EXPERIMENTAL PHYSICAL CHEMISTRY

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Fifth Edition

McGRAW-HILL BOOK COMPANY, INC.
New York · Toronto · London · 1956

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Library of Congress Catalog Card Number 56-6892

THE MAPLE PRESS COMPANY, YORK, PA.

PREFACE

To illustrate the principles of physical chemistry, to train in careful experimentation, to develop familiarity with apparatus, to encourage ability in research—these are the purposes of this book, as stated in the first edition a quarter of a century ago. In each revised edition an attempt has been made to keep pace with the new developments in physical chemistry and to have the book representative of the teaching of the laboratory course in physical chemistry at the University of Wisconsin.

There are many more experiments in this book than can be performed by any one student. Selection will be made on the basis of the time and apparatus available and on the capacity and ultimate aims of the student. If an experiment is too short, the student will find interesting projects under Suggestions for Further Work; if it is too long, the instructor may designate parts of the Procedure to be omitted.

The imperative is not used. Procedures are described, but orders are not given. The student must study the experiment first and then plan his work—a method which develops both his power and his interest.

The high cost of laboratory apparatus restricts the choice of experiments, particularly where classes are small. Nevertheless, there has been no hesitation in introducing advanced apparatus and concepts. If students are not given an opportunity to become familiar with a variety of modern developments and new techniques, they will be handicapped in their later practice of chemistry. Space for additional material has been obtained by abbreviating parts of the last edition and omitting some of the older classical experiments which have found their way into first- and second-year chemistry courses.

All the experiments previously used have been reviewed, and changes have been made in the light of continuing class experience. Experiments in newly developing fields have been added, such as chromatographic adsorption, differential thermal analysis, and high-vacuum technique.

The second part of the book describes apparatus and technique, particularly for more advanced work. It is designed not only to encourage students to undertake special work, but to aid them in later years in the solution of practical problems. No claim whatsoever is made for completeness. In their selection of material the authors have been guided simply by their own experience.

This edition, like its predecessors, owes much to many people—students, laboratory assistants, and teachers in other universities and colleges—who, over the years, have offered thoughtful criticisms and provided many worthwhile suggestions for improvements. The authors wish particularly to acknowledge the aid of Professor C. Daniel Cornwell and the teaching assistants who have been eager to test new experiments. They wish to acknowledge also the help of Professor George W. Murphy who shared in the writing of the fourth edition. They appreciate the suggestions of Lawrence Barlow concerning equipment. They extend their thanks to Harry A. Schopler for the drawings, to Mary Lou Margrave for the careful typing and assembling of the manuscript.

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PART I

LABORATORY EXPERIMENTS

CHAPTER 1

GASES

1. GAS DENSITY

This experiment illustrates the simplest and most direct method for determining the molecular weight of a gas. The method to be used was devised by Regnault. The density of a gas is determined also by means of a density balance.

Theory. According to the ideal-gas law

$$pv = \frac{g}{M} RT \tag{1}$$

where p = pressure
v = volume
T = absolute temperature (t°C + 273.1°)
g = weight of gas of molecular weight M

For the evaluation of the ideal-gas constant R, measurements with a substance of known molecular weight are required. The scale of atomic and molecular weights is defined by taking atmospheric* oxygen as 32 g mole^{-1}. Careful experiments have shown that the pressure-volume product for 32 g of oxygen at 0°C approaches 22.414 liter-atm as the pressure approaches zero. Thus from measurements of p and v for a known weight g of gas at a known absolute temperature T, a value of the molecular weight M may be calculated. For permanent gases and pressures of the order of atmospheric pressure, this value of M is reasonably accurate, but, strictly speaking, Eq. (1) is obeyed exactly only at vanishingly low pressures.

In the second part of the experiment the density of a gas is determined conveniently by means of a density balance. The principle of Archimedes is used, according to which the upward force is equal to the weight of the gas displaced. A large glass bulb on a balance beam is counterpoised with a weight. A reference gas such as oxygen is admitted and its pres-

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* The atomic-weight scale used by physicists is somewhat different because 16 is taken as the atomic weight of the most abundant isotope of oxygen (O^{16}) rather than of normally occurring oxygen. The ratio of an atomic weight on the physical scale to that on the chemical scale is 1.000272.

sure adjusted. The density at this pressure p_1 of the reference gas of molecular weight M_1 may be written as

$$\left(\frac{g}{v}\right)_1 = \frac{p_1 M_1}{RT} \tag{2}$$

If the apparatus is evacuated and another gas admitted, the pressure has to be adjusted to a different value in order to obtain a zero reading on the balance. At this new pressure the density of the gas of molecular weight M_2 is the same as that given by Eq. (2). If the temperature is constant,

$$p_1 M_1 = p_2 M_2 \tag{3}$$

Thus, for gases which obey the ideal-gas law this equation offers a convenient method for determining the molecular weight of an unknown gas.

Apparatus. A 200-ml thin-walled bulb with a small capillary-stopcock; counterpoise of same volume; analytical balance; vacuum-pump and manometer assembly; gas-density balance; barometer; carbon dioxide; other gases.

Procedure. Gases are weighed in the glass bulb shown in Fig. 1. The evacuated bulb is first weighed, and it is then weighed after filling to a known pressure with a gas, the molecular weight of which is to be determined.

In weighing large glass vessels it is necessary to maintain uniform conditions. The bulb is wiped with a clean damp cloth and allowed to stand in the balance for 5 or 10 min to come to constant weight. A counterpoise, consisting of a closed glass bulb of practically the same volume, is used on the opposite balance pan to minimize errors due to adsorption of moisture and changes in buoyancy of the air due to barometric fluctuations.

The assembled apparatus is shown in Fig. 1. The pressure is read to a fraction of a millimeter on a closed-end manometer. The pressure inside the glass bulb *B*, in millimeters of mercury, is equal to the difference in height of the mercury menisci in the two limbs of the manometer. The tube at the base of the manometer has a small bore to prevent splashing the mercury when the pressure is raised or lowered suddenly.

The bulb is first evacuated to 1 mm or less with a motor-driven oil pump that is properly protected by use of a suitable trap. Water and other liquids must not be allowed to get into the oil of the vacuum pump. In order to obtain a steady pressure, it is important that the system be free of leaks, as proved by evacuating the bulb and observing that the mercury levels in the manometer remain constant when the connection to the pump is closed. Leaks at the rubber connections may be stopped by substituting new gum rubber which fits tightly over the glass tubes and by winding wire around the connection, which is then painted with a solution of Glyptal resin.

The bulb is removed from the rubber connecting tube, wiped with a clean damp (not wet) lintless cloth, and allowed to hang in the balance for 5 or 10 min to come to constant weight. The counterpoise, wiped in the same way, is used on the opposite pan.

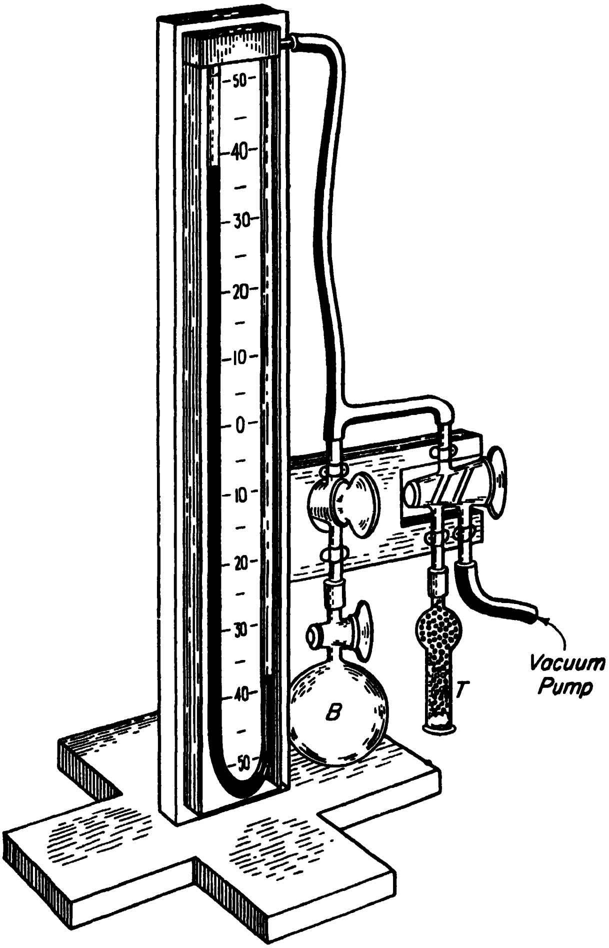

FIG. 1. Manometer and vacuum system for gas-density measurements.

The bulb is replaced in the apparatus and subjected to a second evacuation, after which it is weighed again. If the two weights do not check, the process is repeated until they do check.

The evacuated bulb is now filled with carbon dioxide or other gas from a tank. A diaphragm regulator connected to the tank is used to regulate the pressure. The bulb is returned to the vacuum system which has previously been evacuated. With the two-way stopcock closed, the stopcock on the bulb is opened and the pressure measured. The temperature of the air in the vicinity of the bulb is recorded. After wiping with a damp cloth and waiting for uniform conditions in the balance case, the bulb of gas is weighed. After weighing, the bulb is again evacuated and filled cautiously with carbon dioxide, the measured temperature and pressure are recorded, and the bulb is weighed.

The weight of carbon dioxide is determined in the same manner at about ¾ and again at about ½ atm. It is essential in this work that there be no leaks.

The density of air or city gas or of some unknown gas or mixture of gases may be determined, introducing the gas through the drying tube *T*.

The volume *v* of the bulb in cubic centimeters is obtained by weighing it empty and filled with distilled water. The bulb is filled by evacuating it, closing the stopcock, immersing the end of the tube in a beaker of distilled water, and then opening it to permit the bulb to fill. A hypodermic syringe may be used to complete the filling of the bulb. The bulb is then emptied by use of a water aspirator and placed in a drying oven. It is evacuated several times while hot to remove the last traces of moisture.

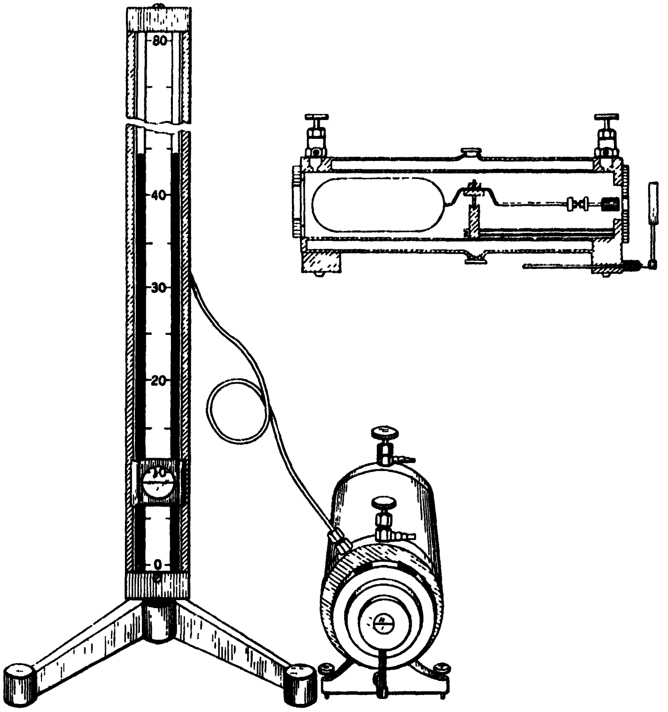

FIG. 2. Gas-density balance.

In the second part of the experiment, the gas-density balance is used to determine the average molecular weight of dry air. A balance developed by Edwards[5] is illustrated in Fig. 2. The case of the balance is connected to a closed-end manometer and has connections for attaching a vacuum pump or tank of purified gas. The window at the end of the balance containing the counterpoise is marked so that the position of the pointer may be determined.

Several readings are made on gas of known molecular weight such as oxygen. The pressure necessary to bring the pointer to the zero point is determined.

The pressure required for a zero balance with air which has been passed through a tower of soda lime to remove water vapor is determined next. In order to fill the gas balance with a new gas, it is evacuated, filled with gas, evacuated, and refilled with gas to sweep out the last traces of the first gas. A second density reading is then taken after further sweeping out with the new gas. If the two readings do not agree, the sweeping process is continued until two successive readings agree closely.

Calculations. If the counterpoise has practically the same volume as the bulb, it is unnecessary to make a correction for the buoyancy of the air (see Appendix).

The weight g of the gas is obtained by subtracting the weight of the dry evacuated bulb from that of the bulb when filled with the gas.

If a closed-end manometer is used, the observed pressure in millimeters of mercury is corrected to 0° by use of the equation

$$p_0 = p - p\,\frac{\alpha t - \beta(t - t_s)}{1 + \alpha t} \tag{4}$$

where p_0, p = corrected and observed pressures
t = centigrade temperature of the manometer
t_s = temperature at which scale was calibrated, normally 20°C
α = mean cubical coefficient of expansion of mercury between 0 and 35°
β = linear coefficient of expansion of the scale material

The value of α is 181.8×10^{-6}, and the value of β is 18.4×10^{-6} for brass. If a wooden scale is used, taking the value of β equal to zero introduces a negligible error, since β for wood is about 5×10^{-6}.

If an open-end manometer is used, the pressure in the bulb is equal to the difference between the corrected barometer pressure (see Appendix) and the manometer pressure corrected by use of Eq. (4).

The molecular weight of carbon dioxide is calculated at each pressure. If carbon dioxide were a perfect gas, the calculated molecular weight would be the same at all pressures. In determining the true molecular weight of a gas, it is necessary to plot the molecular weight obtained at different pressures and extrapolate to zero pressure. If the precision of the data warrants, a more accurate value of the molecular weight of carbon dioxide may be obtained in this way.

The mean molecular weight of air is calculated from measurements with the gas-density balance by using Eq. (3) and compared with the average molecular weight obtained from the known composition of air.

Practical Applications. The formula of a chemical compound may be calculated from the molecular weight, together with the atomic weights, and the percentage composition found by chemical analysis. In the most accurate work globes of 8 to 20 liters have been used, and corrections were made for the loss of buoyancy of the globe when it contracted on evacuation.[1] The determination of the density of ammonia gas by Dietrichson and coworkers[4] illustrates the experimental techniques used in accurate work. Birge and Jenkins[2] have discussed the methods for extrapolating to the limiting gas density and the errors involved. The work of Cady and Rarick[3] indicates the high precision with which molecular weights may be determined with a gas-density balance.

The chemical equilibrium between different gases may often be calculated from the density of the equilibrium mixture of gases.

Suggestions for Further Work. The accurate determination of the molecular weight of hydrogen gas by this method constitutes a real test of a student's care and skill.

The molecular weights of other gases may be determined. Small tanks of methane, ethylene, nitrous oxide, Freon, and other gases can be purchased.

The percentage composition of a mixture of two gases such as oxygen and carbon dioxide may be determined from the density of the mixture.

More exact values of the molecular weights may be calculated with equations of state such as those of Berthelot, van der Waals, or Beattie and Bridgman. However, the use of these equations requires a knowledge of certain constants characteristic of the gas which will not be available for an unknown gas.

The gas-density balance is well adapted to measuring the density of a mixture of gases. For example, the carbon dioxide content of the exhaled breath may be determined by blowing the breath through a calcium chloride drying tube and a cotton packing into the balance.

In the analysis of a mixture of gases, the density in grams per liter is determined with the balance, and the density of each pure gas at the same pressure is known. A formula is derived that will give the percentage composition corresponding to the observed density at the observed pressure. It is assumed that any interaction among the different gases leading to density changes is negligible in the experiments described here.

References

1. Baxter and Starkweather, *Proc. Nat. Acad. Sci. U.S.*, **12**, 699 (1926).
2. Birge and Jenkins, *J. Chem. Phys.*, **2**, 167 (1934).
3. Cady and Rarick, *J. Am. Chem. Soc.*, **63**, 1357 (1941).
4. Dietrichson, Bircher, and O'Brien, *J. Am. Chem. Soc.*, **55**, 1-21 (1933).
5. Edwards, *Ind. Eng. Chem.*, **9**, 790 (1917).

2. VAPOR DENSITY

This experiment illustrates a practical method for determining the molecular weight of a volatile material. It provides excellent practice in the use of simple physical-chemical apparatus.

Theory. The density of a vapor is more easily determined than the density of a gas because the substance may be weighed accurately when condensed to a liquid at room temperature. Very accurate vapor-density results have been obtained in this way.[3] When only moderate accuracy is required, however, of the various methods available that of Victor Meyer[4] is the simplest and the one most frequently used.

A known weight of liquid is vaporized in a chamber maintained at an appropriate and constant high temperature. The air displaced from the chamber is cooled to room temperature and its volume carefully measured. Substitution of air for the actual vapor thus provides a means of determining the volume the known weight of vapor would have occupied at room temperature if it could be cooled without condensation.

It should be noted that it is not necessary that the temperature of the vaporization chamber be known, but it must be constant.

Apparatus. Modified Victor Meyer apparatus; gas burette and leveling bulb; 1° thermometer; barometer; glass bulblets; carbon tetrachloride, benzene, acetone, or chloroform; water aspirator; large and small test tube.

Procedure. A modified form of Victor Meyer apparatus is shown in Fig. 3. The outer jacket *A* is made from a Pyrex tube (5 by 40 cm). A cork holds the inner vaporizer tube in the outer jacket, through which live steam is passed. At the bottom of the jacket is sealed a small tube through which the excess steam and condensed water are led to the sink. A can made of sheet copper, provided with a safety tube, serves as a steam generator. The vaporizer tube is fitted with a rubber stopper through which passes the brass tube *D*. This central tube carries three or four disks *G* nearly filling the cross section of the vaporizer tube, the purpose being to reduce the rate of diffusion of the vapor produced when the bulblet is broken. The disks are cut from thin metal and provided with central holes so that they can slip over the supporting tube. They are soldered in position or supported by rings or wire twisted around the tube. Mica disks and a glass tube are used for corrosive gases.

At the bottom of tube *D* a hole is drilled through both walls. The bent tail of the bulblet *F* is inserted into these holes when a run is begun. A loosely fitting brass rod passes through the tube and into the rubber tubing *J* connected at the top, being held in position by a rubber-tubing clamp at the top. Positive breakage of the glass tail is accomplished by pushing the brass rod down.

The little bulblet is made by drawing out 4-mm soft-glass tubing, as

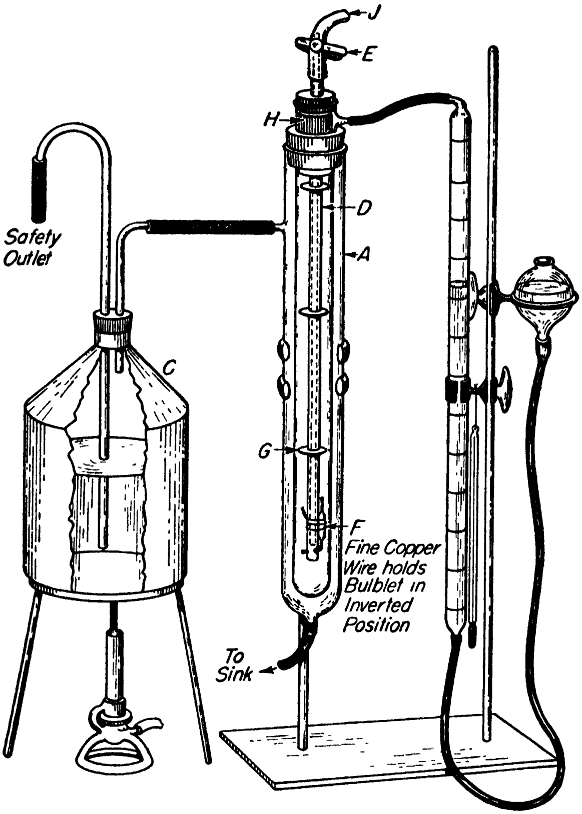

FIG. 3. Modified Victor Meyer apparatus.

suggested by Fig. 4. The tubing is rotated evenly during the heating operation. The micro flame shown is formed by a jet of gas issuing from a capillary section drawn at the end of a Pyrex tube. After drawing, bending, and sealing the tail, the bulblet is weighed on an analytical balance. About 0.1 ml of the liquid to be used is placed in a miniature test tube ($\frac{3}{8}$ by 2 in.), and the latter is then placed in a large test tube (1 by 6 in.) with the open bulblet capillary dipping into the liquid. A stopper with outlet tube is fitted to the large test tube, which is then attached by vacuum tubing to the aspirator and evacuated. The vacuum may be broken by suddenly removing the tubing, whereupon the liquid will rise into the bulblet. The remaining capillary end is then sealed off with the micro flame about an inch from the end, care being taken that no liquid is present in the immediate area of heating and that the flame does not strike the open end of the capillary, where it can deposit condensed water. The bulblet with its liquid and the sealed-off end are then weighed again to obtain the weight of the liquid. Any liquid remaining in the sealed-off end must be removed before weighing. Because leaking bulblets are the main cause of difficulty in this experiment, the quality of the seals made should be tested. The bulblet, in a *dry* miniature test tube, is returned to the filling apparatus which is then evacuated as well as possible with the water aspirator. Any serious deficiency in the seals will become obvious.

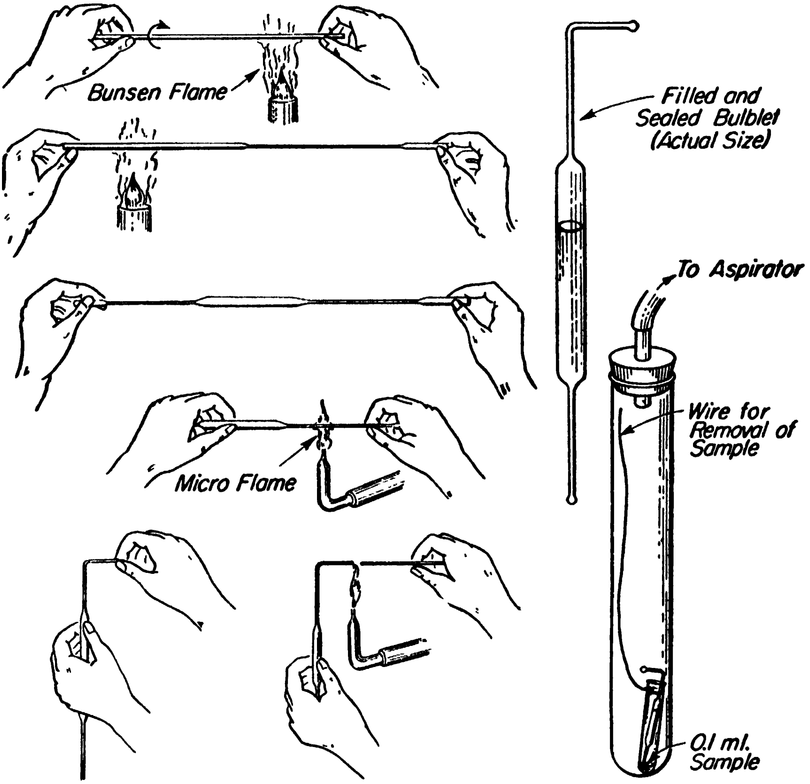

FIG. 4. Preparation and filling of Victor Meyer bulblet.

The vaporizer tube is swept out with a gentle current of air drawn through the tube *D* by an aspirator attached to *J* after steam has been passing through the jacket for some minutes. During this operation the rubber stopper should be loosened to provide an air entrance. The apparatus is assembled with the sealed bulblet as shown, and after steam has passed through the jacket for at least 10 min, it is tested for leaks and for thermal equilibrium by closing the screw cock *E* and lowering the leveling tube. If the water in the burette does not continue to fall when the leveling bulb is maintained in a steady position, the apparatus is tight and in thermal equilibrium.* The leveling bulb is then raised until the two liquid levels are exactly equal, and the reading of the burette is recorded.

The brass rod is now pushed down sufficiently to break off the lower capillary tip of the bulblet, whereupon the liquid vaporizes quickly. As the vaporization takes place, the leveling tube is lowered so as to maintain nearly equal pressure inside and outside the apparatus to prevent possible leakage. When the hot air displaced into the gas burette cools, a slight contraction may be noted. When the level of the liquid in the burette ceases to change position, the levels of the liquid are carefully adjusted to exactly the same height, and the final reading of the volume is made. After the apparatus has stood for some time, the volume of the measured air decreases, because of diffusion of the vapor from the vaporizer into the cooler parts of the apparatus where it condenses. Obviously the final reading must be taken before this occurs. The temperature is taken from a thermometer hanging by the burette. For more precise work, the measuring tube may be jacketed with a concentric tube containing water and a thermometer.

Carbon tetrachloride, benzene, or any low-boiling liquid may be used. The material must be pure. Two or more determinations are made until satisfactory checks are obtained. After each determination the vapor is removed before a second experiment is started, for an excessive volume of vapor leads to condensation in the connecting tube.

The molecular weights of one or more unknowns are to be determined, duplicate determinations being made as usual. The apparatus should not be dismantled until the calculations have been made and the results checked.

Calculations. The pressure is read from the barometer and corrected to 0°C with tables or by calculations (see Appendix). The correction amounts to 2 or 3 mm. Another correction should be made for water vapor in the measured volume. The partial pressure of water in the gas burette is equal to $P^0_{H_2O}$, the vapor pressure of water at the corresponding temperature. The air introduced from the vaporization tube has a partial pressure of water vapor, $rP^0_{H_2O}$, determined by the relative humidity r of the laboratory air. The latter may be determined with a sling psychrometer or, more conveniently, a hair hygrometer reading directly in relative humidity. The difference in partial pressure of water between saturated air and the unsaturated laboratory air is subtracted from the barometer reading P_{bar}. This correction assumes that no diffusion of

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* *H* is a bakelite or hard-rubber plug of slightly smaller outside diameter than the inside diameter of the vaporizer tube. This practically eliminates the dead air space at the top where the vaporizer tube is not in actual contact with the steam. The result is more rapid attainment of thermal equilibrium.

water vapor into the vaporization tube occurs during the preliminary phases of the experiment, and becomes less accurate if the experiment requires an extended time.

The molecular weight M of the vapor is calculated from the familiar equation

$$pv = \frac{g}{M} RT$$

where p = pressure, atm
$= P_{\text{bar}} - P^0_{\text{H}_2\text{O}}(1 - r)$
v = volume of displaced air, ml
T = absolute temperature at which volume is measured
g = weight of liquid taken
R = gas constant, 82.05 ml-atm deg^{-1} mole^{-1}

The averaged results are compared with the accepted values, and the percentage error is calculated. A reasonable error involved in each reading is estimated, the various causes of error are enumerated, and the accuracy attainable is discussed critically.

Practical Applications. The determination of the molecular weight is useful in identifying a chemical compound and in establishing its formula.

When gases dissociate on heating, the equilibrium may be studied quantitatively through density measurements.

Suggestions for Further Work. The densities of several organic or inorganic vapors may be measured. For substances having boiling points above 80°, some liquid boiling higher than water must be used to generate vapor for the jacket,[2] or a furnace may be used for extreme temperatures.[5] The jacket should be at a temperature at least 20° above the boiling point of the substance whose vapor density is being determined, because of the failure of the gas laws to apply to vapors that are near the condensation point.

Better results are obtained by using van der Waals' equation or Berthelot's equation. A convenient form of the latter is

$$M = g\frac{RT}{pV}\left[1 + \frac{9}{128}\frac{p}{p_c}\frac{T_c}{T_s}\left(1 - 6\frac{T_c^2}{T_s^2}\right)\right]$$

where p_c = critical pressure
T_c = critical temperature of compound used
T_s = temperature of steam jacket

Such an equation is obviously of no use in the case of an unknown compound, since the critical temperature and pressure will not be known. It has been used, however, for testing the reliability of apparatus on known substances.

References

1. Evans, *Ber.*, **35,** 958 (1913).
2. Harris and Meyer, *Ber.*, **27,** 1482 (1894), and earlier papers.
3. Kretschmer and Wiebe, *J. Am. Chem. Soc.*, **76,** 2579 (1954).
4. Meyer, *Ber.*, **11,** 1867 (1878).
5. Meyer and Meyer, *Ber.*, **12,** 1112 (1879).

CHAPTER 2

OPTICOCHEMICAL METHODS

3. REFRACTOMETRY

Experience is obtained in the operation of different kinds of refractometers. They are used to analyze mixtures, to test for purity, and to aid in determinations of molecular structure.

Theory. Whenever a beam of light passes into a transparent medium, a small part is reflected while the other part is propagated and continues as the *refracted ray*. This refracted ray does not continue in the same direction as the incident ray, unless it is perpendicular to the boundary. The light ray is bent at the point it leaves the first material and enters the second. The angle this ray makes with a line drawn perpendicular to the surface of the second medium at the point where the light enters is known as the *angle of refraction*. The index of refraction n, of any medium with reference to air, is defined as the ratio of the velocity of light in air to the velocity of light in that medium. It is given by the equation $n = \sin i/\sin r$, where i is the angle of incidence and r is the angle of refraction. The index of refraction is characteristic of each particular substance, and its measurement is a matter of considerable practical importance.

The refractive index of a liquid varies with temperature and pressure as the number of molecules in the path of the light is changed, but the *specific refraction* r defined by Lorenz and Lorentz is independent of these variables. On the basis of the electromagnetic theory of light, Lorenz and Lorentz have shown that

$$r = \frac{n^2 - 1}{n^2 + 2}\frac{1}{d} \tag{1}$$

where d is the density. The *molar refraction* is equal to the specific refraction multiplied by the molecular weight. The molar refractions of a large number of organic and inorganic compounds have been determined, and it has been found that many atoms and groups of atoms always contribute the same definite amount to the molar refraction of any compound in which they are found. Tables of atomic refractions[2,3,5] are useful in determining the structure of molecules, because the sum of the refractions for the atoms and for the structural features in a proposed structure should add up to give a total which is equal to the experimentally determined molar refraction. For example, dimethyl ether $(CH_3)_2O$ and ethanol C_2H_5OH have the same atoms; but in the ether, oxygen has a different atomic refraction than in alcohol.

Apparatus. Abbe refractometer; immersion refractometer; benzene, carbon tetrachloride, chloroform, ethyl acetate, ethylene chloride, *n*-heptane, methyl acetate, potassium chloride.

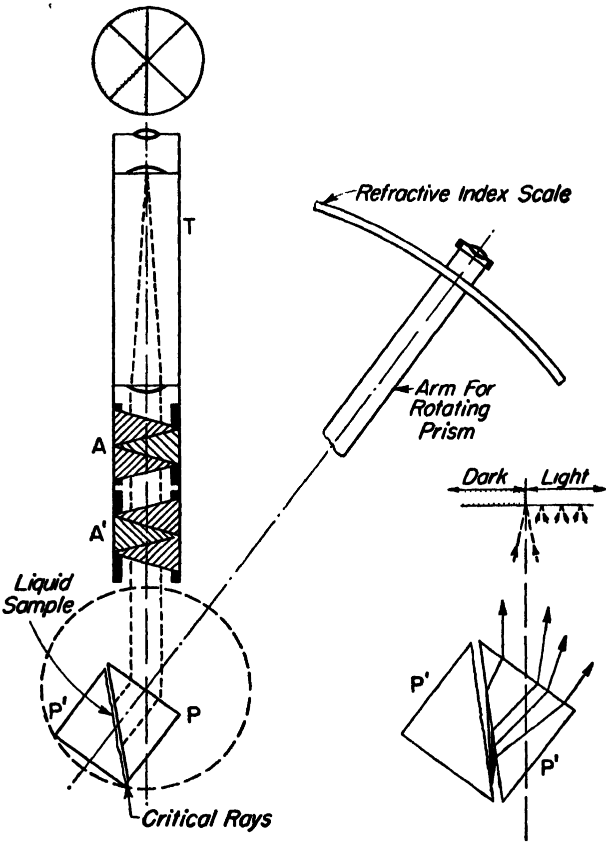

FIG. 5. Optical path in Abbe refractometer.

Procedure. The Abbe refractometer will be used for organic liquids which have widely different refractive indices, and the immersion refractometer will be used for aqueous solutions.

Both refractometers make use of the principle of the grazing angle. The field of vision in the telescope will show a light field and a dark field, in which the sharp line of demarcation corresponds to the grazing angle. The Abbe refractometer is shown in Fig. 5.

White light from a frosted electric-light bulb is used for convenience, and if it were not for the compensating Amici prism of different kinds of glass in the telescope, the line of demarcation between the dark and light fields would be colored and indistinct because the refraction of light is different for different wavelengths. The light of different wavelengths is dispersed by the refractometer prism, by the first compensating prism A', and by the sample of liquid. Since the extent of the dispersion differs for each liquid, the second compensating prism A is adjusted manually so that its dispersion is exactly equal and opposite to the dispersion produced by the refractometer and the liquid. A knurled ring in the middle of the telescope barrel is turned until the compensation is complete and the color fringes disappear, leaving a sharp line of demarcation between the two parts of the field.

Although white light is used, the refractive index measured, n_D, is for the D line, 5893 A, because the Amici compensating prisms are constructed with special glasses so that light of this wavelength is not deviated, but all other light is deviated.

The Abbe refractometer has two prisms, the first of which, P', has a ground-glass face. It is used to confine the thin sample of liquid and to illuminate it with scattered light. The upper prism, P, is the refracting prism. The prisms are jacketed so that the temperature may be controlled to 0.2° with water from a thermostat. The refractometer prism is rotated by a protruding arm so as to set the edge of the shadow directly on the intersection of the cross hairs as shown in Fig. 5.

The prisms are opened like jaws after turning the lock nut, and they are wiped with lens tissue paper, care being taken not to scratch the prism surfaces. A few drops of liquid are placed on the face of the lower prism, and the prism jaws are then closed and locked. The compensating ring is turned to eliminate color fringes. The telescope is set in a convenient position, and the mirror is adjusted to reflect the light from a frosted electric lamp into the refractometer. The prism is rotated by means of the arm until the border between the dark and light fields passes exactly through the intersection of the cross hairs. The telescope eyepiece is adjusted until the cross hairs are in good focus, and the eyepiece on the movable arm is adjusted to give a sharp focus on the scale. The scale is graduated directly in terms of refractive index calculated for the glass used in the prism as shown on page 350. The reproducibility of the individual readings on the scale is ±0.0002 in refractive index. Accurate temperature control is important because the refractive indices of many organic liquids change 0.0004 per degree. After a liquid is used, it is absorbed with lens paper or rinsed off with a volatile liquid in which it is soluble.

The refractive indices of pure methyl acetate, ethyl acetate, ethylene chloride, chloroform, and heptane are measured with the Abbe refractometer. The molar refraction of each compound is calculated from the refractive index and density at the temperature of the measurement. The densities may be calculated from the equations given in the International Critical Tables, or the values given in Table 1 may be used.

TABLE 1. DENSITY AT 25°, GRAMS PER MILLILITER

Benzene	0.8734	Ethyl acetate	0.8941
Butanol	0.8064	Ethylene chloride	1.2464
Carbon tetrachloride	1.5844	*n*-Heptane	0.6794
Chloroform	1.4797	Methyl acetate	0.9277
Diethyl ether	0.7103		

The molar refractions are compared with the values found in tables or with the sum of the atomic refractions if the molar refractions are not available. If there is a serious discrepancy, the liquids may be impure. Redistillation with an efficient fractionating column (page 83) should give considerably improved values. In fact purification is often continued until further purification gives no further change in refractive index.

The atomic and group refractions are calculated from the molar refractions and compared with values given in the literature. The difference between the methyl acetate and ethyl acetate molar refractions is equal to the CH_2 refraction. The molar refraction of ethylene chloride $C_2H_4Cl_2$ minus twice the CH_2 refraction is the refraction of two Cl. Proceeding in this way the refractions for CH_2, Cl, H, and C are calculated. The H refractions calculated from data on chloroform and heptane are compared. Assuming an uncertainty of ± 0.0003 in the refractive indices and ± 0.001 in the densities, the possible error in the hydrogen refraction is calculated.

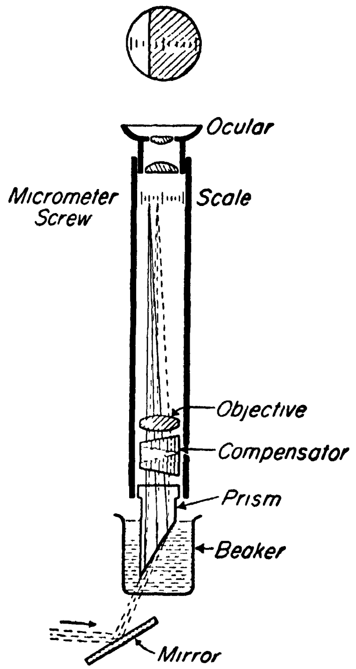

FIG. 6. Immersion refractometer.

The *immersion refractometer* is shown in Fig. 6. Light which hits the face of the prism, at all angles up to the grazing angle, is refracted to give a light field. The sharp edge between the dark and light field is read directly on a transparent scale.

Three solutions of pure KCl are made up accurately with concentrations varying from 2 to 10 g in 100 g of water. The solutions must be mixed thoroughly by pouring back and forth into a beaker. Several small beakers, each containing a pure liquid or a solution, are set into the rack in the thermostat, care being taken to avoid flooding.

The refractometer is hung on the wire frame by means of the hooks near the eyepiece, so that the prism dips into the solution. The mirror is adjusted so that the light from the lamp, which is placed in front of and slightly above the bath, is reflected through the thermostat and beaker and into the refractometer. If the half-shadow is not well defined, the mirror and lamp should be adjusted. Special care must be taken to avoid chipping the edge of the exposed prism.

As with the Abbe refractometer, a compensating prism is incorporated so that n_D is obtained using white light. The ring which encircles the barrel is turned until the compensator eliminates the color fringe. The reading is taken by noting the position on the scale of the border line between the dark and light fields. The micrometer is set at zero when the scale is read. Fractions of a scale division are determined by turning the micrometer screw and scale until the edge of the shadow touches the nearest line on the scale.

Check readings are taken, and then the beakers are refilled for a second series of readings. Refractive index is plotted against composition, and from this graph the concentration of a solution of unknown concentration is determined.

Tables accompanying the instrument are used to convert scale readings into n_D. This conversion is unnecessary in analysis, when the concentrations of the known solutions ·are plotted directly against the scale readings.

Practical Applications. Measurements of the indices of refraction are helpful in identifying and establishing purity, in determining the molecular structure of organic compounds, and in the quantitative analysis of certain types of solutions.

The Abbe refractometer has a number of special applications, particularly in food analysis and in the testing of oils. It covers a wide range of refractive indices, and uses but a very small amount of sample.

The immersion refractometer is very sensitive over a narrow range of refractive index and is therefore well suited to the measurement of the refractive index of solutions. This fact makes possible the quantitative analysis of solutions. A refractometer with interchangeable prisms is available, covering several different ranges.

Suggestions for Further Work. Refractive indices of additional compounds and binary mixtures may be determined. The refractive indices of solids may be determined, as described on page 351.

The refractive indices of diethyl ether and butanol may be determined to indicate the difference between the atomic refraction of ether oxygen and hydroxyl oxygen.

If a Pulfrich refractometer is available, it may be used with a mercury H-4 lamp or a Geissler tube to give refractive indices with somewhat greater accuracy. The refractive index may be measured at different wavelengths to obtain molecular dispersions.

References

1. Annual Tables of Physical Constants and Numerical Data, Sec. 921C, National Research Council, Frick Chemical Laboratory, Princeton, N.J. (1941).
2. Bauer and Fajans *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Chap. 20, Interscience Publishers, Inc., New York (1949).
3. Daniels and Alberty, "Physical Chemistry," John Wiley & Sons, Inc., New York (1955)
4. Gibb, "Optical Methods of Chemical Analysis," McGraw-Hill Book Company, Inc., New York (1942).
5. International Critical Tables, Vols. I, VII McGraw-Hill Book Company, Inc., New York, (1928).
6. Swietoslawski, Atomic Refractions, *J. Am. Chem. Soc.*, **42**, 1945 (1920).

4. SPECTROPHOTOMETRY

This experiment illustrates the use of a photoelectric spectrophotometer, which is used to map spectra and to analyze a binary mixture of colored substances in solution.

Theory.[4,8] The spectrophotometer consists of a monochromator and a photocell detector. In other words it separates the radiation into separate narrow wavelength regions by refraction or diffraction and measures the intensity in each region. The light is spread out into a spectrum by a prism or a diffraction grating. Improved gratings are now made with the lines ruled at a definite angle so as to throw most of the radiation into the first-order spectrum, thus increasing the energy available and improving the purity. The purest light is obtained with a double monochromator with two prisms or gratings. In order to make the radiation monochromatic in this way the intensity is greatly reduced, and only recently have instruments in which the energy is measured directly by electrical means become available for general laboratory use. Photoelectric tubes and amplifying circuits are used in some types. In others a barrier-layer cell and sensitive galvanometer are used. The intensity-indicating device (galvanometer, milliammeter, or potentiometer) is set to read 100 per cent transmission on a scale for the pure solvent, and the percentage transmission $100I/I_0$ is then equal to the reading on the same scale for the solution. This adjustment is made by reducing or augmenting the incident light intensity or by attenuating the output from the photoelectric cell.

The spectrophotometer can be used in the ultraviolet and infrared as well as in the visible regions of the spectrum. Powerful tungsten lamps, Corex cells and optical parts, and sensitive photocells permit measurements to 3000 A. In the infrared, optical parts of sodium chloride permit an extension to 15 μ and with potassium bromide to 25 μ. More materials are "colored" in the ultraviolet than in the visible, and in the infrared almost all substances are "colored." In fact, there are so many overlapping absorption bands in the infrared that analysis by the spectrometer may be complicated. A thermopile must be used for measuring the intensity of transmitted light in the infrared.

The advantage of a sensitive spectrophotometer is obvious. The complete spectrum is quickly obtained with percentage transmissions at each wavelength. The true color of a material or solution may be defined in quantitative terms. The wavelengths of maximum absorption are quickly found, and then the spectrophotometer with a narrow slit is set directly at a suitable absorption band for a series of measurements at different dilutions.

All types of monochromators have certain features in common. The wavelength to be used is selected by turning a knob which moves a prism or diffraction grating. Since there is some current from the photocell even when the shutter between it and the sample compartment is closed, a dark-current rheostat is provided so that the instrument will read exactly zero per cent transmission when the shutter is closed. When the shutter is open and a reference cell containing solvent is in the light path, the instrument is then set to read 100 per cent transmission by changing the sensitivity of the amplifier or by adjusting the slit from the monochromator. As the slit is opened to provide greater intensity of light, a wider range of wavelengths is included in the beam. Therefore, at wavelengths where the transmission varies rapidly with wavelength, the slit width should be kept as narrow as possible consistent with stable operation of the spectrophotometer. After these adjustments have been made, the per cent transmission of a solution may be measured directly. A number of spectrophotometers are available commercially. The *Beckman Model B spectrophotometer* (Fig. 7) employs a prism monochromator and is suitable for measurements in the region 325 to 1,000 mμ. One millimicron (mμ) is equal to ten angstroms. A line-operated tungsten source is used.

The Beer-Lambert law may be written in the form

$$\log (I_0/I) = A = abc \tag{1}$$

where the quantity $\log (I_0/I)$ is referred to as the *absorbancy* (A)* of the sample. For a solution of a solute which does not associate or dissociate, the absorbancy is directly proportional to the thickness of solution b and its concentration c. Since the absorbancy depends only upon the per cent transmission, the scale of the spectrophotometer may be graduated in absorbancy so that a number proportional to concentration may be

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* The term optical density is also used to designate this quantity. In Eq. (1) the terminology introduced by the Bureau of Standards (Letter Circ., **LC-857**, May 19, 1947) is used.

read directly. The proportionality constant a is referred to as the *absorbancy index,** or if the concentration is expressed in moles per liter, as the *molar absorbancy index,* a_M. The absorbancy index of a solute varies with the wavelength of light, solvent, and temperature. It is conveniently determined from the slope of a plot of log (I_0/I) versus c.

The absorbancy of a multicomponent system is equal to the sum of the absorbancies due to the individual components if they do not interact with each other. Thus,

$$\log (I_0/I) = A = (a_1c_1 + a_2c_2 + \cdots)b \tag{2}$$

where $c_1, c_2, \ldots$ are the concentrations of the (noninteracting) components having absorbancy indices of $a_1, a_2, \ldots$.

In a binary solution only two terms appear in Eq. (2). Thus, if the optical density of the solution is determined at two suitable wavelengths, and if the absorbancy indices are known for each component at each wavelength, the individual concentrations can be computed by solving the two simultaneous equations of the form of Eq. (2). The extension to any number of components is obvious.

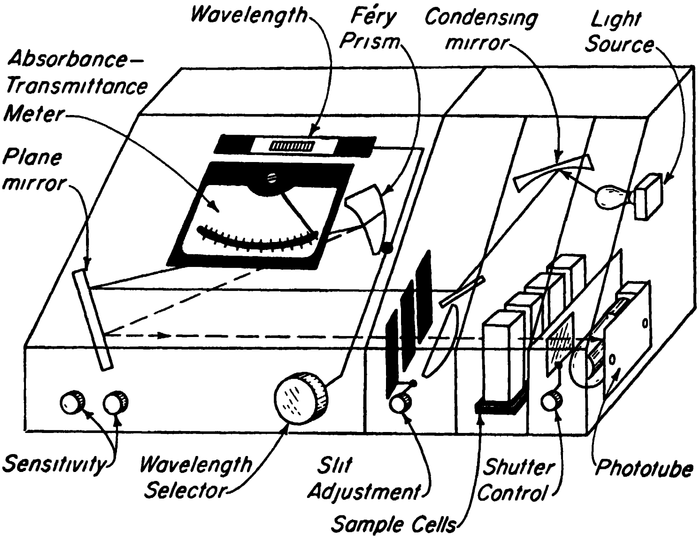

FIG. 7. Spectrophotometer.

Apparatus. Photoelectric spectrophotometer; three cells; volumetric flasks and pipettes; cupric chloride and cobalt chloride or red and green dyes suitable for analysis as a binary system.

Procedure. The instructions for using the particular instrument in the laboratory should be read. The light source and photocell circuits of

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* This quantity has also been called the extinction coefficient.

the instrument are turned on, and the instrument is allowed to warm up. Most spectrophotometers require a warm-up period in order to give their most stable operation.

For accurate work it is necessary to take into account differences between different spectrophotometer cells (cuvettes). Spectrophotometer cells may be imperfect in two ways:

1. The light transmissions of different cells filled with a nonabsorbing solvent (for example, water in the visible region) may not be the same. This results from imperfections in the cell windows.

2. The optical paths through the cells may not be the same. This error could be detected by measuring the light transmissions of a series of cells filled with an absorbing solution. If different cells give different absorbancies after correction for item 1, the optical paths are different. The paths through the cells are directly proportional to the corrected absorbancies.

In order to correct for the first effect, the light transmissions are determined for the cells filled with the nonabsorbing solvent. The cells are cleaned and filled with distilled water and placed in the spectrophotometer. The cell with the highest light transmission is chosen as the reference cell, and the per cent transmission is adjusted to 100 with this cell in the optical path. The other cells are then placed in the optical path and the absorbancies (A_c) read. In accurate work it is necessary to determine this correction at each wavelength used.

Subsequent experimental absorbancy measurements on solutions are corrected to actual sample absorbancy A by subtracting the A_c value for the particular cell used.

Example: $A_{exp} = 0.219$ is obtained in a cell for which $A_c = 0.011$. Thus, the actual sample absorbancy is $A = 0.219 - 0.011 = 0.208$.

In measuring the absorbancy of solutions the greatest accuracy is obtained if the concentration is such as to give a per cent transmission in the range 20 to 60 per cent (absorbancy 0.7 to 0.2). It can be shown that if the error in the measurement of per cent transmission is a constant per cent transmission, then the greatest accuracy is obtained at 37 per cent transmission (absorbancy 0.44).

Stock solutions of the two colored solutes are prepared in 100-ml volumetric flasks at concentrations recommended by the instructor (0.1 M for $CuCl_2$ and $CoCl_2$ in 0.005 M HCl). Solvent is placed in the spectrophotometer cell having the greatest transmission, and the two colored solutions are placed in two cells for which the absorbancy corrections are known. The absorbancies are measured from 400 mμ to 700 mμ at intervals of 10 mμ. The corrected absorbancies for the solutions are plotted versus wavelength, and two wavelengths are chosen for analyzing mixtures.

A known mixture and an unknown mixture of these solutes are to be analyzed, and so two wavelengths for this analysis are chosen. For example, if red and green dyes are used, these wavelengths are chosen so that at one wavelength the red dye absorbs strongly and the green dye absorbs weakly, while at the other wavelength the situation is reversed.

It is necessary to determine whether Beer's law is obeyed for both solutions at these wavelengths. The stock solutions of each are diluted with 0.005 N HCl to obtain solutions 0.75, 0.50, 0.25, and 0.125 as concentrated. The absorbancies for each solution are determined at both wavelengths.

The absorbancy of a solution containing equal volumes of the two stock solutions is measured at the two wavelengths as a test of the additivity of the absorbancies of the two solutes in a mixture. An unknown solution of the two solutes, prepared by the instructor, is measured at the two wavelengths.

Calculations. Graphs are prepared of absorbancy versus wavelength for the two substances studied. Graphs of absorbancy versus concentration for the two solutes at the two wavelengths are constructed. The absorbancy indices are calculated from the slopes of straight lines passing through the origin ($A = 0$ at $c = 0$).

The concentrations of the known and unknown mixtures are calculated from the absorbancies measured at the two wavelengths using two simultaneous equations of the type of Eq. (2). The uncertainty in these analyses resulting from the estimated uncertainty in the measurement of absorbancy and the uncertainties in the absorbancy indices are indicated.

Practical Applications. The color of nearly any commercial product can be described quantitatively with the spectrophotometer and checked for uniformity.

The spectrophotometer and the photoelectric colorimeter can be used for the determination of traces of mercury, benzene, and other organic vapors in air by the measured absorption of ultraviolet light.[5]

Suggestions for Further Work. The color of some common material may be described quantitatively by determining its absorption spectrum and plotting the percentage transmission at the different wavelengths. A dilute solution of ink, blood, paint, or an acetone extract of chlorophyll, a flower petal, or a food material may be used. Colored glass filters may be checked.

The emission spectrum of a mercury-vapor lamp may be plotted. The H-4 lamp is convenient.

Colorless or slightly colored salts in solution can often be made intensely colored by the addition of certain organic compounds. To illustrate this, a solution of potassium dichromate may be run through with the spectrophotometer. Then a little diphenylcarbazide is added to a very dilute solution (10^{-5} M), and a different and more intense color is produced. The spectrum of this solution is plotted. The absorption at 5000 A follows Beer's law and is suitable for accurate analysis.

It is possible to study equilibria in solution if the reactant and product have different colors. Graphs showing log (I/I_0) plotted against concentration are prepared for ferric ion with dilute hydrochloric acid (to prevent hydrolysis) and for the deep red

$FeCNS^{++}$ of ferric thiocyanate containing an excess of potassium thiocyanate.[1] Then the concentration of each in solutions containing different ratios of Fe^{+++} and CNS^- is determined by setting the spectrophotometer at a definite absorption band for each. An equilibrium constant may be calculated. Other equilibria that may be studied in this way involve iodine and the triiodide ion formed in a solution of iodine in potassium iodide, or iodine chloride formed from iodine and chlorine in a solution of carbon tetrachloride.

An interesting equilibrium constant has been determined for the association of the ions of methylene blue and of thionine, using a spectrophotometer. The monomer of methylene blue absorbs at 6565 A and the dimer at 6000 A. Beer's law is not followed on account of this association. The equilibrium constant is determined by extrapolating the absorbancy index to infinite dilution as described by Rabinowitch and Epstein.[7]

References

1. Bent and French, *Ind. Eng. Chem., Anal. Ed.*, **13**, 568 (1941); Peters and French, *Ind. Eng. Chem., Anal. Ed.*, **13**, 605 (1941).
2. Brode, "Chemical Spectroscopy," John Wiley & Sons, Inc., New York (1947).
3. Cary and Beckman, *J. Opt. Soc. Amer.*, **31**, 682 (1941).
4. Gibb, "Optical Methods of Chemical Analysis," McGraw-Hill Book Company, Inc., New York (1942).
5. Hanson, *Ind. Eng. Chem., Anal. Ed.*, **13**, 119 (1941).
6. Mellon, "Analytical Absorption Spectroscopy," John Wiley & Sons, Inc., New York (1950).
7. Rabinowitch and Epstein, *J. Am. Chem. Soc.*, **63**, 69 (1941).
8. West *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Chap. 21, Interscience Publishers, Inc., New York (1949).

5. POLARIMETRY

Experience is gained in the operation of the polarimeter and its use in the characterization of optically active compounds.

Theory.[4] On passage into an anisotropic crystal, ordinary nonpolarized light is resolved into two plane-polarized components, whose planes of polarization are mutually perpendicular. The velocities of propagation of these two components through the crystalline medium are different because of the difference in the index of refraction of the medium for the two differently polarized rays. This makes possible the elimination of one component to provide a source of plane-polarized light. The common Nicol prism is constructed by cutting a calcite prism in half along a suitable diagonal plane and cementing the sections together with Canada balsam. At the calcite—Canada balsam interface, one component is totally reflected to the side, where it is absorbed by a coating applied to the prism. The other component, for which the refractive index of the balsam and the calcite are almost equal, is freely transmitted.

Certain substances possess the power of rotating the plane of polarization of plane-polarized light. This phenomenon is observed in some gases and in many crystals, liquids, and solutions. In the case of crystals the rotation may be due to the arrangement of the atoms in the molecules (sucrose), or it may be due to the lattice structure of the crystal (quartz). Optical activity arises when the structure of a molecule is such that it may exist in nonsuperimposable mirror-image forms. The presence in the molecule of an asymmetric carbon atom (one for which all four attached groups are different) leads to such a structure and is the most common, but not the only, cause of optical activity. Optical activity is common, for example, in inorganic compounds; $[Rh\{(HN)_2SO_2\}_2(H_2O)_2]^-$, an inorganic ion, has been resolved into its two optically isomeric forms.[8] The explanation of the origin and mechanism of optical rotatory power is a difficult theoretical problem which is progressing toward a quantitative solution.[6]

Compounds of chemical interest are ordinarily studied in solution. The magnitude of the optical rotation is affected by the concentration of the solution, the length of the path of the light in the solution, the wavelength of the light, the temperature, and the nature of the solvent. To eliminate some of these variables, the specific rotation $[\alpha]_\lambda^t$ for a given wavelength λ at a given temperature t is defined by the relation

$$[\alpha]_\lambda = \frac{100\alpha}{lc} = \frac{100\alpha}{lpd}$$

where α = observed angle of rotation
l = length of light path, *decimeters*
c = concentration of solute, g solute/100 ml solution
p = concentration of solute, g solute/100 g solution
d = density of solution, g/ml

The specific rotation is usually referred to the sodium 5890-5896 A doublet termed the D line, or to the mercury line at 5460 A, which is to be preferred for work of high accuracy.[1,4]

The magnitude of the optical rotation is measured with a polarimeter, which consists primarily of two Nicol prisms, between which the optically active substance is placed. When the second Nicol, known as the *analyzer*, is placed at right angles to the first, no light can pass through, but when a substance that is capable of rotating the plane of polarized light is inserted between the Nicols, light can again be seen through the analyzer. The angle through which the analyzer must be turned to darken the field again is the measure of optical rotation. If the analyzer is turned clockwise to restore darkness, the substance is said to be dextrorotatory. If darkness reappears when the analyzer is turned counterclockwise, it is levorotatory. The angle could be read when the field is darkest, but the error would be large. It is much better to compare the field with another field of nearly the same brightness, as is done in the half-shadow or triple-shadow polarimeter.

The principle of the Landolt-Lippich triple-shadow polarimeter is illustrated in Fig. 8. Behind the large polarizing Nicol prism *P* are placed two auxiliary Nicols, *P*′ and *P*″, whose planes of polarization have been adjusted to make an angle θ with that of the principal polarizing prism *P*. The angle θ may be adjusted to optimum conditions which will depend on the intensity of the light and the transparency of the liquid. When the analyzer *A*, whose orientation is indicated by the instrument scale, is turned so that it is at right angles with the main polarizing Nicol, the central strip of the field, as viewed through the magnifying eyepiece, is dark and the sides are lighter, as shown at I. When the analyzer is turned through the small angle θ to cross with the smaller Nicols, the sides are dark and the central strip is lighter, as shown at II. When the analyzing Nicol is turned back through half of this small angle, it gives a uniform field as shown at III. This proper setting is readily found, and the corresponding reading of the scale is recorded. The double-field polarimeter (Laurent type) employs only one auxiliary Nicol prism which covers half the field of the polarizing prism. The field of view is hence

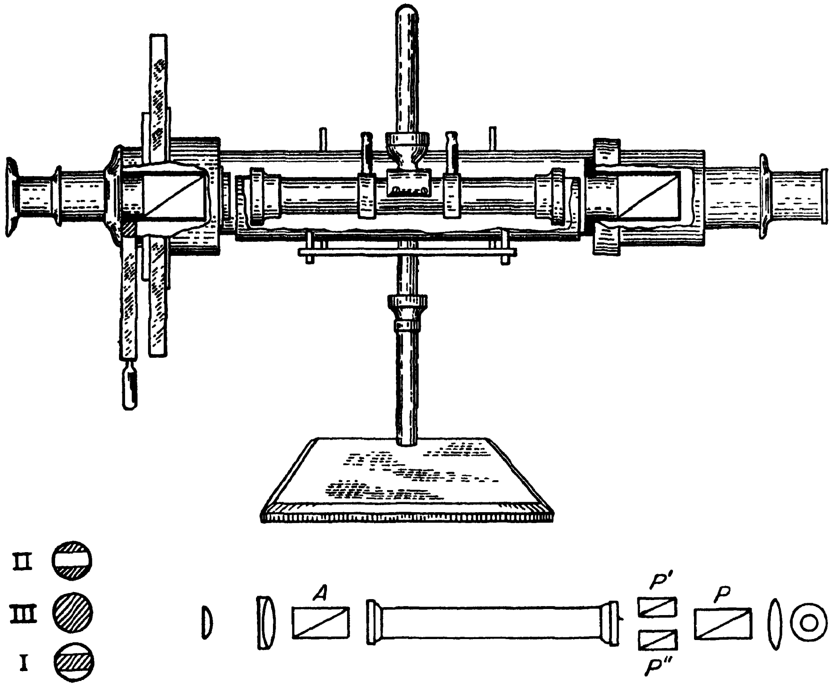

FIG. 8. Polarimeter.

divided into two parts, and the reference analyzer setting is again that which gives a uniformly illuminated field. The scale is usually graduated directly into quarters of degrees, and with the aid of verniers and a magnifying lens, the angles may be read to 0.01°.

Apparatus. Polarimeter; sodium-vapor lamp and mercury-vapor lamp or other sources of monochromatic light; sugar solutions; filters.

Procedure. Solutions of approximately 5, 10, and 15 g of sugar are made up to volume in 100-ml volumetric flasks. The crystallized sucrose should be heated to 105°, cooled in a desiccator, and weighed out accurately. The solution is mixed thoroughly by pouring it from the filled volumetric flask into a clean dry beaker and back again, repeating the process several times. Inadequate mixing is the most common source of error in this experiment.

Monochromatic light sources must be used with the polarimeter because of the existence of rotatory dispersion; the angle of rotation depends on the wavelength of the light used. To demonstrate this phenomenon for sucrose, the sodium-vapor lamp is supplemented as a light source by a mercury-vapor lamp, such as Type H-4, with which filters* are used to isolate the strong lines in the visible region at 5780 A (yellow), 5460 A (green), and 4358 A (blue). For accurate work a monochromator is used to ensure adequate quality of illumination. The light source should be placed at the proper focal distance from the end of the polarimeter (about 20 cm) and should not be close enough to heat the instrument. It must be carefully positioned on the optical axis of the instrument to ensure uniform illumination of the polarizer.

The tube is rinsed and filled with distilled water, as full as possible, and the cap is screwed on, not tightly enough to cause strain as this would produce an additional optical rotation. Any small air bubble remaining is driven up into an enlargement, above the line of vision. The glass plates at the ends must be clean, and the exposed surface must be dry. The analyzer is rotated until the field is uniform, and several readings are taken. The average gives the zero point. The setting of the analyzer should always be approached from the same direction in order to maintain identical mechanical conditions. The zero reading is subtracted from the readings on the optically active material. It should be taken at the beginning and end of each set of determinations.

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* Wratten filters may be obtained from the Eastman Kodak Co., for the yellow line No. 22, for the green line No. 77, for the blue line No. 40. The glass-filter combinations supplied by the Corning Glass Works may also be used. An excellent liquid filter solution for the 4358 A line is described in Chap. 24. Some polarimeters are equipped with a removable glass filter, for use with the sodium D line source, which must be removed when other wavelengths are employed.

The tube is next rinsed two or three times with the sugar solution and filled as before; three or more readings are taken. The difference between this average reading and the zero reading gives the rotation. For each solution the rotation is measured for each wavelength of light available. The concentration of sugar in an unknown solution is determined by measuring the rotation.

Calculations. The specific rotation of sucrose is calculated for each of the wavelengths employed from the observed optical rotations for the pure sucrose solutions. The results are compared with the values given in tables.[5] The change with temperature of the specific rotation of sucrose in water solution is approximately −0.02 per cent/°C in the neighborhood of room temperature and is essentially independent of wavelength.

Plots are made of optical rotation versus concentration for each wavelength and of specific rotation versus wavelength. The concentration of sucrose in the solution of unknown concentration is determined.

Practical Applications. Optical rotation is used in identifying materials and in determining the structure of organic compounds.[4] It finds important applications in quantitative analysis, as, for example, in the determination of the concentration of sugar in solutions.[1,2] Certain chemical changes may be followed without disturbing the system, as, e.g., in the rate of inversion of cane sugar by catalysts (described in Exp. 28).

Suggestions for Further Work. Other substances which are optically active, such as tartaric acid or camphor, may be studied in the same manner as sugar. Nonaqueous solutions may be used, e.g., camphor in benzene, carbon tetrachloride, and acetone.[7] The influence of solvent on the optical rotation of the solute has not yet found quantitative explanation.

References

1. Bates *et al.*, Polarimetry, Saccharimetry and Sugars, *Natl. Bur. Standards Circ.*, **C440** (1942).
2. Browne and Zerban, "Physical and Chemical Methods of Sugar Analysis," 3d ed., John Wiley & Sons, Inc., New York (1941).
3. Gilman, "Organic Chemistry," 2d ed., John Wiley & Sons, Inc., New York (1943).
4. Heller *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Chap. 23, Interscience Publishers, Inc., New York (1949).
5. International Critical Tables, Vol. II, McGraw-Hill Book Company, Inc., New York (1928).
6. Kauzmann, Walter, and Eyring, *Chem. Revs.*, **26,** 339 (1940).
7. Landolt, "The Optical Rotary Power of Organic Substances and Its Practical Applications," Chemical Publishing Company, Inc., Brooklyn, N.Y. (1902).
8. Mann, *J. Chem. Soc.*, **1933,** 412.

CHAPTER 3

THERMOCHEMISTRY

6. HEAT OF COMBUSTION

Experience is gained in the operation of a combustion bomb and in the calculation of calorimetric data.

Theory.[6,11] Among thermochemical reactions the oxidations are the most common and the most important. Nearly all organic compounds can be oxidized completely, and the reactions proceed rapidly. Accurate measurements of the heats of reaction are therefore possible, and the heats of combustion are used extensively in the various calculations of thermochemistry.

A powerful oxidizing agent is needed to oxidize all the material rapidly and completely, and in accurate work the material is burned in a heavy steel bomb with oxygen under a pressure of about 25 atm. A special acid-resisting steel alloy is used in the construction of the bomb because water and nitric acid (originating from nitrogen in the bomb either from the air initially present or as an impurity in the oxygen) are always produced in the combustion. In the case of compounds containing nitrogen or sulfur, considerable amounts of acid may be formed. Special techniques have been developed to improve the oxidation of compounds containing halogen atoms.[5]

The adiabatic-jacket method[1,7] of calorimetry is convenient; it eliminates the cooling correction by keeping an outer bath always at the same temperature as the calorimeter. In highly precise work, however, corrections must also be made for the heat of stirring of the calorimeter, evaporation of water from the calorimeter, etc. It should be noted also that the cooling correction which is required when an isothermal jacket is used can be made with a high degree of accuracy;[2] its elimination by the adiabatic method is a convenience in work of moderate accuracy[2,11] but not a necessity. In the exacting modern research measurements, the isothermal-jacket method is used almost exclusively.

The experimental heat of reaction is calculated as

$$\Delta E = -c\Delta T \qquad (1)$$

Here c represents the total heat capacity of the calorimetric system (commonly determined by measurements with a combustion standard such as benzoic acid for which the value of ΔE is known), and ΔT is the rise in temperature resulting from the thermochemical reaction. The minus sign is required to indicate that heat is evolved, since both c and ΔT are positive quantities. The reaction takes place at constant volume, and the heat is represented by ΔE, the change of internal energy. The heat of reaction per gram or per mole is calculated from the weight of sample used.

The most important physical-chemical use of heat of combustion data is in the calculation of standard heats of formation for compounds with the aid of the accurately known standard heats of formation of carbon dioxide and water. For this calculation there is required the value of the standard heat of combustion, ΔH^0, which is the enthalpy change in the combustion reaction per mole for specified standard reference states of the products and reactants. The direct experimental measurement yields the value of ΔE_B, the heat of reaction per mole for the reaction as carried out in the bomb. It is necessary first to calculate ΔE^0, the internal energy change for the standard reaction, from ΔE_B by correcting for the differences between experimental conditions and those for the standard reaction. The method for making this correction was devised by Washburn[12] and has been summarized by Sturtevant.[11] This correction may be as large as several tenths of a per cent and is quite important in view of the precision of 0.01 per cent attained in modern research. The standard heat of combustion, ΔH^0, may then be calculated:

$$\Delta H^0 = \Delta E^0 + \Delta(PV) \tag{2}$$

Ignoring changes in volume due to solids or liquids and assuming that the gases present behave ideally, a sufficiently accurate assumption,

$$\Delta(PV) = (n_2 - n_1)RT \tag{3}$$

where n_2 = number of moles of gaseous products
n_1 = number of moles of reacting gases
R = gas constant (1.987 cal deg^{-1} mole^{-1})
T = absolute temperature

Apparatus. Parr, Emerson, or other adiabatic calorimeter; pellet press; two thermometers graduated to 0.01°; iron wire; benzoic acid, naphthalene, sugar; 0.1 N sodium hydroxide.

Procedure. A typical calorimeter is shown in Fig. 9. A little less than 1 g of the material to be oxidized is pressed into a pellet with the pellet machine to prevent incomplete burning due to mechanical loss of material during the combustion. The weight of the pellet is obtained. Coal and some other materials are difficult to make into pellets, and under these conditions the material is simply weighed in the pan and packed around the ignition wire.

The pellet is placed in the sample pan. The ends of the weighed ignition wire are attached to the two terminals. The wire loop is adjusted to give firm contact with the pellet. The wire should not touch the sample pan. The bomb is set into a steel receptacle on a firm table, and the cover is placed carefully in position. The heavy assembly ring is then screwed down, clamping the cover firmly on the bomb. The final tightening is accomplished with the help of a spanner wrench with a handle 50 or 100 cm long. The surfaces on which the closure is effected must be kept scrupulously clean, and every precaution must be taken to avoid marring them. When the bomb is dismantled, they should be protected by being placed only on a clean, soft surface, e.g., a folded towel. Recently a Parr bomb of new design has become available in which the cover can be screwed down adequately by hand.

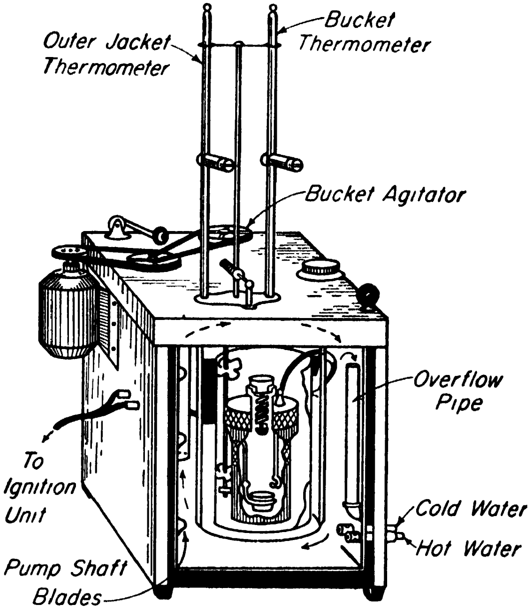

FIG. 9 Adiabatic combustion calorimeter (Parr).

The adapter, which is connected by a metal tube to an oxygen tank, is then connected to the bomb. With the Emerson bomb, the bomb needle valve is opened slightly, and oxygen is admitted slowly until the pressure gauge connected to the oxygen line reads 25 atm. The bomb valve and tank valve are then closed, and the pressure in the oxygen line is relieved by opening the auxiliary relief valve. The adapter is then removed from the bomb. With the Parr bomb, the bomb valve is operated automatically by the gas pressure.

Approximately 2,000 ml of water, the temperature of which has been adjusted approximately to room temperature, is weighed into the calorimeter can, which is then transferred to the adiabatic jacket. The ignition wires are connected to the bomb, and the bomb is placed in the water. With the Parr bomb, one ignition wire is connected to the terminal on the cover, the other to the calorimeter can, which is in electrical contact with the bomb. A possible ignition circuit is shown in Fig. 10. This transformer-coupled circuit is recommended because it provides isolation from the 110-volt line, one side of which is grounded.

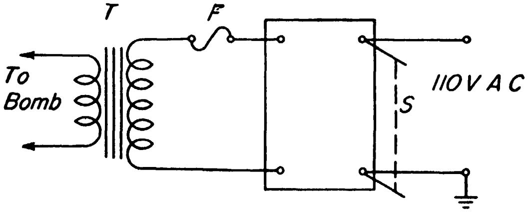

FIG. 10. Ignition circuit for bomb calorimeter: *F*, 5-amp fuse; *T*, step-down transformer, secondary rating about 14 volts at 5 amp (two filament transformers with primaries connected in parallel and secondaries in series can be used); *S*, DPST switch, preferably interlock type, as Insuline Corp. of America No. 1280.

The water in the calorimeter can must cover the bomb completely. If gas bubbles escape from the bomb, the assembly ring must be tightened, or the bomb gaskets may need replacement. If the charge is ignited while a leak is present, the bomb may be seriously damaged.

The cover of the calorimeter chamber is set in place, and the thermometers and stirrer are lowered into position. The jacket is then heated by closing its electrical circuit to bring its temperature within 0.02 to 0.03° of that of the water in the calorimeter can. Alternating current passes directly through the water of the outer jacket in the Emerson calorimeter. *Tap water* should be placed in the jacket; only under rare circumstances should sodium chloride or other electrolyte be used. In the Parr calorimeter the outer jacket is heated by running in water from a reservoir heated either by gas or electricity. In this type the water circulates through the cover also. In either type, cold water is added directly to reduce the jacket temperature.

Thermometers reading in the 20 to 30° range are preferred, but Beckmann thermometers may be used if care is taken to set them to read nearly alike. For precise work the thermometer in the calorimeter can must be calibrated, and the precautions described in Chap. 20, which are required to ensure accuracy in measurements with mercury thermometers, must be carefully observed. A matched pair of calorimeter thermometers graduated to 0.01° is preferred. Where the highest possible accuracy is required, a platinum resistance thermometer[2] is employed. The initial temperature must be such that the mercury is on the lower part of the scale, for if the rise in temperature is sufficient to cause the mercury to go above the top of the scale, the determination is lost.

The stirrer is started, and the thermometer in the inner can is read for a few minutes to make sure that equilibrium has been attained and that there is no further change in temperature. This temperature is recorded as the initial temperature. The ignition switch is then closed; as soon as the charge has been fired, as shown by the indicating lamp in the ignition circuit or by a rise in temperature in the calorimeter can, the switch is opened in order to prevent heating by passage of electricity through the water of the inner calorimeter.

The temperature of the calorimeter rises very quickly at first, and the jacket temperature is kept as close as possible to that of the calorimeter can by closing the heating-circuit switch* as required or, in the Parr calorimeter, by admitting hot water as needed. The temperature rise will become slower, and after 4 or 5 min the temperature again becomes stationary. During the rapid change of temperature it may not be possible to keep the two thermometers reading exactly alike, but toward the end of the experiment the difference can be reduced to a few hundredths of a degree.

When the final temperature has been reached, as evidenced by the fact that there is no further change, the bomb is removed, the pressure is relieved by opening the needle valve (Emerson) or depressing the valve stem (Parr), and the cover is removed. The bomb is rinsed out with a little water, which is then titrated with 0.1 N sodium hydroxide to determine the amount of nitric acid formed from the nitrogen of the air originally present and from the nitrogen contained in the compound, if any. The weight of the unoxidized iron wire is determined. The bomb and calorimeter are thoroughly cleaned and dried in preparation for the next determination.

Two determinations are made with benzoic acid for calculating the heat capacity of the calorimeter, and two determinations with a substance whose heat of combustion is accurately known, such as naphthalene or sugar. The materials must be highly purified. The heat of combustion of a sample of coal or other "unknown" may then be measured.

Calculations. The heat capacity of the calorimeter includes the heat

* No part of the Emerson calorimeter should be touched while the heating-circuit switch is closed.

required to raise the bomb, thermometer bulb, calorimeter can, stirrer, and other accessories through 1°. It cannot be calculated accurately from the specific heats of the materials but must be determined experimentally under actual working conditions.

For every gram of benzoic acid burned in the bomb, 6,318 cal of heat[4] is evolved in the calorimeter, and for every gram of iron wire oxidized, 1,600 cal is introduced. The total heat supplied to the calorimeter is calculated from the weights of benzoic acid and iron wire oxidized, and the heat produced by the formation of nitric acid. The heat evolved in the formation of dilute aqueous nitric acid from nitrogen, oxygen, and water may be taken as 13,800 cal mole^{-1}.

The heat absorbed by the water in the calorimeter can is obtained by multiplying the observed temperature rise by the heat capacity of the water, which is obtained from the mass of water used and the specific heat of water; the latter may be taken as 0.999 cal g^{-1} deg^{-1}. The difference between the total heat evolved and the heat absorbed by the water represents the amount of heat absorbed by the calorimeter. The heat capacity of the calorimeter is obtained by dividing this difference by the temperature rise.

The heat of combustion of the naphthalene or other substance can then be calculated. The heat capacity of the calorimeter is added to the heat capacity of the water used in the determination, and the sum is multiplied by the temperature rise to give the total heat evolved. From this quantity are subtracted the heats evolved by the oxidation of the known weight of iron wire oxidized and by the oxidation of nitrogen to nitric acid, giving the heat of combustion of the material under investigation.

The experimental heat of combustion ΔE_B is reported for each substance in terms of both calories per gram and calories per mole. Assuming that the difference between ΔE_B and ΔE^0 is negligible, the standard heat of combustion ΔH^0 is calculated by use of Eqs. (1) and (2), and the standard heat of formation of the known compound is calculated, using the values -94.05 and -68.32 kcal for the standard heats of formation of carbon dioxide and liquid water, respectively. The calculated value is compared with the accepted value.[3,9,10]

Practical Applications. Various heats of reaction and heats of formation can be calculated from the heats of combustion. For example, the heat of oxidation of carbon to form carbon monoxide may be obtained by subtracting the heat of combustion of carbon monoxide from the heat of combustion of carbon. Heats of isomerization of organic compounds, which cannot be measured directly, may also be determined indirectly through heat-of-combustion measurements.[6] The heats of formation obtained from heat-of-combustion measurements on the compounds concerned may be combined with entropy data derived from specific-heat measurements to permit the calculation of equilibrium constants from thermochemical data alone.[11]

The heating value of fuels and the so-called "caloric value" of foods may be determined directly by this method.

Suggestions for Further Work. The heat of combustion of other pure organic compounds may be determined and compared with the accepted values.

The heating value of various samples of coal or food may be determined. These materials cannot readily be made into pellets, and they are placed in the sample pan around the ignition wire. The oxygen must be admitted slowly to prevent scattering of the powder. With coal a 0.5-g sample is sufficient.

Liquids may be used if they are sealed off in thin, flat glass bulbs[6,8] and weighed. A weighed quantity of benzoic acid or naphthalene is placed on the bulb, and its combustion breaks the glass and permits combustion of the liquid. Obviously the heat released by burning the benzoic acid must be subtracted from the total heat released.

References

1. Daniels, *J. Am. Chem. Soc.*, **38,** 1473 (1916).
2. Dickinson, *Natl. Bur. Standards (U.S.), Bull.*, **11,** 189 (1915).
3. International Critical Tables, Vol. V, p. 162, McGraw-Hill Book Company, Inc., New York (1928).
4. Jessup, *J. Research Natl. Bur. Standards*, **29,** 247 (1942).
5. Popoff and Shirokich, *Z. physik. Chem.*, **A167,** 183 (1933).
6. Prosen and Rossini, *J. Research Natl. Bur. Standards*, **27,** 289 (1941).
7. Richards, *J. Am. Chem. Soc.*, **31,** 1275 (1909).
8. Richards and Barry, *J. Am. Chem. Soc.*, **37,** 993 (1915).
9. Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Standards Circ.*, **500** (1952).
10. "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44 Report, Carnegie Press, Pittsburgh (1955).
11. Sturtevant *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Chap. 14, Interscience Publishers, Inc., New York (1949).
12. Washburn, *J. Research Natl. Bur. Standards*, **10,** 525 (1933).

7. HEAT OF IONIC REACTIONS

This experiment gives practice in a simple calorimetric determination and illustrates the heat effects accompanying certain inorganic reactions.

Theory. For chemical processes at constant pressure, in which the only work done is expansion work, the heat absorbed is equal to the enthalpy change of the system. When two solutions are mixed and allowed to react in a Dewar flask, the total enthalpy remains constant; but a measurement of the temperature change together with knowledge of the heat capacity of the product system makes it possible to calculate the enthalpy change at the initial temperature. The total enthalpy change which is zero may be divided into two parts, that for the reaction and that for the heating of the solutions. If the temperature rise is ΔT and the heat capacity of the final system is c_p

$$0 = \Delta H + c_p \Delta T$$

or $$\Delta H = -c_p \Delta T \qquad (1)$$

Since ΔH is defined as the heat absorbed, it is negative for an exothermic reaction.

The neutralization of a solution of an acid HA by a solution of a base BOH is represented by the equation

$$HA \cdot xH_2O + BOH \cdot yH_2O = BA \cdot (x + y + 1)H_2O$$

where x = number of moles of water per mole of acid
y = number of moles of water per mole of base

When HA, BOH, and BA are strong electrolytes, it is found that the enthalpy change at 25° is very close to −13.67 kcal mole^{-1}. Comparison with this value of the enthalpy changes for weak electrolytes indicates the nature of the heat effects of processes other than $H^+ + OH^- = H_2O$.

In this experiment 0.5 N HCl is added to an equal volume of 0.5 N NaOH to produce 0.25 N NaCl. The reaction may be written

$$HCl \cdot 100H_2O + NaOH \cdot 100H_2O = NaCl \cdot 201H_2O$$

the molar ratio of 100 corresponding to an approximately 0.5 N solution. When the equation is written in this form, the extensive tabulation of heat-of-formation data by Bichowsky and Rossini[1] or the Bureau of Standards[6] may be used directly. The heat of formation ΔH_f of a substance is the enthalpy change for the reaction in which a mole of the substance is formed from elements in their standard states. Thus, to obtain the heat of reaction, we have

$$\begin{aligned}\Delta H_{291} &= \Delta H_f(NaCl \cdot 200H_2O) + \Delta H_f(H_2O) - \Delta H_f(HCl \cdot 100H_2O) \\ &\qquad - \Delta H_f(NaOH \cdot 100H_2O) \\ &= -97.12 - 68.37 - (-39.38) - (-112.10) \\ &= -14.01 \text{ kcal*}\end{aligned}$$

All the data given by Bichowsky and Rossini are for 18°C or 291°K. A conversion may be made to another temperature using the heat-capacity data in Table 1. Thus, for 25°C

$$\begin{aligned}\Delta H_{298} &= \Delta H_{291} + [C_p(\text{products}) - C_p(\text{reactants})](298 - 291) \\ &= -14.01 + (3.607 - 1.785 - 1.774)(7) \\ &= -13.67 \text{ kcal}\end{aligned}$$

Apparatus. Two vacuum bottles with ring stirrers (Exp. 12); 0.5 N NaOH; 0.5 N HCl; barium chloride; potassium sulfate; two 100-ml pipettes; Beckmann thermometer or calorimeter thermometer.

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* Figures given here and elsewhere in the book are for the defined calorie, which is equal to 4.1840 abs joules or 4.1833 int joules.

Procedure. Cylindrical vacuum bottles make excellent calorimeters because they reduce the cooling corrections to a very low value.[3] A wide-mouthed vacuum bottle of the pint size is convenient for many experiments. The bottle is provided with a cork, an accurate thermometer, and a ring stirrer of glass tubing, preferably of small heat capacity. The arrangement is like that shown in Fig. 19, Exp. 12. A thermometer graduated to 0.1° is satisfactory for some experiments, but a calorimeter thermometer or Beckmann thermometer graduated to 0.01° is more desirable. A Beckmann thermometer is adjusted to read near the bottom of the scale; otherwise the mercury thread may go above the top of the scale during the reaction. Continuous vigorous stirring is essential in all calorimetric measurements. A stirrer of the propeller type, driven by a motor, is better than the hand stirrer.

If a solution of 0.5 N sodium hydroxide free from carbonate is not available as a stock reagent, it may be prepared according to the method given in Chap. 26, under Sodium Hydroxide, and titrated against standard acid.

The dry calorimeter is weighed to 0.1 g on the platform balance, exactly 150 ml of NaOH is pipetted in, and the bottle is reweighed. The weighings are necessary for a calculation of the heat capacity of the solution. A volume of 0.5 N hydrochloric acid solution slightly in excess of that required to neutralize the NaOH solution is added to the second vacuum bottle. Since the acid is in excess, there is more than enough to neutralize the alkali, and thus the exact amount is not important except as it affects the heat capacity of the solution. After the experiment is completed, the solution should be tested with a drop of phenolphthalein. If an alkaline reaction appears, the experiment is worthless because the acid is too dilute and the base is not used up.

The thermometer is set into the stopper of the vacuum bottle containing the hydrochloric acid solution, and the ring stirrer is adjusted so that there is no possibility of hitting and breaking the thermometer bulb. For a permanent piece of equipment, the thermometer jacket made from polystyrene tubing as shown in Fig. 19 is recommended. After a steady temperature is obtained the same thermometer is used to measure the temperature of the sodium hydroxide solution. It is allowed to drain while touching the side of the bottle and is then rinsed with water and wiped dry before inserting in the other vacuum bottle.

The acid solution is then poured into the vacuum bottle containing the sodium hydroxide with rapid stirring, and the time is noted. The mixture is stirred constantly, and the temperature is read every minute for several minutes until the rate of temperature change becomes small and constant. When the experiment is complete, the calorimeter is reweighed to determine the weight of the hydrochloric acid solution added.

Check determinations are made on the heat of neutralization of hydrochloric acid and sodium hydroxide, and the average is used for calculating the heat capacity of the calorimeter.

In the same manner the heat of neutralization of acetic acid and sodium hydroxide is obtained by use of duplicate determinations.

The heat of precipitation of lead iodide is next determined. The reaction may be written

$$Pb(NO_3)_2 \cdot 100H_2O + 2(KI \cdot 50H_2O) = PbI_2(c) + 2(KNO_3 \cdot 100H_2O)$$

All operations can be carried out gravimetrically, starting with solutions of composition $Pb(NO_3)_2 \cdot 100H_2O$ and $KI \cdot 50H_2O$. In order to keep the final volume comparable with that in the preceding experiments, about 28 g of KI is weighed out and water is added in the proportion 50 moles of water per mole of KI. The $Pb(NO_3)_2$ solution is prepared by dissolving about 2 per cent in excess of that required by the equation in the appropriate weight of water. The solutions are mixed after their temperatures have been measured as described above, the temperature rise is measured, and a duplicate determination is made.

As an alternative to the determination of the heat of precipitation of PbI_2, the heat of formation of cupric ammonia complexes may be determined. If sufficient ammonium hydroxide is added, the reaction is

$$CuSO_4 + 4NH_3 = Cu(NH_3)_4SO_4$$

A 0.05 M solution of $CuSO_4$ is suitable, and an excess of ammonium hydroxide over that required by the preceding equation is added. Since this reaction goes to completion only at a rather high ammonia concentration, the heat evolved depends upon the concentration of ammonium hydroxide used. A value of ΔH for the above reaction of 18.9 ± 0.8 kcal mole^{-1} has been reported [*C.A.*, **47,** 10327*e* (1953)].

Calculations. The time-temperature curves are plotted, starting with the time of mixing. The nearly straight line that is obtained shortly after mixing is extrapolated back to the time of mixing. The difference between this extrapolated temperature and the initial temperature which the system would have if the solutions were brought into contact without reaction is ΔT in Eq. (1). The initial temperature may be calculated from the temperatures of the initial solutions, their weights, and the specific-heat data in Table 1.

The heat capacity of the final system, c_p in Eq. (1), is equal to the sum of the heat capacities of the reaction products and the calorimeter. The heat capacities of the solutions may be calculated from the data in Table 1. The concentrations of the solutions used are sufficiently close to those in the table for direct use.

TABLE 1. SPECIFIC HEATS IN THE TEMPERATURE RANGE 18 TO 25°C

Solution	Specific heat, cal g^{-1} deg^{-1}	Reference
$NaOH \cdot 100H_2O$	0.969	Richards and Gucker, *J. Am. Chem Soc.*, **51,** 712 (1929)
$HCl \cdot 100H_2O$	0.965	Richards, Mair, and Hall, *J. Am. Chem. Soc.*, **51,** 727 (1929)
$H_2SO_4 \cdot 200H_2O$	0.975	International Critical Tables, Vol. V, 115
$HC_2H_3O_2 \cdot 100H_2O$	0.989	Richards and Gucker, *loc. cit.*
$HNO_3 \cdot 100H_2O$	0.958	Richards and Rowe, *J. Am. Chem. Soc.*, **43,** 770 (1921)
$NaCl \cdot 201H_2O$	0.980	Gillespie, Lambert, and Gibson, *J. Am. Chem. Soc.*, **52,** 3806 (1930)
Na_2SO_4 $401H_2O$	0.976	Randall and Rossini, *J. Am. Chem. Soc.*, **51,** 323 (1929)
$NaC_2H_3O_2 \cdot 201H_2O$	0.983	Richards and Gucker, *loc. cit.*
$NaNO_3 \cdot 201H_2O$	0.974	Randall and Rossini, *loc. cit.*
$NH_4OH \cdot 50H_2O$	0.999	"Handbook of Chemistry and Physics"
$CuSO_4 \cdot 50H_2O$	0.841	*Ibid.*
$CuSO_4 \cdot 100H_2O$	0.908	*Ibid.*
$PbI_2(s)$	0.042	Lange, "Handbook of Chemistry"
$KNO_3 \cdot 100H_2O$	0.943	Randall and Rossini, *loc. cit.*
$Pb(NO_3)_2 \cdot 100H_2O$	0.85	International Critical Tables, Vol. V, 122
$KI \cdot 50H_2O$	0.826	Rossini, *J. Research Natl. Bur. Standards*, **7,** 47 (1931)

The heat capacity of the calorimeter is obtained by introducing a known quantity of heat into the calorimeter and measuring the temperature rise. The known quantity of heat may be computed from the heat of neutralization of HCl and NaOH, which was found on page 36 to be 13.67 kcal mole^{-1} at 25°C. The heat capacity of the calorimeter may be considered constant, since virtually the same volume of solution was used in each determination.

With the heat capacity of the calorimeter thus determined, the heat of neutralization of sodium hydroxide and acetic acid and the heat of precipitation of lead iodide may be calculated using Eq. (1). The heats are converted to molar quantities and compared with those computed from heat of formation data.

Practical Applications. Measurements of heats of neutralization are of value in studying the properties of electrolytes. This simple type of calorimeter is useful and adequate for the determination, with moderate accuracy, of the heat of most ordinary reactions in solution.

Suggestions for Further Work. Miller, Lowell, and Lucasse[4] suggest studies with sulfamic, acetic, monochloroacetic, oxalic, and tartaric acids neutralized with NaOH and with NH_4OH to illustrate various factors involved in neutralizations.

Pattison, Miller, and Lucasse[5] describe procedures for determining heats of several types of reactions with a simple calorimeter:

A gas is evolved:

1. Decomposition of H_2O_2 using MnO_2 as a catalyst
2. Reaction of HCl with calcium carbide

Undissociated molecule or complex ion formed:

3. Reaction of $Hg(NO_3)_2$ with NaCl

Oxidation-reduction:

4. Reaction of $KBrO_3$ and HBr

Precipitate formed:

5. Reaction of NaOH with $MgSO_4$ and with $Al_2(SO_4)_3$

Organic:

6. Reaction of acetic anhydride with NaOH
7. Reaction of hydroxylamine and acetone

Solution:

8. Solution of anhydrous and hydrated sodium acetate

Dilution:

9. Dilution of ethyl alcohol with water
10. Dilution of H_2SO_4 with water

References

1. Bichowsky and Rossini, "Thermochemistry of the Chemical Substances," Reinhold Publishing Corporation, New York (1936).
2. Kegeles, *J. Am. Chem. Soc.*, **62**, 3230 (1940).
3. Mathews and Germann, *J. Phys. Chem.*, **15**, 73 (1911).
4. Miller, Lowell, and Lucasse, *J. Chem. Educ.*, **24**, 121–122 (1947).
5. Pattison, Miller, and Lucasse, *J. Chem. Educ.*, **20**, 319–326 (1943).
6. Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Standards, Circ.*, **500** (1952).
7. Sturtevant *in* Weissberger (ed.), "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, p. 731, Interscience Publishers, Inc., New York (1949).

8. HEAT OF SOLUTION

The integral heat of solution of potassium nitrate in water is determined as a function of concentration. These results permit the calculation of differential heats of solution and integral heats of dilution.

Theory. The quantitative study of the thermal effects which accompany the dissolution of a solute in a pure solvent or a solution has been systematized through the introduction of the concepts of the integral and differential heats of solution.

The integral heat of solution at a particular concentration is the heat of reaction $\Delta H_{\text{I.S.}}$* at a specified temperature and pressure when one mole of solute is dissolved in enough pure solvent to produce a solution of the

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* Because the processes considered here take place at constant pressure and only *pv* work is done, the heats of reaction are given by the corresponding enthalpy changes.

given concentration. Thus, if one mole of solute is dissolved in 500 g of water at constant T and P, the heat of reaction gives the value of the integral heat of solution at the concentration 2 molal.

The differential heat of solution, $\Delta H_{\text{D.S.}}$, may be visualized as the heat of solution of a mole of solute in a quantity of solution, of given concentration, so large that the addition of one more mole of solute does not change the concentration appreciably. Correspondingly, if the addition of dm moles of solute to a finite quantity of solution produces at constant T and P the infinitesimal heat effect δq, the differential heat of solution at the concentration of the solution is the ratio $\delta q/dm$. The differential heat of solution obviously cannot be determined accurately through direct experimental measurement, but it can be evaluated indirectly from a knowledge of the integral heat of solution:

$$\Delta H_{\text{D.S}} = \frac{d(m\Delta H_{\text{I S.}})}{dm} \tag{1}$$

This relation may be clarified as follows. The quantity $(m\Delta H_{\text{I.S.}})$ represents the heat effect for the production of a solution containing m moles of solute and 1,000 g of solvent. The differential $d(m\Delta H_{\text{I.S}})$ then represents the difference in the heats of solution of $(m + dm)$ and m moles of solute, respectively, in 1,000 g of solvent, and thus gives the heat effect accompanying the dissolution of dm moles of solute in a solution of molality m containing m moles of solute and 1,000 g of solvent. The ratio $d(m\Delta H_{\text{I.S.}})/dm$ then is the heat of solution per mole of solute in a process conforming exactly to the definition given for the differential heat of solution.

From their definitions, the integral and differential heats of solution become identical as the concentration of the solution approaches zero. The difference between the two increases in general with increasing concentration; it is ordinarily small in the dilute solution range, but may be quite marked at higher concentrations.

The magnitudes of these heats of solution depend specifically on the solute and solvent involved. The value of the heat of solution at high dilutions is determined by the properties of the pure solute and by the interactions of the solute with the solvent. As the concentration of the solution increases, the corresponding changes in the differential and integral heats of solution reflect the changing solute-solvent and solute-solute interaction effects.

In the hypothetical case of a solid which dissolves in a given solvent to form ideal solutions, the integral and differential heats of solution become identical, independent of concentration, and numerically equal to the molar heat of fusion of the solid to give the (supercooled) liquid at the temperature of the solutions. Such behavior is approximated in some real cases, which involve nonelectrolyte solutes and, preferably, nonpolar solvents. For electrolytic solutes no such interpretation is possible, because of the marked solute-solvent and solute-solute interactions encountered.

The *integral heat of dilution*, $\Delta H_{D,m_1 \rightarrow m_2}$, between two molalities m_1 and m_2 is defined as the heat effect, at constant temperature and pressure, accompanying the addition of enough solvent to a quantity of solution of molality m_1 containing one mole of solute to reduce the molality to the lower value m_2. The process to which the integral heat of solution at molality m_2 refers is equivalent to the initial formation of the more concentrated solution of molality m_1 followed by its dilution to the lower molality m_2; the integral heat of dilution is thus equal to the difference of the integral heats of solution at the two concentrations involved:

$$\Delta H_{D,m_1 \rightarrow m_2} = \Delta H_{\mathrm{I.S.}}(m_2) - \Delta H_{\mathrm{I.S.}}(m_1) \tag{2}$$

Apparatus. Heat-of-solution calorimeter; sensitive mercury thermometer (18 to 31° in 0.01° divisions); thermistor thermometer with Wheatstone bridge and lamp and scale galvanometer; calibrated ammeter with 1-amp scale; 6-volt storage battery; stop watch or electric timer; six weighing bottles or 10-ml Erlenmeyer flasks with stoppers; potassium nitrate; switch and wire.

Procedure.[5] This experiment illustrates the special advantage that endothermic reactions offer for calorimetric measurements. When the reaction absorbs heat, the cooling effect may be balanced with electrical heating to prevent any change of temperature. It thus becomes unnecessary to know the heat capacity of the calorimeter or of the solution being studied. No cooling correction is necessary, and the method is simpler than the ordinary adiabatic method.

The essential features of a suitable calorimeter for work of moderate precision are shown in Fig. 11. The vacuum bottle minimizes heat exchange between the solution and the surroundings. A mechanical stirrer is used to provide the efficient and uniform stirring essential to the rapid dissolution of the solute. The rate of stirring, however, should be kept as low as efficiency permits to minimize the energy introduced by stirring. The stirrer shaft should be of a poor heat conductor, and proper bearings must be provided to eliminate as far as is possible heat generation by friction. (The shaft bearings may advantageously be located above the calorimeter proper.) A belt-and-pulley drive is used to keep the heat transfer by conduction and radiation from the motor at a minimum.

The calorimeter heating element should have a low temperature coefficient of resistance, a low time lag in transferring heat to the solution, and must be isolated from the solution. These requirements can conveniently be met by use of copper-sheathed, fiber-glass insulated constantin wire.* The copper sheath, soldered to the resistance wire at one end, serves as one electrical lead. At the other end, the sheath is cut back to expose a short section of the wire, to which an enameled copper lead wire is then soldered. A section of copper sheath from which the resistance wire has been removed is slipped over the lead wire, and a water-tight joint† is made between the two sections, as shown, for example, in Fig. 11. The copper-lead assembly should remain immersed for some distance past the

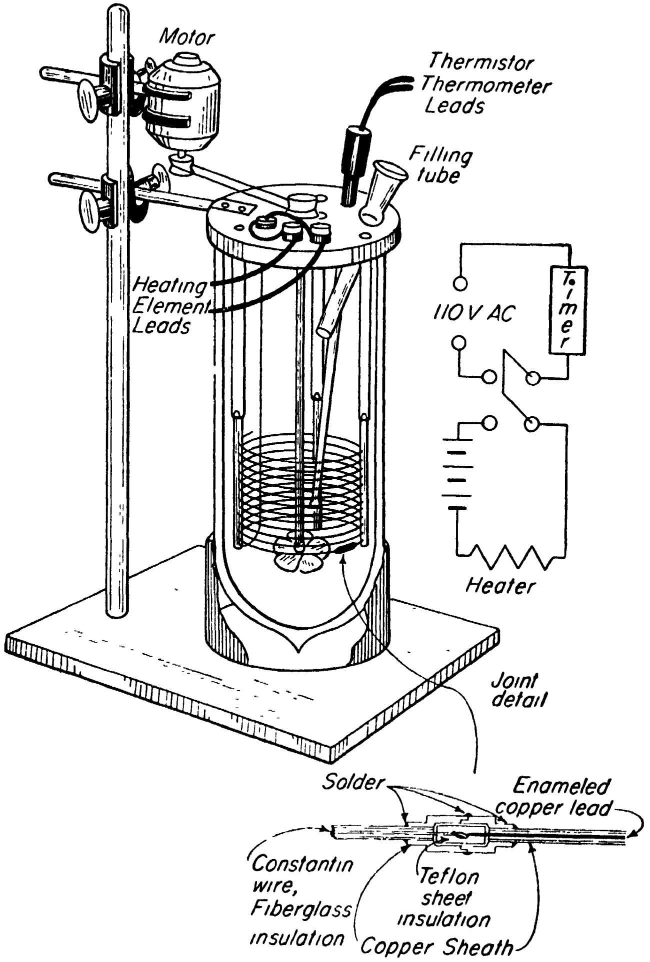

FIG. 11. Calorimeter for measuring heats of solution.

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* This wire assembly is made by the Precision Tube Company, Inc., Philadelphia, Pa., under the name Precision Coaxitube.

† The brass junction elements can be prepared at any machine shop.

joint to ensure its temperature equilibration with the solution. A heater resistance of about 7 ohms, as given by about 5 ft of 24-gauge constantin wire, is recommended because the current obtained by use of a 6-volt storage battery can be determined accurately with a 1-amp ammeter.

As temperature indicator, a sensitive mercury thermometer may be used, but a thermistor thermometer* is recommended because of its rapid and sensitive response to temperature changes. A conventional student d-c Wheatstone bridge with lamp and scale galvanometer readily makes available a thermometric sensitivity of the order of a millidegree.

Six samples of pulverized potassium nitrate, three of about 8 g and one each of 3, 4, and 5 g, are transferred to numbered weighing bottles which are then stoppered and weighed. About 200 ml of distilled water, which has been carefully adjusted to room temperature, is weighed into the vacuum bottle, and the calorimeter assembled. The thermistor thermometer is connected to the Wheatstone bridge, and the stirrer is started. The thermometer resistance is checked by means of the bridge; if the water temperature was properly adjusted as specified above, the resistance will soon show only a very slow decrease due to the temperature rise caused by stirring.

When this condition has been reached, the position of the galvanometer light balance is noted as a reference point for later use, and the first determination is started by adding the 3-g sample of potassium nitrate through the sample tube. The emptied weighing bottle is set aside to be reweighed later. The heating circuit switch is then closed, and the timer started simultaneously. It is convenient to use an electric timer so that the two circuits may be closed at once by use of a double-pole switch. The heating current is recorded, and any salt adhering to the surface of the sample tube is pushed down with a blunt glass rod or a camel's-hair brush.

The extent of the bridge unbalance is checked at frequent intervals as indicated by the magnitude of the galvanometer deflection; *the bridge dial settings are not changed.* When the unbalance has been reduced far enough so that the galvanometer light spot remains on the scale, the galvanometer circuit switch is closed and the heating current and timer are turned off. The number n of scale divisions traversed thereafter by the spot due to the lag in the heater and thermometer is noted. The heating current and timer are switched on again and turned off when the light spot has reached the point n scale divisions short of the initial balance reference point. The spot will then come to rest very close to the latter, and in this way the final temperature of the solution is matched to the initial temperature. The total heating time is recorded.

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* Available from E. H. Sargent and Co., Chicago.

The thermometer bridge balance is checked, and the second determination is made as above after addition of the 4-g sample. Since heat exchange with the surroundings is influenced by the magnitude of the temperature differential between the calorimeter and the room, the solute may profitably be added gradually during the heating period rather than all at once. The remaining samples are used in turn to extend the concentration range studied to near 2 molal. The empty weighing bottles are then reweighed.

A check is also made on the work of stirring. After the last heat of solution run is made, the temperature change due to continued stirring is followed for 15 to 30 min, and the average rise per second due to the work of stirring determined. The heating current is then turned on for 5 min and the resulting temperature rise noted. In this last work a sensitive mercury thermometer may be substituted for the thermistor type, or a calibration of the latter made to permit calculation of the actual temperature rise from the observed resistance change.

Calculations. The electrical energy E dissipated in a heater of resistance R* ohms because of the passage of a current i amperes for a time t seconds is given by the relations

$$E = i^2Rt \text{ joules} = \frac{i^2Rt}{4.184} \text{ cal} \tag{3}$$

The energy input per second due to the work of stirring is calculated by multiplying the electrical energy input per degree rise in temperature as determined in the final heating period by the corresponding temperature rise per second due to the work of stirring.

The total energy input required to restore the system to its initial temperature following the addition of each solute sample can then be calculated by adding the total work input due to stirring during the heating period to the electrical energy dissipated in the heater. The contribution of the work of stirring will be relatively small.

For each solution the total number of moles of solute present and the corresponding total energy input from the beginning of the experiment are calculated. The molality of the solution and the integral heat of solution at that concentration are then determined. The integral heat of solution $\Delta H_{\text{I S.}}$ is plotted against the molality, and the differential heat

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* The resistance of the heater will be increased by the flow of current because of the increase in the wire temperature. The required resistance value may be calculated by determining the potential drop across the heater, by use of a potentiometer, and dividing it by the current flowing. The latter in turn may be evaluated by measuring the potential drop across a relatively small standard resistance connected in series with the heater. An ammeter connected in the line can be calibrated simultaneously.

of solution is evaluated at 0.5 and 1.5 molal by use of the relation

$$\frac{d(m\Delta H_{\mathrm{I.S.}})}{dm} = \Delta H_{\mathrm{I.S}} + m\frac{d\Delta H_{\mathrm{I.S.}}}{dm} \tag{4}$$

This method is employed, rather than direct use of Eq. (1), to minimize the uncertainty in the calculated values due to the difficulty of determining accurately the slope of a curve.

The integral heats of solution at 0.5, 1, and 1.5 molal are obtained by interpolation, and the integral heats of dilution from 1.5 to 1 molal and 1 to 0.5 molal are evaluated. The various experimental results are compared with accepted values.[3,4]

Practical Applications. Integral heat of solution data are often required in energy-balance calculations for chemical processes for engineering purposes. They are also used in the indirect evaluation of standard heats of formation of compounds for which heats of reaction in solution must be utilized. Measurements of the integral heat of solution may be used for the calculation of integral heats of dilution when no direct determinations of the latter are available. The differential heat of solution at saturation determines the temperature coefficient of solubility of the solute[6] (compare Exp. 23).

Suggestions for Further Work. The method here described is suitable for measurements on most endothermic reactions. The apparatus may be used for exothermic reactions by determining the temperature rise due to the reaction, then cooling the system to the initial temperature and reheating it through the identical temperature range by means of the electrical heating coil. It can be used also for the measurement of the specific heats of pure liquids or solutions after the heat capacity of the calorimeter has first been established by use of pure water as a standard.

The heat of solution of urea may be determined as typical of a nonelectrolyte. The individual samples used should be larger (about 15 g) because of the smaller heat of solution. The heats of solution of urea, phenol, and the compound $(NH_2)_2CO \cdot 2C_6H_5OH$ are measured separately, and the heat of formation of the compound calculated.[2] The compound is prepared by fusing 9.40 g of phenol with 3 g of urea in a test tube immersed in boiling water.

The heat of hydration of calcium chloride may be determined indirectly from measurements of the endothermic heat of solution of $CaCl_2 \cdot 6H_2O$ and the exothermic heat of solution of $CaCl_2$. A test of the equipment and operating technique may be made by measuring the relatively small heat of solution of sodium chloride. Comparison data for concentrations up to 1.3 molal have recently been given by Benson and Benson.[1]

References

1. Benson and Benson, *Rev. Sci. Instr.*, **26**, 477 (1955).
2. Campbell and Campbell, *J. Am. Chem. Soc.*, **62**, 291 (1940).
3. Lange and Mondheim, *Z. physik. Chem.*, **150A**, 349 (1930).
4. Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Standards, Circ.*, **500** (1952).
5. Sturtevant *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Chap. 14, Interscience Publishers, Inc., New York (1949).
6. Williamson, *Trans. Faraday Soc.*, **40**, 421 (1944).

CHAPTER 4

LIQUIDS

9. VAPOR PRESSURE

In this experiment the vapor pressure of a liquid is measured at several temperatures. Experience is gained in finding empirical equations to fit experimental data. The empirical constants are interpreted in terms of thermodynamic relations.

Theory. Vapor pressure is defined as the pressure of the vapor that is in equilibrium with a liquid. Molecules are flying off continuously from the surface of the liquid because of their kinetic energy, and molecules are leaving the gas phase and going back into the liquid. When the rates of these two processes are equal, a dynamic equilibrium is said to exist. In a closed vessel, the equilibrium pressure is quickly established; but in an open vessel where the vapor can diffuse away, the liquid continues to evaporate indefinitely.

When the temperature is raised, the vapor pressure increases, because more molecules gain sufficient kinetic energy to break away from the surface of the liquid. When the vapor pressure becomes equal to the pressure of the gas space, the liquid boils. The temperature at which the vapor pressure reaches 760 mm Hg is the *standard* boiling point.

An important relation, known as the Clausius-Clapeyron equation, connects the heat of vaporization of a liquid and the temperature coefficient of the vapor pressure. It may be expressed in several forms, the most convenient of which are

$$\frac{1}{p}\frac{dp}{dT} = \frac{d \ln p}{dT} = \frac{\Delta H_{\text{vap}}}{RT^2} \tag{1}$$

or the integrated expression,

$$\log \frac{p_2}{p_1} = \frac{\Delta H_{\text{vap}}}{2.303R} \frac{(T_2 - T_1)}{T_2 T_1} \tag{2}$$

where p_2, p_1 = vapor pressures at temperatures T_2 and T_1

ΔH_{vap} = molar heat of vaporization

R = gas constant

ΔH_{vap} and R are usually expressed in calories.

Apparatus. Vacuum system consisting of water aspirator, ballast tank, mercury manometer, and connections; Ramsay-Young vapor-pressure tube; one or more liquids chosen from carbon tetrachloride, acetone, chloroform, benzene, alcohol, water, or other liquid boiling below 100°.

Procedure. Ramsay-Young Method.[2] The apparatus is shown in Fig. 12. A long Pyrex tube *A*, about 25 mm in diameter, has a ground-glass joint at the top. Into this joint fits a special dropping funnel *B*, which is so constructed that the pressure above the liquid surface is always the same as that in the system, thus ensuring uniform liquid flow rates at all pressures. The stopcock plug is scored with a sharp file in the manner indicated to provide close flow control. A thermometer *C* is

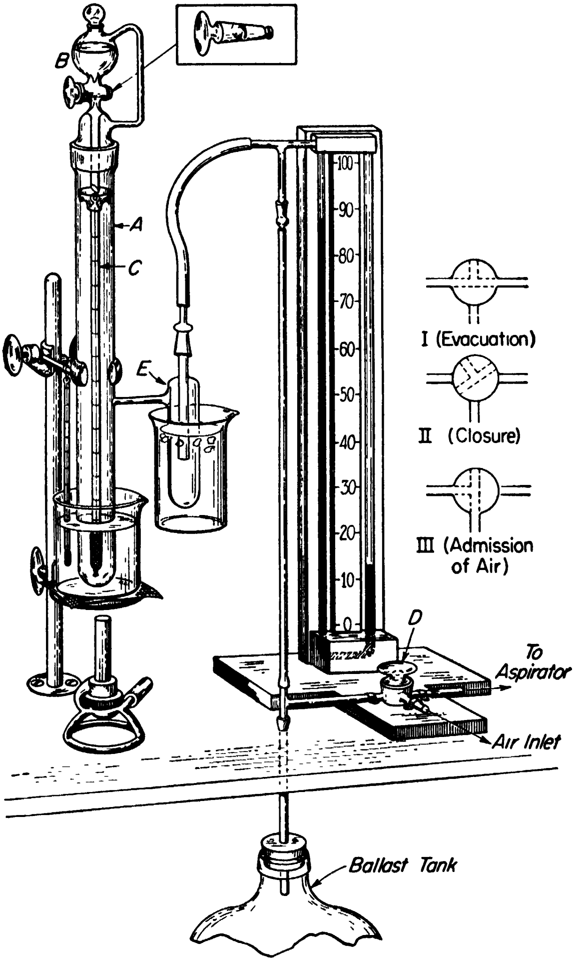

FIG. 12. Ramsay-Young vapor-pressure apparatus.

supported at the top by a glass bushing, which is held in tube *A* by indentations in the glass. The thermometer should have a range of 0 to 100°C graduated in 0.1 or 0.2° divisions. A hygrometer wick or layer of muslin cloth surrounds the thermometer bulb and is tied on with thread.

The vacuum system consists of an aspirator connected through a three-way T stopcock *D* to a ballast tank of 10 liters or more capacity.* This tank prevents sudden pressure surges from upsetting the equilibrium. Connections between the various parts of the apparatus can be made with rubber vacuum hose, but Tygon tubing is better.

A trap *E* cooled by ice is provided between the vapor-pressure tube and the vacuum system to condense the organic vapor.

The stopcocks and the stopper of the dropping funnel are greased, if this has not already been done. For acetone or most other organic liquids which may be under study a special grease must be used which is not dissolved by such materials.†

If a liquid different from the one being studied has been used previously in the apparatus, the system must be cleaned out and the liquid completely removed.

The system is now tested for leaks. With stopcock *D* in position I the system is evacuated as far as possible, and the system is then closed off from the aspirator (stopcock position II). If the apparatus has been in previous use, the manometer will rise slowly as residues of liquid evaporate in the system. If the manometer rises slowly to a somewhat higher point and stays there, the apparatus may be considered leak-tight. If leakage is indicated by a continuing manometer rise, the source must be located and eliminated. Air may be introduced into the apparatus via stopcock position III.

After testing for leaks, about 40 ml of acetone is introduced into the dropping funnel, which is then stoppered. The system is evacuated as far as possible, and stopcock *D* is closed (position II).

The stopcock of the separatory funnel is opened carefully, and liquid is allowed to run down the thermometer stem at such a rate that 4 or 5 drops of liquid fall off from the cloth wrapping of the thermometer bulb each minute. The water bath surrounding the flask is kept about 20° above the temperature registered by the thermometer bulb, and the flow of liquid is adjusted so that each drop evaporates before the next one falls.

The liquid on the cloth around the thermometer bulb is heated by

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* Stainless-steel tanks which were widely used by the Army air forces for breathing oxygen make excellent ballast tanks. These may be available at surplus-property supply houses. If an ordinary glass bottle is used, it should be wrapped in heavy wire mesh or placed in a wooden box to eliminate hazards due to flying glass in case of breakage when evacuated.

† Nonaq grease, sold by the Fisher Scientific Co., Pittsburgh, Pa., is satisfactory.

condensation of vapor and by radiation from the flask, and cooled by evaporation until a steady temperature is registered. This is the boiling temperature of the liquid at the pressure registered on the manometer, unaffected by superheating.

After the thermometer and manometer become steady, the two readings are recorded, and the stopcock of the reservoir bottle is opened to the air. The pressure is increased about 100 mm, and a second observation is made when equilibrium has been reached. The observations are continued less frequently at higher pressures, at least five readings in all being taken before atmospheric pressure is reached.

By starting at atmospheric pressure and going to lower pressures, another set of observations can be made.

Two complete experiments are performed, one with ascending temperature and one with descending temperature.

Calculations. Two types of graphs are plotted. In one the vapor pressures are plotted against the temperatures, and in the second the logarithms of the vapor pressures are plotted against the reciprocals of the *absolute* temperatures. Values taken from the literature are plotted also.

If a given set of points thus plotted differs appreciably and in a regular manner from another set, separate smooth lines may be drawn through different sets. If, however, substantially all the points lie close to a single line, one will suffice.

The second graph is nearly a straight line, represented by the equation

$$\log p = \frac{-A}{T} + B$$

The constants A and B may be found by using the two-point formula for the straight line, using two points directly on the line and far apart. The empirical equation plotted in this way is tested by substituting into it one or two of the observed temperatures and solving for the corresponding vapor pressures. The calculated vapor pressures should agree closely with the observed pressures.

The heat of vaporization of the liquid may be obtained from the straight-line graph. The integration of Eq. (1) shows that the slope of the line is equal to $-\Delta H_{vap}/2.303R$. At any temperature, ΔH_{vap} may be calculated by multiplying the slope of the line by $-2.303R$. The assumptions made in the derivation of the Clausius-Clapeyron equation limit the accuracy of the heats of vaporization calculated in this way. This uncertainty may be eliminated by proper use of the Clausius equation provided the equation of state of the real vapor and the density of the liquid are known.[1]

Practical Applications. Vapor-pressure measurements are important in all distillation problems and in the calculation of certain other physical properties. They are used in the correction of boiling points and in the recovery of solvents. The concentration of vapor in the gas phase may be regulated nicely by controlling the temperature of the liquid. Humidity conditions, which are so important in many manufacturing processes, depend largely on the vapor pressure of water.

Suggestions for Further Work. The vapor pressures of other liquids may be determined, using, if possible, liquids whose vapor pressures have not yet been recorded in tables. The sublimation temperature of a solid may be obtained by covering the thermometer bulb with a thin layer of the solid. The equation for the straight line for the graph of log p against $1/T$ may be determined not by visual graphing but by the method of least squares or by other analytical methods (Chap. 17). It is instructive to check this visual evaluation of the straight-line constants with the least-squares evaluation.

The vapor pressure may be determined by an entirely different method, evaluating the amount of liquid evaporated by a measured volume of air, as described in Chap. 21.

References

1. Brown, *J. Chem. Educ.*, **28**, 428 (1951).
2. Ramsay and Young, *J. Chem. Soc.*, **47**, 42 (1885).
3. Willingham, Taylor, Pignocco, and Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

10. SURFACE TENSION

Four different methods are used for determining surface tensions of liquids. The effect of temperature on surface tension is investigated.

Theory.[1,2] The molecules at the surface of a liquid are subject to the strong attractive forces of the interior molecules. A resultant force, whose direction is in a plane tangent to the surface at a particular point, acts to make the liquid surface as small as possible. The magnitude of this force acting perpendicular to a unit length of a line in the surface is called the *surface tension*. The surface, or interface, where the tension exists is between the liquid and its saturated vapor in air, usually at atmospheric pressure. A tension may also exist at the interface between immiscible liquids; this is commonly called the *interfacial tension*. The dimensions of surface tension are force per unit length and are commonly expressed in the cgs system as dynes per centimeter.

In order to illustrate the above definition of surface tension, we shall consider the principles involved in the four methods of measurement discussed in this experiment and shown in Fig. 13. Surface tension is a property of an interface. Usually it is measured by balancing it along a certain boundary line against an equal force which can be measured.

In the *capillary-rise* method, the liquid rises, owing to its surface tension, in a capillary tube immersed in it (provided that the liquid wets the tube). The circular boundary line is located at some point above the meniscus and has a length $2\pi r$, where r is the inside tube radius. The surface tension γ is thus $f/2\pi r$, where f is the force acting perpendicular to the boundary and in the plane of the surface. At equilibrium the downward force mg due to gravity prevents the liquid from rising higher in the capillary. Here m is the mass of liquid in the capillary and g is the acceleration of gravity. For a liquid of density d rising to a height h in the capillary, this downward force is πr^2hdg. At equilibrium this force is just balanced by the vertical component of force, $f \cos \theta = 2\pi r\gamma \cos \theta$, where θ is the contact angle of the liquid with the vertical side wall of the capillary. For water and most organic liquids this contact angle is practically zero; this means that the surface of the liquid at the boundary is parallel with the wall of the capillary. Setting the two forces equal we have, for zero contact angle,

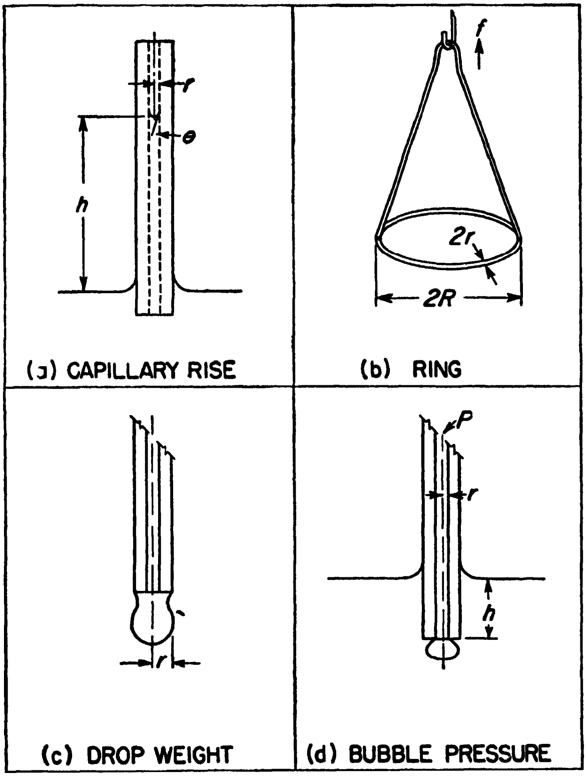

FIG. 13. Principles of four surface-tension methods.

$$2\pi r\gamma = \pi r^2hdg$$

$$\gamma = \tfrac{1}{2}hrdg \qquad (1)$$

In the *ring* method, a platinum-iridium ring in the surface of the liquid is supported by a stirrup attached to the beam of a torsion balance. The ring is pulled upward from the liquid by turning the torsion wire, thus applying a force which is known from calibration of the instrument. For an idealized system, the force just necessary to separate the ring from the liquid is equal to $4\pi R\gamma$, where R is the mean radius of the ring. Doubling of the perimeter $2\pi R$ arises from the fact that there are two boundary lines between liquid and wire, one on the outside and one on the inside of the ring. This treatment holds for liquids with zero contact angle, a condition usually met, and for an ideal situation where the ring holds up a thin cylindrical shell of liquid before the break occurs, a condition which is not met. Actually the shape of the liquid held up influences the force necessary for breaking away. The shape is a function of R^3/V and R/r, where V is the volume of liquid held up and r is the radius of the wire. The surface tension is thus given by the equation

$$\gamma = \frac{f}{4\pi R} F \tag{2}$$

where f = maximum force registered on torsion-balance scale
F = correction factor due to shape of liquid help up and the ring dimensions

These factors have been determined experimentally by Harkins and Jordan.[2,4] Over extreme variations of R^3/V and R/r, F varies between about 0.75 and 1.02. In ordinary cases it is close to 1.

In the *drop-weight* method, a drop forms at the end of a tube, and the boundary line is the outside perimeter of the tube, $2\pi r$. When the drop just detaches itself, the downward force on the drop, mg, is equal to the force acting upward, $2\pi r\gamma$. Actually, only a portion of a drop falls, and Harkins and Brown[2,3,5] propose the equation

$$m_i g = 2\pi r\gamma \tag{3}$$

where m_i is the mass of an "ideal" drop. An equation which is equivalent to Eq. (3) and more convenient to use is $\gamma = \frac{mg}{r} \cdot F$, where F is an empirically determined function of V/r^3 and V is the actual volume of the drop. Values of F are given in Table 2.

In the *bubble-pressure* method, a gas bubble is forced through a tube immersed in the liquid, and the maximum pressure before the bubble detaches itself is measured. The boundary line on which the forces act is the inside perimeter of the tube at the edge. The force holding the bubble to the tube is $2\pi r\gamma$, and the force tending to detach the bubble is equal to the pressure p times the cross-sectional area of the tube (πr^2), or $\pi r^2 p$. These two forces are equal when the pressure is at a maximum; hence

$$2\pi r\gamma = \pi r^2 p_{\max} \tag{4}$$

or

$$p_{\max} = \frac{2\gamma}{r}$$

This pressure is the difference between the measured manometric pressure $p_{\max}$ (in excess of atmospheric) and that due to the immersion, hdg. Substituting these quantities into Eq. (4) and solving for γ, we have

$$\gamma = \frac{r}{2}(p_{\max} - hdg) \tag{5}$$

Surface tension decreases as the temperature rises and is practically unaffected by changes in total area, pressure, or volume. The surface tension becomes zero at the critical point. The temperature coefficient of surface tension, $d\gamma/dT$, is of importance in the thermodynamic treatment of surfaces. The surface energy per unit area E_A of a film is given by the equation[2]

$$E_A = \gamma' - T\frac{d\gamma'}{dT} \tag{6}$$

where γ' = work done on increasing the surface by 1 cm^2

$-T(d\gamma'/dT)$ = heat absorbed during the process, sometimes called the latent heat

The negative of the temperature coefficient of surface tension, $-(d\gamma/dT)$, is the surface entropy S_A per unit area. Equation (6) is the two-dimensional analogue of the Gibbs-Helmholtz equation.

Apparatus. Assembly for surface-tension measurements by capillary-rise, ring, drop-weight, and bubble-pressure method; organic liquid such as acetone or absolute ethyl alcohol.

A. COMPARISON OF THE METHODS

Procedure. The four methods for measuring surface tension described above are to be compared by careful measurements on a single organic liquid. Acetone or absolute ethyl alcohol is suggested. Distilled water is used for calibration purposes.

The *capillary-rise* apparatus is shown in Fig. 14. The capillary tube is provided with engraved millimeter graduations. It is cleaned with *hot* cleaning solution, rinsed with distilled water and then with the liquid to be used.* The test tube must be cleaned in the same manner.

The assembled apparatus is placed in a 25° thermostat, and pure liquid is poured into the test tube to a depth of several centimeters. The stopper is replaced; a clean dust-free rubber tube is fitted with a loose wad of cotton to keep out dirt and spray and attached to the projecting tube as shown. After coming to the temperature of the thermostat, the liquid in the capillary is raised slightly by gently blowing into the rubber tube

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* In case a liquid is used which is immiscible with water, an intermediate rinsing with acetone is necessary. Air from pressure lines should not be blown through the capillary, since it is contaminated with oily substances.

and allowed to fall back to its equilibrium level. Then it is depressed by slight suction and again allowed to come to equilibrium. If the capillary is clean, the reading on the scale after equilibrium is attained should be the same after raising the level as after depressing it.

The difference in the level of the liquid in the capillary tube and in the test tube is read on the scale, the bottom of the meniscus being read in each case. A wide test tube gives a more nearly flat meniscus. Four or five measurements are made on the liquid, and the results are averaged.

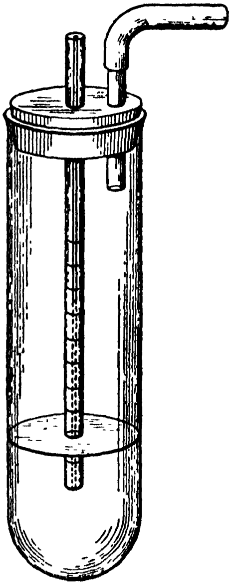


FIG. 14. Capillary-rise apparatus for measuring surface tension.

The radius of the tube is obtained by observing the capillary rise with pure water, the surface tension of which is known to be 71.8 dynes/cm at 25°C. At least five observations are made. The average value of h is obtained from the scale readings, and r is obtained by solving Eq. (1), using the known value of γ.

The DuNouy tensiometer is illustrated in Fig. 15. It is a widely used example of the *ring method.*

The ring of platinum-iridium wire is cleaned with *hot* cleaning solution, thoroughly rinsed with warm distilled water, and dried by carefully touching with a clean filter paper or cloth and allowing to stand in the air. Occasionally, the ring may be heated momentarily in a bunsen flame if further cleaning is necessary. It must not be touched with the fingers, and care should be used not to bend it. The apparatus is adjusted by hanging the ring in the hook and turning the knob at the right until the pointer is at zero. The setscrew at the back is then turned until the lever nearly touches the arm at the left. It must not actually touch, but the gap must be very small. The platform holding the watch glass with the liquid is now raised until the liquid just touches the ring. The knob at the right is then turned slowly and steadily until the ring is suddenly torn from the surface of the liquid. The guard above the lever is adjusted so that the ring cannot be thrown off the edge of the watch glass.

As the pointer is turned, the ring pulls away slightly from the watch glass before it breaks the film, and the beam is raised above the original horizontal position. To compensate for this error, the platform is lowered gradually while the pointer is turned, so that the beam is at its horizontal position when the ring is pulled off. If this adjustment is not made, the readings will be too high.

Several readings are taken on the liquid, and the average is computed. The temperature is determined by immersing a thermometer with a small bulb (Anschuetz type) in the liquid. Unfortunately, close temperature control is not convenient with this instrument.

After the determinations have been made, the instrument is calibrated over the range of scale readings involved. The ring is dried, a weighed square of paper is inserted, and a fractional-gram weight is added. The pointer is turned until the lever just barely clears its support and lies in its standard horizontal position. The weight of paper and fractional-gram weight divided by the scale reading and multiplied by 981 gives the value in dynes of 1 scale division. The calculation is repeated once or twice, using more weights.

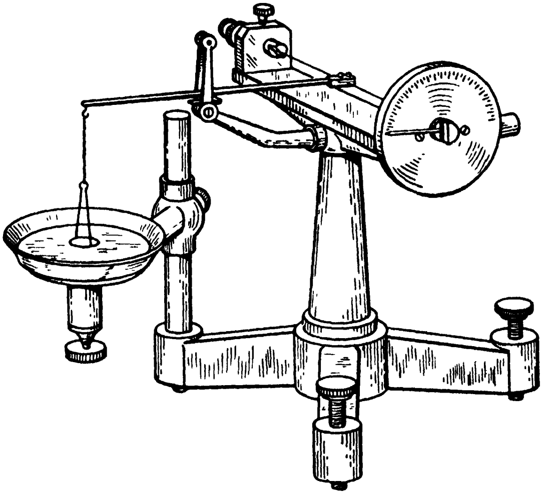


FIG. 15. DuNouy ring-pull apparatus for measuring surface tension.

A useful form of *drop-weight* apparatus is shown in Fig. 16. The end of the capillary is ground flat and polished. It must be free from chips in order to obtain reproducible results, and to this end a permanent guard tube surrounds it.

Before the performance of the experiment the bulb and capillary should be scrupulously cleaned with hot cleaning solution, followed by rinsings with distilled water and the liquid to be studied. After the apparatus has been conditioned and assembled, a dried weighing bottle* is weighed and placed in the protecting bottle, which is then screwed into the cap. A small air vent is provided in the cap to keep pressure from building up inside. The assembly is now introduced into the thermostat.

The liquid whose surface tension is to be measured is added through the side tube and capillary, and the liquid levels are adjusted until the

*A very thin layer of stopcock grease applied to the ground joint of the weighing bottle will prevent loss by evaporation in subsequent weighings.

time of formation of a drop is of the order of 5 min. The difference in liquid level to meet this requirement is ordinarily less than 1 cm. The apparatus may be tipped at first to get the liquid started in the capillary.

The first drop is allowed to form over the relatively long period of time in order to saturate the space within the container. After the detachment of this first drop, additional liquid is added to the side tube, or slight pressure is carefully applied to increase the drop rate. Care must be taken that each drop falls only under the influence of gravity. After the first drop, 30 sec should suffice for the formation of each of the others. A total of 20 to 25 drops should be adequate for the determination.

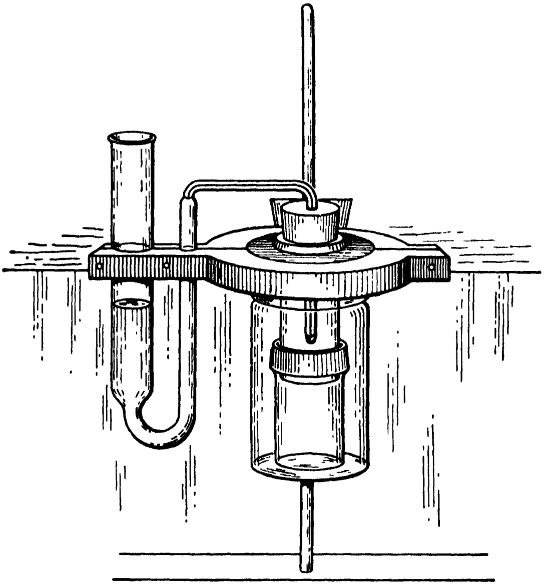


FIG. 16. Drop-weight apparatus for measuring surface tension.

If the radius of the capillary is not known, it may be measured with a comparator microscope.

The *bubble-pressure* apparatus is shown in Fig. 17. The tube may be prepared by drawing a larger tube down so that its bore radius is about 0.3 mm. A sharp fracture at the end of the tube is obtained by scratching the thin wall of the tube with a broken fragment of unglazed porcelain and breaking the tube at this scratch point. The capillary is mounted vertically and connected by rubber tubing to the manometer.

The beaker is nearly filled with the liquid whose surface tension is to be determined, and the tip of the capillary tube is immersed to a known depth below the surface of the liquid. Two or three centimeters depth of immersion is suggested. By a simple manipulation the water level in one of the leveling tubes may be maintained at some convenient reading. The levels are slowly raised to give the difference in height (hydrostatic pressure) which is required to detach an air or gas bubble from the end of the capillary tube. Four or five measurements are made for the liquid, and the average is used in the computations. The experiments are performed at 25°C.

The radius of the capillary tube at the point of formation of the bubble is obtained by observing the maximum bubble pressure with pure water, the surface tension of which is known to be 71.8 dynes cm^{-1} at 25°C. The average values of the maximum bubble pressure and depths of immersion of capillary are used with Eq. (5) to calculate the effective radius of the tube.

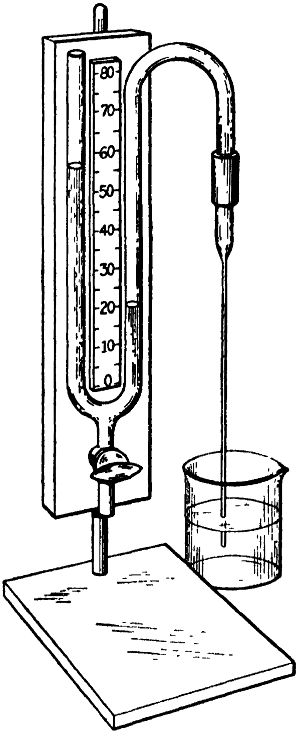


FIG. 17. Bubble-pressure apparatus for measuring surface tension.

B. SURFACE TENSION AS A FUNCTION OF TEMPERATURE

Procedure. The surface tension of acetone is measured by the capillary-rise method at 0° using an ice bath and at three other temperatures, 25, 35, and 50°, using thermostats if they are available. A hand-regulated bath may be used for less accurate work, and a thermometer should be immersed directly in the liquid.

Calculations. The surface tension of the liquid as determined by the different methods is computed, using Eqs. (1), (2), (3), and (5). The density of the liquid may be found in tables.

The value of R/r for the ring of 4-cm perimeter usually supplied with the commercial-type student ring-method instrument may be taken as 40 unless a different value is specifically given. The volume of liquid held up, V, is calculated from the density and the reading on the dial scale, which can be converted to mass of liquid. Correction factors to be applied in Eq. (2) are given in Table 1 for $R/r = 40$ and for different values of R^3/V. For other values of these parameters the works of Harkins and Jordan[2,4] must be consulted. If the temperature of the liquid differs much from 25°, a correction to this temperature may be estimated from the temperature coefficient of surface tension determined in procedure B.

TABLE 1. CORRECTION FACTORS FOR THE RING METHOD
$(R/r = 40)$

R^3/V	F	R^3/V	F
0.30	1.038	0.80	0.923
0.40	0.996	0.90	0.913
0.50	0.969	1.00	0.905
0.60	0.950	1.10	0.897
0.70	0.935	1.20	0.890

Correction factors for the drop-weight calculation are given in Table 2. The volume of the drop is calculated from its known density and the experimentally determined weight. Values of V/r^3 between 1 and 3 give the best results. For values of F outside the limits of Table 2, the tables of Harkins and Brown[2,3,5] are to be consulted.

TABLE 2. EXPERIMENTAL VALUES OF DROP-WEIGHT CORRECTIONS

V/r^3	F
2.995	0.261
2.637	0.262
2.341	0.264
2.093	0.265
1.706	0.266
1.424	0.265
1.211	0.264
1.124	0.263
1.048	0.262

The surface tensions determined by the four methods are compared with the literature values, and the percentage deviations are computed.

The surface tensions determined in procedure B are then plotted as ordinates against temperature as abscissa. The slope of the line is determined and the surface energy computed [Eq. (6)] in ergs per square centimeter at some representative temperature.

Practical Applications. Surface tension is an important phenomenon in the study of emulsions and colloid chemistry. It is an important factor in the concentration of ores by the flotation process. Surface-tension measurements find valuable applications in the biological sciences, particularly in bacteriology; the movement of the moisture of the soil and the passage of sap in plants are only two of the many agricultural phenomena that involve surface tension.

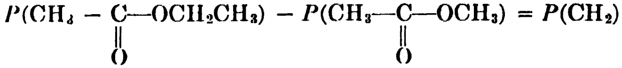
The *parachor* P is defined by the equation

$$P = \frac{M\gamma^{1/4}}{d_l - d_v}$$

where M = molecular weight
d_l = density of liquid
d_v = density of saturated vapor

Usually d_v is so small compared with d_l that it can be neglected. It is found that a parachor value can be assigned to each atom in an organic molecule and that the molecular parachor depends in part also on structural features. It is possible then to determine the presence of structural groups in an organic compound from the difference between the experimentally determined molecular parachor and the sum of the atomic parachors.

Suggestions for Further Work. A table of atomic parachors can be set up by measurements of surface tension of the following liquids: ethyl acetate, methyl acetate, *n*-heptane, chloroform, and ethylene bromide. The densities of these compounds may be found in Experiment 3. The individual parachors are calculated and atomic parachors computed according to the following scheme:



$$P(CH_3-\underset{\underset{O}{\|}}{C}-OCH_2CH_3) - P(CH_3-\underset{\underset{O}{\|}}{C}-OCH_3) = P(CH_2)$$

$$P[CH_3-(CH_2)_5-CH_3] - 7P(CH_2) = 2P(H)$$

$$P(CH_2) - 2P(H) = P(C)$$

$$P(CHCl_3) - P(C) - P(H) = 3P(Cl)$$

$$P(C_2H_4Br_2) - 2P(C) - 4P(H) = 2P(Br)$$

The capillary-rise method is best for these determinations.

Measurements are made so rapidly with the DuNouy apparatus that the surface tension of a large number of liquids and solutions may be determined. If a solute lowers the surface tension, it concentrates in the outer layers of the solution, but if it increases the surface tension of the solution, it is driven away from the surface. Surface tension then is never increased very much by the addition of a solute, but it may be decreased by a considerable amount. This theory may be checked by a number of determinations.

References

1. Bikerman, "Surface Chemistry," Academic Press, Inc., New York (1948); "Foams," pp. 161–169, Reinhold Publishing Corporation, New York (1953).
2. Harkins *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I Part I, Chap. 9, Interscience Publishers, Inc., New York (1949).
3. Harkins and Brown, *J. Am. Chem. Soc.*, **41,** 519 (1919).
4. Harkins and Jordan, *J. Am. Chem. Soc.*, **52,** 1751 (1930).
5. International Critical Tables, Vol. IV, p. 435, McGraw-Hill Book Company, Inc., New York (1928).
6. Mills and MacKenzie, *J. Am. Chem. Soc.*, **76,** 2672 (1954).

11. VISCOMETRY

Experience is given in the determination of viscosities of pure liquids and mixtures by using a capillary-tube method. Densities are measured with a Westphal balance.

Theory. Resistance is offered when one part of a liquid is moved past another. The coefficient of viscosity is a measure of this internal friction or resistance to flow.

The viscosity of a liquid is usually measured by observing the rate of flow of the liquid through some form of capillary tube. For accurate viscosity determinations, a steady flow parallel to the axis of the tube must be maintained, and its rate must not exceed a certain value which is dependent on the viscosity of the liquid and the radius of the tube.

The law that describes the viscous flow of liquids through such tubes was first deduced by Poiseuille. This law gives the relation between the coefficient of viscosity, η, the volume v of liquid flowing across the whole cross section of the tube in time t, the pressure p, and the radius r and length l of the tube. It is expressed as follows:

$$\eta = \frac{\pi p r^4}{8vl} t \tag{1}$$

The derivation of this equation depends upon a simple and useful principle. In the viscometer the liquid flows as coaxial cylinders would move. As this experiment is performed the downward flow, caused by the gravitational force, is opposed by the force of internal friction. In the "steady state" the two forces are equal, and it is only necessary to provide suitable mathematical descriptions of each of them to come quickly to Eq. (1).

The experimental determination of the absolute viscosity of a liquid is a difficult task, but the measurement of relative viscosity, the ratio of the viscosity of a liquid to that of some standard liquid such as water, is simple and adequate for most purposes. If necessary, the absolute viscosity may be calculated from a knowledge of the absolute viscosity of the reference liquid.[5] In a simple viscometer, the pressure* driving a liquid of viscosity η_1 through the capillary depends on the difference in liquid level h, the density d_1, and the acceleration due to gravity, g, and is given by the expression hgd_1. If *exactly* the same volume of a second liquid of viscosity η_2 is introduced into the tube, the pressure driving this liquid through the tube is equal to hgd_2, where d_2 is the density of the second liquid. By Eq. (1), the viscosity is proportional to the pressure and the time of efflux for the same volume. Hence,

$$\frac{\eta_1}{\eta_2} = \frac{d_1 t_1}{d_2 t_2} \tag{2}$$

Comprehensive discussions of viscometers of various types have been given by Reilly and Rae,[4] Barr,[1] and Hatschek.[2] McGowry and Mark[3] have discussed the use of the Ostwald viscometer in organic chemistry. The temperature effect on viscosity and the viscosity of mixtures is treated by Hatschek.[2]

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* Actually part of the driving pressure is utilized in imparting kinetic energy to the liquid (compare Chap. 21). In the case of relative viscosities this correction is negligible if a standard liquid is chosen whose viscosity is close to that of the liquid being studied.

Apparatus. Viscometer; stop watch; thermostat with glass window; 10-ml graduated pipette; Westphal balance or other means for determining densities; acetone, benzene, carbon tetrachloride, or other organic liquids.

Procedure. The viscometer shown in Fig. 18 is the Ostwald modification of Poiseuille's apparatus. Since the glassware is very fragile, the method of clamping shown is suggested for minimum breakage hazard.

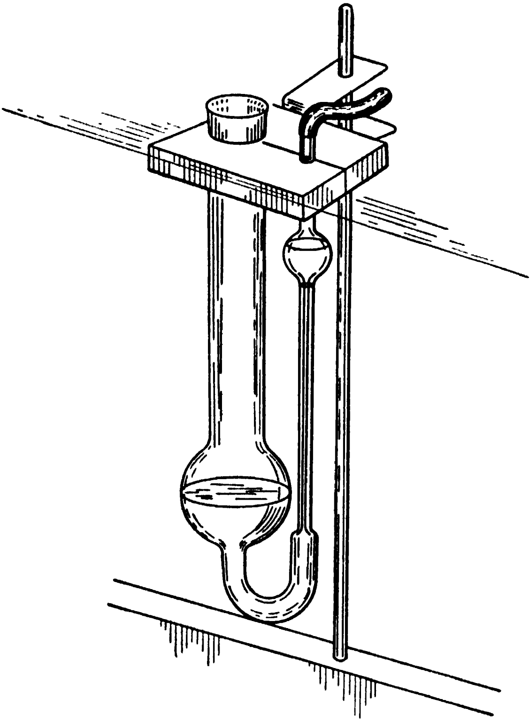

FIG. 18. Ostwald viscometer.

After the viscometer has been thoroughly cleaned with hot sulfuric acid and potassium dichromate, it is rinsed and dried by aspirating through it *clean* air from the laboratory. Traces of oil from compressed air or other dirt may cause serious errors. The viscometer is clamped vertically in the thermostat in such a position that it can be viewed easily, and an exactly specified quantity of water is added from a pipette. The liquid surface in the lower bulb at the start should be as much below the center of the bulb as it is above at the end of the experiment. A dust-free rubber tube loosely plugged with cotton is attached to the smaller tube, and the liquid is drawn up into the enlarged bulb and above the upper mark.

The liquid is then allowed to flow down through the capillary, and the stop watch is started when the meniscus passes the upper mark and stopped when it passes the lower mark. Four or five check determinations on the time of outflow are made. If they do not agree closely, the tube should be cleaned again.

The measurements are repeated on two or three pure organic liquids such as acetone, carbon tetrachloride, benzene, and methanol, drying the viscometer each time before the new liquid is added.

A determination is made on an "unknown" liquid or mixture of liquids.

The relative viscosities of solutions of acetone and water are measured by making up by volume solutions of 5, 10, 20 and 40 mole per cent. Solutions of methanol and water or pairs of organic liquids may be used instead of acetone and water.

The mole fraction N_1 of a component of a binary solution is given by

$$N_1 = \frac{n_1}{n_1 + n_2} = \frac{g_1/M_1}{g_1/M_1 + g_2/M_2} = \frac{v_1d_1/M_1}{v_1d_1/M_1 + v_2d_2/M_2}$$

where n = number of moles
g = number of grams
M = molecular weight
v = volume, milliliters,
d = density, g ml^{-1}

The subscripts refer to the two components. The volumes of the two components required for preparing convenient volumes of the solutions of definite mole fractions are calculated by using this equation.

It is necessary to determine the density of *each* pure liquid and of *each* solution studied in the viscometer. A Westphal balance, or better, a chainomatic density balance may be used.

Calculations. The relative viscosities are calculated, using Eq. (2). The relative viscosities are then changed to absolute viscosities in poises by multiplying by the absolute viscosity of water, given at several temperatures in Table 1. When possible, the absolute viscosities are compared with accepted values given in tables.

TABLE 1. VISCOSITY OF WATER AT VARIOUS TEMPERATURES

t°C	0	5	10	15	20	25	30	35
η, millipoises	17.94	15.20	13.10	11.45	10.09	8.95	8.00	7.26

The measurements on solutions are best represented by means of a curve in which the composition in mole per cent is plotted along the X-axis, and the viscosity relative to that of water is plotted along the Y-axis. The shape of the curve obtained in this manner gives information concerning the changes that take place upon solution.

Practical Applications. Viscosity measurements are important in lubrication and in the movement of liquids through pipes. They find application also in physiological studies.

Suggestions for Further Work. Other pairs of liquids may be chosen from among the following list, which includes some that form ideal solutions, some that indicate some type of chemical interaction, and others that show a breaking down of larger units into smaller molecules in the presence of the second liquid: acetone-chloroform; benzene-nitrobenzene; carbon tetrachloride–ethanol; chloroform-ethanol; ethanol-methanol; benzene–carbon tetrachloride.

The viscosity of a liquid may be determined at several different temperatures to test the empirical relation that the logarithm of the viscosity is a linear function of the reciprocal of the absolute temperature for nonassociated liquids. The viscosity of nitrobenzene may be determined, for example, at 25°, at 50°, using a hot water bath, and at the temperature of boiling water. The density of nitrobenzene is 1.17 at 50° and 1.123 at 100°. $\log \eta$ is then plotted against $1/T$.

Another interesting study lies in testing the suggestion that the longer the molecule, the greater the viscosity.

Viscosity measurements on solutions of highly polymerized linear molecules have acquired considerable significance. Work of this type is done in Exp. 43.

If the reciprocal of viscosity (the fluidity) of a solution is plotted against mole fraction, a straight line is obtained when the solution is ideal, i.e., when the components have no apparent chemical effect on each other and the properties of the two components are additive. It is interesting to apply this test to these or other solutions.

Viscosities may be determined by the method of the falling sphere (Chap. 21). A 2-mm ball bearing is allowed to drop through 25 cm in a 30-cm tube, and the times of fall are observed. The results are compared with those obtained with the capillary tube.

References

1. Barr, "Viscometry," Oxford University Press, New York (1931).
2. Hatschek, "The Viscosity of Liquids," George Bell & Sons, Ltd., London (1928).
3. McGowry and Mark *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Part I, Chap. 8, Interscience Publishers, Inc., New York (1949).
4. Reilly and Rae, "Physico-chemical Methods," D. Van Nostrand Company, Inc., New York (1953).
5. Swindells, Coe, and Godfrey, *J. Research Natl. Bur. Standards*, **48**, 1 (1952).

CHAPTER 5

SOLUTIONS

12. DEPRESSION OF THE FREEZING POINT

The lowering of the freezing point constitutes one of the simplest and most accurate means of determining the apparent molecular weight of a solute. It is of practical value and is important in theoretical studies of solution behavior.

Theory. The addition of a solute to a liquid decreases the tendency of the solvent molecules to escape into the gas phase, i.e., it lowers the partial vapor pressure of the solvent. When the partial vapor pressure of the solvent is lowered, the temperature of freezing is also lowered because the vapor-pressure curve of the solvent in the solution intersects the sublimation curve of the solid at a lower temperature. The solid phase, which is assumed to be pure solvent, separates when the temperature is lowered to a point where the partial vapor pressure of the solvent is just infinitesimally greater than the sublimation pressure of the solid. The extent of the freezing-point depression depends on the concentration, and the following quantitative relation holds for ideal dilute solutions:

$$M = \frac{1{,}000K_f g}{G\Delta T_f} \tag{1}$$

In this equation, M is the apparent molecular weight of the solute, and ΔT_f is the observed depression of the freezing point caused by the addition of g grams of solute to G grams of solvent. The constant K_f is called the *freezing-point constant,* or *molal depression.* It is characteristic of the solvent and corresponds to the depression per gram molecule of solute dissolved in 1,000 g of solvent. In solutions of moderate concentration, Eq. (1) is not exact but is sufficiently good for practical molecular-weight determinations. Values of K_f and related data for several substances are given in Table 1.

The molal freezing-point depression may be calculated from the heat of fusion of the solvent per gram l_f, the freezing point T_f,* and the gas con-

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* As is customary, T represents absolute temperature and t designates centigrade temperature.

TABLE 1. MOLAL FREEZING-POINT CONSTANTS

Solvent	Freezing point, °C	Molal depression, K_f	Heat of fusion l_f, cal g^{-1}
Acetic acid	16.7	3.9	43.2
Barium chloride	962	108	27.8
Benzene	5.5	5.12	30.1
tert-Butanol[a]	25.1	8.37	21.88
Camphor	178.4	37.7	10.74
Cyclohexane	6.5	20.0	7.4
Cyclohexanol[b]	25.1	37.7	4.27
sym-Difluorotetrachloroethane[c]	24.7	37.7	
Fluoropentachloroethane[c]	99.9	42.0	
Heptachloropropane[d]	29.5	12.0	
Naphthalene	80.2	6.9	36.0
Nitrobenzene	5.7	8.1	22.46
Phenol	42	7.27	29.0
Tribromophenol	95	20.4	13.4
Water	0.0	1.855	79.67

[a] Getman, *J. Am. Chem. Soc.*, **62**, 2179 (1940).

[b] Wilson and Heron, *J. Soc. Chem. Ind. (London)*, **60**, 168 (1941).

[c] Berstein and Miller, *J. Am. Chem. Soc.*, **62**, 948 (1940).

[d] Boeseken and Benedictus, *Rec. trav. chim.*, **37**, 121 (1918). This compound is obtainable from Halogen Chemicals, Inc., Columbia, S.C.

stant R, by the following equation (van't Hoff):

$$K_f = \frac{RT_f^2}{1{,}000 l_f} \qquad (2)$$

The separation of pure solvent in the solid form increases the concentration of the remaining solution, and this increase may be considerable, particularly if the solution has been supercooled. Any error due to the change in concentration is avoided by determining the concentration in equilibrium with the solid phase at the temperature recorded. Satisfactory results can be obtained, however, by weighing out solute and solvent to give a known initial concentration, provided that supercooling is kept to a low value by seeding with a small crystal of the solid phase at the proper temperature.

METHOD A

Apparatus. Vacuum bottle with cork and ring stirrer; freezing-point thermometer (+1.00 to −1.00° graduated to 0.01°) or Beckmann thermometer; 10-ml weighing bottle; burette; 10-ml pipette; potassium chloride; 0.1 *N* silver nitrate; 5 per cent potassium chromate solution; distilled water.

Procedure. A small vacuum bottle (1 pt) is provided with a cork, through which passes the 0.01° thermometer and a ring stirrer as shown in Fig. 19. For apparatus which is in continuous daily use it is best to protect the fragile thermometer bulb with a tube of polystyrene which has been liberally perforated to allow freedom of liquid flow around the bulb. A stirrer made of polystyrene rod is preferable to one made of glass.* The bottle is filled about one-third full with distilled water which has been chilled in an ice bath, and an equal volume of clean cracked or finely divided ice is added. The pieces of ice in a clean beaker are rinsed two or three times with distilled water in order to remove any electrolytes. The rinsing water itself is cooled nearly to zero in order to prevent the melting of more ice which might introduce additional impurities.

If the ice is not pure, the freezing point of the ice bath will decrease as more and more of the ice becomes melted. If this decrease is enough to interfere with the accuracy of the experiments, it will be necessary to prepare pure ice by freezing distilled water in an electric refrigerator or in a salt and ice bath.

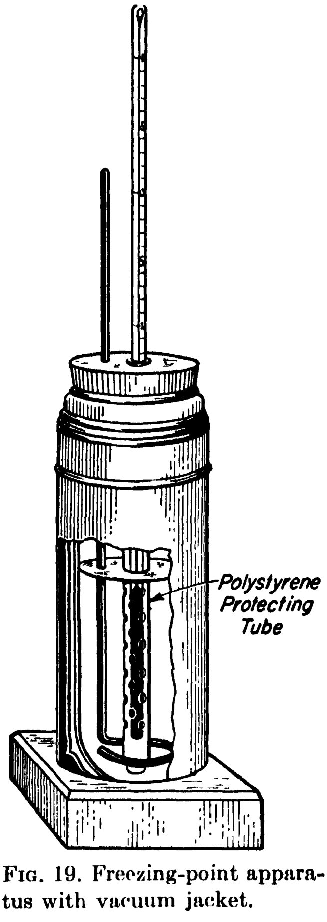

FIG. 19. Freezing-point apparatus with vacuum jacket.

The ice and water in the bottle are stirred vigorously until a steady temperature is attained. Thermometers reading from +1.0 to −2.0° are very convenient for aqueous solutions. The thermometer is tapped gently just before reading. If a Beckmann thermometer is used, it is adjusted so that the mercury comes near the top of the scale at the freezing point of the pure solvent. It is set in the manner described in Chap. 20 (under supervision).

The water is drained off and replaced by a chilled solution of potassium chloride in distilled water which contains about 2 g per 100 ml. The solution and ice are stirred thoroughly until a constant temperature is reached, whereupon the temperature is recorded and a sample is removed with a 10-ml pipette, with the tip touching the bottom of the flask to pre-

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* Polystyrene is thermoplastic and can be bent by heating in a drying oven or well above the flame of a bunsen burner.

vent sucking in little pieces of ice. Since the weight of solute per 1,000 g of solvent is needed for the calculation, the contents of the pipette are drained into a weighing bottle and weighed to 0.01 g. The sample is titrated with 0.1 *M* silver nitrate solution, using a 5 per cent solution of potassium chromate as indicator. The silver nitrate solution is standardized against known weights of potassium chloride. The ice-solution mixture is stirred again, a second temperature reading is obtained, and another aliquot is removed for weighing and titration.

The solution is diluted with chilled distilled water to give a concentration about half as great, and the above procedure is repeated to obtain two independent temperature readings and concentrations.

Calculations. The freezing-point depression ΔT_f is the difference between the temperature of freezing water and the freezing solution. The apparent molecular weights of potassium chloride are calculated for the four experiments by use of Eq. (1). These results are discussed in the light of the estimated experimental uncertainty.

Potassium chloride is a strong electrolyte which is completely dissociated, and the depression of the freezing point would be twice that of an undissociated solute except for the interionic attraction. Accordingly, the depression will be somewhat less than twice the value calculated on assumption of no dissociation; the apparent molecular weight will be somewhat more than half the true value, and the interionic effects will be greater in the more concentrated solutions.

METHOD B

Apparatus. Beckmann molecular-weight apparatus; Beckmann thermometer; benzene; cyclohexane, or other cryoscopic liquid; naphthalene or other solute; unknown organic compound.

Procedure. The Beckmann freezing-point apparatus is shown in Fig. 20.* The innermost tube contains the solvent or solution being studied, in which is immersed the Beckmann thermometer set at the proper range. A heavy wire ring stirrer is provided, bent so that it does not strike the thermometer bulb. The side arm is for the purpose of admitting the solvent and solute.

The tube is surrounded by an air jacket to reduce the cooling rate, and this in turn is immersed in the jar of liquid kept about 3° below the expected freezing point. If benzene or cyclohexane is used, the temperature of the outer bath may be kept uniform by floating a few pieces of ice on top of the water and stirring with the large ring stirrer.

About 20.0 ml of benzene, or other quantity accurately measured to

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* The apparatus shown is of commercial design and is obtainable from supply houses.

0.1 ml or less and sufficient to cover the thermometer bulb fully, is introduced from a pipette in such a manner that none of the liquid adheres to the sides of the tube.

The benzene is cooled quickly until it starts to freeze, and then it is warmed slightly and set into the jacket in the freezing mixture. The stirrer is operated vigorously. Temperatures are taken at various time intervals. The stationary temperature at which the solid and liquid phases are in equilibrium is the freezing point of the solvent. If a stationary temperature is not obtained the experiment should be repeated with benzene which has been recrystallized. The thermometer must be tapped *gently* before a reading is taken. The system is warmed, and the freezing point is again determined, the above operations being repeated. If supercooling occurs, the solid will not separate until the temperature is below the correct freezing point; then the temperature will rise as heat is evolved by the solidification. The temperature will rise to a steady sta-

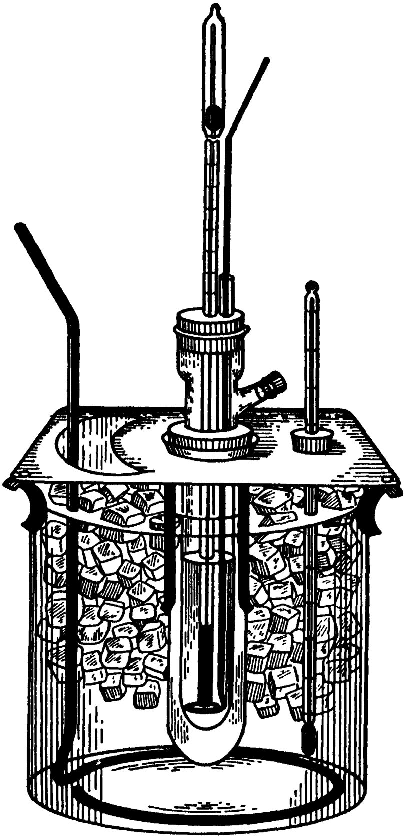

FIG. 20. Beckmann freezing-point apparatus.

tionary temperature if the solvent is pure. The supercooling may be relieved by vigorous stirring, but in extreme cases it may be necessary to add a very small crystal as a nucleus for crystallization.

A sufficient quantity of solute to give a depression of about 1 or 2° is pressed out in a tablet machine and weighed accurately. It is introduced into the apparatus through the side arm, and the freezing point is determined as described for pure benzene, time-temperature readings again being taken. Supercooling must be minimized, and for this purpose seeding is nearly always essential. The small crystal is introduced by means of a precooled glass rod when the freezing point is approached, as determined by a previous rough determination. A second determination may be made after the addition of another weighed amount of solute.

This method uses smaller quantities of material and is suitable for all types of solutions. It can be used for any weighable solute and is not limited to solutions that can be readily analyzed. Liquids may also be used as solutes.

Calculations. The cooling curves are plotted. For the pure solvent the plateau or stationary temperature is taken as the freezing point. For the solution the temperature at which the slope first decreases is the freezing point, but if supercooling has occurred the maximum in the curve is taken.

The molecular weight of the known solute is calculated, the percentage error being computed.

Practical Applications. The freezing-point method is the simplest and perhaps the most accurate method for determining molecular weights in solution. It is useful in establishing the formulas of organic substances.

The freezing-point method constitutes one of the best ways for obtaining the activities of solute and solvent for thermodynamic calculations.

Suggestions for Further Work. Several different ionizing and nonionizing solutes may be investigated in water and in benzene and other solvents. The degree of dissociation of monochloroacetic acid in water may be determined, using concentrations of 0.25 *N* and below.

According to the best technique,[3] twin flasks are used, one for the pure solvent and one for the solution, and the temperature difference is determined with a sensitive thermocouple. The thermocouple described in Chap. 20 may be used; it is calibrated with the hydrochloric acid solutions in a test tube, vigorously stirred, and cooled with salt and ice until the first ice appears and a steady deflection is obtained. Exactly 0.25 *N* hydrochloric acid has a freezing point of −0.890°. By this method the activities of solvent and solute can be determined at various concentrations.[2] Very careful technique is required.

Conditions for obtaining an ice bath constant to 0.001° are described by White.[5] The ice in a covered beaker is protected against melting with a second ice bath, and pure chilled water is passed through the inner bath at intervals to remove solutes from the surface of the ice.

The solutions may be analyzed conveniently with an immersion refractometer.

A number of the solvents listed in Table 1 may be employed for determining the molecular weights of organic compounds. A large freezing-point constant is desirable in order to obtain the greatest depression. *tert*-Butanol and cyclohexanol have relatively large constants and are not very expensive, but they are hygroscopic and require careful technique to prevent absorption of water vapor during manipulation. Phenol is even more hygroscopic. *sym*-Difluorotetrachloroethane and fluoropentachloroethane have favorable constants but are not readily available. Heptachloropropane has a large constant and convenient melting point and is not very expensive. Camphor has been used extensively for molecular-weight determinations after the method of Rast.[1] In this method the solidified solution is contained in a melting-point capillary tube, and the melting point is determined and compared with that of the pure solvent under controlled conditions. Very small samples can be handled by this method.

References

1. Gattermann and Wieland, "Laboratory Methods of Organic Chemistry," p. 86, The Macmillan Company, New York (1937).
2. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 284, McGraw-Hill Book Company, Inc., New York (1923).
3. Scatchard and Benedict, *J. Am. Chem. Soc.*, **58**, 837 (1936), and earlier papers.
4. Skau and Wakeham *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Chap. 3, Interscience Publishers, Inc., New York (1949).
5. White, *J. Am. Chem. Soc.*, **56**, 20 (1934).

13. ELEVATION OF THE BOILING POINT

The boiling points of a solution and the pure solvent are determined and used for calculating the molecular weight of the nonvolatile solute.

Theory. When a nonvolatile solute is dissolved in a solvent, the vapor pressure of the latter is decreased; as a consequence the boiling point of the solution is higher than that of the solvent. The extent of the elevation depends upon the concentration of the solute, and for *dilute*, ideal solutions it may be shown that

$$\Delta T_b = K_b m \tag{1}$$

where ΔT_b = elevation of the boiling point for a solution of molality m over that of the pure solvent

K_b = a constant characteristic of the solvent called the *boiling-point constant*, or the *molal elevation of the boiling point*

This relation permits calculation of the molecular weight of the solute, since it may be transformed into the equivalent form

$$M = \frac{1{,}000K_b g}{G\Delta T_b} \tag{2}$$

where ΔT_b = elevation of the boiling point for a solution containing g grams of solute of molecular weight M in G grams of solvent of boiling-point constant K_b

It should be noted that even for ideal solutions the foregoing relations are valid only if the solution is dilute, i.e., if the mole fraction of solute is small.

For a given solvent K_b may be evaluated experimentally as the boiling-point elevation per mole of solute per 1,000 g of solvent by measurements using dilute solutions of a solute of known molecular weight. Alternatively it may be calculated from the relation

$$K_b = \frac{RT_b^2}{1{,}000 l_v} \tag{3}$$

where T_b = absolute temperature of the boiling point of the solvent
l_v = latent heat of vaporization of the solvent per gram at that temperature

The foregoing equations do not hold exactly for dilute real solutions but will give results of fair accuracy in cases in which the departure from ideality is small. A more complicated and rigorous thermodynamic calculation[10] is required when this method is applied to the accurate determination of the properties of nonideal solutions. Valuable information concerning aqueous solutions of electrolytes has been obtained in this way.[3, 10]

In order to determine the boiling temperature of a solution, the thermometer must be in contact with the solution, not in the vapor as in the case of a pure liquid. The elimination of any superheating of the liquid phase is therefore particularly important and is usually accomplished by means of the vapor lift pump described below; electrical heating may be used to minimize the initial degree of superheating of the solution. The method of Landsberger,[5] preferably as modified by McCoy,[6] may also be used; solvent vapor is passed into the solution, where it condenses, and the heat of condensation raises the solution to the boiling point. In this way radiation and conduction of heat from a body at a higher temperature are avoided, and superheating is eliminated.

Apparatus. Boiling-point apparatus of the Cottrell type; Beckmann thermometer or other thermometer graduated to 0.01°; carbon tetrachloride; benzoic acid; diphenyl.

Procedure. The elevation of the boiling point of carbon tetrachloride is studied for two types of solutes, represented by diphenyl and benzoic acid, and the corresponding molecular weight of each is calculated.

A commercially available boiling-point apparatus of the Cottrell type[1,2,11] is shown in Fig. 21. The Davis[2] or the Cottrell-Choppin[9] apparatus also may be obtained from supply houses. A quantity of the solvent, weighed to 0.1 g and sufficient to come a centimeter or so below the thermometer bulb, is placed in the tube, and a Beckmann thermometer or other thermometer graduated to 0.01° is put into place. The liquid level must always be below the lower end of the glass thermometer shield. The apparatus is clamped in a vertical position and heated with a small gas flame. *The shield shown in Fig. 21 is a convenient means of keeping drafts of air away.* The purpose of the small inverted funnel, which is raised above the bottom on small projections, is to catch the bubbles of vapor and direct them through the center tube and three vertical tubes. As the bubbles discharge through these outlets, they direct three sprays of liquid and vapor against the thermometer; any superheated solution comes to full equilibrium with the vapor by the time it gets to the thermometer bulb.

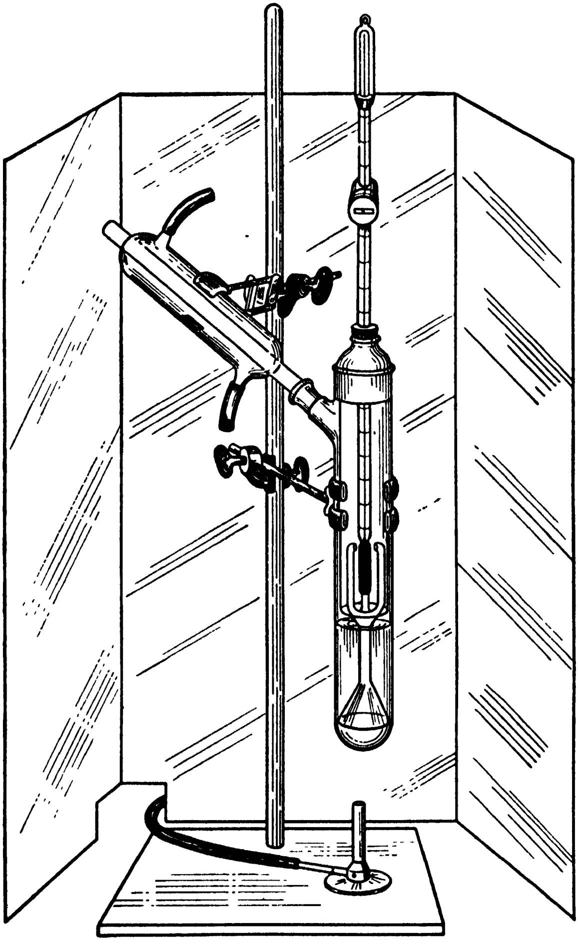

FIG. 21. Cottrell boiling-point apparatus.

If the liquid does not pump steadily over the thermometer bulb, the rate of heating is changed. The flame should be adjusted so that ebullition takes place primarily within the funnel in order to produce the most efficient pumping action. The rate of heating should not be so high as to drive the liquid condensate film too close to the end of the condenser since this may result in marked loss of solvent and also cause superheating. A metal chimney placed around the burner facilitates adjustment of the rate of heating.

An absolutely constant boiling-point reading cannot be expected, but when equilibrium has been reached the observed temperature will fluctuate slightly around a mean value and in particular will not show a slow drift except when there is a corresponding drift in barometric pressure. The thermometer, which must be handled carefully, is tapped *gently* before a reading is taken. Since the boiling point is sensitive to changes in pressure, the barometer should be read just after the temperature reading is recorded.

After the boiling point of the pure solvent has been determined, the burner is turned off and the liquid allowed to cool. The condenser is then removed, and a weighed quantity of benzoic acid sufficient to produce a 1 to 5 per cent solution is added. To prevent loss, the benzoic acid is made up into a pellet in a pellet machine before weighing, or is placed into a short glass tube and rammed tight with a central rod acting as a plunger.

The steady boiling point of the solution is determined in the manner previously described. The determinations on solvent and corresponding solution should follow one another closely so as to minimize the effect of changes in barometric pressure. A second determination may then be made in a more concentrated solution by adding a second pellet of benzoic acid. In each case, the barometric pressure is recorded just after the temperature reading is made.

The boiling point of a fresh sample of carbon tetrachloride is determined, and the elevation of the boiling point measured for diphenyl as solute. Here again two determinations are made.

Serious error can result from failure to wait for equilibrium to be attained and the thermometer reading to become adequately constant before the observation is recorded. Other large experimental errors may be caused by fluctuations in atmospheric pressure or by an appreciable loss of solvent vapor through the condenser. The first difficulty may be met by making corrections for pressure changes, by employing a manostat to ensure a constant pressure, or by using two sets of apparatus at the same time, one for solvent and one for solution. The second problem may be solved by analyzing the solution after the determination of the boiling point. A sample is withdrawn with a pipet and weighed in a weighing bottle. The solvent is then evaporated in a current of air, and the residue is weighed.

Calculations. The molecular weight is calculated by means of Eq. (2), using the values for K_b shown in Table 1. The pressure corrections for K_b, shown in the last column, are applied if the corrected barometric pressure is not close to 760 mm.

TABLE 1. MOLAL BOILING-POINT CONSTANTS[a]

Solvent	Boiling point at 760 mm	Molal boiling-point constant K_b	$\frac{\Delta K_b}{\Delta P(\text{mm})}$
Acetone	56.0	1.71	0.0004
Benzene	80.2	2.53	0.0007
Bromobenzene	155.8	6.20	0.0016
Carbon tetrachloride	76.7	5.03	0.0013
Chloroform	60.2	3.63	0.0009
Ethanol	78.3	1.22	0.0003
Ethyl ether	34.4	2.02	0.0005
Methanol	64.7	0.83	0.0002
Water	100.0	0.51	0.0001

[a] Hoyt and Fink, *J. Phys. Chem.*, **41**, 453 (1937).

The necessary correction to ΔT_b required by a difference in the barometric pressures at the times the boiling points of the solvent and solution were recorded may be made by use of Eq. 1 of Exp. 9. For this purpose, it is assumed that dp/dT, the derivative of vapor pressure with respect to temperature, may be set equal to $\Delta p/\Delta T$.

The calculated molecular weights are compared with the corresponding formula weights, in the light of the estimated experimental error. The percentage errors in the determinations are calculated.

Practical Applications. Many materials cannot be vaporized for direct determinations of the vapor density without decomposition. In such cases the material is dissolved in a suitable solvent, and the elevation of the boiling point furnishes a rapid and convenient method for determining the molecular weight. Molecular weights of substances in solution, however, are often different from the values found from vapor-density measurements.

Activities of solutes forming nonideal solutions may be determined by the boiling-point method.[10]

Suggestions for Further Work. A more elaborate and accurate method may be used in which a thermocouple gives directly the difference in boiling point between the solvent and solution in two different vessels.[8]

The determinations of molecular weight may be made at a number of concentrations and the values extrapolated to infinite dilution. Only in this way can a reliable value for the molecular weight be obtained.[7]

The molecular weights of several different organic solids may be obtained, using e.g., urea, naphthalene, oxalic acid, or sugar. The abnormal properties of aqueous electrolytic solutions may be demonstrated.

A solvent may be used for which the value of K_b is not given. The constant K_b may be evaluated by experiment with solutes of known molecular weight or by calculation from the formula given above.

The molecular weight of benzoic acid may be determined from measurements on solutions in a polar solvent such as ethanol, and the result compared with that obtained with the nonpolar solvent.

Caution is required when an inflammable solvent is used.

References

1. Cottrell, *J. Am. Chem. Soc.*, **41,** 721 (1919).
2. Davis, *J. Chem. Educ.*, **10,** 47 (1933).
3. Harned, *J. Franklin Inst.*, **225,** 623 (1938).
4. Hoyt and Fink, *J. Phys. Chem.*, **41,** 453 (1937).
5. Landsberger, *Ber.*, **31,** 458 (1898).
6. McCoy, *Am. Chem. J.*, **23,** 353 (1900).
7. Mair, *J. Research Natl. Bur. Standards*, **14,** 345 (1935).
8. Pearce and Hicks, *J. Phys. Chem.*, **30,** 1678 (1926).
9. Rogers, Knight, and Choppin, *J. Chem. Educ.*, **24,** 491 (1947).
10. Smith, *J. Am. Chem. Soc.*, **61,** 497–503 (1939).
11. Washburn and Read, *J. Am. Chem. Soc.*, **41,** 729 (1919).

14. LIQUID-VAPOR EQUILIBRIA IN BINARY SYSTEMS

Boiling-point and vapor-composition data for a binary solution may be presented in a graph of temperature against composition. Data for such a plot are obtained in this experiment in which the liquid and vapor compositions are determined refractometrically.

Theory. The composition of the vapor in equilibrium with a solution of two volatile liquids is different from that of the solution if the partial pressures of the two components are different.

In an ideal solution each component exerts a partial pressure p which is equal to the vapor pressure p^0 of the pure component multiplied by its mole fraction N in the solution. This is expressed by

$$p = Np^0 \tag{1}$$

In most solutions, however, there is some type of influence of one component on the other so that Eq. (1) does not hold. There may be a tendency for chemical reaction, forming a compound as, for example, in a solution of chloroform and acetone. In other solutions the presence of the second liquid breaks down the larger units of the first liquid and renders the first liquid more volatile.

If a liquid has a low vapor pressure, it has a high boiling temperature, and, in general, the boiling-point–composition curves are just opposite in character to the vapor-pressure–composition curves.

In an ideal solution the vapor and liquid composition curves run smoothly between the two boiling points, but in a nonideal solution, the increase or decrease in volatility due to the influence of the other component may be sufficient to cause a minimum or a maximum in the boiling-point curve (corresponding to a maximum or a minimum in the vapor-pressure curve). Hydrochloric acid and water offer a good illustration of a pair that has a maximum boiling point. Benzene and ethanol is an example of a pair of liquids exhibiting a minimum boiling point.

Comprehensive discussions of vapor-liquid equilibria in various systems may be found in the works of Young,[12] Robinson and Gilliland,[9] and Dodge,[4] and an extensive table of azeotropes has been compiled by Horsley and coworkers.[6]

Apparatus. Distilling apparatus as illustrated in Fig. 22; pipette of about 1 ml; resistance wire for electric heater; step-down transformer (110 to 6 volts); thermometer graduated to 0.1°; refractometer with thermostated prism; weighing bottle; benzene; ethanol.

Procedure. The apparatus which is shown in Fig. 22 may be readily constructed from a 50-ml distilling flask. Superheating is avoided by internal electric heating with a resistance coil.

The heating coil of No. 26 nichrome wire about 14 cm long is wound in the form of a helix about 3 mm in diameter. It is soldered to No. 14 copper wire leads set into the cork. The coil should touch the bottom. A small step-down transformer capable of at least 25 watts output is used.

Other types and sizes of resistance wire may be used, but the current should be such that the wire is heated to a dull red heat when out in the open air. A heater of 2 ohms operating at 6 volts is satisfactory.

A thermometer graduated to 0.1° and reading from 50 to 100° serves very well, but any accurate thermometer with large 1° divisions will do. A short length of glass tubing surrounds the bulb of the thermometer; this enables the boiling liquid to circulate over the entire thermometer bulb. The bulb must not touch the heating coil.

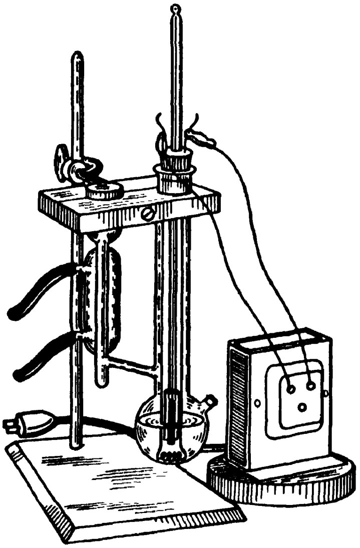

FIG. 22. Apparatus for determining the vapor compositions of binary mixtures.

The arm of the distilling flask is bent upward to act as a reflux condenser; at the bottom of the bend is a bulb of about 1 ml capacity to act as a pocket for retaining condensed distillate as it flows down from the short condenser.

The transformer is adjusted so that the liquid boils vigorously at a constant rate, and the vapor condenses in the reflux condenser. Additional regulation may be accomplished with a rheostat, if necessary. The boiling is continued until the pocket below the reflux condenser has been thoroughly rinsed out with condensed liquid and the thermometer reading has become constant. The approach to equilibrium is hastened by stirring the liquid in the pocket with a long glass rod. The current is then turned off, and samples of about 1 ml are taken with a small tube or pipette from the distillate in the pocket and then from the residue in the flask through the side arm. The sample of distillate is removed by inserting the end of the pipette through the open end of the reflux condenser directly into the pocket below. A dry pipette should be used for taking the samples. The refractive indices of the samples are determined with a refractometer (Exp. 3). Samples for this determination may be preserved for a short time in small *stoppered* vials or test tubes, but errors caused by partial evaporation of the samples must be considered. It is important to close the jaws of the refractometer quickly to avoid evaporation from the liquid film on the prism.

About 25 ml of benzene is measured into the flask, and its boiling point is determined. Boiling points and refractive indices of the residue and distillate are then determined after successive additions of 0.2, 0.5, 1, 5, 5, and 5 ml of ethanol. The refractive indices are used to obtain the mole fractions of ethanol in these solutions.

In order to construct a plot of refractive index versus mole per cent ethanol, the refractive indices are determined for the pure benzene and ethanol and for a series of solutions containing accurately known weights of benzene and ethanol. Mixtures about 5 ml in volume containing approximately 1 volume of ethanol to 1, 3, and 6 volumes of benzene are convenient.

The boiling flask is drained and dried, and about 25 ml of ethanol is introduced for a boiling-point determination. Boiling points and compositions of the residue and distillate are then determined after successive additions of benzene as follows: for example, 2, 4, 5, 7, and 10 ml.

The barometer should be read occasionally. In case the atmospheric pressure changes considerably, it is necessary to estimate a correction for the boiling point, taking an average correction for the two liquids as an approximation. Such a correction may usually be avoided by performing all of the distillation experiments within a few hours.

Calculations. The refractive indices of the weighed samples and the pure liquids are plotted against the compositions of the solutions expressed in mole fractions (defined in Exp. 11) of ethanol. The composition of each sample of distillate and residue may then be determined by interpolation on this graph.

In a second graph two curves are plotted: one in which boiling temperature is plotted against the mole fraction of ethanol in the residue, and one in which the same boiling temperatures are plotted against the mole fraction of ethanol in the distillate. The composition in terms of mole fraction of ethanol is plotted along the horizontal axis. For such a plot different symbols should be used for the two sets of points.

The significance of this graph is discussed with regard to the feasibility of separating benzene and ethanol by fractional distillation.

Practical Applications. Vapor-composition curves are necessary for the intelligent separation of liquids by distillation. Fractional distillation under controlled conditions is essential in the purification of liquids and in many industries such as the petroleum industry and solvent industries.

Suggestions for Further Work. Solutions of chloroform and acetone, giving a maximum in the boiling-point curve, may be studied in exactly the same manner described for ethanol and benzene.

The maximum in the boiling-point curve of hydrochloric acid and water occurs at 108.5° and a composition of 20.2 per cent hydrochloric acid at a pressure of 760 mm. The distillate at the maximum boiling point is so reproducible in composition at a given pressure and so easily obtained that it may be used to prepare solutions of HCl for volumetric analysis. A solution of hydrochloric acid is made up roughly to approximate the constant-boiling composition, and after boiling off the first third, the remaining distillate is retained. The barometer is read accurately, and the corresponding composition is obtained from the literature.[1,5,6]

Solutions of chloroform and methanol, giving a minimum in the boiling-point curve, may be studied by using a Westphal density balance for determining the compositions instead of a refractometer. A density-mole-fraction curve is plotted, and the compositions of the samples are determined by interpolation. Since larger samples are needed for the density measurements, more material and a larger flask are required.

The gas-saturation method for vapor-pressure measurements may be used in studying binary liquids. Using this technique, Smyth and Engel[11] have determined vapor-pressure-composition curves for a number of ideal and nonideal types.

Vapor-liquid equilibria at different total pressures provide an interesting study. The acetonitrile-water system has an azeotrope which varies considerably in composition as the pressure is reduced.[7] Othmer and Morley[8] describe an apparatus for the study of vapor-liquid compositions at pressures up to 500 psi. The earlier papers of Othmer may be consulted for a number of binary vapor-liquid equilibria.

References

1. Bonner and Branting, *J. Am. Chem. Soc.*, **48**, 3093 (1926).
2. Carney, "Laboratory Fractional Distillation," The Macmillan Company, New York (1949).
3. Daniels and Alberty, "Physical Chemistry," John Wiley & Sons, Inc., New York (1955).
4. Dodge, "Chemical Engineering Thermodynamics," Chaps. XII, XIII, McGraw-Hill Book Company, Inc., New York (1944).
5. Foulk and Hollingsworth, *J. Am. Chem. Soc.*, **45**, 1220 (1923).

6. Horsley and co-workers, "Azeotropic Data," Advances in Chemistry Series, American Chemical Society, Washington, D.C. (1952); Tables of Azeotropes and Non-Azeotropes, *Anal. Chem.*, **19**, 508–600 (1947).
7. Othmer and Josefowitz, *Ind. Eng. Chem.*, **39**, 1175 (1947).
8. Othmer and Morley, *Ind. Eng. Chem.*, **38**, 751 (1946).
9. Robinson and Gilliland, "The Elements of Fractional Distillation," 4th ed., McGraw-Hill Book Company, Inc., New York (1950).
10. Rogers, Knight, and Choppin, *J. Chem. Educ.*, **24**, 491 (1947).
11. Smyth and Engel, *J. Am. Chem. Soc.*, **51**, 2646, 2660 (1929).
12. Young, "Distillation Principles and Processes," Macmillan & Co., Ltd., London (1922).

15. FRACTIONAL DISTILLATION

In this experiment the efficiencies of packed and unpacked columns are compared at total reflux. The separation of a binary mixture by fractional distillation is studied by using refractive-index measurements to analyze the distillate.

Theory. The separation of liquids by distillation is one of the oldest and most important operations of chemistry, but considerable improvement has been made in recent years in the design of apparatus for fractional distillation. The developments in petroleum refining and the need for increased efficiency in laboratory operations and purification have been largely responsible for these improvements. More recently the concentration of isotopes has made still greater demands on fractional distillation.

The separation of two liquids which is obtained by a simple vaporization and condensation (as in Exp. 14) is not great except in the case of liquids with widely differing boiling points. Greater separation may be achieved by a series of simple distillations, but this is laborious. The same result is obtained by using a fractionating column through which the vapor is passed and brought into contact with part of the condensate flowing down the column. The less volatile components in the ascending vapor are condensed in such a column, and the more volatile components are boiled out of the descending liquid phase, so that distillation through the column is equivalent to a number of successive simple distillations. Greater separation is obtained in a fractionating column if most of the vapor condensed at the top of the column is returned as reflux. The reflux ratio is defined as the ratio of the volume of liquid returned to the column per unit time, to the volume of distillate collected in the same time interval.

It is necessary to insulate or heat a fractionating column so that the net condensation in the column will not be too great. The temperature will be lower at the top of the column where the more volatile component is concentrated than at the bottom. The purpose of the packing is to provide good contact between the vapor and liquid phases in the column, but it is undesirable for the packing to hold a large amount of liquid relative to the volume of the batch being distilled because of the resulting decrease in sharpness of separation. A number of types of packing are listed on page 373.

The study of the efficiency of different distilling columns has been put on a quantitative basis by the invention of the term *theoretical plate.* The number of theoretical plates in a column is equal to the number of successive infinitesimal vaporizations at equilibrium required to give the measured separation. Thus, a theoretical plate may be visualized as a section of the distilling column of such length that the vapor leaving at the top of the section corresponds in composition to the equilibrium vapor of the liquid leaving at the bottom of the section. An ordinary 1-cm tube 1 m long might be equivalent to only 1 theoretical plate, whereas the same tube filled with adequate packing can give the equivalent of 20 or more theoretical plates. A column with 12 theoretical plates is adequate for the practical separation of benzene (bp 80.1°) and toluene (bp 110.8°). The number of theoretical plates required for a given separation increases when the reflux ratio is decreased.

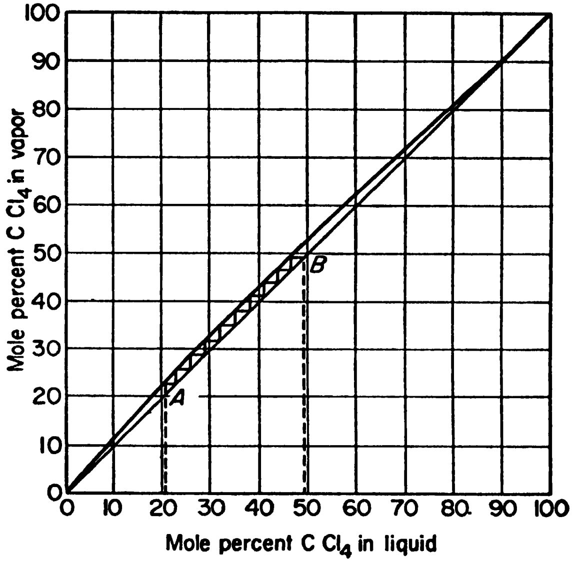

FIG. 23. Vapor-liquid graph for calculating the number of theoretical plates.

The number of theoretical plates cannot be determined from the geometry of the distilling column; it is calculated from the separation effected with a liquid mixture for which the liquid-vapor equilibrium data are fully known. As an example, the determination of the number of theoretical plates in a column by a distillation of a mixture of carbon tetrachloride and benzene is illustrated in Fig. 23. This figure is a plot of the mole per cent of carbon tetrachloride in the vapor in equilibrium with liquid having the composition given on the abscissa. A sample of the distillate obtained under conditions of practically total reflux had composition *B*, and the residue in the distilling pot had composition *A*. The compositions of residue and distillate are marked on the 45° line, and a series of vertical and horizontal lines is drawn stepwise from *A* as shown until the composition of the distillate is reached. Each vertical line drawn corresponds to an ideal distillation step in which there is derived from a liquid solution a vapor having the equilibrium composition for the given liquid. Each horizontal line corresponds to a condensation in which vapor is completely condensed to give a liquid of the same composition as the vapor. The number of these vertical line steps minus 1 is equal to the number of theoretical plates in the fractionating column. The liquid-vapor surface in the distillation pot acts as 1 theoretical plate.

Depending upon the construction of the distillation column, the number of theoretical plates may vary somewhat with the rate of entry of vapor into the bottom of the column and the rate of return of liquid from the top of the column. In the case of small-scale laboratory columns it is found that the actual separations obtainable at finite reflux ratios are, in general, lower than would be predicted from the number of theoretical plates determined at total reflux.

The number of theoretical plates in a column under actual operating conditions may be determined by the method of McCabe and Thiele.[6] In this method the number of theoretical plates is obtained by plotting a curve representing mole fraction of the more volatile component in the binary mixture in the vapor phase versus its mole fraction in the liquid phase and counting steps between this curve and the *operating line*, rather than the 45° line, which is used for the calculation of theoretical plates at total reflux. The operating line is a straight line drawn through the 45° line at the composition of the distillate with a slope equal to $R/(1 + R)$, where R is the reflux ratio. The student is referred to chemical engineering books[1,8] for a complete description of the use of this important concept in actual separations by fractional distillation.

Apparatus. Vigreux column; vacuum-jacketed packed columns; still head with cold thumb and thermometer; glass-cloth-covered heating mantle; variable autotransformer; distilling flask; 100-ml graduated cylinder; small test tubes and corks; Abbe refractometer; carbon tetrachloride; chloroform; benzene.

Procedure. Two types of fractionating columns are to be employed, such as unpacked columns of the Vigreux type and vacuum-insulated columns of the bubble-plate type or columns packed with double cones of metal screen (Stedman), stainless-steel saddles, or glass helices. A distillation apparatus with a vacuum-jacketed fractionating column is illustrated in Fig. 24. The unpacked column and one of the packed columns are compared by determining the number of theoretical plates for each at total reflux, using solutions of benzene and carbon tetrachloride. Samples from the distilling pot and distillate are to be analyzed, and measurements of refractive index with an Abbe refractometer are convenient for this purpose.

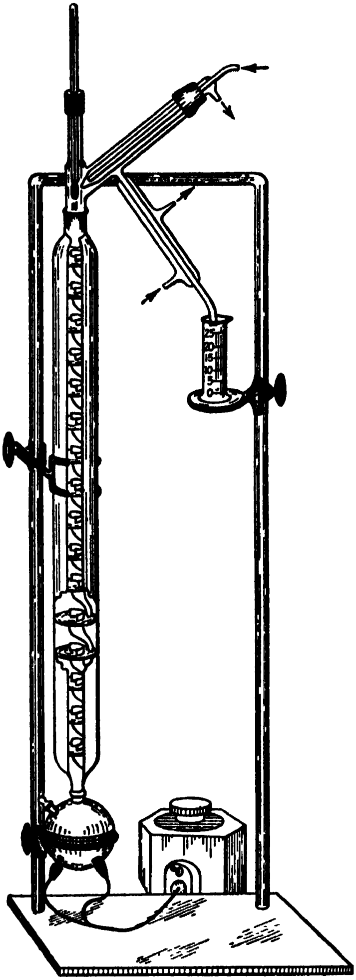

FIG. 24. Bubble-plate fractionating column.

About 10 ml of carbon tetrachloride and 40 ml of benzene are mixed and placed in the distillation pot, which is attached to the Vigreux column. The distilling pot is heated with an electric heating mantle controlled with a variable autotransformer. The liquid is boiled vigorously until condensation takes place in the distilling head, and then the heating is decreased so that the column does not become flooded. The cold-thumb condenser should be in such a position that all the condensate is returned to the column.

After equilibrium is attained as indicated by the fact that the temperature at the thermometer is constant, a sample of the material at the top of the column is taken. The cold-thumb condenser is partially withdrawn so that most of the condensate is collected in the graduate. The first two or three drops are discarded, and then a 1-ml sample is collected for analysis with the Abbe refractometer. The use of this instrument is described in Exp. 3. The electrical heater is then turned off, and a sample of the liquid (about 1 ml) is removed through the side arm of the distillation pot, using a pipette or tube. It is to be emphasized that the efficiency of the column determined by use of these two samples is the efficiency essentially at total reflux, since the column is brought to equilibrium at total reflux and only a small sample is withdrawn from the column. A finite reflux ratio is necessarily used in collecting the sample, but it has a negligible effect on the composition of the sample as long as the sample taken is small.

The above procedure is repeated using a packed fractionating column or a bubble plate column rather than the Vigreux column. The packed column requires a longer time to come to equilibrium.

While equilibrium is being established in the fractionating column, refractive-index measurements with an Abbe refractometer are made on pure benzene, pure carbon tetrachloride, and two or three mixtures of known composition. These measurements are used for the determination of the compositions of samples of distillate and residue.

The packed column is used next to demonstrate the separation of two liquids. The column and distilling pot are emptied and dried, and 30 ml of chloroform and 30 ml of benzene are introduced. The reflux condenser is set for a reflux ratio of from 5:1 to 10:1, and the liquid is distilled and collected in a graduated cylinder. A 1-ml sample is collected in a small stoppered tube after every 3 ml of distillate, and the thermometer reading is recorded graphically as a function of the percentage of total volume which has distilled over. The refractive indices are then recorded together with the total volume distilled over.

Calculations. The refractive indices of benzene, carbon tetrachloride, and the known mixtures of the two are plotted on coordinate paper on which the mole per cent of carbon tetrachloride is plotted along the X-axis from 0 to 100. A smooth curve is drawn through these points.

The numbers of theoretical plates effective in the Vigreux column and in the packed column at total reflux are calculated with the help of a large graph in which the mole per cent of the more volatile component in the vapor is plotted against the mole fraction of this component in the liquid, as indicated in Fig. 22. The data required for the benzene–carbon tetrachloride system are given in Table 1.

TABLE 1. LIQUID AND VAPOR COMPOSITION OF MIXTURES OF CARBON TETRACHLORIDE AND BENZENE AT 760 MM AND AT TEMPERATURES BETWEEN THE BOILING POINTS[7]

Mole per cent CCl_4 in liquid...	0	13 64	21 57	25 73	29 44	36 34	40 57	52 69	62 02	72.2
Mole per cent CCl_4 in vapor .	0	15 82	24 15	28 80	32.15	39.15	13 50	51 80	63.80	73 3

The effectiveness of various types of packing or construction of the fractionating column may be compared by calculating the length equivalent to 1 theoretical plate. The length of packing per theoretical plate is called the *height equivalent per theoretical plate, H.E.T.P.* The value of H.E.T.P. is calculated for the various columns used.

The effectiveness of the chloroform-benzene distillation is illustrated by plotting on the same graph the refractive indices of the samples collected during the distillation and the corresponding temperatures against the percentage of the total volume of the mixture distilled. For a column with a large number of plates operated at a high reflux ratio, a square step-shaped curve would be obtained, the refractive index of the distillate changing abruptly from that of the more volatile component to that of the less volatile component when the former has all been distilled out.

Suggestions for Further Work. Additional pairs of liquids may be separated by fractionation with an efficient column. A mixture of carbon tetrachloride and toluene may be used to determine the number of theoretical plates. The data for this system are given in Table 2.

TABLE 2. LIQUID AND VAPOR COMPOSITIONS OF MIXTURES OF CARBON TETRACHLORIDE AND TOLUENE[7]

Mole per cent CCl_4 in liquid .	0	5 75	16 25	28 85	42.60	56.05	64.25	78 20	94.55
Mole per cent CCl_4 in vapor .	0	12 65	31 05	49.35	64 25	75.50	81 22	89 95	97.35

Some of the various types of packing referred to in Chap. 21 may be compared by determining the H.E.T.P. for each.

An impure liquid, such as a low-grade technical benzene, is purified by fractionating with a 10:1 reflux ratio, and the purification is followed by refractive-index measurements on the distillate. Liquids for use in the laboratory may be advantageously purified in this way.

A commercial gasoline may be separated into fractions of different boiling-point ranges.

The value of a fractionating column depends not only on the number of theoretical plates but also on the amount of liquid held up by the packing.[4,8] Equilibrium conditions are attained more rapidly if the holdup of the column is small. The amount of liquid held up may be determined at the end of an experiment by removing the heating bath, taking out the column and blowing dry air through it, and condensing the material in a weighed U tube surrounded by a freezing bath of dry ice. When the packing is completely dry, the increase in weight of the U tube gives the weight of the liquid held up in the column.

References

1. Badger and McCabe, "Elements of Chemical Engineering," Chap. IX, McGraw-Hill Book Company, Inc., New York (1936).
2. Bowman *in* Gruse and Stevens: "The Chemical Technology of Petroleum," Chap. VII, McGraw-Hill Book Company, Inc., New York (1942).
3. Carney, "Laboratory Fractional Distillation," The Macmillan Company, New York (1949).
4. Collins and Lantz, *Ind. Eng. Chem., Anal. Ed.*, **18**, 673 (1946).
5. McCabe and Thiele, *Ind. Eng. Chem.*, **17**, 605 (1925).
6. Morton, "Laboratory Technique in Organic Chemistry," McGraw-Hill Book Company, Inc., New York (1938).
7. Perry, "Chemical Engineers' Handbook," 3d ed., Sec. 9, McGraw-Hill Book Company, Inc., New York (1950).
8. Robinson and Gilliland, "The Elements of Fractional Distillation," 4th ed., McGraw-Hill Book Company, Inc., New York (1950).
9. Williams and Glazebrook *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. IV, Chap. 2, "Distillation," Interscience Publishers, Inc., New York (1951).

16. PARTIAL MOLAL PROPERTIES OF SOLUTIONS

The accurate determination of the density of a liquid and the precise mathematical treatment of the properties of solutions are studied.

Theory.[3,4] The quantitative study of solutions has been greatly advanced by the introduction of the concept of partial molal quantities. A property of a solution, e.g., the volume of a mixture of alcohol and water, changes continuously as the composition is changed, and considerable confusion existed formerly in expressing these properties as a function of composition. G. N. Lewis emphasized the use of the exact and simple methods of the differential calculus and defined the *partial molal property* of a component of a solution as follows: Let G represent any extensive property of a binary solution; at constant temperature and pressure, G then will be a function of the two independent variables n_1 and n_2 which represent the numbers of moles of the two components present. The partial molal property of component 1 is then defined by the relation

$$\bar{G}_1 = \left(\frac{\partial G}{\partial n_1}\right)_{n_2,T,P} \tag{1a}$$

Similarly for component 2,

$$\bar{G}_2 = \left(\frac{\partial G}{\partial n_2}\right)_{n_1,T,P} \tag{1b}$$

The partial molal quantity is designated by a bar above the letter representing the property and by a subscript which indicates the component to which the value refers. The usefulness of the concept of partial molal quantities lies in the fact that it may be shown mathematically[3,4] that

$$G(n_1,n_2) = n_1\bar{G}_1 + n_2\bar{G}_2 \qquad (T,P \text{ constant}) \tag{2}$$

Any extensive property of the solution may be expressed in this manner in terms of partial molal properties, which themselves are functions of the concentration of the solution, the temperature, and the pressure and must be evaluated by means of experimental measurements. The activity a_i of a component of a solution is defined in terms of its relative partial molal free energy $\bar{F}_i - \bar{F}_i^0$, and the calculation of heats of reaction for solution systems requires a knowledge of the relative partial molal enthalpies $\bar{H}_i - \bar{H}_i^0$ for all the components.

In the case of the volume of the solution, Eq. (2) gives directly

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \qquad (T,P \text{ constant})$$

The partial molal volumes $\bar{V}_1$ and $\bar{V}_2$ may be evaluated from density measurements on the solutions. The graphical methods described fully by Lewis and Randall[3] may be used in the treatment of the data; of these the use of the apparent molal volume ϕ_V is particularly convenient for binary solutions.

The apparent molal volume is defined by the relation

$$\phi_V = \frac{V - n_1 v_0}{n_2} \qquad (T,P \text{ constant}) \tag{3}$$

where V = volume of solution containing n_1 moles solvent, n_2 moles solute

v_0 = molar volume of pure solvent at given T,P

Since $V = n_2\phi_V + n_1 v_0$,

$$\bar{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{n_1,T,P} = \phi_V + n_2\left(\frac{\partial \phi_V}{\partial n_2}\right)_{n_1,T,P} \tag{4a}$$

and

$$\bar{V}_1 = \frac{V - n_2\bar{V}_2}{n_1} = \frac{1}{n_1}\left[n_1 v_0 - n_2^2\left(\frac{\partial \phi_V}{\partial n_2}\right)_{n_1,T,P}\right] \tag{4b}$$

In terms of the experimentally measured density d and the molecular weights M_1 and M_2 of the two components,

$$\phi_V = \frac{1}{n_2}\left(\frac{n_1M_1 + n_2M_2}{d} - n_1 v_0\right) \tag{5}$$

When the molal concentration scale is used, $n_2 = m$, the molality, and

n_1 is equal to the number of moles of solvent in 1,000 g of solvent, so that

$$\phi_V = \frac{1}{m}\left[\frac{(1{,}000 + mM_2)}{d} - \frac{1{,}000}{d_0}\right] = \left[\frac{1{,}000}{mdd_0}(d_0 - d) + \frac{M_2}{d}\right] \quad (6)$$

where d_0 = density of pure solvent

d = density of solution of molality m of solute of molecular weight M_2

The second expression is particularly convenient for actual calculations.

The use of the apparent molal volume in this determination is advantageous because the error involved in the graphical determination of the derivative of a function is encountered only in the evaluation of the term giving the difference between the partial molal volume and the apparent molal volume.

The partial molal volume may be visualized by considering a large reservoir of a solution of given composition, so large that the addition of one more mole of a component will not appreciably alter the concentration. If now one mole of component 1 is added to this large reservoir of solution, the increase in the volume of the solution is equal to the partial molal volume of component 1 at the indicated concentration, temperature, and pressure. The magnitude of the partial molal volume depends upon the nature of the interactions between the components of the solution under the given conditions; the effects of these interactions are difficult to predict theoretically, but the over-all result is readily expressed mathematically, as already shown. In the special case of an ideal solution, the partial molal volume of any component at any concentration is equal to the molal volume of the pure liquid component at the temperature and pressure of the solution.

The concept of the partial molal quantity may, of course, be applied to solutions containing more than two components. The extension of Eqs. (1) and (2) to the general case is discussed in detail elsewhere.[3,4]

Apparatus. Pycnometers; thermostat; balance; six small glass-stoppered bottles or flasks; sodium chloride.

Procedure.[1] Solutions of sodium chloride in water containing approximately 2, 4, 8, 12, and 16 per cent sodium chloride by weight are prepared. The salt and water are weighed out accurately into a weighing bottle or glass-stoppered flask, care being taken to prevent evaporation of the volatile solvent. A total volume of about 75 ml of each solution is required for the execution of duplicate determinations.

The density of each solution is determined accurately at 25.0°C. A pycnometer of the Weld or Ostwald-Sprengel type shown in Fig. 25 may be used. The pycnometer is dried carefully, weighed, then filled with distilled water and placed in the thermostat for 10 or 15 min.

With the Ostwald-Sprengel pycnometer, the quantity of liquid is then adjusted so that the liquid meniscus is at the mark on the horizontal capillary when the other capillary arm is filled. This adjustment may be made by tilting the completely filled unit slightly and withdrawing liquid slowly from the other capillary by touching a piece of filter paper to it. The pycnometer is removed from the thermostat, wiped dry with a lintless cloth, and the caps placed on the capillary arms. It is allowed to stand in the balance case for a few minutes before being weighed.

The Weld pycnometer is initially filled to bring the liquid level about halfway up the throat T of the reservoir R. The pycnometer is placed in the thermostat with the cap C in position to prevent evaporation from the exposed liquid surface. When temperature equilibrium has been reached, the cap C is removed and the plug P is inserted. A moderate pressure is sufficient to seat the plug firmly. Any excess liquid on the tip of the plug is wiped off with a piece of filter paper, care being taken to avoid removing liquid from the plug capillary in the process. The pycnometer is then removed from the thermostat, wiped dry with a lintless cloth, and the (dried) cap C put in place. It is allowed to stand in the balance case for a few minutes before being weighed.

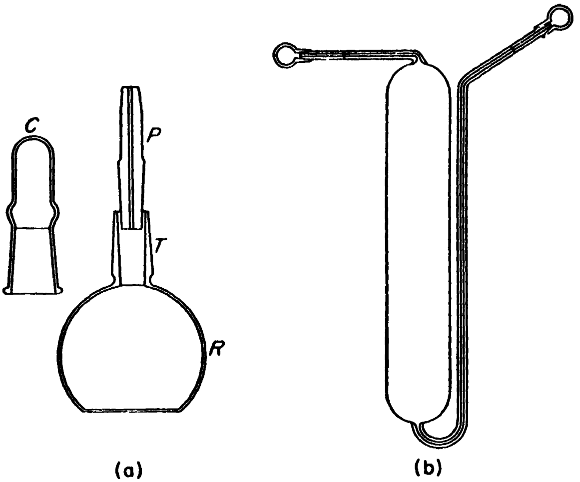

FIG. 25. (*a*) Weld pycnometer; (*b*) Ostwald-Sprengel pycnometer.

In this fashion, duplicate determinations are made of the weight of liquid required to fill the pycnometer at the thermostat temperature, for water and for each of the solutions previously prepared. Two pycnometers may be used to advantage so that one may be weighed while the other is in the thermostat.

Calculations. The weights of the water and of the various salt solutions held by the pycnometers are corrected to vacuum as described in

Chap. 21. The density of water at 25°C is taken as 0.99707 g ml^{-1} for the calculation of the volumes of the pycnometers. The density of each solution is then calculated by dividing its vacuum weight by the appropriate pycnometer volume.

The concentration of each solution is expressed in terms of the molal concentration scale, and the apparent molal volume is determined at each concentration. The uncertainty in the apparent molal volume introduced by an uncertainty of 0.02 per cent in the density is computed for each solution.

By means of Eqs. (4*a*) and (4*b*) the partial molal volumes of solute and solvent are evaluated at each concentration. In this case $n_2 = m$, the molality, and n_1, the number of moles of solvent associated with n_2 moles of solute, is equal to 55.51, i.e., 1,000/18.016. It is convenient in the case of an electrolytic solution to plot ϕ_V against $m^{1/2}$* instead of against m, and to utilize the relationship

$$\left(\frac{\partial \phi_V}{\partial m}\right)_{n_1,T,P} = \frac{1}{2m^{1/2}}\left[\frac{\partial \phi_V}{\partial (m^{1/2})}\right]_{n_1,T,P} \tag{7}$$

A second method is also used for the evaluation of $\bar{V}_2$. The volume of solution containing 1,000 g of solvent is plotted against the molality m. The slope of the tangent to the curve at any chosen concentration gives directly the value of $\bar{V}_2$. The values given by this method are compared with those obtained by the preceding method.

Practical Applications. The use of partial molal quantities is fundamental in the application of thermodynamics to solution systems.

Suggestions for Further Work. Other solutions may be investigated. The system benzene-carbon tetrachloride[6] exhibits nearly ideal behavior. The system ethanol-water[5] provides an example of nonideal behavior and is particularly interesting in the region from 0 to 15 mole per cent ethanol.

References

1. Bauer *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Chap. 6, Interscience Publishers, Inc., New York (1949).
2. Gucker, *J. Phys. Chem.*, **38**, 307 (1934).
3. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," pp. 37ff., McGraw-Hill Book Company, Inc., New York (1923).
4. MacDougall, "Thermodynamics and Chemistry," 3d ed., pp. 23ff., John Wiley & Sons, Inc., New York (1939).
5. Osborne, McKelvey, and Bearce, *Natl. Bur. Standards* (*U.S.*), *Bull.*, **9**, 424 (1913).
6. Wood and Brusie, *J. Am. Chem. Soc.*, **65**, 1891 (1943).

17. STEAM DISTILLATION

Steam distillation is used to illustrate the distillation of two immiscible liquids.

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* Where the highest accuracy is required, the concentration is expressed on the molar scale rather than the molal scale.[2]

Theory. When two immiscible liquids are heated, each exerts its own vapor pressure independent of the other. When the sum of the vapor pressures of the two liquids becomes equal to the atmospheric pressure, the two distill over together, and the temperature of distillation and the composition of the distillate remain constant until one of the liquids is entirely evaporated.

The composition of the distillate is fixed by the vapor pressures and the molecular weights. The higher the vapor pressure of a liquid, the greater is the number of molecules in the vapor phase; and the larger the molecular weight, the greater is the weight of material evaporated for a given number of molecules. Steam distillation is similar to vacuum distillation, in that the liquid distills over and condenses at a temperature much below its normal boiling point.

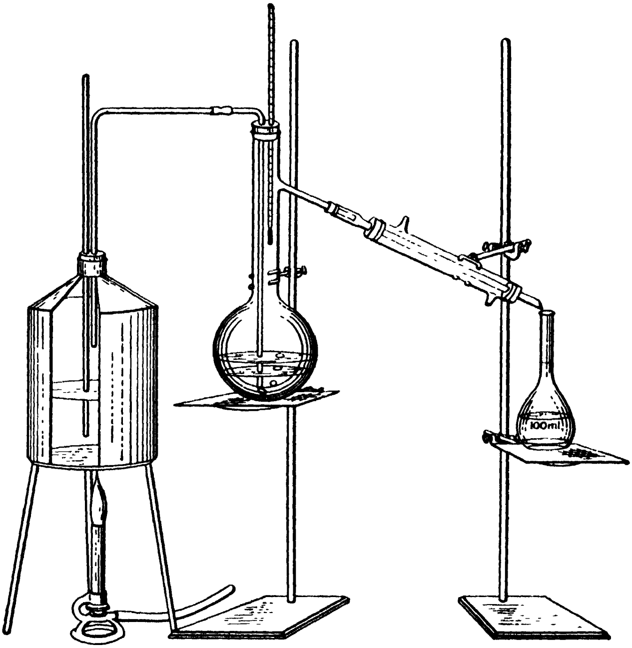

FIG. 26. Apparatus for steam distillation

Apparatus. Barometer; 500-ml distilling flask; condenser; two 100-ml volumetric flasks; 10-ml graduated cylinder; 0.1° thermometer; steam generator; glass tubing.

Procedure. A 500-ml distilling flask is connected to a condenser, and steam is introduced from a generator, made of a metal can provided with a two-hole stopper carrying the exit tube and a 50-cm safety tube, which extends to the bottom of the can. If too great a pressure is built up, it is relieved by forcing out the liquid in the safety tube. The apparatus is shown in Fig. 26.

The steam-inlet tube at the bottom of the flask has a number of small holes so that the steam will come in contact with a larger surface and thus become saturated more quickly with the vapor of the other liquid. A thin bulb is blown on the end of a glass tube, and many small holes are poked through it, using the sharpened end of a file which has been heated to redness.

Steam is passed through the flask to correct for the exposed stem and errors in the thermometer. The true temperature of the steam is determined by reading the barometer (corrected to 0° as given in the Appendix) and finding in tables the boiling point of water at this pressure. The difference between this temperature and the thermometer reading gives the correction which must be added or subtracted. This correction is applicable only when the thermometer is in the same position and the room temperature is approximately the same.

About 100 ml of nitrobenzene is introduced into the flask, and steam is forced through the heavy nitrobenzene layer. When the temperature becomes constant, two 100-ml volumetric flasks are allowed to fill to the mark with the distillate and are set aside to allow the two layers to separate.

If the distillation is too rapid, an insufficient quantity of nitrobenzene will distill over. Most of the water layer is poured from the collected samples, and the volume of the nitrobenzene layer is carefully measured after transferring it to a small cylinder graduated to 0.1 or 0.2 ml. All the nitrobenzene including small drops clinging to the sides of the flask must be rinsed out into the cylinder.

The meniscus of the nitrobenzene is inverted when covered with water, and an error is introduced if the reading is taken in the usual manner, because the cylinder is calibrated for a meniscus that is convex to the bottom. Two or three milliliters of nitrobenzene is placed in the cylinder and covered with a little water. The difference between the level of *this* meniscus and the level *after* pouring in the nitrobenzene from the flask gives the correct volume of nitrobenzene carried over by the steam.

Steam distillation of oleic acid is carried out in the same manner as has been described for nitrobenzene.

Calculations. The weight of each component in the distillate is proportional to the vapor pressure and to the molecular weight, as shown by the following relation:

$$\frac{\text{Weight}_A}{\text{Weight}_B} = \frac{\text{vapor pressure}_A \times \text{molecular weight}_A}{\text{vapor pressure}_B \times \text{molecular weight}_B} \qquad (1)$$

The experimental data may be used to calculate one of the several different quantities given in Eq. (1). In this experiment, it is the vapor pressure of nitrobenzene which is calculated. The weight of nitrobenzene is determined from the volume of the condensed liquid, its density being 1.204 g cm^{-3} at 20° and 1.197 g cm^{-3} at 25°. The weight of water is then calculated, and the molecular weights are obtained from the atomic weights, assuming no association in the gas phase. The only unknown then is the vapor pressure of nitrobenzene at the temperature of the steam distillation. The vapor pressure of water at the temperature of distillation is found from tables by interpolation.

The vapor pressure of the water and the vapor pressure of nitrobenzene should add up to give the observed barometric pressure except for a small error due to a very slight solubility of the two liquids in each other.

The vapor pressure of oleic acid is calculated from the barometric pressure and the vapor pressure of water as found in tables, assuming that the solubilities of the liquids are negligible. The number of grams of water required to steam-distill a gram of oleic acid is then calculated and compared with the experimentally determined amount. The density of oleic acid at 20° is 0.891.

Practical Applications. When a liquid decomposes at its normal boiling point, it should be distilled at a lower temperature either by vacuum distillation or by distillation with steam or other immiscible liquid. The apparatus for steam distillation is simpler than that required for vacuum distillation, but the process is limited to those liquids which are immiscible with water. Water is the most common liquid used in the distillation of immiscible liquids on account of its cheapness and its low molecular weight.

Suggestions for Further Work. Other liquids may be steam-distilled, such as aniline, fats, oils, and mercury.

Having determined the vapor pressure at the temperature of the steam distillation and knowing the boiling point at 760 mm from tables, the heat of vaporization of nitrobenzene is calculated using the Clausius-Clapeyron equation given in Exp. 9.

References

1. Carlson *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. IV, Chap. 3, "Distillation," Interscience Publishers, Inc., New York (1951).
2. Morton, "Laboratory Technique in Organic Chemistry," pp. 124-146, McGraw-Hill Book Company, Inc., New York (1938).

CHAPTER 6

HOMOGENEOUS EQUILIBRIA

18. EQUILIBRIUM IN ORGANIC LIQUIDS

This experiment illustrates the determination and calculation of apparent equilibrium constants.

Theory. An acid and an alcohol combine to form an ester and water; the ester hydrolyzes to give the acid and alcohol. The two opposing reactions proceed until an equilibrium is reached with all four compounds present in definite concentrations. The equilibrium constant K gives a measure of the relation between the activities of the products and the reacting materials. When the equilibrium constant has been determined, it is possible to calculate the yield that may be expected from any given concentration of reacting materials.

When concentrations are used in calculating the equilibrium constant, the equilibrium constant is in error on account of the failure of the mass law, particularly at high concentrations. An accurate value of the equilibrium constant is obtained by using activities instead of analytically determined concentrations. Activities may be determined by vapor-pressure measurements or by other methods. Details are given by Lewis and Randall.[6] In many cases, however, the equilibrium constant may be calculated with fair accuracy from the concentrations.

The equilibrium is sometimes reached very slowly, particularly in organic reactions, and it may be necessary to raise the temperature or to use a catalyst.

The equilibrium between ethanol, acetic acid, ethyl acetate, and water is studied in this experiment, and the reaction is catalyzed by the addition of hydrochloric acid. Its concentration is great enough to change the character of the water and alter the numerical value of the equilibrium constant,[5] but the results are fairly constant for a given concentration of hydrochloric acid. The hydrochloric acid is added merely as a catalyst to hasten the reaction, and it takes no part in the stoichiometric reaction.

Apparatus. Burette; 5-ml pipette; 2-ml pipette; 1-ml pipette; fourteen 50-ml glass-stoppered bottles; 0.5 N sodium hydroxide; phenolphthalein, ethyl acetate, concentrated hydrochloric acid, glacial acetic acid, absolute ethanol.

Procedure. A 3 *N* hydrochloric acid is prepared by diluting concentrated hydrochloric acid. It is mixed with ethyl acetate and other materials in 50-ml glass-stoppered bottles, in the following proportions:

(*a*) 5 ml 3 *N* HCl + 5 ml water
(*b*) 5 ml 3 *N* HCl + 5 ml ethyl acetate
(*c*) 5 ml 3 *N* HCl + 4 ml ethyl acetate + 1 ml water
(*d*) 5 ml 3 *N* HCl + 2 ml ethyl acetate + 3 ml water
(*e*) 5 ml 3 *N* HCl + 4 ml ethyl acetate + 1 ml ethanol
(*f*) 5 ml 3 *N* HCl + 4 ml ethyl acetate + 1 ml acetic acid
(*g*) 5 ml 3 *N* HCl + 4 ml ethanol + 1 ml acetic acid

Duplicate determinations are made as usual. Each of the bottles is stoppered immediately and allowed to stand in a warm place for at least 48 hr and preferably for a week, with occasional shaking. It is necessary that the stoppers fit tightly to prevent evaporation. A thermostat is unnecessary because this equilibrium is affected only slightly by temperature changes.

The weight of each material is determined by discharging the pipette directly into a glass-stoppered weighing bottle and weighing. In this way the following weighings are made:

5 ml 3 *N* hydrochloric acid
5 ml and 2 ml ethyl acetate
1 ml and 4 ml ethanol
1 ml acetic acid
5 ml, 3 ml, and 1 ml water

The drainage of the pipettes will not always be uniform, but the error involved in using a pipette is not serious for the present work.

After standing, each solution is titrated with the 0.5 *M* sodium hydroxide, using phenolphthalein as an indicator.

Calculations. The original weight of ethyl acetate is obtained by weighing the liquid ethyl acetate discharged from the pipette. The original weight of acetic acid and ethanol in (*e*), (*f*), and (*g*) is obtained in the same way. The weight of water is obtained by adding the weight of pure water to the water contained in the 3 *N* hydrochloric acid. The latter is calculated by subtracting the weight of the hydrochloric acid, obtained by titration, from the weight of the 5 ml of hydrochloric acid solution.

The amount of acetic acid at equilibrium is obtained by subtracting the number of milliliters of sodium hydroxide used in solution (*a*) from the number used for the final equilibrium titration. The former is a measure of the hydrochloric acid, and the latter is a measure of both the hydrochloric acid and the acetic acid at equilibrium. The difference, then, gives the amount of acetic acid at equilibrium. In (*f*) and (*g*), acetic acid is added to the original solution, and this amount must be used in calculating the equilibrium amounts of the other reactants. For every mole of acetic acid produced in the reaction, 1 mole of ethanol is produced, 1 mole of water disappears, and 1 mole of ethyl acetate disappears.

If the number of moles of each of the four materials in the original mixture and the number of moles of acetic acid produced in the reaction are known, the equilibrium constant K_N may be computed. It is defined as

$$K_N = \frac{N_{\mathrm{CH_3COOC_2H_5}} N_{\mathrm{H_2O}}}{N_{\mathrm{C_2H_5OH}} N_{\mathrm{CH_3COOH}}}$$

where N represents mole fraction.

As indicated in the opening paragraphs, the value K_N obtained in this way is not particularly constant. It deviates more and more as the concentrations of the reactants and products are increased. Thus, the values of K_N which are obtained are apparent ones; true equilibrium constants can be obtained by the use of activities in place of concentrations.

Practical Applications. In planning any chemical synthesis, it is desirable to know what yield of material may be expected from a given concentration of reacting materials. Such a calculation may be made when the value of the equilibrium constant is known, provided that the reaction is fast enough to come to equilibrium in the time allowed.

Suggestions for Further Work. Similar experiments may be carried out with other esters.

More significant results are obtained without the use of a catalyst, but under these conditions it is necessary to heat the mixture to about 150° in sealed tubes to effect an equilibrium within a couple of days. If sufficient precautions are taken to avoid danger from bursting tubes, the equilibrium constant may be determined by titrating mixtures that have been weighed out, sealed off in small glass tubes, and heated. The original work of Berthelot and St. Gilles[3] may be repeated.

The equilibrium involved in the reaction between acetaldehyde and alcohol to give acetal and water may be studied.[2] A little hydrochloric acid is used as a catalyst, and the equilibrium concentration of the acetaldehyde is determined volumetrically by the sulfite method,[1] with thymolphthalein as indicator.[4]

Another example of an equilibrium in a liquid system is the dissociation of the amyl ester of dichloroacetic acid into the acid and amylene. It was investigated by Nernst and Hohmann.[7]

References

1. Adams and Adkins, *J. Am. Chem. Soc.*, **47**, 1358 (1925).
2. Adkins and Adams, *J. Am. Chem. Soc.*, **47**, 1368 (1925).
3. Berthelot and St. Gilles, *Ann. chim. et phys.* (3), **65**, 385 (1862); **68**, 225 (1863).
4. Deyrup, *J. Am. Chem. Soc.*, **56**, 60 (1934).
5. Jones and Lapworth, *J. Chem. Soc.*, **99**, 1427 (1911).
6. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," pp. 254–290, McGraw-Hill Book Company, Inc., New York (1923).
7. Nernst and Hohmann, *Z. physik. Chem.*, **11**, 352 (1893).

19. DISSOCIATION OF NITROGEN TETROXIDE

The equilibrium constant for a reaction is determined as a function of temperature, and the corresponding heat of reaction is calculated.

Theory. Nitrogen tetroxide dissociates in accordance with the reaction

$$N_2O_4 = 2NO_2$$

If the equilibrium degree of dissociation is represented by α, an initial one mole of undissociated N_2O_4 gives at equilibrium $(1 + \alpha)$ moles of gas, $(1 - \alpha)$ moles of N_2O_4, and 2α moles of NO_2. The equilibrium mole fraction of N_2O_4 is then $(1 - \alpha)/(1 + \alpha)$, and that of NO_2 is $2\alpha/(1 + \alpha)$. When the partial pressure of each constituent is set equal to the product of its mole fraction and the total pressure P, the equilibrium constant for the reaction takes the form

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha}P\right)^2}{\frac{1-\alpha}{1+\alpha}P} = \frac{4\alpha^2P}{1-\alpha^2} \tag{1}$$

Since the volume of a gas phase at constant temperature and pressure is proportional to the number of moles of gas present, the density d of the equilibrium gas mixture is related to d_0, the density corresponding to undissociated N_2O_4 at the same temperature and pressure:

$$\frac{d_0}{d} = \frac{1+\alpha}{1} \tag{2}$$

Since the molecular weight of a gas is directly proportional to its density at constant temperature and pressure, the value of α is given by

$$\alpha = \frac{d_0 - d}{d} = \frac{M_0 - M}{M} \tag{3}$$

where M_0 = molecular weight of N_2O_4 = 92.06

M = average molecular weight of equilibrium gas mixture

Equations (1), (2), and (3) apply when the gas mixture is considered to be an ideal mixture of perfect gases.

The standard free-energy change for a reaction can be calculated from the thermodynamic equilibrium constant:

$$\Delta F^0 = -RT \ln K = -2.303RT \log K \tag{4}$$

The determination of the equilibrium constant at a series of temperatures permits the evaluation of the standard heat of reaction by application of the Gibbs-Helmholtz equation in the form

$$\Delta H^0 = -T^2\left(\frac{d\Delta F^0/T}{dT}\right) = 2.303RT^2\left(\frac{d\log K}{dT}\right)$$
$$= -2.303R\left(\frac{d\log K}{d1/T}\right) \qquad (5)$$

When the plot of log K versus $1/T$ is a straight line the standard heat of reaction is constant over the temperature range involved and may be calculated from the slope of the line. When the line is not straight the heat of reaction depends on the temperature, but the slope of a tangent drawn at a point corresponding to any temperature will give the heat of reaction at that temperature.

Apparatus. Two gas-density bulbs; counterpoise bulb of same capacity, small adjustable thermostat; cylinder of nitrogen tetroxide.

Procedure. Gas-density bulbs of about 200 ml capacity with capillary glass stopcocks are used for determining the density of the dissociation mixture. Nitrogen tetroxide attacks ordinary stopcock greases, but its effect on petroleum jelly or silicone grease is negligible during the period of the experiment if a minimum amount is used in lubricating the plug.

Two bulbs are evacuated to 1 mm or less with the vacuum system described in Exp. 1, and weighed to 0.1 mg, using a bulb of similar volume as counterpoise. The student should refer to Exp. 1 for comments concerning the weighing procedure.

The bulbs are filled from a small cylinder of nitrogen tetroxide. *Caution: Nitrogen tetroxide is corrosive and very poisonous. All operations should be carried out in a well-ventilated hood.* The outlet from the cylinder is fitted with a short length of Tygon tubing.* A small plug of glass wool may be inserted in this tube before attaching the bulb in order to keep any debris which may be present in the system from entering the bulb. It is removed after filling. The valve on the cylinder is opened slightly to sweep the air out of the tube (a couple of seconds will suffice), and the outlet from the gas-density bulb is then attached to the tube. The cylinder valve and the glass stopcock are opened wide, in that order. The bulb should be completely filled at the vapor pressure of N_2O_4 in about 30 sec. The valve and the stopcock are then closed and the bulb removed from the tubing. The temperature must be higher than 21.5°, the boiling point of N_2O_4. Both bulbs are filled, each determination being made in duplicate.

A small thermostat which permits rapid temperature setting is very convenient for this experiment. Alternatively, a large beaker of water

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* Tygon is the trade-mark of the U.S. Stoneware Company of Akron, Ohio, for a polyvinyl chloride plastic. It is superior to rubber in resistance to N_2O_4.

heated by a bunsen burner or immersion electric heater may be used, although control by this method is more difficult.

The bulb is placed in the small thermostat, which is first set at the lowest temperature to be used (about 30°). The stopcock is opened momentarily at intervals of 2 or 3 min during the period of thermostating, and the gas is allowed to escape until no more brown fumes are seen to issue from the opening. The bulb is closed and again weighed;* care must be taken to ensure uniform weighing technique. Time should be allowed for moisture equilibrium between the bulb and the air in the balance case to be attained and for the bulb to cool to the temperature of the balance.

The bulb is now placed in a thermostat at a temperature approximately 10° higher, and the above procedure repeated. The same measurements are made every 10° up to 60°.

The volume of the bulb may be determined from the weight of water it can hold. The bulb is evacuated two or three times with a water aspirator in order to remove all corrosive nitrogen tetroxide. It is then evacuated with the aspirator, the stopcock closed, and the end of the tube immersed in a beaker of distilled water. The stopcock is then opened to permit the bulb to fill. A hypodermic syringe with a long needle may be used to complete the filling of the bulb. The bulb is then weighed, and from the weight of water it holds the volume is calculated by use of the data on the density of water given in the Appendix.

The bulb is then emptied, with the help of the water aspirator, and placed in a drying oven. It is evacuated several times while hot to assist in the drying process.

The barometric pressure must be taken at the time of the experiment for use in subsequent calculations.

Calculations. The average molecular weight of the gas at each temperature is computed by use of the ideal-gas law (compare Exp. 1). The corresponding values of the degree of dissociation and the equilibrium constant are calculated by application of Eqs. (3) and (1). A plot is made of log K against $1/T$, and the equation is found of the line considered to best represent the set of points. The standard heat of reaction is calculated from the slope of the line. The standard free-energy change for the reaction is calculated for 25°C.

Practical Applications. The determination of equilibrium constants is of fundamental importance in industrial work, where the yield under specified conditions must be known.

Suggestions for Further Work. A glass-diaphragm manometer may be used for studying this equilibrium at various pressures.[5]

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* After removing the bulb from the thermostat, the temperature regulator should be reset to a point approximately 10° higher. The thermostat will then be approaching the new temperature while weighings are being made.

A simple photometer may be used for determining the partial pressure of NO_2 in the mixture.[3]

The dissociation of N_2O_4 in carbon tetrachloride solution may be studied.[1]

Other rapid reversible dissociations such as that of phosphorus pentachloride and ammonium chloride may be studied at higher temperatures. The method of Victor Meyer (Exp. 2) is suitable for these determinations.

References

1. Atwood and Rollefson, *J. Chem. Phys.*, **9**, 506 (1941).
2. Giauque and Kemp, *J. Chem. Phys.*, **6**, 40 (1938).
3. Harris and Siegel, *Ind. Eng. Chem., Anal. Ed.*, **14**, 258 (1942).
4. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," p. 561, McGraw-Hill Book Company, Inc., New York (1923).
5. Verhoek and Daniels, *J. Am. Chem. Soc.*, **53**, 1250 (1931).

CHAPTER 7

HETEROGENEOUS EQUILIBRIA

20. DISTRIBUTION OF A SOLUTE BETWEEN IMMISCIBLE SOLVENTS

A study is made of the equilibrium distribution of a solute between two immiscible solvents. Quantitative measurements are made of the amount of a solute extracted by an immiscible solvent. Distribution studies of this type give evidence of association or dissociation of the solute.

Theory. When two immiscible solvents are in contact with each other, a dissolved substance will distribute itself between the two according to a definite equilibrium. The ratio of the concentrations of substance A in the organic phase, $c_{A,\text{org}}$, and aqueous phase, $c_{A,\text{aq}}$, at equilibrium gives the distribution coefficient K:

$$K = \frac{c_{A,\text{aq}}}{c_{A,\text{org}}} \tag{1}$$

The distribution coefficient K defined by Eq. (1) is not a true equilibrium constant because it involves concentrations rather than activities, and it may vary somewhat with the concentration of the solute. If the molecular weight of the solute is different in the two phases, the magnitude of the distribution coefficient will change rapidly with the concentration if calculated by Eq. (1).

When the molecular weight of a solute is different in the two solvents, the ratio of the concentrations in the two phases is not constant, and conversely, if the ratio varies considerably with concentration, it may be inferred that the molecular weight of the solute is not identical in the two solvents. If, for example, a substance is associated to form a polymer of n units in the organic phase,

$$\underset{\substack{\text{organic}\\ \text{phase}}}{A_n} \rightleftharpoons \underset{\substack{\text{aqueous}\\ \text{phase}}}{nA} \tag{2}$$

The corresponding distribution coefficient is

$$K = \frac{c^n_{A,\text{aq}}}{c_{A,\text{org}}} \tag{3}$$

where the subscripts indicate the phase. Here the denominator should strictly be $c_{A_n,\text{org}}$, but since n is unknown when the concentrations are calculated from the analytical data, the concentrations in both phases are expressed on the basis of the unassociated molecular weight. This calculation gives the distribution coefficient a value different from that which it would have if calculated from c_{A_n} but does not affect its constancy when c is changed. If the association is not complete, the value of n calculated from Eq. (3) will not be a whole number and may vary with concentration. Similar considerations apply when the solute is dissociated as well as when it is associated.

The carboxylic acids are suitable for a study of this type because they generally form double molecules in nonpolar solvents or in the gas phase but exist as single molecules in polar solvents such as water. Some carboxylic acids, e.g., acetic acid, are so weak that their ionization in water can be practically neglected, but others, e.g., trichloroacetic acid, are almost entirely ionized.

Extraction with several portions of solvent is more efficient than with a single portion of the same total volume. In the case of phase distributions which satisfy Eq. (1), it is possible to derive a generalized formula which will show the amount remaining unextracted after a given number of operations. If V milliliters of solution initially containing x_0 grams (or equivalents) of a substance are repeatedly extracted with v milliliters of an immiscible solvent, we may calculate the number of grams x_n remaining unextracted after n extractions as follows: After one extraction the concentration in the original solution will be x_1/V and in the extracting phase $(x_0 - x_1)/v$. Therefore, the distribution coefficient is

$$\frac{x_1/V}{(x_0 - x_1)/v} = K \tag{4}$$

$$x_1 = x_0\left(\frac{KV}{KV + v}\right) \tag{5}$$

After a second extraction x_2 grams (or equivalents) remain in the original solvent. Thus,

$$x_2 = x_1\left(\frac{KV}{KV + v}\right) = x_0\left(\frac{KV}{KV + v}\right)^2 \tag{6}$$

The second form is obtained by substitution for x_1 by use of Eq. (5).

After n extractions the quantity remaining in the original solvent is

$$x_n = x_0\left(\frac{KV}{KV + v}\right)^n \tag{7}$$

Craig and others[1,3] have designed various pieces of apparatus for carrying out multiple extractions conveniently. A countercurrent distribution apparatus is analogous to a distillation column in that separation is achieved by many two-phase distributions. Such countercurrent distribution experiments may be used not only for the purpose of fractionation but also for the characterization of unknown organic compounds.

Since the distribution coefficients for organic acids and bases between aqueous solutions and immiscible organic solvents depend markedly on the pH of the aqueous phase, multiple extractions with various buffer solutions may be used to separate various organic acids, such as the penicillins.[4]

Apparatus. Three 100-ml separatory funnels; three 100-ml Erlenmeyer flasks; 100-ml volumetric flask; 25-ml pipette; 10-ml pipette; 1.0 *N* acetic acid or trichloroacetic acid or other acid; glacial acetic acid; carbon tetrachloride; ether; 0.5 *N* sodium hydroxide; 0.01 *N* sodium hydroxide.

Procedure. One hundred milliliters each of approximately 0.50 *N*, 1 *N*, and 2 *N* solutions of acetic acid in water are prepared. Twenty-five milliliters of each of the three solutions is pipetted into closed 100-ml separatory funnels, and to each is added 25 ml of diethyl ether. Closed rubber tubes are put over the outlets to keep out the water of the thermostat, and the separatory funnels are set in a thermostat at 25° for 20 min or more, with frequent shaking.

After the solutions have come to equilibrium, the separatory funnels are removed from the thermostat and the lower layers run out into beakers, care being taken to let none of the upper layer go through. Ten-milliliter samples of each of the lower layers are taken rapidly and drained into Erlenmeyer flasks for titration with sodium hydroxide, using phenolphthalein as an indicator. Samples of the upper layers are removed from the separatory funnels with 10 ml pipettes, care being taken to avoid sucking up any of the lower layer. The aqueous and ether solutions are titrated with 0.5 *N* NaOH. Check titrations should be made in each case.

A second set of experiments is carried out in the same way, using 25-ml aliquots of carbon tetrachloride instead of ether. Ten-milliliter aliquots of the CCl_4 phases are measured rapidly in order to prevent loss due to evaporation. The CCl_4 phases are titrated with 0.01 *N* sodium hydroxide.

In titrating the acid dissolved in carbon tetrachloride or ether, an equal volume of water is added initially, and it is necessary to shake vigorously to accelerate the passage of dissolved acid across the surface and into the water layer and thus reduce the time required for elimination of the fading end point.

Calculations. The concentrations of acid in the two layers in the distribution experiments are calculated in moles per liter, and the distribution coefficients are calculated with Eq. (1). Plots of log $c_{A,\mathrm{org}}$ versus log $c_{A,\mathrm{aq}}$ are also constructed and the value of n calculated. If the value of n is not equal to unity, a hypothesis is suggested to explain the results.

As an illustration of the application of the distribution coefficient, the concentration of acetic acid remaining in the ether phase is calculated for the following cases:

1. 50 ml of 1.0 N acetic acid in ether is extracted with 50 ml of water.
2. 50 ml of 1.0 N acetic acid in ether is extracted with five 10-ml portions of water.

Practical Applications. Extraction of a solute by shaking a solution with another immiscible solvent is an operation that is used extensively in organic chemistry. The efficiency of the operation may be calculated when the distribution coefficient is known.

The escaping tendency of a solute determines its distribution into a second solvent, and the activity of the solute may be calculated from distribution data.[6]

The concentration may be determined without disturbing the equilibrium in the solution. For example, in a solution containing iodine dissolved in a solution of potassium iodide, the amount of free iodine cannot be determined by titration, because as soon as the iodine is removed, the potassium triiodide which is present in solution dissociates and keeps up the supply of iodine. The solution may be shaken with a little carbon tetrachloride, and the free iodine distributes itself between the two liquids. The concentration of iodine in the carbon tetrachloride layer may be determined without the complication of the potassium triiodide compound; the concentration of free iodine in the aqueous solution may be obtained by multiplying the concentration in the carbon tetrachloride solution by the distribution ratio between carbon tetrachloride and water.

In some cases, the degree of hydrolysis of a salt may be determined by measuring the distribution ratio of the acid or base when shaken with an immiscible solvent.

The extraction of uranium from its ores and the separation of uranium from its fission products in atomic-energy operations often make use of solvent extraction with an organic solvent which is immiscible with water.

Suggestions for Further Work. Other distribution systems may be studied, such as the following:

Hydrochloric acid between water and benzene.[5]

Salicylic acid or picric acid between water and benzene, and between water and chloroform as a function of the pH of the aqueous phase.

Iodine between potassium iodide solution and carbon tetrachloride.

Uranyl nitrate between water and ether or between water and tributyl phosphate. The extraction of uranyl nitrate into the organic phase is improved by the addition of nitric acid.

As an example of the distribution of an inorganic salt between immiscible solvents, the distribution of ferric chloride between ether and water may be studied. The salting-out effect is illustrated by the addition of excess sodium chloride or calcium chloride to the aqueous phase.

References

1. Craig, *J. Biol. Chem.*, **155**, 519 (1944).
2. Craig and Craig *in* Weissberger (ed.): "Physical Methods of Organic Chemistry," Vol. III, Interscience Publishers, Inc., New York (1950).

3. Craig, Golumbic, Mighton, and Titus, *J. Biol. Chem.*, **161,** 321 (1945).
4. Craig, Hogeboom, Carpenter, and du Vigneaud, *J. Biol. Chem.*, **168,** 665 (1947).
5. Hinshelwood and Knight, *J. Chem. Soc.*, **1927,** 466.
6. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," pp. 260, 331, McGraw-Hill Book Company, Inc., New York (1923).

21. THREE-COMPONENT SYSTEMS

Solubility data involving three different substances are plotted on triangular graph paper.

Theory. According to the phase rule of Gibbs the variance v (number of degrees of freedom) of a system at equilibrium is equal to the number of components c minus the number of phases p plus 2, provided that the equilibrium is influenced only by temperature, pressure, and concentration.

$$v = c - p + 2 \tag{1}$$

In considering systems at sufficiently high pressures to eliminate the vapor phase, the pressure does not have to be specified and the phase rule is written

$$v = c - p + 1 \tag{2}$$

If in addition the temperature is held constant

$$v = c - p \tag{3}$$

so that for a three-component system $v = 3 - p$. Thus, there are two degrees of freedom if a single phase is present, and one degree of freedom if two phases are present.

It is convenient to represent a three-component system on a triangular diagram such as that illustrated in Fig. 27.

In an equilateral triangle, the sum of the perpendiculars from a given point to the three sides is a constant. The perpendicular distance from each apex, representing a pure compound, to the opposite side is divided into 100 equal parts, corresponding to per cent, and labeled along the side at the right of the perpendicular. A point situated on one of the sides of the triangle indicates that there are two components with the percentage concentration indicated. The composition corresponding to any point within the triangle is obtained by measuring on these coordinates the distance toward apex A, the distance toward B, and the distance toward C. These three distances representing percentages always add up to 100. For example, point M represents the composition 30 per cent A, 60 per cent B, and 10 per cent C. If the figure is turned successively with each apex at the top, the scale of percentage composition for the component, corresponding to this apex, is found at the right.

Several different types of ternary systems are possible depending upon whether one, two, or three pairs of the liquids are partially miscible in each other. In the typical system illustrated in Fig. 27, *A* and *C* are partially miscible while pair *A* and *B* and pair *B* and *C* are completely miscible. Mixtures having compositions lying below the curve will separate into two phases, while all other mixtures form homogeneous solutions. For example, mixture *O* will separate into two phases *K* and *L*, and the line connecting these conjugate ternary solutions in equilibrium with each other is called a *tie line*. It is an important characteristic of a ternary diagram that the relative amounts of phases *K* and *L* are proportional to the lengths *OL* and *OK*, respectively. These tie lines slope upward to the right, indicating that component *B* is relatively more soluble in the phase rich in *C* than it is in the phase rich in *A*.

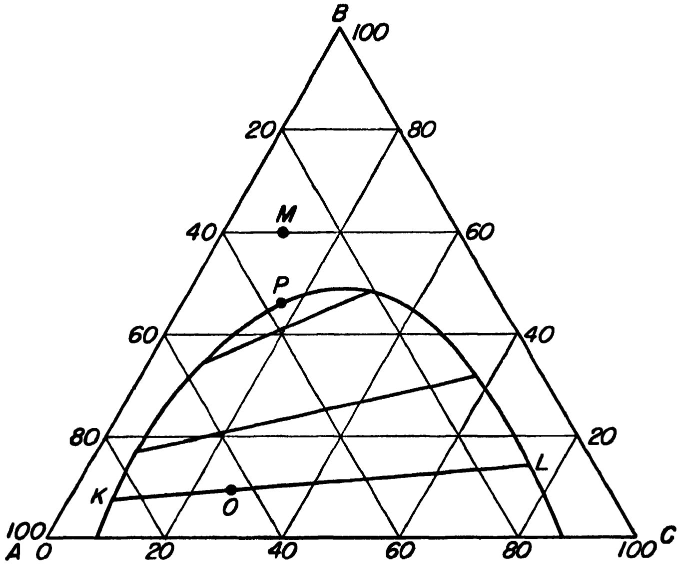

FIG. 27. Three-component system.

As the amount of component *B* is increased, the compositions of the conjugate solutions approach each other. At point *P* the two conjugate solutions have the same composition, so that the two layers have become one: this is called the *plait point*.

Apparatus. Thermostat (25°); three burettes (25 ml); six glass-stoppered bottles (50 ml); one 5-ml pipette; small separatory funnel; Westphal density balance; chloroform; acetic acid; 0.2 *N* sodium hydroxide.

Procedure. The solubility relations of the three-component system chloroform–acetic acid–water are studied in this experiment. The tie lines may be determined conveniently by titrating the acetic acid in the two separate liquid phases which are in equilibrium with each other.

Three burettes are set up containing water, chloroform, and acetic acid. The density of each liquid is determined on the Westphal balance, and solutions of accurately known concentration are prepared containing approximately 10, 25, 40, and 60 per cent by weight acetic acid in water. About 20 g of each is sufficient. These four solutions are placed in 50-ml glass-stoppered bottles and set in a thermostat at 25°. After coming to temperature, they are removed as necessary and titrated with chloroform. During the titration, the bottle is shaken vigorously after each addition of chloroform, and the end point is taken as the first perceptible cloudiness.

Samples of approximately 10, 25, 40, and 60 per cent acetic acid in chloroform are then prepared and titrated to cloudiness with water at the thermostat temperature. The percentage by weight of each component present at the appearance of the second phase is calculated, and the compositions are plotted on the ternary diagram.

The tie lines are determined by preparing about 40 ml of mixtures of accurately known concentrations containing approximately 10, 20, 30, and 40 per cent acetic acid with 45 per cent chloroform in each case, the remainder being water. These two-phase mixtures are prepared in the glass bottles which are then stoppered, shaken, and allowed to equilibrate in the 25° thermostat. After equilibrium has been reached and the phases have been separated by means of a separatory funnel, the density of each phase is determined with the Westphal balance, and 5-ml aliquots are titrated with 0.2 *N* sodium hydroxide, using phenolphthalein as indicator.

Calculations. The percentage by weight of chloroform, acetic acid, and water for each of the mixtures that showed the first indication of turbidity is plotted on triangular graph paper.

The determination of the acetic acid concentrations allows the compositions of the conjugate phases to be located on the two-phase curve. It may be assumed that the more dense phase is the one rich in chloroform. The total compositions of the two-phase mixtures are also plotted on the triangular graph, and the tie lines should pass through these points.

The phases present at each area and line are recorded, and the effect of adding more of the components at significant points is described.

Practical Applications. The properties of many systems are conveniently described with the help of triangular graphs. The increase in mutual solubility of two liquids due to the addition of a third is of practical as well as theoretical importance. Calculations in two-phase extraction processes may be carried out, using triangular diagrams.

Suggestions for Further Work. The solubility and tie-line determinations may be repeated at a different temperature. As the temperature is raised, the area under the curve corresponding to the region of two liquid phases becomes smaller, because the liquids become more soluble in each other. Several isothermal lines may be drawn on the same diagram, or a space model may be constructed with temperature as the vertical axis and the triangular diagrams lying in horizontal planes. A triangular-prism space model may be made for the liquid-solid phases in the system diphenyl-diphenylamine-benzophenone.[3]

The systems benzene-water-alcohol and cyclohexane-water-alcohol studied by Washburn and his associates illustrate the effect of increasing the hydrocarbon-chain length in the alcohol homologous series.[5]

The system water–ether–succinic nitrile furnishes an example of a three-component system containing three pairs of partially miscible liquids. The system water–methyl acetate (or ethyl acetate)–*n*-butyl alcohol is an example of a system in which two of the pairs of liquids are partially miscible while the third pair is completely miscible.

References

1. Findlay, "The Phase Rule," Longmans, Green & Co., Inc., New York (1938); Dover Publications, Inc., New York.
2. Glasstone, "Textbook of Physical Chemistry," pp. 790–812, D. Van Nostrand Company, Inc., New York (1946).
3. Lee and Warner, *J. Am. Chem. Soc.*, **55**, 309, 4474 (1933).
4. Rhodes, "Phase Rule Studies," Chaps. V and VI, Oxford University Press, New York (1933).
5. Washburn *et al.*, *J. Am. Chem. Soc.*, **53**, 3237 (1931); **54**, 4217 (1932); **56**, 361 (1934); **57**, 303 (1935); **59**, 2076 (1937); **61**, 1694 (1939), **68**, 235 (1946).

22. FREEZING-POINT DIAGRAMS

This experiment illustrates the use of cooling curves to establish the phase diagram for a binary system. It illustrates also the use of the thermocouple.

Theory.[1] The purpose of the experiment is to obtain data by thermal analysis for constructing a phase diagram which indicates the solid and liquid phases that are present at each temperature and composition. Mixtures are made up arbitrarily, and the temperatures at which solid phases appear are indicated by typical nonuniformities in the cooling curves. A slower rate of cooling is obtained during the change in state because the heat evolved by solidification partly offsets the heat lost by radiation and conduction to the colder surroundings.

A. AN ALLOY SYSTEM

Apparatus. Six Pyrex test tubes fitted with thermocouple wells and spacers; tin, lead, and their binary mixtures; benzoic acid; Chromel-Alumel thermocouple and potentiometer; electric furnace or Méker burner; large test tube, spacer, and rack; aluminum foil; watch or electric clock; vacuum bottle.

Procedure. A suggested sample tube-cooling jacket combination is shown in Fig. 28. The brass spacers center the thermocouple well in the sample tube, and the latter in the cooling jacket. The steel sample cup* is highly recommended; if the metals are heated directly in glass tubes, considerable breakage trouble is inevitable because of the difference in the coefficients of expansion of the metal and glass. The aluminum foil is used inside the outer cooling jacket to prevent too rapid heat loss by radiation.

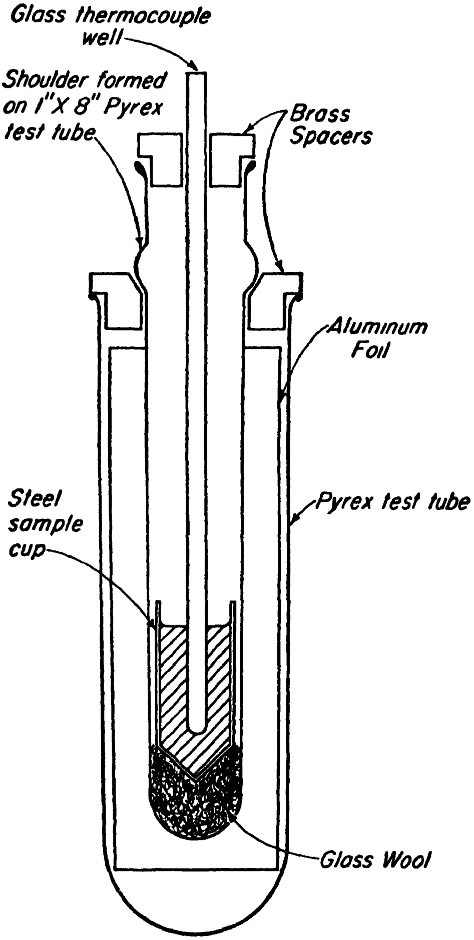

Fig. 28. Sample tube and cooling jacket.

The Chromel-Alumel thermocouple is calibrated before use; the known freezing-point temperatures of benzoic acid (121.7°), tin (232°), bismuth

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* The cups are made by drilling out a short piece of steel rod and can readily be made at very moderate cost at any machine shop. Corrosion of the steel by the liquid metals is negligible in comparison with the rate of deterioration of the latter due to oxidation.

(271°), and lead (327°) are employed as reference temperatures for this calibration. The tube containing a particular metal is heated* until the material has just melted completely. If the tube is markedly overheated oxidation may be more serious, and furthermore a large number of readings of no practical value will be required at the beginning of the subsequent measurements. The Pyrex tube containing the metal cup is then transferred to the outer cooling jacket, and the time-temperature curve determined.

One end of the thermocouple is placed in the thermocouple well of the sample tube; the other end is placed in a tube in an ice bath contained in a vacuum bottle. The thermocouple leads are connected to a potentiometer designed for thermocouple use; for the present application the commonly available 0-to-16-millivolt range is appropriate. The potentiometer is adjusted as required to balance the changing electromotive force of the thermocouple as the sample cools. Time and voltage (temperature) readings are recorded approximately every quarter minute, until the results indicate that the freezing point (or, for a mixture, the eutectic temperature) has been reached as illustrated in Fig. 29.

Cooling curves are then determined for the following mixtures:

(*a*) Lead, 90 per cent; tin, 10 per cent
(*b*) Lead, 80 per cent; tin, 20 per cent
(*c*) Lead, 60 per cent; tin, 40 per cent
(*d*) Lead, 40 per cent; tin, 60 per cent
(*e*) Lead, 20 per cent; tin, 80 per cent

A thin layer of powdered graphite may be placed over the metals and alloys to minimize oxidation.

The cooling curves may be drawn directly by use of a recording potentiometer. The thermocouple is connected to the recorder, and the working junction is placed in the well of the heated sample tube. The instrument range switch is set to position the recorder pen at the high end of the scale. The setting used is marked on the chart, and the chart-drive switch is turned on; as the sample cools, the time-temperature curve is automatically drawn on the chart.

B. AN ORGANIC COMPOUND SYSTEM

Apparatus. Ten freezing-point tubes with varying compositions of phenol and *p*-toluidine; larger tube for slow cooling; 0 to 50° thermometer with 0.1 or 0.2° divisions.

Procedure. Phase relationships can be illustrated by use of mixtures

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* The Fieldner volatile-matter furnace, obtainable at supply houses, is recommended for this experiment, since it permits the tubes to be heated in the vertical position. The furnace temperature may be controlled conveniently by use of a Variac or other variable autotransformer.

of organic compounds as well as metal-alloy systems. For example, compound formation between the components is shown by the system phenol-*p*-toluidine. *These compounds must be handled with great care to avoid contact with the skin.*

For the system assigned, a set of about 10 freezing-point tubes should be prepared to cover the composition range from one pure component to the other. The compounds are weighed out carefully into ½- by 6-in. test tubes; about 6 g total mixture weight is sufficient. A prepared tube is heated until the mixture is completely melted, and a thermometer, of appropriate range and graduated to 0.1°, is suspended in the liquid by use of a cork bored to fit the stem snugly. The tube is placed in a cooling jacket, as described above. For mixtures with low freezing points the cooling tube may be immersed in a beaker of crushed ice or an ice-salt mixture; such cooling baths are stirred intermittently to keep their temperature uniform. A time-temperature record is made as described under procedure A; the readings are continued until the sample has solidified. It may be helpful to stir the liquid *carefully* with the thermometer, or a stirrer made of nichrome or other inert wire, with a nonconducting handle, may be used. The mixture may be melted again and a check run made. The thermometer is then removed carefully and cleaned before use in the next sample studied. The procedure is repeated with each of the mixtures.

Pure materials should be employed in preparing the mixtures for study. Compounds which are subject to air oxidation or which tend to absorb moisture or carbon dioxide may be conserved by sealing them off in an all-glass freezing-point tube with a Dewar seal at the re-entrant thermometer well. The materials are introduced into the tube through a side arm which is then sealed off. A small amount of a light oil or other suitable liquid is placed in the well to assure good heat transfer to the thermometer bulb. It should be noted, however, that a unit of this type may give trouble because of excessive supercooling.

A thermocouple may be used instead of a thermometer; it can be calibrated by use of compounds which have known melting points in the temperature range of interest.

A major experimental problem in this work is supercooling, i.e., failure of crystallization to take place at the proper temperature. Actually, a *small* extent of supercooling is useful, since then when crystallization does start the crystals formed are dispersed widely through the liquid and equilibrium between the solid and liquid phases is more easily maintained. If supercooling seems too great, the experiment is repeated with more vigorous stirring at the appropriate stages. Supercooling may usually be avoided by dropping in a "seed crystal" of the solid material.

Calculations. In the interpretation of actual time-temperature records, care must be taken that spurious irregularities, due to instrumental and other experimental errors, are avoided.

The various experimental cooling curves are drawn as plots of potentiometer readings versus times of observation. The voltages corresponding to the freezing points of the substances used as calibration standards are determined (Fig. 29*a*). A thermocouple calibration curve is constructed from the set of voltage-temperature points so obtained. For each mixture studied the temperatures at the characteristic transformation points (initial crystallization of solid, crystallization of eutectic mixture, etc.) can then be obtained from its cooling curve (Fig. 29).

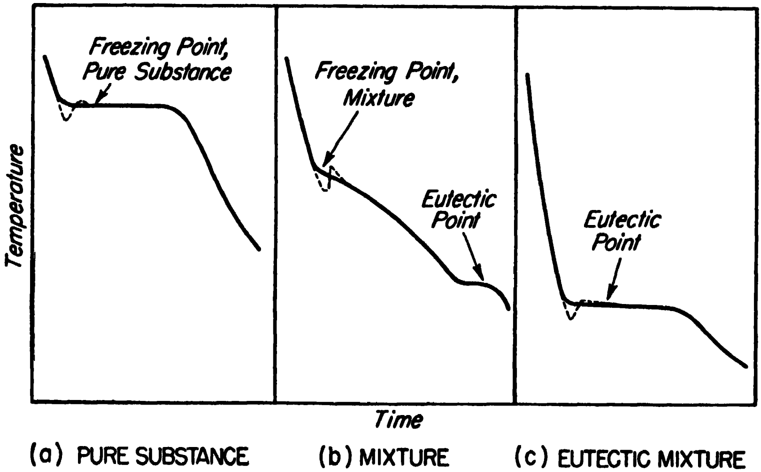

FIG. 29. Typical cooling curves (dashed portions illustrate supercooling effects).

A third graph is then prepared by plotting these transformation temperatures against the compositions of the mixtures. Lines are drawn through the points to complete the phase diagram in conventional form. Each area, line, and invariant point on the diagram is discussed briefly in terms of the phase rule.

Practical Applications. The method of thermal analysis illustrated in this experiment is a basic procedure in the study of phase relationships. A maximum in the freezing-point–composition curve indicates the existence of an intermediate compound, and the composition of the compound is given by the highest point on the composition-temperature curve, for this represents the melting point of the pure compound.

Temperature-composition curves and other phase diagrams are of great value in the technical study of alloys and in the recovery of a salt by crystallization from a mixture of salts.

Suggestions for Further Work. The following pairs of organic compounds are suitable for study: urea-phenol, naphthalene-nitrophenol, acetamide–β-naphthol,

β-naphthol–p-toluidine, phenol–α-naphthylamine, diphenylamine-naphthalene. A number of phase diagrams in organic systems are discussed by Kofler[3] and by Skau and Wakeham.[4] Interesting inorganic systems may be selected by reference to the diagrams given in the International Critical Tables.[2]

Fractional crystallization is an effective method of purification. A new application has been developed in which an impure solid is melted and frozen in a long tube. The freezing point of the impure material is determined. The long tube of thin glass filled with the solid is mounted horizontally, and with a small flame or electric heater a molten zone is moved along the whole length of the tube from one end to the other. The impurities are literally chased along to one end where they accumulate. After traversing the tube once the heating zone is moved again along the whole tube in the same direction. To illustrate this "zone" purification, a 4-mm Pyrex tube is filled with impure naphthalene. An impurity may be added to the naphthalene. The material is melted at one end, and the molten zone is moved to the other end by use of a loop of hot resistance wire. The freezing-point curves of samples taken from the two ends of the tube are compared. The constancy of the freezing point throughout the whole solidification from start to finish is one of the best criteria for purity.

References

1. Findlay, "The Phase Rule," Longmans, Green & Co., Inc., New York (1938); Dover Publications, New York.
2. International Critical Tables, Vols. II, IV, McGraw-Hill Book Company, Inc., New York (1928).
3. Kofler, "Thermo-Mikro-Methoden," Verlag Chemie, GmbH., Weinheim/Bergstrasse, Germany (1954).
4. Skau and Wakeham *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Chap. 3, Interscience Publishers, New York (1949).

23. SOLUBILITY AS A FUNCTION OF TEMPERATURE

The determination of solubility and the calculation of the heat of solution at saturation are illustrated in this experiment.

Theory. When a chemical system is in equilibrium, no apparent change takes place, but a dynamic equilibrium is assumed with two opposing reactions proceeding at the same rate. One of the simplest cases of equilibrium is that of a saturated solution, in which molecules leave the solid and pass into solution at the same rate at which the molecules in solution are deposited on the solid. The solubility of a solid, i.e., the concentration in a saturated solution, is then a special case of an equilibrium constant.

The relation between an equilibrium constant and the absolute temperature developed by van't Hoff is one of the most important equations in chemistry. The mathematical relation is

$$\frac{d \ln s}{dT} = \frac{\Delta H}{RT^2} \tag{1}$$

and in the integrated form

$$\log s = \frac{-\Delta H}{2.303R}\frac{1}{T} + \text{constant} \tag{2}$$

or

$$\log \frac{s_2}{s_1} = \frac{\Delta H(T_2 - T_1)}{2.303R(T_2T_1)} \tag{3}$$

where s_2, s_1 = solubilities, usually expressed in moles/1,000 g of solvent, at the absolute temperatures T_2 and T_1

R = gas constant

ΔH = heat of solution per mole

In this integration ΔH is assumed to be constant, an assumption that is not entirely justified. The derivation of this equation and similar ones is discussed by Hildebrand and Scott.[2] The exact calculation of heats of solution from solubility data for nonideal systems requires information on the activity coefficient as described by Williamson.[7]

The heat of solution with which we are concerned here is the heat absorbed when 1 mole of the solid is dissolved in a solution that is already practically saturated. It differs from the heat of solution at infinite dilution, which is the heat of solution usually given in tables, by an amount equivalent to the heat of dilution from saturation to infinite dilution.

Apparatus. Ice bath at 0°; large test tube; 0.5 *N* sodium hydroxide; oxalic acid; 0.1° thermometer; 10-ml pipette; 10-ml weighing bottle.

Procedure. The solubility of oxalic acid is determined at 25, 20, 15, and 0°, or at other convenient temperatures below room temperature; the temperature is read to 0.1° with a thermometer immersed in the solution. The 15° temperature is achieved by adding small amounts of ice or ice water as necessary to the thermostat.

For the solubility determinations a test tube, thermometer, and stirrer similar to that shown in Fig. 20 on page 69 are used. The stirrer is made from a small rod of glass or polystyrene, bent into a ring of such size that it cannot hit the thermometer bulb. It is moved up and down vigorously by hand. The air jacket between the test tubes is provided to reduce the rate of cooling or heating. A simple thermostat improvised from a large beaker and a small motor-driven stirrer may be used. A 10-ml sample is removed with a pipette, drained into a weighing bottle, and weighed to 0.01 g.

Distilled water in large test tubes is saturated with oxalic acid by dissolving crystals at a higher temperature and then cooling to the required temperature so that some of the dissolved material is crystallized out. When the equilibrium is approached in this way, from the side of supersaturation rather than from the crystal side, the equilibrium is attained rapidly. For this reason, if the thermostat temperature is not constant, a falling temperature may not be serious, but a rising temperature may introduce a considerable error.

To prevent sucking small crystals into the pipette along with the solution, a small piece of filter paper is wrapped around the tip of the pipette and fastened with thread or a small rubber band. The filter paper is removed before draining the pipette. The solution is then titrated with 0.5 *N* sodium hydroxide using phenolphthalein as an indicator.

Duplicate determinations are made at each temperature.

Calculations. The solubility in moles per 1,000 g of solvent is calculated at each of the four temperatures and compared with the accepted values. It is interesting to compare these values with the solubilities calculated in moles per liter.

The logarithm of the solubility in moles per 1,000 g of solvent is plotted against the reciprocal of the absolute temperature, and a smooth curve is drawn through the four points. If the heat of solution were constant and there were no complicating reactions, such as ionization, the line would be straight. Tangents are drawn at 25 and 0°, and the heat of solution is determined at the two temperatures with the help of Eq. (2).

Practical Applications. The solubility of a substance may be calculated at other temperatures when it has been determined at two different temperatures. The results are more accurate when the heat of solution is not affected by temperature or when the temperature range is small. Solubility may be used as a criterion of purity and as a means of studying intermolecular forces.[6]

Suggestions for Further Work. The solubility of other materials may be determined in a similar way, benzoic acid or succinic acid for example, or other solids having low solubility and easy methods of analysis. Nonaqueous solvents may be used also.

Boric acid may be used instead of oxalic acid for this experiment. It is titrated by using phenolphthalein as an indicator and adding 10 to 20 ml of neutral glycerin to give a sharp end point.

The solubility-product rule and the effect of other salts on solubility may be illustrated by determinations of the solubility of a slightly soluble salt such as silver bromate in the presence of common ions, ammonium hydroxide, and other salts.

The influence of salts in reducing the solubility of benzoic acid may be determined.[1] The salting-out constant thus obtained can be used for calculating activity coefficients.

In Eq. (2) it is assumed that the heat of solution is independent of temperature, but this assumption is not often justified. The equation may be made exact by introducing terms for the heat capacity of the solute and solvent and for the solution.

References

1. Goeller and Osol, The Salting-out of Molecular Benzoic Acid in Aqueous Solutions, *J. Am. Chem. Soc.*, **50,** 2132 (1937).
2. Hildebrand and Scott, "Solubilities of Non-Electrolytes," American Chemical Society Monograph, Reinhold Publishing Co., New York (1950).

3. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3d ed., Vol. I, D. Van Nostrand Co., New York (1940).
4. Seidell, "Solubilities of Organic Compounds," 3d ed., Vol. II, D. Van Nostrand Co., New York (1941).
5. Seidell and Linke, "Supplement to Solubilities of Inorganic and Organic Compounds," 3d ed., Vol. III, D. Van Nostrand Co., New York (1952).
6. Vold and Vold *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Chap. 7, Interscience Publishers, Inc., New York (1949).
7. Williamson, *Trans. Faraday Soc.*, **40**, 421 (1944).

24. TRANSITION TEMPERATURE

In this experiment the determination of the transition temperature between different crystal forms is illustrated by three experimental methods.

Theory. When a substance changes from one crystal form into another, the change is accompanied by an absorption or evolution of heat and by other phenomena such as changes in vapor pressure, volume, or color. The temperature at which such a change takes place reversibly is called the *transition temperature.*

A transition temperature may be determined by a cooling or heating curve, in which temperature is plotted against time. Thus, for example, if water is cooled sufficiently, its temperature will fall continuously until 0°C is reached. After staying at 0° until all the water has frozen, the temperature will again continue to fall. The heat evolved on freezing counterbalances the heat losses and maintains the system at the freezing temperature as long as any liquid water is left.

The transition temperature of sodium sulfate is to be studied.[2] This is the temperature at which hydrated sodium sulfate is in equilibrium with the anhydrous form.

$$Na_2SO_4 \cdot 10H_2O \rightleftharpoons Na_2SO_4 + 10H_2O$$

Under these conditions there are two components, sodium sulfate and water, and four phases, anhydrous sodium sulfate, hydrated sodium sulfate, solution, and vapor. According to the phase rule, $v = c - p + 2$ (page 105), the variance is zero, and there is only one temperature and pressure at which all these phases can be in equilibrium. This temperature is 32.38°C, and it is just as definite as the freezing temperature of water where there are one component and three phases.

Apparatus. Two large test tubes; 0.1° or 0.01° thermometer, 0 to 50°C; four weighing bottles; desiccator; dilatometer; stirrer; anhydrous sodium sulfate; hydrated sodium sulfate.

A. THERMOMETRIC METHOD

Procedure. An 8-in. test tube is set into a larger one which serves as an air jacket. A thermometer, graduated to 0.1° and reading from 0 to 50°, is fitted into a cork in the mouth of the smaller test tube. A vertical stirrer is made by bending the end of a plastic (polystyrene) or glass rod of small diameter into a ring. The stirrer ring is nearly as large as the test tube so that it cannot be displaced laterally and break the thermometer bulb at its center.

Hydrated sodium sulfate is made by preparing a saturated solution of sodium sulfate at about 32°, using about 50 g $Na_2SO_4 \cdot 10H_2O$ and 50 ml water, and cooling in an ice bath. The crystals formed are removed and drained on filter paper. Preferably they are placed in a Büchner funnel and attached to a suction pump. The last mother liquor may be squeezed out effectively by placing a piece of thin rubber sheet over the rim of the funnel in such a way that the atmospheric pressure forces the rubber down against the crystals. A second crystallization is carried out. The $Na_2SO_4 \cdot 10H_2O$ crystals are then placed in closed bottles, and about one-tenth is placed on paper or trays to dry out. They lose water and leave white anhydrous Na_2SO_4. This process of losing water is called efflorescence.

The twice-crystallized $Na_2SO_4 \cdot 10H_2O$ is then mixed with a little anhydrous sulfate. The inner tube is filled with the crystals and heated to 34 or 35°, inserted in the outer jacket, and set into a beaker of water at room temperature. The mixture is stirred continuously, and the temperature is recorded. Temperature readings are plotted against time.

The horizontal part of the graph near 32.4° is of interest. It is unnecessary to take many readings before and after this region is reached. If the temperature drops so slowly as to prolong the experiment unduly, the tubes may be set into colder water. If the temperature falls much below 32.4° without becoming constant, the solution has become supersaturated and a crystal of $Na_2SO_4 \cdot 10H_2O$ should be dropped into it.

Impurities in the salt or inaccuracies of the thermometer will introduce errors. To eliminate the first source of error, the sodium sulfate is crystallized until two successive crystallizations give the same transition temperature. Usually one or two crystallizations are sufficient.

The thermometer is checked in an ice bath.

Calculations. Curves are plotted, with time on the X-axis and temperature on the Y-axis. When the transition temperature remains unchanged after successive recrystallizations, the salts may be considered pure and the horizontal part of the curve may be taken as 32.383°C.

The correction for the thermometer at 0° is determined from the reading in the ice bath, and the correction at 32.383° is determined from the transition temperature.

B. SOLUBILITY METHOD

Procedure. The solubility of sodium sulfate is as follows:

	$Na_2SO_4 \cdot 10H_2O$				Na_2SO_4			
Temperature, °C	0	20	25	30	32.38	35	40	50
Solubility, moles/1,000 g. . .	0.342	1.33	1.96	2.88	3.50	3.45	3.40	3.28

Since a $Na_2SO_4 \cdot 7H_2O$ is known, the saturated solution is seeded with a sample of $Na_2SO_4 \cdot 10H_2O$. These solubilities may be verified by maintaining the saturated solution at a given temperature for 5 min with stirring and then discharging a 10-ml pipette full of the clear solution into a small weighed weighing bottle and weighing to 0.1 g. Four bottles may be used at once for four different temperatures. A piece of filter paper is tied over the tip of the pipette while drawing up the saturated solution and removed when the pipette is drained. The solutions are evaporated to dryness, dried in an oven at 100 to 105°, cooled after the stopper is inserted, and weighed to 0.01 g.

A few perfect crystals of $Na_2SO_4 \cdot 10H_2O$ are dried with filter paper and weighed quickly. They are heated at 100 to 105°, cooled in a desiccator or weighing bottle, and weighed. The heating is repeated until a constant weight is obtained. The number of moles of water per mole of sodium sulfate is calculated for the hydrated crystals.

Calculations. A graph is drawn showing the solubility plotted against the temperature, using the data given in the table, together with any points determined experimentally. There are two solubility curves, one for the anhydrous salt, the other for the hydrated salt, and the intersection of the two curves gives the transition temperature. This value for the transition temperature is compared with those obtained by the thermometric and dilatometric methods.

C. DILATOMETRIC METHOD

Procedure. There is an appreciable change in volume when $Na_2SO_4 \cdot 10H_2O$ is dehydrated at 32.38° and undergoes transition into anhydrous Na_2SO_4 and water. This change is measured in a dilatometer which is made by fusing a capillary tube 3 mm inside diameter and 15 cm long to a Pyrex tube about 1 cm in diameter and 5 cm long. A millimeter scale is attached firmly to the stem with sealing wax, giving the appearance of a large thermometer.

The tube is filled more than half full at room temperature with finely crushed pure hydrated crystals of $Na_2SO_4 \cdot 10H_2O$, forced in through the smaller tube with a stiff wire. Saturated solution is added to fill the bulb using a hypodermic syringe with a long needle, and the dilatometer is rotated to obtain a saturated solution, and then it is heated to about 30°. The saturated solution containing the large excess of $Na_2SO_4 \cdot 10H_2O$ crystals is adjusted so that its level is nearly at the bottom of the scale. The dilatometer is then placed in a large beaker of water and heated slowly at a constant rate. The level and temperature are recorded at suitable intervals and plotted against time. An abrupt change in the rate of rise of the solution level is observed at the transition temperature. This temperature is recorded.

Suggestions for Further Work. The heat absorbed in the dissociation of $Na_2SO_4 \cdot 10H_2O$ may be measured calorimetrically with an electric heating coil or in any other way to be devised by the student.

Assuming 1 cal of heat from the sun per square centimeter per minute for an 8-hr period, calculations are made on the solar heating area required and the pounds of anhydrous sodium sulfate required to give the heat storage equivalent to 100 lb of coal.

The sodium sulfate dilatometer is next used as a radiation meter to determine the number of calories absorbed by radiation in a given time from sunlight or from a nearby 200-watt lamp. A few drops of India ink or a little black nigrosine dye is added, and the tube is placed nearly horizontal, half immersed in a bath of $Na_2SO_4 \cdot 10H_2O$ and Na_2SO_4, maintaining the temperature at 32.38°. The radiation is absorbed at 32.38° and causes some $Na_2SO_4 \cdot 10H_2O$ to become dehydrated and give an increase in volume. The dilatometer increase then is a measure of the radiation received, after making a correction for any change of volume due to other heating or cooling effects as determined in a control experiment when the dilatometer is shielded from radiation. The dilatometer readings may be calibrated with radiation of known intensity as measured with a General Electric radiation meter, which reads directly in cal min^{-1} cm^{-2}.

The calibration may be effected also with the help of a vacuum-jacketed bottle used as a calorimeter. The dilatometer is placed in the calorimeter with water at 32.38°. A measured quantity of heat is introduced with an electric heating coil, while stirring. The temperature of the calorimeter water remains constant, and the rise in the dilatometer capillary per calorie of absorbed heat is then calculated.

The colorimetric method, which is perhaps the most obvious, may be illustrated with cuprous mercuric iodide ($2CuI \cdot HgI_2$), which changes color at 67.5°C. The transition from one solid phase to another in the absence of a solution is very slow, and the time lag is sufficient to cause errors of several degrees. A little cuprous mercuric iodide is placed in a thin melting-point tube and attached to an ordinary thermometer. On heating very slowly in a small beaker of water, the color change may be detected. The reverse change is observed when the water is cooled very slowly. The average of several determinations is taken as the transition temperature, and the agreement is better the slower the change in temperature.

The transition temperature of sulfur may be obtained by determining the solubility curve of monoclinic and rhombic sulfur in nitrobenzene between 80 and 120°.

Practical Applications. The transition temperature having been determined, it is possible to control the product that crystallizes out. Below 32.38° the hydrated form crystallizes out, and above 32.38° the anhydrous form is obtained. Considerations of this kind are important in the production of many salts on a commercial scale.

The transition temperatures of salts are used in standardizing thermometers. Sodium sulfate is the most commonly used substance, because the temperature is fairly close to room temperature and because the salt can be easily purified.

Transition temperatures are also used to give a warning when a bearing becomes overheated. The bearing is painted with a paint that contains a substance giving a decided change in color when the transition temperature is exceeded. A series of lacquers is available in which special organic and inorganic powders are incorporated so as to give color changes at specified temperatures. They are convenient for determining the actual surface temperature of hot pipes and engineering equipment.

The transition of sodium sulfate has been utilized for storing solar energy for the heating of a house in winter. Obviously an extra storage capacity for heat is necessary to carry through the nights and dark days.[3] The efficiency of sodium sulfate in heat storage may be compared with that of water, heated rocks, and other hydrated salts.

References

1. Findlay, Campbell, and Smith, "The Phase Rule and Its Applications," Dover Publications, New York (1951).
2. Richards, *J. Am. Chem. Soc.*, **36**, 485 (1914).
3. Telkes, "Solar Heat Storage," *in* Daniels and Duffie: "Solar Energy Research," University of Wisconsin Press, Madison, Wis. (1955).

25. DIFFERENTIAL THERMAL ANALYSIS

This experiment illustrates the use of differential thermal analysis. Differential thermograms are obtained which show the dehydration of inorganic salts and the thermal decomposition of an organic and an inorganic compound.

Theory. Differential thermal analysis is concerned with the determination of heat absorbed or evolved by a material on heating. The sample under investigation together with a sample of inert material is placed in a furnace. The temperature of the furnace is raised at a constant rate, and the *difference* in temperature between the active and inert samples (ΔT) is observed as a function of furnace temperature (T). If no reaction takes place, both samples will remain at the same temperature. If the active sample undergoes an endothermic reaction such as loss of water of hydration, it will experience a thermal lag. When the reaction is complete, no more heat is absorbed and a steady state is again attained where ΔT is zero. Hence a plot of ΔT versus T starting at zero, rising to a maximum, and dropping again to zero is expected.

The temperature at which ΔT first begins to depart from zero is the temperature at which the rate of reaction becomes appreciable. It is generally higher than the temperature at which the hydrates are in equilibrium with the water vapor in the air. It will vary somewhat with the apparatus used and procedure followed.

The area under the peak is proportional to the heat transferred by the reaction giving rise to the peak.

Apparatus. Differential thermal analyzer and accompanying circuit; $CuSO_4 \cdot 5H_2O$; $BaCl_2 \cdot 2H_2O$; $CdCl_2 \cdot 2\frac{1}{2}H_2O$; $KHCO_3$; potassium acid phthalate.

Procedure. Apparatus which is suitable for work up to 360° is shown in Fig. 30. It consists of two aluminum or brass cylinders 4 in. in diameter, the lower one, *A*, containing the thermocouples *TC* and the upper, *B*, serving as sample holder and furnace. The holes for the powdered samples *s* are ¼ in. in diameter. The thermocouples are made of 28-gauge platinum-platinum, 10% rhodium wire. It is important that the thermocouple junctions be as small as possible since the sensitivity is very much dependent on their mass. The heating coil consists of 7½ feet of No. 24 nichrome wire. It is insulated from the block by asbestos sheet. The outer casing of *B* is cut from Transite. The thermocouple is connected to a Leeds and Northrup model 2430 galvanometer *C* (or other suitable galvanometer) by way of the circuit in Fig. 30. Resistor *V* serves as a voltage divider to control the sensitivity; $R + V$ is adjusted to the critical damping resistance for the galvanometer. An approximately constant rate of temperature rise is obtained by periodically advancing the setting of the Variac which controls the input to the furnace. There is a 1° mercury thermometer in well *T*.

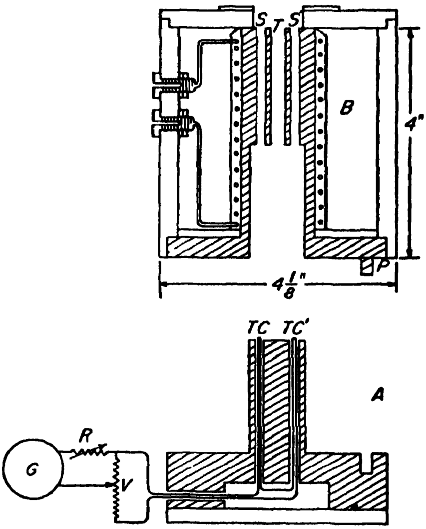

FIG. 30. Apparatus for differential thermal analysis.

The sample is mixed with some inert material such as Al_2O_3 or SiO_2. Silicon dioxide, of course, is not inert at high temperatures if the sample being studied is highly basic, and Al_2O_3 cannot be used at high temperatures with acidic or basic materials. The same inert material is used in the reference sample holder. This dilution with an inert material prevents fusion on the thermocouple wires and makes the thermal conductivities and heat capacities of the active and reference sample approximately the same. If this condition is not met, the base line will drift, i.e., ΔT will depart from zero even in the absence of a reaction. This drift will be particularly pronounced when the rate of temperature rise is changing, as when the heater is first turned on. If a serious base-line drift is observed even when the above precautions have been observed, the samples have not been uniformly packed and should be repacked.

Samples of $BaCl_2 \cdot 2H_2O$, $CuSO_4 \cdot 5H_2O$, $CdCl_2 \cdot 2\frac{1}{2}H_2O$, $KHCO_3$, and potassium acid phthalate are ground to approximately 100 to 200 mesh. They are mixed with an equal quantity of SiO_2 or calcined Al_2O_3 of the same mesh size. Approximately 0.12 g of the sample mixture is placed in one of the sample holders, and 0.12 g of the inert material in the other. The samples are firmly packed down with a small rod. All the reactions observed are endothermic. The galvanometer scale should be so moved that the pointer has room for travel. An initial setting of 3 on a scale running 0 to 10 where increasing readings indicate an endothermic reaction is advisable. The proper sensitivity setting will have to be determined by trial and error since this depends very much on the heat capacity of the thermocouple junction. The experiment with $BaCl_2 \cdot 2H_2O$ should be carried to 250°, $CuSO_4 \cdot 5H_2O$ to 350°, $CdCl_2 \cdot 2\frac{1}{2}H_2O$ to 200°, $KHCO_3$ to 260°, and potassium acid phthalate to 330°. Galvanometer readings are recorded every 5 deg until the reaction occurs, then every degree. A determination with inert material in both sample holders should be performed to determine how much of the pattern is due to spurious fluctuations.

Calculations. Curves are plotted, ΔT versus T, for each of the five compounds. They are critically discussed in view of the known chemical behavior of these compounds[2,4,8,7] and in view of the theory of differential thermal analysis.

Practical Applications. Each maximum or peak in a differential thermogram corresponds to a separate reaction or transition. Thus Guth and coworkers[3] observed several peaks in the oxidation of praseodymium and terbium indicating the presence of intermediate oxides. Smothers[10] observed the solid state reaction between NaOH and Al_2O_3. Since each substance gives a characteristic differential thermogram, Morita and Rice[6] have suggested that differential thermal analysis be used for the characterization of complex organic substances. Morehead and Daniels[5] have measured energy storage in certain minerals which resulted from bombardment by α particles. The method has been used for years to characterize complex minerals and constituents of soils.[9]

Suggestions for Further Work. Differential thermograms of several inorganic compounds which are suitable for study are given by Barshad.[1] Semiquantitative estimates of heats of reaction or transition can be made if the apparatus is calibrated. Determinations are made on substances of known heats of fusion, and the heat corresponding to a unit area is determined. The heats of fusion of *m*-dinitrobenzene (mp 90°), *o*-dinitrobenzene (mp 117°), benzoic acid (mp 122°), $AgNO_3$ (mp 212°) and $NaNO_2$ (mp 307°) are suitable.[10] A preliminary estimate of the precision of this method can be made by considering the first two peaks for $CuSO_4 \cdot 5H_2O$. The heats of reaction are as follows:

$$CuSO_4{\cdot}5H_2O = CuSO_4{\cdot}3H_2O + 2H_2O(g) \qquad \Delta H_{298} = 26.2 \text{ kcal mole}^{-1}$$
$$CuSO_4{\cdot}3H_2O = CuSO_4{\cdot}H_2O + 2H_2O(g) \qquad \Delta H_{298} = 27.3 \text{ kcal mole}^{-1}$$

Since the heats of reaction for these two processes are almost equal, the areas should be approximately the same.

References

1. Barshad, *Am. Mineralogist*, **37**, 667 (1952).
2. Borchardt, *J. Chem. Educ.*, **33**, 103, (1956).
3. Guth *et al.*, *J. Am. Chem. Soc.*, **76**, 5239, 5249 (1954).
4. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Longmans, Green & Co., Inc. (1922).
5. Morehead and Daniels, *J. Phys. Chem.*, **56**, 546 (1952).
6. Morita and Rice, *Anal. Chem.*, **27**, 336–339 (1955).
7. Selected Values of Thermodynamic Properties, *Natl. Bur. Standards, Circ.*, **500** (1952).
8. Sidgwick, "Chemical Elements and Their Compounds," Oxford University Press, New York (1950).
9. Smothers, "Bibliography of Differential Thermal Analysis," University of Arkansas, Fayetteville, Ark. (1951).
10. Smothers and Chiang, *Proc. Intern. Symposium Reactivity of Solids*, pp. 501–504 (1952).

CHAPTER 8

CHEMICAL KINETICS

26. HYDROLYSIS OF METHYL ACETATE

From experimental data on the rate of a chemical reaction the specific reaction-rate constants are calculated for two different temperatures, and from these the energy of activation is determined.

Theory.[1,4] In chemical kinetics the term *rate of reaction* refers to the time rate of change, dc/dt, of the concentration of some constituent of interest. The *reaction-rate constant*, or *specific reaction rate*, k, is a proportionality factor which relates the rate of reaction to reactant concentrations on which it depends.

A *first-order reaction* is one whose rate is found by experiment to be proportional to the concentration of the reacting substance:

$$-\frac{dc}{dt} = kc \tag{1}$$

Integration of this equation gives the equivalent expressions

$$-2.303 \log c = kt + \text{constant} \tag{2a}$$

$$k = \frac{2.303}{t_2 - t_1} \log \frac{c_1}{c_2} \tag{2b}$$

$$k = \frac{2.303}{t} \log \frac{c_0}{c} \tag{2c}$$

where c = concentration of reactant at time t

c_0, c_1, c_2 = concentrations at times $t = 0$, t_1, and t_2, respectively

For the first-order reaction, k is numerically equal to the fraction of the substance which reacts per unit time, and is usually expressed in reciprocal seconds or minutes. It should be noted that for a first-order reaction the specific reaction rate can be determined without information on the initial reactant concentration or even as to the absolute concentrations at various times, provided that a quantity directly proportional to the concentration can be determined.

The kinetics of *second-order reaction* is described by the equation

$$-\frac{dc_A}{dt} = kc_Ac_B \tag{3}$$

where c_A and c_B represent the concentrations of two reactants. If in this case one reactant is present in sufficiently large excess, its concentration will remain essentially constant while that of the other constituent undergoes a marked change; the reaction will then appear to be first-order.

From the kinetic viewpoint, most chemical reactions are complex, the reaction mechanism consisting of several successive steps, each of which will normally be either first- or second-order. Several different reaction mechanisms, each complex, may be involved. Another typical complication arises with reactions which proceed to an equilibrium state rather than to completion; in these cases the reverse reaction becomes important as equilibrium is approached. The concentration of a catalyst may also be an important variable.

The hydrolysis of methyl acetate presents a number of interesting kinetic aspects. The reaction, which is extremely slow in pure water, is catalyzed by hydrogen ion:

$$CH_3COOCH_3 + H_2O + H^+ \rightleftharpoons CH_3COOH + CH_3OH + H^+$$

The reaction is reversible, so the net rate of hydrolysis at any time is the difference between the rates of the forward and reverse reactions, each of which follows the simple rate law given by Eq. (3). Thus,

$$-\frac{dc_{CH_3COOCH_3}}{dt} = k_1'c_{H_2O}c_{CH_3COOCH_3} - k_2c_{HC_2H_3O_2}c_{CH_3OH} \tag{4}$$

where k_1' is the specific rate constant for the forward reaction and k_2 for the reverse reaction. For dilute solutions, water is present in such large excess that its concentration undergoes a negligible change while that of the methyl acetate is changed considerably. For this case Eq. (4) may be written

$$-\frac{dc_{CH_3COOCH_3}}{dt} = k_1c_{CH_3COOCH_3} - k_2c_{HC_2H_3O_2}c_{CH_3OH} \tag{5}$$

In the early stages of the hydrolysis, the concentrations of acetic acid and methanol remain small enough so that the term involving them is negligible, and the reaction appears to be of first order:

$$-\frac{dc_{CH_3COOCH_3}}{dt} = k_1c_{CH_3COOCH_3} \tag{6}$$

The value of k_1 can then be determined by one of the methods conventional for first-order reactions.

Evaluation of k_1 at the different temperatures permits the calculation of the *heat of activation*, ΔH_a, for the forward reaction:

$$\frac{d \ln k_1}{dT} = \frac{\Delta H_a}{RT^2} \tag{7}$$

or

$$\log \frac{k_{1,T_2}}{k_{1,T_1}} = \frac{\Delta H_a}{2.303R}\,\frac{T_2 - T_1}{T_2T_1} \tag{8}$$

In obtaining the integrated form, it is assumed that ΔH_a is a constant. The heat of activation is usually expressed in calories per mole and is interpreted as the amount of energy the molecules must have in order to be able to react.

An explicit solution to the kinetic equation may also be written for the case where the reverse reaction cannot be ignored. If the concentration of methyl acetate is a moles per liter initially, and $(a - x)$ moles per liter at time t, then Eq. (5) can be written as

$$-\frac{d(a-x)}{dt} = \frac{dx}{dt} = k_1(a - x) - k_2x^2 \tag{9}$$

since for each mole of methyl acetate hydrolyzed one mole each of acetic acid and methanol are produced. Integration of this relation gives

$$t = \frac{1}{k_1\left(\frac{4ak_2}{k_1} + 1\right)^{1/2}} \ln \frac{2a + x\left[\left(\frac{4ak_2}{k_1} + 1\right)^{1/2} - 1\right]}{2a - x\left[\left(\frac{4ak_2}{k_1} + 1\right)^{1/2} + 1\right]} \tag{10}$$

Consideration of the relation between k_2, k_1, the equilibrium concentrations of the reactants, and the equilibrium constant K_h for the hydrolysis reaction, as given by the law of mass action, permits the elimination of k_2 to give

$$t = \frac{1}{k_1\left(\frac{4a}{K_h c^0_{\mathrm{H_2O}}} + 1\right)^{1/2}} \ln \frac{2a + x\left[\left(\frac{4a}{K_h c^0_{\mathrm{H_2O}}} + 1\right)^{1/2} - 1\right]}{2a - x\left[\left(\frac{4a}{K_h c^0_{\mathrm{H_2O}}} + 1\right)^{1/2} + 1\right]} \tag{11}$$

Here $c^0_{\mathrm{H_2O}}$ represents the concentration of water present, which is treated as a constant in accordance with the assumption made in obtaining Eq. (5) from Eq. (4).

Apparatus. Thermostats at 25 and 35°; three 250-ml, two 125-ml Erlenmeyer flasks; 5-ml pipette; 100-ml pipette; stop watch or electric timer; methyl acetate; 2 liters 0.2 N sodium hydroxide; 500 ml 1 N hydrochloric acid; distilled water; ice.

Procedure. The concentration of methyl acetate at a given time is determined through titration of samples with a standard sodium hydroxide solution; the success of the experiment depends chiefly on the care used in pipetting and titrating. The sodium hydroxide solution used should be prepared by dilution of a saturated stock solution to minimize the amount of carbonate present and hence to reduce the fading of the phenolphthalein end point. It is not necessary, however, to use CO_2-free distilled water, because the amount of carbonate introduced in this way is negligible when titrating with 0.2N sodium hydroxide.

A test tube containing about 12 ml methyl acetate is set into a thermostat at 25°C. Approximately 250 ml of standardized 1 N hydrochloric acid is placed in a flask clamped in the thermostat. After thermal equilibrium has been reached (10 or 15 min should suffice), several 5-ml aliquots of the acid are titrated with the standard sodium hydroxide solution. Then 100 ml of acid is transferred to each of two 250-ml flasks clamped in the thermostat, and 5 min allowed for the reestablishment of thermal equilibrium. Precisely 5 ml of methyl acetate is next transferred to one of the flasks with a clean, dry pipette; the timing watch is started when the pipette is half emptied. The reaction mixture is shaken to provide thorough mixing.

A 5-ml aliquot is withdrawn from the flask as soon as possible and run into 50 ml of distilled water. This dilution slows down the reaction considerably, but the solution should be titrated at once; the error can be further reduced by chilling the water in an ice bath. The time at which the pipette has been half emptied into the water in the titration flask is recorded together with the titrant volume. Additional samples are taken at 10-min intervals for an hour; then at 20-min intervals for the next hour and a half. A second determination is started shortly after the first one to provide a check experiment.

In similar fashion, two runs are made at a temperature of 35°. Because of the higher rate of reaction, three samples are first taken at 5-min intervals, then several at 10-min intervals, and a few at 20-min intervals. It is convenient to start the check determination about a half hour after the first experiment is begun.

Calculations. The titrant volume at time t, V_t, measures the number of equivalents of hydrochloric acid and acetic acid then present in the 5-ml reaction-mixture aliquot. Let V_T represent what the titrant volume per 5-ml aliquot would be *if* the hydrolysis were complete. Then $V_T - V_t$ measures the number of equivalents of methyl acetate remaining per 5-ml aliquot at time t, because one molecule of acetic acid is produced for each molecule of methyl acetate hydrolyzed. The corresponding concentration of methyl acetate in moles per liter is $N(V_T - V_t)/5$, where N is the normality of the sodium hydroxide solution.

If the reaction actually proceeded to completion, V_T could be measured directly by titration of an aliquot from the equilibrium mixture. An appreciable amount of unhydrolyzed methyl acetate is present at equilibrium, however, so V_T must be *calculated.*

Let the volume of sodium hydroxide solution required to titrate a 5-ml aliquot of the original 1 N HCl solution be V_x. Let V_s represent the initial volume of the hydrochloric acid–methyl acetate solution. Then the volume of sodium hydroxide required to neutralize the hydrochloric acid present in any 5-ml aliquot of the reaction mixture is $100V_x/V_s$, if it is assumed that the total volume of the reaction mixture remains constant at V_s as the reaction proceeds. The weight of methyl acetate initially present in 5 ml of the reaction mixture is $5d_2 \cdot (5/V_s)$, where d_2 represents the density of methyl acetate at the given temperature; this corresponds to $25d_2/V_sM_2$ equivalents of methyl acetate, where M_2 represents the molecular weight of the ester, 74.08. The number of milliliters of sodium hydroxide solution of normality N required to titrate the acetic acid produced by the complete hydrolysis of this quantity of ester is $(25d_2/V_sM_2)(1000/N)$. It follows that

$$V_T = \frac{100V_x}{V_s} + \left(\frac{25d_2}{V_sM_2}\frac{1000}{N}\right) \tag{12}$$

The methyl acetate does not dissolve to form an ideal solution in water, so that the correct value for V_s is not 105 ml, as might first be assumed, but should be taken as 104.6 ml. The further change in volume due to the hydrolysis reaction is negligible, because the reactants and products are reasonably similar. The density of methyl acetate in grams per milliliter may be taken as 0.9273 at 25° and 0.9141 at 35°.

The value of V_T is calculated for each kinetic experiment by means of Eq. (12). For each run a tabulation is made of the times of observation and the corresponding values of V_t and $(V_T - V_t)$.

Two graphs are then prepared. For each temperature a composite plot is made of log $(V_T - V_t)$ versus t; the points obtained in the two runs can be identified by use of circles and squares. The straight line which is considered to best represent the experimental results is drawn through each set of points, and the specific reaction rates for the two temperatures are calculated from the slopes of the two lines, in accordance with Eq. (2*a*). It is not necessary to calculate the actual concentrations of methyl acetate, since a plot versus t of log $(V_T - V_t)$ has the same slope as a plot of log $[(V_T - V_t)(N/5)]$.

Comparison values of k_1 are calculated at each temperature from several sets of points by use of Eq. (2*b*), to illustrate the dependence of the calculated rate constant on the particular pair of points chosen, and hence emphasize the advantages of the averaging achieved in the graphical method. It should be noted that it is not significant to substitute an explicit averaging of the values of k obtained from the successive observations by means of Eq. (2*b*).[7]

From the rate constants found for the two temperatures, the heat of activation is calculated by use of Eq. (8).

Practical Applications. The rate of a chemical reaction is important in determining the efficiency of many industrial reactions. In organic reactions particularly, where there is the possibility of several reactions going on simultaneously, the kinetic considerations will often be no less important that the equilibrium relationships.

Suggestions for Further Work. The integration of Eq. (9) to give Eqs. (10) and (11) may be checked to illustrate a typical transformation in chemical kinetics. The integral involved is given in mathematical tables.

Instead of estimating by eye the "best" straight-line representation of the plot of log $(V_T - V_t)$ versus time, the method of least squares may be used (Chap. 17).

Different acid concentrations or other acids may be used;[5] the influence of neutral salts may be studied.[2] Nonaqueous solvents may be used,[3] and methyl acetate may be replaced by other esters,[6] higher temperatures being used if necessary.

References

1. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Company, New York (1949).
2. Duboux and deSousa, *Helv. Chim. Acta*, **23**, 1381 (1940).
3. Friedman and Almore, *J. Am. Chem. Soc.*, **63**, 864 (1941).
4. Frost and Pearson, "Kinetics and Mechanisms," John Wiley & Sons, Inc., New York (1953).
5. Griffith and Lewis, *J. Chem. Soc.*, **109**, 67 (1916).
6. Harned and Pfansteil, *J. Am. Chem. Soc.*, **44**, 2193 (1922).
7. Rosevearc, *J. Am. Chem. Soc.*, **53**, 1651 (1931).

27. SAPONIFICATION OF ETHYL ACETATE

This experiment illustrates a second-order reaction for which a second-order constant may be calculated. A conductometric method or a titrimetric method may be used for following the course of the reaction.

Theory. The second-order reaction studied in this experiment is the saponification of ethyl acetate by sodium hydroxide.

$$CH_3COOC_2H_5 + Na^+ + OH^- \rightarrow CH_3COO^- + Na^+ + C_2H_5OH$$

The hydroxyl ion and ethyl acetate are the reacting materials, the sodium ion being incidental.

The rate of the second-order reaction, dx/dt, is proportional to the concentration of each of the two reacting materials, as expressed in the equation

$$\frac{dx}{dt} = k(a - x)(b - x) \tag{1}$$

where x = number of moles per liter reacting in time t
a = initial concentration of ethyl acetate
b = initial concentration of the hydroxyl ion
k = specific reaction rate

On integration for $a \neq b$, it is found that

$$k = \frac{2.303}{t(a - b)} \log \frac{b(a - x)}{a(b - x)} \tag{2}$$

On integration for the case in which $a = b$,

$$k = \frac{1}{ta}\frac{x}{a - x} \tag{3}$$

A solution containing sodium hydroxide and ethyl acetate undergoes a marked decrease in conductance with time because the highly conducting hydroxyl ion is replaced by the poorly conducting acetate ion during the reaction. Accordingly, a conductance bridge can be used to study the progress of the reaction.[5] An alternative procedure is to withdraw samples from the reaction mixture at definite intervals, discharge them into excess standard HCl solution, and back-titrate with standard NaOH.

A. CONDUCTANCE METHOD

Apparatus. Two 250-ml glass-stoppered volumetric flasks; two 250-ml Erlenmeyer flasks; bottle-type conductance cell, conductance bridge; tall glass-stoppered weighing bottle; ethyl acetate; standardized sodium hydroxide; 25-ml burette; 1-ml graduated pipette; 25-ml pipette; 50-ml pipette; thermostats at 25 and 35°; stop watch or timer.

Procedure. Standard solutions of ethyl acetate and sodium hydroxide having exactly the same normality are prepared. This requires careful technique.

Enough pure ethyl acetate is pipetted into a weighed weighing bottle containing about 5 ml of water to prepare 250 ml of 0.02 *M* solution. The bottle is reweighed, the solution transferred quantitatively to a volumetric flask with rinsing, and distilled water is added to the mark. The exact normality is calculated.

The same volume of NaOH whose normality is exactly equal to that of the ethyl acetate is prepared by quantitative dilution of standardized 0.5 *N* stock reagent.

The flasks containing these solutions and a 250-ml flask containing distilled water are clamped in the 25° thermostat and allowed to come to temperature equilibrium before use.

The conductance bridges described in Exp. 29 and Chap. 22 are satisfactory for this experiment. A compact bridge utilizing an electron-ray tube or "magic eye" as a null indicator is convenient. The student is referred to Chap. 9 for information on the theory and practice of conductance measurements. The Freas-type conductance cell shown in Fig. 31 is recommended.

The conductance bridge is set up near the thermostat, and a conductance cell which has been rinsed with distilled water is brought to thermostat temperature.

Into another 250-ml flask is pipetted exactly 25 ml of ester solution, 25 ml water, and 50 ml NaOH solution in that order. The flask is swirled rapidly in the thermostat as the NaOH is introduced and the stop watch started after about half has been added. The conductance cell is quickly rinsed with a few milliliters of the mixture and then filled about two-thirds full. Conductance readings are begun as soon as the cell can be returned to the thermostat. Readings are taken up to an hour or so, every 2 or 3 min at first, with intervals lengthened as time goes on so that a total of about 15 readings is obtained. The solution is then returned to the mixing flask, which is stoppered and set aside for conductance readings after at least 24 hr have elapsed, when the reaction will have been completed.

For the next experiment, the proportions of ester and base are reversed, and the experiment is repeated.

Next, equal volumes of the base and ester solutions are mixed, and readings are taken for about an hour at 25°C. With solution and apparatus transferred to the 35° thermostat, the experiment is repeated with equal volumes of the reactants. In this experiment with exactly equal concentrations of the two reactants it is possible to obtain the specific rate constants without waiting for a final reading after the reaction is completed.

Calculations. The number of moles per liter, x, reacting in time t is given in terms of the conductances $y_0 = 1/R_0$, $y_t = 1/R_t$, and $y_\infty = 1/R_\infty$ at the times 0, t, and ∞, respectively, by

$$\frac{x}{c} = \frac{y_0 - y_t}{y_0 - y_\infty} = \frac{1/R_0 - 1/R_t}{1/R_0 - 1/R_\infty} \tag{4}$$

where c is a or b, whichever is smaller. Rather than calculating x by using Eq. (4) and substituting into Eq. (2), considerable labor in computation may be saved by substituting Eq. (4) into Eq. (2) and rearranging to obtain Eq. (5) and (6).

For $b > a$, where b is the initial concentration of base,

$$\frac{k(b - a)t}{2.303} + \log\left(\frac{bf}{a}\right) = \log\frac{fR_\infty - R_t}{R_\infty - R_t} \tag{5}$$

where $f = R_0[R_\infty - (R_\infty - R_0)(b/a)]^{-1}$.

For $a > b$

$$\frac{k(a - b)t}{2.303} + \log\left(\frac{ag}{b}\right) = \log\frac{gR_\infty + R_t}{R_\infty - R_t} \tag{6}$$

where $g = R_0[(R_\infty - R_0)(a/b) - R_\infty]^{-1}$.

A plot of resistance versus time is prepared and extrapolated back to zero time to obtain the value of R_0. Plots of $\log [(fR_\infty - R_t)/(R_\infty - R_t)]$ or $\log [(gR_\infty + R_t)/(R_\infty - R_t)]$ versus t are prepared, and the specific reaction-rate constant k is calculated by use of Eq. (5) or (6).

When the concentrations of the two reactants are the same, Eq. (3) may be used. Upon introduction of conductances or resistances, Eq. (3) becomes

$$k = \frac{1}{ta}\frac{y_0 - y_t}{y_t - y_\infty} = \frac{1}{ta}\frac{1/R_0 - 1/R_t}{1/R_t - 1/R_\infty} \tag{7}$$

Rearrangement of Eq. (7) leads to

$$\frac{1}{R_t} = \frac{1}{R_\infty} + \frac{1}{kat}\left(\frac{1}{R_0} - \frac{1}{R_t}\right) \tag{8}$$

The specific reaction-rate constant k is calculated from a plot of $1/R_t$ versus $(1/R_0 - 1/R_t)/t$.

From the values of k at 25 and 35° the heat of activation, ΔH_a, is calculated by use of Eq. (8) of the preceding experiment.

B. TITRATION METHOD

Apparatus. Two Erlenmeyer flasks (2,000 ml); two 250-ml Erlenmeyer flasks; 50-ml pipette; 50-ml burette, stop watch; ethyl acetate; standardized sodium hydroxide; 0.02 M hydrochloric acid; thermostat.

Procedure. Since the end points are much sharper if no carbonate is present, about 3 liters of carbon dioxide-free distilled water is first prepared. The water may be boiled, or a stream of air may be passed through a tower of soda lime and bubbled through the water in a vigorous stream for 10 to 15 min.

Pure ethyl acetate is dissolved in water to give about 800 ml of 0.01 M solution. Two liters of 0.02 M sodium hydroxide which is free from carbonates (see page 469) is prepared. It is important that the concentration of sodium hydroxide be exactly twice that of the ethyl acetate. Exactly 250 ml of each solution is placed in clean Erlenmeyer flasks, and these flasks are clamped in the 25° thermostat and allowed to come to temperature equilibrium.

The reaction is started by pouring the ethyl acetate solution rapidly into the sodium hydroxide solution and shaking thoroughly. The stop watch is started.

Fifty-milliliter samples are withdrawn and titrated after about 2, 5, and 8 min. The time of discharge of the pipette is noted accurately, and the sample is discharged as rapidly as possible into a known excess of 0.02 M hydrochloric acid. A fast-flowing pipette is used. The solution is then titrated with 0.02 M sodium hydroxide using phenolphthalein as an indicator. Further samples are titrated after longer intervals of time as the reaction slows down. The last 100 ml or more is stoppered and allowed to stand for a day or two to give the final titration value after the reaction has gone to completion.

A second experiment is started about half an hour later, when the first reaction has slowed down somewhat. If the first titrations cannot be made fast enough to permit proper sampling, the samples may be kept in stoppered bottles after acidifying.

The experiment is repeated with the same conditions except with the ethyl acetate half as concentrated.

Calculations. The initial concentrations of ethyl acetate, a, and sodium hydroxide, b, in the reaction mixture are calculated in moles per liter.

The decrease in concentration, x, of sodium hydroxide and ethyl acetate at any time t is calculated by subtracting the concentration of NaOH at time t from its original concentration in the reaction mixture.

As a check the initial concentration of ethyl acetate may be calculated from the difference between the initial concentration of NaOH and that after the reaction mixture has stood for a day or two so that the reaction goes to completion.

The specific reaction rate constant k is calculated by use of Eq. (2) or, if the initial concentrations a and b are equal, from Eq. (3). In the first case, $\log [b(a - x)/a(b - x)]$ is plotted against t, and in the second case, $x/(a - x)a$ is plotted against t.

Practical Applications. The calculations in this experiment are typical for a second-order reaction, and the influence of concentration of either reacting material on the velocity of the reaction may be calculated quantitatively.

Suggestions for Further Work. The rates of saponification of other esters may be determined. Methyl acetate saponifies rapidly; consequently it should be studied at lower temperatures. The more complicated esters saponify more slowly, and they may be studied conveniently at higher temperatures. The saponification rate is the same with all strong bases, but with weak bases the reaction is complicated and depends on the degree of dissociation of the base.

References

1. Amis, "Kinetics of Chemical Change in Solution," The Macmillan Company, New York (1949).
2. Frost and Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York (1953).
3. Laidler, "Chemical Kinetics," McGraw-Hill Book Company, Inc., New York (1950).
4. Moelwyn-Hughes, "Kinetics of Reactions in Solution," Oxford University Press, New York (1947).
5. Walker, *Proc. Roy. Soc. (London)*, **A78**, 157 (1906).

28. INVERSION OF SUCROSE

This experiment illustrates the use of the polarimeter and the calculation of reaction-rate constants. The catalysis of a hydrolytic reaction by hydrochloric acid and monochloroacetic acid is studied.

Theory. The kinetic equations are discussed in Exp. 26.

The inversion of cane sugar can be followed without disturbing the system. The angle of rotation of polarized light passing through the solution is measured with a polarimeter. The reaction is

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O + H^+ \rightarrow \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6} + H^+ \tag{1}$$

The sucrose is dextrorotatory, but the resulting mixture of glucose and fructose is slightly levorotatory because the levorotatory fructose has a greater molar rotation than the dextrorotatory glucose. As the sucrose is used up and the invert sugar is formed, the angle of rotation to the right (as the observer looks into the polarimeter tube) becomes less and less, and finally the light is rotated to the left. The rotation is determined at the beginning (α_0) and at the end of the reaction (α_∞), and the algebraic difference between these two readings is a measure of the original concentration of the sucrose. It is assumed that the reaction goes to completion, and practically no sucrose remains at "infinite" time. At any time t, a number proportional to the concentration c of sucrose is obtained from the difference between the final reading and the reading (α_t) at the time t. Thus, the specific reaction-rate constant may be calculated using the equation

$$k = \frac{2.303}{t} \log \frac{\alpha_0 - \alpha_\infty}{\alpha_t - \alpha_\infty} \tag{2}$$

The reaction proceeds too slowly to be measured in pure water, but it is catalyzed by hydrogen ions. The water is in such large excess that the reaction follows the equation for a first-order reaction, although two kinds of molecules are involved in the reaction.

Guggenheim[6] has described a method for calculating the rate constant of a first-order reaction without an infinite time value. This method is useful if the reaction does not go to completion in one laboratory period and has the added advantage that each plotted point does *not* depend upon a *single* observation of the reading at time infinity.

The Guggenheim method may be applied directly if data are taken at equal time intervals. If the data are taken at unequal time intervals, a plot of concentration, angle of rotation, or other measure of the extent of reaction versus time (t) is prepared and a smooth curve drawn. The required data may be read from this curve.

The data are arranged in two sets. For each observation (c_1) at time t in the first set, another observation (c_2) is taken at time $t + \Delta t$, where Δt is a fixed time interval. If a plot of log ($c_1 - c_2$) versus t is prepared, the points will fall on a straight line of slope $-k/2.303$. The constant time interval Δt may be taken as approximately one-half the duration of the experiment. If Δt is too small, there will be a large error in $c_1 - c_2$.

The equation for this method may be derived as follows: From the integrated form of the first-order-reaction differential equation,

$$c = c_0 e^{-kt} \tag{3}$$

Thus the concentrations c_1 and c_2 at two times differing by Δt are

$$c_1 = c_0 e^{-kt} \tag{4}$$
$$c_2 = c_0 e^{-k(t+\Delta t)} \tag{5}$$

Subtracting,

$$c_1 - c_2 = c_0 e^{-kt}(1 - e^{-k\Delta t}) \tag{6}$$

Taking logarithms,

$$\log (c_1 - c_2) = -kt/2.303 + \log [c_0(1 - e^{-k\Delta t})] \tag{7}$$

Thus, the slope of a plot of $\log (c_1 - c_2)$ versus t is $-k/2.303$.

If instead of measuring concentration directly some linear function X of the concentration, say optical rotation, is measured, an equation of the same form as Eq. (7) applies. For example, if

$$X = ac + b \tag{8}$$
$$c_1 - c_2 = (X_1 - X_2)/a \tag{9}$$

and

$$\log (X_1 - X_2) = -kt/2.303 + \log [ac_0(1 - e^{-k\Delta t})] \tag{10}$$

Apparatus. Polarimeter (described in Exp. 5); mercury-vapor lamp with filters (Chap. 24) or sodium-vapor lamp; thermostat and circulating pump; two water-jacketed polarimeter tubes; pure sucrose; 100 ml of 4 N hydrochloric acid; 100 ml of 4 N monochloroacetic acid.

Procedure. Twenty grams of pure cane sugar (sucrose) is dissolved in water (filtered, if necessary, to give a clear solution) and diluted to 100 ml.

Two jacketed polarimeter tubes are connected in series with the circulating water from a thermostat at 25°. A zero reading is taken with a mercury-vapor lamp and Corning glass filters arranged to transmit only the green light (Chap. 24). A sodium-vapor lamp is equally satisfactory.

After letting the sugar solution and a solution of exactly 4 N hydrochloric acid solution stand in the thermostat for a few minutes, 25 ml of each are mixed together thoroughly. One of the polarimeter tubes is rinsed out with successive small portions of the solution, and then the tube is filled with the solution and stoppered. The second tube is filled, in a similar manner, with a mixture of the sugar solution and exactly 4 N monochloroacetic acid solution (exactly 25 ml of each). The tubes are filled as soon as possible after mixing, so that an early reading of the angle of rotation may be obtained.

The time of the first reading is recorded, and polarimeter readings of the hydrochloric acid solutions and the corresponding times are taken as rapidly as convenient (10 min) over a period of 1 hr or so. As the reaction slows down, the observations may be taken less frequently. The observations should extend over a period of 3 hr or more. The reaction goes much more slowly with the monochloroacetic acid, and the readings are taken less frequently. They are taken at convenient intervals of time when the polarimeter is not being used for readings on the solution containing hydrochloric acid.

The final readings (α_∞) are taken after the solutions have stood in a tightly stoppered flask long enough for the reaction to be completed, at least 2 days for the hydrochloric acid and a week for the monochloroacetic acid. If it is not convenient to obtain the final reading for the monochloroacetic acid, it may be assumed that α_∞ will be the same as for the hydrochloric acid.

Calculations. A plot of $\alpha_t - \alpha_\infty$ versus time is prepared. As stated before, the concentration of sucrose is proportional to $\alpha_t - \alpha_\infty$ where α_t is the angle of rotation at time t and α_∞ is the final angle (negative in this particular case). The logarithms of ($\alpha_t - \alpha_\infty$) are plotted against time. Plotting the logarithms of ($\alpha_t - \alpha_\infty$) gives the same slope as plotting the logarithms of ($\alpha_t - \alpha_\infty$) multiplied by a constant. The best straight lines are drawn through the points, one for the hydrochloric acid and one for the monochloroacetic. The specific reaction-rate constants k are calculated from the slopes of the lines.

In calculating the results of this experiment at least one set of data is treated by the Guggenheim method for comparison with the usual method. If the infinite time reading cannot be obtained conveniently, this method may be used exclusively.

A calculation is made to show what the concentration of sucrose was in each case exactly 10 hr after starting the reaction. The precision of this calculation is estimated.

Practical Applications. These are discussed under Exp. 25.

Suggestions for Further Work. Some suggestions for further work are discussed under Exp. 25.

Trichloroacetic acid and sulfuric acid, and other acids, each 4 N, may be used as catalysts. Trichloroacetic acid is about as strongly dissociated as hydrochloric acid. (**Caution**: It is corrosive.) The relative acid strengths of monochloroacetic acid and trichloroacetic acid are to be explained on the basis of molecular structure.

The activation energies may be obtained by running a second set of determinations, using water pumped from a thermostat at 35° or at 15°.

The effect of ionic strength on the rate of this reaction[2] may be investigated. The effect of changing the dielectric constant may be investigated by adding ethanol or dioxane.[1]

Volume changes as measured continuously in a dilatometer may be used to follow the course of a reaction. The hydrolysis of acetal[3,4] is a good example. At 25°, 0.0005 M HCl is mixed quickly with enough acetal from a graduated pipette to make the solution 0.15 M with respect to acetal. The solution is transferred immediately to a dilatometer through a tightly fitting stopcock, and the rise of the liquid in the capillary is recorded at frequent intervals. The logarithm of the final reading minus the reading at time t is plotted against time and the specific rate constant is calculated. A second experiment may be carried out with 0.05 M acetic acid instead of the hydrochloric acid.

References

1. Amis and Holmes, *J. Am. Chem. Soc.*, **63**, 2231 (1941).
2. Amis and Jaffe, *J. Chem. Phys.*, **10**, 598 (1942).
3. Brönsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).
4. Ciapetta and Kilpatrick, *J. Am. Chem. Soc.*, **70**, 639 (1948).
5. Frost and Pearson, "Kinetics and Mechanism," John Wiley & Sons, Inc., New York (1953).
6. Guggenheim, *Phil. Mag.* (7), **2**, 538 (1926).
7. Pennycuick, *J. Am. Chem. Soc.*, **48**, 6 (1926).
8. Scatchard, *J. Am. Chem. Soc.*, **48**, 2259 (1926).

CHAPTER 9

ELECTRIC CONDUCTANCE

29. CONDUCTANCE BEHAVIOR OF WEAK AND STRONG ELECTROLYTES

In this experiment practice is obtained in the measurement of the electrical conductance of solutions. The influence of concentration on the conductance of weak and strong electrolytes is studied, and the dissociation constant of a weak acid is determined.

Theory.[4,6,7] The specific resistance of an electrolytic solution is defined as the resistance in ohms of a column of the solution 1 cm long and 1 cm^2 in cross section. The specific conductance L is the reciprocal of the specific resistance and could be evaluated from a resistance measurement with a cell having a volume of 1 cm^3 and constructed with plane-parallel electrodes 1 cm^2 in area and 1 cm apart. The usual conductance cell does not satisfy these requirements, but it is possible to determine the value of a constant and characteristic factor k called the *cell constant*, such that

$$Lr = k \tag{1}$$

where r is the resistance of the actual cell containing an electrolytic solution of specific conductance L. The numerical value of k for a particular cell is determined experimentally by use of a standard solution of known specific conductance. For this purpose a solution of potassium chloride of accurately known specific conductance[3] is used; for 0.02 N KCl, for example, the specific conductance L is 0.002768 $\text{ohm}^{-1}\ \text{cm}^{-1}$ at 25°C. The observed resistance r for the potassium chloride solution is multiplied by the known specific conductance to obtain the cell constant. The specific conductance of any solution may then be calculated by using the same equation and substituting the known value of the cell constant and the observed resistance.

The equivalent conductance, which is the conductance in reciprocal ohms of a solution containing 1 g-equiv of solute when placed between plane-parallel electrodes of suitable height 1 cm apart, is calculated from the relation

$$\Lambda = LV \tag{2}$$

where V is the volume of solution in cubic centimeters which contains 1 g-equiv weight of solute.

In general, pure solvents are poor conductors of electricity, but when acids, bases, or salts are dissolved in them, the conductance is increased, sometimes to a very large extent.

The conductance of these solutions is the result of the actual movement of ions through the solution to the electrodes. When two electrodes of an electrical circuit are placed in a solution, the cations (+) are attracted to the negative pole (cathode), and the anions (−) are attracted to the positive pole (anode). Changes in the conductance of an electrolytic solution due to variations in concentration may result from changes both in the number and in the mobility (p. 152) of the ions present.

Strong electrolytes are those like sodium chloride which are largely dissociated into electrically charged ions even in fairly concentrated solutions, and weak electrolytes are those like acetic acid which are only slightly dissociated into ions even in dilute solutions.

The difference in behavior between a weak and a strong electrolyte becomes evident when the equivalent conductances of their solutions are plotted as a function of the concentration, especially in the dilute region. The equivalent conductance for the strong electrolyte approaches a definite value at infinite dilution, but that of the weak electrolyte cannot be extrapolated to a definite value because the slope of the curve is still changing appreciably at the lowest concentrations at which accurate experimental measurements can be made. When the electrolyte is weak, the increase observed in the equivalent conductance on dilution is due largely to an increase in the number of ions present, corresponding to a higher degree of dissociation as the solution is diluted. This is the basis of the theory of Arrhenius, proposed in 1887, which has been so successful in describing quantitatively the behavior of solutions of weak electrolytes.

The increase of the equivalent conductance of solutions of strong electrolytes with dilution in the low-concentration range is not due to an increase in dissociation, because the dissociation is already complete, but to an increased mobility of the ions. In a concentrated solution of a highly ionized strong electrolyte, the ions are close enough to one another so that any one of them in moving is influenced not only by the electrical field impressed across the electrodes but also by the field of the surrounding ions. The ionic velocities are, then, dependent upon both forces. Arrhenius attempted to treat the electrolytic-conductance behavior of the strong electrolytes in the way in which he had successfully treated the weak electrolytes; such a treatment is, however, inconsistent with the fact discovered by Kohlrausch that a plot of the equivalent conductance of a strong electrolyte against the square root of the concentration is very nearly linear. More recently Debye and Hückel and Onsager have been able to calculate the effect of the surrounding ions on the mobility of any given ion and have obtained results entirely consistent with the experimental facts. Complete dissociation is here assumed.

A great deal more effort has been devoted to the study of the conductance behavior of aqueous solutions than of nonaqueous solutions, but the newer theories as expounded by Debye, Onsager, Kraus, Fuoss, and others are being applied to the nonaqueous solutions, which are now receiving more attention than formerly.

The apparent dissociation constant for a typical weak electrolyte such as acetic acid may be calculated as

$$K_a = \frac{\alpha^2 c}{1 - \alpha} \tag{3}$$

where α = degree of dissociation
c = concentration of solute, moles/liter

According to the Arrhenius theory, the value of α at any concentration is given by the relation

$$\alpha = \frac{\Lambda}{\Lambda_0} \tag{4}$$

where Λ = equivalent conductance at concentration c
Λ_0 = equivalent conductance at infinite dilution

In the case of a weak electrolyte the value of Λ_0 cannot be obtained by the extrapolation to infinite dilution of results obtained at finite concentrations but must be calculated from results obtained with strong electrolytes by means of the law of Kohlrausch concerning the additivity of ionic conductances at infinite dilution. Thus, for a weak acid HR, the value of Λ_0 may readily be determined from a knowledge of the values of Λ_0 for HCl, NaCl, and the sodium salt, NaR, of the weak acid:

$$\Lambda_{0,\mathrm{HR}} = \Lambda_{0,\mathrm{HCl}} + \Lambda_{0,\mathrm{NaR}} - \Lambda_{0,\mathrm{NaCl}}$$

Alternatively, the relation

$$\Lambda_{0,\mathrm{HR}} = l_{0,\mathrm{H}^+} + l_{0,\mathrm{R}^-}$$

may be used directly. The value of l_{0,H^+}, the limiting conductance of the hydrogen ion, is obtained as the product of Λ_0 for HCl and the limiting value of the transference number at infinite dilution of the hydrogen ion in HCl solutions. For the evaluation of l_{0,R^-} similar measurements on solutions of the sodium salt of the weak acid are used. The Λ_0 values for the strong electrolytes are obtained by extrapolating to infinite dilution the values of the equivalent conductance at finite dilutions.

The relation expressed by Eq. (3) is derived by assuming that the ions and undissociated molecules behave as ideal solutes. The calculation of the degree of dissociation by means of Eq. (4) would be accurate if the ionic mobilities were independent of the concentration. Neither of these assumptions is exactly true, but they may safely be adopted in routine work of moderate accuracy. Where high accuracy is required, a more elaborate method[4,7] of calculation must be employed.

Apparatus. Wheatstone bridge assembly; conductance cell; source of alternating current; earphones; conductance water; platinizing solution; *exactly* 0.02 N potassium chloride solution; 0.05 N solution of acetic acid; 0.02 N solutions of hydrochloric acid, sodium chloride, and sodium acetate; thermostat at 25°C; 50- and 100-ml volumetric flasks.

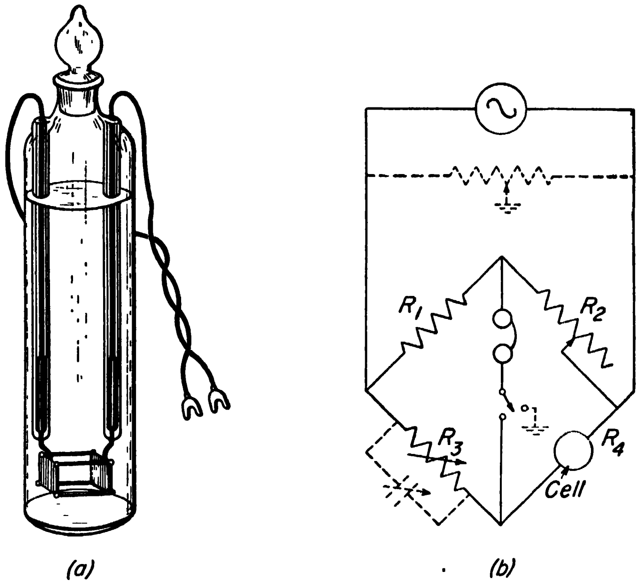

FIG. 31. Apparatus for conductance measurements. (*a*) Freas conductance cell; (*b*) Wheatstone bridge circuit.

Procedure. The principle of the Wheatstone bridge should be thoroughly understood. The basic apparatus is shown in Fig. 31. The dotted elements of the circuit diagram may be incorporated for increased accuracy; their functions are explained in Chap. 22. For the bridge circuit of Fig. 31 the condition for resistive balance is

$$R_4 = R_3 \frac{R_2}{R_1}$$

The quantity R_2/R_1 is commonly called the *bridge ratio;* in conventional student Wheatstone bridges switch selected ratios in decimal steps from 10^{-3} to 10^3 are available. The variable standard resistor R_3 consists normally of four decade resistors giving, respectively, steps of 1,000, 100, 10, and 1 ohms.

The conductance cell or other unknown resistance is connected as R_4. The 1,000-ohm decade switch is set to 1, and the other three decade switches to 0, and the oscillator and detector connected to the bridge. The detector switch is closed, and the ratio dial set at the position giving the smallest detector output. The several decade resistors are successively adjusted (*starting with the largest and working down*) to determine the value of R_3 giving minimum detector output. It should be noted that this setting should be verified by approach from both the high and low resistance sides. If a Wagner ground is being used, the detector is then switched to the ground connection and the Wagner ground branch balanced. The detector is switched back to the bridge proper, and a better bridge-balance setting obtained. This sequence of operations is repeated until both bridge and Wagner ground balances are obtained simultaneously. The value of R_4 is then equal to the product of R_3 and the bridge ratio.

The Freas-type conductance cell shown in Fig. 31 is particularly suitable for student conductance measurements. The four corners of the thin platinum squares are anchored to a glass frame. The cell is readily filled and emptied, and the volume of solution required is small. For all conductance measurements the cell is immersed in a thermostat, preferably at 25°C regulated to 0.02°.

The electrodes of the conductance cell must have an adherent coating of platinum black and should be immersed in distilled water whenever the cell is not in use. If the electrodes are allowed to dry out, it is difficult to rinse out electrolytes from them, and it is advisable to dissolve off the coating with aqua regia (under the hood) and plate out a fresh deposit as described in Chap. 22. The electrodes and cell are rinsed out thoroughly, first with distilled water and then with conductance water (Chap. 22) which is especially pure water prepared by multiple distillations. The conductance cells must be handled with great care; the electrodes must not be touched, and they must not be moved with respect to each other during the course of an experiment.

The cell is filled with conductance water, inspected to make sure there are no air bubbles at the electrodes, and its resistance is measured; it is then rinsed, refilled, and the resistance measured again. This process is repeated until the resistance has become essentially constant, showing that contaminating electrolytes in the cell have been rinsed out. The cell resistance will not become absolutely constant because the conductance water is very pure and traces of electrolytes insignificant in the later measurements will produce noticeable fluctuations. The specific conductance of the water used should be about 5×10^{-6} ohm^{-1} cm^{-1} or less, corresponding to a resistance of 200,000 ohms or more in a cell of unit cell constant. At these high resistances an accuracy of more than two significant figures is difficult to obtain without special precautions. For the other solutions studied, a precision of the order of a few tenths of a per cent should be obtained in the resistance measurements.

When the cell is clean, as shown by a reasonably constant high resistance with conductance water, it is rinsed two or three times with 0.02 *N* potassium chloride solution and the resistance then determined with this solution filling the cell. Additional measurements are made on fresh samples of the solution until successive determinations agree closely. The purpose of these measurements is to secure data for the calculation of the cell constant.

The cell is emptied and rinsed with the next solution for which the conductance is to be measured. It is advisable to make check determinations on each solution to make sure that the cell was thoroughly rinsed.

One hundred milliliters of 0.05 *N* acetic acid is prepared by quantitative dilution of 1 *N* stock solution with conductance water, and its concentration is verified by titration with standard sodium hydroxide. After the conductance of this solution has been determined, a 0.025 *N* solution is prepared by quantitative dilution of the 0.05 *N* acetic acid for a second conductance measurement. In this fashion, conductance measurements are made on 0.05, 0.025, 0.0125, 0.00625, 0.00312, and 0.00156 *N* acetic acid solutions. The successive dilutions must be made with great care because the propagation of error will otherwise become excessive.

Conductance measurements are then made on solutions of hydrochloric acid, at concentrations of 0.02, 0.01, 0.005, 0.0025, and 0.00125 *N*. The solutions are prepared as above by quantitative dilution of a stock solution with conductance water. These measurements provide data illustrating the conductance behavior of solutions of strong electrolytes and data for the calculation of the equivalent conductance at infinite dilution for acetic acid.

Calculations. The cell constant for the conductance cell is determined by means of Eq. (1) and the known specific conductance of the potassium chloride solution. The specific conductances of the conductance water and of the various solutions are then calculated. The specific conductance of the solute in each case is evaluated as the difference between the specific conductance of the particular solution and that of the solvent used. The equivalent conductance of the solute is then calculated for each solution.

For each of the solutes a plot is made of equivalent conductance versus the square root of the concentration; for the hydrochloric acid an extrapolation* of the experimental data to zero concentration is made for the

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* The reliability of the various experimental points should be considered in making this extrapolation.

evaluation of the equivalent conductance at infinite dilution. The value so obtained is combined with values of Λ_0 for sodium chloride and sodium acetate taken from the literature to give the equivalent conductance at infinite dilution for the acetic acid. A second calculation of this quantity is made by use of the values of Λ_0 for the sodium acetate and hydrochloric acid solutions and the values 0.449 and 0.821, respectively, for the transference numbers at infinite dilution of the acetate ion of sodium acetate and the hydrogen ion of hydrochloric acid at 25°.

The apparent dissociation constant K_a for the acetic acid is then calculated at each concentration by use of Eqs. (3) and (4) and the value of Λ_0 for acetic acid obtained as described above. No such calculations should be carried out for strong electrolytes, since the equations given are without significance for them.

The data and the results of this experiment may be conveniently tabulated under the following column headings: concentration, milliliters containing 1 g-equiv of solute, resistance in ohms, specific conductance, equivalent conductance, degree of dissociation, and dissociation constant. Wherever possible the results are compared with accepted values,[4,6,7] and any discrepancies arising are discussed in the light of the sources of experimental error.

Practical Applications. The next experiment in this chapter illustrates applications of conductance measurements to chemical problems. To illustrate their application to engineering chemistry, it may be mentioned that measurements of this sort have been used to measure the flow of water in streams, to determine the total solids in water, and to test for pollution of water.

Suggestions for Further Work. The influence of substitution and structure on the dissociation constants of organic acids may be studied. For example, the dissociation constants of mono- and dichloroacetic acids and propionic acid may be determined and compared with the dissociation constant of acetic acid. In the same way the influence of substituting amino or nitro groups into benzoic acid may be studied.

The conductance behavior of potassium iodide when dissolved in acetone, dioxane, ethanol, and mixtures of these solvents with water may be studied.

A conductance cell of the type described by Nichol and Fuoss[5] may be constructed. This cell utilizes shielded cylindrical electrodes arranged so as to eliminate stray capacitance shunting the electrolytic resistance.

References

1. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2d ed., Reinhold Publishing Corporation, New York (1950).
2. International Critical Tables, Vol. VI, pp. 229ff., McGraw-Hill Book Company, Inc., New York (1928).
3. Jones and Bradshaw, *J. Am. Chem. Soc.*, **55**, 1780 (1933).
4. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York (1939).
5. Nichol and Fuoss, *J. Phys. Chem.*, **58**, 696 (1954).

6. Robinson and Stokes, "Electrolyte Solutions," Academic Press, Inc., New York (1955).
7. Shedlovsky *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed. Vol. I, Part II, Chap. 25, Interscience Publishers, Inc., New York (1949).

30. APPLICATIONS OF CONDUCTANCE MEASUREMENTS

This experiment illustrates several of the practical uses of conductance measurements.

A. SOLUBILITY BY CONDUCTANCE MEASUREMENTS

Theory.[4] In a saturated solution of a difficultly soluble salt, the solution is so dilute that its equivalent conductance may be assumed to be practically equal to the limiting value obtained by extrapolation to infinite dilution; in other words, the effects of interionic attraction are negligible.

If the specific conductance L of the saturated solution and the specific conductance of the water used as solvent are determined, the specific conductance of the ions of the salt may be calculated by simple subtraction.

$$L_{\text{solution}} - L_{\text{water}} = L_{\text{ions}}$$

By definition the equivalent conductance Λ is given by the expression

$$\Lambda = L_{\text{ions}}V = L_{\text{ions}}\frac{1{,}000}{c}$$

where V = volume containing 1 g-equiv of solute, ml
c = concentration, g-equiv/liter

Making use of the approximation that Λ may be replaced by Λ_0, the equivalent conductance at infinite dilution, it follows that

$$c = \frac{1{,}000L_{\text{ions}}}{\Lambda_0}$$

Apparatus. Same as in Exp. 29 except that a conductance cell with large electrodes placed a short distance apart should be used; lead sulfate or other difficultly soluble salt.

Procedure. The cell constant for the conductance cell employed and the specific conductance of the water used, at 25°C, are determined as described under Exp. 29. The lead sulfate, strontium sulfate, calcium fluoride, or silver iodate whose solubility is to be determined is shaken repeatedly with conductance water to remove any soluble impurities. The substance thus prepared is suspended in conductance water in an Erlenmeyer flask which has been thoroughly cleaned and rinsed with conductance water. The suspension is warmed moderately, then placed in the thermostat at 25°C and stirred vigorously until it has come to equilibrium at the temperature of the thermostat. The specific conductance of this solution is determined by repeated measurements on fresh samples of the solution until a constant value is obtained. The samples are withdrawn through a glass-wool filter, if necessary, to eliminate particles of the solid phase.

Calculations. The solubility of the salt is calculated by means of the equation already given. The concentration c in gram equivalents per liter is changed to grams per 100 g of solvent, on the assumption that the density of the solution is equal to that for water, and compared with the accepted value.

Values of Λ_0 are obtained from tables of equivalent conductances,[3] or, using Kohlrausch's law, by adding the ionic conductances[2,3,5,6] involved.

Practical Applications. This experiment indicates a method by which the solubility of many difficultly soluble salts may be determined. Although of restricted utility, it serves as a convenient check when applied to the solubility of certain salts whose analytical determination is difficult. The solubilities at several temperatures below 25° are measured by withdrawing samples at lower temperatures and measuring the conductances at 25°.

Suggestions for Further Work. Solubility measurements may be made on less soluble salts such as silver chloride or barium sulfate. Very pure conductance water is necessary, and carbon dioxide from the air must be excluded.

References

1. Böttger, *Z. physik. Chem.*, **46**, 521 (1903).
2. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," p. 172, Reinhold Publishing Corporation, New York (1950).
3. International Critical Tables, Vol VI, pp. 230ff., McGraw-Hill Book Company, Inc., New York (1930).
4. Kohlrausch and Rose, *Z. physik. Chem.*, **12**, 234 (1893).
5. MacInnes, "The Principles of Electrochemistry," p. 342, Reinhold Publishing Corporation, New York (1939).
6. Robinson and Stokes, "Electrolyte Solutions," Academic Press, Inc., New York (1955).

B. CONDUCTOMETRIC TITRATIONS

Theory.[1,4,6] That the end point of a neutralization reaction involving a strong acid and a strong base may be indicated by conductance measurements will be evident from the following consideration: when the strong base is added gradually to the solution of the strong acid, the fast-moving hydrogen ions are gradually removed with the formation of water molecules and are replaced by the cations of the base, which have an ionic mobility that is usually not more than one-fifth or one-sixth that of the hydrogen ions. The salt formed, as well as the acid and base, is largely ionized, so the change in conductance arises from the difference in the mobilities of the ions. The conductance of the solution continues to decrease until all the hydrogen ions have disappeared (except those due to the dissociation of the water), i.e., until the acid has been neutralized. If the addition of the base is continued, the conductance of the solution will again increase, because the number of ions in the solution will be increased and because of the higher mobility of the hydroxyl ions. The neutralization of a strong base by addition of a strong acid leads in the same way to a minimum conductance at the end point.

When the acid or base is weak, the salt that is formed represses the ionization still further. Under these conditions the curve may be quite different from that given by a strong acid with a strong base.[3]

The conductometric test for an end point is not limited to neutralization reactions; it can be used with reactions involving the precipitation of an insoluble compound or the formation of complex ions and double salts. In any application, best results are obtained when the volume of the solution is not greatly increased during the titration, and, accordingly, the reagent added should be concentrated.

Apparatus. Wheatstone bridge and accessories, as in Exp. 29; conductance cell suitable for titration; 0.5 *M* solutions of hydrochloric acid, sodium hydroxide, acetic acid, ammonium hydroxide.

Procedure. A known volume (about 10 ml) of 0.5 *M* hydrochloric acid is placed in the conductance cell and diluted to a volume of 100 ml. The cell resistance is then measured in the usual manner. Standard 0.5 *M* sodium hydroxide is titrated into the cell by means of a burette. After the addition of each small increment of base, the solution is well mixed and the cell resistance is measured. It will be found that the resistance will first increase, and then, after a certain point, it will decrease. If a plot is made of the reciprocal of the cell resistance against the volume of base added, the end point of the neutralization reaction will be indicated by a sharp minimum in the curve. If both the acid and base are strong, the titration may be carried out equally well by adding the acid to the base.

When it is desired to make a conductometric determination of the amount of a weak acid, such as acetic acid, the strong base must be added to the acid solution. Since the weak acid is but slightly ionized, the initial conductance of the solution is low. As strong base is titrated into the system, the acid of low conductance is converted into completely ionized salt, and the conductance increases gradually and almost linearly. After the acid is completely neutralized, the addition of excess base gives rise to a still sharper, nearly linear increase in conductance. The equivalence point again is determined by the intersection of the two straight lines, but in this case both lines have positive slopes when conductance is plotted against the volume of base added.

A 10-ml sample of 0.5 M acetic acid is measured into the conductance cell, diluted to 100 ml, and titrated with 0.5 *M* sodium hydroxide solution.

It is also possible to follow conductometrically the neutralization of a weak acid by a weak base. Another 10-ml sample of 0.5 *M* acetic acid is measured out, diluted, and titrated with 0.5 *M* ammonium hydroxide solution.

Calculations. The results of the experiment are most readily presented in the form of curves in which the number of milliliters of titrant is plotted as abscissa against the reciprocal of the measured cell resistance as ordinate. The equivalence point for the titration is found in each case at the intersection of two straight lines. This method assumes that the volume change which takes place in the course of a titration can be neglected. If desired, a correction may be made for the volume change by multiplying each observed conductance (reciprocal resistance) by the term $(V + v)/V$, where V is the initial volume of the solution and v is the volume of reagent added up to that point.

In the case of the titration of acetic acid with ammonium hydroxide, an explanation of the shape of the curve obtained is to be given in terms of the ionic equilibria involved.

Practical Applications.[4] Conductometric titration has been applied successfully to a number of problems in chemical research. It was used by Tosterud[7] to study the formation of compounds between the alkali fluorides and aluminum fluoride similar to the well-known salt $3NaF \cdot AlF_3$. The formation of complex ions in solution has been studied in a number of cases by use of the method of this experiment.

The method is particularly useful in determining the end point of a reaction in colored or turbid solutions. This application is illustrated by the work of Harned[2] on the quantitative determination of copper and nickel sulfates in solution.

The conductometric method may be applied to the determination of the end points of other analytical precipitations. It is particularly suited to determinations in which the precipitate formed is soluble to an appreciable extent in the solution, a circumstance which would cause a low result in a gravimetric analysis but which is often without influence upon the end point as determined conductometrically. The concentration of Ba^{++} ions or Pb^{++} ions in solution may be determined by titration with solutions containing a known concentration of $Cr_2O_7^{--}$ or SO_4^{--} ions; the determination of magnesium sulfate by titration with sodium hydroxide may also be carried out conductometrically.

Suggestions for Further Work. The titrations discussed under Practical Applications provide a number of possibilities for further work. The concentration of sodium acetate in a solution may be determined by titration with a strong acid such as hydrochloric acid.

References

1. Furman *in* Taylor: "Treatise on Physical Chemistry," 2d ed., pp. 936-943, D. Van Nostrand Company, Inc., New York (1931).
2. Harned, *J. Am. Chem. Soc.*, **39**, 252 (1917).

3. Kolthoff, *Ind. Eng. Chem., Anal. Ed.*, **2**, 225 (1930).
4. Kolthoff and Laitenen, "pH and Electrotitrations," John Wiley & Sons, Inc., New York (1941).
5. Robinson and Stokes, "Electrolyte Solutions," Academic Press, Inc., New York (1955).
6. Shedlovsky *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Chap. 25, Interscience Publishers, Inc., New York (1949).
7. Tosterud, *Ind. Eng. Chem., Anal. Ed.*, **48**, 1 (1926).

CHAPTER 10

ELECTRODE PHENOMENA

31. TRANSFERENCE NUMBER OF THE HYDROGEN ION BY THE MOVING BOUNDARY METHOD

The moving-boundary method offers the most accurate method for the determination of transference numbers of both cations and anions, and such a determination, together with a measurement of specific conductivity, may be used to calculate ionic mobilities.

Theory. In the moving-boundary method, an initially sharp boundary between two electrolyte solutions having either the same anion or the same cation is subjected to an electric field. If the two solutions have different cations, a boundary will move toward the cathode with the velocity of the cation in the solution into which the boundary moves. In order to obtain a sharp moving boundary, it is important that the boundary be made to move into the solution containing the cation with the higher mobility. The latter solution is called the "leading" solution, and the other solution, the "indicator" solution.

In this experiment an electrolysis is used to form the indicator solution. The anode in the moving-boundary apparatus is made of metallic cadmium, so that $CdCl_2$ is formed by the passage of current. A boundary between the solutions of cadmium chloride and hydrochloric acid will leave the face of the electrode and move up the tube as illustrated in Fig. 32. Since the cadmium ion has a much lower mobility than the hydrogen ion, this moving boundary is very sharp. As the boundary moves upward, the common-ion constituent, which is the chloride ion in this example, moves downward across the boundary and eventually accumulates around the anode. Electrical neutrality is preserved in the solution near the electrode owing to the fact that only a fraction of the cadmium ions which are formed by the electrolysis of the anode is necessary for the maintenance of the growing column of indicator solution. This concentrated solution of cadmium chloride which accumulates at the anode may be seen at the conclusion of the experiment by tipping the tube so that the heavy solution falls down the tube.

When 1 faraday F of electricity passes through a tube containing such a boundary, there will be a movement of 1 equiv of electrolyte through a hypothetical plane in the solution. Since the transference number n_c of the cation is the fraction of the current carried by the cation, n_c equivalents of the cation will move toward the cathode. The transference number is equal to the product of the volume ΔV in liters moved through by the boundary per faraday and the concentration c of the cation in equivalents per liter.

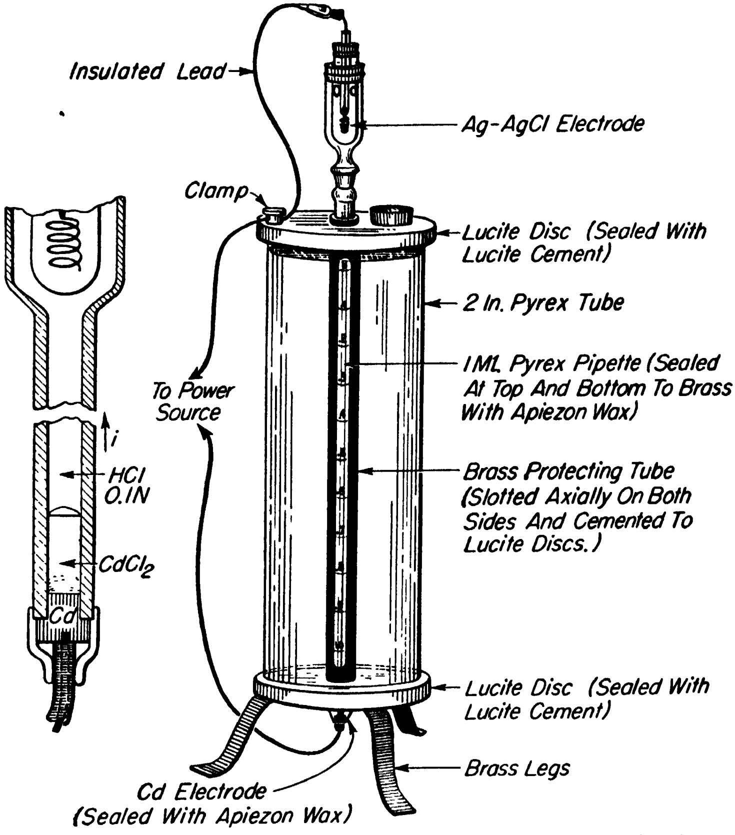

FIG. 32. Apparatus for the moving-boundary method for the determination of transference numbers.

$$n_c = c\Delta V \tag{1}$$

If the boundary sweeps through volume Δv milliliters during the passage of i amperes for Δt seconds, the volume ΔV in liters per faraday is readily calculated from

$$\Delta V = \frac{\Delta v \mathrm{F}}{1{,}000 i \Delta t} \tag{2}$$

Combining Eqs. (1) and (2),

$$n_c = \frac{\mathbf{F}c\Delta v}{1{,}000i\Delta t} \tag{3}$$

One faraday **F** is equivalent to 96,500 coulombs (or amp-sec). The same equation may be used to calculate anion transference numbers if the salts forming the boundary have the same cation but different anions.

Very accurate values of transference numbers and ionic mobilities may be determined by the moving-boundary method because the boundary remains sharp and does not diffuse. To explain this, we must consider the electric field strength (or potential gradient) in the graduated tube. The force causing the ions to move is proportional to the electric field strength E' in practical volts per centimeter, which is

$$E' = \frac{i}{AL} \tag{4}$$

where A = cross-sectional area of tube, cm^2

L = specific conductivity of solution, ohm^{-1} cm^{-1}

The average velocity $\Delta x/\Delta t$ of an ion in the direction of the field is directly proportional to the electric field strength:

$$\frac{\Delta x}{\Delta t} = uE' \tag{5}$$

Substituting Eq. (4) into Eq. (5),

$$u = \frac{A\Delta xL}{i\Delta t} = \frac{\Delta vL}{i\Delta t} \qquad \text{cm}^2\ \text{sec}^{-1}\ \text{volt}^{-1} \tag{6}$$

where Δv is the volume in cm^3. The ionic mobility u is equal to the velocity of the ion in a unit electric field (1 volt cm^{-1}), as may be seen from Eq. (5).

In our experiment, the $CdCl_2$ solution below the boundary has a specific conductivity L which is lower than that of the hydrochloric acid solution because it is more dilute and the Cd^{++} ion has a lower mobility than the H^+ ion. By reference to Eq. (4) it is seen that the electric field strength is greater in the $CdCl_2$ solution below the moving boundary than in the HCl solution above the boundary. Therefore, if H^+ ions diffuse into the $CdCl_2$ solution below the boundary, they will encounter a high field strength and will be rapidly sent up to the boundary. On the other hand, if Cd^{++} ions diffuse ahead of the boundary, they will have a lower velocity than the hydrogen ions because of their lower mobility and will soon be overtaken by the boundary. This so-called "adjusting effect" keeps the boundary sharp.

The ionic mobility of the leading ion in the boundary may be calculated from the boundary velocity $\Delta x/\Delta t$ using Eqs. (4) and (5). The ionic mobility of the following ion could be calculated if the specific conductance of the following solution were known. By use of the preceding equations, it may be shown that the transference number and mobility of the cation are related by

$$n_c = \frac{96{,}500 u_c c}{1{,}000 L} \tag{7}$$

where c is the concentration of HCl in equiv liter^{-1}.

Apparatus. Glass assembly shown in Fig. 32 fitted with cadmium and silver silver chloride electrodes; d-c power supply; 0.1 N HCl solution; methyl violet indicator.

Procedure. The adaptation of this method for use as a laboratory experiment is described by Longsworth.[4] The glass capillary tube is made of a 1-ml Pyrex pipette graduated every 0.1 ml and having an inside diameter of about 2 mm. The capillary is rinsed several times with 0.1 N hydrochloric acid containing methyl violet indicator. Only enough methyl violet to give a distinguishable color in the capillary tube is required. The indicator should be added to the acid just before the start of the experiment, because the color will fade. The rinsing of the capillary may be aided by the use of a wood or glass rod which just fits in the capillary and is used as a plunger. It is important to dislodge any bubbles at the lower end of the tube. Next the electrode chamber is filled with hydrochloric acid, and the silver–silver chloride electrode is inserted.

It is necessary to immerse the tube in which the boundary moves in a water bath, in order to dissipate the heat which is developed in the tube by the passage of the electric current.

The electrodes are connected to a source of direct current capable of delivering 2 to 4 milliamp. It is most convenient if the current through the capillary is kept constant during the experiment. If the applied voltage is constant, the current through the capillary will decrease during the experiment, because as the boundary ascends the tube, the length of the column of indicator electrolyte increases correspondingly, and this solution is a poorer conductor than the one it replaces. The potential applied to the cell must therefore be continually increased in order to maintain a constant current. This may be done by one of two methods: (*a*) part of the current supply may be shunted across a rheostat which has a sliding contact, and by manual adjustment of this contact a constant current through the cell may be maintained; (*b*) a power supply designed to produce a constant current with minimum adjustment, such as that of Bender and Lewis,[1] may be used. This method has the advantage that attention may be focused on the determination of the boundary velocity. The current may be measured using a low-range milliammeter, or if greater accuracy is required, by measuring the potential drop across an accurately known series resistance with a potentiometer.

The time, to the nearest second, at which the boundary crosses successive graduations is obtained with the aid of a stop watch.

A second experiment is performed at a different current.

Calculations. Values of the transference number of the hydrogen ion are calculated by the use of Eq. (3) and a plot of Δv versus t. In the regions of the tube near the cadmium electrode, the movement of the hydrogen ion may be retarded because of the diffusion of the $CdCl_2$ solution.

The specific conductance of 0.1 N hydrochloric acid is 0.03913 ohm^{-1} cm^{-1} at 25°. The specific conductance of a solution *slightly* different from 0.1 N may be calculated assuming that the specific conductance is directly proportional to concentration. The hydrogen-ion mobility is calculated from the experimental data by using Eq. (6). The chloride ion transference number and mobility are calculated by using the relation $n_{H^+} + n_{Cl^-} = 1$.

Practical Applications. The moving-boundary method for the determination of ionic mobilities has been particularly useful in the study of proteins. Electromigration methods have been used for the separation of isotopes.[2]

Suggestions for Further Work. If the current is regulated very closely and the moving-boundary tube is calibrated, the variation of the transference number and mobility of hydrogen ion may be determined, using 0.01 and 0.05 N hydrochloric acid. The apparatus may also be used to determine the transference number of cations which yield colored solutions.

The transference number of potassium ion in 0.1 N potassium chloride may be determined with the same apparatus. In this case, the boundary is visible only because of the difference in the refractive indices of the two solutions. Longsworth[4] has described a simple optical arrangement for the location of the boundary.

References

1. Bender and Lewis, *J. Chem. Educ.*, **24**, 454 (1947).
2. Brewer, Madorsky, Taylor, Dibeler, Bradt, Parham, Britten, and Reid, *J. Research Natl. Bur. Standards*, **38**, 137 (1947).
3. Daniels and Alberty, "Physical Chemistry," John Wiley & Sons, Inc., New York (1955).
4. Longsworth, *J. Chem. Educ.*, **11**, 420 (1934).
5. MacInnes, "Principles of Electrochemistry," Reinhold Publishing Corporation, New York (1939).
6. Robinson and Stokes, "Electrolyte Solutions," Academic Press, Inc., New York (1955).

32. TRANSFERENCE NUMBER OF THE SILVER ION BY THE HITTORF METHOD

The transference number of the silver ion may be determined by chemical analysis of solutions before and after electrolysis. High accuracy is required in the analytical procedure.

Theory. When an electrical current is passed through an electrolyte solution, the current is carried by ions, and an oxidation reaction occurs at the anode while reduction occurs at the cathode. If the electrolysis of silver nitrate solution is carried out by using silver electrodes, the number of equivalents of silver ion formed at the anode (+) is equal to the number of gram atoms of metallic silver formed at the cathode (−).

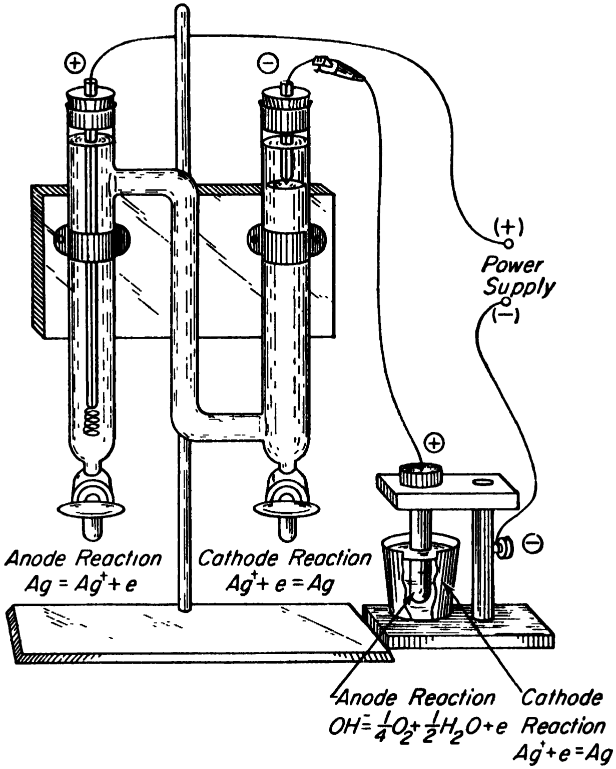

FIG. 33. Hittorf apparatus for the determination of transference numbers.

However, the concentration of silver ions in the regions surrounding the two electrodes depends not only upon the duration of electrolysis and upon the current used, but also upon the mobilities of the silver and nitrate ions. Hittorf (1853) was the first to make use of this fact to determine transference numbers.

The construction of the electrolysis cell used in this experiment is illustrated in Fig. 33. At the anode an equivalent of silver ion goes into solution per faraday of current passed and less than one equivalent of silver ions is transported out of the arm by ion migration. Therefore, the solution around the anode becomes more dense during electrolysis, and so the anode is placed at the bottom of the chamber and the connecting arm is placed at the top. On the other hand, silver is plated out on the cathode faster than it migrates into the cathode chamber so that the solution in the surrounding region becomes lighter than the initial solution and tends to rise to the top. Therefore, the cathode is placed at the top of its chamber and the connecting arm is placed at the bottom. When the apparatus is constructed in this way, the concentration changes are restricted to as small as possible volumes in the anode and cathode chambers, and the concentration of the solution in the connecting arm is unchanged if the duration of the electrolysis is not too long.

The transference number of an ion may be defined as the fraction of the total current through the solution carried by that ion. If x faradays of charge are passed between the electrodes, then x equivalents of silver ion would disappear from the cathode chamber if there were no migration of silver ion. However, if only y equivalents of silver disappear from the cathode chamber, y being less than x because of migration of silver ions toward the negative electrode, $x - y$ is the number of equivalents of silver ion which have migrated into the cathode chamber during the passage of x faradays of charge. Thus, the fraction of the current carried by silver ions is

$$n_c = \frac{x - y}{x} \tag{1}$$

The transference number of the silver ion, n_c, may also be calculated from the change in concentration in the anode chamber. Here x equivalents of silver ion are formed by the electrode reaction, but the increase in the number of equivalents of silver ion in this compartment is only z because of the migration of silver ions away from the positive electrode. The number of equivalents of silver ion which have migrated out of the anode chamber is $x - z$, so that the fraction of the current carried by the silver ions is

$$n_c = \frac{x - z}{x} \tag{2}$$

If analyses were simultaneously carried out for nitrate ion, it would be found that the nitrate concentration would have increased in the anode chamber and decreased in the cathode chamber. The transference number of the anion may also be calculated from

$$n_c + n_a = 1 \tag{3}$$

since the sum of the transference numbers of anion and cation must be unity.

In order to calculate the ionic mobilities, it is also necessary to have information concerning the specific conductance of the solution as discussed in Exp. 31.

Apparatus. Transference-number cell with silver electrodes; source of 90 to 110 volts direct current; milliammeter; 0.05 molal silver nitrate; 0.02 *N* potassium thiocyanate; silver coulometer; ferric sulfate.

Procedure. The transference number of silver ion in 0.05 molal silver nitrate solution is to be determined in this experiment, and the transference number of the nitrate ion calculated, using Eq. (3). The apparatus which is illustrated in Fig. 33 is filled with a 0.05 molal solution of silver nitrate, and the silver electrodes are put in place.

The silver coulometer is filled with a solution containing 15 per cent by weight of silver nitrate in water. The silver anode is wrapped in filter paper to prevent particles from falling from the anode onto the cathode. The platinum crucible is cleaned with dilute nitric acid, rinsed thoroughly, heated at 110°, cooled in a desiccator, and weighed. The silver crystals deposited on the cathode will not adhere unless the surface is clean.

The electrical connections are made as illustrated in the figure and a current of 0.01 amp is passed through the solution for a period of time of 120 min or more, accurately measured by means of an electric clock. Currents of greater magnitude should not be used on account of the heating effect of the current which causes convection currents. It is convenient to use a current-regulated power supply since then the total quantity of electricity involved is accurately given by the product of current and time.

While the electrolysis is in progress, 10 ml aliquots of the 0.05 molal silver nitrate solution are titrated, using a standard solution of KCNS (about 0.02 *N*). This solution may be standardized against a weighed quantity of $AgNO_3$. A few milliliters of ferric sulfate solution made slightly acid with nitric acid is used as an indicator.

After the current has been turned off, slightly more than 50 ml of solution is withdrawn from the anode chamber by means of the stopcock, and exactly 50 ml is measured with a pipette and titrated. Then about 10 ml more is run into the beaker, which still contains a few milliliters remaining from the first sample, and 10 ml is withdrawn and titrated. This procedure is repeated until titration of two successive 10-ml aliquots yields a titer that agrees within experimental error with the initial value. Since the concentration changes in the electrode compartments are small, it is necessary that these analyses be performed with the utmost care.

Solutions from the cathode chamber are titrated as follows. The 50-ml pipette is inserted under the surface of the solution just far enough to remove 50 ml of solution. This is then emptied into a beaker and titrated. A 10-ml pipette is then inserted into the cathode solution just far enough to remove 10 ml of solution. The pipette is drained, and the solution titrated. This procedure is repeated until the titer of two of these 10-ml aliquots agrees within the experimental error with that of the initial solution. If the titrations cannot be completed in one laboratory period, the solutions should be withdrawn from the Hittorf apparatus as described and placed in separate flasks for titration during the next period.

The silver nitrate solution from the coulometer is then poured into the silver residue bottle, and the crucible is washed carefully with distilled water. Then it is heated in an oven at 110°, cooled in a desiccator, and weighed.

If possible, the electrolysis experiment should be repeated.

Calculations. The transference number of the silver ion is calculated from the analyses of the solutions in both the anode and cathode compartments. The quantity of electricity in faradays (x) is obtained from the weight of silver deposited in the coulometer and from the product of current and time. One faraday (96,500 coulombs) corresponds to 107.88 g of silver.

The decrease (y) in the number of equivalents of silver ion in the cathode compartment is calculated. The total number of equivalents of silver in the aliquots titrated is computed, and subtracted from the number of equivalents of silver ion in the same volume of the initial solution. This calculation involves an approximation since it is assumed that equal volumes of the various solutions contain equal weights of water. The transference number of silver ion is computed by use of Eq. (1).

The increase (z) in the number of equivalents of silver ion in the anode compartment is calculated. The total number of equivalents of silver in the aliquots titrated is computed. and from this number is subtracted the number of equivalents of silver ion in the same volume of the initial solution. The transference number of silver ion is calculated by use of Eq. (2).

The nitrate ion transference number is calculated by using Eq. (3).

Practical Applications. Transference numbers have an important application to the so-called "electromotive-force cells with transference." In this type of cell, there is a potential difference, which cannot be directly measured, established at the surface of contact of the two solutions of different concentration. This potential difference is due to a migration of the ions from the concentrated to the dilute solution, and it becomes zero only when the anion and cation have the same velocity. It is, however, possible to approximate the magnitude of this potential by certain formulas which have been proposed and which always involve a knowledge of the magnitude of the transference numbers. For further details, Reference 6 may be consulted.

A less general application is the use of transference data to obtain information concerning the composition of complex ions. For example, if a solution of $KAg(CN)_2$ is electrolyzed, it is found that the concentration of the silver actually increases in the anode compartment, showing that the silver is contained in a complex negative ion.

Suggestions for Further Work. The transference number of cupric ion may be determined by the Hittorf method, using the same apparatus, by substituting copper electrodes and filling the apparatus with 0.05 *M* cupric sulfate solution. After the experiment, the anode and cathode solutions are analyzed for copper. One convenient method is to add ammonium hydroxide drop by drop until the precipitate just clears and then add 5 ml of glacial acetic acid and 3 g potassium iodide. The iodine liberated is titrated with thiosulfate, using soluble starch as an indicator. Each mole of iodine (I_2) formed corresponds to 2 moles of copper.

In certain cases transference numbers may be determined by electromotive-force measurements. Mason and Mellon[5] have shown this method may be used as a convenient laboratory experiment to determine the cation transference number in HCl solutions. The cells used are

I. H_2 (1 atm)|HCl(a_1)|HCl(a_2)|H_2 (1 atm)
II. H_2 (1 atm)|HCl(a_1), AgCl|Ag + Ag|AgCl, HCl(a_2)|H_2 (1 atm)

Cell I involves transference whereas cell II does not. The electromotive forces of these cells are

$$\text{I.}\quad E_t = 2n_c \frac{RT}{\mathbf{F}} \ln \frac{a_2}{a_1}$$

$$\text{II.}\quad E = 2\frac{RT}{\mathbf{F}} \ln \frac{a_2}{a_1}$$

The transference number of the cation is obtained by division.

$$n_c = \frac{E_t}{E}$$

References

1. Glasstone, "An Introduction to Electrochemistry," D. Van Nostrand Company, Inc., New York (1942).
2. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2d ed , Reinhold Publishing Corporation, New York (1950).
3. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York (1939).
4. MacInnes and Longsworth, *Chem. Revs.*, **11**, 171 (1932), and preceding papers.
5. Mason and Mellon, *J. Chem. Educ.*, **16**, 512 (1939).
6. Pearce and Mortimer, *J. Am. Chem. Soc.*, **40**, 509 (1918).
7. Robinson and Stokes, "Electrolyte Solutions," Academic Press, Inc., New York (1955).

33. THE DROPPING-MERCURY ELECTRODE

This experiment illustrates the use of the current-voltage curves obtained with the dropping-mercury electrode in the qualitative and quantitative analysis of reducible and oxidizable solutes.

Theory.[2,3] In electrolysis a potential difference is impressed between two electrodes immersed in a solution. The decomposition potential is defined as the potential difference required to cause continuous electrolysis to take place. This potential depends not only on the standard electrode potentials involved, but also on the composition of the solution and on surface effects. In ordinary electrolysis the current which flows increases continuously as the voltage is increased beyond the decomposition potential, but if one electrode is a microelectrode, i.e., of very small dimensions, such as the dropping-mercury electrode, current-voltage curves can be obtained whose unusual characteristics lead to important practical applications.

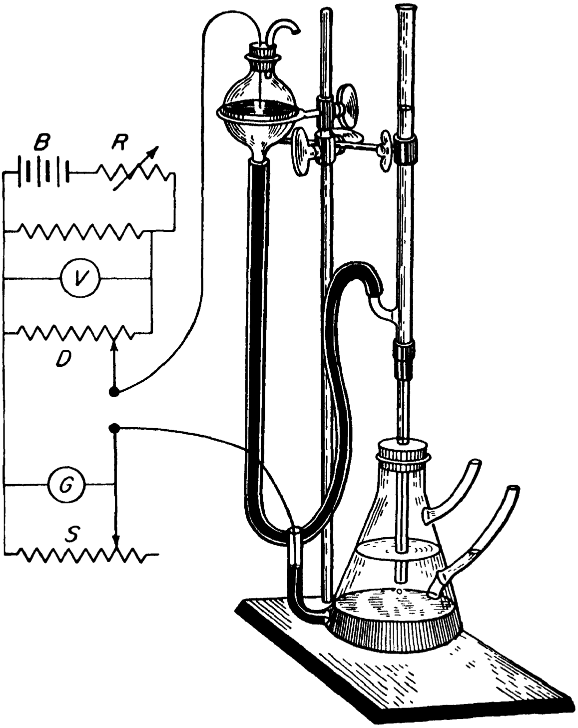

FIG. 34. Schematic diagram of a polarograph.

In the dropping-mercury electrode, mercury flows through a section of fine-bore capillary tubing in a succession of small drops which grow to a maximum diameter of about 0.5 mm before breaking away. The experimental arrangement used in the determination of current-voltage curves with the dropping-mercury electrode is shown in Fig. 34. Variation of the resistance *R* in series with the battery *B* permits adjustment of the potential drop, measured by the voltmeter *V*, across the precision voltage divider *D*. Any desired fraction of this potential drop can then be applied across the electrolysis cell by adjustment of the setting of *D*. The resulting current is measured by the galvanometer *G*; the shunt *S* is used to bypass current around the galvanometer when reduced current sensitivity is required. For a given applied voltage, the current increases to a maximum value as the drop grows in size. The average current during the life of the drop is the important quantity measured; a long-period galvanometer is used to facilitate the determination of this average current.

Following the terminology introduced by Heyrovsky, the pioneer in this field, the current-voltage curve obtained with the dropping-mercury electrode is commonly called a *polarogram*, and the instrument used in its determination a *polarograph*. The latter term applies in particular to the automatic instruments in which the applied potential is gradually changed by use of a motor-driven potential divider, and the corresponding galvanometer deflections recorded on photographic paper mounted on a drum whose rotation is coupled mechanically to that of the potential divider. Alternatively, the galvanometer is replaced by a strip-chart recorder. The various commercial instruments and their characteristics are described in several places.[2,3]

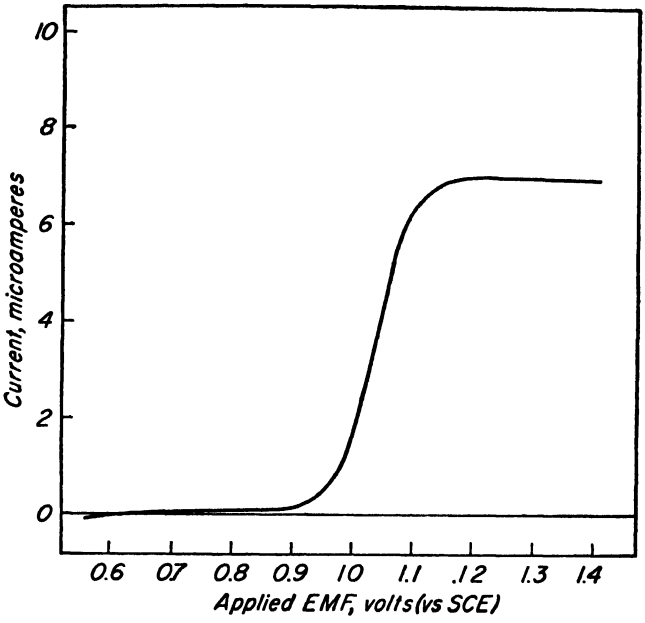

FIG. 35. Current-voltage curve for reduction at the dropping-mercury cathode.

A typical average current-voltage curve obtained with a solution 0.001 *M* in $ZnSO_4$ and 0.1 *N* in KCl is shown in Fig. 35. For low applied voltages there results only a very small current called the *residual current*. This current includes contributions from the *condenser current*, the current required to charge the individual drop to the applied potential, and the *electrolysis*, or *faradaic*, *current* resulting from the reduction of impurities such as traces of dissolved oxygen, mercury ions, etc. It should be noted that the applied voltage is the potential relative to the anode. A mercury pool electrode in a 0.1 N KCl solution assumes a potential essentially equal to that of the decinormal calomel electrode. As may be seen from a table of standard electrode potentials, an electrode potential of -1.0 volt relative to the decinormal calomel electrode corresponds at 25°C to -0.665 volt relative to the standard hydrogen electrode, or -0.910 volt versus the saturated calomel electrode (s.c.e). The latter is commonly used in accurate work as the reference electrode in reporting the potential of the dropping-mercury electrode.

After the decomposition potential is passed, the current first increases rapidly with increasing voltage, then levels off at an essentially constant value because a state of extreme concentration polarization is reached at the dropping-mercury electrode. The two processes which can bring zinc ions to the electrode are transference and diffusion. The large excess of the supporting electrolyte, potassium chloride, reduces the transference number of the zinc ion to such a low value that transport of zinc ion by transference is made negligible. The zinc ions thus move to the electrode by diffusion, for which the number arriving per unit time is determined by the concentration gradient from the body of the solution to the mercury-drop surface. As the applied electromotive force is increased the electrolysis current increases, and correspondingly the concentration of the reducible ion at the electrode surface is decreased below the value for the body of the solution. The concentration difference so produced increases with increased applied voltage until the concentration of reducible ions at the electrode surface becomes negligible. The cathode is then said to be "concentration-polarized." At this point the average rate of diffusion of reducible ions to the electrode becomes constant, because the driving force for diffusion, the concentration difference between the body of the solution and at the electrode surface, has become constant. The average electrolysis current, therefore, remains constant as the applied voltage is further increased, except for a slight increase due to a change in the residual current, until the voltage becomes large enough to produce another chemical reaction at the cathode.

The diffusion-limited contribution to the electrolysis current is called the *diffusion current* for the ion. It may best be determined by subtracting from the total current at a voltage on the flat part of the curve the corresponding residual current evaluated in a second run on a solution identical with the first except for the omission of the reducible ion in question. Alternatively, the residual-current contribution may be found by extrapolation to the appropriate voltage of the residual-current line determined at lower applied voltages.

A theoretical equation describing the average diffusion current was first derived by Ilkovic:[2,3]

$$i_D = 607nD^{1/2}m^{2/3}t^{1/6}C$$

where i_D = average diffusion current, μamp
n = number of electrons transferred in the electrode reaction (e.g., 1 for reduction of Ag^+, 2 for Zn^{++}, etc.)
D = diffusion coefficient of reducible species, $cm^2\ sec^{-1}$
m = rate of flow of mercury, mg sec^{-1}
t = drop time, sec
C = concentration of reactant, millimoles $liter^{-1}$

Simplifying assumptions made in the derivation of this equation prevent it from being exact, but do not in general affect its usefulness in practical work. The Ilkovic equation is valuable because it permits a quantitative prediction of the influence of the several factors involved. It is important to note that the proportionality between i_D and C is a direct consequence of the concentration polarization of the dropping electrode.

The *half-wave potential*, $E_{1/2}$, for the current-voltage "wave" for a particular constituent is the value of the applied voltage for which the current (corrected for the residual-current contribution) is equal to one-half the limiting diffusion current. When the electrode reaction is reversible, a study of the effect on the half-wave potential of variation in the composition of the solution has been made to yield information of thermodynamic interest on complex ions, etc.,[2,3] through consideration of the system as a special type of electromotive-force cell. For simple ions, such as Tl^+, Zn^{++}, etc., which are reduced rapidly and reversibly at the dropping-mercury electrode with the formation of an *amalgam* at the drop surface, the half-wave potential is constant and independent of the concentration of the reducible ion when the temperature and supporting electrolyte concentration are constant. In principle the half-wave potential in such cases thus provides a means of identifying the material responsible for a wave, but in practice this is of little value unless auxiliary information is available to limit the possibilities.

Since oxygen is readily reduced at the dropping-mercury electrode and thus interferes with the current-voltage curves of other substances, it must ordinarily be removed from the solution to be electrolyzed. This may be accomplished by bubbling an inert gas such as nitrogen through the solution before (but not during) the electrolysis. Oxygen interference may also be eliminated by addition of sodium sulfite to neutral or alkaline solutions, to the extent of about 1 g per 100 ml of solution.

Another complication encountered is the appearance of a maximum in the current-voltage wave. The maximum is caused by a streaming of the solution past the drop surface; this stirring effect destroys the concentration polarization of the electrode, and consequently the current can increase beyond the diffusion-limited value. These maxima may usually be eliminated by the addition to the solution of small amounts of adsorbable materials such as gelatin, dyes, etc., which are not reduced at the given potential. Such maximum suppressors may produce undesirable effects as well, however, so that their characteristics should be carefully checked in each pertinent case.

In analytical work the optimum concentration range extends from about 10^{-2} to 10^{-5} molar. The dropping-mercury electrode may be used at potentials from approximately $+0.2$ to -2.0 volts versus the saturated calomel electrode. On the positive side the limit is set by the anodic dissolution of mercury; the extended negative range is made possible by the high overvoltage of hydrogen on mercury. An additional advantage results from the amalgamation of most metals by mercury, which permits their reduction at the dropping-mercury electrode at less negative potentials than otherwise would be required.

Initial work in polarography was centered on the obvious analytical applications. The continuing development of the field, however, has included significant contributions to problems of physical-chemical interest, and it forms an important aspect of modern electrochemistry. An excellent introduction to the theory and practice of polarography has been given by Meites,[3] while the monograph of Kolthoff and Lingane[2] provides a comprehensive survey of the field. Applications to organic chemistry in particular are treated by Müller,[4] and Delahay[1] has given a comprehensive treatment of the newer instrumental methods in electrochemistry.

Apparatus. Dropping-mercury electrode and circuit elements; gelatin or Triton X-100 solution; KCl; $ZnCl_2$; $CdCl_2$; $MnCl_2$; nitrogen tank or sodium sulfite; unknown.

Procedure. Directions will be provided by the instructor for the operation of the polarograph to be used. The recommended cell assembly is shown in Fig. 34. The capillary tip is about 5 or 10 cm long. The appropriate tubing is available from supply houses, or an adequate substitute may be obtained by drawing out a section of ordinary capillary tubing and cutting it off in the constricted section. The mercury used must be of high purity (Chap. 26), and a connecting tube of polyethylene is recommended. If rubber tubing is substituted, pure gum tubing should be used. It should be boiled with concentrated sodium hydroxide solution to remove sulfur compounds and carefully rinsed before use.

The mercury flow should be started, by increasing the height of the mercury column, *before* the electrode is immersed in any solution. It is best to allow the mercury to flow continuously through the whole laboratory period rather than to stop it and clean the tip between determinations. The electrode is then immersed in the first solution to be studied and the mercury height adjusted to give a drop time between 3 and 6 sec. The electrodes are then connected to the polarograph, and a series of current-voltage readings made for the applied potential range 0 to −2 volts. The current will rise sharply in the neighborhood of −2 volts because the decomposition potential for potassium ion has been reached. For each voltage setting the *average* galvanometer deflection is recorded. The galvanometer shunt is adjusted as required to give an accurately measurable deflection for the current involved. The actual electrolysis current is obtained as follows:

$$i = asg^0$$

where i = current, μamp
a = galvanometer deflection, mm
g^0 = basic galvanometer deflection sensitivity, μamp mm^{-1}
s = shunt reduction factor

The value of g^0 is characteristic of the galvanometer used; if it is not specified for the instrument employed, it can be calculated by determining the deflection obtained for a known voltage with a known resistance of about 100,000 ohms substituted for the electrolysis cell.

Solutions of $CdCl_2$, $ZnCl_2$, and $MnCl_2$ are first studied, with potassium chloride as the supporting electrolyte. The solutions are made 0.1 N in KCl, and 0.001 N in the reducible ion. To suppress maxima, 0.1 ml of a 0.2 per cent stock solution of Triton X-100* is added for each 10 ml of solution being analyzed. Gelatin may also be used as a maximum suppressor; it should be used in amounts not exceeding 0.01 per cent by addition of the necessary quantity of a *fresh* 0.5 per cent stock solution prepared from high-quality gelatin.

A sample of the first solution is placed in the working cell containing a large mercury pool electrode, and nitrogen is bubbled through the solution to remove dissolved air. The dropping-mercury electrode is then inserted to complete the cell assembly, and the current-voltage curve determined. The other two solutions are then treated similarly.

Measurements are next made on a series of solutions of $CdCl_2$ to test the relation between the concentration and the diffusion current. Concentrations of 10^{-2}, 5×10^{-3}, 10^{-3}, 5×10^{-4}, and 10^{-4} equiv of $CdCl_2$ per liter are used, with 0.1 N KCl as supporting electrolyte. A maximum suppressor is not required in this case. An appropriate voltage is selected on the basis of the previous work, and the corresponding residual current is determined by a measurement on the supporting electrolyte

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* Manufactured by the Rohm and Haas Co., Philadelphia, Pa.

solution itself. The diffusion current is also determined for an unknown solution of $CdCl_2$ in 0.1 *N* KCl.

Finally, a polarogram is obtained for a solution prepared by mixing equal volumes of the 0.001 *N* $CdCl_2$ and $ZnCl_2$ solutions prepared earlier, to illustrate the successive discharge of two different reducible ions. A maximum suppressor is required here.

The cell is then removed and a beaker placed below the electrode to catch the flowing mercury. The electrode is rinsed with distilled water, then dried carefully with filter paper, care being taken to remove water from the end of the capillary. The mercury flow is permitted to continue for several minutes, and the reservoir is then lowered to stop the flow.

Calculations. The several complete current-voltage curves are plotted; the half-wave potentials are determined for the various ions, and the results compared with accepted values.[2]

A graph of diffusion current versus concentration is prepared for the $CdCl_2$ solutions, and the concentration of $CdCl_2$ in the unknown solution is obtained by its use.

Practical Applications. A knowledge of the decomposition potential is important in the calculation of the energy requirements in an electrolytic process such as electroplating.

The dropping-mercury electrode has been applied in analysis for a large variety of substances, both inorganic and organic. The analyses can be made quickly, and often with very small quantities of material. Each analysis, however, must be regarded as empirical and reliable only when checked against known concentrations of the same material.

The polarographic determination of dissolved oxygen has proved useful in respiration studies and various biological investigations.[5]

Suggestions for Further Work. The reduction of oxygen at the dropping-mercury electrode may be investigated, and the efficiency of the methods previously recommended for the removal of oxygen from the solutions studied may be checked. Oxygen is reduced irreversibly at the dropping-mercury electrode in two steps; the first wave is associated with the reduction of oxygen to hydrogen peroxide, and the second corresponds to the reduction of hydrogen peroxide. The marked maximum otherwise associated with the first wave is readily suppressed in the conventional fashion.

The influence of complex ion formation may be illustrated by comparison of the polarograms obtained for lead ion in 1 *N* NaOH and 0.1 *N* KCl as supporting electrolyte. The following reference oxidation potentials are pertinent: Hg,Hg_2Cl_2; KCl (0.1 *N*), −0.355 volt; Hg,HgO,NaOH (1 *N*), −0.140 volt. The values given are for 25°C and are referred to the standard hydrogen electrode.

Directions for a number of other interesting experiments have been given by Meites.[3]

References

1. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York (1954).

2. Kolthoff and Lingane, "Polarography," 2d ed., Interscience Publishers, Inc., New York (1952).
3. Meites, "Polarographic Techniques," Interscience Publishers, Inc., New York (1955).
4. Müller *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. 1, Part II, Chap. 28, Interscience Publishers, Inc., New York (1949).
5. Petering and Daniels, *J. Am. Chem. Soc.*, **60**, 2796 (1938).

CHAPTER 11

ELECTROMOTIVE FORCE

34. SINGLE-ELECTRODE POTENTIALS

In this experiment measurements are made of the oxidation potentials of several metals. Experience is gained in the use of the potentiometer and the electrochemical conventions.

Theory. Every electrochemical cell consists of two single electrodes or half-cells. One electrode tends to lose electrons in the process of oxidation and is called the anode. The other tends to gain electrons in the process of reduction and is called the cathode. The voltage of the cell is a measure of the difference in the tendencies of the two electrodes to lose electrons, and it is also a measure of the tendency of the corresponding cell reaction to take place. In order to correlate cell voltages with cell reactions as written on paper, it is necessary to follow certain conventions. These conventions must apply to both positive and negative ions and to both oxidation and reduction reactions.

The potential of a single electrode depends on the ease with which electrons are lost and on the effective concentration of the ions surrounding the electrode. The absolute values of the electrode potentials are not known with certainty, and so the hydrogen electrode (page 174) at one atmosphere pressure of gas and unit activity of hydrogen ions is taken as the reference electrode with an assigned standard electrode potential of zero.

A standard metal metal ion electrode and a standard hydrogen electrode form a cell which is written as follows:

$$M;\ M^+\ (a = 1)\|\mathrm{H}^+\ (a = 1);\ \mathrm{H}_2\ (1\ \mathrm{atm}),\ \mathrm{Pt} \qquad (1)$$

where the vertical parallel bars indicate that the junction potential, between the two different electrolytic solutions, is practically eliminated by connection through a salt bridge of potassium chloride or some other salt in which the two ions have substantially the same transference numbers. When the concentration of the ions is such that their activity is unity, as indicated in cell (1) by $a = 1$, the electrode potential is designated as E^0 and is equal to the standard oxidation potential.

The voltage of a cell is the algebraic sum of the oxidation potential for the electrode written at the left and the reduction potential of the electrode written at the right. By convention the chemical reaction corresponding to a given cell is written so that electrons move from left to right outside the cell.[3]

The electrode potential changes with the activity of the ions. The fundamental equation governing the effect of activity of ions on the voltage is

$$E = E^0 - \frac{RT}{n\mathbf{F}} \ln Q \tag{2}$$

where R = gas constant, 8.314 joules deg^{-1} mole^{-1}
$\mathbf{F}$ = faraday, 96,500 coulombs equiv^{-1}
n = number of faradays for the reaction as written
Q = activity quotient

$$Q = \frac{a_G^g a_H^h}{a_A^a a_B^b} \tag{3}$$

for the generalized reaction $aA + bB = gG + hH$.

The type of cell used in the laboratory may be written as follows for a monovalent metal ion:

$$\text{M; M}^+(a)\|\text{KCl (sat); Hg}_2\text{Cl}_2\text{, Hg} \tag{4}$$

The electromotive force of this cell is given by

$$E = E^0_{\text{M;M}^+} - \frac{RT}{\mathbf{F}} \ln a_{\text{M}^+} + E_{\text{KCl(sat);Hg}_2\text{Cl}_2\text{,Hg}} + E_j \tag{5}$$

where $E^0_{\text{M;M}^+}$ is the oxidation potential for the metal electrode, $E_{\text{KCl(sat);Hg}_2\text{Cl}_2\text{,Hg}}$ is the reduction potential (i.e., the oxidation potential with its sign reversed) of the saturated calomel electrode, and E_j is the liquid junction potential which is made very small by the use of the KCl bridge.

For the cells involving divalent metal ions

$$\text{M; M}^{++}(a)\|\text{KCl (sat); Hg}_2\text{Cl}_2\text{, Hg} \tag{6}$$

the electromotive force is given by

$$E = E^0_{\text{M;M}^{++}} - \frac{RT}{2\mathbf{F}} \ln a_{\text{M}^{++}} + E_{\text{KCl(sat);Hg}_2\text{Cl}_2\text{,Hg}} + E_j \tag{7}$$

Equations (5) and (7) are to be used for calculating E^0 for the metal electrodes. For this purpose it is necessary to know the activities a_{M^+} and $a_{\text{M}^{++}}$ or the activity coefficients γ_{M^+} and $\gamma_{\text{M}^{++}}$ in the expressions $a_{\text{M}^+} = \gamma_{\text{M}^+}m$ and $a_{\text{M}^{++}} = \gamma_{\text{M}^{++}}m$. However, it is not possible to determine single-ion activity coefficients by rigorous thermodynamic methods, and so it is necessary to use the mean ionic activity coefficients given later in Table 1. In the limit of infinite dilution these two types of activity coefficients become equal to unity because of the definitions of the standard states.

The activity coefficients γ_A and γ_B of the cation A and anion B in electrolyte solutions are given by

$$\gamma_A = \frac{a_A}{m_A} \qquad \gamma_B = \frac{a_B}{m_B} \tag{8}$$

where a = activity
m = molality

The mean ionic activity coefficient $\gamma_\pm$ is defined by

$$\gamma_\pm = \frac{a_\pm}{m_\pm} \tag{9}$$

For the electrolyte $A_{\nu_+}B_{\nu}$ which dissociates into ν_+ positive ions and ν_- negative ions, the mean ionic activity $a_\pm$ is defined by

$$a_\pm = (a_A^{\nu_+} a_B^{\nu})^{1/\nu} \tag{10}$$

where $\nu = \nu_+ + \nu_-$, and the mean ionic molality $m_\pm$ is defined by

$$m_\pm = [(\nu_+ m)^{\nu_+}(\nu_- m)^{\nu_-}]^{1/\nu} \tag{11}$$

where m is the molality of the salt. Thus the mean ionic molality of a salt like NaCl is m, for a salt like Na_2SO_4 it is $4^{1/3}m$, and for a salt like $MgSO_4$ it is m. By substituting Eqs. (10) and (11) into (9) it is readily shown that

$$\gamma_\pm = (\gamma_A^{\nu_+}\gamma_B^{\nu_-})^{1/\nu} \tag{12}$$

Apparatus. Potentiometer; electrodes of cadmium, copper, lead, silver, zinc; electrode vessels; calomel electrode (saturated potassium chloride); standard cell; dry cells; key; 0.100 M solutions of cadmium chloride, copper sulfate, lead nitrate, silver nitrate, zinc sulfate; 2 N ammonium nitrate solution; 100-ml volumetric flask; one 10-ml pipette.

Procedure. In this experiment, the single-electrode potentials of cadmium, copper, lead, silver, and zinc are to be determined using 0.1 and 0.01 M solutions. The 0.1 M solutions are prepared carefully by weighing out the salts with due allowance for water of crystallization, or better, by determining the concentration by analytical methods. The 0.01 M solutions may be prepared by pipetting exactly 10 ml of the 0.1 M solution into a 100-ml volumetric flask and diluting with distilled water.

The electrodes of zinc and lead are prepared by pouring the molten metal from a small porcelain crucible into a glass tube and setting a copper wire into the upper end for a terminal. When cold, the glass tube is broken and removed. For the copper electrode a wire of large diameter is used. The electrodes may be amalgamated, to give a steady potential, less affected by mechanical strains. It should be remarked, however, that the potential of an amalgamated electrode is not necessarily exactly that of the pure metal. The electrode is placed in a beaker of dilute acid with a drop of mercury, and a small brush or cloth is used to spread the mercury over the surface of the electrode.

The silver electrode may be prepared by electroplating spongy silver on a platinum-wire cathode in a silver cyanide (**caution**) solution, using a silver or platinum anode. A single dry cell gives sufficient voltage. Pure silver wire or strip may also be used for the cathode. The silver electrode is not amalgamated.

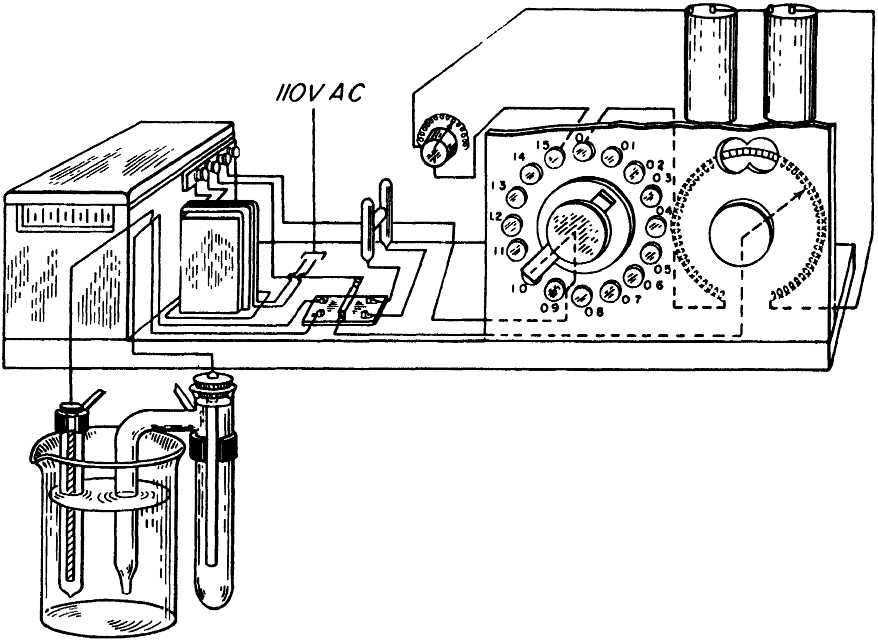

FIG. 36. Measurement of electrode potentials with the potentiometer.

For best results the aqueous solutions should be bubbled out with a stream of hydrogen or purified nitrogen, to remove dissolved oxygen.

The experimental assembly is shown in Fig. 36.

The electrodes are mounted in rubber stoppers and set tightly into vessels having side arms to provide liquid contact with a reference electrode. The snugly fitting stopper prevents the solution from siphoning out of the electrode vessel.

A saturated calomel electrode is used for the reference electrode. In the commercially available type shown later in Fig. 40, a thread of glass fibers wet with KCl solution performs the function of a salt bridge to minimize the liquid-junction potential. In the case of the silver electrode, it is necessary to connect the silver and calomel electrodes through a beaker of 2 *N* ammonium nitrate which is set between the silver electrode and the calomel cell to act as an auxiliary salt bridge which prevents precipitation of silver chloride.

The electromotive force of this cell, with the metal electrode and calomel cell, is determined by means of the potentiometer. The principle of the potentiometer is shown in Fig. 37, in which the electromotive forces, or potentials, of two cells *A* and *B* may be balanced. A wire *RS*, of uniform and high resistance, is stretched along a linear scale. The current is supplied by cell *B*, whose electromotive force is larger than that of cell *A*. Since the wire is of uniform resistance and the same current passes through each section of it, there will be a uniform fall of potential per unit length in the direction *R* to *S*. To measure an unknown electromotive force (cell *A*), a second circuit containing a key, galvanometer, and sliding contact is necessary. The positive terminal of cell *A* is connected opposite the positive terminal of cell *B*, at *R*. The sliding contact *T* is moved along the wire, until there is no deflection of the galvanometer *G* when the key *K* is pressed. If the sliding contact is moved too far to the right, the galvanometer will deflect in one direction; if too far to the left, the galvanometer will deflect in the other direction. If the potential drop per unit length of the slide wire is known from the potential difference between *R* and *S* and the distance between *R* and *S*, the electromotive force of cell *A* may be determined directly from the length *RT*. Then, when the setting at *T* gives no galvanometer deflection, the ratio *RT*/*RS* gives the ratio of the voltage of cell *A* to the potential difference between *R* and *S*.

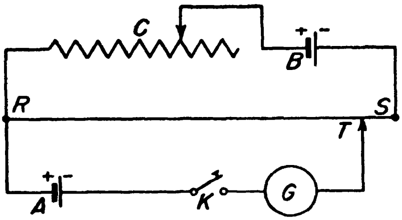

FIG. 37. Simple potentiometer circuit.

Potentiometers are designed so that the fall of potential per unit length of wire is adjusted to some decimal fraction of a volt, and the unknown voltage is then read directly from the scale. This direct reading is accomplished by means of the rheostat *C*, using a Weston cell in place of cell *A*. The Weston standard cell has a voltage of 1.0186 volts at 20°. The point *T* is moved to a position such that there are 1018.6 divisions of the wire between *R* and *S*. The current from the cell *B* through the wire is then changed by the adjustable resistance *C* until the galvanometer shows no deflection, signifying that the fall of potential along *RT* is 1.0186 volts, and the difference of potential per unit length is 1 millivolt. Having once adjusted the potentiometer with the rheostat *C* against the standard cell, the readings thereafter are given directly in voltages. A common type of laboratory potentiometer assembly is shown in Fig. 36 in which the resistance *RS* of Fig. 37 is conveniently arranged in coils for direct use in decimal units. The potentiometer is balanced with the standard cell by the rheostat *C* and used thereafter as a direct reading instrument for determining the voltage of any cell *A* which is smaller than that of cell *B*.

It is important to note in which direction the current is flowing and to record which is the positive electrode, i.e., the electrode connected to the positive terminal of the potentiometer when the circuit is balanced. If there is any doubt as to which is positive, the circuit may be compared with one in which an ordinary dry cell is used. In this cell the zinc is negative and the carbon electrode is positive. The negative terminal is the one that gives a blue color when the wires are both touched to a piece of moist litmus paper. If the galvanometer always deflects in the same direction no matter how the potentiometer is set, the terminals of the unknown cell must be reversed to obtain a point of balance.

Calculations. Cells (4) and (6) have been written for the case that oxidation occurs spontaneously at the metal electrode. If this is the case, the metal electrode is the negative electrode; that is, it is the one connected to the negative terminal of the potentiometer. If the metal electrode is the positive electrode, the representations of the cells in (4) and (6) are reversed, and the signs in Eqs. (5) and (7) are reversed.

The standard oxidation potentials E^0 of the metals are calculated from the experimental data by using the mean ionic activity coefficients given in Table 1. They are then compared with the values found in standard reference tables.

TABLE 1. MEAN ACTIVITY COEFFICIENTS OF ELECTROLYTES AT 25°C

Electrolyte	Concentration		
	0.001 *M*	0.01 *M*	0.1 *M*
Cadmium chloride	0.819	0.524	0.228
Copper sulfate	0.69	0.40	0.16
Lead nitrate	0.89	0.69	0.37
Silver nitrate	0.95	0.90	0.731
Zinc sulfate	0.700	0.387	0.150
Sodium chloride	. . .	0.9032	0.7784
Hydrochloric acid	0.9656	0.9048	0.7964

Practical Applications. If the standard electrode potentials of the metals studied are arranged in order, the metals will be found to fall into their respective positions in the electromotive-force series.

When the value of E^0 is known, it is a simple matter to calculate the activity of the ions from the measurement of E in a given solution, using Eq. (7). This method of determining activities finds many important uses.

Suggestions for Further Work. It is of interest to study the effect of continued dilution of the metallic ions surrounding an electrode upon its potential. It has been suggested in the experiment that 0.01 M and 0.1 M salt concentrations be used. By making further careful dilutions of these solutions, it is possible in principle to extrapolate to zero concentration where the activity coefficients approach unity. However, the experimental errors become very large at these high dilutions. For evaluating γ and E^0 it is necessary to use some function of the molality which will give a straight line when plotted against the molality and thus permit accurate extrapolations to infinite dilution from data at moderate concentrations where the accuracy is good. The values of E^0 and γ for hydrochloric acid are determined in Exp. 35.

The effect on the single-electrode potential of bending or straining the electrode is sufficient to be measured by means of the student potentiometer, except in the case of the softest of the metals.

References

1. Bockris, "Electrochemistry," Academic Press, Inc., New York (1954).
2. Conway, "Electrochemical Data," Elsevier Press, Inc., Houston, Tex. (1952).
3. Daniels and Alberty, "Physical Chemistry," Chap. XVI, John Wiley & Sons, Inc., New York (1955).
4. Dole, "Principles of Experimental and Theoretical Electrochemistry," McGraw-Hill Book Company, Inc., New York (1935).
5. Glasstone, "Introduction to Electrochemistry," D. Van Nostrand Company, Inc., New York (1942).
6. Harned and Ehlers, *J. Am. Chem. Soc.*, **54**, 1350 (1932).
7. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2d ed., Reinhold Publishing Corporation, New York (1950).
8. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York (1952).
9. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," Chaps. XV and XXX, McGraw-Hill Book Company, Inc., New York (1923).
10. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York (1939).

35. THE HYDROGEN ELECTRODE

This experiment illustrates the use of the hydrogen electrode which is the standard reference electrode for electromotive-force studies. A cell consisting of a hydrogen electrode and a silver–silver chloride electrode is used to determine the standard potential of the silver–silver chloride electrode and the activities of hydrochloric acid solutions.

A. THE HYDROGEN ELECTRODE

Theory. A cell involving a hydrogen electrode is illustrated in Fig. 38. A hydrogen electrode is formed by bubbling pure hydrogen gas over a wire or small foil with a specially prepared surface which is able to catalyze the reaction

$$\tfrac{1}{2}H_2(g) = H^+ + e$$

thus establishing equilibrium between hydrogen molecules and the hydrogeni ons in the solution in which the electrode is immersed. The hydrogen electrode is designed so that a platinized platinum wire is partly covered by the solution. As hydrogen is passed into the side arm and bubbles out into the solution, the level of the solution at the wire rises and falls so that the wire is alternately bathed in hydrogen and in the solution. The hydrogen electrode cannot be used in the presence of certain substances like H_2S, cyanides, and arsenic compounds which inhibit the catalysis of the electrode process.

The potential of a hydrogen electrode half-cell is given by

$$E = -\frac{RT}{\mathbf{F}} \ln \frac{a_{H^+}}{p_{H_2}^{1/2}} \qquad (1)$$

since the standard potential of the hydrogen electrode is conventionally assigned a value of zero at all temperatures. When used in conjunction with a saturated calomel electrode as illustrated in Fig. 38, the cell may be represented by

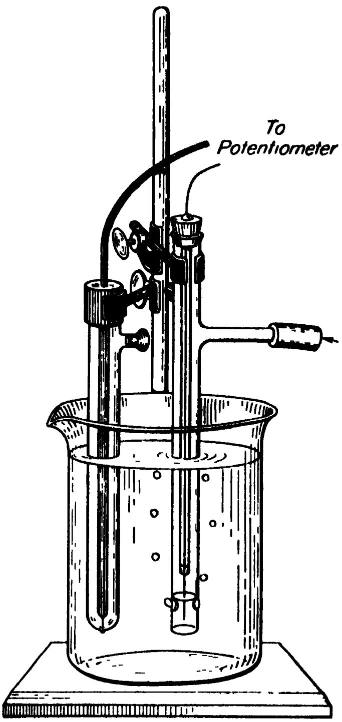

FIG. 38. Hydrogen electrode and calomel electrode.

$$\text{Pt; } H_2,\ H^+(a) \| \text{KCl (sat); } Hg_2Cl_2,\ Hg$$

where $\|$ indicates the liquid junction between the saturated KCl solution and the acid solution. This cell operates spontaneously with oxidation occurring at the left electrode. Thus, this electrode is connected to the negative terminal of the potentiometer, and the electrode at the right is connected to the positive terminal. The electromotive force of this cell is given by

$$E = E^0_{\text{KCl(sat)};Hg_2Cl_2,Hg} - \frac{RT}{\mathbf{F}} \ln \frac{a_{H^+}}{p_{H_2}^{1/2}} + E_j \qquad (2)$$

where $E^0_{\text{KCl(sat)};\text{Hg}_2\text{Cl}_2,\text{Hg}}$ is the standard reduction potential of the saturated calomel electrode, and E_j is the potential caused by the liquid junction which is assumed to be independent of the concentration of the acid solution. The standard reduction potential is the negative of the standard oxidation potential. Equation (2) may be rearranged to

$$-\log a_{\text{H}^+} + \frac{1}{2}\log p_{\text{H}_2} = \frac{E - E^0_{\text{KCl(sat)};\text{Hg}_2\text{Cl}_2,\text{Hg}} - E_j}{2.303RT/\mathbf{F}} \tag{3}$$

The activity of hydrogen ions may be expressed in terms of the pH which is $-\log a_{\text{H}^+}$. Thus

$$\text{pH} = \frac{E - E^0_{\text{KCl(sat)};\text{Hg}_2\text{Cl}_2,\text{Hg}} - E_j}{2.303RT/\mathbf{F}} - \frac{1}{2}\log p_{\text{H}_2} \tag{4}$$

where the partial pressure of hydrogen above the solution, p_{H_2}, is given in atmospheres. For the saturated calomel electrode, $E^0_{\text{KCl(sat)};\text{Hg}_2\text{Cl}_2,\text{Hg}} + E_j$ is taken to have the value 0.2444 volts at 25°. A value of 0.2802 volt would be used for the calomel electrode containing 1 N KCl at 25°. Values for other temperatures and other reference electrodes are given by Bates.[1]

Since it is not possible to know individual ion activities, the pH scale is a conventional one.[1] Although glass electrodes are widely used for the determination of pH, the hydrogen electrode is the standard in this field.

Apparatus. Potentiometer and accessories; hydrogen electrode; calomel electrode; 0.5 N hydrochloric acid (with normality accurately known); 0.5 N (approximate) sodium hydroxide.

Procedure. A known volume of 0.5 N hydrochloric acid (say 25 ml) is placed in a beaker, and the hydrogen electrode and saturated calomel electrode are immersed as illustrated in Fig. 38. Hydrogen from a tank is allowed to bubble slowly through the glass hood of the hydrogen electrode. For research purposes it is necessary to remove any oxygen and carbon dioxide in the hydrogen. Unless found to be free from sulfur, all the rubber tubing used should be boiled in concentrated sodium hydroxide solution and thoroughly rinsed.

The student should be familiar with the principle and operation of the potentiometer before starting the experiment (see Exp. 34 and Chap. 22). Since the cell operates spontaneously with oxidation occurring at the hydrogen electrode, the hydrogen electrode is connected to the negative terminal of the potentiometer and the calomel electrode to the positive terminal. The circuit is closed only momentarily with the tapping key to find the point of balance because any appreciable passage of current will polarize the electrodes.

The initial voltage should be approximately 0.26 volt; otherwise, the electrode is not functioning properly. Replatinizing the electrode will usually correct faulty behavior of a hydrogen electrode. When the electrode is properly platinized, a steady voltage should be reached in half a minute or so. After adding a drop of phenolphthalein solution, approximately 0.5 N sodium hydroxide is added slowly from a burette, and the solution is stirred after each addition. At first about 5 ml is added at a time, but as the neutral point is approached, readings are taken more frequently, and after passing the end point, larger amounts can again be added. The exact end point should be found by accurate drop-by-drop titrations so that the pH at which the phenolphthalein changes color can be calculated. The addition of alkali is continued until the voltage has become practically constant.

The barometric pressure is read so that the partial pressure of hydrogen above the solution may be calculated.

To prepare the hydrogen electrode, it is wiped as clean as possible and dipped for a few seconds into warm aqua regia, under the hood. The electrode is then platinized, i.e., coated with a deposit of platinum black, by electrolyzing the electrode as the negative pole in a 1 per cent solution of platinic chloride. Another platinum wire serves as the anode, and the potential is supplied by two dry cells connected in series. The electrolysis is allowed to continue for several minutes. The electrodes are then placed in a small beaker of distilled water to which a drop of concentrated sulfuric acid has been added, and the electrolysis is allowed to proceed as before. This treatment produces hydrogen and removes any impurities. The electrode should be kept in distilled water until used; it should never be allowed to dry out. Electrodes must be replatinized from time to time, as the coating of platinum black becomes "poisoned" with use.

Calculations. Graphs are drawn in which the numbers of milliliters of sodium hydroxide solution added are plotted as abscissas against voltage as ordinates. The steepest part of the curve corresponds to the end point. This volume is used for calculating the normality of the sodium hydroxide from the known normality of the original hydrochloric acid solution. The hydrogen-ion activity of a given solution is calculated by means of Eq. (4) from the observed voltage E of the cell. The partial pressure of hydrogen above the solution is calculated by subtracting the vapor pressure of water from the barometric pressure. The hydrogen-ion activities and pH values corresponding to the voltages at which phenolphthalein changes color may now be calculated.

B. ELECTROMOTIVE FORCE CELL WITHOUT TRANSFERENCE

The liquid junction in the cell used in the first part of this experiment contributes a potential difference which cannot be determined with exactness. Such cells are therefore not suitable for accurate thermodynamic measurements. The problem of the liquid junction potential is avoided in cells such as

$$\text{Pt, } H_2\text{; } HCl(a)\text{; } AgCl\text{; } Ag$$

which contain a single electrolyte solution. The cell reaction is

$$\tfrac{1}{2}H_2 + AgCl = Ag + H^+ + Cl^-$$

and the electromotive force of the cell is given by

$$E = E^0 - \frac{RT}{\mathrm{F}} \ln \frac{a_{H^+}a_{Cl^-}a_{Ag}}{a_{AgCl}a_{H_2}^{1/2}} \tag{5}$$

where E^0 is the standard reduction potential for the silver–silver chloride electrode. The activities of Ag and AgCl are unity because of the presence of the solid phases, and $a_{H^+}a_{Cl^-}$ may be written as $\gamma^2 m^2$, where γ is the mean ionic activity coefficient and m is the molality.

$$E = E^0 - \frac{RT}{\mathrm{F}} \ln \frac{\gamma^2 m^2}{p_{H_2}^{1/2}} \tag{6}$$

At atmospheric pressures it is satisfactory to assume that the activity of hydrogen gas is given by its pressure in atmospheres.

The value of the standard potential for the silver–silver chloride electrode has been determined[2,3] in very careful research in which the Debye-Hückel theory is used to guide the extrapolation of experimental values to $m = 0$, where γ is taken to be unity. The values of the reduction potential at 20, 25, and 30° are 0.22557, 0.22234, and 0.21904 volt, respectively. Thus, a measurement of the electromotive force of a cell at a particular hydrogen pressure and molality of hydrochloric acid makes it possible to calculate the mean ionic activity coefficient of hydrochloric acid by use of Eq. (6).

Apparatus. Potentiometer and accessories; hydrogen electrode and tank of hydrogen; silver–silver chloride electrode; approximately 2 *N* HCl of accurately known molality.

Procedure. The construction of the cell is illustrated in Fig. 39. If silver–silver chloride electrodes are not available, they may be prepared from a piece of platinum wire (No. 26) about 7 mm in length coiled into a helix and sealed into a glass tube as illustrated in Fig. 39. The electrode is cleaned in warm 6 *N* nitric acid, and silver is electrodeposited from a silver nitrate solution. The surface of the deposit is then converted to silver chloride by electrolysis as the anode in 1 *N* HCl solution. Too thick a coat of silver chloride will make the electrode response sluggish. The electrodes are immersed in distilled water for storage.

These electrodes are subject to an aging effect during the first 20 to 30 hr after preparation and are sensitive to traces of bromide in the solutions. In the presence of air the potential is slightly more positive than for an air-free solution probably because of a slight decrease in the concentration of chloride ion within the interstices of the electrode by the reaction

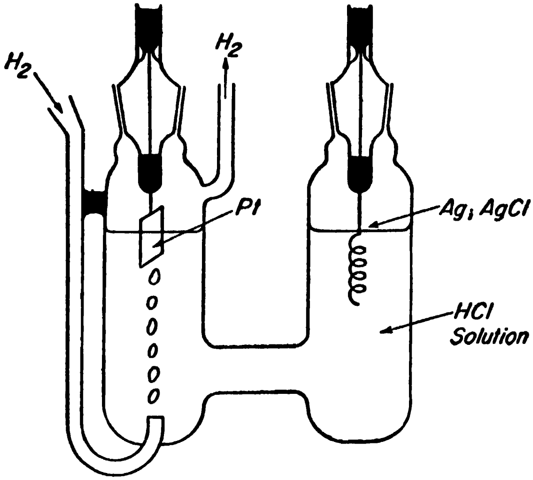

FIG. 39. Cell without transference for the determination of the activity of the hydrochloric acid in solution.

$$2Ag + 2HCl + \tfrac{1}{2}O_2 = 2AgCl + H_2O$$

These effects all have to be taken into account in work of the highest precision.

The electromotive forces of the cell containing 2 *N*, 1 *N*, 0.5 *N*, 0.25 *N*, and 0.125 *N* hydrochloric acid are measured at a constant temperature, preferably 25°. The barometric pressure is recorded.

Calculations. The molalities of the hydrochloric acid solutions are calculated from the known normalities by use of density data which may be obtained from a handbook. Since several solutions are involved, it will be convenient to prepare a plot of molality against normality.

The partial pressure of hydrogen above the solution is taken to be equal to the difference between the barometric pressure and the vapor pressure of water. In more accurate work the vapor pressure of the solution would have to be known. The pressure in Eq. (6) must be expressed in atmospheres.

The mean ionic activity coefficients of the various hydrochloric acid solutions are calculated by use of Eq. (6). A plot of activity coefficient versus molality is prepared, and a comparison with the literature values is made.

Suggestions for Further Work. Measurements may be made in the concentration range 0.005 to 0.05 molal, and the data extrapolated by use of the Debye-Huckel theory to obtain a value of E^0. Other cells suitable for study are

$$\text{Hg, Hg}_2\text{Cl}_2\text{, HCl}(m)\text{, H}_2\text{; Pt}$$
$$\text{Ag; AgBr, HBr}(m)\text{, H}_2\text{; Pt}$$

References

1. Bates, "Electrometric pH Determinations," p. 201, John Wiley & Sons, Inc., New York (1954).
2. Daniels and Alberty, "Physical Chemistry," p. 445, John Wiley & Sons, Inc., New York (1955).
3. Harned and Owen, *J. Am. Chem. Soc.*, **55**, 1350, 2179 (1933).
4. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2d ed., Reinhold Publishing Corporation, New York (1950).
5. MacInnes, "The Principles of Electrochemistry," Reinhold Publishing Corporation, New York (1939).
6. Pinching and Bates, *J. Research Natl. Bur. Standards*, **37**, 311 (1946).
7. Ricci, "Hydrogen Ion Concentration," Princeton University Press, Princeton, N.J. (1952).

36. THE GLASS ELECTRODE

The use of the glass electrode for the determination of pH is illustrated by the titrations of phosphoric acid and glycine. The preparation of buffers of given pH and the determination of buffer capacity are introduced.

Theory. The theory of pH measurements is discussed in Exp. 35.

The glass electrode has several advantages over the hydrogen electrode for the measurement of pH. The glass electrode functions in both oxidizing and reducing media and in the presence of proteins and sulfur compounds, all of which interfere with the use of platinized platinum.

The glass electrode consists of a thin membrane of soft glass enclosing a dilute solution of potassium chloride and acetic acid in which is immersed a platinum wire coated with Ag-AgCl. The variation of the potential of a glass electrode with varying hydrogen-ion concentration is the same as that of a hydrogen electrode.* A number of theories for the action of a glass electrode have been proposed.[1,5] A saturated calomel electrode is used in conjunction with the glass electrode so that the cell may be represented diagrammatically as follows.

$$\mathrm{Ag,\ AgCl;\ KCl,\ CH_3CO_2H}\overset{\text{glass membrane}}{\Vert}\text{unknown solution}\overset{\text{salt bridge}}{\Vert}\mathrm{KCl\ (sat);\ Hg_2Cl_2,\ Hg}$$

The construction of commercially available electrodes is illustrated in

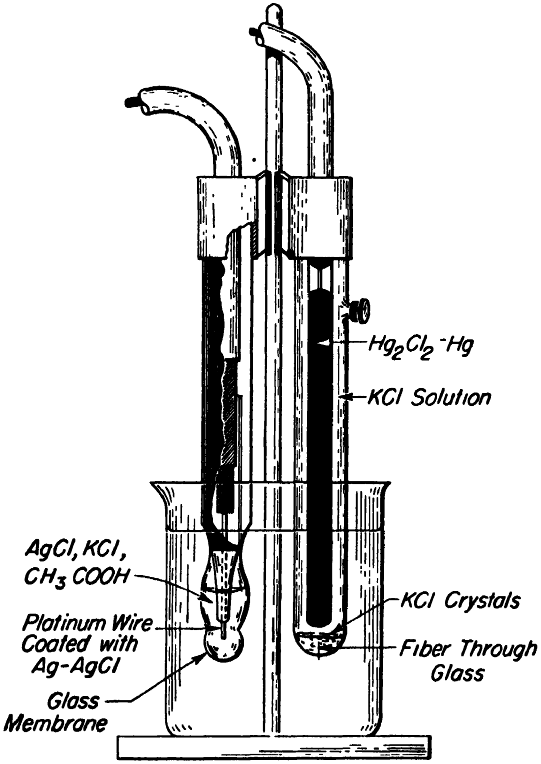

FIG. 40. Glass-electrode–calomel-electrode assembly.

Fig. 40. The electromotive force of this cell cannot be measured with a potentiometer because of the high resistance of the glass membrane. For this reason an electronic voltmeter is used. The glass-electrode potential changes 0.0591 volt/pH unit at 25°C, and pH meters are graduated directly in terms of pH. According to the simplified theory, two solutions of the same hydrogen-ion activity, with the glass membrane interposed,

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* At pH's above 10 it is necessary to correct for response to Na^+ ions unless special glasses are used.

should show no potential difference. However, glass electrodes usually do show a small potential (asymmetry potential) under these conditions, and for this reason it is necessary to set the pH meter periodically by using a buffer of known pH. Some useful buffers for this purpose studied by MacInnes[4] are given in Table 1.

TABLE 1. pH VALUES OF STANDARD BUFFERS

Buffer	12°C	25°C	38°C
CH_3CO_2H(0.1 *N*), CH_3CO_2Na(0.1 *N*)	4.650	4.640	4.635
Potassium acid phthalate (0.05 *M*)	4.000	4.000	4.015

The pH of a mixture of a weak acid or base and its salt may be calculated from the mass-action equilibrium formulation.

$$K = \frac{[H^+][A^-]}{[HA]} \tag{1}$$

HA represents a weak acid. Upon taking the logarithm of this equation and rearranging, we obtain

$$\text{pH} = \text{p}K + \log \frac{[A^-]}{[HA]} \tag{2}$$

where pK is equal to $-\log K$. Note that if the concentrations of the acidic and basic forms of the buffer are equal, $[A^-] = [HA]$, and

$$\text{pH} = \text{p}K = -\log K$$

This fact may be used to determine ionization constants of rather weak acids and bases. The pH of the buffer depends upon the ratio of the concentrations of these two forms and not on the total amounts. However, the capacity of a buffer to resist changes of pH produced by the addition of acid or alkali depends upon the concentrations of the two forms present. The slope of a plot of equivalents of acid or base added per liter of buffer versus pH is sometimes called the ***buffer capacity***. The buffer capacity may be calculated from the concentrations of the salt and undissociated acid using Eq. (3) (see Reference 6):

$$\frac{dB}{d(\text{pH})} = \frac{2.3[A^-][HA]}{[A^-] + [HA]} \tag{3}$$

Here B represents the number of equivalents of acid or base added per liter of buffer. The buffer capacity is a maximum at pH = pK. At 1 pH unit away from the pK a buffer is about 33 per cent as effective.

The pK value of a weak acid determined with Eq. (2) depends upon the salt concentration since the equilibrium expression [Eq. (1)] has been written in terms of concentrations rather than activities. The value of the ionization constant of a weak acid or base determined by titration is frequently referred to as the apparent ionization constant to distinguish it from the thermodynamic ionization constant obtained by extrapolation to infinite dilution.

The titration of a polybasic acid such as phosphoric acid, using a pH meter, may be used to evaluate the ionization constants. The successive ionizations of phosphoric acid may be represented as follows:

$$H_3PO_4 \rightleftharpoons H_2PO_4^- + H^+$$

$$K_1 = \frac{[H_2PO_4^-][H^+]}{[H_3PO_4]} = 7.5 \times 10^{-3} \qquad pK_1 = 2.124 \tag{4}$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{--} + H^+$$

$$K_2 = \frac{[HPO_4^{--}][H^+]}{[H_2PO_4^-]} = 6.2 \times 10^{-8} \qquad pK_2 = 7.206 \tag{5}$$

$$HPO_4^{--} \rightleftharpoons PO_4^{---} + H^+$$

$$K_3 = \frac{[PO_4^{---}][H^+]}{[HPO_4^{--}]} = 4.8 \times 10^{-13} \qquad pK_3 = 12.32 \tag{6}$$

The third dissociation takes place at such a high pH that it cannot be studied in dilute aqueous solutions. The first two end points can be recognized by the large change in pH for a small addition of base.

At the pH at which the second acid group is half neutralized, the hydrogen-ion activity is equal to the equilibrium constant K_2.

The pK values for ionizations (4), (5), and (6) are the thermodynamic values.[3] At 0.1 ionic strength the value of pK_2 is 6.80. The ionic strength is half the sum of the concentrations of the ions multiplied by their valence squared.

In aqueous solution pure glycine exists as a dipolar ion (zwitter ion), as evidenced by the high dielectric constant which is measured. When glycine is titrated with acid, the hydrogen ions react with the carboxyl group as illustrated by the reverse of Eq. (7). When half the carboxyl groups have reacted, the hydrogen-ion activity is equal to the equilibrium constant K_1. The corresponding pH is $-\log K_1 = 2.35$. When neutral glycine is titrated with sodium hydroxide, the hydrogen on the amino group is titrated as indicated by Eq. (8). The equilibrium expressions for these reactions are written as follows:

$$\underset{\substack{\text{form present in}\\ \text{acid solution}}}{{}^{+}H_3NCH_2CO_2H} \rightleftharpoons \underset{\text{dipolar ion}}{{}^{+}H_3NCH_2CO_2^-} + H^+ \qquad (7)$$

$$K_1 = \frac{[{}^{+}H_3NCH_2CO_2^-][H^+]}{[{}^{+}H_3NCH_2CO_2H]} = 4.47 \times 10^{-3} \qquad pK_1 = 2.35$$

$$\underset{\text{dipolar ion}}{{}^{+}H_3NCH_2CO_2^-} \rightleftharpoons \underset{\substack{\text{form present in}\\ \text{alkaline solution}}}{H_2NCH_2CO_2^-} + H^+ \qquad (8)$$

$$K_2 = \frac{[H_2NCH_2CO_2^-][H^+]}{[{}^{+}H_3NCH_2CO_2^-]} = 1.66 \times 10^{-10} \qquad pK_2 = 9.78$$

The three dissociable hydrogens of phosphoric acid are equivalent in H_3PO_4, and so the question as to which H^+ dissociates first does not arise. In the case of glycine there are two possibilities and various types of evidence including the high dielectric constant of neutral solutions of glycine indicate that the carboxyl group is the stronger acid group.

Apparatus. pH meter with glass electrode and calomel electrode; bottle of standard buffer; 0.1 *N* acetic acid; 0.1 *N* sodium acetate; 0.1 *M* phosphoric acid; glycine.

A. TITRATION OF PHOSPHORIC ACID

Procedure and Calculations. Twenty-five milliliters of 0.1 *M* H_3PO_4 is titrated with 0.1 *N* NaOH. The pH is measured after each addition of about 5 ml of base, except near the end points, where more readings are taken. In order to determine the pH range for the color change of a typical indicator, a few drops of phenolphthalein solution are added before the titration. The color change of the indicator is noted during the titration. The pH of the solution is plotted versus volume of sodium hydroxide added, and the ionization constant K_2 is calculated.

B. BUFFERS

Procedure and Calculations. The following buffer solutions are carefully prepared, using volumetric equipment:

Solution	ml 0.10 *N* HAc	ml 0.10 *N* NaAc
1	95	5
2	50	50
3	5	95

The pH of each solution is determined with the pH meter and compared with the values calculated from Eq. (2). Since acetic acid is a weak acid, it does not contribute appreciably to the acetate concentration of these buffers, so that the acetate-ion concentration is determined only by the amount of sodium acetate added. Four milliliters of 0.1 *N* sodium hydroxide is added to each of the above buffers, and the pH again measured. Four milliliters of 0.1 *N* sodium hydroxide is added to 100 ml of distilled water, and the pH change noted. The ratios $\Delta B/\Delta(\text{pH})$ of the numbers of equivalents of base added per liter of buffer to the changes in pH are calculated and compared with the buffer capacities calculated by using Eq. (3).

C. TITRATION OF GLYCINE

Procedure and Calculations. Two approximately 250-mg portions of glycine are weighed and dissolved in 30 ml of distilled water. One portion is titrated with 0.1 *N* NaOH and the other with 0.1 *N* HCl, the pH being recorded at six to eight intervals. No definite end points are obtained, however, since they occur in such strongly acidic or basic solutions that a large amount of the added acid or base is required to change the pH.

The titration curves are plotted by graphing the volume of acid added to the left of the origin on the horizontal axis and the volume of base added to the right with the pH plotted as ordinate. In a second figure the pH is plotted versus the number of equivalents of acid or base which have reacted per mole of glycine. The number of equivalents of hydrogen ion or hydroxyl ion which have reacted with glycine is the difference between the number of equivalents of acid or base added and the number of equivalents remaining free in solution (calculated from the pH and the volume of solution being titrated). The calculations are most conveniently arranged in tabular form. The corrected titration curve is plotted, and the pK' values of glycine calculated from it.

Practical Applications. The rates of many reactions depend markedly upon the pH, and therefore solutions in which such reactions are carried out must be buffered. Industrially, pH is frequently controlled by automatic devices which add acid or base depending upon the potential of a glass electrode. The pH meter is particularly important in biological research.

Suggestions for Further Work. The glass electrode may be used for the measurement of the pH of a wide variety of miscellaneous substances, e.g., milk, sour milk, blood, orange juice, lemon juice, water extract of soil, tap water, tap water from which carbon dioxide has been expelled. If a mixture of acids which have pK's differing by about 2 (e.g., hydrochloric acid, acetic acid, and lactic acid) is titrated with the pH meter, it is possible to determine the amount of each acid present.

Measurements of pH may be used to determine the degree of hydrolysis of salts, providing the salts have been carefully purified and pure water is used. While aqueous solutions of salts of strong acids and strong bases are neutral, solutions of salts of strong acids and weak bases are acidic, and solutions of salts of weak acids and strong bases are basic. To illustrate this, the pH values of solutions of sodium chloride, sodium acetate, ammonium acetate, and aniline hydrochloride may be measured. The degree of hydrolysis x is calculated from $x = (OH^-)/c$ or $x = (H^+)/c$, depending upon whether the solution is basic or acidic. The concentration of the salt in equivalents per liter is represented by c. The experimentally determined degrees of hydrolysis are compared with the values calculated from the ionization constants in the literature.

References

1. Bates, "Electrometric pH Determinations," John Wiley & Sons, Inc., New York (1954).
2. Daniels and Alberty, "Physical Chemistry," John Wiley & Sons, Inc., New York (1955).
3. Harned and Owen, "The Physical Chemistry of Electrolytic Solutions," 2d ed., Reinhold Publishing Corporation, New York (1950).
4. MacInnes, "The Principles of Electrochemistry," Chap. 15, p. 258, Reinhold Publishing Corporation, New York (1939).
5. Michaelis *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Chap. 27, Interscience Publishers, Inc., New York (1949).
6. Van Slyke, *J. Biol. Chem.*, **52**, 525 (1922).

37. FREE ENERGY AND THE EQUILIBRIUM CONSTANT

This experiment illustrates the important relation between equilibrium constants and free energy and connects chemical and electrical measurements through thermodynamics. Practice is obtained in the use of the potentiometer, the volumetric analysis of silver, and certain inorganic preparations.

Theory. One of the most important equations of physical chemistry is that connecting the free-energy change ΔF^0 with the equilibrium constant K for a chemical reaction:

$$\Delta F^0 = -RT \ln K \tag{1}$$

This equation becomes exact if the equilibrium constant K is expressed in terms of activities, and it is useful as an approximate equation when activities are replaced by concentrations.

The free-energy change involved in a chemical reaction may be obtained by addition and cancellation of several reactions, in the same way that heats of reaction are obtained from thermochemical equations. Tables of free-energy values are being accumulated which will eventually permit a calculation of the equilibrium constant for most chemical reactions. It is possible also to calculate free energies from heats of reaction and entropy values, the latter being obtained from specific-heat measurements down to absolute zero.

When it is realized that an equilibrium constant enables one to calculate just how far the chemical reaction can go, the importance of these free-energy tables is apparent. Through these thermodynamic relationships, the concentration of products at equilibrium can be predicted when the concentration of the reacting materials is known. If the reaction is slow, considerations of reaction rate may, however, become more important than considerations of free energy and equilibrium.

The free-energy change in a chemical reaction may be determined most directly, and frequently with high accuracy, by measuring the voltage of the reversible cell for which the cell reaction is the reaction under consideration.

Cells with liquid junctions between the different electrolytes cannot be given exact thermodynamic treatment, but they can give a useful result if the liquid junctions have been practically eliminated by a salt bridge. Such cells are used widely in pH measurements; they are to serve in another way in this experiment.

The reaction

$$\mathrm{Fe^{++} + Ag^{+} = Ag + Fe^{+++}} \qquad (2)$$

is particularly suitable for testing Eq. (1), because the equilibrium is quickly reached, the equilibrium constant is easily obtained by volumetric analysis, and the free-energy change may be calculated from the voltage of the cell

$$\mathrm{Pt;\ Fe^{++},\ Fe^{+++} \| Ag^{+};\ Ag} \qquad (3)$$

Apparatus. Two 150-ml glass-stoppered bottles; platinum electrode; silver electrode; two half-cells (Fig. 41); crystallizing dish; calomel cell; potentiometer assembly; 0.1 *M* ferric nitrate in 0.05 *M* nitric acid; 0.1 *M* silver nitrate; 0.1 *M* potassium thiocyanate, ferrous sulfate, barium nitrate; purified nitrogen or carbon dioxide.

A. TITRATION METHOD

Procedure. Precipitated silver is prepared by dissolving about 7 g of silver nitrate in water and adding an excess of copper wire. The precipitate of silver is filtered and rinsed with distilled water until the rinsings give no test for copper ion with ammonia solution. The yield is split between the two glass-stoppered bottles to each of which is added 100 ml of a solution which is 0.100 *M* in ferric nitrate and 0.05 *M* in nitric acid. The nitric acid reduces hydrolysis of the ferric salt. Purified nitrogen (page 395) or carbon dioxide is bubbled slowly through the solution for a few minutes to sweep out dissolved oxygen; the glass joint is greased, and the bottle tightly stoppered. Oxidation of ferrous ions by dissolved air constitutes one of the greatest difficulties in this experiment.

The two bottles are heated to about 50°; they are removed and shaken at frequent intervals and then set aside to stand for at least 24 hr. Procedure B may be performed while equilibrium is being attained.

When equilibrium has been reached, the solutions are analyzed for silver ions. A 25-ml sample of the solution is titrated with 0.1 *M* potassium thiocyanate, the ferric nitrate already in solution serving as an indicator. The potassium thiocyanate solution is standardized with the 0.1 M silver nitrate solution, an equal volume of the ferric nitrate solution being added as indicator.

The titrations should be made as soon as the stoppers are removed in order to avoid air oxidation of ferrous ion.

B. POTENTIOMETRIC METHOD

Procedure. Twenty milliliters of 0.1 M ferric nitrate in 0.05 M nitric acid is mixed with 20 ml of freshly prepared ferrous nitrate solution. The latter is prepared by mixing equal portions of 0.2 M ferrous sulfate and 0.2 M barium nitrate. The barium sulfate is allowed to settle for a few minutes in a stoppered vessel; the resulting solution is decanted into one of the half-cells, and the rubber stopper which holds the platinum electrode is sealed tightly in place. It is just as important to prevent air oxidation here as in the procedure for method A, and to this end the use of purified nitrogen or carbon dioxide over the solutions may be advisable. The presence of a small amount of suspended barium sulfate in the solution should not affect the results.

Into the other half-cell are placed 0.1 M silver nitrate and the silver electrode, with the rubber stopper seating tightly. The side arms in both half-cells must be completely filled.

The two half-cells and the calomel cell are now set up as shown in Fig. 41. The crystallizing dish contains saturated ammonium nitrate solution, which acts as a salt bridge.

The principle of the potentiometer should be fully understood (Exp. 34 and Chap. 22).

Three potentials are determined between the following pairs of electrodes: silver against calomel, ferrous-ferric against calomel, and silver against ferrous-ferric. In each case, time should be allowed for a steady potential to be reached.

The silver residues in both procedures are to be placed in a special recovery bottle.

Calculations. The fundamental equation is

$$E = \frac{RT}{n\mathrm{F}} \ln K - \frac{RT}{n\mathrm{F}} \ln \frac{a^x_{\text{products}}}{a^y_{\text{reactants}}}$$

in which products are defined as the materials at the right of the equality sign and reactants as the materials at the left, and x and y refer to the coefficients in the balanced chemical equation. When the activities a are unity, the potential is defined as E^0, and then $E^0 = (RT/n\mathrm{F}) \ln K$.

The concentration of silver ion in the equilibrium solution is calculated from the potassium thiocyanate titration. The concentration of the

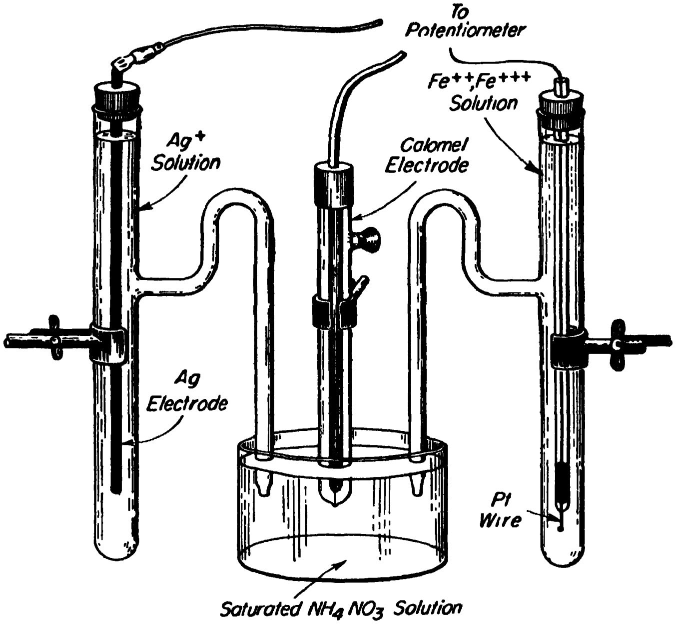


FIG. 41. Measurement of electrode potentials for calculating the free-energy change in chemical reactions.

ferrous iron is the same as that of the silver, and the concentration of ferric iron is calculated by subtracting the concentration of ferrous iron from the concentration of ferric iron originally present. The equilibrium constant K is calculated as follows:

$$K = \frac{c_{\mathrm{Fe}^{+++}}}{c_{\mathrm{Fe}^{++}} \cdot c_{\mathrm{Ag}^{+}}}$$

The activity of silver atoms does not appear in the calculation, because it is kept constant by the presence of the solid silver. The electrochemical reactions at the two electrodes corresponding to the cell given by Eq. (3) are

$$\mathrm{Fe}^{++} = \mathrm{Fe}^{+++} + e$$

and

$$\mathrm{Ag}^{+} + e = \mathrm{Ag}$$

The oxidation potential $E^0_{\mathrm{Pt;Fe}^{++},\mathrm{Fe}^{+++}}$ may be calculated from the electromotive force E_{I} of the cell

$$\mathrm{Hg},\ \mathrm{Hg_2Cl_2};\ \mathrm{KCl\ (sat)}\|\mathrm{Fe}^{+++}(a_{\mathrm{Fe}^{+++}}),\ \mathrm{Fe}^{++}(a_{\mathrm{Fe}^{++}});\ \mathrm{Pt} \qquad \text{(I)}$$

Assuming that the junction potential is negligible,

$$E_{\mathrm{I}} = E^0_{\mathrm{Hg,Hg_2Cl_2,KCl(sat)}} - E^0_{\mathrm{Pt,Fe}^{++},\mathrm{Fe}^{+++}} - 0.0591 \log \frac{a_{\mathrm{Fe}^{++}}}{a_{\mathrm{Fe}^{+++}}}$$

where $E^0_{\mathrm{Hg,Hg_2Cl_2,KCl(sat)}}$ is the oxidation potential for the saturated calomel electrode.

If $a_{\mathrm{Fe^{++}}}$ is set equal to $a_{\mathrm{Fe^{+++}}}$ when $c_{\mathrm{Fe^{++}}} = c_{\mathrm{Fe^{+++}}}$

$$E^0_{\mathrm{Pt;Fe^{++},Fe^{+++}}} = -E_{\mathrm{I}} + E^0_{\mathrm{Hg,Hg_2Cl_2,KCl(sat)}}$$

The value of $E^0_{\mathrm{Pt;Fe^{++},Fe^{+++}}}$ found is compared with that given in tables.

The oxidation potential $E^0_{\mathrm{Ag;Ag^+}}$ may be calculated from the electromotive force E_{II} of the cell

$$\mathrm{Hg,\ Hg_2Cl_2;\ KCl\ (sat)} \| \mathrm{Ag^+}(a_{\mathrm{Ag^+}});\ \mathrm{Ag} \qquad \text{(II)}$$

Assuming that the junction potential is negligible,

$$E_{\mathrm{II}} = E^0_{\mathrm{Hg,Hg_2Cl_2;KCl(sat)}} - E^0_{\mathrm{Ag;Ag^+}} - 0.0591 \log \frac{1}{a_{\mathrm{Ag^+}}}$$

Thus

$$E^0_{\mathrm{Ag;Ag^+}} = -E_{\mathrm{II}} + E^0_{\mathrm{Hg,Hg_2Cl_2;KCl(sat)}} - 0.0591 \log \frac{1}{a_{\mathrm{Ag^+}}}$$

Then for the cell

$$\mathrm{Pt;\ Fe^{++}}(a_{\mathrm{Fe^{++}}}),\ \mathrm{Fe^{+++}}(a_{\mathrm{Fe^{+++}}}) \| \mathrm{Ag^+}(a_{\mathrm{Ag^+}});\ \mathrm{Ag} \qquad \text{(III)}$$

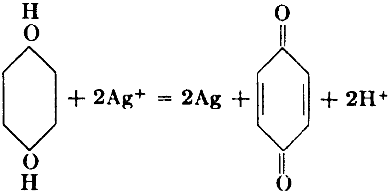
$$\begin{aligned} E^0 &= E^0_{\mathrm{Pt,Fe^{++},Fe^{+++}}} - E^0_{\mathrm{Ag,Ag^+}} \\ &= 0.0591 \log \frac{a_{\mathrm{Fe^{+++}}}}{a_{\mathrm{Fe^{++}}} a_{\mathrm{Ag^+}}} = 0.0591 \log K \end{aligned}$$

The value of K is calculated from this equation and compared with the value of K obtained by direct analysis. The agreement can be only approximate, because analytically determined concentrations, rather than activities, are used for calculating K from the equilibrium mixture and for determining $E^0_{\mathrm{Pt.Fe^{++},Fe^{+++}}}$, but since the solutions are fairly dilute the error is not great. The contact potential between the unlike solutions is another source of considerable error.

Practical Applications. An equilibrium constant for a chemical reaction can be calculated when the free-energy change is known. In accumulating tables of free energies for this purpose, the direct electromotive-force measurement of reversible cells constitutes one of the most valuable methods. The equilibrium constants for various reactions may be calculated from the oxidation-reduction potentials.

Suggestions for Further Work. The results may be made considerably more accurate by carrying out the measurements with a series of more dilute solutions and evaluating $\log K$ and E^0 by extrapolation to infinite dilution, where the concentrations and activities become identical. More accurate determination of ferric iron is advisable, using reduction with zinc and titration with potassium permanganate. Better results are obtained with perchlorates instead of nitrates.[3]

The oxidation of hydroquinone by silver ion is an excellent reaction[2] to study because the equilibrium constant can be determined accurately by iodiometric titration, and because dissolved oxygen from the air does not affect the results. The reaction is



and the cell by which the equilibrium constant can be calculated is

Pt, quinhydrone; $H^+ \| Ag^+$; Ag

The dissociation pressure of copper oxide or mercuric oxide may be calculated from electromotive-force measurements of suitable cells.

References

1. Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Company, Inc., New York (1923).
2. Livingston and Lingane, *J. Chem. Educ.*, **15**, 320 (1938).
3. Schumb and Sweetser, *J. Am. Chem. Soc.*, **57**, 871 (1935).

38. THERMODYNAMICS OF ELECTROCHEMICAL CELLS

The electromotive force of a cell is measured at different temperatures, and the heat of the reaction is calculated by means of the Gibbs-Helmholtz equation.

Theory. The following reaction[2] is studied:

$$Zn(Hg) + PbSO_4(s)^* = ZnSO_4 \text{ (0.02 molal)} + Pb(Hg) \qquad (1)$$

The heat evolved in the direct, irreversible reaction may be measured directly in a calorimeter under conditions where no useful work is performed, or it may be calculated indirectly from electrical measurements. Since the measurement of electrical quantities is very precise, the latter method is often more accurate than the direct calorimetric method.

Instead of placing zinc amalgam directly in contact with lead sulfate and carrying out the reaction irreversibly, the same reaction may be brought about reversibly by the electrochemical cell represented as

$$Zn(Hg);\ ZnSO_4 \text{ (0.02 molal)};\ PbSO_4(s),\ Pb(Hg) \qquad (2)$$

Electrical work is defined as the product of the potential and the charge carried through the circuit. When the cell operates reversibly, the electrical work done is determined by the free-energy change accompanying the cell reaction:

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[*] The symbol (*s*) refers to the solid state. Zn(Hg) and Pb(Hg) are two-phase systems consisting of an intermetallic compound, e.g., Pb_2Hg, in equilibrium with a saturated liquid amalgam.

$$\Delta F = -n\mathrm{FE} \tag{3}$$

where E = cell potential for reversible operation

nF = total charge flow for completion of cell reaction as written

n = number of faradays transferred for completion of cell reaction as written

F = faraday, 96,500 coulombs equiv^{-1}

Thus, for the above reaction, ΔF is the free-energy change attending the reaction of 1 mole of zinc in accordance with Eq. (1). It can be determined by measuring the cell potential for reversible operation, such as is adequately approached in voltage measurements with a potentiometer, which draws only a minute current from the cell. The use of the potentiometer is described under Exp. 34.

At constant temperature and pressure, the heat effect accompanying the direct irreversible reaction in which only *pv* work is done is equal to ΔH, the change in enthalpy for the process, while for the reversible execution of the reaction it is equal to $T\Delta S$, where ΔS is the corresponding change in entropy. The difference in these two quantities determines the electrical work done in the reversible process, since for the specified conditions of constant temperature and pressure $\Delta F = \Delta H - T\Delta S$. If $\Delta S > 0$, the electrical work done is greater than that equivalent to ΔH; the energy balance is achieved through heat absorbed by the cell from its surroundings in constant-temperature operation. If $\Delta S < 0$, heat is given up to the surroundings in the reversible operation of the cell at constant temperature and the electrical work becomes less than that equivalent to ΔH.

According to the Gibbs-Helmholtz equation,

$$\Delta F - \Delta H = T\left(\frac{\partial \Delta F}{\partial T}\right)_p = -T\Delta S \tag{4}$$

Since $\Delta F = -n\mathrm{FE}$,

$$\Delta H = -n\mathrm{FE} + n\mathrm{F}T\left(\frac{\partial \mathrm{E}}{\partial T}\right)_p \tag{5}$$

$$\Delta S = n\mathrm{F}\left(\frac{\partial \mathrm{E}}{\partial T}\right)_p \tag{6}$$

These equations are subjected to experimental test in this experiment. The cell voltage and its temperature coefficient are determined, and the value of ΔH obtained by use of Eq. (5) is compared with the literature value for the heat of reaction found calorimetrically.

Apparatus. H-type cell, preferably with sintered-glass disk in connecting arm; mercury; granular zinc; granular lead; zinc sulfate; lead sulfate; mortar and pestle; thermostats at several temperatures from 0 to 40°, or rapidly adjustable thermostat in this range; potentiometer assembly.

Procedure. The cell represented by (2) is particularly suited for experimental study. It is a cell *without transference;* i.e., it has no liquid junction and therefore no uncertain junction potential, provided the effect of the slight solubility of lead sulfate is considered negligible.

The H-type cell is shown in Fig. 42. For preparing these cells, sintered-glass disks sealed into straight tubes are available from supply houses. The coarse grade of sintered glass is preferred. Alternatively, an open tube plugged with clean glass wool may be used. The purpose of this disk or plug is to prevent solid lead sulfate from contaminating the zinc half-cell. Contact with the amalgam electrode is obtained by platinum wires sealed into the end of a glass tube. Mercury is placed in this tube, and the leads from the potentiometer dip into the mercury.

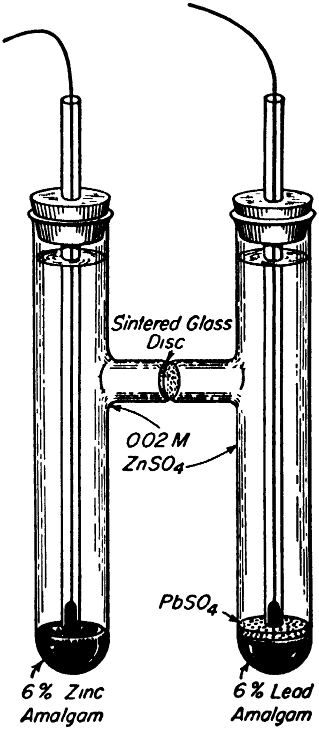

FIG. 42. Electrochemical cell for determination of thermodynamic functions.

About 500 ml of 0.02 *molal* $ZnSO_4$ is prepared. To 100 ml of this solution is added about 2 g of lead sulfate, and the mixture is shaken vigorously.

In all precise potential work, oxygen must be carefully excluded from the cell. If a nitrogen tank and purification train (page 395) are available, the solutions containing pure $ZnSO_4$ and $ZnSO_4 + PbSO_4$ are swept out with nitrogen during the preparation of the amalgams.

The amalgams are prepared by grinding the granular metal with mercury under a little dilute (0.5 *N*) H_2SO_4 in a mortar. The amalgams should be about 6 per cent of Zn or Pb by weight. The sulfuric acid prevents an oxide scum from forming on the surface and hastens the amalgamation. Some grinding of the zinc with mercury should be done before adding the acid; otherwise the granules will tend to float on the acid. The amalgams are carefully rinsed with distilled water and with three or four portions of $ZnSO_4$ solution; they are then transferred to their respective arms of the cell. If the zinc amalgam has thickened to form a sludge, moderate warming will render it mobile.

Zinc sulfate solution is added to the zinc electrode, and the $ZnSO_4$-$PbSO_4$ suspension to the lead electrode, care being taken not to allow excessive mixing of the two solutions. The platinum-glass leads are then introduced with the platinum completely immersed in the amalgam.

The potential is to be determined at several temperatures in the range 0 to 40°. Temperature intervals of 10 or 15° are convenient. For careful work the cell should be thermostated. The cell may take so long to reach equilibrium that a manually controlled bath cannot be recommended. A well-stirred ice bath is used for the 0° measurement.

Readings of the potential at each temperature are taken at intervals until a value constant within a few tenths of a millivolt is obtained; this value is taken to be the cell potential for reversible operation at the particular temperature. If erratic operation or continual drift of the cell voltage occurs, a new cell should be set up.

The first set of readings may be recorded starting at 0° and increasing the temperature. A check run is then made with descending temperature, starting at the highest point in the previous set.

Calculations. The potential is plotted against the absolute temperature and $(\partial E/\partial T)_p$ is obtained by drawing a tangent to the curve. The estimated reliability of the voltage measurements should be considered in drawing the curve.

Values of ΔF, ΔH, and ΔS are calculated for 25°C by use of Eqs. (3), (5) and (6), for both joules and calories as the energy unit. The heat of reaction for direct irreversible reaction is compared with that for the reversible case.

The value here obtained for ΔH is compared with that calculated for the cell reaction by use of calorimetrically determined heats of formation.[8] The heats of formation of the saturated zinc and lead amalgams are negligible[1,3] for the purposes of this calculation.

Practical Applications. The relation between ΔF and ΔH discussed in this experiment was studied down to low temperatures by Richards and led to the first expression of what is now known as the third law of thermodynamics.

Suggestions for Further Work. Various other cells may be studied, including a copper-zinc cell, in which ΔH and ΔF are nearly equal, a copper-lead cell, where ΔH is less than ΔF, and a silver-zinc cell, where ΔH is greater than ΔF.

Cadmium and cadmium sulfate may be used in place of zinc and zinc sulfate in the apparatus of this experiment.[5]

By extending these measurements to several different concentrations, it is possible to obtain the E^0 of the cell, the activity coefficients, heats of transfer, and the partial and integral heats of dilution of $ZnSO_4$[2,4] or of $CdSO_4$.[6]

In the case of the cadmium-lead system, thermodynamic data may be obtained for reactions involving the pure metals, using measurements of the electromotive force of the Cd-Cd amalgam couple by LaMer and Parks,[7] and of the Pb-Pb amalgam couple by Gerke.[3] The latter reference contains a wealth of practical information on the techniques of precise potential measurements.

References

1. Clayton and Vosburgh, *J. Am. Chem. Soc.*, **58**, 2093 (1936).
2. Cowperthwaite and LaMer, *J. Am. Chem. Soc.*, **53**, 4333 (1931).

3. Gerke, *J. Am. Chem. Soc.*, **44**, 1684 (1922).
4. LaMer and Cowperthwaite, *J. Am. Chem. Soc.*, **55**, 1004 (1933).
5. LaMer and Parks, *J. Am. Chem. Soc.*, **53**, 2040 (1931).
6. LaMer and Parks, *J. Am. Chem. Soc.*, **55**, 4343 (1933).
7. LaMer and Parks, *J. Am. Chem. Soc.*, **56**, 90 (1934).
8. Selected Values of Chemical Thermodynamic Properties, *Natl. Bur. Standards, Circ.*, **500** (1952).

39. POTENTIOMETRIC TITRATIONS

The important relation connecting electromotive force with concentration is applied to two oxidation-reduction reactions and one precipitation reaction. The practical applications in analysis are apparent. Indicators that change color at definite oxidation-reduction potentials are illustrated.

Theory.[2,5] A potentiometric titration is one in which the end point is detected by measuring the change in potential of a suitable electrode during the titration. The electrode whose potential indicates the change in activity or concentration of the ion being titrated is called the "indicator electrode."

When a substance takes on electrons, it is reduced, and when it loses electrons, it is oxidized. Reduction occurs, then, at the cathode where the electrons are transferred from the cathode to the surrounding ions, leaving the electrode positively charged, and oxidation occurs where the ions give up electrons at the anode.

The determining factor in the potential of the indicator electrode is the ratio of the activities a of the oxidized and reduced forms of the ion. A general reduction reaction may be written

$$\text{Ox} + e = \text{Red}$$

where e equals electron and Ox and Red refer to the oxidized and reduced states. The formula giving the electrode potential E for any mixture of these oxidized and reduced forms is

$$E = E^0 - \frac{RT}{\mathbf{F}} \ln \frac{a_{\text{red}}}{a_{\text{ox}}} \tag{1}$$

where E^0 equals the standard electrode potential.

This equation is of fundamental importance because it connects chemical equilibria and electrochemical measurements with reversible electrodes. It is useful in determining the concentration of ions. In titration curves the equation itself determines the shape of the curve and the numerical value of E^0 determines its position on the potential scale.

In order to use this equation quantitatively, it is necessary to have reversible electrodes, but the end point in a titration curve can be determined empirically without the use of this theoretical equation and with electrodes that are not necessarily reversible. Under these conditions the end point is indicated by a rapid change in voltage when a small amount of reagent is added. The steepest part of the curve, when voltage is plotted vertically against the number of milliliters of reagent added, indicates the point at which the two reactants are present in chemically equivalent amounts.

In certain types of precipitation reactions the potential of the indicator electrode remains constant as more of the titrating solution is added, because the concentration of added ions is fixed by the solubility. When all the material has been precipitated, however, the concentration of the added ions increases sharply and the electrode potential registers a sudden change.

The potentiometric titration has been shown to have great merit in the establishment of the oxidation-reduction levels of certain indicators such as methylene blue. In turn, the indicators serve to determine the characteristic potentials in organic oxidation-reduction systems.[1,7]

Apparatus. Potentiometer assembly; bright platinum electrode; calomel electrode; tungsten electrode; silver electrode; two burettes; 0.01 M solutions of the following reagents: ferrous sulfate, potassium dichromate, zinc sulfate, potassium ferrocyanide, ceric sulfate (in 0.5 M H_2SO_4), potassium chloride, silver nitrate; diphenylamine; *o*-phenanthroline–ferrous ion (Ferroin).

Procedure. The arrangement of apparatus for a typical potentiometric titration is shown in Fig. 43. For titrations with the bimetallic electrode systems to be described, the calomel electrode may be replaced by a tungsten electrode and the platinum by silver. A stirrer, preferably of the magnetic type, may also be provided. The potential measured on a uniformly stirred and a quiet solution may be somewhat different, particularly in the case of bimetallic electrode systems. However, a steady potential should be obtained in either case, and the sharp change at the end point will be duplicated regardless of stirring. The potential of an irreversible electrode (e.g., tungsten) is also strongly dependent on its surface condition; accordingly, before each titration the oxide layer or other contamination is removed from the electrode with fine emery paper.

Twenty-five milliliters of the ferrous sulfate solution is placed in the beaker with 100 ml of water; a few milliliters of concentrated sulfuric acid is added cautiously, and the potassium dichromate solution is titrated into the beaker from a burette with vigorous stirring. At first several milliliters are added at a time, but as the point of equivalence is approached, smaller and smaller volumes are added. The potential rises slowly at first, then rapidly, and then slowly again after the dichromate is present in excess. The voltages and burette readings are recorded for graphing.

A second set of readings may be taken in which 25 ml of the potassium dichromate solution is placed in the beaker and titrated with the ferrous sulfate solution in the burette.

Colored indicators, similar to indicators that are used for neutralization reactions, are available for oxidation and reduction reactions. They change color at definite oxidation potentials, just as the acid indicators change at definite hydrogen-ion activities. They find uses in biochemical problems.

The application of such indicators may be illustrated by diphenylamine, first used for this purpose by Knop.[4] When it is oxidized to give a compound which may be reduced to diphenylbenzidine, the color is changed from pale green to intense blue. Ferric ions tend to produce the blue color because the oxidation potential is so close to that of the ferrous-ferric system. However, if the ferric ions are removed as fast as formed by having phosphoric acid present, the blue color is not produced until all the ferrous ion in solution has been oxidized by the dichromate.

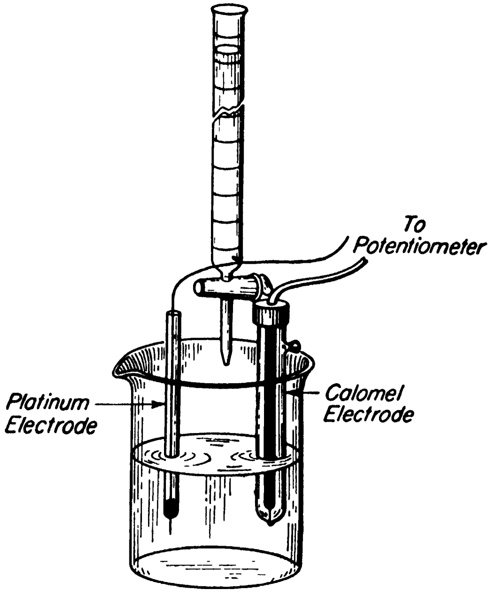

FIG. 43. Apparatus for potentiometric titrations.

Another indicator that is useful in the study of the reaction between ferrous iron and dichromate solution is *o*-phenanthroline–ferrous ion (Ferroin[3]). The red complex ferrous ion is oxidized to the pale-blue complex ferric ion at a relatively high level on the oxidation-reduction scale. The color change is relatively slow in titration with the dichromate solution, but sharp and distinct in the reverse titration.

The above titration is repeated twice, first with a small amount of diphenylamine and then with *o*-phenanthroline–ferrous ion added; the potentials at which the color changes occur are recorded and converted into the potential referred to the standard hydrogen electrode.

For a second experiment the precipitation of zinc with potassium ferrocyanide is suggested.[8] Twenty-five milliliters of 0.01 *M* zinc sulfate is placed in the beaker. An accurately measured excess of 0.01 *M* potassium ferrocyanide is thoroughly mixed with the sample, which is then allowed to stand at room temperature for 15 min. The precipitated sample is diluted to a total volume of 125 ml, and the platinum and tungsten electrodes are inserted in the solution. The excess ferrocyanide is titrated with 0.01 *M* ceric sulfate, potentiometer readings being taken as in the preceding experiment.

For a third experiment, chloride ion is titrated with silver nitrate solution using a silver-tungsten electrode pair. A platinum-tungsten pair may also be used. Twenty-five milliliters of 0.01 *M* potassium chloride solution is diluted to 125 ml with distilled water. One milliliter of 1:1 H_2SO_4 is added. This solution is titrated with 0.01 *M* silver nitrate, potentiometer readings being taken in the usual fashion.

Calculations. The titration curves for the ferrous sulfate and potassium dichromate are plotted; the observed voltages are plotted against the number of milliliters of reagent added, and the end point is determined from the steepest part of the curve. The validity of Eq. (1) can be checked approximately in the following manner: The concentrations of ferrous and ferric ions are calculated after several representative additions of dichromate, using the known molarities of the two reagents for the calculation. Assuming that the ferrous- to ferric-ion concentration ratio is equal to the ion activity ratio, these values are inserted into Eq. (1) along with the literature value for E^0, and the potential is calculated. The points are located on the titration plot and compared with experimental values. Exact correspondence should not be expected, since the above assumption is only approximately correct, and since some air oxidation of the ferrous ion may have occurred.

A second graph is prepared in which $\Delta E/\Delta C$ is plotted against C where E represents the potential and C the total number of milliliters. The quantity $\Delta E/\Delta C$ is a maximum at the equivalence point.

The voltages at which the oxidation-reduction indicators change color are compared with the accepted voltages as given in tables.

The titration curves for the zinc ferrocyanide and silver chloride systems are plotted with voltages as ordinate and milliliters of reagent added as abscissa. In these cases Eq. (1) does not apply at all, since irreversible electrode systems were used. Nevertheless, the sharp break in the voltage locates the end point of the titration accurately.

Practical Applications. Potentiometric titrations can be carried out advantageously for many oxidation-reduction, or precipitation, reactions. They are usually more accurate than titrations depending on other volumetric indicators, and they can be used when no suitable indicator is available. They can be used equally well in clear, colored, or turbid solutions. Neutralization titrations are considered in Exp. 35.

Suggestions for Further Work. Any of the oxidants potassium dichromate, potassium permanganate, or ceric sulfate may be used for titrating ferrous or ferrocyanide ion.

Iodine solutions are readily titrated potentiometrically with sodium thiosulfate, or vice versa.

References

1. Clark, "Topics in Physical Chemistry," 2d ed., The Williams & Wilkins Company, Baltimore (1953).
2. Furman, *Ind. Eng. Chem., Anal. Ed.*, **14**, 367 (1942).
3. Hume and Kolthoff, *J. Am. Chem. Soc.*, **65**, 1895 (1943).
4. Knop, *J. Am. Chem. Soc.*, **46**, 263 (1924).
5. Kolthoff and Furman, "Potentiometric Titrations," 2d ed., John Wiley & Sons, Inc., New York (1931).
6. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York (1952).
7. Neilands and Stumpf, "Outlines of Enzyme Chemistry," John Wiley & Sons, Inc., New York (1955).
8. Sturgis, *Ind. Eng. Chem., Anal. Ed.*, **11**, 267 (1939).

CHAPTER 12

DIELECTRIC CONSTANT

40. DIELECTRIC CONSTANT AND DIPOLE MOMENT. CAPACITANCE DETERMINATIONS BY THE RESONANCE METHOD

In this experiment the dipole moment of a polar molecule is determined; the necessary dielectric-constant measurements are made by the resonance method.

Theory. A *dielectric* is a medium which under the influence of an electric field is capable of storing energy in the field. This storage of electrical energy in a static form is accomplished practically by means of the capacitor, or condenser, which in its simplest form consists of two conductors separated by a dielectric. The dielectric must obviously have insulating properties, but the property of permitting energy storage is distinct from that of offering a high resistance to the passage of an electric current, and two materials which possess essentially the same specific resistance will not in general show the same ability for energy storage in an electric field. Since an electric field can be established in a vacuum, and electrical energy stored thereby, a vacuum is a dielectric,* and it is the standard with reference to which the dielectric properties of other mediums are measured.

If a condenser composed of two parallel plates with a vacuum dielectric is connected to a battery or other source of electrical potential, electrons will be removed from one plate and supplied to the second. This transfer of electrons cannot continue indefinitely, however, since it progressively becomes more difficult to remove an electron from the first plate, where a deficiency now exists, and more difficult to force an electron on the second plate, where an excess is present. As the transfer process proceeds, a difference in potential between the two plates is produced, and when this potential becomes equal in magnitude to that of the source, the net transfer of electrons will stop. It is found that the quantity q of electricity which must be moved from one plate to the other in order to produce a potential difference V between the plates is given by

$$q = CV \tag{1}$$

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* Condensers with vacuum dielectric are not just a convenient fiction, but are used in radio-frequency power-generating equipment.

where C is called the *capacitance* of the condenser and is a constant under any given set of conditions, i.e., fixed area and separation of plates, etc. When q is expressed in coulombs and V in volts, the capacitance C is expressed in a unit called the *farad.* For practical purposes this unit is too large, so that C is usually expressed in microfarads (1 μf $= 10^{-6}$ farad) or micromicrofarads (1 $\mu\mu$f $= 10^{-6}\ \mu$f $= 10^{-12}$ farad).

There is energy stored in the condenser because of the work done in the charging process. This energy may be calculated in nontechnical fashion as follows: If the charge q coulombs is moved in t seconds, the average charging current is $q/t = CV/t$ amperes; the average potential against which this current is delivered is $V/2$ volts. The work done and hence the energy stored are then given by

$$E = i_{\text{avg}} V_{\text{avg}} t = \frac{CV^2}{2} \text{ joules} \tag{2}$$

If now the vacuum dielectric is replaced by a material dielectric, it will be found that the capacitance of the condenser has been increased. The ratio of the capacitance C_x of the condenser with the given dielectric to its capacitance C_0 with a vacuum dielectric is called the *dielectric constant* ϵ of the dielectric medium. From Eq. (2) it is seen that the energy stored in the condenser has also been increased by the substitution of a material dielectric for the vacuum dielectric.

If we consider first the simplest case of a gaseous dielectric composed of nonpolar molecules, the interactions between which are negligible, this increase in the energy stored is due to the strain created in the molecules under the stress of the electric field in the condenser. Under the influence of the electric field the molecules become polarized; i.e., an actual displacement of electrons takes place within a molecule, the centers of charge of negative and positive electricity are separated, and the normally nonpolar molecule acquires an electric moment. The magnitude of this *induced* moment depends on the intensity of the field acting on the molecule, upon the characteristic properties of the molecule itself, and upon the orientation of the molecule with respect to the direction of the field. Because of thermal agitation a single molecule will in a period of time assume all possible orientations with reference to a fixed direction, and in terms of the average properties—it is average properties that are determined experimentally—we have

$$\bar{m} = \alpha F \tag{3}$$

where $\bar{m}$ = average electric moment per molecule
F = electric field intensity
α = a positive molecular property called the *polarizability* of the molecule

The energy stored in the dielectric through this polarization process depends upon the magnitude of this induced moment per molecule and the number n of molecules per cubic centimeter, and will be reflected in the magnitude of the dielectric constant. A straightforward application of electrostatic theory leads to the relation

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi n\alpha \tag{4}$$

This relation is usually transformed by multiplying both sides by the ratio of the molecular weight M to the density d in grams per cubic centimeter to define a new quantity P called the *molar polarization:*

$$P = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} = \frac{4}{3}\pi\frac{nM}{d}\alpha = \frac{4}{3}\pi N\alpha \tag{5}$$

where $$\frac{nM}{d} = \text{the Avogadro number } N$$

Equation (5) is called the Clausius-Mosotti equation. The molar polarization is a molecular property which gives information concerning the electrical properties of the molecule.

If the polarizability α is a constant, the molar polarization P will also be constant, and in particular will be independent of the temperature. Experimental measurements of densities and dielectric constants show that this is indeed true for many gases and vapors. Even for some liquids (such as benzene and carbon tetrachloride), where interactions between the molecules are certainly greater than in the gas phase, the molar polarization is very nearly independent of the temperature.

There exists, however, a second class of compounds for which the molar polarization is abnormally large and is found to be a function of the temperature, even when calculated from measurements made on the material in the gas phase. This result indicates that the polarizability depends upon the temperature, a fact which has been explained by Debye[2] by assuming that even in the absence of an electric field the molecules concerned possess an electric moment, or dipole moment.

Again considering the material to be in the gaseous state, in the absence of the electric field there will be no net electric moment per molecule in any specified direction, because over a period of time the thermal motion of the molecules causes them to take up all possible orientations relative to the specific direction. In the presence of an electric field, two effects must now be considered. First, there will be a distortion of the electronic configuration of the polar molecule just as for a nonpolar molecule. Second, there will be a tendency for the polar molecules to align themselves in the direction of the field, giving rise now to a net electric moment, in the direction of the field, due to their orientation. This tendency toward a specific orientation is opposed by the forces of thermal agitation, which tend to produce a completely random orientation. If the polar molecule were to move out of alignment with the field, potential energy would be acquired; if this potential energy of the molecule were large compared with the average energy of thermal agitation, then a practically complete alignment of the dipoles in the field would take place, because the average molecule could never acquire enough energy to move in opposition to the field. The energy of thermal agitation is $\frac{3}{2}kT$ per molecule where $k = R/N$. At room temperature it is 6.2×10^{-14} erg/molecule. The maximum energy of a dipole of magnitude μ electrostatic units in an electric field of strength F is μF ergs. Assuming a dipole moment of 5×10^{-18} esu, which is large for ordinary molecules, and a field of strength 1 esu of potential per centimeter (300 volts cm^{-1}) the maximum energy of the dipole in the field is 5×10^{-18} erg, or approximately 0.01 per cent of the average energy of thermal agitation. It is thus obvious that nothing like a complete alignment of the dipoles in the field is possible.

The orientation of the dipoles in the field, while incomplete, will be no longer random. Orientations in which the dipole is close to alignment with the field will be favored over those in which the dipole is opposed to the field, so that there will be a contribution to the average electric moment per polar molecule due to this tendency of the molecule to orient itself in the electric field. This contribution $\bar{m}_0$ can be shown to be given by the relation

$$\bar{m}_0 = \frac{\mu^2 F}{3kT} \tag{6}$$

There will also be a contribution $\bar{m}_d$ to the electric moment per molecule from the deformation of the molecule, which, as for a nonpolar molecule, will be proportional to the field strength:

$$\bar{m}_d = \alpha_0 F$$

The total average electric moment per polar molecule $\bar{m}$ in the presence of the field will then be

$$\bar{m} = \alpha F = \left(\alpha_0 + \frac{\mu^2}{3kT}\right) F \tag{7}$$

Correspondingly, the expression for the molar polarization becomes

$$P = \frac{4}{3}\pi N\alpha = \frac{\epsilon - 1}{\epsilon + 2}\frac{M}{d} = \frac{4}{3}\pi N\left(\alpha_0 + \frac{\mu^2}{3kT}\right) = \frac{4}{3}\pi N\alpha_0 + \frac{4\pi N\mu^2}{9kT} \tag{8}$$

The contribution to the molar polarization from the distortion of the molecule by the electric field is called the *distortion polarization* P_D and that due to the orientation of the permanent dipoles in the field is referred to as the *orientation polarization* P_μ

$$P = P_D + P_\mu \qquad P_D = \frac{4}{3}\pi N\alpha_0 \qquad P_\mu = \frac{4}{3}\pi N\frac{\mu^2}{3kT} \tag{9}$$

Measurements of the dielectric constant and density of the polar gas at different temperatures thus may be combined to permit a determination of both the dipole moment and the mean polarizability of the molecules. A plot of P versus $1/T$ will be a straight line of slope equal to $\frac{4}{9}\pi N(\mu^2/k)$ and intercept equal to $\frac{4}{3}\pi N\alpha_0$. When applicable, this is the best method for the determination of the dipole moment.[11] Unfortunately such measurements on materials in the gas phase are not practical for most compounds of chemical interest. A second method may be used, however, which permits a determination of the dipole moment of a compound from dielectric-constant and density measurements at constant temperature made on dilute solutions of the polar material in a *nonpolar* solvent.

Let the solution contain, per cubic centimeter, n_1 nonpolar solvent molecules of polarizability α_1 and molecular weight M_1, and n_2 polar solute molecules of polarizability α_2 and molecular weight M_2. If ϵ_{12} is the dielectric constant of the solution, then we can write [compare Eq. (4)]

$$\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2} = \frac{4}{3}\pi(n_1\alpha_1 + n_2\alpha_2) \tag{10}$$

For the transformation of this equation to a more useful form, the following relationships are required:

$P_1 = \frac{4}{3}\pi N\alpha_1$ = molar polarization of solvent in solution
$P_2 = \frac{4}{3}\pi N\alpha_2$ = molar polarization of solute in solution
N = Avogadro number
$f_1 = \dfrac{n_1}{n_1 + n_2}$ = mole fraction of solvent in solution
$f_2 = \dfrac{n_2}{n_1 + n_2}$ = mole fraction of solute in solution
$d_{12} = \dfrac{n_1M_1 + n_2M_2}{N}$ = density of solution
M = molecular weight
ϵ_1 = dielectric constant of pure solvent
P_1^0 = molar polarization of pure solvent

It may be shown that Eq. (10) can be transformed to read

$$\frac{\epsilon_{12} - 1}{\epsilon_{12} + 2}\,\frac{(f_1M_1 + f_2M_2)}{d_{12}} = f_1P_1 + f_2P_2 = P_{12} \tag{11}$$

where P_{12} is termed the molar polarization of the mixture. If we now assume that the solvent in the solution retains the properties that it exhibits when pure, an assumption which is justified for *dilute* solutions, then

$$P_1 = P_1^0 = \frac{\epsilon_1 - 1}{\epsilon_1 + 2}\frac{M_1}{d_1} \tag{12}$$

$$P_2 = \frac{P_{12} - f_1 P_1^0}{f_2} \tag{13}$$

When the value of P_2 is calculated from measurements made on solutions of different concentrations, it is found that P_2 is a function of the concentration. This is to be expected, since in the derivation of Eq. (4) it is assumed that there are no interactions between the molecules. In the case of the dilute solution, there are three kinds of interactions involved: interactions between solvent molecules, between solvent molecules and solute molecules, and between two solute molecules. The molar polarization of a nonpolar compound such as benzene is found to be practically the same whether calculated from measurements on the vapor or on the liquid. Thus, interactions of the first kind are unimportant. The interactions between the polar solute molecules and those of the nonpolar solvent are more important, but their effect is detected only in the most accurate measurements (Exp. 41). As two polar molecules approach one another, however, there takes place a very strong interaction, which is the primary cause of the observed dependence of P_2 on the concentration.

Since the magnitude of the interaction depends on the distance between the dipoles, the extrapolation of the observed P_2 values to infinite dilution will yield a value P_2^0 for the molar polarization of the solute which is free from the effect of dipole-dipole interaction. (This procedure is comparable to the use of the method of limiting densities for the accurate determination of the molecular weight of a real gas.) Then, since the only interactions of consequence have been eliminated,

$$P_2^0 = P_{2_D}^0 + P_{2_\mu}^0 = \frac{4}{3}\pi N\alpha_0 + \frac{4}{3}\pi N\frac{\mu^2}{3kT} \tag{14}$$

The extrapolation itself is often arbitrary because use is not made of the form of the deviation function. There are several modes of procedure by which greater convenience as well as greater accuracy can be achieved in the determination of the polarization P_2^0, one of which is the use of an analytical approach originally proposed by Hedestrand.[7]

The value of μ can be calculated if the distortion polarization $P_{2_D}^0$ can be evaluated. This is readily done with adequate accuracy by means of the relation

$$P^0_{2_D} = \frac{n^2 - 1}{n^2 + 2}\frac{M_2}{d_2} = M_2r \tag{15}$$

where M_2r is the molar refraction of the solute and can be calculated either from the measured refractive index n and density d_2 of the solute or by means of tables of atomic and structural refractions. With results obtained for the D line of sodium, Eq. (15) will not hold exactly, but since for a polar molecule $P^0_{2_D}$ is generally small compared with P^0_2, a moderate error in the determination of $P^0_{2_D}$ will exert a negligible effect on the final value for the dipole moment.

The relation expressed by Eq. (15) arises because, according to the electromagnetic theory, the square of the refractive index of a medium will be equal to the dielectric constant of the medium if both quantities are measured for electromagnetic waves of the same frequency. For frequencies as high as optical frequencies, such as that of the sodium D line, the contribution to the dielectric constant due to the partial orientation of the dipoles in the field vanishes. For the production of the preferred orientation under the influence of an electric field, the whole polar molecule must rotate to a greater or lesser extent. For this process there is required a finite time, which depends on the size and shape of the molecule, the viscosity of the solvent, and the temperature. With small molecules under normal working conditions, this time is short enough (about 10^{-10} sec) that the orientation effect persists to frequencies much higher than those regularly used in dipole-moment measurements; such frequencies are ordinarily of the order of 10^6 cycles/sec or less. For optical frequencies, where 1 half-cycle lasts for approximately 10^{-15} sec, there is just not time enough for the orientation of the dipole in the field to take place before the field changes direction. The distortion effect still persists, however, because the inertia of the electrons is so low that they can readily shift at the rate required to follow the high-frequency field.

For large molecules such as protein molecules, the orientation contribution drops out at frequencies readily employed in experimental work, and information concerning the size and shape of the molecules has been derived from studies of the dielectric constants of their solutions as a function of the frequency.[3]

Apparatus. Resonance-type apparatus for measurement of dielectric constant; nitrobenzene or other polar compound; benzene or other nonpolar solvent; pycnometer or Westphal balance.

Procedure.[5,11] In order to use the equation $\epsilon = C_x/C_0$ for accurate determinations, elaborate calibrations for lead-wire and stray-capacitance effects are necessary. For the work of the laboratory it is convenient to use a dielectric cell which is arranged so that capacitance measurements are made with a variable condenser rather than with one having fixed plates. Measurements can then be made of capacitance differences between two fixed positions (*a* and *b*) of the rotor plates, first when the plates of the condenser are in air, and then when they are immersed in the liquid or solution. It is possible to use air, rather than a vacuum, as the reference medium because the dielectric constant of air, while not unity, is very close to unity.

The dielectric constant of the liquid is obtained by dividing the difference in capacitance between the positions *a* and *b* when the plates are immersed in the liquid by the corresponding difference with air as the dielectric, or

$$\epsilon = \frac{C_{b,\text{liq}} - C_{a,\text{liq}}}{C_{b,\text{air}} - C_{a,\text{air}}} \tag{16}$$

This relation holds because the total capacitance of two condensers connected in parallel is equal to the sum of the capacitances of the individual condensers.

In this experiment the capacitance measurements are to be made by a resonance method. This method is capable of giving quite accurate results,[4] although it does not possess the extremely high accuracy possible with the heterodyne-beat method. On the other hand, it has the tremendous advantage that it is suitable for work with liquids having an appreciable electrical conductance.

If a secondary circuit containing a parallel combination of inductance L and capacitance C is loosely coupled,* either inductively or capacitatively, to a primary source of alternating current, there will be produced in the secondary circuit an alternating current and across it an alternating potential. If the frequency f of the source and the inductance L of the secondary circuit are fixed, the secondary current and voltage will vary as the capacitance C is changed. For some critical capacitance value C_r the current or energy in the secondary circuit will have a maximum value; the secondary circuit is then said to be in *resonance* with the electrical field of frequency f. The value of C_r will be given very closely by the relation $C_r = 1/(2\pi f)^2L$, but the important fact here is that there exists a unique capacitance value C_r for which resonance is obtained and which therefore provides a reference point for the capacitance increment measurements required for dielectric-constant calculations by means of Eq. (16).

The standard apparatus assembly for the resonance method is sche-

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* When two inductances are so placed that lines of flux from one cut the turns of the other, they are said to be inductively coupled. For loose coupling comparatively few of the lines of flux from the first inductance link with the second.

matically represented in Fig. 44. The capacitance in the secondary circuit is a parallel combination of the dielectric-constant cell C_x, a calibrated precision-tuning condenser C_s, and a coarse-tuning condenser C_a. The secondary circuit is loosely inductively coupled to the oscillator, which generates a constant-frequency current which flows through the plate-circuit tank coil L_p. The rotor of the empty dielectric cell is set in position *a* (minimum capacitance). The precision condenser is set near the high end of its range and the secondary circuit brought to resonance by adjustment of the coarse-tuning condenser C_A. The condition of resonance may be indicated by a maximum in the voltage across the tuned circuit as measured by a *vacuum-tube* voltmeter, or by a minimum in the d-c plate current of the oscillator tube. The critical capacitance setting corresponding to resonance is now located precisely by means of the precision condenser. The rotor of the cell is then moved to position *b*, after which the condition of resonance is reestablished by resetting the precision condenser, *the coarse-tuning condenser remaining unaltered.* Since the total capacitance of the secondary circuit always has the value C_r at resonance, the capacitance increment in the cell, $C_{b,\text{air}} - C_{a,\text{air}}$, is equal to the decrease in the capacity of the standard condenser required to reestablish resonance. These same operations are carried out with a solution as the dielectric to obtain $C_{b,\text{liq}} - C_{a,\text{liq}}$, and the dielectric constant of the liquid is calculated by means of Eq. (16). For accurate work the standard condenser must be carefully calibrated.[11]

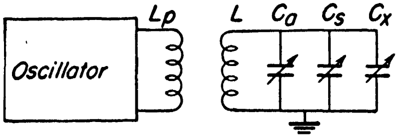


FIG. 44. Schematic representation of standard resonance apparatus.

An alternative resonance circuit which is particularly suitable for student use is shown in Fig. 45; its operation is described in greater detail elsewhere.[1] The 6E5 tuning-eye tube shown above acts both as an oscillator tube and as a resonance detector. The piezoelectric quartz crystal in the grid circuit of the tube acts like a tuned circuit whose natural frequency depends upon its thickness and upon the orientation of the plate relative to the crystal axes of the quartz crystal from which it was cut. Because of this property of the crystal, oscillations will begin in the circuit when the natural frequency of the plate tuning circuit *LC*, i.e., the frequency $f = 1/2\pi \sqrt{LC}$, is adjusted to that of the quartz crystal by suitable setting of the variable condensers shown. The coupling in this system—i.e., the means by which energy can be transferred between the plate and grid circuits—is achieved through the plate-grid capacitance in the tube. The plate and grid act as the two plates of a condenser of small capacitance which permits some passage of alternating current.

If the capacitance in the plate tuning circuit is increased from low capacitance, when the natural frequency of the circuit approaches that of the quartz crystal, oscillation sets in, and the tuning eye of the tube begins to close. As the capacitance is further increased, oscillation will cease abruptly, with a corresponding sudden increase in the shadow angle. As the tuning capacitance is gradually increased, then, the shadow angle will first gradually decrease to a minimum and then will suddenly widen as oscillation ceases. This critical off-resonance capacitance setting, characterized by the sudden widening of the shadow angle, is the reference point for capacity measurements with this circuit.

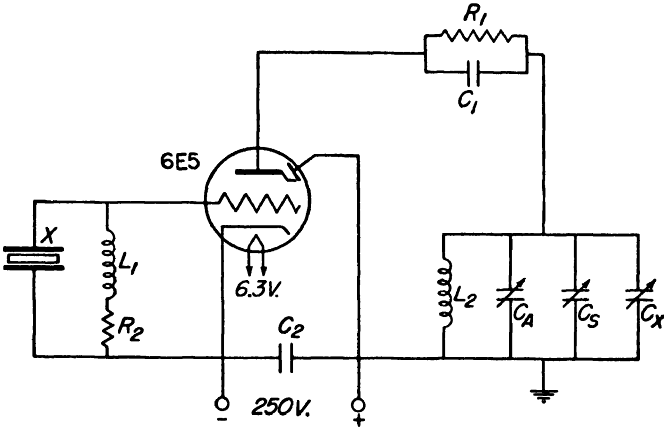


FIG. 45. Dielectric-constant meter circuit: R_1 = 150,000 ohms; R_2 = 40,000 ohms; L_1 = 2.5-millihenrys R.F. (radio-frequency) choke; X = 1-megacycle quartz crystal; C_S = 150-μμf variable air condenser, precision type; L_2 = inductance: 60 turns, No. 25 enameled wire, close-wound on 1½-in.-diameter coil form; C_1 = 0.001-μf 450 W.V. (working-voltage) condenser; C_2 = 0.01-μf 450 W.V. condenser; C_X = dielectric-constant cell; C_A = 150-μμf variable air condenser.

As before, the dielectric cell containing the desired medium is set for minimum capacitance, the standard condenser is set near the upper limit of its usable range, and the adjusting condenser tuned to bring the plate circuit to resonance, as shown by the response of the tuning-eye tube. The critical capacitance setting is then located exactly by means of the standard condenser. The capacitance of the cell is raised to its maximum value, and the condition of resonance is reestablished by resetting the standard condenser, *the adjusting condenser remaining unaltered.* The capacitance increment in the cell is equal to the decrease in the capacitance of the standard condenser required to compensate for it. These same operations are carried out with air as the dielectric, and the dielectric constant of the medium is calculated by means of Eq. (16).

A suitable dielectric-constant cell may be made from a midget variable condenser, the number of rotor and stator plates of which is adjusted to give a convenient capacitance increment. The condenser, which should have two rotor bearings, is mounted on a hard-rubber plate. An insulated arm is fastened to the rotor shaft, and two brass pins are driven into the hard-rubber plate to provide reproducible minimum and maximum capacitance settings. The cell is connected to the rest of the circuit by means of coaxial cable and cable connectors. A small Berzelius type of beaker (i.e., lipless) may be used as a liquid container; it should be surrounded by a grounded metal shield, which can be fastened to the top plate for support, in order to minimize stray-capacitance effects.

Dielectric-constant measurements are made on benzene and on dilute solutions of nitrobenzene or other polar molecule in benzene. Concentrations suggested for the work are 1, 2, 3, and 4 mole per cent of solute. Approximately 100 ml of each solution is made up by weight; an *accurate* balance must be used for these weighings. The densities of the solutions are also measured, either pycnometrically or by means of the Westphal balance.

Calculations. The object of the experiment is to determine the dipole moment of a polar molecule. For the computation it is required to evaluate the molar polarization of this solute at infinite dilution, P_2^0. In the Hedestrand procedure which we adopt it is assumed that for the dilute solutions which are involved, the dielectric constants and densities can be accurately expressed as linear functions of the mole fraction of the solute, thus

$$\epsilon_{12} = \epsilon_1 + af_2$$

and

$$d_{12} = d_1 + bf_2$$

Here ϵ_1 and d_1 represent the dielectric constant and density, respectively, of the solvent at the temperature at which the measurements have been made. The coefficients a and b are obtained from appropriate plots of ϵ_{12} and d_{12} against f_2. The quantities ϵ_1 and d_1 are characteristic of the actual solvent sample used in the experiment. The values of ϵ_{12} and d_{12} are then substituted into the equation,

$$P_2 = \frac{1}{f_2}\left[\left(\frac{\epsilon_{12}-1}{\epsilon_{12}+2}\right)\left(\frac{f_1M_1+f_2M_2}{d_{12}}\right) - f_1\left(\frac{\epsilon_1-1}{\epsilon_1+2}\right)\left(\frac{M_1}{d_1}\right)\right] \tag{17}$$

a modified form of Eq. (11). In this way there can be obtained an expression for P_2 as a function of f_2 which is valid in the dilute solution range. The limiting value of P_2, i.e., P_2^0, may be evaluated by setting f_2 equal to zero, in which case

$$P_2^0 = A(M_2 - Bb) + Ca$$

where $A = \dfrac{\epsilon_1 - 1}{\epsilon_1 + 2}\dfrac{1}{d_1}$

$B = M_1/d_1$

$C = \dfrac{3M_1}{(\epsilon_1 + 2)^2 d_1}$

Halverstadt and Kumler[6] have described a modification of the Hedestrand procedure. Other pertinent comments about the computations have been given by Kwestroo and associates.[8]

The orientation polarization $P^0_{2\mu}$ is then calculated by means of Eqs. (14) and (15), and from it the value of the dipole moment of the molecule is obtained, since

$$P^0_{2\mu} = \frac{4}{3}\pi N \frac{\mu^2}{3kT}$$

or

$$\mu = 0.0127 \times 10^{-18} \sqrt{P^0_{2\mu}T}$$

Practical Applications. Electric-moment data have contributed much to the solution of chemical and physical problems. Since the electric moment is a measure of the electrical symmetry or lack of symmetry in a molecule, its determination may assist in the solution of problems of molecular structure. Such data have also contributed to the improvement of our understanding of association and compound formation in solution, and of resonance effects in polar molecules, directive influences in reactions of organic chemistry, and energy losses in commercial materials.

Suggestions for Further Work. The electric moments of a series of ortho-, meta-, and para-like disubstituted benzene derivatives may be determined to show the effect of the change of position of groups on the polarity of a molecule.

References

1. Bender, *J. Chem. Educ.*, **23**, 179 (1946).
2. Debye, "Polar Molecules," Reinhold Publishing Corporation, New York (1929).
3. Elliott and Williams, *J. Am. Chem. Soc.*, **61**, 718 (1939); Williams, *Trans. Faraday Soc.*, **30**, 723 (1934).
4. Groves and Sugden, *J. Chem. Soc.*, **1934**, 1094.
5. Hartshorn, "Radio-frequency Measurements by Bridge and Resonance Methods," John Wiley & Sons, Inc., New York (1941).
6. Halverstadt and Kumler, *J. Am. Chem. Soc.*, **64**, 2988 (1942).
7. Hedestrand, *Z. physik. Chem.*, **B2**, 428 (1929).
8. Kwestroo, Meijer, and Havinga, *Rec. trav. chim.*, **73**, 717 (1954).
9. LeFevre, "Dipole Moments," 3d ed., Methuen & Co., Ltd., London (1954).
10. Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Company, Inc., New York (1955); *Chem. Revs.*, **6**, 549 (1929).
11. Smyth *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Chap. 24, Interscience Publishers, Inc., New York (1949).

41. DIELECTRIC CONSTANT AND DIPOLE MOMENT. CAPACITANCE DETERMINATIONS BY THE HETERODYNE-BEAT METHOD

The heterodyne-beat method of determining the dielectric constant of a solution is the one most commonly used by chemists for dipole moment studies. It is illustrated in this experiment.

Theory.[4,5] In order to obtain the electric moment of a molecule in solution, dielectric-constant and density determinations are required. The pertinent theory has been outlined in Exp. 40. For accurate measurements of the dielectric constants of liquids and solutions having extremely low conductance, the heterodyne-beat method is probably the best available at the present time. The principle on which it is based is schematically represented in Fig. 46.

A radio-frequency signal of constant frequency f_0, generated by a fixed-frequency oscillator, and a second signal of frequency f, generated by a variable-frequency oscillator, are fed into a "mixer" tube whose function is to produce in its output voltage a component of frequency $|f - f_0|$. This difference frequency, or beat frequency, will be in the audio range when f and f_0 are nearly equal and can be detected by earphones or other suitable means.

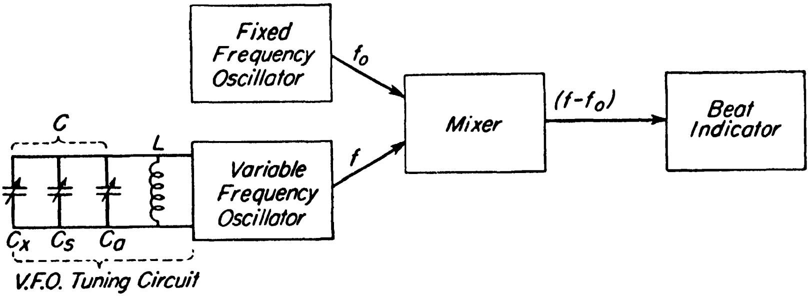


FIG. 46. Principle of the heterodyne-beat method: C_x, dielectric-constant cell; C_s, precision condenser; C_a, rough tuning condenser.

The frequency of the variable oscillator will be given very closely by the relation

$$f = \frac{1}{2\pi \sqrt{LC}}$$

where L and C represent the inductance and capacitance in the oscillator tuning circuit; for complete stability of all other circuit elements, the frequency is uniquely determined by the value of the tuning capacitance. If, for some capacitance setting, $f \gg f_0$, the beat frequency will be outside the audible range. An increase in C will lower the beat frequency, which will pass through the audible range from high pitch to low and will reach zero when $f = f_0$. A further increase in C will again produce a beat note, which now will increase with C until it passes beyond audibility. The reference point for the measurement of capacitance increments by the heterodyne-beat method is the critical capacitance setting corresponding to a selected beat frequency, which is usually zero beat.

The potential accuracy of the heterodyne-beat method is very high. Since the inductance L is constant, differentiation of the frequency-determining relation gives

$$\frac{\Delta f}{f} = -\frac{1}{2}\frac{\Delta C}{C}$$

If the fixed oscillator frequency is 1 megacycle, (1,000 kilocycles) and a beat frequency of 5 cycles/sec can be distinguished from zero beat, the detectable change of capacitance in the circuit is 1 part in 100,000. Actually it is possible to locate zero beat to within 1 cycle/sec or less, yielding a potential sensitivity of the order of 1 part per million. The accuracy actually attained in practice is, of course, limited by the efficiency of the experimental equipment employed.[5]

Apparatus. The principle of the operation of the heterodyne-beat method for the measurement of capacitance (and dielectric constant) has been indicated. There are a number of vacuum-tube circuit combinations which are suitable. Several of them are described in the LeFevre[4] and Smyth[5] monographs, so that no details will be given here. In addition, there are required a pycnometer or Westphal balance, a nonpolar solvent, and polar substances such as nitrobenzene or acetonitrile, etc.

Procedure. Except for the different method of locating the critical capacitance settings, the dielectric-constant determinations on the dilute benzene or hexane solutions of the substance whose electric moment is desired are carried out as described under Exp. 40. Density measurements are also made on the solutions.

Calculations. From the experimentally determined concentrations, dielectric constants, and densities of the solutions employed, the dipole moment of the solute molecule is calculated as explained under Exp. 40.

Practical Applications. The introduction of the heterodyne-beat method for the determination of the dielectric constant made possible for the first time really accurate determinations of the electric moments of gaseous molecules.[1,3,6] With the increased accuracy obtainable in the case of liquids, it is possible to study the effect of a change of nonpolar solvent on the magnitude of the measured electric moment of a given solute molecule. A slight but definite dependence upon the dielectric constant of the solvent medium has been established.[2]

Suggestions for Further Work. The dipole moment of a less polar molecule such as chloroform may be determined. Careful attention to detail is required for accurate results in such work.

References

1. Debye, "Polar Molecules," Reinhold Publishing Corporation, New York (1929).
2. Frank, *Proc. Roy. Soc. (London)*, **A152**, 171 (1935).
3. Hurdis and Smyth, *J. Am. Chem. Soc.*, **64**, 2829 (1942).
4. LeFevre, "Dipole Moments," 3d ed., Methuen & Co., Ltd., London (1954).
5. Smyth *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Chap. 24, Interscience Publishers, Inc,. New York (1949); Smyth, "Dielectric Behavior and Structure," McGraw-Hill Book Company, Inc., New York (1955).
6. Zahn, *Phys. Rev.*, **24**, 400 (1924).

CHAPTER 13

COLLOIDS

42. VISCOSITY OF HIGH-POLYMER SOLUTIONS

Viscosity determinations are very important in the study of high polymers. Using simple viscosity measurements, the average molecular weight of the polymer may be determined and certain qualitative conclusions may be made as to the general form of the macromolecules in solution.

Theory. Einstein[2] showed that the viscosity η of a dilute suspension of small rigid spheres is given by

$$\eta = \eta_0\left(1 + \frac{5}{2}\phi\right) \quad \text{or} \quad \frac{(\eta/\eta_0) - 1}{\phi} = \frac{\eta_{sp}}{\phi} = \frac{5}{2} \tag{1}$$

where η_0 = viscosity of solvent

ϕ = total volume of spheres per milliliter of suspension

Since $(\eta/\eta_0) - 1$ occurs frequently in the theory of the viscosity of solutions, it is given a special symbol and name: η_{sp}, specific viscosity. The viscosity increment is greater than $5/2$ for nonspherical high-polymer molecules.

In the case of polymer solutions it is not possible to calculate the volume occupied by polymer in an unambiguous way, and so concentrations are generally expressed in terms of weight of polymer per unit volume (usually 100 ml). It is necessary to extrapolate η_{sp}/c to zero concentration since this ratio depends upon concentration. Plots of η_{sp}/c versus c are generally linear in the low-concentration range, and the extrapolated value is called the intrinsic viscosity,[6] $[\eta]$.

$$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} = \lim_{c \to 0} \frac{1}{c} \ln\left(\frac{\eta}{\eta_0}\right) \tag{2}$$

where c is the number of grams of polymer in 100 ml of solution. In order to show that η_{sp}/c and $(1/c) \ln (\eta/\eta_0)$ extrapolate to the same limit at zero concentration, the logarithmic function may be expanded as an infinite series

$$\ln \frac{\eta}{\eta_0} = \ln (1 + \eta_{sp}) = \eta_{sp} - \frac{\eta_{sp}^2}{2} + \cdots$$

Since the second and higher order terms in η_{sp} become negligible compared to the first as concentration approaches zero, the functions given in Eq. (2) extrapolate to the same limit.

The following equation expresses the relation between intrinsic viscosity and the molecular weight of the high polymer.

$$[\eta] = KM^a \tag{3}$$

The exponent *a* is a function of the geometry of the molecule in solution and varies from 0.5 for tightly curled polymer molecules to about 1.7 for rigidly extended molecules. The constants *a* and *K* depend upon the type of polymer, the solvent, and the temperature of the viscosity determinations; they are determined experimentally by measuring the intrinsic viscosities of polymers for which the molecular weight has been determined by an independent method, such as osmotic pressure. The values of *K* and *a* listed in Table 1 have been determined for fractionated polymers, which are more homogeneous than the unfractionated polymer studied in the laboratory.

TABLE 1. PARAMETERS FOR EQ. (3)[a]

Polymer	Solvent	Temp, °C	*K*	*a*
Cellulose acetate	Acetone	25	1.49×10^{-4}	0.82
Polyisoprene	Toluene	25	5.02×10^{-4}	0.67
Polystyrene	Toluene	25	3.7×10^{-4}	0.62
GR-S copolymer	Toluene	30	5.4×10^{-4}	0.66
Methyl methacrylate	Benzene	25	0.94×10^{-4}	0.76
Polyisobutylene	Toluene	20	3.6×10^{-4}	0.64

[a] Goldberg, Hohenstein, and Mark, *J. Polymer Sci.*, **2**, 502 (1947).

In addition to yielding molecular weights, viscosity measurements give us some insight into the general form of polymer molecules in solution.[1,7] A long-chain molecule in solution takes on a somewhat kinked or curled shape, intermediate between a tightly rolled up mass and a rigid linear configuration. Presumably all possible degrees of curling are represented, owing to the internal Brownian movement of the flexible chains. In a "good" solvent, i.e., one which shows a zero or negative heat of mixing with the polymer, the polymer molecule is rather loosely extended, as represented in Fig. 47*a*, and the intrinsic viscosity is high. In a "poor" solvent, i.e., one in which the polymer dissolves with absorption of heat (positive heat of mixing), the segments of the polymer molecule attract each other in solution more strongly than they attract solvent molecules, and the result is that the molecule assumes a more compact shape as illustrated in Fig. 47*b*. Consequently in a "poor" solvent the intrinsic viscosity would be lower than in a "good" solvent.

Apparatus. Ostwald viscometer; stop watch; pipettes; 25-ml volumetric flasks; polymer sample;* toluene; methanol.

Procedure. Solutions of the polystyrene sample of unknown molecular weight are prepared in a good solvent (toluene) and a poor solvent (a mixture of toluene and methanol). Since the polymer may dissolve rather slowly, warming in a water bath may be used to accelerate solution. When this is done, the solution should be cooled to 25° before adding solvent to bring the meniscus up to the mark on the volumetric flask.

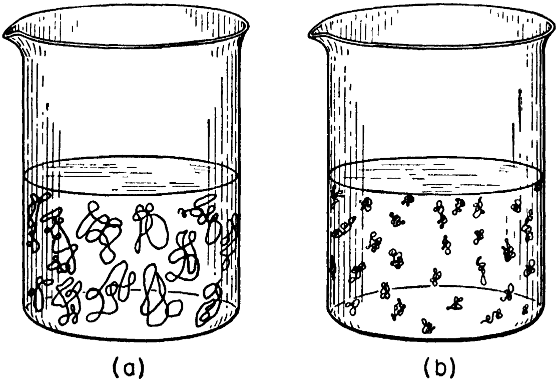


FIG. 47. Long-chain polymer molecules in (*a*) a "good" solvent; (*b*) a "poor" solvent.

1. 500 mg of polystyrene is dissolved in toluene and diluted to exactly 25 ml in a volumetric flask.
2. One hundred milliliters of a solution containing 15 per cent methanol and 85 per cent toluene by volume is prepared. Again 500 mg of polystyrene is dissolved in this solvent and diluted to exactly 25 ml. The remaining solvent is required for dilutions and a flow-time determination.

After the viscometer has been thoroughly cleaned with cleaning solution, it is rinsed and dried by aspirating through it clean air from the laboratory. It is important for the viscometer to be perfectly dry inside before organic solvents are added.

The flow time of the viscometer is determined for toluene and for the methanol-toluene solvent as described in Exp. 11. The flow time for the solution of polystyrene in toluene is determined. The sample is then diluted by a factor of 2, and the flow time determined. The accuracy of the dilutions may be improved by use of two calibrated pipettes, one calibrated for *withdrawal* of solution and the other for *delivery* of solvent.

* Dow polystyrenes DS-15, -25, and -65 are satisfactory for this experiment.

This dilution is repeated until the relative viscosity of the polymer solution becomes so close to 1 that there is a large error in the specific viscosity. Since the densities of the dilute polymer solutions are not significantly different from that of the solvent, it is unnecessary to determine the densities.

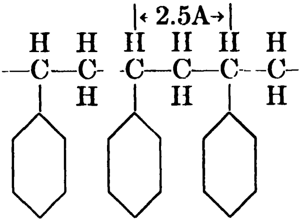
The same procedure is now repeated with the solution of polystyrene in methanol-toluene, in this case diluting with the mixed solvent.

Since methanol is a nonsolvent for polystyrene, the addition of further quantities will cause precipitation of the polymer. The per cent methanol by volume required to cause the first turbidity is determined by titrating a few milliliters of the solution of polystyrene in toluene.

Notice: Before the viscometer is allowed to dry inside, it should be rinsed thoroughly with toluene so that a film of polymer will not be left in the capillary.

Calculations. The intrinsic viscosity is obtained by plotting η_{sp}/c and $(1/c) \ln (\eta/\eta_0)$ versus c (in grams polymer per 100 ml of solution) for the solution of polystyrene in toluene. The intrinsic viscosity in methanol-toluene is determined by a similar graph. The advantage of the double extrapolation is that the intercept may be determined more precisely than by using only one straight line. Using the values of K and a given in Table 1, the molecular weight of the sample of polystyrene is calculated from its intrinsic viscosity in toluene. It should be realized that this is an average molecular weight, some of the molecules being larger and some smaller.

An estimate as to the size of the average polystyrene molecule in the sample is obtained by calculating the volume of one molecule from the molecular weight using 0.903 g/ml for the density of polystyrene. The radius of the molecule is calculated, assuming the molecule to be spherical. The length of the extended polymer molecule is calculated assuming the length per monomer unit is 2.5 A. The actual shape of the polystyrene molecule in solution is intermediate between the spherical and stretched-out forms and depends upon the solvent and temperature.



Practical Applications. Determination of the molecular weight of synthetic rubber, resins, and cellulose plastics is important because the physical properties of these materials depend markedly on molecular weight.

Suggestions for Further Work. The general subject of the viscosity of polymer solutions has been well reviewed in the literature,[3,7] where suggestions for further work may be found.

Viscosity determinations at higher concentrations are used to show that the linear relation between η_{sp}/c and c does not hold at higher concentrations. Polystyrene may be separated into several fractions by precipitating part of it with methyl alcohol. The average molecular weight of each fraction is determined by means of viscosity determinations.

For a given polymer $[\eta]$ may be determined for various concentrations of nonsolvent and plotted against per cent nonsolvent.[1]

References

1. Alfrey, Bartovics, and Mark, *J. Am. Chem. Soc.*, **64**, 1557 (1942).
2. Einstein, *Ann. Physik*, **19**, 259 (1906); **34**, 591 (1911).
3. Ewart *in* Kraemer (ed.), "Advances in Colloid Science," Vol. II, Interscience Publishers, Inc., New York (1946).
4. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N.Y. (1953).
5. Goldberg, Hohenstein, and Mark, *J. Polymer Sci.*, **2**, 502 (1947).
6. Kraemer, *Ind. Eng. Chem.*, **30**, 1200 (1938).
7. Mark and Tobolsky, "Physical Chemistry of High Polymeric Systems," 2d ed., Interscience Publishers, Inc., New York (1950).
8. Van Holde and Alberty, *J. Chem. Educ.*, **26**, 151 (1948).

43. DETERMINATION OF THE OSMOTIC PRESSURE OF A SOLUTION OF A HIGH POLYMER

The number average molecular weight of a sample of polystyrene is calculated from the osmotic pressure of a solution of the polymer in methyl ethyl ketone.

Theory. Of the four colligative properties of solutions, boiling-point elevation, freezing-point lowering, vapor-pressure lowering, and osmotic pressure, only the latter is useful in determining the molecular weights of solutes in the colloid size range synthetic high polymers, proteins, and polysaccharides. For example, an aqueous solution containing 10 g liter^{-1} of a solute of molecular weight 100,000 would have a boiling-point elevation of 5×10^{-5} deg, a freezing-point lowering of 2×10^{-4} deg, a vapor-pressure lowering of 5×10^{-5} mm of Hg, but an osmotic pressure of 25 mm of water.

When a solution and the pure solvent are separated by a semipermeable membrane (that is, one which permits the passage of molecules of solvent from one side to another, but not molecules of solute), solvent molecules will pass through the membrane into the solution or in the opposite direction, depending upon the pressure difference across the membrane. The *osmotic pressure* is the excess pressure which must be applied to the solution to prevent the flow of solvent. Since at equilibrium the fugacity of the solvent is the same in the solution phase as in the pure solvent phase, the relation of osmotic pressure to molecular weight may be derived thermodynamically.[3] The basic thermodynamic equation is

$$\pi = \frac{RT}{\bar{V}_1} \ln \frac{f_1^0}{f_1} \tag{1}$$

where π = osmotic pressure
R = ideal-gas constant
T = absolute temperature
$\bar{V}_1$ = partial molal volume of the solvent
f_1^0 = fugacity of the pure solvent at 1 atm pressure
f_1 = fugacity of the solvent in the solution at 1 atm pressure

If it is assumed that (1) fugacities may be replaced by vapor pressures, (2) Raoult's law applies to the solvent in dilute solutions of the polymer, and (3) $\bar{V}_1$ may be replaced in dilute solutions by the molar volume of the solvent, Eq. (1) becomes

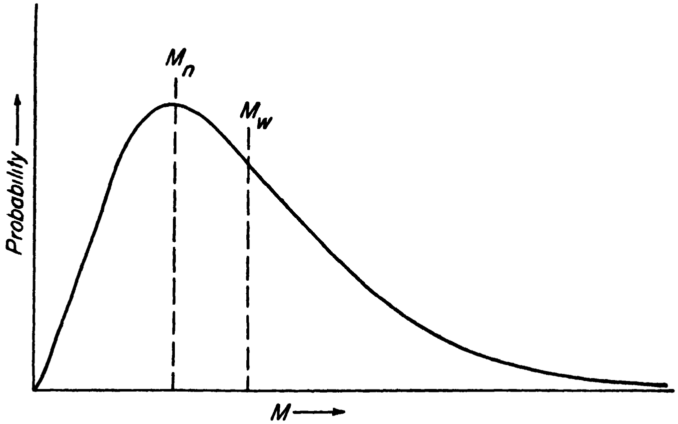


FIG. 48. Probability of molecules of molecular weight M for a high polymer. The values of M_n and M_w for this molecular-weight distribution are shown.

$$\lim_{c \to 0} \frac{\pi}{c} = \frac{RT}{M} \tag{2}$$

where c = concentration (weight of polymer per unit volume of solution)
M = molecular weight of the polymer.

The limiting value of π/c is obtained by plotting π/c versus c and extrapolating linearly to $c = 0$.

In the case of a synthetic polymer all of the molecules do not have the same weight, and so it is necessary to deal with average molecular weights. Several types of average may be considered.[4] In the case of most polymers, whether natural or synthetic, the molecular-weight distribution may be represented by a plot versus M of the probability of a particular molecular weight as illustrated in Fig. 48.

The probability may be expressed as the fraction of material with molecular weight in the range M to $M + dM$. Different experimental methods yield different types of average molecular weight. Since the osmotic pressure depends on the number of molecules per unit volume without regard to their size, Eq. (2) yields the *number average molecular weight,* which is expressed by

$$M_n = \frac{\sum_i n_i M_i}{\sum_i n_i} \tag{3}$$

where n_i is the number of molecules of weight M_i.

In contrast, the weight average molecular weight is expressed by

$$M_w = \frac{\sum_i n_i M_i^2}{\sum_i n_i M_i} \tag{4}$$

The viscosity method (Exp. 42) yields a molecular weight which is closely, but not exactly, related to M_w. The weight average molecular weight must obviously be greater than the number average molecular weight for a heterogeneous substance. If all the molecules have the same weight, $M_n = M_w$.

A general review of osmotic-pressure measurements has been written by Wagner.[6]

The osmometer to be used is of the Schultz-Wagner[5] type, which is illustrated in Fig. 49. It consists of a graduated capillary (0.75 to 1.0 mm inside diameter) attached to a short section of larger tubing (12 mm inside diameter) which has a ground lower surface against which the membrane is held by a brass clamp. The purpose of the lower plate is to hold the membrane tightly against the glass tubing and to support the membrane so that it will not bulge out and stretch during the experiment. The osmometer is filled with polymer solution by use of a syringe with a long

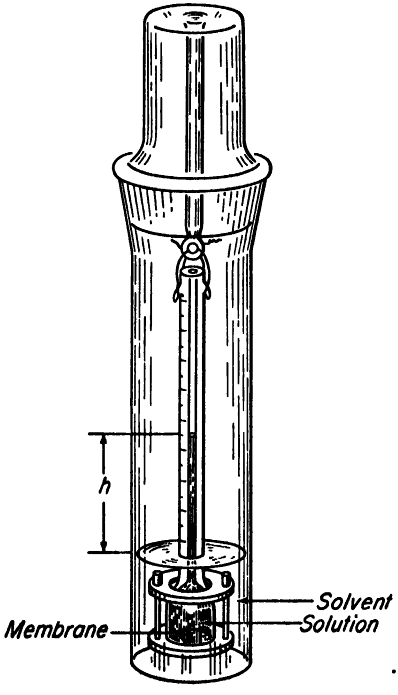


Fig. 49. Simple osmometer.

stainless-steel needle. This method of filling the osmometer has the advantage that ground-glass joints and valves are avoided so that possibilities for leaks are reduced to a minimum.

Since the permeability of a membrane to various types of solvents may be very different, osmotic-pressure measurements may be made more rapidly with one solvent than with others. In the case of cellophane membranes, Browning and Ferry[1] showed that equilibrium is reached more rapidly with methyl ethyl ketone than with benzene or toluene.

DuPont Cellophane 600 is soaked overnight in 30 per cent sodium hydroxide and washed for a few minutes in progressive dilutions of sodium hydroxide and then water. This treatment is necessary to increase the porosity of the membrane. The progressive dilutions of alkali are essential to avoid wrinkling of the membrane. The membranes are then washed in progressively more concentrated solutions of methyl ethyl ketone in water and stored in methyl ethyl ketone, making it unnecessary for each student to carry out the sodium hydroxide treatment.

Apparatus. Two Schultz-Wagner osmometers; polystyrene; methyl ethyl ketone; 5-ml syringe with long stainless-steel needle; volumetric flasks; cellophane membranes.

Procedure. Since it is necessary to correct the observed meniscus height for the capillary rise of the solution, this correction may be determined before making the osmotic-pressure measurements. It is satisfactory to assume, for the purpose of this experiment, that the capillary rise for the polystyrene solution will be the same as for methyl ethyl ketone.

Data required for making another correction should also be obtained before assembling the osmometer. The need for this further correction arises since the equilibrium height in the capillary is, in general, different from the initial height. If the equilibrium height of the meniscus is greater than the initial height, solvent has passed into the polymer solution, and so the equilibrium polymer solution is more dilute than the original solution. In order to compute the equilibrium concentration it is necessary to know the volume of the osmometer bulb and the radius of the capillary. The volume of the bulb may be determined with sufficient accuracy by measuring the volume of water required to fill it, and the radius of the capillary may be calculated from the capillary rise of methyl ethyl ketone. The surface tension of pure methyl ethyl ketone is 23.9 dynes cm^{-1} at 25°, and its density at 25° is 0.803 g cm^{-3}.

A weighed sample of polystyrene is dissolved in methyl ethyl ketone, and the solution is diluted to the desired volume in a volumetric flask. A suggestion as to the concentration to use may be obtained from an instructor. Since 2 to 4 days are required for equilibration, two osmometers should be set up at one time. The osmotic pressures for several concentrations of the same polymer are measured. The concentrated solution may be diluted quantitatively to provide more dilute solutions for measurement.

In assembling the osmometer it is important to keep the membrane moistened with methyl ethyl ketone, as the value of the sodium hydroxide treatment will be lost if the membrane is allowed to dry out.

Two disks of a smooth hard filter paper are moistened with methyl ethyl ketone and placed on the bottom brass plate. The filter paper serves as a support for the membrane so that it cannot sag into the holes and facilitates a good seal between the membrane and the ground-glass surface of the osmometer bulb. The membrane is placed on the filter paper, and the glass osmometer tube is attached. The knurled nuts are tightened with the fingers. The polystyrene solution is placed in the osmometer by use of a syringe with a long stainless-steel needle, taking care to avoid trapping bubbles at any point. **Precaution:** The syringe and needle should be rinsed out with methyl ethyl ketone after being used to transfer the polymer solution so that no polystyrene residue will be left in them. Since methyl ethyl ketone is a solvent for many of the plastics used in the construction of fountain pens and pencils, carelessness may result in damage to writing equipment.

Enough methyl ethyl ketone is placed in the outer glass tube so that the meniscus comes on the lower part of the graduated capillary when the osmometer is hung in the tube.

The height of the liquid column in the capillary is set at a value several centimeters above, or below, that expected at equilibrium. If it is possible to use two osmometers for each solution, the height is set higher than the expected pressure in one and lower in the other. The osmometer is then suspended in methyl ethyl ketone so that the membrane is completely immersed.

The osmometers are placed in the air thermostat, and after allowing some time for temperature equilibration, an initial reading is taken. Readings are then taken at intervals over a period of two or more days.

An unfractionated polymer sample contains molecules of a wide range of molecular weights, and some of the lowest molecular-weight material may diffuse through the membrane. If there is appreciable leakage of low-molecular-weight material, a constant osmotic pressure will not be obtained. The low-molecular-weight material may be eliminated by precipitating about 75 per cent of the polymer by the addition of methyl alcohol to a solution in benzene. The lowest molecular-weight fraction will remain in the supernatant liquid. The precipitate may be dissolved in benzene and dried by vacuum sublimation of the benzene to obtain a porous preparation of polystyrene which can be readily redissolved.

Calculations. Plots of height (h) versus time are useful in determining the equilibrium pressure.

The ratio of equilibrium pressure π (corrected for the surface-tension rise) to the equilibrium concentration is plotted versus concentration, and the value of π/c at zero concentration is obtained by extrapolation. If the range of values of π/c is within the range of experimental error, the best horizontal line is drawn through the points. The number average molecular weight is calculated from the extrapolated value of π/c by use of Eq. (2). As an illustration, $\pi/c = 220\ \text{cm}^4\ \text{g}^{-1}$ at 25°, where π is pressure in centimeters of methyl ethyl ketone solution and c is concentration in g cm^{-3}. Before calculating M, it is convenient to convert this intercept to atm liter g^{-1} which yields

$$\pi/c = \frac{(220\ \text{cm}^4\ \text{g}^{-1})(0.803\ \text{g cm}^{-3})}{(13.6\ \text{g cm}^{-3})(76.0\ \text{cm Hg atm}^{-1})(1{,}000\ \text{cm}^3\ \text{liter}^{-1})}$$

$$= 170 \times 10^{-6}\ \text{atm liter g}^{-1}$$

$$\lim_{c \to 0} \frac{\pi}{c} = \frac{RT}{M}$$

$$170 \times 10^{-6}\ \text{atm liter g}^{-1} = \frac{(0.0825\ \text{liter atm deg}^{-1}\ \text{mole}^{-1})(298\ \text{deg})}{M}$$

$$M = 144{,}000\ \text{g mole}^{-1}$$

Practical Applications. Since the properties of a solid plastic or synthetic rubber will depend upon the molecular weight of the polymer, the measurement of osmotic pressure is widely used in industry. The viscosity method which is also used is illustrated in Exp. 42.

Suggestions for Further Work. The molecular weight of a sample of polystyrene may be determined in another solvent. Although the number average molecular weight obtained from the intercept of a plot of π/c versus c should be the same, the slope may be quite different.[2] On the other hand, the slopes for a series of polystyrene samples of different molecular weight in a given solvent will be very nearly the same.

The polymer sample may be fractionated by dissolving it in a good solvent and partially precipitating it by the addition of a poor solvent, for example, methyl alcohol. The molecular weights of the polymer in the precipitate and in the solution phase may be shown to be different by osmotic-pressure measurements.

References

1. Browning and Ferry, *J. Chem. Phys.*, **17**, 1107 (1949).
2. Flory, *J. Am. Chem. Soc.*, **65**, 373 (1943).
3. Flory, "Principles of Polymer Chemistry," pp. 273–282, Cornell University Press, Ithaca, N.Y. (1953).
4. Palit, *J. Chem. Educ.*, **24**, 199 (1947).
5. Wagner, *Ind. Eng. Chem., Anal. Ed.*, **16**, 520 (1944).
6. Wagner *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Interscience Publishers, Inc., New York (1949).

44. ADSORPTION FROM SOLUTION

Quantitative measurements of adsorption by an ion-exchange resin are made. The isothermal data are expressed by means of an equation, and the regeneration of the adsorbent is illustrated.

Theory. Solids have the property of holding molecules at their surfaces, and this property is quite marked in the case of porous and finely divided material. Various forces are involved, ranging from those which are definitely physical in nature to those which are referred to as chemical. Adsorption is frequently quite specific, so that one solute may be adsorbed selectively from a mixture.

In the case of so-called "exchange adsorbents," the adsorption is actually a chemical reaction in which an ion is liberated from the adsorbent as another is "adsorbed." The softening of water, using naturally occurring or synthetic zeolites, is an example of this phenomenon. An important advance in the field of exchange adsorbents was made by Adams and Holmes[1] in 1935 when they discovered that phenol-formaldehyde resins exhibited ion-exchange properties. The advantage of synthetic resins is that the exchange adsorption properties may be varied at will by the selection of the reactants for the polymerization reaction.[3,6,7,8] For example, the condensation of polyhydric phenols with formaldehyde yields resins which adsorb calcium ions, liberating hydrogen ions or sodium ions.

$$2\text{NaR} + \text{Ca}^{++} \rightleftharpoons \text{CaR}_2 + 2\text{Na}^+$$
$$2\text{HR} + \text{Ca}^{++} \rightleftharpoons \text{CaR}_2 + 2\text{H}^+$$

Here NaR represents the sodium salt of the cation-exchange resin, and HR represents the acid form. By treating the exhausted resin with an excess of Na^+ or H^+, the reactions may be reversed, regenerating the resin.

Synthetic resins prepared by condensing aromatic amines with formaldehyde exhibit anion-exchange, or acid-adsorbent, properties as illustrated by the following equation:

$$\text{RX} + \text{HCl} \rightleftharpoons \text{RX}\cdot\text{HCl}$$

where RX represents the anion-exchange resin. The capacity of a resin ranges from about 4 to 9 milliequiv of acid per gram of dry resin. In this case the regeneration is accomplished by treating the exhausted resin with a solution of sodium carbonate.

$$\text{RX}\cdot\text{HCl} + \text{Na}_2\text{CO}_3 \rightarrow \text{NaCl} + \text{NaHCO}_3 + \text{RX}$$

By passing water successively through columns of base-exchange (hydrogen form) and acid-binding resins, deionized water comparable in quality to distilled water may be obtained.

The amount of solute adsorbed by a given quantity of adsorbent increases with the concentration of the solution. In some cases the layer of adsorbed molecules is only one molecule deep, and further adsorption ceases when the surface of the crystal lattice is covered. The equilibrium between the dissolved solute and the material adsorbed also depends upon the nature of the solvent and the temperature, the amount adsorbed increasing at lower temperatures.

The relation between the amount adsorbed and concentration may be represented by the adsorption isotherm of Freundlich

$$\frac{x}{m} = kc^n \tag{1}$$

where x = weight of material adsorbed by m grams of adsorbing material
c = concentration in solution
n = constant ranging from 0.1 to 0.5
k = another constant

Although k varies considerably with the temperature and nature of the adsorbent, the ratio of k for two different adsorbents is maintained in different solutions. By taking the logarithm of Eq. (1) we obtain

$$\log \frac{x}{m} = n \log c + \log k \tag{2}$$

According to this equation a plot of log (x/m) versus log c is a straight line, and the constants may be evaluated from the slope n and the intercept log k. The equation of Freundlich is purely empirical in nature.

The adsorption equation of Langmuir is based upon a theoretical consideration of the process of adsorption. This equation may be written

$$\frac{x}{m} = \frac{\alpha c}{1 + \beta c} \quad \text{or} \quad \frac{c}{x/m} = \frac{1}{\alpha} + \frac{\beta}{\alpha} c \tag{3}$$

where α and β are constants. For cases in which this equation represents the data, $c/(x/m)$ may be plotted as a linear function of c, and the constants evaluated from the slope β/α and intercept $1/\alpha$. The Langmuir equation differs from the Freundlich equation in that the adsorption approaches a finite limit as the concentration is increased.

In the expression of the experimental results it is the *form* of the Langmuir equation which is used. This equation is actually one description of the law of mass action. This may be seen in the following argument. Suppose we use the symbol R for the part of the resin which combines with a hydrogen ion according to the reaction

$$R + \text{H}^+ \rightleftharpoons R\text{H}^+$$

The constant for the association is $K = \dfrac{c_{RH^+}}{c_{H^+}c_R}$, or $c_{RH^+} = Kc_{H^+}c_R$.

The total resin concentration is $c_{R,(t)} = c_{RH^+} + c_R$, so that

$$c_{RH^+} = Kc_{H^+}(c_{R,(t)} - c_{RH^+})$$

Thus
$$\frac{c_{RH^+}}{c_{R,(t)}} = \frac{Kc_{H^+}}{1 + Kc_{H^+}}$$

The ratio $c_{RH^+}/c_{R,(t)}$ represents the number of moles of bound hydrogen per mole of resin combining sites, and the expression for it is formally the same as the Langmuir fraction.

Apparatus. Twelve 250-ml Erlenmeyer flasks; two burettes; 1 *N* acetic acid; 0.1 *N* sodium hydroxide; anion-exchange resin* or as an alternative, highly activated adsorbent charcoal; 100-ml volumetric flask; weighing bottle.

Procedure. The exchange resin consists of particles (approximately 20 to 50 mesh) which are kept in a regenerating solution of 8 per cent sodium carbonate when not in use. The carbonate solution is decanted and the resin rinsed with three portions of distilled water, allowing the resin to settle before each decantation. The loss of finer particles during decantation is not serious.

The resin is now collected on a filter and pressed to remove excess moisture. Twelve samples of damp resin of approximately 2 g in weight are weighed to ±10 mg. Two additional samples of the resin weighed at the same time are placed in the oven and dried at 110°C to constant weight. In the calculations, the adsorption x/m is calculated on the basis of the dry resin. To obtain the percentage of moisture in the wet resin, a sample may be taken for drying both before and after the weighing of the equilibrium samples.

Acetic acid solutions of different concentrations are made by running out 1 *N* acetic acid from a burette and diluting to 100 ml with water; 50, 25, 10, 5, 2.5, and 1 ml are diluted with distilled water to 100 ml. Each solution is transferred to a 250-ml Erlenmeyer flask, and 2 g of wet exchange resin (or 1 g of adsorbent charcoal) is then added to each flask. The solutions are set up in duplicate. The solutions are agitated and allowed to stand overnight or longer. A thermostat is unnecessary if the room temperature is fairly constant.

After equilibrium has been reached and the resin has settled, a suitable volume (5 or 25 ml, depending on the concentration) is pipetted from the clear supernatant solution in each flask and titrated with 0.1 *N* sodium hydroxide. Whenever the titration volume falls below 25 ml, the base may be diluted by a known ratio, such as 1:1. Blank determinations should be made on all distilled water used for this purpose.

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* Amberlite IR-4B is satisfactory and is obtainable from chemical supply houses.

The experiment may be repeated with oxalic acid instead of acetic acid.

After the experiment has been completed, the resin is regenerated by the addition of 10 ml of 8 per cent by weight Na_2CO_3 per gram of resin and returned to the stockroom.

Calculations. The total weight of acetic acid in each solution is calculated from the data of the original solutions, and titration gives the weight remaining in 100 ml of the solution after shaking with adsorbent. The difference gives directly the weight of acetic acid adsorbed by the m grams of adsorbent.

The normality of the solution in equilibrium with the adsorbed acetic acid is calculated from the sodium hydroxide titrations, and the values of x/m are plotted against these equilibrium concentrations.

A plot of $c/(x/m)$ versus c is prepared, and the constants α and β of Eq. (3) are computed.

Practical Applications. The adsorption isotherm or equivalent form is important in the quantitative expression of the adsorption process, and as such it finds use in some dyeing and in various purification processes. It is useful also for the description of the adsorption of gases.

Ion-exchange resins are important in softening water, recovering ions from solutions of low concentration, and separating the rare earths.[9]

Suggestions for Further Work. If the system is in equilibrium, the same results should be obtained whether approached from concentrated or from more dilute solutions. Equilibrium may be tested by repeating the adsorption experiments and then diluting the solution with water after it has stood with the adsorbent. Acetic acid should be released by the adsorbent, and the final values of x/m and c should still fall on the same curve.

Various other materials may be adsorbed—weak acids, or bases. Ammonium hydroxide is suitable if a cation exchange resin is used.

The adsorption isotherm may be tested nicely with dyes adsorbed on charcoal, the initial and final concentrations of dye in solution being obtained with a colorimeter. The difference between the two readings gives a measure of the quantity of dye adsorbed by the charcoal. Methyl violet and malachite green are suitable dyes.

The adsorption experiments may be carried out at 0°C and at elevated temperatures.

The values of the constants k and n in Eq. (1) are compared for the different materials and temperatures.

References

1. Adams and Holmes, *J. Soc. Chem. Ind. (London)*, **54**, 1-67 (1935).
2. Alexander, "Colloid Chemistry," Vol. I, Reinhold Publishing Corporation, New York (1926).
3. Edwards, Schwartz, and Boudreaux, *Ind. Eng. Chem.*, **32**, 1462 (1940).
4. Glasstone, "Textbook of Physical Chemistry," pp. 1194–1210, D. Van Nostrand Company, Inc., New York (1946).
5. Morton, "Laboratory Technique in Organic Chemistry," Chap. IX, McGraw-Hill Book Company, Inc., New York (1938).

6. Myers *in* Kraemer (ed.): "Advances in Colloid Science," Vol. II, Interscience Publishers, Inc., New York (1942).
7. Myers and Eastes, *Ind. Eng. Chem.*, **33**, 1203 (1941).
8. Myers, Eastes, and Myers, *Ind. Eng. Chem.*, **31**, 1138 (1939).
9. Spedding, *et al.*, *J. Am. Chem. Soc.*, **69**, 2777, 2786, 2812 (1947).

45. ADSORPTION OF GASES

In this experiment the amounts of gas adsorbed at various pressures on activated charcoal or silica gel are determined by a volumetric method.

Theory. Adsorption is a process whereby gases or solutes are attracted and held to the surface of a solid. The material adsorbed is called the adsorbate, and the material on which it is adsorbed is called the adsorbent. Often the force of attraction is physical in nature, involving an interaction between dipoles or induced dipoles, but sometimes the force of attraction involves chemical bonds, as when oxygen is adsorbed on charcoal. In many cases the layer of adsorbed molecules is only one molecule deep, an atom of adsorbent at the surface being unable to take part in the attractive force beyond the first molecule of adsorbate. Since the amount of gas which is adsorbed is proportional to the amount of surface exposed, the good adsorbents are those which have enormous surface areas, such as activated charcoal or silica gel; but adsorption of gases at low temperatures has been measured on clean glass surfaces, mercury surfaces, and metallic wires. Sometimes the large surface is produced by a cellular structure originally present in the plant, as in the case of charcoal.

If the adsorbent is porous on a submicroscopic scale, so-called capillary condensation may take place below the normal saturation pressure. This type of adsorption can be distinguished from the unimolecular-layer type of adsorption by heats of adsorption and by other criteria.

The experimental data for adsorption are plotted as "adsorption isotherms," in which the quantity of gas adsorbed (expressed as milliliters at 0° and 760 mm) per gram of adsorbing material is plotted against the equilibrium pressure.

In many cases of adsorption it is possible to relate the amount of adsorbed material to the equilibrium pressure, using the empirical equation of Freundlich,

$$v = kp^n \tag{1}$$

where v = number of milliliters of gas, corrected to 0° and 760 mm, adsorbed per gram of adsorbing material

p = pressure

The constants k and n may be evaluated from the slope and intercept of the line obtained when $\log v$ is plotted against $\log p$.

One of the most successful theoretical interpretations of gas adsorption is that of Langmuir,[4,5] who considered adsorption to distribute molecules over the surface of the adsorbent in the form of a unimolecular layer. Consideration of the dynamic equilibrium between adsorbed and free molecules leads to the following relation:

$$\frac{p}{v} = \frac{p}{v_u} + \frac{1}{kv_u} \tag{2}$$

where p = gas pressure
v = volume of gas (at S.T.P.) adsorbed per gram of adsorbent
v_u = volume of gas (at S.T.P.) adsorbed per gram of adsorbent when unimolecular layer is complete
k = constant characteristic of adsorbent-adsorbate pair

Thus, if p/v is plotted against p, a straight line will be obtained if the Langmuir Equation (2) applies. The slope of the line is equal to $1/v_u$; when the line is extrapolated to low pressures, as $p \rightarrow 0$, p/v approaches the finite limit $1/kv_u$. The values of the constants in the Langmuir equation may also be obtained by plotting $1/v$ versus $1/p$.

By postulating the building up of multimolecular adsorption layers on a surface, Brunauer, Emmett, and Teller[1,2,3] have extended the Langmuir derivation for unimolecular layer adsorption to obtain an isotherm equation for the more complicated case. The extension is not without some empiricism, yet it is often useful. Thus, knowing the volume of gas required to form a complete unimolecular layer over the surface of the adsorbent, it is possible to compute the surface area of the adsorbent, if it is assumed that each molecule of the adsorbate occupies the volume that it would occupy if the density of the unimolecular film is the same as that of the liquid adsorbate at the same temperature.

A graph of adsorption data giving the pressure as a function of temperature for a specific volume of gas adsorbed is referred to as an isostere. Such graphs bear a close resemblance to graphs in which the vapor pressure is plotted against the temperature, and the heat of adsorption, $q_{\text{isosteric}}$, may be calculated in a manner similar to that used for calculating the heat of vaporization of a liquid using the following modification of the Clausius-Clapeyron equation, thus

$$\ln \frac{p_1}{p_2} = \frac{q_{\text{isosteric}}(T_1 - T_2)}{RT_1T_2} \tag{3}$$

where p_1 = equilibrium pressure for a given amount of gas adsorbed at T_1
p_2 = equilibrium pressure of the same amount of gas adsorbed at T_2

By calculating $q_{\text{isosteric}}$ for different volumes of gas adsorbed, the variation of heat of adsorption with volume adsorbed may be found. A variation of heat of adsorption with the volume adsorbed indicates changes in the magnitude of the forces between the adsorbent and the adsorbate.

Apparatus. Apparatus as shown in Fig. 50, consisting of a mercury manometer, a mercury-filled gas burette, six stopcocks, and a ground-glass joint; vacuum pumps; tanks containing methyl chloride or other suitable gas; adsorbent charcoal or silica gel.

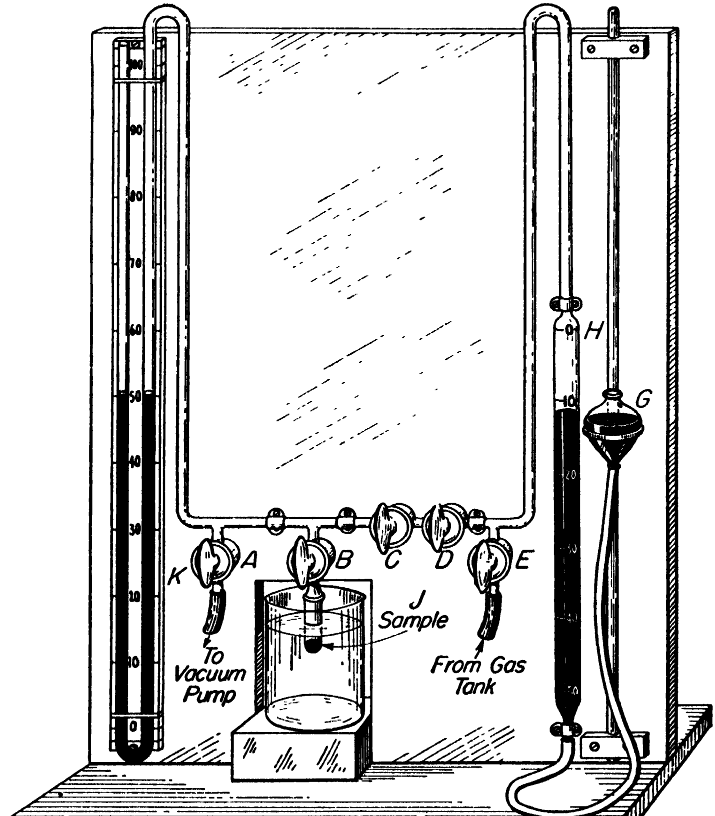

FIG. 50. Gas-adsorption apparatus.

Procedure. The flexible Tygon connecting tube from the gas tank attached to E is flushed out by removing the ground-glass tube J and opening the stopcocks E, D, C, and B. Stopcock E is closed; the tube J is replaced; the leveling bulb of mercury is lowered as far as possible; and the whole system is evacuated with a vacuum pump through stopcock A. Stopcock D is closed, and methyl chloride is admitted through E until the burette H is filled at atmospheric pressure. Stopcock E is then closed, and the leveling bulb G is adjusted carefully until the gas in the burette is at exactly atmospheric pressure. The volume of gas in the burette is then recorded.

The amount of gas which is adsorbed by the adsorbent is to be determined by measuring the volume of gas which must be admitted from the burette in order to give a specified pressure. Part of the gas from the burette is adsorbed, but an additional part, known as the "dead volume," is needed for filling the apparatus up to the given pressure at which the adsorption measurement is made. The dead volume of the apparatus between the manometer *K* and the stopcock *D* is determined by finding the volume of gas admitted from the burette which is necessary to produce a given pressure in the absence of any adsorbing material in *J*.

The apparatus is first tested for leakage by observing the manometer. There should be no detectable change in the levels of the manometer *K* over a period of at least 5 min when the apparatus is evacuated. Then gas from the burette is admitted into the system through stopcocks *C* and *D* until the pressure in the apparatus is about 50 mm, and the exact manometer reading, burette readings, and temperature of the room are recorded. These data are used for calculating the dead volume of the gas under standard conditions. The dead volume is determined in a similar manner at pressure increments of about 100 mm. The burette is refilled when necessary by closing stopcock *D*, opening stopcock *E*, and lowering the leveling bulb *G*.

The volume of methyl chloride adsorbed by activated charcoal at a given pressure is determined by placing 0.080 to 0.100 g of the charcoal in the ground-glass tube *J*, inserting it at *B*, and placing a beaker of water at room temperature around it. Stopcocks *C* and *D* are closed, and the charcoal is outgassed for 5 min by evacuating through *A*. Methyl chloride is then admitted from the burette until the pressure is about 50 mm. The pressure will decrease as the gas becomes adsorbed on the charcoal, but after 5 min or so there is no tendency toward further change if the pressure is kept constant. The two stopcocks *C* and *D* with the intervening space of about 0.05 ml volume provide a convenient means for introducing gas into the system in small amounts so as to maintain the pressure constant. (A much longer time is required to reach equilibrium if a given quantity of gas is introduced and allowed to decrease in pressure until reaching an equilibrium.) When equilibrium has been reached and no more additions of gas are necessary to maintain the pressure, the volume of gas introduced from the burette is recorded.

This operation is repeated by using pressure increments of 30 to 50 mm up to about 250 mm and then using increments of about 100 mm up nearly to atmospheric pressure.

The adsorption measurements on charcoal are then repeated at 0° by using an ice bath in the beaker which surrounds the adsorbent.

Calculations. Part of the gas introduced from the burette is adsorbed on the charcoal, and part remains in the manometer and connecting tubes. The volume of gas adsorbed at a given equilibrium pressure is obtained by subtracting the dead-space volume in the apparatus from the total volume of gas introduced from the burette. The dead volume in milliliters at a given pressure is obtained by interpolation on a line obtained by plotting the corrected dead volume against the pressure measured in the absence of any adsorbent. All these observed volumes are reduced by calculations to the volumes of gas at 0° and 760 mm. When several additions of gas have been made to the adsorbent, giving a specified equilibrium pressure, they are all added together to obtain the total volume. The volume v adsorbed per gram of charcoal is then determined by dividing the corrected volume by the weight of the adsorbent.

Three graphs are drawn to interpret the adsorption. In the first graph, the corrected volume of gas, v, adsorbed per gram of adsorbent is plotted vertically, and the equilibrium pressures are plotted horizontally.

In the second graph, log v is plotted against log p in accordance with the Freundlich equation [(1)], and the constants k and n are calculated for the equation $v = kp^n$ as discussed on page 225.

In the third graph, the values of p/v are plotted against p to evaluate the constants k and v_u of the Langmuir equations [(5) and (6)], and the constant v_u is used for calculating the surface area of the adsorbent.

The volume of one molecule in the layer of adsorbate is calculated on the assumption that the molecule has the same volume as a molecule in the liquid state. The number of molecules in the unimolecular layer is calculated by dividing the volume v_u of adsorbate in the unimolecular layer by the volume of a mole of the gas, 22,400, and multiplying by the Avogadro number 6.02×10^{23}. Then the volume of a molecule of adsorbate is calculated by dividing the volume of a mole of the material in the liquid state (obtained from tables of liquid densities) by the Avogadro number. The surface area covered by a single molecule is equal to the two-thirds power of the volume of the molecule. The surface area of a gram of adsorbent is equal, then, to the number of molecules in the saturated unimolecular layer multiplied by the cross-sectional area of a molecule.

The isosteric heat of adsorption is computed by Eq. (3) for several different volumes of gas adsorbed, and these values are plotted against the volume adsorbed. This plot is then used to interpret qualitatively the forces which exist between the adsorbent material and the gas being adsorbed.

Practical Applications. The adsorption of gases is used for purification and recovery of vapors. Solvent vapors are adsorbed from a stream of gas by adsorption in activated charcoal or silica gel and then recovered in concentrated form by heating the adsorbent to drive out the adsorbed vapors.

The drying of air is carried out on a large scale by adsorbing the water vapor with silica gel. When the silica gel becomes saturated, it is reactivated by heating to about 150° to expel the water and prepare the adsorbent for another cycle of adsorption.

High vacuum is conveniently produced in a vessel by connecting to a tube containing an adsorbent at liquid-air temperatures.

The effective surface of powders and catalysts is determined by measuring the amount of gas adsorbed. The adsorption of nitrogen on material at the temperature of liquid air has been used in such determinations.

Measurements of the Brunauer, Emmett, and Teller[2] (BET) constants are carried out on a routine basis in some catalyst testing programs.

Suggestions for Further Work. The experiments and calculations may be repeated, using 0.5 g of silica gel instead of 0.1 g of activated charcoal. The silica gel should be activated by evacuating the system while gently heating the sample at *J* to about 150° with a bunsen flame.

Other gases and vapors may be used instead of the methyl chloride, e.g., ammonia, sulfur dioxide, or Freon, with suitable weights of adsorbents.

In general, the higher the boiling point of a liquid, the higher is the temperature at which the adsorption experiments should be carried out.

Different grades of silica gel and activated charcoal may be used for adsorption experiments.

The rate of adsorption may be studied by maintaining the pressure as nearly constant as possible and measuring the volume adsorbed at different times. The rate of adsorption at different temperatures may be studied.

References

1. Brunauer, "Physical Adsorption," Chaps. I-IV, p. 222, Princeton University Press, Princeton, N.J. (1945).
2. Brunauer, Emmett, and Teller, *J. Am. Chem. Soc.*, **60**, 310 (1938).
3. Emmett, *Ind. Eng. Chem.*, **29**, 639 (1945).
4. Kraemer, Williams, and Alberty *in* Taylor and Glasstone: "A Treatise on Physical Chemistry," 3d ed., Vol. II, Chap. V., D. Van Nostrand Company, Inc., New York (1951).
5. Langmuir, *J. Am. Chem. Soc.*, **38**, 2267 (1916); **40**, 1361 (1918).

46. SEDIMENTATION RATE AND PARTICLE-SIZE DISTRIBUTION

The measurement of the velocity of sedimentation of particles in the earth's gravitational field or a centrifugal field gives valuable information concerning their size. When the dispersed particles are so large that they exceed the limit of colloidal dimensions and when the density of the particle relative to that of the suspension medium is sufficiently great, they settle out under the force of gravitation. By measuring rates of sedimentation, particle size and size distribution determinations can be made with finely divided solids for which other sizing methods would be impractical or impossible.

Theory. The constant velocity with which a spherical particle falls in a liquid may be expressed with a relatively simple law. The force of friction resisting the fall of the particle is $6\pi\eta r(dx/dt)$, and the force of gravity acting on the particle is mg, or $\frac{4}{3}\pi r^3(d_p - d_m)g$. In these expressions η is the viscosity of the liquid, r is the radius of the particle, dx/dt is the velocity of fall of the particle, d_p and d_m are the densities of the particle and of the suspension medium, m is the effective mass of a particle, and g is the acceleration due to the earth's gravitational field. The force of gravity and the force of friction are exactly opposed and equal when the particle falls with constant velocity, and

$$6\pi\eta r \frac{dx}{dt} = \frac{4}{3}\pi r^3(d_p - d_m)g$$

or

$$r = \sqrt{\frac{9}{2}\eta \frac{dx/dt}{(d_p - d_m)g}} \tag{1}$$

This equation is known in the literature as Stokes' law.

Thus, if the sedimentation rate of spherical particles is measured, and the viscosity of the liquid, the difference in density between the particle and the liquid, and the constant of the sedimentation field are known, the particle size can be calculated. This statement is true for sedimentations in an ultracentrifuge as well as for ordinary sedimentations, and a very large number of determinations of the size of particles has been made by using the formula of Stokes. If the particles are asymmetric in shape, the exact particle size cannot be obtained in this way, but there may be evaluated an "equivalent radius," or the radius of an imaginary spherical particle of the same substance with the same observed velocity of sedimentation. The particle must possess some appreciable degree of asymmetry before this factor makes a marked difference in sedimentation rates.

Apparatus. Sedimentation-tube assembly; finely divided solid, such as lead sulfate; gum arabic; stop watch.

Procedure. The apparatus, Fig. 51, consists of an inclined capillary side tube, C, containing the suspension medium, in this case water, connected to the main vessel, A, at the sampling level. At equilibrium, the water column will have a height greater than that of the suspension in the large tube, since the suspension of the dense powder has a higher density than the pure suspension medium. As the suspended solid settles out below the sampling level, the density of the suspension becomes less, and the levels in the two tubes approach the same value. It is the measurement of the excess height in the inclined capillary tube as a function of time which provides a curve showing the variation of the mean density of the suspension between its surface and the sampling level.

The capillary side arm is bent to a small angle to provide means to make a more accurate estimate of the difference in the levels in the two tubes. The apparatus is adjusted with the aid of the spirit level and the leveling screw to ensure accuracy of the side-arm angle.

Enough $PbSO_4$ is weighed out to make about 150 ml of a 3 per cent suspension. The powder is mixed with 2 or 3 ml of 5 per cent gum arabic solution and about 1 ml of 5 per cent lead nitrate solution. This mixture is rubbed well on a glass plate with a spatula, the purpose being to break up the agglomerates of small particles. The paste is now transferred to the mixing flask and diluted with distilled water.

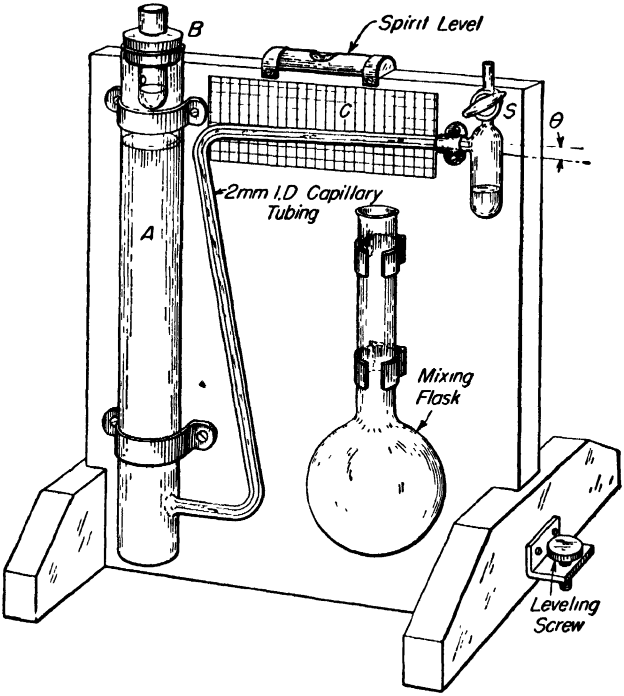

FIG. 51. Sedimentation-tube assembly.

The sedimentation tube and its side arm are cleaned thoroughly with hot cleaning solution and rinsed with distilled water. This preliminary treatment is of the utmost importance, since the slightest trace of foreign matter will cause sticking of the meniscus. With the stopcock open the apparatus is filled with distilled water to such a height that the meniscus in the side tube rests near the lower end of the inclined part of the capillary. The top height in the large tube, A, is marked, and the distance between this mark and the sampling level is measured to give the height h. The water is then drawn up to a point on the scale near the further end of the inclined capillary tube. The stopcock is closed and the large tube emptied. The suspension is now poured in to the top height mark and the suspension is stirred. After opening the stopcock, the level in the capillary is read at suitable intervals of time. At least 5 hr of settling should be allowed if lead sulfate is used. For other materials longer periods may be required.

Distilled water placed in the reservoirs of B and below S serves to minimize errors due to evaporation in the sedimentation tube.

It is also necessary to measure the inside diameter of the tube for use in the calculations. The tangent of the angle θ of inclination of the side tube is read from the graph-paper backing as ordinate divided by abscissa.

Calculations. The relationship between the weight of material, M_t, which settles out in time t and the horizontal displacement of the meniscus, x, is found in the following way:

$$a = \frac{D}{d}h - h = x \tan \theta \qquad (2)$$

where a = the difference in height of the menisci in the two tubes
D = mean density of the suspension
d = density of the suspension medium, in this case, water
h = distance from the sampling level to the meniscus in the large tube
x = length of the base as determined from positions of the meniscus
θ = angle the capillary tube makes with the horizontal

The weight of the material which settles past the sampling level is obtained from densities and volumes. Thus,

$$D = \frac{v_s d - v_m d + M}{v_s}$$

where v_s = volume of the suspension corresponding to the height h
v_m = volume of the medium displaced, i.e., the volume of the solid
M = weight of solid phase in the suspension above the sampling level

Now, if S is the specific gravity of the solid,

$$D = \frac{Sv_s d - Md + MS}{v_s S}$$

Substitution of this expression in Eq. (2) leads to the desired relationship, namely,

$$M = \frac{Sv_s d \cdot x \cdot \tan \theta}{h(S - d)} = kx \qquad (3)$$

The weight of material, M_t, which has settled below the sampling level in time t is simply the difference between the weight initially, $M_0 = kx_0$, and that at time t, kx.

$$M_t = k(x_0 - x) \tag{4}$$

where x_0 = initial horizontal position of the meniscus ($t = 0$)
x = horizontal position of meniscus at time t
k = proportionality constant, which is computed from Eq. (3), using data to be found in the standard handbooks and certain apparatus constants

From Eq. (4) the weight M_t settled below the side-arm entrance may be calculated after any time. A sedimentation curve may then be constructed by plotting the weight settled against time. The time scale is then converted to particle size by the use of Stokes' law. Tangents are drawn on this plot at times corresponding to equal particle-size intervals. The difference between the intercepts of any two tangents on the ordinate corresponds to the percentage of material in the size interval at whose limits the tangents were drawn.

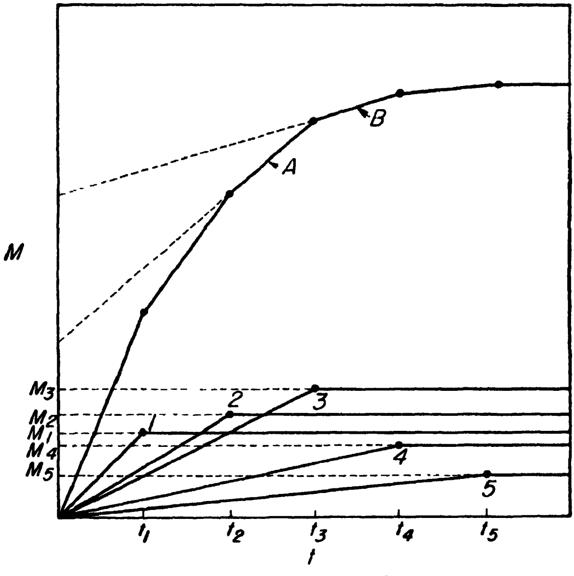

FIG. 52. Hypothetical mass-time curve.

This can perhaps best be seen from the construction of a synthetic curve similar to the experimental one, except that only a few sizes of particles are allowed, thus giving rise to a plot of connected straight segments. If all particles in a sample were of exactly the same size, the sedimentation "curve" would look like one of the curves labeled from 1 to 5 in the lower part of Fig. 52. For example, in curve 3 the sediment collects at a uniform rate until time t_3 is reached, when all the material M_3

will have settled out, and no further change in M with time occurs; t_3 will thus be the time required for this particular size of particle to fall the distance h in the sedimentation tube. The equation for the curve is $M = m_3t$ for $t < t_3$, where m_3 is the slope, and $M = M_3$ for $t > t_3$.

If five sizes of particles are present together, the sedimentation curve will assume the form of the upper curve in the figure. Any point on this curve for a given time is obtained by summing corresponding points on all of the individual curves. It can be verified by inspection that the equation of straight line segment A, for example, is

$$M = (m_3 + m_4 + m_5)t + M_1 + M_2 \qquad t_2 < t < t_3$$

Now this particular segment is tangent to the sedimentation curve between t_2 and t_3, and according to this equation the intercept on the weight axis is simply the total weight of material having sizes which have completely settled out at time t_2. The intercept of segment B is then $M_1 + M_2 + M_3$, and the difference between the two intercepts is just M_3, which is the weight of material in size class 3 (*i.e.*, between 2 and 4).

In practice an infinite variety of sizes is present, and a smooth curve is obtained. The above analysis can be readily extended to this case.

A plot of intercept differences for equal size intervals versus average radius is the particle size distribution curve which is desired.

Practical Applications. Knowledge of particle size and size distribution is finding important use in the cement, ceramic, ore flotation, photographic emulsion, and paint pigment technologies. The rate of settling of precipitates is often important in analytical chemistry. Relationships between size and the behavior of soils, the stability of pastes, etc., have been recognized for a long time.

Suggestions for Further Work. Sedimentation studies with typical soils, paint pigments, or cements may be carried out, and more complete mathematical analyses of the distribution curves may be attempted.

The weight of particles settling from a suspension may be determined directly by suspending a pan from one arm of a balance in the medium. When carefully done, this method is capable of considerable precision.[3,4]

At least in principle, the use of floats of known density might eliminate many of the practical difficulties of the sedimentation tube method used in this experiment.[1] Presumably problems encountered in the construction of suitable floats could be solved to provide a more accurate measure of the small density differences which are involved.

References

1. Berg, *Ingeniørvidenskab. Skrifter, Danish Acad. Tech. Sci.*, No. 2 (1940).
2. Kelly, *Ind. Eng. Chem.*, **26,** 928-930 (1924); "Colloid Symposium Monograph," Vol. 2, pp. 29–36 (1925).
3. Oden *in* Alexander: "Colloid Chemistry," Vol. I, Reinhold Publishing Corporation, New York (1928).
4. Svedberg and Rinde, *J. Am. Chem. Soc.*, **45,** 943 (1923).
5. Wiegner, *Landwirtsch. Vers.-Sta.*, **91,** 41 (1918).

47. ION-EXCHANGE CHROMATOGRAPHY

The separation of cations by means of elution from a cation exchange resin with a complexing reagent is illustrated.

Theory. Ion exchange is essentially nothing more than a chemical reaction which proceeds by double decomposition. A familiar example of this type of reaction is

$$2NaCl + H_2SO_4 \rightarrow 2HCl \uparrow + Na_2SO_4$$

Ion exchange works exactly the same way with a large, insoluble synthetic molecule taking part. A cation exchange resin is a macromolecular acid having sulfonic, phenolic, or carboxylic groups. Just as H_2SO_4 and HCl ionize into H^+ ions and SO_4^{--} or Cl^- ions, a cation exchange resin can dissociate into H^+ ions and the insoluble macromolecular anion, usually designated by R^-. Dowex-50 is a resin of the sulfonic acid type. Other cations can replace the hydrogen in the resin just as the sodium replaces the hydrogen in the H_2SO_4 in the reaction as written above. If, for example, a solution of $NiCl_2$ and $CoCl_2$ is poured on the column, the following reactions take place:

$$Ni^{++} + H_2R \rightleftharpoons NiR + 2H^+ \quad (1)$$

$$Co^{++} + H_2R \rightleftharpoons CoR + 2H^+ \quad (2)$$

The "capacity" of a resin is the maximum number of equivalents of cation which may be bound on one gram of resin. If a resin of sufficiently high capacity is used, all the Ni^{++} and Co^{++} ions will be adsorbed in a relatively narrow band at the top of the column. Note that these reactions are reversible; i.e., if an acid, say HCl, is poured on the column, the increase in the hydrogen-ion concentration will cause the equilibrium to shift to the left and the metal ions will be replaced on the resin by hydrogen ions.

If a bed of resin is arranged in column form and metal ions are adsorbed in the top layer, they may be washed through the column by a flow of solvent, the rate of transport of the ions being dependent upon their equilibrium concentration in the *solution*. As the equilibrium solution is washed down the column, the adsorbed ions at the upper edge of the band dissociate into solution and a certain portion of the ions carried to the layer of fresh resin becomes adsorbed by the resin.

The affinity of the resin for a metal ion is affected by two factors, the radius of the hydrated ion and the valence of the ion. Thus, two different metal ions will be held by the resin to different extents. A separation of the two ions might then be achieved by taking advantage of this difference in the affinity of the two ions for the resin. Although this difference is sometimes quite small, it can be accentuated by use of a complexing agent (such as citrate buffer or tartrate buffer) which effectively removes metal ions from the solution and competes with the resin for the cations. The speed with which a given ion moves down the resin column is then dependent upon the affinity of the resin for the ion and the extent to which the ion is complexed by the complexing agent.

When a solution of ammonium citrate (of a pH at which nickel citrate complex ions are formed) is passed through a resin column on which nickel ion has been adsorbed at the top, the following reversible reaction is set up:

$$2NH_4^+ + NiR \rightleftharpoons (NH_4)_2R + Ni^{++} \qquad (3)$$

At the same time, the citrate anion of average charge $-m$ (represented by A^{-m}) reacts with the Ni^{++} ion as indicated by the reversible reaction

$$Ni^{++} + xA^{-m} \rightleftharpoons NiA_x^{2-xm} \qquad (4)$$

where x is the number of anions which complex with each nickel ion. The fraction of the total nickel found in each form, i.e., as Ni^{++}, NiR_2, and NiA_x^{2-xm}, is determined by the equilibrium constants for reactions (3) and (4). A similar set of two reactions occurs for the Co^{++} ion. Now, if these two equilibrium constants for the nickel reactions are sufficiently different from those for the cobalt reactions, a separation may be achieved. By using a complexing agent, there are two equilibrium constants instead of one with which to work.

The process may be visualized as follows (again using the nickel as an illustration). When the nickel chloride solution is poured on the column, the nickel is adsorbed in a narrow band at the top.

$$Ni^{++} + (NH_4)_2R \rightleftharpoons NiR + 2NH_4^+ \qquad (5)$$

When ammonium citrate buffer is passed into the column, the Ni^{++} ion is complexed, thereby shifting the equilibrium of reaction (5) to the left. The nickel in solution moves down the column to a region of "fresh" resin $(NH_4)_2R$. This amounts to increasing the concentration of $(NH_4)_2R$ which shifts the equilibrium of reaction (5) to the right again; i.e., the Ni^{++} ion is readsorbed. Thus, as the solution passes down the column, the Ni^{++} is successively adsorbed and desorbed in a process similar to fractional distillation in which a substance is successively vaporized and condensed. The same process is going on with the Co^{++} ions. Thus, the small differences in equilibrium constants are made use of many times, with the result that a better separation is achieved by column operation than in a batch experiment. When citrate buffers of higher pH are used, reaction (4) is displaced to the right and the metal ions are eluted more rapidly from the column.

Apparatus. Ion exchange column filled with Dowex-50; citrate buffer (50 g citric acid monohydrate and 1 g phenol per liter of water adjusted to pH 3.30–3.40 with concentrated aqueous ammonia); $NiCl_2$; $CoCl_2$; two 25-ml graduates; spectrophotometer; spectrophotometer cells; lens tissue; long tube with bulb.

Procedure. The experimental arrangement for this experiment is illustrated in Fig. 53. It is assumed that the resin has been completely freed of nickel and cobalt and has been washed with distilled water. If it is not certain that this has been done, the column is washed with about 300 ml of 2*N* HCl followed by about 300 ml of distilled water. Washing may be stopped when the effluent is basic to methyl orange (about pH 4.5).

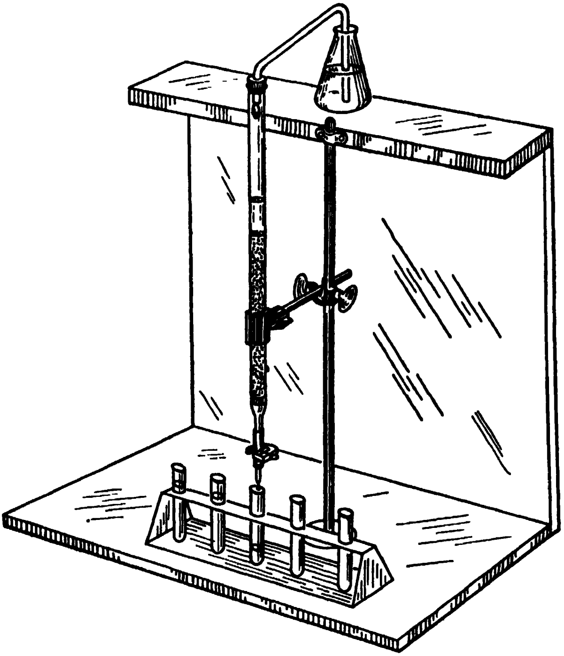

FIG. 53. Ion-exchange column.

Quantities of nickel and cobalt chlorides containing 200 mg of the metal are weighed out, mixed, and dissolved in a small quantity of distilled water (not over 20 ml). In order to save time, it is advisable to suck out the water above the resin bed by using a long glass tube and rubber bulb before pouring on the solution of the metals. The solution containing metal ions is poured on the top of the resin bed and allowed to flow into the column. If distilled water is then poured carefully into the tube above the resin bed, it will form a layer above the salt solution and there will be an adequate head to force the solution through the column. A siphon is connected to the column, and about 150 ml of distilled water is allowed to flow through it. If the washings are colorless, they are discarded.

The distilled water above the column is then withdrawn with the long glass tube and bulb, and citrate buffer is poured on the column. A large container of citrate buffer is connected by means of a siphon. The rate of elution is controlled by means of a pinch clamp so that the flow rate is 2.5 to 3.0 ml min^{-1}. Twenty-five-ml samples of the effluent are collected until the first nickel appears, and from that point on 10-ml samples are collected. For each fraction the volume and time are recorded (the flow rate may be checked from these data), and a test tube full of the solution is corked for analysis.

Since the cobalt tends to tail out through a large volume, the last bit may be removed by washing the column with 2 N HCl and then with distilled water (at least 300 ml).

The solutions are analyzed directly with a spectrophotometer. It has been found convenient to analyze for cobalt at a wavelength of 510 mμ and nickel at 650 mμ. A small amount of nickel does not interfere with the analysis for cobalt, and vice versa. The concentrations are read directly from plots of absorbancy [log (I_0/I)] (Exp. 4) versus concentration of nickel or cobalt; these are provided in the laboratory or determined separately.

Calculations. The concentrations of nickel and cobalt in the various fractions are plotted versus volume of effluent. The quantities of nickel and cobalt recovered from the column are calculated from the concentrations and volumes of the fractions. The per cent recovery is computed.

Practical Applications. Chromatographic adsorption is finding many applications. It is widely used for qualitative analysis of organic compounds and for the separation of different compounds in a mixture of biological materials. It has been used even for the separation of isotopes.[5]

Suggestions for Further Work. The influence of pH, rate of elution, or ratio of weight of metal to weight of resin may be investigated.

A vertical tube packed with powdered sugar under the proper conditions may be used for separating by chromatographic adsorption the various plant pigments obtained by crushing leaves and treating them with petroleum ether.

References

1. Block, Durrum, and Zweig, "Paper Chromatography and Paper Electrophoresis," Academic Press, Inc., New York (1955).
2. Cassidy *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. V, Interscience Publishers, Inc., New York (1951).
3. Roberts, Willeford, and Alberty, *J. Chem. Educ.*, **29**, 545 (1952).
4. Series of papers on the separation of rare earths and radioisotopes by ion exchange, *J. Am. Chem. Soc.*, **69**, 2769–2881 (1947), especially Tompkins, Khyn, and Cohn, p. 2769.
5. Spedding, Powell, and Svec, *J. Am. Chem. Soc.*, **77**, 6125 (1955).
6. Tompkins, *J. Chem. Educ.*, **26**, 32, 92 (1949).

CHAPTER 14

PHOTOCHEMISTRY

48. PHOTOLYSIS OF URANYL OXALATE

This experiment gives practice in studying the influence of several variables on the rate of a photochemical reaction. The quantitative effect of time, volume, distance, and concentration is to be determined. The experiment illustrates also the calculation of radiation intensities by the use of an actinometer.

Theory. Oxalic acid is transparent except in the shorter ultraviolet. Uranyl ions in water absorb light of wavelength shorter than about 4360 A. The absorbed light energy is simply degraded into heat. However, when uranyl ions are mixed with oxalic acid, they tend to interact, as shown by the fact that the absorption of light by the uranyl solution is increased by the addition of the *transparent* oxalic acid. Because of this loose intermediate compound between the oxalic acid and the uranyl ions, the oxalic acid is decomposed by the light which the uranyl ions absorb. This transfer of energy by a light-absorbing molecule to another molecule is sometimes called *photocatalysis.* Usually the formation of some kind of a compound or loose union is necessary before energy can be transmitted from one molecule to another.

The reaction is

$$UO_2^{++} + H_2C_2O_4 + \text{light} \rightarrow UO_2^{++} + H_2O + CO + CO_2$$

and the amount of oxalic acid decomposed is readily determined by titration with potassium permanganate before and after exposure. It is so simple to measure and so reproducible that it is widely used as an actinometer for measuring by chemical means the intensity of radiation in the ultraviolet and violet regions of the spectrum.

Apparatus. A capillary mercury-vapor lamp AH-5 and transformer; four 1-in. Pyrex test tubes; shielding box with cover; 10- and 25-ml pipettes; 1 liter 0.02 *M* oxalic acid; 1 liter 0.02 *M* uranyl nitrate; 2 liters 0.02 *N* potassium permanganate; burette; 2 Erlenmeyer flasks.

Procedure. A ventilated wooden box about 50 by 80 cm is fitted with a cover. The inside is rendered nonreflecting by painting with lampblack in dilute varnish. Two semicircles are drawn on the cover with radii of 15 and 30 cm. Along each are bored four holes, 15 cm apart in the smaller circle and 30 cm in the larger circle, for holding the 1-in. test tubes. A Mogul lamp socket pointing downward is fastened to the cover at the center of the semicircles. It, too, is painted dull black.

A General Electric AH-5 mercury-vapor lamp is screwed into the socket and connected to the special transformer. Although the lamp is shielded by a box, ultraviolet-absorbing glasses must always be used to protect the eyes if there is any exposure to the lamp.

Oxalic acid is weighed out accurately to give 1 liter of a standard solution. It should be about 0.02 N in oxalic acid. This solution is then used to standardize the 0.02 N permanganate solution. All the oxalic acid solutions are titrated by placing them in Erlenmeyer flasks, acidifying with dilute sulfuric acid and heating before adding the permanganate from a burette. The approximately 0.02 M uranyl nitrate solution is prepared by weighing out uranyl nitrate from a weighing bottle.

Each of four Pyrex test tubes is filled with 25 ml of the oxalic acid solution and 25 ml of the uranyl nitrate solution, well mixed. The lamp is turned on for 5 min to reach steady conditions, and then the four tubes are inserted quickly in the first circle 15 cm from the center of the lamp. After 10 to 30 min, depending on the intensity of the light, all the tubes are removed quickly and titrated with permanganate. The titrations are compared with the titration obtained with the same volume of the original unexposed solution. The decrease of the volume of the $KMnO_4$ solution required for titration is a measure of the amount of oxalic acid decomposed by the light. If there is a variation of more than a few per cent among the different tubes in the decrease in volume of potassium permanganate solution required, the lamp is turned or the tubes are spaced differently so as to obtain a more uniform distribution of light.

Pyrex glass absorbs all the radiation below about 3000 A, but the greater portion of the radiation emitted by the lamp is of longer wavelength than this.

In a second experiment the four test tubes are removed one at a time after suitable time intervals, such as 5, 10, 20, 40 min.

Additional determinations are made, usually four at a time, to determine the influence of (*a*) distance from the lamp, (*b*) volume of solution in the test tube, and (*c*) concentration of uranyl nitrate. The experiments are to be planned so that the maximum information is obtained with the minimum number of experiments, so that check determinations are obtained, and so that *only one variable is changed at a time.* Obviously, for the best use of time the titrations should be made while the next set of solutions is being irradiated.

If the line voltage fluctuates, all four determinations will be affected equally, and even in passing from one set to another any variations in the intensity of the light will tend to average out over an extended exposure.

Calculations. The numbers of moles of acid decomposed are plotted against the times of exposure. The rate of the reaction is determined as a function of the different variables. The influence of the other variables is represented graphically or mathematically in some suitable form. Explanations are then sought which will account quantitatively for the effect of each variable.

The number of ergs of radiant energy absorbed per second is calculated for the 50 ml of solution. The effective radiation lies between 3200 A, the absorption limit of Pyrex, and 4400 A, the absorption limit of uranyl ion, and the average is taken as 3800 A. The average quantum yield is 0.57 molecule of oxalic acid decomposed per photon absorbed.[1] The energy of each photon or quantum is $h\nu$, where h is Planck's constant, 6.62×10^{-27} erg sec, and ν is the frequency of light. The number of molecules of oxalic acid decomposed is 6.02×10^{23} times the number of moles.

Practical Applications. Ultraviolet light is used in the treatment of skin disease and rickets and for other purposes. The irradiation of foods with ultraviolet light assures an adequate supply of vitamin D. In chemical kinetics the mechanisms of certain reactions may be studied advantageously by exciting the molecules photochemically.

The quantitative measurement of the radiation intensity is important in all cases, and the photolysis of uranyl oxalate offers a convenient and accurate chemical means for obtaining this quantity.[1]

Suggestions for Further Work. The absolute measurements of energy may be checked directly with a thermopile and standard lamp as given on page 449, using a cell with flat Pyrex windows instead of test tubes and suitable filters to absorb the light of wavelength longer than 4400 A (page 445).

Other photodecompositions catalyzed by uranyl ion include the decarboxylation of malonic acid.

Other reactions may be studied. The quantum yield may be determined by chemical analysis assuming that the same number of photons of light is absorbed by 0.01 *M* uranyl nitrate in all the solutions.

Ferric ion, which also acts as a photocatalyst in the decomposition of oxalic acid, may be studied in a manner similar to that used for uranyl ion.[2]

References

1. Leighton and Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).
2. Livingston, *J. Phys. Chem.*, **44**, 601 (1940).
3. Noyes and Leighton, "Photochemistry of Gases," Reinhold Publishing Corporation, New York (1941).
4. Rollefson and Burton, "Photochemistry," Prentice-Hall, Inc., New York (1939).

49. PHOTOHYDROLYSIS OF MONOCHLOROACETIC ACID

This experiment gives practice in the use of the actinometer and the calculation of the quantum yield—the number of molecules reacting per photon or quantum of light actually absorbed by the solution. It requires a quartz mercury-vapor lamp rich in light of 2537 A, but no optical instruments or quartz cells are needed.

Theory. Monochloroacetic acid hydrolyzes according to the reaction

$$CH_2ClCOOH + H_2O = CH_2OHCOOH + HCl$$

At room temperature the reaction is practically negligible, but when activated by ultraviolet light of 2537 A, which monochloroacetic acid absorbs, the reaction goes more rapidly. Not every molecule that absorbs a quantum of light undergoes reaction with the water, because some molecules lose their excess energy before they can react. On the average the chance of reaction is about 1 in 3, giving a quantum yield of 0.31 at 25°.[3,4,5] At 70° the quantum yield is 0.69.

The number of quanta of light absorbed by the monochloroacetic acid solution is calculated from data on the extent of reaction produced in samples of an actinometer solution. These samples, together with samples of monochloroacetic acid, are placed similarly with respect to the radiation source. The quantum yield for the actinometer and the relative absorbancies of the actinometer and unknown solutions must be known. The actinometer consists of a solution of uranyl nitrate and oxalic acid and is described in the preceding experiment.

Apparatus. Germicidal mercury-vapor lamp available at electric-fixture stores; four small rectangular plastic dishes or small crystallizing dishes; 50-ml pipette; two burettes; potentiometer; silver electrodes; calomel electrode; 200 ml 0.2 *M* uranyl nitrate; 200 ml 0.02 *M* oxalic acid; 500 ml 0.025 *N* potassium permanganate; 200 ml 0.1 *M* monochloroacetic acid, freshly prepared: 200 ml 0.005 *M* mercuric nitrate; 200 ml 0.005 *M* silver nitrate; sodium nitroprusside.

Procedure. The amount of monochloroacetic acid hydrolyzed is compared with the amount of oxalate decomposed under the same conditions of light absorption. The second reaction is used as an actinometer for calculating the quantum yield of the first. The absorbancy indices for the two solutes are not equal, but for the concentrations and thicknesses used, the actinometer solution absorbs practically all of the incident light up to 4360 A while the monochloroacetic acid solution absorbs completely the light at 2537 A and does not absorb at longer wavelengths of the mercury arc. The high-voltage "cold" mercury lamp used emits radiation in which approximately 85 per cent of the light has a wavelength of 2537 A. Not all the remaining 15 per cent is absorbed by the uranyl oxalate.

In making up the solutions, the oxalic acid is weighed out accurately so that it may be used to standardize the potassium permanganate solution. An equal volume of the uranyl nitrate solution is mixed with the oxalic acid solution. The monochloroacetic acid need not be made up accurately because the determination of the chloride ion, produced by the ultraviolet light, is the only analytical measurement which is made.

The apparatus is shown in Fig. 54. Four rectangular dishes of the type used for ice cubes are filled with 50 ml of solution and placed in line under two germicidal ultraviolet lamps of the type sold for refrigerator and hospital use. The lamps are mounted parallel in the top of a wooden box provided with a hanging hinged door in front to protect the eyes from the ultraviolet light. To prevent overheating, air at about 15 $\text{ft}^3\ \text{min}^{-1}$ is drawn through the box along the lamps by an exhaust fan.

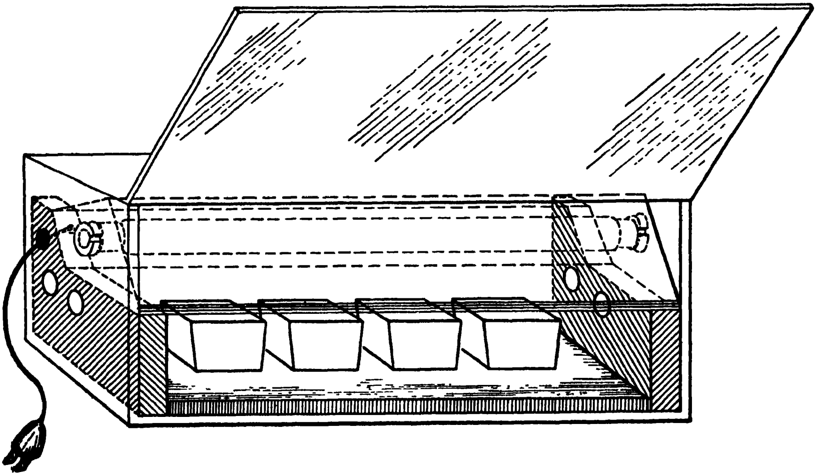

FIG. 54. Apparatus for the photohydrolysis of monochloroacetic acid.

Since the light intensity varies in different positions, the actinometer solution is placed in the first and third positions with the monochloroacetic acid solution in the second and fourth positions. The time of exposure is recorded. It should be long enough (over 2 hr) to give a satisfactory titration.

The uranyl oxalate is titrated with the 0.02 N potassium permanganate after adding an excess of dilute sulfuric acid and heating. The two monochloroacetic acid solutions are titrated with the 0.01 N mercuric nitrate. The amount of photochemical reaction is so small and the solutions are so dilute that sharp end points cannot be expected. They are, however, adequate for the kinetic measurements involved.

The titration of the chloride ion produced by the photohydrolysis of the monochloroacetic acid depends on the fact that the mercuric ions are removed with chloride ions in the form of undissociated mercuric chloride molecules, according to the reaction $Hg^{++} + 2Cl^- = HgCl_2$. After sufficient mercuric ions have been added to react with the chloride ions present, further addition gives a precipitate of white mercurous nitroprusside which is observed as a slight turbidity.

The irradiated monochloroacetic acid is transferred to a 100-ml flask, and about 0.1 ml of a 10 per cent solution of sodium nitroprusside is added, from a dark bottle, before titration; the solution is brought to a pH of about 7 with sodium hydroxide; and approximately 0.005 *M* mercuric nitrate is run in from a burette until a faint, permanent turbidity is detected. The approximately 0.005 *M* mercuric nitrate solution is standardized against a standard solution of HCl or NaCl under conditions similar to those used in the experiment. A blank run is made with the nitroprusside in water alone, and the volume of mercuric nitrate solution necessary to give detectable turbidity is subtracted from the titration reading for the standardization and for the photolysis determination.

Instead of determining the extent of photohydrolysis by titration with mercuric nitrate, it may be determined by potentiometric titration in an alternative procedure using a silver electrode similar to that described in Exp. 39. Two silver wire electrodes are used, one of which is placed in about 0.01 *M* $AgNO_3$, and connected through a salt bridge of ammonium nitrate to a beaker containing the monochloroacetic acid and the second silver electrode. The two electrodes are connected to a potentiometer, and the voltage is plotted after each addition of 0.005 *M* $AgNO_3$. The silver ions added are precipitated as silver chloride, and the voltage remains nearly constant, until the chloride ion is all used up. The voltage changes rapidly then with each small addition of silver nitrate. The steepest part of the titration curve gives the end point.

In a check experiment the uranyl oxalate solution may be placed in the first and second containers, and the monochloroacetic acid in the third and fourth.

Calculations. The number of molecules of oxalic acid decomposed (the number of moles times 6.02×10^{23}) is calculated from the difference in the volumes of permanganate solution required to titrate the oxalic acid solution before and after exposure to the light. The number of photons absorbed by the actinometer is calculated from the fact that 1 photon decomposes on the average 0.57 molecule of oxalic acid.[2] The number of photons received by the two actinometer dishes is added to give the number of photons received by the two monochloroacetic acid samples. This number is reduced by 15 per cent to obtain the number of photons absorbed by the monochloracetic acid, thus allowing for the radiation absorbed by the actinometer but not by the monochloroacetic acid solution. The number of molecules of monochloroacetic acid hydrolyzed is calculated from the number of chloride ions produced as determined by titrating with mercuric nitrate or silver nitrate. This number divided by the number of photons absorbed gives the quantum yield.

Quantum yields should be independent of the length of exposure. This fact may be checked by comparing experiments with different lengths of exposure. The accuracy is greater for the longer exposures.

Practical Applications. These experiments illustrate the use of the actinometer in measuring quantitatively the intensity of radiation and the determination of the efficiency of photochemical reactions.

Suggestions for Further Work. A better method[3] for measuring the energy absorption consists in making a determination with a flat quartz dish containing a concentrated solution of monochloroacetic acid, which absorbs the light of 2537 A, placed over the uranyl oxalate dish. In a second experiment the upper quartz dish contains water. The titration *a* obtained for uranyl oxalate with the monochloroacetic acid filter gives a measure of the number of quanta of wavelength longer than 2537 A, and the titration *b* with the water gives a measure of all the radiation absorbed by uranyl oxalate together with a correction for losses of light from the filter due to reflection—amounting to about 4 per cent each at the air-quartz interface and at the air-solution interface. If the titration obtained in the absence of an upper filter solution is denoted by *c*, the corrected titration for light of 2537 A alone is $c - (c/b)a$.

The bleaching of dyes such as methylene blue or malachite green may be followed colorimetrically, using as standards various concentrations of the unbleached dyes.

The photodecomposition of hydrogen peroxide may be followed by titration with potassium permanganate. This is a chain reaction subject to catalytic influences. Chain reactions give large quantum yields and do not require micro methods for chemical analysis.

The photobromination of cinnamic acid in carbon tetrachloride provides a good experiment.[1] The quantum yield shows that the reaction is a chain reaction. It increases when dissolved oxygen is removed by boiling under reduced pressure produced by a water aspirator. Equal portions of 0.005 *M* bromine in carbon tetrachloride and 0.01 *M* cinnamic acid in carbon tetrachloride are mixed and placed in the light. The bromine adds to the double bond when exposed to light, and the decrease in free bromine is determined by adding potassium iodide solution and titrating with standard sodium thiosulfate. The bromine removal may be determined also by absorption of light and the application of Beer's law.

References

1. Bauer and Daniels, *J. Am. Chem. Soc.*, **56**, 387, 2014 (1934).
2. Leighton and Forbes, *J. Am. Chem. Soc.*, **52**, 3139 (1930).
3. Noyes and Leighton, "The Photochemistry of Gases," pp. 82 85, Reinhold Publishing Corporation, New York (1941).
4. Smith, Leighton, and Leighton, *J. Am. Chem. Soc.*, **61**, 2299 (1939).
5. Thomas, *J. Am. Chem. Soc.*, **62**, 1879 (1940).

50. PHOTOGRAPHY

The theory and practice of photography are introduced in this experiment.

Theory. In the development of photography, the art has been ahead of the science, but good progress is now being made toward understanding the action of light on the photographic plate.

A photographic plate or film has on its light-sensitive surface what is known as a photographic *emulsion*, consisting essentially of a suspension of exceedingly fine grains of silver bromide in gelatin. These grains of silver bromide have been sensitized in the process of manufacture of the emulsion, either by heating the emulsion or by treating it with a small amount of ammonia. Sometimes these two processes are combined. The ordinary photographic paper for making prints by contact printing has a similar emulsion, with silver chloride or silver bromide as the sensitive material.

When sensitized grains of silver halide in the gelatin are exposed to light, they are activated in such a way that they are more easily reduced to silver by a suitable mild reducing agent. The effect produced by the action of light is called the *latent image*. Nuclei are produced in the silver halide crystals by the light, and when the plate is immersed in a solution of the proper reducing activity (reduction potential in the electromotive-force series), each grain containing a nucleus is reduced to silver. This process is called *development*, and the reducing solution is called a *developer*. The silver halide grains that do not contain nuclei are reduced only after a much longer period of development. The production of nuclei for the latent image depends upon the presence of imperfections in the crystal produced by impurities or strains[4] formed during the nucleation and crystallization. The light energy produces electrons and positive holes which are trapped at imperfections in the crystal, giving mobile silver and halogen atoms which start reaction with the developer. A diffusion of the silver and halogen atoms to the surface of the grain is involved.[4]

After development the plate is *fixed*. In this process the unreduced grains of silver halide are dissolved in sodium thiosulfate ("hypo"), leaving behind the grains which had light-induced nuclei and which were accordingly reduced by development to give black grains of silver. The parts of the plate that received the brightest light when the plate was exposed become the darkest when the plate is developed and fixed, and the finished plate is called a *negative*.

After fixation is complete, the plate is washed and thoroughly dried. A photographic printing paper is then placed behind and firmly in contact with the negative (in a printing frame) and exposed to light; the development and fixing described above are repeated on the paper. The lightest spots on this print correspond to the darkest spots on the negative, and accordingly they correspond to the lightest parts of the original.

The camera and lens are devices for projecting upon the plate an image of the object to be photographed, and the shutter regulates the time of exposure. The shutter is also provided with an adjustable diaphragm to control the aperture of the lens which is used.

The amount of change produced on the plate by the action of the light is, of course, dependent upon the amount of light energy acting. Obviously, the same amount of light can be admitted through the lens by using (*a*) a small aperture and long exposure or (*b*) a large aperture and short exposure. Better definition and greater depth of focus are obtained by the use of a small aperture. In portrait work, however, great depth of focus is not desired; hence a large aperture should be used. In photographing landscapes, it is best to "stop down," as far as light conditions permit, for the longest exposure practicable, viz., 0.04 sec, if the camera is held in the hand.

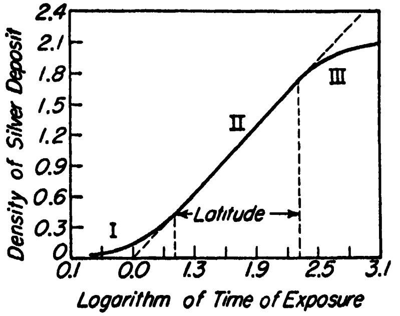

FIG. 55. Characteristic curve for the exposure of a photographic plate.

In a perfect negative, i.e., one which has silver deposits in the various areas proportional in amount to the intensities of light reflected from the corresponding areas of the objects being photographed, the densities of the deposit are proportional to the logarithm of the corresponding exposure. If a series of identical plates are given exposures increasing in geometrical progression (so that their logarithms increase in arithmetical progression), and all plates are subjected to exactly the same process of development, a curve is obtained that shows the density of the developed photographic silver image as a function of the logarithm of the exposure, known as the *characteristic curve* of the film or plate. It has the general form shown in Fig. 55.

If the exposures are such as to bring the photographic plate into the region of the straight line, II, excellent results will be obtained. Good results may often be obtained, however, when the exposure is somewhat less, in the curved part I, because the failure to give direct proportionality between density and exposure is partly compensated for in the printing of the positive.

The use of an exposure meter is recommended with proper attention to the exposure index of the particular type of film or plate used. These indices are supplied by the manufacturer and recorded on the box containing the films.

Emulsions with large grains (silver halide crystals) are faster. They are not suitable for enlargements or lantern slides, and for these a finer-grained, slower emulsion is used.

Apparatus. Camera; plates; plateholder; electric lights; focusing cloth; exposure meter; developer; fixer; photographic paper; darkroom with red light.

Procedure. A line drawing is held securely in a vertical position, squarely in front of the camera and illuminated evenly by two 200-watt frosted lamps* backed by white reflectors of painted metal or of white cloth. The lights are so placed as to avoid any reflection into the lens. The camera is moved forward or backward until the image is of the right size to fit the plate, and the lens is focused until the image stands out sharply on the ground glass in the back of the camera. A hand lens is useful in getting the exact focus.

The plateholder is loaded in the darkroom with two plates. The emulsion side is arranged to face the lens. If a cut film is used, it is slipped into a film sheath, and this is then placed in the holder as if it were a plate. A *process* plate is used for contrast such as is desired for a line drawing. If it is desired to take a photograph of an ordinary object, a plate of normal contrast is used. The length of exposure may be determined with an exposure meter of the photovoltaic type held near to the object to be photographed.

In computing the exposure, the dial of the exposure-meter calculator is adjusted for the exposure index of the particular film or plate used. The diaphragm openings in the camera shutter have different values, depending on the system used, U.S. or f. At a setting of 16, the two systems have identical areas of diaphragm opening (also U.S. 8 $= f/11$, and U.S. 32 $= f/22$). In the f system, the diaphragm opening represented by $f/16$ means that the diameter of the opening is one-sixteenth of the focal length of the lens. With the setting of $f/16$ and a process plate, an exposure of about 10 sec or less is appropriate, but the exact exposure is obtained from the exposure meter. Two pictures are taken, one with a slightly longer exposure than estimated and one with a shorter exposure.

After the camera has been focused, the loaded plateholder is inserted in the back of the camera, without changing the position of the camera. The shutter is closed, the diaphragm is adjusted to the desired opening, and the slide is pulled out of the plateholder. After exposure, the slide is immediately replaced. It is a convention that the black side of the handle on the slide is always placed outward after the plate has been exposed.

Three trays containing developer, water and fixing bath are placed near the red lamp in the darkroom.† At 20°C, the image appears in 15 to 20 sec, but development should be continued until the details in the

---

* Photoflood lamps may be used and the time of exposure considerably reduced. These lamps have a relatively short life and should not be left burning. A double-pole double-throw switch can be used so as to have the lamps connected in series during the operation of focusing and connected in parallel for the few seconds during which the exposure is made.

† If *panchromatic* plates or films are used the development must be carried out in total darkness.

shadows are brought out, usually requiring about 3 min. Control of temperature is very important, as a few degrees of change greatly influence the action of the developer. The proper point at which development should be stopped must be learned by experience. The plate is then rinsed to remove alkali and placed in the fixing bath for about 20 min, or at least 5 min after all the halide (white) is apparently removed from the plate. After fixing, the plate is washed for at least half an hour in running water, placed on a rack, and allowed to dry. Upon completion of washing, the surface of the wet plate should be swabbed off (lightly) with wet absorbent cotton before drying. This removes any possible sediment that may have collected on the gelatin surface.

The dry negative is set in a printing frame, a piece of printing paper is placed face down on the negative so that the emulsion side of the paper is in contact with that of the negative, and the frame is closed and exposed for a few seconds to an electric light, at a suitable distance, e.g., 2 ft. Ordinary Velox or Azo F4 or other contrast paper is used for photographs of line drawings. For portraits or landscapes a paper giving less contrast is used. For printing, a dim light may be used instead of the red lamp.

To ascertain the proper printing time, several small strips of paper are placed in the plateholder and given preliminary exposures, each succeeding exposure being double the preceding one. By development of these strips, the proper length of exposure is quickly determined. A properly exposed print takes 60 to 90 sec for development. Development should not be too prolonged, nor should it be necessary to remove the print quickly to save it. As soon as the print has acquired the desired intensity, it is rinsed in a dilute acetic acid solution (5 per cent). This rinsing neutralizes the alkali and stops development and greatly reduces the tendency of the print to stain in the fixing solution. While in the fixing solution, the prints should be moved frequently. Complete removal of the fixing solution by rinsing is important. The drippings from the wet prints are allowed to fall into a dilute alkaline permanganate solution. If the permanganate retains its color, the "hypo" has been removed.

Ready-mixed developers may be purchased, or the developer may be prepared from the formula which accompanies the plate or film.

A suitable formula for process plates or contrast plates or films is prepared by mixing the two following solutions *A* and *B*.

Solution A		*Solution B*	
Water	100 ml	Water	100 ml
Hydroquinone	2.5 g	NaOH	4 0 g
Na_2SO_3	2.5 g		
KBr	2.5 g		

The following solution is recommended for fixing plates or prints:

Solution A		*Solution B*	
Water	500 ml	Glacial acetic acid	10 g
"Hypo" ($Na_2S_2O_3 \cdot 5H_2O$, crude)	125 g	Powdered alum	10.5 g
		Na_2CO_3	10 5 g
		Water	75 ml

The water of solution *A* may be heated to dissolve the "hypo" quickly, but it must be cooled before solution *B* is added.

The reagents are added in the order given, and when they are fully dissolved, the hardening solution *B* is poured into the thiosulfate or "hypo" solution *A* slowly, with stirring. The "hypo" must be *fully* dissolved before adding the hardener; otherwise, sulfur will be deposited. The "hypo" solution must not be hot, because then sulfur will be deposited.

Various printing papers are available. The glossy-surfaced papers, such as press bromide, are suitable for photographs of line drawings and apparatus. Prints on such paper are allowed to dry on smooth ferrotype plates. The prints are laid face down on the highly polished plate, and the excess of water is removed by blotting and rolling the print into intimate contact with the plate. In order to prevent prints from sticking, the metal plate must be thoroughly clean. It should frequently be rubbed with a clean cloth, having on its surface a few drops of pure light oil or a few drops of a dilute solution of paraffin in benzene. The plate must then be rubbed with a clean cloth, until apparently free from oiliness.

Instead of taking a photograph of a line drawing, it may be more instructive to make a photograph and print of an emission or absorption spectrum.

Calculations. The function of each of the ingredients in the developer and the fixing bath is to be explained. A brief discussion of the camera and lens should be included also.

Practical Applications. The practical applications of photography are too many to be enumerated.[6,7,9] Many operations in physical chemistry depend on photographic methods, e.g., spectrography.

Suggestions for Further Work. Photographs of objects as well as line drawings may be taken, e.g., a laboratory apparatus setup, or enlargements may be made from plates or films.

Photomicrographs are made by inserting the top of the microscope into the lens holder of the camera with a special light-tight adapter. The microscope is focused so that the image on the ground glass is sharp. A small magnifying glass should be used in this operation; it is used to best advantage on a clear glass instead of a ground glass. It is often convenient to have a large microscope cover glass cemented on the ground side of the ground glass to give a transparent area for better focusing with a lens. A 200-watt lamp may be used as a source of light, and a screen of ground glass placed near the object helps to make the illumination uniform. Special effects may be obtained by staining the slide and using color filters. Specially sensitized plates are necessary when stains are used. These are useful in photographing colored objects. They are known as panchromatic plates and must be developed in complete darkness, as must also the specially sensitized plates used in spectroscopy.

References

1. Arenson, *J. Chem. Educ.*, **18**, 122 (1941).
2. Boircher, "Fundamentals of Photography," D. Van Nostrand Company, Inc., New York (1940).
3. "Elementary Photographic Chemistry," Eastman Kodak Company.
4. Evans, Hedges, and Mitchell, Theory of Photographic Sensitivity, *J. Photographic Sci.*, **3**, 1–11 (1955).
5. James and Higgins, "Fundamentals of Photographic Theory," John Wiley & Sons, Inc., New York (1948).
6. Mack and Martin, "The Photographic Process," McGraw-Hill Book Company, Inc., New York (1939).
7. Matthews and Crabtree, Photography as a Recording Medium for Scientific Work, *J. Chem. Educ.*, **4**, 9 (1927).
8. Mees, "The Theory of the Photographic Process," The Macmillan Company, New York (1942).
9. Neblette, "Photography, Its Principles and Practice," 5th ed., D. Van Nostrand Company, Inc., New York (1955).

51. SPECTROMETRY AND SPECTROGRAPHY

The calibration and use of a spectrometer or spectrograph are illustrated in this experiment. The study of typical emission spectra is used to emphasize theoretical and practical applications.

Theory.[1,3,4] The passage of polychromatic light through a prism or its reflection from a ruled grating results in the dispersion of the light into its various wavelengths. The visible range of the spectrum so produced extends from the violet at about 4000 A to the deep red at about 7500 A. The angstrom unit, named after the Swedish physicist, was originally defined as 10^{-8} cm. It is now defined as 1/6,438.4696 of the wavelength of the cadmium red line, under carefully specified conditions, which thus becomes the primary standard of wavelength, and is designated as A. Wavelengths of other lines used as secondary standards have been measured relative to the primary standard with a precision as high as 0.0001 A, and the primary standard is known in terms of the standard meter bar to about 1 part in 10,000,000. For all but the most accurate work, 1 A can still be taken to be 10^{-8} cm.

For many purposes it is convenient to characterize spectral lines in terms of *wave number*, $\tilde{\nu}$, which is the reciprocal of the wavelength in centimeters. For example, the wave number of the green line in the mercury arc spectrum is $1/(5460.73 \times 10^{-8}$ cm), or 18,312.6 cm^{-1}.

A sketch of a simple spectrograph is shown in Fig. 56. The collimator renders the rays of light parallel, the prism refracts them to an extent depending on their wavelength, and the spectrum is observed at the focal plane of the camera lens. The collimator is essentially a tube provided with a convex lens at one end and a narrow adjustable slit at the other, the slit being at the principal focus of the lens so that the light enters the prism as a parallel beam. The prism illustrated is of the constant-deviation type and can be regarded as built up of two 30-60° prisms which perform the separation of the rays and a 90° totally reflecting prism. The prism is rotated by means of the screw *A* which moves a lever arm fastened to the prism table. A scale also driven by the screw indicates the wavelength centered in the field.

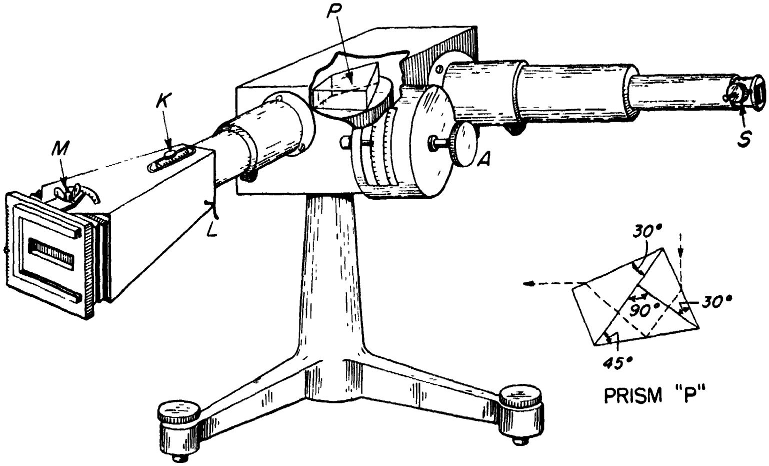

FIG. 56. Constant-deviation spectrograph.

Specially sensitized photographic plates, made by the Eastman Kodak Company, are available for overlapping wavelength ranges from the far ultraviolet to the near infrared; for the visible spectrum panchromatic film is also useful. Glass prisms and lenses restrict observations to wavelengths from about 3600 to 10,000 A. For the ultraviolet region quartz or fluorite optics are used, while infrared prism spectrometers employ NaCl, KBr, and CsBr prisms with special detectors. Reflection gratings avoid the problem of light absorption by prisms and can provide high dispersion and resolution of the spectrum.

The instrument shown in Fig. 56 can be used as a spectrometer for visual work by replacement of the camera by an eyepiece assembly containing a cross hair. The wavelength of a spectral line brought to the cross hair is read directly on the wavelength scale. In another common type of spectrometer the spectrum lines are seen superimposed on an illuminated scale, relative to which the various line positions are read. The scale must be calibrated by use of lines of known wavelength.

The conditions required for the production of emission spectra (high temperature–low voltage arc, or high voltage discharge) are such that only for atoms and very simple molecules can the emission spectrum be studied; for complex molecules the methods of absorption spectroscopy must be used. For atoms the emission lines originate in a change in the electronic energy of the atom. According to the quantum theory, the electronic energy of a particular kind of atom can have only certain discrete and characteristic values. For a gas such as helium, under ordinary conditions all but a negligible fraction of the atoms will be in the lowest electronic-energy state. In the high voltage gas discharge tube, however, atoms are raised to various high energy states. When such an excited atom drops back to a lower energy level, the energy balance is maintained by the emission of radiation which is observed as one of the characteristic emission lines of the atom. The frequency of the emitted radiation is given by the quantum condition

$$h\nu = E_2 - E_1 = hc\tilde{\nu} \tag{1}$$

where h = Planck's constant
ν = frequency
E_2 = energy of higher energy state
E_1 = energy of lower energy state
c = velocity of light
$\tilde{\nu}$ = wave number

The emission spectrum of a diatomic molecule, as obtained from a discharge tube, is a superposition of the spectra of the molecule and of the atoms produced by its dissociation. Because changes in quantized energies of vibration and rotation are possible for molecules as well as changes in electronic energy, the emission spectrum of a diatomic molecule is quite complex. It consists of a series of bands of lines, each band corresponding to a particular change in electronic energy combined with various smaller changes in rotational and vibrational energies.

The theoretical calculation of the electronic energy levels of complex atoms is quite difficult, but for atomic hydrogen, the simplest atom, the following result has been obtained for the wave numbers $\tilde{\nu}$ of the emission lines:

$$\tilde{\nu} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{2}$$

where R = Rydberg constant, 109,677.76 cm^{-1}
n_1, n_2 = integral quantum numbers characterizing initial and final energy states

For a given value of n_1, successive higher values of n_2 produce a series of lines. For $n_1 = 2$, this series of lines lies in the visible region of the spectrum. The Lyman series, for which $n_1 = 1$, is found in the ultraviolet range, and other series corresponding to $n_1 = 3, 4$, etc., lie in the infrared region. It is interesting to note that the relation expressed by Eq. (2) was found empirically by Balmer to represent the visible emission lines of atomic hydrogen long before the first theoretical derivation of the formula was achieved by Bohr.

A. SPECTROSCOPE

Apparatus. Spectroscope; platinum (or nichrome) wire; frosted electric light; chlorides of alkali and alkaline earth metals; mercury-vapor lamp.

Procedure. The spectroscope is set up in a darkened room; a small electric light is placed in position as required to produce in the eyepiece field a scale image that is clear but not too bright. The mercury-vapor lamp is placed in front of the slit, and the slit adjusted to give spectral lines which are narrow and sharp. The scale is calibrated by use of the mercury spectrum; the wavelengths of the various lines are obtained from Fig. 128. If a wavelength spectrometer (Fig. 56) is used, the wavelength scale calibration is checked.

Various salts are then volatilized in a colorless bunsen-burner flame placed at least 15 cm in front of the slit to avoid injury to the spectrometer. A platinum wire* sealed into a glass handle is thoroughly cleaned, dipped into a small beaker of hydrochloric acid, and heated in the flame. The process is repeated (with fresh samples of acid) until a negligible discoloration of the flame is produced. The wire is then plunged while red-hot into a salt held on a watch glass. The holder is then fastened in a clamp to support the wire in the flame, at a level below the slit to avoid interference from the continuous spectrum emitted by the incandescent solid.

The scale readings of the various lines seen are recorded to permit the determination of the corresponding wavelengths by use of a plot of scale reading versus wavelength for the known reference lines. The red lines of lithium and potassium, at 6710 and 7680 A, respectively, can be used to extend the scale calibration into the red region of the spectrum.

Difficulty may be experienced in detecting the violet lines of potassium and calcium, since they are faint and disappear soon after the salt is placed in the flame. The difficulty may be overcome by using an ample supply of salt, reducing the scale illumination to a minimum, widening the slit, and taking a reading as soon as possible after the salt is introduced. After the line positions have been located, the slit may be narrowed to obtain readings of greater accuracy.

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* Nichrome wire may also be used.

Unknown salts or mixtures of salts are then analyzed qualitatively, the elements present being identified through the determination of the wavelengths of their prominent lines for comparison with results tabulated in wavelength tables given in handbooks, etc. Only the lines specified in the tables as strongest need be considered. If the unknowns are not easily volatilized, they should be moistened with hydrochloric acid. The yellow doublet line of sodium (components at 5896 and 5890 A) is so intense that it appears in the spectrum of almost every salt because of the presence of small amounts of sodium as an impurity.

B. SPECTROGRAPH

Apparatus. Spectrograph; panchromatic film; plateholder; mercury-vapor lamp; argon, helium, hydrogen, nitrogen and mercury-argon discharge tubes; discharge-tube transformer; photographic developer and fixer solutions; sample undeveloped film; microscope comparator.

Procedure. The spectrograph focusing is checked by examination of the spectrum from a mercury-vapor lamp* placed in front of the slit. The slit width should be set to give a narrow line (about 0.1 mm) but should not be so small as to require inconveniently long exposures; a slit height of about 8 mm is recommended. The lines should be in good focus in all parts of the spectrum; if this is not the case, further adjustment of the instrument should be made in accordance with the instructions furnished by the manufacturer, or with *expert* assistance.

The panchromatic film, which is employed because of its sensitivity to the entire visible range of the spectrum, must be handled in complete darkness. The film is placed in the holder with the emulsion side out; this operation is facilitated by preliminary examination of a sample undeveloped film. Some holders are designed for use with cut film only, but others accommodate film or plates. In the latter case the film is placed in a metal film sheath for support before being put into the plateholder.

The spectrograph shutter is closed, the holder is attached to the camera, and the black slide covering the film is withdrawn. By means of the rack and pinion control provided, the plateholder position is adjusted so that the top edge of the film is in position for the first exposure. The shutter is then opened, and the spectrum of the mercury-vapor lamp is recorded. The proper exposure times for this and the other spectra studied depend on the characteristics of the particular spectrograph and light sources used. Approximate exposure times for the various spectra should be specified by the instructor as reference data for this experiment. For a new source, a set of trial exposures varying between wide

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* The General Electric H-2 or H-4 mercury-vapor lamp is recommended. Either lamp requires a special transformer for its operation.

limits may first be taken and the optimum exposure time selected on the basis of these results.

The plateholder is moved up 1 cm, as indicated on the adjacent scale, and the next spectrum recorded. Exposures are thus taken of the argon, helium, hydrogen, and nitrogen discharge-tube spectra. The discharge tubes should be placed in position immediately in front of the slit. **Caution:** The operating voltage for these tubes is several thousand volts. A switch in the transformer primary circuit is used to control the discharge tube; the intensity can be varied by a resistance connected in the primary circuit. Alternatively, an autotransformer may be used to supply the primary voltage.

A second mercury spectrum is recorded as the last exposure on the film. The order in which the spectra are taken is recorded.

The plateholder is taken to the darkroom. The film is developed in total darkness in D-19 developer (5 min), rinsed in distilled water, and fixed in F-5 acid fixer (15 min), as described in Exp. 50. It is then washed in running water for 30 min and air-dried.

A straight line is marked on the film with a needle, connecting a sharp line in the upper mercury spectrum with the corresponding line in the lower. The distance of each of the mercury lines from this reference line is obtained using a comparator; the film is mounted between two pieces of *plate* glass, to keep it flat, with the emulsion side up. A preliminary dispersion curve is drawn through a plot of wavelength versus displacement in millimeters from the reference line; the wavelengths of the mercury lines are obtained from Fig. 128. With this curve, lines in the helium spectrum listed in handbooks are identified; their positions relative to the reference line provide additional points to define the dispersion curve more accurately.

The displacements of several lines in the argon spectrum from the reference line are determined, together with those of the several lines of the Balmer series identified in the hydrogen spectrum. The comparator settings should all be approached from the same direction to eliminate difficulties from backlash and looseness in adjustment. From the known order of the exposures, the individual spectra can readily be identified because of the distinctive band structure of the nitrogen spectrum.

If a comparator is not available, an enlargement of the film may be made and the line positions measured with an accurate steel rule.

Calculations. The wavelengths found for the argon lines by means of the dispersion curve are compared with literature values. The wavelengths for the Balmer lines are calculated by use of the theoretical formula of Eq. (2) and compared with those found experimentally. No measurements on the nitrogen spectrum are made, but the features of the spectrum are carefully noted.

Practical Applications. The spectrograph has been one of the most useful tools in the advancement of science, particularly in the fields of chemistry, physics, and astronomy. With it, most of the elements and many compounds may be identified and a quantitative analysis obtained, even with minute quantities. It has aided in establishing the structure of organic compounds. It has been responsible for the discovery of many of our elements. It has made possible a determination of the composition and temperature of the sun and stars. Even the velocities of some of the stars have been calculated with its help. Intelligent advances in photochemistry demand a complete knowledge of absorption spectra, and a spectrometer furnishes the best source of monochromatic illumination for controlled experiments in that branch of physical chemistry.

The nature of the absorption spectrum, whether continuous or discontinuous, is of value in interpreting the mechanism of the molecular absorption and the nature of certain photochemical reactions.

Suggestions for Further Work. The absorption spectrum of potassium permanganate or of a dye solution may be obtained by placing an absorption cell in front of the slit and illuminating it with a small, frosted electric-light bulb. Potassium permanganate and especially salts of neodymium and praseodymium give fairly sharp bands in sufficiently dilute solutions.

Several suitable experiments on band spectra of diatomic molecules have been suggested by Davies.[2]

References

1. Brode, "Chemical Spectroscopy," John Wiley & Sons, Inc., New York (1943).
2. Davies, *J. Chem. Educ.*, **28,** 474 (1951).
3. Harrison, Lord, and Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York (1948).
4. Herzberg, "Atomic Spectra and Atomic Structure," Prentice-Hall, Inc., New York (1937).

52. RAMAN SPECTRUM

The Raman spectra of chloroform and benzene are obtained, using the 4358 A mercury line for excitation. The Raman frequency shifts are measured and compared with the infrared absorption frequencies of the compounds.

Theory.[4,6,11] When a transparent and homogeneous medium is traversed by a beam of light, laterally diffused radiation may be observed. This phenomenon, termed the scattering of light by the medium, is a universal property of matter and had been under experimental and theoretical investigation for a number of years when in 1928 Raman discovered, in the scattered light, weak radiation of discrete frequencies not present in the monochromatic incident light and characteristic of the material under investigation. The term *Raman effect* refers to the production of these altered frequencies, whose complement constitutes the Raman spectrum.

The Raman effect arises from an exchange of energy between the scattering molecule and a photon of the incident radiation, which results in a transition of the molecule from one of its discrete energy states to another and a compensating change in the energy, and hence in the frequency, of the photon. The fundamental equation is

$$h\nu + E_1 \rightleftharpoons h\nu' + E_2 \tag{1}$$

where h = Planck's constant
ν = frequency of incident photon
ν' = frequency of scattered photon
E_1, E_2 = initial and final energy states of the molecule

The Raman line of frequency ν' is called a "Stokes line," if $\nu > \nu'$, and an anti-Stokes line, if $\nu' > \nu$. The Stokes lines correspond to transitions in which the molecule is raised from a lower to a higher energy state at the expense of the photon, the anti-Stokes lines to transitions in which the molecule drops from an excited state to a lower energy level and gives up energy to the photon. Hence any permitted transition can give rise to both a Stokes and an anti-Stokes line, of which the former will be stronger because of the relatively small number of molecules in the higher energy states. Theory and experiment are in good agreement on the ratio of the intensities of the Stokes and anti-Stokes lines corresponding to a given transition.[1]

The difference in frequency between the Raman line and the exciting line is independent of the frequency of the incident light and is a measure of the separation of two energy states of the molecule. It is called the Raman frequency shift, or Raman frequency, and is ordinarily expressed in wave numbers, or cm^{-1} (compare page 255). Thus

$$\Delta\tilde{\nu} = \frac{\nu - \nu'}{c} = \frac{(E_2 - E_1)}{hc} \tag{2}$$

where c is the velocity of light. For polyatomic molecules, only changes in the vibrational contributions to the energy are ordinarily observed in the Raman effect. The total vibrational contribution is the sum of the contributions of all the vibrational degrees of freedom of the molecule; for a particular vibrational degree of freedom, this contribution can have only values given by

$$E_i = (n + \tfrac{1}{2})hc\tilde{\nu}_i \qquad n = 0, 1, 2, 3, \ldots \tag{3}$$

where $\tilde{\nu}_i$ = corresponding fundamental vibrational frequency, cm^{-1}
n = vibrational quantum number

It follows from Eqs. (2) and (3) that in the Raman spectrum of a polyatomic molecule there will be found:

1. Frequency shifts equal to fundamental vibrational frequencies of the molecule, corresponding to transitions between adjacent energy levels associated with a single vibrational frequency. These lines are ordinarily the strongest Raman lines.
2. Frequency shifts equal to linear combinations (sums and differences) of several fundamental frequencies, due to simultaneous changes in the energy associated with the several modes of vibration concerned.
3. Frequency shifts equal to integral multiples of the fundamental vibrational frequencies, due to the less common transitions between nonadjacent levels associated with a single frequency. These lines are usually very weak.

Corresponding to each fundamental vibrational frequency there is a "normal mode of vibration," the complete description of which involves the specification of the motion undergone by each atom in the molecule. Any vibrational motion of the molecule can be represented as a superposition of the different normal modes with appropriate amplitudes. In general, *all* the atoms in the molecule are involved in each normal mode of vibration, but it has been found experimentally and explained theoretically that the presence of various groups in the molecule can give rise to characteristic vibrational frequencies irrespective of the nature of the rest of the molecule.[5] Thus, all aliphatic nitriles have a characteristic frequency of approximately 2,100 cm^{-1} which is associated with the stretching of the carbon-nitrogen triple bond. These group frequencies are often useful in the identification of structural features through the Raman spectrum.

Intramolecular vibrations also give rise to absorption bands in the infrared region of the spectrum at frequencies equal to fundamental vibrational frequencies and their harmonics and combinations. The quantum theory permits a prediction from the structure of a molecule of the number of fundamental vibrational frequencies, etc., that will be observed in the Raman spectrum and in the infrared absorption spectrum. Different rules are found to apply to the two different types of spectra, which thus yield complementary information in the study of molecular vibrations. A given vibrational frequency may be detected only in the Raman effect, only in the infrared spectrum, or in both. Conversely, from a comparison of the infrared and Raman spectra of a compound important information concerning the structure of the molecule may be obtained.

Most studies of Raman spectra have been made on materials in the liquid state. The introduction of special techniques for the Raman spectroscopy of gases[12] has been an important recent development in this field.

Apparatus. Spectrograph; photographic plate or film; AH-2 mercury-vapor lamps and transformers; Raman tube; glass water jacket; chloroform and benzene; filter jacket; filter solution; argon-mercury tube, helium tube; transformer.

Procedure. A typical apparatus assembly is shown in Fig. 57. A spectrograph of fairly large aperture is needed; the common wavelength spectrometer of aperture about $f/16$ gives quite satisfactory results with a slit width of 0.1 to 0.2 mm. Eastman Type 103a-J spectrographic plates are recommended, although the slower panchromatic film can also be used.

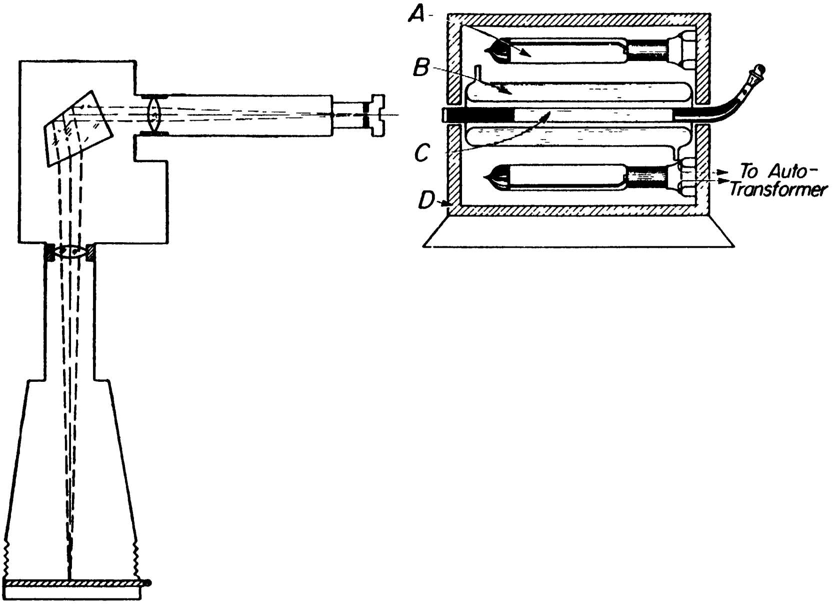

FIG. 57. Apparatus for Raman spectra.

The intense source of light necessary is best provided by a bank of AH-2 mercury-vapor lamps, *A*, which yield sharp lines and comparatively little continuous background in the visible region. A separate transformer is required for each lamp, and a 15-min warm-up period is required to bring the lamps to maximum brilliance.

The liquid to be examined is contained in the Raman tube *C*, of diameter approximately 16 mm and with a plane glass window sealed on the front end.* Except for the window and the section directly opposite the lamps, the tube is painted black to minimize the amount of light reflected rather than scattered into the spectrograph. The Raman tube is protected from the heat generated by the lamps by the glass water jacket *B*,

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* Such tubes are readily available on special order from manufacturers of scientific glassware.

through which tap water is circulated. The entire excitation unit is enclosed in a light-tight box *D*, to keep stray light from entering the spectrograph.

The Raman tube is filled with the desired liquid and placed in the jacket, which should be so adjusted that the axis of the tube coincides with the optic axis of the spectrograph collimator. Improper alignment of the Raman tube is the greatest source of trouble in this experiment. The exposure times required may be minimized by use of a suitable condensing lens selected in accordance with the recommendations of Nielsen.[8] After the two Raman exposures have been made, several reference spectrum exposures are made by means of a mercury-argon discharge tube, placed immediately in front of the spectrograph slit, for use in the construction of a dispersion curve for the spectrograph. Greater accuracy in the latter task is facilitated by superposition of a helium spectrum on the mercury-argon spectrum. The exposure times required for the several spectra depend upon the apparatus used, for which specific recommendations must be provided.

An unfiltered mercury-lamp source will yield spectra clearly showing the excitation of Raman lines by both the 4047 and 4358 A mercury lines. An effectively monochromatic 4358 A light source may be obtained by use of a filter solution* in a filter jacket surrounding the Raman tube but inside the water jacket. Alternatively, a filter jacket may be ring-sealed to the Raman tube, or an appropriate coating may be applied to the Raman tube itself.[3]

Calculations. The Raman lines, which do not appear on the simple spectrum of the mercury lamp, may be seen at the sides of the 4358 A exciting line. Their wavelengths are determined, as described on page 260, by means of a dispersion curve based on the standard values for the wavelengths of the mercury, argon, and helium lines; the photographic enlargement method mentioned can facilitate measurements on the weaker Raman lines, which often are difficult to see under the magnification given by a comparator. The frequencies, expressed in wave numbers, of the Raman lines and of the exciting line are calculated. The Raman frequency shifts for the compounds are then determined and compared with the principal infrared absorption frequencies given in Table 1.

For chloroform, agreement is obtained between the Raman shifts and the infrared absorption frequencies listed. For benzene no such coincidences actually occur; this is an example of the so-called "mutual exclusion rule" for molecules which, like benzene, possess a center of symmetry. In such a case the Raman-active fundamentals are not infrared

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* A solution containing 0.01 per cent crystal violet and 4 per cent *p*-nitrotoluene in ethyl alcohol is recommended. (**Fire hazard.**)

TABLE 1. PRINCIPAL INFRARED ABSORPTION FREQUENCIES OF CHLOROFORM AND BENZENE[a]

$\tilde{\nu}_{\text{vacuum}}$, cm^{-1}

$CHCl_3$	C_6H_6
260	671
364	1,037
667	1,485
760	1,807
1,205	1,964
3,033	3,045
	3,099

[a] Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York (1945).

active, and vice versa. It is readily seen that the application of this rule can be complicated by the experimental uncertainties in the Raman and infrared data.

Practical Applications. Many uses have been discovered for the Raman spectra, and these are described in the voluminous literature published since the effect was discovered in 1928. A knowledge of the fundamental vibrational frequencies of the molecules is required for the theoretical calculation of the thermodynamic properties of gases by statistical methods, and the structures of molecules can be deduced through a study of the Raman and infrared spectra. Raman spectra have also found application in the qualitative[2] and quantitative[10] analysis of multicomponent systems and in the determination of the degree of dissociation of strong electrolytes in aqueous solution.[9]

Suggestions for Further Work. The Raman spectra of other liquids may be determined. A comparison of the Raman spectra of the two geometric isomers *cis*- and *trans*-dichloroethylene provides an interesting study. Infrared data are available for these compounds.[5]

References

1. Chien and Bender, *J. Chem. Phys.*, **15,** 376 (1947).
2. Cleveland, *J. Am. Chem. Soc.*, **63,** 622 (1941).
3. Glockler and Haskin, *J. Chem. Phys.*, **15,** 759 (1947).
4. Herzberg, "Molecular Spectra and Molecular Structure," Vol. I, "Diatomic Molecules," Prentice-Hall, Inc., New York (1939).
5. Herzberg, "Infra-red and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Company, Inc., New York (1945).
6. Murphy, *J. Opt. Soc. Amer.*, **30,** 396 (1940).
7. Murray and Stevenson, *J. Am. Chem. Soc.*, **66,** 812 (1944).
8. Nielsen, *J. Opt. Soc. Amer.*, **20,** 701 (1930); **37,** 494 (1947).
9. Redlich and Biegeleisen, *J. Am. Chem. Soc.*, **65,** 1883 (1943).
10. Rosenbaum, Martin, and Lauer, *Ind. Eng. Chem., Anal. Ed.*, **18,** 731 (1946).
11. Sutherland, "Infra-red and Raman Spectra," Methuen & Co., Ltd., London (1936).
12. Welsh, Stansbury, Romanko, and Feldman, *J. Opt. Soc. Amer.*, **45,** 338 (1955).

CHAPTER 15

RADIOACTIVE ISOTOPES AND TRACERS

53. THE GEIGER-MÜLLER COUNTER

This experiment provides experience in the use of the Geiger-Müller counter and scaling circuit for the characterization of radioactive materials.

THE MAXIMUM ENERGY OF β^- PARTICLES

Theory.[1,4,7] The β^- particles (negatrons) which are emitted by radioactive nuclei originate in a nuclear transformation in which a neutron is changed into a proton and a β particle is released. The negatrons emitted do not all have the same energy; there is a continuous distribution of energy among them, as is shown by Fig. 58. The maximum energy E_{max} is characteristic of the nuclear transformation concerned. The complete distribution curve of Fig. 58 may be established experimentally by means of the electromagnetic β-ray spectrograph,[2,5,6] but the value of E_{max} may be estimated by simpler measurements.

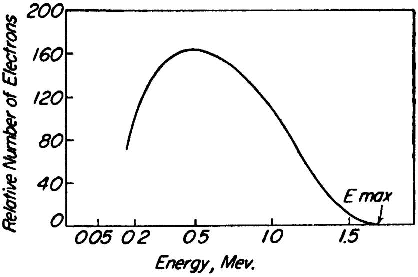

FIG. 58. Energy-distribution curve for β particles of P^{32}. (*After Lyman.*[5])

When high-velocity electrons enter a material medium, they undergo collisions with the electrons of the molecules or atoms they encounter; in these collisions they lose energy and are slowed down and eventually stopped. The distance that the electron can travel in the medium depends upon its initial energy and upon the electron density in the material and is called the range of the electron in the absorbing substance. The range will vary for different substances if expressed in terms of centimeters, but if it is expressed in terms of mass per square centimeter, it is almost independent of the identity of the absorbing material. This result follows from the fact that the number of electrons per unit mass is *nearly* the same for all atoms, so that there will be approximately the same number of electrons in equal masses of two different materials.

The range of a β particle in an absorber will then depend on the initial energy of the particle, and the maximum range will be determined by the value of $E_{\max}$. From an experimentally determined value of the maximum range, the corresponding value of $E_{\max}$ may be obtained by interpolation on a standard curve established by measurements with β particles for which the values of $E_{\max}$ have been found by means of the magnetic spectrograph. The range determination is made by finding the thickness of a suitable absorbing material, such as aluminum, which is required to prevent the passage of any β particles from the source. The range is most easily determined by measuring the counts per minute obtained with various absorber thicknesses and estimating from a plot (of the logarithm of the number of counts per minute against absorber thickness) the absorber thickness through which β particles can no longer be detected above the background. This visual method is capable of high accuracy in cases where γ rays are not present or are present in such low intensity that their contribution to the counting rate is negligible.

A more generally applicable method has been suggested by Feather;[3] the absorption curve for a selected β emitter, for which the range is known, is used as a standard for the determination of the range for β radiation from another source. The primary reference standard for this work has been radium E (5d Bi^{210}), but UX_2 (1.14m Pa^{234}) has also been recommended.[4] For the β particles of UX_2, the range has been found[3] to be 1,105 mg cm^{-2}.

The detection and counting of the transmitted β particles is accomplished by means of the Geiger-Müller tube and a scaling circuit. The statistical considerations concerning the accuracy of counting-rate determinations are outlined in Chap. 17. A useful relation to remember is that the statistical uncertainty in a total of *n* counts is approximately equal to the square root of *n*.

Apparatus. Geiger-Müller tube and mount; scaling circuit; impulse register; electric timer or stop watch; aluminum absorbers; radioactive substances such as phosphorus 32, UX_2 (Pa^{234}) in equilibrium with uranium, etc.*

Procedure. The Geiger-Müller tube, shown in Fig. 59, the impulse register and the electric timer are connected to the scaling unit. With all switches in the *off* position and the high-voltage control in the *low* position, the unit is connected to the 110-volt a-c line. The main power switch is then turned on and a warm-up period of 2 min allowed. The high-voltage switch can then be turned on, and when the applied potential has registered on the voltmeter, the counting switch is thrown on and a radioactive sample is placed under the tube on the top shelf. The high-

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* Radioactive reference sources of many types may be obtained from Tracerlab, Inc., Boston, Mass.

voltage control is now turned up *slowly*, until the starting potential for the particular tube in use is reached, when counts will be recorded by the scaling unit as shown by the response of the neon interpolation bulbs.

The number of counts in a period of 2 min* is determined at this voltage; duplicate determinations are made. The counting switch is turned off, and the reset switch momentarily depressed to extinguish the interpolation lights and clear the scaling circuit. The reading of the impulse register is then recorded, the timer reset to zero, and the counting switch turned on for an accurately measured period of 2 min. At the end of the counting period the counting switch is turned off, and the counting time is recorded, together with the new reading of the impulse register and the number of counts recorded on the interpolation tubes. If a scale-of-64 scaling circuit is employed, the total number of counts is given by

$$N = 64(n' - n) + I$$

where n' = final reading of impulse register
n = initial reading of impulse register
I = counts registered by interpolation tubes

The value of I is obtained by adding together the numbers over those neon tubes which are lit up.

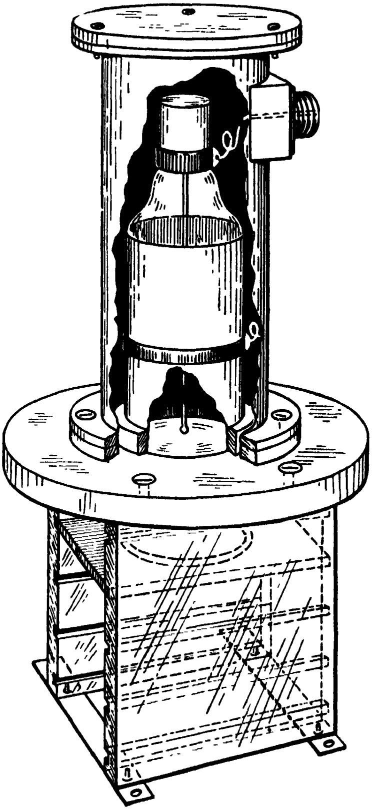

FIG. 59. Geiger-Muller tube and sample holder.

The voltage applied to the Geiger-Müller tube is raised in successive steps of 25 volts, and the number of counts in a 2-min period is determined at each voltage until three successive counting rates agree within ± 10 per cent, showing that the plateau for the tube has been reached (Chap. 25). The operating voltage so found is employed in all subsequent counting work. *Under no circumstances should the posted maximum voltage for the counter tube be exceeded, since higher voltages will cause severe damage or destruction of this sensitive and expensive instrument.*

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* If the activity of the sample is low, sufficient counting time should be allowed to give approximately 2,000 counts.

The number of counts in a 10-min period is next determined with no sample in the holder or near the Geiger-Müller tube. The counts registered, which are due to cosmic rays and stray radiation in the laboratory due to contamination with radioactive materials, comprise the "background" of the laboratory, which contributes to the observed counting rate in any measurement. Radioactive materials, including radium-activated luminous watch dials, should be kept remote from the counter tube. (When maximum accuracy is required, as with weakly radioactive samples, heavy lead shields may be placed around the counting tube to reduce the background.)

A sample containing phosphorus 32 (or other single β emitter) in sufficient quantity to give an initial counting rate of 5,000 to 10,000 counts per minute is then placed on the second shelf of the mount, and the number of counts in a 2-min period is measured. The counting rate is then determined with a series of aluminum absorbers placed on the first (top) shelf; thicknesses of approximately 50, 100, 200, 400, 800, and 1,200 mg cm^{-2} are used singly and in combinations until an essentially constant counting rate is obtained, showing that all the β particles from the source are being absorbed. Longer counting periods will be necessary as the counting rate grows smaller; a minimum of 300 counts should be recorded in any period.

When this procedure is carried out for the β radiation from ${}_{91}Pa^{234}$ as obtained from a standard sample of uranyl nitrate or, preferably, of U_3O_8, the sample must be covered by a thin aluminum foil of *known* thickness (about 30 mg cm^{-2}) to cut out completely the soft β radiation and α particles from the ${}_{90}Th^{234}$ with which the ${}_{91}Pa^{234}$ is in equilibrium.

To illustrate some of the complications which may be encountered in practical work, an absorption curve is then determined for a material which produces either a strong γ-ray contribution to the counting rate in addition to a β particle (as 5.3y Co^{60}) or two β particles of *different energies.* Additional absorbers in the thin range may be required here.

Data are then taken to illustrate the random nature of the radioactive-disintegration process. A sample of low activity is placed in the Geiger-Müller tube mount in the position where a counting rate of approximately 100 counts per minute is obtained. The number of counts in each of a series of 20 or more accurately measured 1-min counting periods is then recorded.

Calculations. The operating voltage for the Geiger-Müller tube at which the counting rates were measured and the normal background of the laboratory in terms of counts per minute are recorded.

The number of counts per minute for each of the steps of the absorption-curve determinations is calculated. A plot is made of the logarithm of the number of counts per minute, background included, against the total absorber thickness for each of the materials studied. The total absorber thickness is the sum of contributions from all the materials between the sample and the sensitive volume of the Geiger-Müller tube. The aluminum absorbers may be calibrated directly; the contribution of the air may be taken as 1 mg cm^{-2} per centimeter of path in air, and that of the window in the Geiger-Müller tube will be specified by the manufacturer. For a mica-window tube it will be approximately 3.5 mg cm^{-2}. Any covering placed over the sample, as in the case of ${}_{91}Pa^{234}$, must be taken into account. Some absorption takes place in the sample itself, but this effect is important only for low-energy particles.

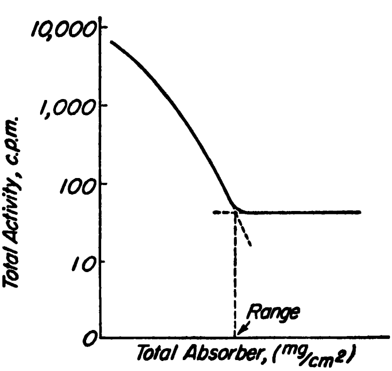

FIG. 60. Visual determination of the range of β particles.

The maximum range of the β particles is estimated visually from the plot for ${}_{15}P^{32}$ or ${}_{91}Pa^{234}$, as indicated in Fig. 60, and the value of E_{max} is obtained by use of Fig. 61. For ${}_{15}P^{32}$ the magnetic-spectrograph value of E_{max} is 1.69 mev (million electron volts). The form of the absorption curve for the other material studied is interpreted qualitatively.

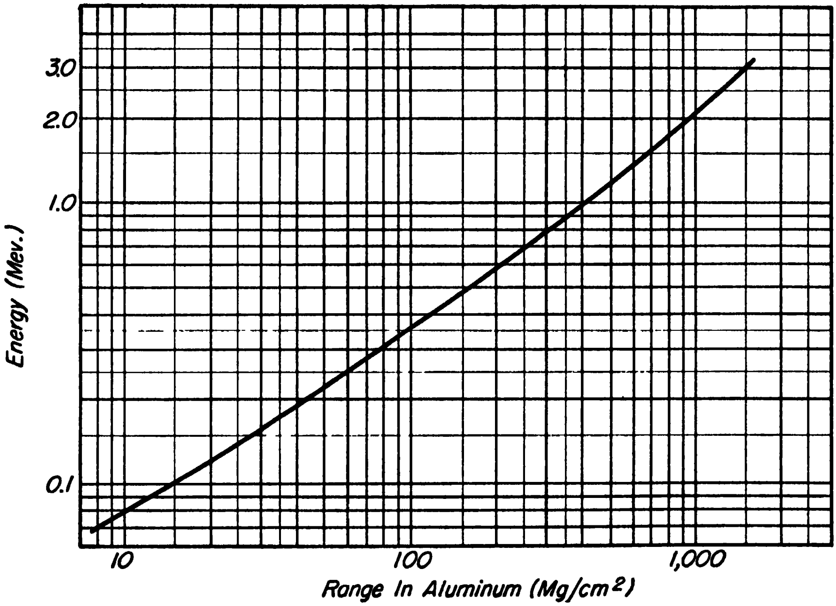

FIG. 61. Range-energy relation for β particles. (*After Glendenin.*[4])

The numbers of counts observed in the series of approximately 1-min counting periods are corrected to the common basis of an exact 1-min counting time; for this calculation, a uniform counting rate in each period is assumed. The average number of counts is determined. The deviations of the individual numbers of counts per minute from the average value are then found and are plotted as in Fig. 80 on page 329.

Practical Applications. The absorption method is a very common and simple procedure for the determination of the energies of the radiations emitted by radioactive materials. Such information is useful in the identification of unknown radioisotopes as isolated, for example, from fission products.

Suggestions for Further Work.[1] The effect of the supporting material on the counting rate obtained for a β-emitting sample may be investigated. A β-ray source, on a very thin plastic or mica sheet, is supported under the counter tube on an aluminum plate with a clearance hole cut through it under the sample, and the counting rate measured. Various metal sheets of differing thicknesses are then placed under the source, and their effects on the counting rate due to back scattering determined. A range of thicknesses can conveniently be obtained in copper; comparison of results obtained with a particular thickness of metals of different atomic number is also pertinent. The effect of the energy of the β radiation may also be checked, by use of a different emitter.

The counting rate obtained with a sample of fixed activity depends on the area over which the sample is distributed as well as the distance from the counting tube. These geometrical factors affecting counting efficiency may be studied.

A correction for the absorption of β particles within the sample itself is necessary when the sample is not negligibly thin. A self-absorption curve may be constructed by measuring the apparent β activity observed with weighed samples of different thickness of the same material. U_3O_8, prepared by thermal decomposition of uranyl nitrate, is a readily prepared source for such work. The various samples should be of the same superficial area and at the same distance from the counter tube. An absorber of about 30 mg cm^{-2} should be placed above the emitter to block out radiation from the ${}_{90}Th^{234}$ present. The sample thicknesses are best characterized in terms of mg cm^{-2}. Self-absorption is a particular problem with β emitters such as C^{14} and S^{35}, for which the maximum β-ray energy is low.

An interesting experiment on the statistics of radioactive measurement is described by Cook and Duncan.[1]

References

1. Cook and Duncan, "Modern Radiochemical Practice," Oxford University Press, New York (1952).
2. Cork, "Radioactivity and Nuclear Physics," D. Van Nostrand Company, Inc., New York (1947).
3. Feather, *Proc. Cambridge Phil. Soc.*, **34**, 599 (1938).
4. Glendenin, *Nucleonics*, **2** (1), 12 (1948).
5. Lyman, *Phys. Rev.*, **51**, 1 (1937).
6. Miller and Curtiss, *J. Research Nat. Bur. Standards*, **38**, 359 (1947).
7. Whitehouse and Putnam, "Radioactive Isotopes," Oxford University Press, New York (1953).

54. THE SZILARD-CHALMERS PROCESS AND THE HALF-LIFE OF RADIOIODINE

In this experiment a radioisotope is prepared by the neutron bombardment process, and its half-life is determined.

Theory.[1,2,9,10] When a slow neutron is captured by a target nucleus, the resulting nucleus is produced initially in an excited energy state and then becomes stabilized through the emission of one or more γ-ray photons. This process is called the (n,γ) reaction, or radiative neutron capture. Because the law of conservation of momentum must be satisfied in the γ-ray emission process, there is conferred upon the recoiling nucleus an abnormally large kinetic energy which is ordinarily very much greater than chemical-bond energies. The result is not only the rupture of the bond originally holding the atom involved in the molecule, but also the breaking of numerous other bonds in other molecules as the recoiling atom expends its excess energy. The atoms and molecular fragments so produced recombine in various ways, and the incorporation of radioactive atoms in appropriate chemical species sometimes permits their chemical concentration. This process of concentration, made possible by the chemical consequences of the nuclear transformation, is commonly called the Szilard-Chalmers process.[8]

When an alkyl iodide, such as ethyl iodide, is irradiated with slow neutrons the (n,γ) reaction on I^{127} produces the radioactive isotope I^{128}. A large fraction of the radioiodine formed ends up in inorganic form, i.e., as molecular iodine, $I^{127}I^{128}$ or HI^{128}, which may be separated from the organic medium by extraction with aqueous sodium hydroxide solution. The "organic yield," the fraction of radioiodine remaining in organic combination, has been found to depend on the structure and phase of the alkyl iodide irradiated and to be influenced also by the presence of added iodine.[4]

Radioactive I^{128} decays to stable Xe^{128} either directly with the emission of a β particle of 2.02-mev maximum energy, or indirectly with the emission of a β particle of 1.59-mev maximum energy to form an Xe^{128} atom in an excited nuclear energy state which immediately becomes stabilized by emission of a γ-ray photon of energy 0.43 mev. (Note that $1.59 + 0.43 = 2.02$.)

The rate of disintegration of a radioisotope $(-dN/dt)$ is proportional to the number, N, of radioactive atoms present:

$$-\frac{dN}{dt} = \lambda N \tag{1}$$

Integrating from $t = 0$, when the number of atoms present is N_0, to time t, when the number of atoms present is N_t,

$$2.303 \log (N_t/N_0) = -\lambda t \tag{2}$$

or

$$N_t = N_0 e^{-\lambda t} \tag{3}$$

In characterizing a radioisotope the half-life, $t_{1/2}$, is more commonly used than the rate constant λ. The half-life is the time required for the number of radioactive atoms to decrease to one-half the number originally present; by setting N_t/N_0 equal to $\frac{1}{2}$ in Eq. (2),

$$t_{1/2} = \frac{2.303 \log 2}{\lambda} = \frac{0.693}{\lambda} \tag{4}$$

If a neutron flux of ϕ neutrons per second per square centimeter is incident upon a thin layer of material containing n nuclei per square centimeter, the number of neutron captures occurring per second is $n\phi\sigma$, where the proportionality factor σ is called the *cross section* for neutron capture. The cross section is commonly reported in terms of *barns* (1 barn $= 10^{-24}$ cm^2), and its value depends on the energy of the incident neutron as well as the identity of the nucleus involved. For I^{127} the cross section σ_a for *slow-neutron* capture is 6.85 barns.

With a small neutron source centered in a flask containing an organic iodide the neutron flux is not constant throughout the medium. The number of radioiodine atoms produced per unit time, however, is constant at a value P determined by the neutron-capture cross section and the radial depth and iodine atom concentration of the medium. The net rate of increase of radioactive atoms is this rate of production minus the rate of disintegration, λN, as given by Eq. (1):

$$\frac{dN}{dt} = P - \lambda N \tag{5}$$

Integration from $t = 0$, $N = 0$, to a later time t, when the number of radioactive atoms is N, gives

$$N = \frac{P}{\lambda}(1 - e^{-\lambda t}) \tag{6}$$

The number of disintegrations per second of the sample is equal to λN:

$$\lambda N = P(1 - e^{-\lambda t}) \tag{7}$$

It is seen that P also represents the limiting activity and that the fraction of this limiting activity attained in time t is

$$\frac{\lambda N}{P} = (1 - e^{-\lambda t}) = 1 - e^{-0.693t/t_{1/2}} \tag{8}$$

For laboratory use an adequate neutron flux can be obtained from a small radium-beryllium source:

$$_{88}\mathrm{Ra}^{226} \rightarrow {}_{86}\mathrm{Rn}^{222} + {}_{2}\mathrm{He}^{4}\ (\alpha \text{ particle})$$
$${}_{2}\mathrm{He}^{4} + {}_{4}\mathrm{Be}^{9} \rightarrow {}_{6}\mathrm{C}^{12} + {}_{0}n^{1}$$

Approximately 10^7 neutrons per second are produced per gram of radium; a typical laboratory source containing 10 mg radium thus provides 10^5 neutrons per second. The neutrons produced may have kinetic energies up to 13 mev, however, and must be slowed down to thermal energies. This is effected by elastic collisions with nuclei. Hydrogen-containing substances make good moderators since the transfer of energy from a neutron to a proton in an elastic collision is very efficient because of the similarity in mass. Thermal neutrons are neutrons which have been slowed down to energies of the magnitude of that of thermal agitation, about RT per mole. Such neutrons are not monoenergetic but are characterized by a Maxwellian distribution of velocities; their *average* energy depends on the temperature of the medium in which they slowed down.

Apparatus. Neutron source* and lead storage shield; remote-handling device; irradiation-flask assembly; irradiation-flask shield; 1-liter separatory funnel; 50-ml pipette; two 150-ml beakers; two 125-ml Erlenmeyer flasks; 25-ml graduate; special sintered-glass filter crucible or small Buchner funnel and filter paper; filter-flask assembly; bunsen burner and ring stand; counting tube, scaler, and timer; ethyl iodide; 0.5 N sodium hydroxide; nitric acid; 0.01 N silver nitrate solution; carbon tetrachloride, iodine.

Procedure. Approximately 10 mg of iodine is weighed out and dissolved in about 850 ml of ethyl iodide in a Pyrex flask. The iodine is added as a scavenger and carrier to improve the recovery of the radioiodine isolated later. The test-tube holder for the neutron source is of *soft glass* because Pyrex glass contains boron, which has a high neutron-capture cross section. It is set in the flask as shown in Fig. 62. The neutron source is then removed from its lead storage housing, by the *instructor*, by means of a remote-handling device, and transferred to the irradiation flask. The irradiation is allowed to proceed for 1 hr.

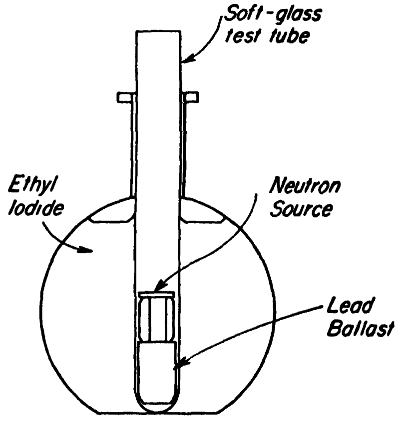

FIG. 62. Irradiation flask assembly.

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* Such sources may be obtained from Atomic Energy of Canada, Limited, Commercial Products Division, P.O. Box 379, Ottawa, Canada.

Caution: The source must always be kept at a safe distance from all personnel.* The radium-beryllium neutron source represents a radiation hazard; γ rays as well as neutrons are emitted. It should be stored in a lead housing and must be handled by means of a remote-control device. It is preferable also to provide lead shielding for the irradiation flask during the irradiation period. The I^{128} is not produced in hazardous amounts, so that the special precautions are required only with the operations involving the neutron source proper.

Because of the relatively short half-life of I^{128}, rapid processing of the irradiated material is essential. During the irradiation period preparations should be carefully made for the subsequent operations. By means of a pipette 50 ml of 0.5 N sodium hydroxide is placed in a 1-liter separatory funnel supported on a ring stand. A 1 N nitric acid solution is prepared by dilution of concentrated acid. A quantity of this acid slightly in excess of that required to neutralize the 50 ml of the sodium hydroxide solution is placed in a 250-ml beaker. It is found by titration, using methyl orange indicator. In separate flasks are placed 15 ml of carbon tetrachloride and 25 ml of a 0.01 N solution of silver nitrate. The auxiliary equipment (filter flask, burner, etc.) is set up, and the counting equipment (Exp. 53) prepared for use at this time.

At the end of the irradiation period the neutron source is returned to storage by the instructor. The ethyl iodide is transferred to the separatory funnel containing the sodium hydroxide solution, and the mixture shaken vigorously. The rapid disappearance of the iodine color from the organic layer indicates the extraction of the iodine into the aqueous phase. The two phases are allowed to separate, and the heavier ethyl iodide layer is run off into the irradiation flask and *reserved for the next irradiation.*

The aqueous phase is extracted with the carbon tetrachloride to remove any residual ethyl iodide. The carbon tetrachloride extract is withdrawn and discarded. The aqueous layer is then drained into the dilute nitric acid; the stirred solution is tested with methyl orange indicator to make sure it is slightly acid. The silver nitrate solution is added and the mixture heated rapidly to boiling to coagulate the silver iodide formed. The precipitate is collected by use of a glass-filter crucible, the body of which has been cut off close to the sintered-glass disc to permit the precipitate to be mounted close to the counter-tube window. Alternatively, filter paper and a small Buchner funnel may be used. The precipitate is washed with distilled water, then with acetone, and air is drawn through to dry it. The crucible (or filter paper) is mounted on an aluminum or

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* Permissable radiation exposures are outlined in Handbook 59 of the National Bureau of Standards, available for 30 cents from the Superintendent of Documents, Washington 25, D.C.

cardboard plate for counting. The number of counts obtained in 1-min counting periods is determined at 2-min intervals for a period of at least 50 min. The laboratory background count is also recorded. (The use of the counting equipment is described under Exp. 53.)

The concentration of radioiodine produced in the Szilard-Chalmers process is possible only because the exchange of iodine between molecular iodine and the organic iodide is slow under the conditions of the experiment. The rapid exchange of iodine between iodide ion and molecular iodine is illustrated in a supplementary procedure.

Ethyl iodide is irradiated as before, except that no carrier iodine is added. The irradiation product mixture is extracted with a solution of 25 mg of potassium iodide in 50 ml of water. The ethyl iodide is reserved for the next irradiation, and the aqueous solution is extracted with carbon tetrachloride to remove any residual organic iodide. The resulting aqueous phase, which contains radioiodine as iodide ion, is shaken in the separatory funnel with 25 ml of carbon tetrachloride containing 10 mg of iodine. The carbon tetrachloride layer is isolated, and the iodine removed from it by extraction with dilute sodium hydroxide. The basic solution obtained is acidified with dilute nitric acid, and silver nitrate solution added. The silver iodide precipitate is collected as before and tested for activity. The presence of radioiodine in this material is evidence of a rapid exchange of iodine between iodide ion and molecular iodine.

Calculations. A plot is made of the logarithm of the number of counts per minute from the radioiodine samples against the time of observation. Limits of uncertainty, obtained by calculation of the corresponding probable errors (compare Exp. 53) are indicated for the various points. The rate constant for the disintegration of I^{128} is determined from the slope of the straight line considered to give the best representation of the experimental results. The half-life of the radioiodine is calculated and compared with the accepted value.

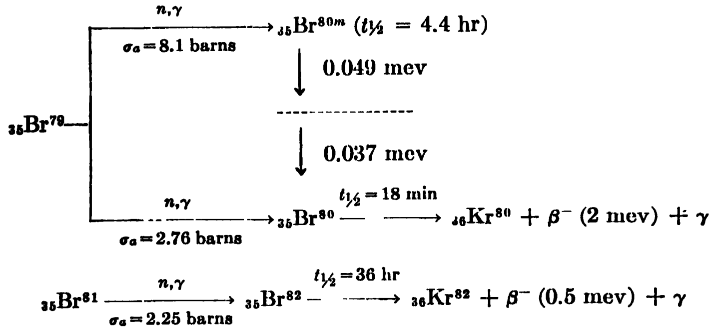
The fraction of the limiting activity obtained in the irradiation period used is calculated. It is shown that Eq. (8) is equivalent to the relation:

$$\frac{\lambda N}{P} = 1 - \frac{1}{2^n} \tag{9}$$

where n is the length of the irradiation period in half-lives of the radioisotope formed.

Practical Applications. Neutron bombardment, particularly in the high neutron fluxes furnished by nuclear reactors, is the most important method for the production of radioisotopes.

Suggestions for Further Work.[1,7] The (n,γ) reaction on bromine may also be studied. The modes of production of the three radioactive species formed and their individual decay schemes may be represented as follows:



The Br^{80} and Br^{80m} constitute a pair of nuclear isomers; the latter is a relatively long lived metastable excited nuclear state of the former. The decay of Br^{80m} to Br^{80} is termed an *isomeric transition*. The 0.049-mev transition occurs almost exclusively by the process of *internal conversion*, in which a direct transfer of energy from the nucleus to an adjacent orbital electron takes place with the resultant ejection of a *conversion electron*. The 0.037-mev transition occurs by conversion electron emission in about half of the events and by γ-ray emission in the other half.

Ethylene dibromide is irradiated for at least 4 hr, and preferably overnight, with the neutron source. The irradiated mixture is extracted with a solution of about 25 mg of potassium bromide in 50 ml of distilled water. (A small amount of a reducing agent such as sodium sulfite may be helpful also.) The aqueous layer is separated, acidified to methyl orange indicator with nitric acid, and silver bromide precipitated by addition of silver nitrate solution. The precipitate is collected as described previously for silver iodide, and the number of counts per minute from the radiobromine sample determined at 2-min intervals for the first half-hour and at longer intervals thereafter. An absorber of thickness about 100 mg cm^{-2} is placed between the sample and the counting tube to absorb the relatively weak β emission from the Br^{82} present. A total counting period of 4 hr or more is recommended. The counting rate initially decreases rapidly as the Br^{80} present disintegrates. Ultimately the rate of decay of Br^{80} becomes equal to its rate of production from Br^{80m}; the activity thereafter decays with a half-life of 4.4 hr. It should be noted that the counts registered here are due to the β-ray emission from the daughter Br^{80} in equilibrium with the Br^{80m}, since the counting efficiency for the accompanying γ rays is negligible relative to that for the β particles. The γ rays are so penetrating that only a few are counted.

A plot is made of the logarithm of the number of counts per minute from the radiobromine sample versus the time of observation. A straight line is drawn through the points corresponding to the later observations, and the half-life of Br^{80m} is calculated from its slope. Data for a corresponding plot for the 18-min activity can be obtained by subtracting from the total numbers of counts per minute at the early times of observation the contributions of the 4.4-hr activity evaluated from the extrapolation of the straight line referred to above (compare Fig. 64).

After the irradiated ethylene dibromide has stood for about 2 hr following the first extraction, a second extraction may be made. The activity thus isolated will decay with a half-life of 18 min. It arises from Br^{80} released from organic combination by bond rupture accompanying the isomeric transition from Br^{80m} by the internal conversion process.

Radiomanganese, Mn^{56}, whose half-life is 2.6 hr, may be isolated by the Szilard-Chalmers process by irradiation of concentrated aqueous potassium permanganate solution.[1,5] The efficiency of the separation depends on the pH of the solution and becomes low when the pH is high.[5]

The nonequivalence of the two sulfur atoms in the thiosulfate ion may be demonstrated[6] by the use of radiosulfur obtained from the Atomic Energy Commission. The maximum β-ray energy for S^{35} is low, 0.165 mev, so that a counting tube with a very thin mica window must be used.

References

1. Cook and Duncan, "Modern Radiochemical Practice," Oxford University Press, New York (1952).
2. Friedlander and Kennedy, "Nuclear and Radiochemistry," John Wiley & Sons, Inc., New York (1955).
3. Hamill, Williams, and Schuler, *J. Chem. Educ.*, **26**, 310 (1949).
4. Levey and Willard, *J. Am. Chem. Soc.*, **74**, 6161 (1952).
5. Libby, *J. Am. Chem. Soc.*, **62**, 1930 (1940).
6. McCool and Hentz, *J. Chem. Educ.*, **32**, 329 (1955).
7. Schuler, Williams, and Hamill, *J. Chem. Educ.*, **26**, 667 (1949).
8. Szilard and Chalmers, *Nature*, **134**, 462 (1934).
9. Willard, *Ann. Rev. Nucl. Sci.*, **3**, 193 (1953).
10. Williams, Hamill, and Schuler, *J. Chem. Educ.*, **26**, 210 (1949).

55. DETERMINATION OF THE HALF-LIFE OF A RADIOISOTOPE, USING A QUARTZ FIBER ELECTROSCOPE

The purpose of this experiment is to illustrate the use of a quartz fiber electroscope for the determination of radioactivity. The half-life of a radioactive isotope is determined.

Theory. The theory of the determination of the half-life of a radioactive isotope has been discussed (Exp. 54).

In addition to the radioelements which occur naturally, approximately 500 radioisotopes have been produced artificially by bombardment with α particles, accelerated protons and deuterons, and especially neutrons. The atomic pile with its high neutron fluxes has made available a number of radioisotopes in large quantities. These isotopes may be obtained from the U.S. Atomic Energy Commission* and are useful for illustrating principles of physical chemistry. It is advisable to use an isotope of short half-life to avoid accumulation of radioactivity in the laboratory due to spillage. Contamination of a laboratory with radioisotopes makes further measurements of radioactivity difficult and may give rise to a health hazard† by producing radioactive dust particles which could be inhaled into the lungs or could get into the stomach.

Phosphorus 32 and silver 111 are short-lived radioisotopes which are

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* Isotopes Branch, U.S. Atomic Energy Commission, Oak Ridge, Tenn.

† See footnote page 276.

relatively inexpensive and are satisfactory for this experiment. Phosphorus 32 is produced by bombarding $KH_2P^{31}O_4$ with neutrons in the pile or nuclear reactor.

$$_{15}P^{31} + n \rightarrow {}_{15}P^{32}$$

Radioactive potassium 42 is also formed but disappears in a few days because of its 12.4-hr half-life. Phosphorus 32 decays with the emission of an electron with 1.69 mev of energy to form a stable sulfur isotope.

$$_{15}P^{32} \rightarrow {}_{16}S^{32} + \beta \qquad t_{1/2} = 14.3 \text{ days}$$

Silver 111 is produced by bombarding palladium metal with neutrons in the pile, by the following steps:

$$_{46}Pd^{110} + n \rightarrow {}_{46}Pd^{111} + \gamma \text{ rays}$$
$$_{46}Pd^{111} \rightarrow \beta + {}_{47}Ag^{111} \qquad t_{1/2} = 26 \text{ min}$$

Silver 111 decays with the emission of a 1-mev β particle.

$$_{47}Ag^{111} \rightarrow {}_{48}Cd^{111} + \beta \qquad t_{1/2} = 7.5 \text{ days}$$

Silver 111 produced in the pile is accompanied by palladium 109, which has a half-life of 13 hr, and palladium 103, which has a half-life of 17 days.

The unit quantity of radioactivity is the curie, which is 3.7×10^{10} disintegrations per second, or 2.2×10^{12} disintegrations per minute. This unit was chosen because it was equal to the experimental value for the disintegration rate of 1 g of radium or of any of the radioactive daughters in equilibrium with 1 g of radium. Since the curie represents a rather high intensity of radiation, the terms millicurie (2.2×10^9 disintegrations per minute) and microcurie (2.2×10^6 disintegrations per minute) are more frequently used in the laboratory.

β rays are generally more penetrating than α particles and less penetrating than γ rays. Depending upon their energy, β particles may traverse paths of less than a centimeter to more than 10 m in air. The loss in energy of a β particle on passing through matter is due to its production of ion pairs along its path. This varies from about 25 pairs per centimeter at 2 mev to about 200 per centimeter at 0.04 mev. The β particles emitted from a given element do not have identical energies, and the energies given above represent the maximum energy. In the case of β particles, the range is expressed as the number of grams of absorber per square centimeter of cross section perpendicular to the path of the particles required for total absorption. This is convenient because the range in various substances is very nearly inversely proportional to the density. For a 1-mev β particle, the range is approximately 0.44 g cm^{-2}, or $0.44/2.7 = 0.16$ cm of aluminum, $0.44/11.3 = 0.039$ cm of lead, or $0.44/0.0012 = 360$ cm of air.

Construction of the Electroscope. Measurement of the rate of the loss of charge of an electroscope due to the ionization current is one of the simplest methods for the quantitative determination of radioactivity. The Lauritsen[6] electroscope represents one design which is widely used and can be used to measure activities as low as several hundred disintegrations per minute.* A schematic diagram of the electroscope is shown in Fig. 63*a*. The gold leaf of the familiar type of electroscope is replaced by a very fine quartz fiber (about 3×10^{-4} cm in diameter and about 0.6 cm long) rendered conducting by a thin deposit of gold. At the free end of the quartz fiber a short quartz segment is attached at right angles, and it is this segment which is observed with the microscope as illustrated in Fig. 63*b*. The other end of the quartz fiber is connected electrically to a metal bar which can be charged to a potential of several hundred volts with a small rectifier or friction charger. The ionization current is determined as the rate of loss of charge from the electroscope as measured by the rate of movement of the quartz fiber over a scale. It is characteristic of this type of electroscope that the rate of movement of the fiber is not the same in all parts of the scale. For this reason the rate of movement of the fiber is determined at different positions on the scale, using a sample of constant radioactivity. A plot of the rate of movement of the fiber versus position on the scale will be nearly horizontal in one region, and quantitative measurements of radioactivity are limited to this plateau.

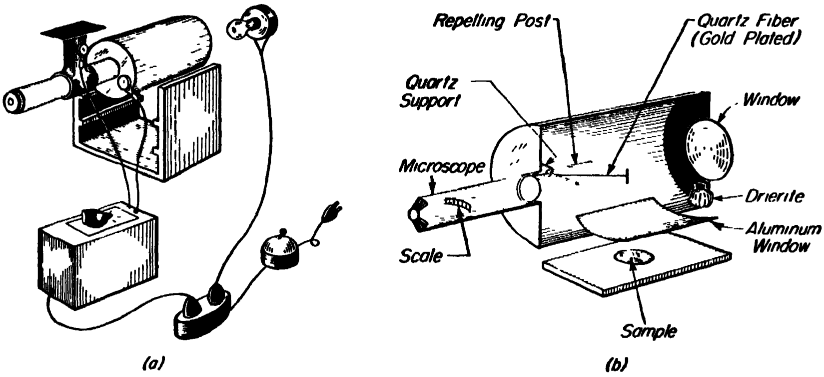

FIG. 63. (*a*) Lauritsen electroscope; (*b*) quartz fiber in electroscope.

Because of the sensitiveness of the quartz fiber to drafts, the ionization chamber is kept closed and protected from drafts and temperature inequalities. A thin aluminum window having a weight of about 5 mg cm^{-2} allows a large fraction of the β particles to enter the electroscope

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* **Quartz fiber electroscopes are available from the Fred C. Henson Co., Pasadena, Calif.**

chamber. A thin lacquer window is required for work with low-energy β and high-energy α rays. It has been found that reproducibility is increased by keeping the inside of the electroscope dry by inclusion of a small bag of Drierite and by discharging the electroscope two or three times, by means of a fairly strong sample, before use.

The sensitivity of a Lauritsen electroscope is such that 1 millicurie of radium at a distance of 1 m produces a movement of 2 to 5 scale divisions per minute. The background due to cosmic rays and low levels of natural radioactivity in the laboratory is approximately 3.1 scale divisions per hour. The electroscope is in general about one-tenth as sensitive as a Geiger counter, but when weak β emitters are counted inside the electroscope, the sensitivity is about the same as that of a Geiger counter. The electroscope may be calibrated to give disintegrations per minute by measuring the rate of discharge for a sample of known activity. It should be remembered that only a fraction of the particles emitted by the sample reach the ionization chamber, because a large fraction of the particles are emitted in other directions and because of absorption.

The measure of the amount of radioactivity present is the difference between the rate of movement of the fiber in the presence of the radioactive sample and the rate of movement of the fiber in the absence of the sample (background). This quantity may be denoted

$$\left(\frac{d}{t}\right)_s - \left(\frac{d}{t}\right)_b$$

where d = distance traversed by the fiber in t seconds
s, b = sample and background, respectively

Preparation of Standard Samples. The following standard samples prepared by using old uranyl nitrate are convenient for checking the electroscope:

Number	Grams of $UO_2(NO_3)_2 \cdot 6H_2O$	Grams of U	Disintegrations per minute from Pa^{234} present
1	0 0343	0 0163	12,000
2	0 0686	0.0326	24,000
3	0 1715	0.0815	60,000

Uranium 238 decays to give a series of daughters, with which it is in equilibrium if the uranium sample is old. From the half-life indicated below, the student should show that 1 g of pure uranium 238 will produce 739,000 disintegrations per minute. Each daughter with which 1 g of uranium 238 is in equilibrium will also emit particles at the rate of

739,000 disintegrations per minute. The uranium sample is covered with aluminum foil 0.11 mm thick (1 cm^2 weighs 30 mg) so that the α particles from uranium 238 and the weak β particles from Th^{234} are stopped and only the β particles from the disintegration of Pa^{234} enter the electroscope.

$$\mathrm{U}^{238} \xrightarrow[t_{1/2} = 4.5 \times 10^{9}\,\mathrm{yr}]{\alpha} \mathrm{Th}^{234} \xrightarrow[24.1\text{ days}]{\beta(0.13\text{ Mev})} \mathrm{Pa}^{234} \xrightarrow[1.14\text{ min}]{\beta(2.32\text{ Mev})} \begin{array}{l}\text{further}\\ \text{radioisotopes}\end{array}$$

Apparatus. Lauritsen electroscope and charger; micropipettes; 1-in. watch glasses; cellophane; collodion; infrared lamp; stop watch; lead sample containers; radioisotope.

Procedure. The plateau of the electroscope is determined by discharging it with one of the more active uranyl nitrate standard samples. The quartz fiber and the repelling post are charged by pressing the red button on the electroscope. The gain on the charger should not be set too high because the quartz fiber may be twisted too far.

Using a stop watch, the time required for the quartz fiber to move several small scale divisions is determined at a number of points along the scale, using a uranyl nitrate sample. The rate of movement of the fiber is plotted versus position on the scale. Since the fiber moves more slowly when the electroscope is almost discharged, measurements need not be made all the way to the end of the scale. Several divisions in the most linear part of the scale are to be used for determinations of radioactivity. The background rate (no sample) is also determined.

The lower shelves in the Lucite sample holder may be used to decrease the rate of discharge of the electroscope for active samples. Increasing the distance between the electroscope and the sample decreases the discharge rate roughly as the inverse square of the distance, but the actual relation must be determined experimentally. The most active uranyl nitrate sample is counted at several distances from the electroscope.

Determination of the Half-life of a Radioisotope. The radioactivity of a sample of a short-lived radioisotope is measured over a period of several weeks to obtain the half-life. Since the activity of the radioisotope is decreasing, the size of the aliquot to be taken for counting purposes is calculated from the initial activity of the radioisotope and its age. A sample giving 100,000 disintegrations per minute is sufficiently active.

Micropipettes calibrated to contain 5 to 100 microliters (λ or μl is used as the symbol) are used for sampling. These pipettes are attached to a 1-ml syringe, using a short piece of small-diameter rubber tubing. Since the pipettes are calibrated "to contain," they must be rinsed with dilute nitric acid several times after delivering the sample and the rinsings added to the sample.

The sample is prepared for counting by evaporating it on a small watch glass, using an infrared heat lamp mounted a few inches above the sample. If too rapid heating is used, the sample will boil and spatter.

The sample is mounted in a piece of cardboard and covered with cellophane fastened down with Scotch tape. The student's name and laboratory period are written on the card, which is filed near the electroscope. The activity of the covered sample is measured several times over a period of two weeks or more.

Calculations. The rate of discharge for the radioisotope sample is plotted versus time in days, and the logarithm of the rate of discharge is also plotted versus time. If a single radioisotope is present, the log plot will be linear and the half-life of the isotope may be calculated from the slope. It is not necessary to know the absolute number of disintegrations in order to determine the half-life. If more than one radioisotope is present, the log plot will be a curve which may be resolved into two or more straight lines. This is illustrated in Fig. 64, which represents the decay of a sample containing Ag^{111} and Pd^{109}. The rate of discharge is plotted on semilog graph paper, and the decay plot for Pd^{109} is obtained by extrapolating the straight-line portion due to Ag^{111} back to the initial time and subtracting the discharge rate due to the Ag^{111} alone from the total discharge rate of the sample.

The rate of discharge with the uranyl nitrate sample of known activity is used to calculate a constant for converting the rate of discharge of the electroscope in divisions per minute to total number of disintegrations per minute in the sample. This proportionality factor will be somewhat different for β particles of different energy.

Practical Applications. Radioisotopes are finding a wide variety of applications in research. By labeling certain atoms in a molecule, it is possible to study reaction mechanisms. Isotope dilution procedures are useful in analysis, especially when it is difficult to isolate the component for which a quantitative analysis is desired. Radioisotopes have been particularly valuable in biological research.

Suggestions for Further Work. The radioactivity of a radioactive ore may be determined.

The adsorption on charcoal of phosphate ion from solution or on an ion-exchange resin may be studied quantitatively using phosphate labeled with P^{32}. The procedure and calculations are similar to those of Exp. 44, except that the radioactivity of small aliquots of solution is determined and the experiment may, therefore, be carried out on a much smaller scale. Special care should be taken to avoid spillage or spattering and to avoid contact with the skin. Paper towels should be laid on the work area, and the test tubes should be handled with tongs.

The solubility product of silver chloride may be determined, using Ag^{111}. It is unnecessary to know the amount of radioactive silver present in absolute units; it may be expressed only in terms of the discharge rate of the electroscope. First a definite volume of radiosilver solution is added to 1 ml of 0.01 *N* silver nitrate, and a slight excess of hydrochloric acid is added to precipitate all the silver. It is convenient to add a volume of silver 111 solution which is fifty to a hundred times larger than that required to discharge the electroscope at a convenient rate. It is important to wash the precipitate several times to free it of other radioactive substances and excess chloride. This may be done by boiling it with 2 ml of distilled water and allowing it to settle. The solubility of silver chloride in water is calculated from the rate with which an aliquot of the saturated solution discharges the electroscope.

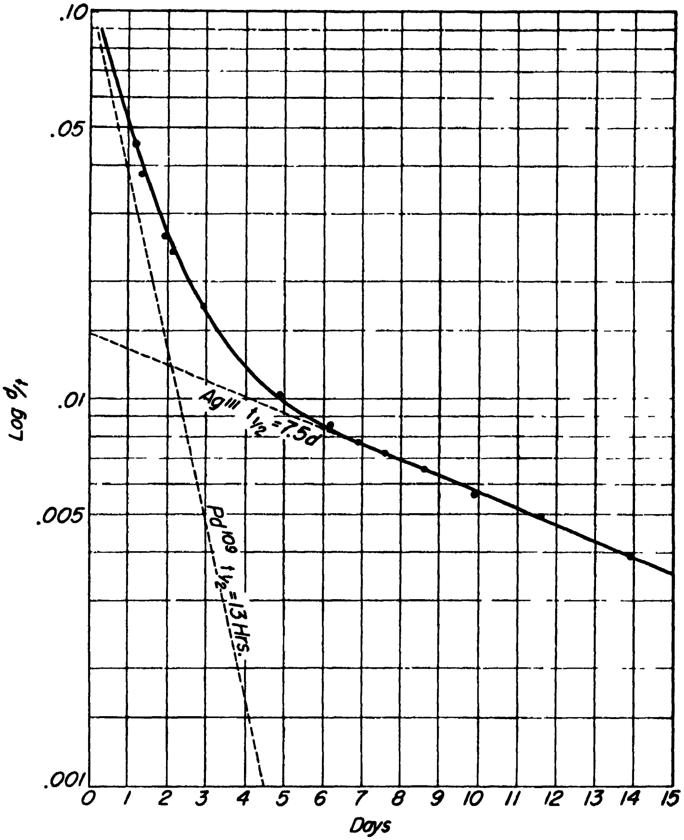

FIG. 64. Decay curve for a mixture of two isotopes.

References

1. Friedlander and Kennedy, "Nuclear and Radiochemistry," John Wiley & Sons, New York (1955).
2. Glasstone, "Sourcebook on Atomic Energy," D. Van Nostrand Company, Inc., New York (1950).
3. Henriques and Margnetti, *Rev. Sci. Instr.*, **17**, 417 (1946).
4. Henriques *et al.*, *Ind. Eng. Chem.*, *Anal. Ed.*, **18**, 349, 415, 417, 420, 476 (1946).
5. Hevesy and Paneth, "Manual of Radioactivity," Oxford University Press, New York (1938).
6. Lauritsen and Lauritsen, *Rev. Sci. Instr.*, **8**, 438 (1937).
7. List of isotopes, U.S. Atomic Energy Commission, Oak Ridge, Tenn.
8. Pollard and Davidson, "Applied Nuclear Physics," John Wiley & Sons, New York (1951).
9. Seaborg, "Artificial Radioactivity," *Chem. Revs.*, **27**, 199 (1940).
10. Wahl and Bonner, "Radioactivity Applied to Chemistry," John Wiley & Sons, New York (1951).

56. EXCHANGE REACTIONS WITH DEUTERIUM OXIDE

By the use of concentrated deuterium oxide it is possible to determine the number of hydrogen atoms in a hydrogen-containing compound which may be exchanged with hydrogen atoms of water. A dry sample of the compound is dissolved in heavy water, and then the heavy water is evaporated by use of a vacuum pump and dry-ice trap. The increase in weight of the compound is due to the substitution of deuterium for hydrogen. Some hydrogen atoms exchange so rapidly that it has not been possible to determine rates, while hydrogen atoms in other positions may exchange very slowly.

Theory. Hydrogen of atomic weight 2, named deuterium, occurs in ordinary hydrogen to the extent of 1 part in 6,700. The existence of this heavier isotope of hydrogen was discovered by Urey. Although the chemical reactions of isotopes are nearly identical, there are very minor differences which show up most prominently in the elements of low atomic weight, and especially in hydrogen. When water is electrolyzed, the hydrogen comes off at the cathode more easily than deuterium, and by fractional electrolysis on a large scale it is possible to prepare pure deuterium oxide, D_2O. In a mixture of water containing equal parts of the light isotope H and the heavy isotope D, it is found that H is liberated by electrolysis about five times as fast as D. In more general terms

$$\frac{dc_D/c_D}{dc_H/c_H} = 0.2$$

Other methods, such as highly efficient fractional distillation on a large scale, are used also to produce an enrichment in deuterium oxide.

Heavy water containing 99.55 per cent D_2O may be purchased from the Stuart Oxygen Company of San Francisco, Calif., for a few cents per gram after first filling out application blanks provided by the U.S. Atomic Energy Commission, Isotopes Division, Oak Ridge, Tenn.

Apparatus. Water containing a known percentage of D_2O; analytical balance; 15-ml weighing bottle; vacuum pump (0.3 μ); drying trap (Fig. 65); Dewar flask; dry ice; hot plate; ammonium sulfate; acetone or trichloroethylene.

Procedure. Ammonium sulfate is satisfactory for this experiment because it is nonvolatile and 6 per cent of its mass is due to hydrogen. One gram of ammonium sulfate is dried by placing it in a weighing bottle in an apparatus such as that illustrated in Fig. 65. The apparatus is evacuated by use of a mechanical vacuum pump. A trap surrounded by dry ice in acetone is placed between the drying chamber and the vacuum pump so that moisture does not get into the oil of the vacuum pump or oil vapor into the sample. The Dewar flask is about one-third filled with liquid, and then crushed dry ice is added (slowly at first). The ammonium sulfate may be dried more quickly if the drying chamber is immersed in a beaker of boiling water.

After the ammonium sulfate has been dried, about 1 g of heavy water is placed on the sample, and the weighing bottle and contents reweighed. The supply of heavy water should be kept stoppered so that D_2O will not exchange with H_2O in the air. The sample must be completely dissolved in the heavy water (by heating if necessary) so that the entire sample has an opportunity to exchange. It is necessary to evaporate the D_2O out of contact with room air so that exchange with ordinary H_2O will not occur. The solution is then frozen in the dry-ice freezing mixture. The weighing bottle is laid almost horizontally in powdered dry ice and rotated so the solution freezes as a thin layer on the walls of the weighing bottle. By freezing a thin layer of large area the rate of sublimation of D_2O can be greatly increased.

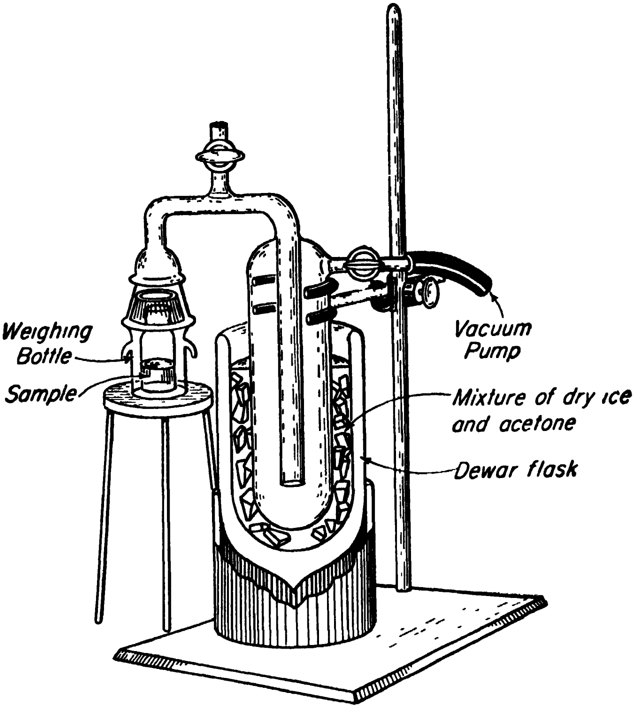

FIG. 65. Apparatus for evaporating heavy water.

The weighing bottle containing frozen solution is placed in the drying apparatus and evacuated. The evaporation of D_2O molecules may not be sufficiently rapid to keep the solution frozen. It is essential that the sample not be allowed to become so warm that bumping occurs, as the sample will be lost in this way. However, if the chamber containing the weighing bottle is kept immersed in ice water, the sample will generally remain sufficiently cold. When the D_2O content has been reduced to the point that there is no longer danger of bubbling, the ice bath is replaced by a beaker of room-temperature water and finally by a beaker of boiling water. By raising the temperature in this way, the drying time is considerably reduced.

The dried salt is weighed and then placed in the drying apparatus for another hour at 100° and reweighed to be sure constant weight has been reached.

The heavy water in the cold trap is thawed out and poured into the bottle for used heavy water.

If a vacuum pump is not available, the experiment may be carried out by passing air dried with Ascarite or other desiccant over the sample. If air is drawn through the sample chamber by use of a water aspirator, a second drying tube should be used to prevent diffusion of ordinary water vapor into the sample chamber.

Calculations. It is desired to determine how many of the hydrogen atoms in the ammonium sulfate molecule can be replaced by deuterium. Only certain types of hydrogen atoms in organic compounds do exchange with the hydrogen atoms in water. If the ammonium sulfate were in equilibrium with pure deuterium oxide, all the readily dissociable hydrogens would be replaced by deuterium. However, the deuterium oxide becomes diluted with ordinary water by the exchange with hydrogen from the ammonium sulfate. Since the ammonium sulfate and heavy water are in equilibrium, the mole fraction of replaceable hydrogens which are replaced by deuterium will be equal to the mole fraction of the deuterium oxide in the water which is in equilibrium with ammonium sulfate.

The mole fraction of D_2O in the water at equilibrium is calculated from the original weight w of heavy water taken, the weight fraction f of D_2O in the original deuterium oxide, and the gain in weight of the ammonium sulfate, $g_2 - g_1$. The total number of moles of water is

$$\frac{fw}{20} + \frac{(1-f)w}{18} \tag{1}$$

This is the number of moles of water added originally, and it is also the total number after exchange, because there is no change in the total number of molecules of D_2O and H_2O, merely a change in the relative proportions of each. The decrease in the number of moles of D_2O as a result of exchange with the ammonium sulfate, leaving deuterium in the ammonium sulfate instead of hydrogen and forming H_2O, is $(g_2 - g_1)/$

$2(D - H)$, where the factor 2 enters because there are 2 atoms of hydrogen per molecule of water. Thus, the mole fraction of D_2O at equilibrium is

$$N_{D_2O} = \frac{(fw/20) - [(g_2 - g_1)/2(D - H)]}{(fw/20) + [(1 - f)w/18]} \tag{2}$$

The gain in weight per mole of ammonium sulfate would be $AN_{D_2O}(D - H)$, where A is the number of gram atoms of hydrogen involved in the exchange equilibrium per gram molecule of ammonium sulfate. Here D and H represent the atomic weights of deuterium and hydrogen, respectively.

The gram-molecular weight of ammonium sulfate is designated by M. If g_1 is the initial dry weight of the ammonium sulfate and g_2 is the weight after exchange, the gain in weight for g_1/M moles of ammonium sulfate is

$$g_2 - g_1 = AN_{D_2O}(D - H)\frac{g_1}{M} \tag{3}$$

Solving for A,

$$A = \frac{(g_2 - g_1)M}{g_1N_{D_2O}(D - H)} \tag{4}$$

Practical Applications. The interest in isotopic hydrogen lies chiefly in the fact that hydrogen atoms can be labeled by their greater weight and followed through various chemical reactions and physical processes. From the final distribution of the heavy and light atoms, much information can be obtained concerning the nature of the process. The applications in biology have been particularly important.

Suggestions for Further Work. Other exchange reactions may be studied, such as acetone with water,[2] or carbohydrates with water.[3]

Significant tracer experiments can be performed also with heavy water containing as little as 10 per cent of deuterium oxide. The density of the water is measured accurately with a pycnometer before and after mixing with a substance which is to be tested for hydrogen-deuterium exchange. The density of deuterium oxide at 25° is 1.1079 times the density of ordinary pure water, and the fraction of the maximum increase in density of a mixture over that of water is proportional to the mole fraction of the deuterium oxide. Experiments on the exchange of hydrogen in ethylene glycol may be carried out, in which a known weight of glycol is mixed with a known weight of dilute heavy water. The water is then separated from the glycol by distillation, and its density redetermined.

The concentration of deuterium in D_2O-H_2O mixtures can be determined by surface tension or by the thermal conductivity[6] of H_2 and D_2.

The main application of this method is to nonvolatile substances of high solubility in water which have a reasonably large percentage change in mass when D is substituted for H. Several organic compounds of interest for this type of work are malonic acid, succinic acid, and malic acid. The hydrogens of —COOH and —OH are expected to exchange instantaneously with the solvent. According to the literature the α-hydrogens of malonic acid are 100 per cent exchanged in 760 hr at 50°. The α-hydrogens in sodium malate are 100 per cent exchanged in 5 hr at 100°. There is no exchange of α-hydrogens of succinic acid in 160 hr at 100°.

References

1. Bonhoeffer, *Trans. Faraday Soc.*, **34**, 252 (1938).
2. Halford, Anderson, and Bates, *J. Am. Chem. Soc.*, **56**, 491 (1934).
3. Hamill and Freudenberg, *J. Am. Chem. Soc.*, **57**, 1427 (1935).
4. Kimball, "Bibliography of Research on Heavy Hydrogen Compounds," McGraw-Hill Book Company, Inc., New York (1949).
5. Kirshenbaum, Murphy, and Urey, "Physical Properties and Analysis of Heavy Water," McGraw-Hill Book Company, Inc., New York (1951).
6. Selwood and Taylor, *J. Am. Chem. Soc.*, **56**, 998 (1934).
7. Urey and Teal, Heavy Hydrogen, *Revs. Modern Phys.*, **7**, 34 (1935).

CHAPTER 16

GENERAL EXPERIMENTAL TECHNIQUES

57. GLASS BLOWING

This experiment offers the opportunity for learning simple techniques used in constructing glass apparatus. Practice is obtained in performing some basic operations in glass blowing.

Theory. Pyrex glass is almost universally used for bench-blown glassware and will be used in this experiment. The disadvantage of the higher softening point of Pyrex is more than compensated for by its lower coefficient of thermal expansion and high strength. The following characteristics of Pyrex and soft glass are of importance to the glass blower:

Characteristic	Pyrex (No. 774)	Soft glass
Softening point	820°C	626°C
Strain point	510°C	389°C
Annealing point	560°C	425°C
Linear coefficient of expansion	32×10^{-7}	90×10^{-7}

Pyrex glass requires an oxygen-air-gas or oxygen-gas flame. When Pyrex is heated above the strain point, harmful strains may be introduced unless the piece is reheated and then cooled slowly and uniformly. Annealing is best done in a furnace which may be heated to 580 to 585°C, but in the laboratory a small piece of glass apparatus may be annealed in a flame. The glass is heated in a soft bushy flame until it is uniformly softened. The working temperature is slowly decreased by manipulating the glass in the cooler parts of the flame, and by lowering the flame temperature, until a layer of soot has been deposited from the smoky flame which is finally used.

A more detailed description of glass blowing than can be given here is to be found in several excellent books listed at the end of the experiment.

Apparatus. Burner; hand torch; oxygen tank; Pyrex glass tubing 10 to 12 mm outside diameter; file or glass knife; 4-mm Pyrex cane (rod); corks; forceps; rubber tubing; Didymium eyeglasses.

Procedure. Practice is obtained in drawing "points" and making bends, straight seals, and T seals. It is essential that all tubing used for glass blowing be clean and dry.

Small tubes and rods are easily cut by making a single file scratch with a sharp file, placing the two thumbs toward each other on either side of the scratch but on the other side of the tubing and breaking with a combined bending and pulling force. It will be found helpful to moisten the scratch before the break is attempted.

In the case of large tubes, a small point of heated glass is touched against one end of the file scratch, and a crack is produced under the file scratch which extends for a short distance beyond. The crack may be extended if necessary by touching the heated glass point to the tube just beyond the end of the crack.

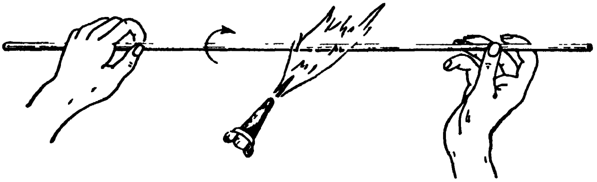

FIG. 66. Glass blowing: rotating the tubing.

The tube may be cracked more neatly and more quickly by wrapping nichrome or other heating wire around the tube over the file scratch. The wire is heated red-hot with an electric current, using a suitable resistance in series.

The proper procedure for lighting a burner is to ignite the gas first, then turn on the air, and lastly turn on the oxygen. The optimum temperature for the flame depends upon the size of the piece being worked and the ability of the operator. A more skillful operator may use a higher temperature which makes possible faster working. The hottest part of a flame is at the tip of the inner cone. Didymium glasses should be worn to protect the eyes from the sodium light produced by the vaporization of sodium from the glass.

The first operation to be learned is uniform rotation of the glass (Fig. 66). A suitable length of tubing 10 to 12 mm outside diameter is selected as a convenient size for practice in this and subsequent operations. The tubing is held by the last three fingers of the left hand, which act as a bearing; the thumb and forefinger are used to rotate the glass. The right hand supports the other end of the tubing. (Left-handed persons may reverse the order given.) Here again, the thumb and forefinger are used to rotate the tube while the other fingers are used mainly for support. The palm of the left hand is downward, while that of the right hand is upward. These positions permit the glass blower to blow into the right-hand end of the tubing, which should be the shorter end. Rotation is in such a direction that the top of the tubing moves away from the glass blower. The right- and left-hand movements are synchronized to prevent twisting of the tubing. The tube is held in a straight line, and bending, pushing, or pulling the glass is avoided except when required for a specific purpose. The student will find that a considerable amount of practice will be required.

The importance of mastering this rotation technique cannot be too strongly emphasized; it is essential for obtaining uniform wall thickness and symmetrical shapes. The student should practice this operation until he gets the "feel" before any glass blowing is tried.

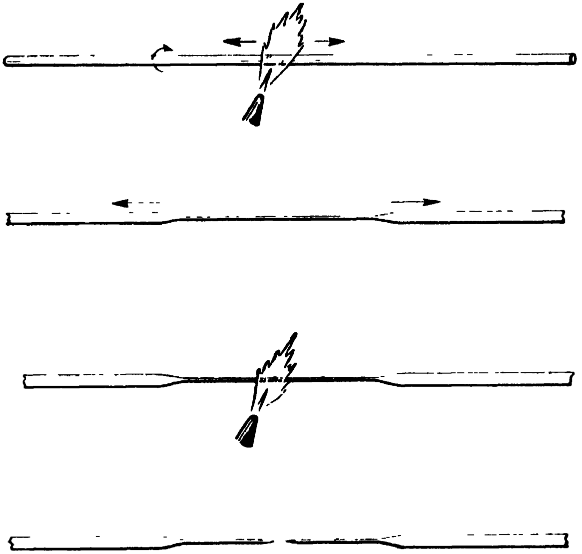

FIG. 67. Glass blowing: pulling a point.

A bend may be made after the tubing has been heated until it is pliable and it has been removed from the fire. In order to obtain a smooth uniform bend, one end of the tube is closed with a cork, and, as soon as the bend is completed, the open end of the tube is blown into with sufficient pressure to eliminate any irregularities in the bend. In order to prevent sagging of a bend, the ends of the tube are bent upward with the heated portion downward.

The next operation is pulling a "point" (Fig. 67). This is an elongation on the end of a tube formed by pulling the tube to a small diameter. Points form convenient handles for holding short pieces of tubing and provide a means for closing the tube and for cutting the glass with the flame. To pull a point, the tube is rotated in the flame so as to heat a length of about ½ in. When the glass is pliable, it is removed from the flame, and while still rotating, it is pulled slowly to a length of 8 or 9 in. The drawn-out portion is melted apart at the center, thus closing both points. If the points do not have the same axis as the tube, it will be necessary to heat at the shoulders where they join the tube to straighten them. The position of the point with respect to the tube is a test of the student's mastery of the rotation technique.

The straight seal is tried next (Fig. 68). One end of the tube to be held in the left hand is stoppered, the tube in the right hand being left open for blowing. The ends of the tubes which are to be sealed together are heated in the flame, with rotation, until softened. The two ends are then pushed together carefully on the same axis, and as soon as the contact is effected, the joint is pulled slightly. The joint is now rotated in the flame until the diameter of the tubing is somewhat decreased and the wall thickness is increased at the point of juncture. While it is still being rotated, the tube is removed from the flame and the joint is blown to a somewhat greater size than the original tubes. The tubing should not be pulled at this point, since this will decrease the wall thickness at the seal. The tubing is now reheated at the enlarged portion until its diameter is decreased; it is then removed from the flame and blown to a slight

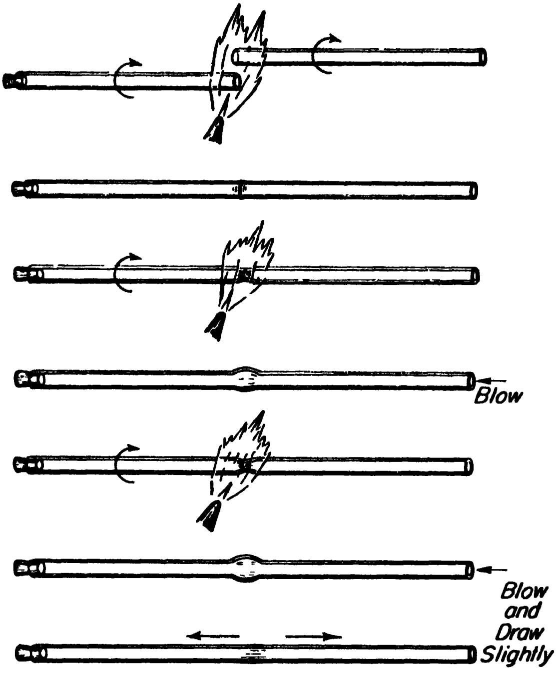

FIG. 68. Glass blowing: the straight seal.

bulge. Before the tube has cooled appreciably, the joint is pulled sufficiently to reduce the diameter to that of the tube. Note that the tubing is continuously rotated in all these operations. If the rotation technique has been mastered, seals which are all but indistinguishable from the remainder of the tubing can be made very quickly. If two pieces of tubing of different diameter are to be joined, the larger is first drawn down and cut off to give an end of the same diameter and wall thickness as the smaller tube.

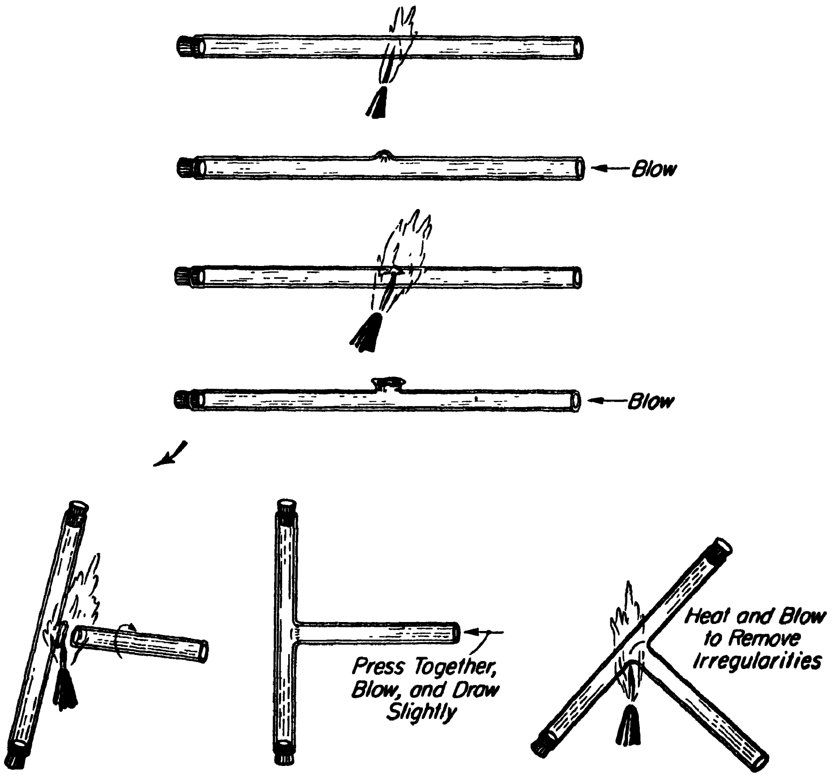

FIG. 69. Glass blowing: the T seal.

The T seal (Fig. 69) presents a different problem, since the tubing cannot be rotated easily except by using a special glass blower's clamp. One end of a tube is closed by a cork, and with a sharp flame a spot on the side of the tube is heated. The heated spot is blown to form a bulge, which is then reheated and blown to a small bulb having thin walls. This bulb is broken and the excess glass chips removed by scraping with wire gauze. The size of the hole thus formed should be about the same size as or slightly smaller than the tube which is to be attached. The other end of the tube with the side hole is now sealed with another cork. The side opening and the end of the tube to be sealed are heated until soft, removed from the flame, and brought quickly together, and given a slight pull as soon as contact has been made. The joint is blown slightly to expand it and to remove any irregularities. If the glass was sufficiently softened when joined, this procedure will result in a good seal; however, should it not appear uniform, small parts can be heated with a sharp flame and then blown to proper size. The entire seal is reheated to remove stresses and to adjust the angle between the tubes.

Suggestions for Further Work. As soon as the student has acquired reasonable proficiency in the above operations, he may proceed to more difficult operations such as joining capillary tubing or small-diameter tubing and making ring seals and closed circuits of tubing. Further directions will be found in the reference books. Flaring the end of the tubing and blowing small bulbs are also good exercises.

Metal-to-glass seals are required in certain types of work. Platinum wire can be sealed into soft glass and also into Pyrex if the diameter is small; these seals, however, are not recommended for vacuum work. Tungsten in small diameters can be sealed directly into Pyrex, and larger diameters can be sealed if an intermediate grading glass is used. Special alloys have been tailored to order for sealing to low-expansion glasses like Pyrex. One or more grading glasses are usually required for the Pyrex-to-metal seal. Kovar* and Fernico† are examples and can be obtained in the form of tubing, wire, and various fabricated shapes, either alone or already sealed to glass. The latter is the preferred way to obtain these materials, since the sealing operation is an art which requires considerable practice. Copper can be sealed into either soft glass or Pyrex by the Housekeeper[4] method, which requires that the copper be very thin where it is sealed to the glass.

References

1. Frary, Taylor, and Edwards, "Laboratory Glass Blowing," 2d ed., McGraw-Hill Book Company, Inc., New York (1928).
2. Heldman, "Techniques of Glass Manipulation in Scientific Research," Prentice-Hall, Inc., New York (1946).
3. "Laboratory Glass Blowing with Pyrex Brand Glasses," Corning Glass Works, Corning, N.Y. (1952).
4. Strong, "Procedures in Experimental Physics," Chap. I, Prentice-Hall, Inc., New York (1939).
5. Wright, "Manual of Laboratory Glass-blowing" Chemical Publishing Co., Brooklyn, N.Y. (1943).

58. HIGH VACUUM

This experiment illustrates some of the elements of importance in the production and measurement of low pressure.

Theory. In vacuum technology, pressures are usually expressed in *microns* of mercury. The cgs unit of pressure, 1 dyne cm^{-2}, is called the *microbar*. The relations between these units can be summarized as follows:

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* Manufactured by Stupakoff Ceramic and Manufacturing Co., Latrobe, Pa.

† Manufactured by General Electric Co., Schenectady, N.Y.

$$1 \text{ micron} = 1\ \mu = 10^{-3} \text{ mm Hg} = 10^{-6} \text{ m Hg} = 1.3332\ \mu\text{bar}$$

The volume unit used commonly is the liter. Quantity of gas, at a particular temperature, is conveniently expressed as liter-microns, or the equivalent in other pressure and volume units.

The speed, S, of a pumping system which is removing gas from a vessel of fixed volume V may be defined* by the relation

$$S = -\frac{dv}{dt} = -\frac{V}{P}\frac{dp}{dt} \tag{1}$$

Here dv represents the volume of gas, measured at the temperature and pressure P of the vessel, removed in the time dt, and dp is the corresponding change in pressure. The pumping speed has the characteristics of *conductance,* since it has the dimensions of volume of gas removed per unit time, and is customarily expressed in liters per second.

The speed of the pumping system determines the time required to reduce the pressure in the volume V from one specified level to another. This problem is considered in detail by Dushman, but for the case where S is *constant* over the range from the initial pressure P_1 to the final pressure P_2, integration of Eq. (1) gives for the required pumping time

$$t_2 - t_1 = \frac{V}{S}\ln\frac{P_1}{P_2} \tag{2}$$

VACUUM PUMPS

In laboratory practice two types of vacuum pumps are commonly employed, mechanical and diffusion pumps. The principle of operation of a typical rotary oil pump is indicated in Fig. 70. The vane V is kept in close contact with the eccentric cylinder C by the spring-loaded rocker arm A. As the cylinder rotates in the oil-filled chamber, air is drawn in at the inlet tube I and driven around to the outlet at O. The vane V and the close fit of the eccentric rotor with the stator produce an efficient pumping action. The entire pump unit is oil-immersed; the ball check shown at O prevents backflow of oil when the rotor is stopped. Commonly two such units, with rotors on a common shaft, are connected in series to form a single compound pump. The pumping speed of such a rotary oil pump depends on its size, but in any case drops off rapidly as

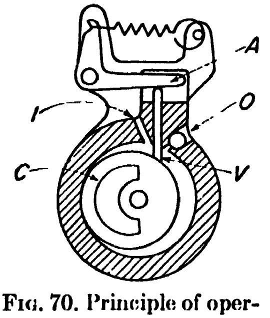

FIG. 70. Principle of operation of a typical rotary oil pump.

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* A more realistic definition takes into account the finite low-pressure limit the pumping system can reach, P_s, and gives $S(P - P_s) = -V\,dp/dt$. If it is assumed that P_s is negligibly small compared to P, Eq. (1) follows directly.

the micron range is approached. Performance curves for typical laboratory pumps are shown in Fig. 71.

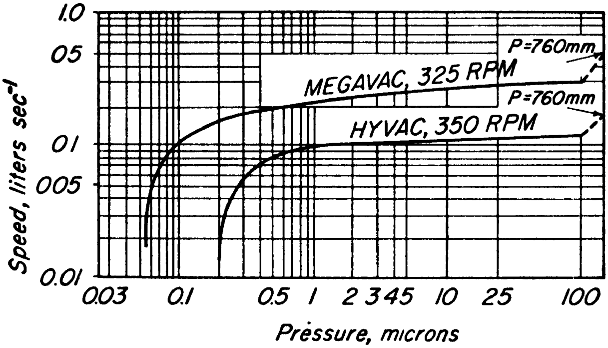

FIG. 71. Performance curves for typical rotary oil pumps.

For efficient pumping at low pressures the diffusion pump is employed. A typical mercury-vapor pump is illustrated in Fig. 72. The pressure in the pump and system is first reduced by means of a rotary oil pump, the *forepump*, connected to the outlet *O*. A high-velocity stream of mercury vapor generated in the boiler by electrical heating is then driven through the nozzle *N*. Air molecules diffuse through the inlet tube *I* into the vapor stream and are driven downward by collisions with mercury atoms. The latter, because of their relatively high mass, are only slightly deflected and proceed to the water-cooled wall where they are condensed and returned to the boiler. The gas molecules are driven down to the outlet where they are removed by the forepump. Very high pumping speeds and low ultimate pressures can be obtained by this pump. The pressure maintained by the forepump must be below a critical value, determined by the diffusion-pump design and the power input to the boiler, if the diffusion pump is to work. This necessary forepressure may be increased by the use of multistage diffusion pumps.

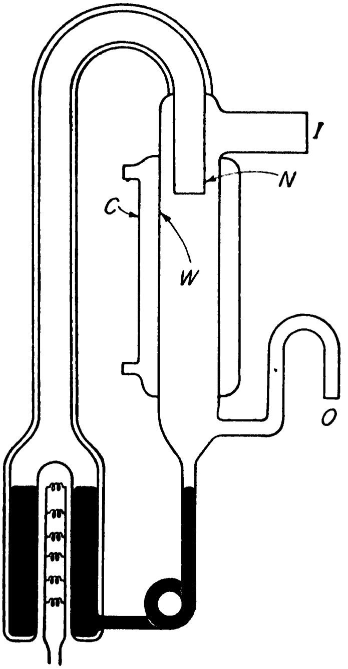

FIG. 72. Typical mercury-vapor diffusion pump.

Mercury as the working fluid has the disadvantage that its vapor pressure at room temperature is relatively high, about 1 μ, so that an efficient cold trap must be used between a mercury-vapor pump and a system in which mercury cannot be tolerated. High-molecular-weight organic pumping fluids, such as butyl sebacate, are commonly used instead of mercury, since they have vapor pressures at room temperature which are negligible for practically all purposes. They are, however, subject to cracking if overheated and must be heated only under vacuum because of susceptibility to air oxidation. The use of silicone pumping fluids offers a solution to these particular problems.

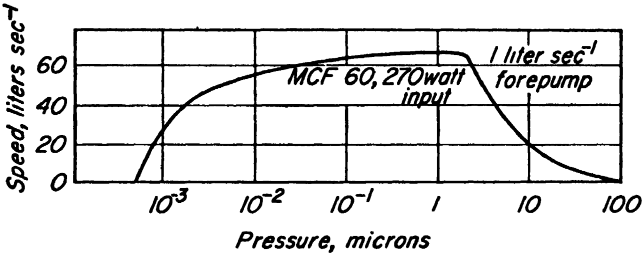

Fig. 73. Performance curve for a small three-stage diffusion pump, type MCF 60, Consolidated Vacuum Corp.

Modern oil diffusion pumps can produce pressures below 10^{-6} mm Hg at room temperature without cold traps, and pumping speeds as high as 20,000 liters sec^{-1} at 10^{-4} mm Hg are available with large-scale commercial units. In Fig. 73 is given a performance curve for the small three-stage commercial pump illustrated in Fig. 74. On the low-pressure side the measured pumping speed drops to zero at a pressure fixed by the vapor pressure of the pumping fluid; the actual pumping speed for *air* remains high at this same pressure, as may be shown by the use of a pressure gauge with a liquid-air trap.

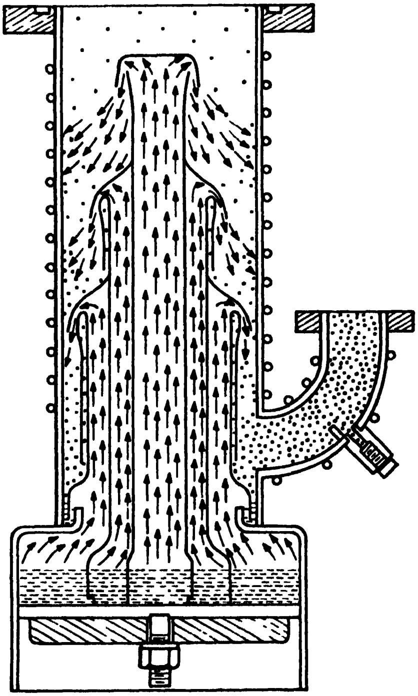

Fig. 74. Three-stage oil diffusion pump, type MCF, Consolidated Vacuum Corp.

A diffusion pump can remove vapors (water, organic liquids) which would condense into the oil of the forepump and seriously impair its performance. Where such a possibility exists the forepump should be protected by a suitable trap. Drying towers filled with solid desiccants, etc., are of limited utility when it is desired to conserve the speed of the pump. Liquid-cooled traps can provide very efficient performance. For routine forepump protection, cooling with solid carbon dioxide is in general adequate; a mixture of solid carbon dioxide and *trichloroethylene* is used. Trichloroethylene is now readily available commercially, and should always be used instead of the inflammable acetone which was commonly used in the past. It should be remembered that the vapor pressure of ice at the temperature of solid carbon dioxide is about 0.1 μ.

Liquid air is a very effective trap refrigerant but involves an explosion hazard if organic materials are brought into contact with it, through breakage of a glass trap, for example. The problem is intensified by the fractionation that takes place on evaporation of the liquid air, which leaves the residual liquid progressively richer in oxygen. Liquid air traps are preferably made of metal, or else a metal jacket should be used around a glass trap so that the latter does not come in direct contact with the liquid air.

Liquid nitrogen has marked advantages over liquid air as a refrigerant because of its chemical inertness. It may be prepared by fractionation of liquid air; if only a moderate quantity is required it may be produced by expansion of tank nitrogen through a throttle valve after precooling by passage through a copper tubing coil immersed in liquid air.

Now coming into use is a new type of pump designed by Herb[4] and associates, called the Evapor-ion pump. In it no coolant traps or baffles are required, nor are there present any of the organic vapors or other volatile materials common to the earlier pumps. It utilizes the gettering action of continuously supplied and evaporated titanium in conjunction with ion pumping to cause gas removal. The lowest pressure obtainable is about 2×10^{-7} mm Hg.

CONDUCTANCE OF A PUMPING SYSTEM

The speed of the pumping system depends not only on the intrinsic speed of the pump proper, S_0, but also on the conductance of the connection between the pump and the vessel to be evacuated. For the connecting tube this conductance, F, relates the quantity Q of gas transferred per unit time to the pressure drop ΔP across the tube:

$$Q = F\Delta P \tag{3}$$

In vacuum work the experimental conditions are in general such that turbulent flow of gas through the connecting tubes is not encountered.

At the higher pressures of interest Poiseuille's law of viscous flow applies:

$$n = \frac{\pi}{256\eta} \frac{d^4}{l} \frac{P_2^2 - P_1^2}{RT} \tag{4}$$

where n = number of moles of gas (assumed to obey ideal-gas law) which flow per second through a cylindrical tube
d = diameter of tube, cm
l = length of tube, cm
P_2, P_1 = inlet and outlet pressures, μbars (i.e., dynes cm^{-2})
η = coefficient of viscosity of the gas, poises, at T°K

Since nRT can be set equal to PV, the quantity of gas Q in microbar cm^3 transferred per second can be written

$$Q = \frac{\pi d^4}{256\eta l}(P_2^2 - P_1^2) = \frac{\pi d^4}{128\eta l} \frac{P_2 + P_1}{2}(P_2 - P_1) \tag{5}$$

As $(P_2 + P_1)/2$ is the average pressure in the tube in microbars, $\bar{P}_{\mu\text{bar}}$, Eq. (3) shows that the conductance F_v of the tube in the viscous flow region is given by

$$F_v = \frac{\pi d^4}{128\eta l} \bar{P}_{\mu\text{bar}} \text{ cm}^3 \text{ sec}^{-1} \tag{6}$$

At very low pressures a different relation obtains because the mechanism of flow changes. As the pressure is reduced the mean free path of the molecules increases; for air at 25°C, the mean free path λ in centimeters is given by $\lambda = 5.09/P_\mu$, where P_μ is the pressure in microns. When the mean free path becomes larger than the diameter of the tube through which the gas is moving, collisions between molecules become of negligible importance compared with collisions of the molecules with the tube walls. The gas is then referred to as a "Knudsen gas," because of the contributions made by the physicist Knudsen to the kinetic theory of gases for such conditions. Each molecule then moves in essential independence of the others. The wall, to an incident molecule, is an extremely rough surface. It is hence legitimate to assume that the direction in which a molecule will bounce off the wall will be independent of the angle of incidence calculated on the assumption of a perfectly smooth surface. The resulting transfer of gas down the tube, termed *molecular flow* by Knudsen, can then be treated by statistical methods to give the following result for a cylindrical tube of diameter d centimeters and length l centimeters:

$$F_m = \frac{1}{3}\sqrt{\frac{\pi}{2}} \frac{1}{\sqrt{\rho_1}} \frac{d^3}{l} \text{ cm}^3 \text{ sec}^{-1} \tag{7}$$

Here ρ_1 is the gas density in g cm^{-3} at a pressure of 1 μbar. It should be noted that in the molecular flow region the conductance is independent of pressure.

At intermediate pressures the flow is partly viscous and partly molecular. The general expression given by Knudsen must be used for this range:

$$F = F_v + F_m Z = F_v + F_m \left(\frac{1 + \dfrac{d\sqrt{\rho_1}}{\eta} \bar{P}_{\mu\text{bar}}}{1 + \dfrac{2.47d\sqrt{\rho_1}}{2\eta} \bar{P}_{\mu\text{bar}}} \right) \text{cm}^3\ \text{sec}^{-1} \qquad (8)$$

For air at 25°C, with the average pressure expressed in microns, d and l in centimeters, and F in liters sec^{-1},

$$F = 0.177 \frac{d^4}{l} \bar{P}_\mu + 12.2 \frac{d^3}{l} Z \qquad (9)$$

$$Z = \frac{1 + 0.246\bar{P}_\mu d}{1 + 0.304\bar{P}_\mu d} \qquad (10)$$

The factor Z varies between 0.81 at high pressures and 1 at low pressures. As pointed out by Hecker,[3] if $\bar{P}_\mu d$ is greater than 1,000, the flow is over 95 per cent viscous, while for $\bar{P}_\mu d$, less than 2 it is over 95 per cent molecular. An alternative criterion for molecular flow given by Knudsen states that the flow is over 95 per cent molecular if d/λ is less than 0.4. The molecular flow range is of primary concern in high-vacuum work, but conductance calculations for the intermediate pressure range are often required in the design of connecting lines between diffusion pumps and forepumps (see below).

The quantity of gas moved per second through two tubes in series is the same for each tube. If the conductances of the tubes are F_1 and F_2, F that of the series combination, $P_3 - P_2$ the pressure drop across the first tube and $P_2 - P_1$ that across the second,

$$Q = F_1(P_3 - P_2) = F_2(P_2 - P_1) = F(P_3 - P_1) \qquad (11)$$

so that

$$\frac{1}{F} = \frac{1}{F_1} + \frac{1}{F_2} \qquad (12)$$

This result may also be obtained by thinking of the conductance as the reciprocal of a resistance to flow. The additivity of resistances in series again leads to Eq. (12).

Bends and elbows in a tube of constant diameter and axial length have relatively little effect on the conductance at low pressures. As the mean free path becomes large compared to the diameter of the tube, however, molecules experience a difficulty getting into the tube from an adjacent region of relatively larger cross section. This difficulty may be characterized quantitatively by a conductance for the tube *entrance,* which for a circular aperture of diameter d can be written approximately as

$$F_0 = \frac{1}{4}\sqrt{\frac{\pi}{2}}\frac{d^2}{\sqrt{\rho_1}} \tag{13}$$

For molecular flow the resultant conductance for a tube plus the entrance is obtained by combining the relations of Eqs. (7) and (13) in accordance with Eq. (12). The result for air at 25°C is

$$F = \frac{9.17d^2}{1 + \frac{3}{4}\frac{l}{d}} \text{ liters sec}^{-1} \tag{14}$$

Consider a composite pumping system of speed S consisting of a pump of speed S_0 in series with a connecting tube of conductance F. The rate Q at which this system removes gas from a vessel where the pressure is P must be equal to SP, from the definition of pumping speed. Similarly $Q = S_0P_0$, where P_0 is the pressure at the pump entrance proper. Also, since the same gas is driven through the conductance F by the pressure drop $(P - P_0)$, $Q = F(P - P_0)$. Hence

$$Q = SP = S_0P_0 = F(P - P_0) \tag{15}$$

and

$$\frac{1}{S} = \frac{1}{S_0} + \frac{1}{F} \tag{16}$$

This relation is of basic importance in vacuum technique. It must be utilized in the design of high-vacuum systems to obtain efficient use of the pump employed.

MEASUREMENT OF SPEED OF VACUUM PUMPS

A number of methods are available for the measurement of the speed of vacuum pumps. The procedure suggested by Howard[5] is convenient for pumps of moderate speed. The apparatus used is shown in Fig. 75. The capillary tube and the 1-mm bore stopcock C, whose plug is grooved slightly at the edge of the hole to facilitate adjustment of the leak rate, permit a slow leakage of air from the 50-ml gas burette B. Initially the stopcock C is closed and the pump set in operation. The mercury leveling tube D is lowered so that stopcock A can be opened to the atmosphere. Stopcock *C* is then opened carefully until the pressure maintained by the pump, as measured by a McLeod gauge connected at *G*, is approximately equal to the pressure for which the pumping speed is to be determined. The pressure in the system is checked periodically, and when it has become constant the mercury level in the burette is raised slowly past the stopcock *A*, which is then closed. The position of the mercury level in the burette, the time, and the barometric pressure are recorded. The leveling bulb is progressively raised as required to keep the pressure in the burette constant as gas is removed by the pump.

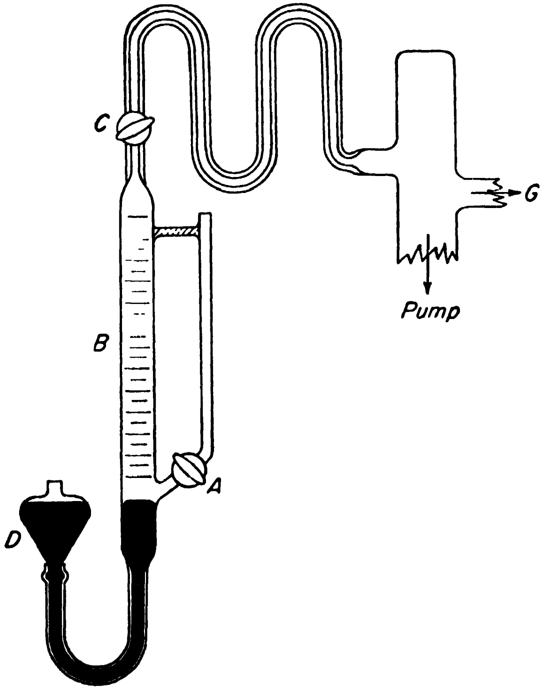

FIG. 75. Apparatus for Howard's method for the measurement of the speed of a pump

When an appropriate volume of air has been pumped out, stopcock *C* is closed and the time and burette reading are recorded. The pumping speed is calculated by multiplying the volume of air removed per second by the ratio of the burette pressure to the pump working pressure.

In another useful method the gas removed by the pump is delivered by a flow tube whose conductance can be calculated; the experimental arrangement is shown in Fig. 76. The bulbs *B*, *B'* should be of about 1-liter volume. The appropriate dimensions for the flow tube depend on the kind of pump under test,[1] but for the smaller laboratory diffusion pumps a tube of 1 cm diameter and 50 cm length can be used for the low-pressure range. Initially the capillary leak (a sensitive high-vacuum needle valve should be used) is closed and the pump started. The leak is then opened gradually until the pressure P_1 has reached the level for which the speed is desired. When the pressures P_2 and P_1 have become constant (as measured by the vacuum gauges G_2 and G_1), the rate of flow of gas through the tube can be evaluated by use of the calculated conductance F of the flow tube:

$$Q = F(P_2 - P_1) \qquad (17)$$

The pump speed is then given by Q/P_1, provided the pump is connected directly to B'. Otherwise the conductance of the connecting tube must be taken into account [compare Eq. (16)].

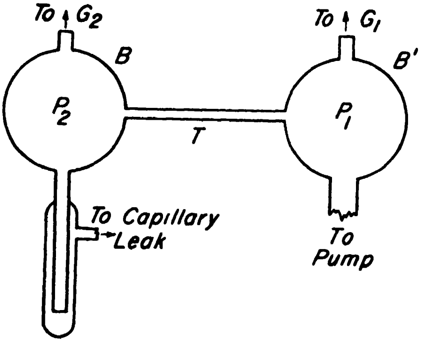

FIG. 76. Apparatus for flow-tube method for pumping-speed determination.

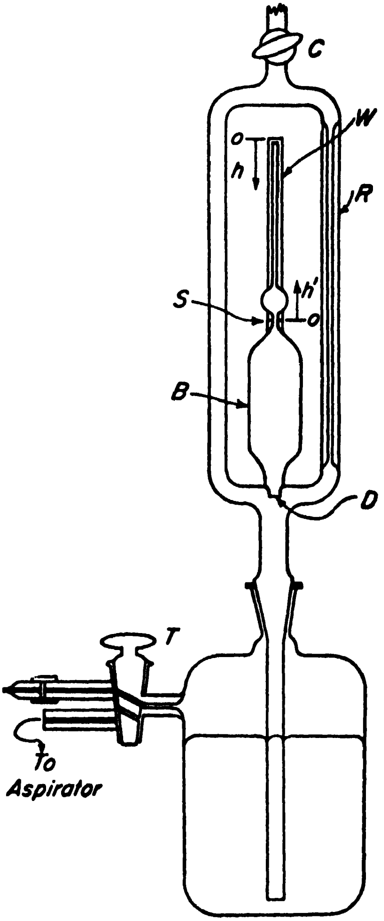

FIG. 77. McLeod gauge.

VACUUM GAUGES

The McLeod gauge, one design of which is shown in Fig. 77, is a basic instrument for low-pressure measurements. A large volume of gas, V, at the unknown pressure p, is compressed to a small volume v, and the corresponding pressure P is measured; p is then calculated from the relation $p = Pv/V$, which holds quite accurately for the low pressures involved. In use, the high-vacuum stopcock C is gradually opened, and as the pressure in the gauge is reduced, the two-way stopcock T is opened carefully to the auxiliary vacuum line to keep the mercury from rising appreciably in the connecting tube. To make a pressure measurement the control stopcock T is opened *slightly* to the atmosphere (a capillary leak here may be used to prevent an undesirable rush of air into the vessel) to produce a slow rise of mercury into the gauge. When the rising mercury reaches the cutoff D, the gas in the gauge bulb B is trapped at the pressure to be determined. For highest sensitivity in the pressure measurements, this gas is compressed until the mercury meniscus in the reference capillary R has reached the level of the top of the gauge capillary W. The difference of h millimeters in the levels of the mercury in the two capillaries represents the final pressure of the compressed gas. The reference capillary is made of the same tubing as the gauge capillary in order to eliminate the effect of the capillary depression.

Previous calibration measurements give the total volume V of the bulb B, and the volume per millimeter length, v_0, of the capillary W. The gas volume at the unknown pressure p is V, while at the final pressure h mm Hg it is v_0h, so that

$$p = \frac{v_0h}{V} \cdot h = \frac{v_0}{V} h^2 \text{ mm Hg} \tag{18}$$

The volumes V and v_0 must be expressed in the same units. The various levels h corresponding to initial gas pressures of 10^{-6}, 10^{-3}, and intermediate values, in millimeters of mercury, are calculated and the gauge calibration scale is constructed. This scale is termed the quadratic scale, or the logarithmic scale.

A different method of operation can be used to extend the range of the gauge to higher pressures than can be measured on the quadratic scale. The gas in the bulb B is compressed until the meniscus *in the bulb* has reached the reference mark S in the lower capillary section. The final volume of the gas is then always equal to the volume V_f of the section above S. The final pressure is read as the height h' millimeters above the level S of the mercury meniscus in the reference capillary R. Then

$$p = \frac{V_f}{V} h \text{ mm Hg} \tag{19}$$

This method thus yields a linear scale. A typical laboratory McLeod gauge will have a range of 10^{-1} to 10^{-6} mm on the quadratic scale, and of 10^{-1} to 2 mm on the linear scale.

After the pressure reading has been made, the stopcock T is opened to the vacuum line and the mercury drawn out of the gauge. When the gauge pressure is raised to the atmospheric level, the reservoir pressure must be increased at the same rate. The care required in this process is one of the main disadvantages of this particular design. In another version the gauge bulb is connected to a tube at least 760 mm long connected to a mercury well provided with a plunger with a threaded top. When the plunger is forced down and the threads engaged, the mercury rises in the gauge. The threaded section facilitates the fine adjustment of the mercury level. The tube and well can be made of metal to provide a very rugged construction.

Small McLeod gauges are available in which a flexible or rotating connection to the system permits the whole gauge to be tipped or rotated as required to force mercury into the gauge bulb.

The sensitivity of the McLeod gauge is governed by the ratio v_0/V. It is not practical to make V larger than 500 ml, because of the weight of such a large volume of mercury. Similarly the capillary diameter should not be less than 0.5 mm because of the tendency of mercury to stick in small capillaries. The mercury used must be quite pure, and the gauge itself carefully cleaned before filling. An efficient cold trap is required when a McLeod gauge is used with a system from which mercury must be excluded. This gauge cannot be degassed, nor can it be used to measure the pressure of a vapor which condenses to a liquid when compressed into the gauge capillary.

The basic importance of the McLeod gauge is that it is an *absolute* pressure gauge, because the calibration scale can be calculated directly from the measured physical characteristics of the instrument. As such it can be used as a reference standard* for the calibration of other types of gauges commonly employed in vacuum work.

At low pressures, the thermal conductivity of a gas becomes directly proportional to the pressure when the distance between the hot and cold surfaces becomes smaller than the mean free path. This property is exploited in the *thermocouple gauge* and the *Pirani gauge.* In the thermocouple gauge a constant current is passed through a resistance wire to the center of which a thermocouple is attached. The temperature of the wire changes as the pressure changes because of the variation of the thermal conductivity of the gas, and this change is indicated by a microammeter connected in series with the thermocouple. The thermocouple gauge is rugged, relatively inexpensive, and has a useful range extending from about 1 to 500 μ. In the Pirani gauge the resistance wire is connected as one arm of a Wheatstone bridge; the extent of the bridge unbalance, as registered by a microammeter connected as the bridge detector, indicates the pressure in the gauge. A second resistance filament, identical to the first but sealed off in a tube under high vacuum, is used in the opposite arm of the bridge to compensate for room-temperature changes, etc., to obtain better gauge performance. The useful range

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* The Knudsen radiometer gauge, discussed in detail by Dushman,[2] is also an absolute gauge, but is much more difficult to construct and use.

of a typical commercial Pirani gauge extends from 1 to 500 μ. The Pirani gauge is subject to erratic zero shift, and its calibration must be checked regularly. A separate calibration is required for every different gas for both of these thermal conductivity gauges.

For measurements of very low pressures *ionization* gauges are employed. The electrode arrangement in the conventional type is similar to that of the triode illustrated in Fig. 110, except that a filamentary cathode and more rugged grid construction are used. Electrons emitted from the heated cathode are accelerated toward the concentric helical grid, which is maintained *positive* with respect to the cathode by a suitable power supply. In collisions between these electrons and gas molecules present, ionization of molecules takes place. The positive ions so produced are attracted to the cylindrical plate, which is made *negative* with respect to the cathode. The resulting current in the plate-cathode circuit is proportional to the pressure of the gas in the gauge provided the electron current from cathode to grid is held constant. The plate current may be measured directly with a microammeter in the less sensitive instruments, but for low-pressure work the potential drop caused by the flow of the current through a series resistance is measured after amplification. The gauge sensitivity is only slightly dependent on the plate potential provided the latter is at least -10 volts relative to the cathode.

This particular electrode arrangement, i.e., plate negative and grid positive, is utilized to provide increased sensitivity. The grid has a relatively small area, so most of the electrons accelerated toward it pass through the helix and continue on toward the plate. As they approach the negative plate they are repelled and move back toward and through the grid. This process continues and increases considerably the average distance traveled in the gauge by the electrons before they are captured by the grid. The lengthened path means an increased number of ionizing collisions with gas molecules, and hence increased gauge sensitivity.

The standard ionization gauge can measure gas pressures as low as 10^{-8} mm Hg. The upper pressure limit is about 5 μ; it is not possible to operate this gauge at higher pressures without harming it. Commonly a thermocouple or Pirani gauge is used to show when the pressure is low enough to permit the operation of the ionization gauge.

A second type of ionization gauge is the Phillips gauge. In this unit a high-voltage ($\sim$2000 volts) discharge is created between a cold cathode and a ring-shaped anode. The resulting current depends on the gas pressure and is measured directly by a microammeter in the grounded side of the high-voltage supply. Small permanent magnets are suitably arranged in the gauge to cause the electrons to move to the anode in spiral paths to obtain increased sensitivity. The Phillips gauge has a range from about 10^{-2} to 25 μ. It is a rugged instrument and remains unharmed when subjected to atmospheric pressure. The discharge aids in the removal of adsorbed surface gases within the gauge, making it unnecessary to degas this gauge for low-pressure measurements. The response of all ionization gauges depends on the nature of the gas present, so separate calibrations are required for different gases. It should be emphasized also that in the use of any vacuum gauge to determine the pressure in a system, particularly if that pressure is not constant, the possible effect of the conductance of the connection to the gauge must be considered.

The general ranges of applicability for the several vacuum gauges are summarized in Table 1.

TABLE 1. RANGES OF VACUUM GAUGES IN MILLIMETERS OF MERCURY

Mercury manometer	1–1000
Butyl phthalate manometer	0.01–10
Pirani gauge	10^{-4}–0.5
Thermocouple gauge	10^{-3}–0.5
McLeod gauge	10^{-6}–2
Phillips gauge	10^{-5}–10^{-2}
Knudsen gauge	10^{-6}–10^{-2}
Ionization gauge	10^{-8}–10^{-3}

One of the basic problems in the attainment of very low pressures is the "outgassing" of surfaces, particularly of metals, as the pressure is reduced, due to the release of adsorbed gases or vapors. The best method for elimination of this interference is a "degassing" procedure in which the system is heated to drive off these materials. Adsorbed water comes off at about 200°C, and other gases, mainly carbon monoxide, at higher temperatures. Obviously, the whole system must be degassed at once for efficient performance, and no materials containing volatile components, such as vacuum waxes, Glyptal, rubber, brass (zinc volatilizes easily), etc., can be present. Without degassing, the best vacuum that can be expected is about 1×10^{-6} mm, and protracted pumping may be required to do this well. For good results vacuum gauges, such as ionization gauges, must be degassed. Ordinarily, provision is made in the gauge-control unit for degassing by electrical heating of the gauge elements.

In any vacuum system connections between the various sections present a problem. In metal systems, flange joints with Neoprene gaskets are often used; for a demountable joint in a section which must be degassed, copper gaskets can be employed. Great convenience can be obtained by use of O-Ring gaskets* with appropriately machined flanges; with these units, connections between metal sections, or between metal

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* O-Ring gaskets are available from Linear, Inc., State Road and Levick St., Philadelphia 35, Pa. The manufacturer's recommendations on their use should be followed in detail.

and glass sections, are easily made, as are effective seals on rotating or sliding rods or tubes which enter the system. For glass systems and moderately high vacua, standard taper joints can be used with vacuum wax or a good grade of vacuum grease. Stopcocks used should be of the specially processed high-vacuum type and of a suitably large bore for the particular application.

LEAK DETECTION

The detection and elimination of leaks is an inevitable step in the setting up of a vacuum system. All leaks must obviously be located, and very small ones may be extremely difficult to find. A complication in the latter case are the so-called "virtual leaks," which actually are due to the continuous evolution of gas inside the system. If it is possible to build up an excess air pressure within the system, leaks may be found by painting the outside in the suspected areas with a soap solution. In glass sections moderate leaks may be found with a Tesla coil; the high-frequency discharge will jump to a pinhole or crack in the glass, illuminating it brightly. Precautions must be taken to avoid puncturing thin-walled areas by use of too violent a discharge. Neither of these first two methods is useful for small leaks.

Because their response depends upon the nature of the gas present as well as its pressure, the thermal conductivity and ionization gauges can be used in leak hunting in appropriate pressure ranges. When the area including the leak is sprayed with acetone, for example, the acetone is drawn into the system and causes a change in the reading of the gauge. The Pirani gauge is considered more sensitive than the thermocouple gauge for this work. The ionization gauge can be used when the leaks are small enough so that an appropriately low pressure can be maintained in the system.

Special leak-detecting units are available commercially. The halogen-sensitive type utilizes the increase in the emission of positive ions (presumably originating from alkali metal impurities) from hot platinum which occurs when halogen-containing molecules strike the electrode surface; carbon tetrachloride, chloroform, or Freon 1-1 are commonly used with this gauge. Extremely high sensitivity is obtained in the helium-leak detector by use of the mass spectrometer principle to obtain a specific response to helium. Leaks are located by virtue of the response when a stream of helium is played over the outside of the system.

The detailed treatment of problems and procedures in vacuum technique given by Dushman[2] is the basic reference in this field. Other general treatments include those of Jnanananda,[6] Reimann,[7] Yarwood,[11] and Hecker.[3] A series of papers on applications of engineering interest and presented at a symposium on high vacuum have been published together.[10] Modern vacuum pumping systems and equipment are also described in a paper by Sullivan.[9]

Apparatus. Rotary oil pump(s); mercury diffusion pump; oil diffusion pump; Howard pumping speed apparatus; flow-tube pumping speed apparatus; McLeod gauge(s); Tesla coil; thermocouple gauge, Pirani gauge, ionization gauge, and control units; acetone.

Procedure. *Part A*. The pumping speed for a rotary oil pump at a pressure near atmospheric is determined by the flow-tube technique. In this case a flow tube 1 m long and of 3 mm internal diameter is suitable; one end is open to the atmosphere, the other is connected to a short section of larger-diameter tubing which leads directly to the pump. A differential manometer is used to measure the pressure drop across the flow tube. One side of this manometer is connected through a stopcock to the low-pressure side of the flow tube, the other is open to the atmosphere. With the stopcock closed, the pump is started. The stopcock is then opened slowly, and when the pressure drop indicated by the manometer has become constant its value is recorded, together with the barometric pressure and the dimensions of the flow tube. It is convenient to use an oil as the manometer fluid; its density will be specified by the instructor.

Part B. The rotary pump is then connected as the forepump for a mercury diffusion pump. The latter is connected to a manifold to which a McLeod gauge and a Howard pumping speed assembly are attached. The stopcocks leading to these two units are closed, and the forepump is started. After a few minutes the stopcock connecting the McLeod gauge is opened, and a pressure measurement is made with the McLeod gauge, as described above. The pressure is rechecked until it has dropped below 100 μ. The water line to the diffusion-pump condenser jacket is then turned on, and power applied to the pump heater. As the pump goes into operation the pressure in the system will drop rapidly, and the McLeod gauge is used to measure the resulting low pressure, which should soon reach 10^{-2} μ. The capillary leak of the Howard apparatus is then opened slowly until a pressure of about 1 μ is found with the McLeod gauge. The pumping speed of the diffusion pump is then determined at this pressure as described under Theory. Finally the mercury is drawn down out of the gauge, and the gauge stopcock is closed. The diffusion pump heater is turned off, then the forepump, and the system slowly opened to the atmosphere by means of a stopcock connected to the forepump line. The gauge is then returned to atmospheric pressure also. After the diffusion-pump boiler has cooled, the condenser water supply is shut off.

Part C. The calibration of a McLeod gauge is undertaken next. A gauge bulb assembly will be supplied by the instructor, together with a piece of the tubing used for the gauge capillary. The clean and dry gauge bulb is weighed empty. It is then filled completely with water to the cutoff at D (Fig. 77) and reweighed. A hypodermic syringe with a long needle will facilitate the filling of the capillary. The temperature of the water is recorded. The bulb is emptied with the help of an aspirator, placed in a drying oven, and reevacuated, with the aspirator, when warm, to assist in drying it. A thread of mercury is drawn into the capillary tube supplied, and its length is measured. The mercury is emptied into a tared weighing bottle, and its weight determined.

Part D. Measurements are made with an oil diffusion pump attached to a flow-tube apparatus like that shown in Fig. 76. It is convenient to use two thermocouple gauges, one to measure the forepressure, and the other on the high vacuum side of the diffusion pump to indicate when it is safe to turn on the ionization gauge connected at G_1. The gauge G_2 may be a Pirani gauge or a Phillips gauge.

All stopcocks connected to the system are closed, the forepump is turned on, and several minutes allowed for the pressure in the system to be reduced below the millimeter level. The thermocouple forepressure gauge is turned on, and when the pressure has dropped below 200 μ, the diffusion-pump heater can be connected. For an air-cooled pump the air supply is turned on, or the water in the case of a water-cooled pump; the manufacturer's operating instructions for the particular pump used should be carefully followed.

While the system pressure is being reduced, the Pirani or Phillips gauge is put into operation. When the pressure has dropped below 1 μ the ionization gauge may be turned on. A pressure of the order of 10^{-2} μ should be reached after the diffusion pump has been in operation for some time. The speed of the latter is then determined for a pressure of about 0.2 μ, following the procedure described in the Theory section. The capillary leak connected to bulb B (Fig. 76) is slowly opened until the pressure P_1 has reached the desired level. The pump is then allowed to operate until the pressures P_2 and P_1 become constant; their values are recorded, together with the dimensions given for the flow tube. The capillary leak must be opened very carefully for the protection of the ionization gauge. It is possible to dispense with the leak by connecting bulb B to the forepump, but the high-vacuum needle valve provides greater versatility.

Part E. The ionization gauge is turned off, and leak detection is illustrated by use of a tube with a pinhole leak in it connected through a high-vacuum stopcock to bulb B. This stopcock is now opened slowly, and the Tesla coil turned on and the discharge played over the tube surface to locate the leak. The readings of the various gauges still in operation are noted. The area around the pinhole is then sprayed with acetone, and the effect on the gauge response noted.

The diffusion-pump heater and the vacuum gauges are turned off. After the pump fluid has cooled, the forepump is stopped and the system pressure raised to 1 atm. This is conveniently done by opening a stopcock connected to the forepump line.

Calculations. *Part A.* The pressure drop across the flow tube used with the rotary oil pump is converted to millimeters of mercury, and the mean pressure in the tube and the pressure at the pump are calculated. The tube conductance in liters per second is calculated by use of Eq. (6), which for air at 25°C may be written as

$$F_v = 0.177 \frac{d^4}{l} \bar{P}_\mu \tag{20}$$

where $\bar{P}_\mu$ is the mean pressure in microns, and d and l are in centimeters. The quantity of gas Q delivered per second to the pump by the flow tube is calculated by use of Eq. (17). Division of Q by the pressure at the pump gives the pump speed.

Part B. The determination of pumping speed by the Howard method has been described in the Theory section.

Part C. The volume V of the McLeod gauge bulb is calculated from the weight of water it holds and the density of the water (page 474). The volume per millimeter length, v_0, of the gauge capillary is calculated from the weight of the mercury thread, its length, and the density of the mercury. A calibration scale for the gauge bulb is drawn for pressure in decade steps from 10^{-6} to 10^{-2} mm Hg, in accordance with Eq. (18).

Part D. The conductance of the flow tube used with the oil diffusion pump is calculated by use of the molecular-flow formula, Eq. (14). The speed of the pump is then calculated as described for the other flow-tube experiment. For this pumping speed there is calculated the diameter for a 20-cm connecting tube necessary to give a conductance which would not reduce the pump speed by more than 10 per cent.

Practical Applications. High-vacuum techniques, fundamental in many research fields in natural science, are finding many practical industrial applications, such as in vacuum furnaces in metallurgy, the application of surface coatings by the vacuum evaporation process, freeze-drying of various materials, vacuum distillation of high-molecular-weight compounds, etc., as well as the more familiar examples of light bulbs, electron tubes, and Dewar flasks.

Suggestions for Further Work. The volume of the McLeod gauge capillary above the reference mark S (Fig. 77) may be determined, and a linear calibration drawn up. The formula for the conductance of an orifice, Eq. (13), may be derived from the relation $n_s = \frac{1}{4}n \sqrt{8kT/m\pi}$ for the number of molecules striking a surface per cm² per second; n represents the number of molecules per cm³ of gas, m is the mass per molecule, k the Boltzman constant, and T the absolute temperature. The effect on the speed of a diffusion pump of variation in the heater-power dissipation or the forepressure may be studied. The conductance formula of Eq. (9) may be checked with tubes of various diameters and lengths. The vacuum evaporation of aluminum may be attempted; directions are given by Strong.[8]

References

1. Backhurst and Kaye, *Phil. Mag.*, **47**, 918 (1924).
2. Dushman, "Vacuum Technique," John Wiley & Sons, Inc., New York (1949).
3. Hecker *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. IV, Part II, Chap. 6, "Distillation," Interscience Publishers, Inc., New York (1951).
4. Herb, Davis, Divatia, and Saxon, *Phys. Rev.*, **89**, 897 (1953); Davis and Divatia, *Rev. Sci. Instr.*, **25**, 1193 (1954).
5. Howard, *Rev. Sci. Instr.*, **6**, 327 (1935).
6. Jnanananda, "High Vacua," D. Van Nostrand Company, Inc., New York (1947).
7. Reimann, "Vacuum Technique," Chapman & Hall, Ltd., London (1952).
8. Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York (1939).
9. Sullivan, *Rev. Sci. Instr.*, **19**, 1 (1948).
10. Various contributors, Symposium on High Vacuum, *Ind. Eng. Chem.*, **40**, 778–847 (1948).
11. Yarwood, "High Vacuum Technique," 2d ed., John Wiley & Sons, Inc., New York (1945).

59. ELECTRONICS

The properties of several types of electron tubes are illustrated by use of simple circuits, and experience is provided with the application of the oscilloscope and other test instruments.

Theory.[1,2,3] Chapter 23 provides a brief introduction to the principles of operation of the tubes and circuits considered here.

Apparatus. Tubes; resistors; condensers; chokes; transformers; breadboard-type circuit assembly boards with binding-post array for connections; 15-ma milliammeter; 22.5-volt battery; oscilloscope;* vacuum-tube voltmeter;* variable-voltage power supply;* tube manual.

Procedure. The various elements required for the circuits to be assembled are provided with leads terminated in spade lugs. A set of binding posts, mounted on a strip of bakelite or other insulator which is fastened to the plywood assembly board, facilitates the required interconnections. The power cord for connection to the 110-volt 60-cycle line is fused and is terminated at an outlet box, fastened to the assembly board, which provides a switch-controlled power outlet. A good ground connection is also provided.

The schematic circuit diagrams may be interpreted with the aid of Fig. 108; the color-code conventions for electronic components are given

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* These instruments can be constructed easily and at relatively low expense from commercially available kits.

in the Appendix. Tube-socket terminals are numbered clockwise as viewed from *below*, starting at the key or gap. The tube manual should be consulted for the terminal connections for the various electrodes. Any unused transformer leads should be connected individually to binding posts to avoid accidental short circuits. All circuit wiring should be carefully rechecked before the power switch is turned on. Circuit adjustments should be made *only* when the power is *off*. Safety precautions in electronics work are emphasized on page 434.

The instructions for the operation of the auxiliary equipment, such as the oscilloscope, should be studied in advance. In use, the ground terminal of the oscilloscope should be connected to the assembly-board ground, and an *insulated* test prod employed to obtain the signal for the oscilloscope input.

Part A. The full-wave rectifier circuit of Fig. 109*c* is assembled, with a 10,000-ohm 25-watt load resistor, a 5Y3 rectifier tube, and a small power transformer such as the Stancor PM 8401. The center tap of the transformer high-voltage secondary winding should be connected to the ground terminal as well as to the load resistor. The power is turned on, and the wave form of the voltage drop across the load resistor is observed with the oscilloscope. The power is then switched off, and the lead *from* one plate of the 5Y3 tube is disconnected from the binding post at which it was connected to the transformer secondary lead. The resulting circuit is that of the half-wave rectifier of Fig. 109*a*. The power is turned on again, and the wave form of the voltage across the load resistor observed.

Part B. The d-c power supply of Fig. 115*a* is constructed, with a resistor R_b of 10,000 ohms (25 watts), a 5Y3 rectifier tube, filter chokes L of 15-henry inductance at 50 ma d-c current, and condensers C of 10-μfarad capacity (450-volt d-c voltage rating). The power is switched on, and the a-c voltage wave forms at the input to the filter section and across the load resistor are observed with the oscilloscope. This a-c ripple voltage is shown to be primarily of 120-cycle frequency by comparison of its wave form with that of a 60-cycle signal obtained from the 6.3-volt filament winding of the power transformer; the center tap of this winding should be grounded.

The effectiveness of the filtering action may be illustrated by comparing the a-c ripple voltages obtained with no filter, a single filter section, and the two-section filter, as measured with a vacuum-tube voltmeter.

When the power is turned off, the filter condensers should be shorted by means of a screwdriver with an *insulated handle* to ensure their complete discharge.

Part C. Amplification by the triode is illustrated with the circuit of Fig. 112. The filament voltage is supplied by the 6.3-volt secondary winding of the power transformer; the center tap of this winding should be grounded. The B battery supply shown may be replaced by the filtered full-wave rectifier supply constructed previously. The input signal for the amplifier is obtained from a 1,000-ohm potentiometer connected across the ungrounded secondary winding of a separate 6.3-volt filament transformer. The potentiometer is adjusted to provide a 1-volt input signal, as measured with the vacuum-tube voltmeter. The alternating voltage developed across the load resistor is also recorded, together with the d-c grid bias and plate supply voltages.

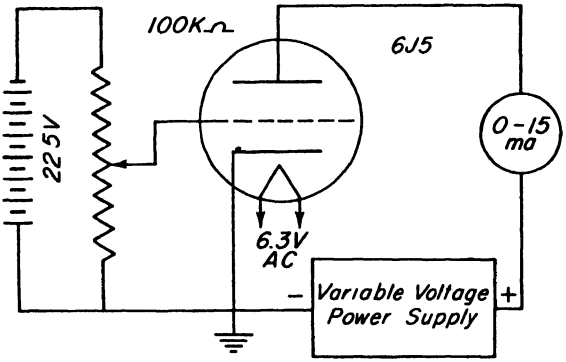

FIG. 78. Circuit for the determination of characteristic curves for a triode.

The input and output a-c voltage wave forms are observed with the oscilloscope. The input voltage is then increased gradually while the output voltage wave form is observed to illustrate the result of overdriving the tube with an excessively large signal.

Part D. Characteristic curves are determined for the 6J5 triode; the circuit arrangement is shown in Fig. 78. The grid bias is set successively at even voltages from 0 to −20 volts, relative to the cathode, as measured by the vacuum-tube voltmeter. For each grid-bias value the plate voltage is increased from zero until a response is noted on the plate milliammeter. The plate current is then determined at 20-volt intervals in plate voltage until the plate dissipation (plate current times plate voltage) approaches 2.5 watts, the maximum rating for this tube.

Part E. The circuit of Fig. 79 is used for the determination of the characteristic curves of the 6AC7 pentode. The power supply constructed in Part B may be used with the 25,000-ohm, 25-watt voltage divider shown to supply the required screen voltage of 150 volts.

The grid bias is set successively at levels of −1.5, −2, and −3 volts relative to the cathode, with the screen voltage constant at 150 volts in each case. For each grid-bias value the plate current is measured at

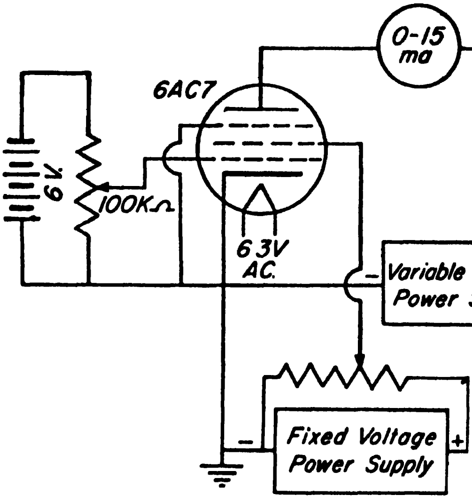

FIG. 79. Circuit for the determination of characteristic curves for a pentode.

10-volt intervals in plate voltage for the first 50 volts, and then at 50-volt intervals to 250 volts.

Calculations. The observed effectiveness of the *LC* filter section used with the full-wave rectifier is compared with the value predicted by the equation

$$\alpha = \frac{\text{alternating voltage at output of section}}{\text{alternating voltage at input of section}} = \frac{1}{(2\pi f)^2LC - 1} \quad (1)$$

where L = choke inductance, *henrys*

C = condenser capacity, *farads* (1 farad = 10^6 μfarads)

f = frequency

For the full-wave rectifier, f is to be taken as 120 cycles. The higher ripple frequencies present (higher multiples of 60 cycles) will be attenuated more than the 120-cycle component. It should be noted that if a choke input filter is to work properly, the first filter choke must have an inductance in henrys at least as great as the net load resistance divided by 1,000, for the full-wave rectifier case.

The characteristic curves for the pentode and triode are plotted as plate current versus plate voltage for the various grid-bias levels. For the triode amplifier circuit of Part C the predicted signal amplification is estimated (page 415) and compared with experimental result.

Practical Applications. Electron tubes and circuits are continuously finding more and more diversified applications in the fields of communication, measurement, and control.

Suggestions for Further Work. The triode relay circuit of Fig. 118, the phototube controlled-relay circuit of Fig. 132, and the constant-current circuit of Fig. 117 may be constructed. Numerous other experiments are described in detail by Muller, Garman, and Droz.[1]

References

1. Muller, Garman, and Droz, "Experimental Electronics," Prentice-Hall, Inc., New York (1945).
2. Reich, "Theory and Application of Electron Tubes," 2d ed., McGraw-Hill Book Company, Inc., New York (1944).
3. Terman, "Radio Engineers' Handbook," McGraw-Hill Book Company, Inc., New York (1943).

PART II

APPARATUS AND METHODS

CHAPTER 17

TREATMENT OF EXPERIMENTAL DATA[1]

ERRORS OF MEASUREMENT

Errors in experimental measurements may be divided into two classes: (*a*) *systematic errors* and (*b*) *random errors*. It is possible to correct for errors of the first type, and they are therefore frequently designated as *corrigible* or *determinate* errors to distinguish them from the random errors which are encountered in all measurements and are beyond the control of the observer. Many systematic errors may be eliminated by the application of familiar corrections. For example, in accurate weighings calibrated weights are used and a buoyancy correction (Chap. 21) is applied if the density of the substance being weighed is appreciably different from that of the weights. In the determination of atmospheric pressure using a mercury barometer, corrections must be applied to allow for the difference between the thermal expansion of mercury and the brass scale (page 472). This is required because 1 atmosphere pressure is defined as the pressure required to support a column of mercury 760 mm in height in an evacuated glass tube at a temperature of 0°C at sea level and at a latitude of 45°. In very precise work it is necessary in addition to correct for the capillary depression of the mercury and for the difference between the acceleration of gravity where the barometer is being used and the defined acceleration at 45° latitude. In calculating the pressure of a gas inside an inverted burette filled with water, it is necessary to subtract the pressure due to water vapor (see Appendix).

In other cases where the theory has not been as well developed, it is necessary to determine corrections experimentally. For example, in the drop-weight method for the determination of surface tension (Exp. 10), corrections which have been determined by using substances of known surface tension are applied. The correction factor to be applied is a function only of r/V^3, where r is the outer radius of the tube and V is the

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[1] Crumpler and Yoe, "Chemical Computations and Errors," John Wiley & Sons, Inc., New York (1940); Worthing and Geffner, "Treatment of Experimental Data," John Wiley & Sons, Inc., New York (1943); Fisher, "Statistical Methods for Research Workers," Oliver & Boyd, Ltd., Edinburgh (1932).

volume of the drop, and therefore does not depend upon the nature of the liquid studied. Such corrections are referred to as empirical corrections.

Systematic errors do not manifest themselves by fluctuations in measurements and cannot be eliminated by merely repeating the measurements, since the same error is involved in each measurement. These errors are, therefore, especially serious and insidious and can be avoided only by careful calibrations and consideration of all possible corrections. Sometimes systematic errors are indicated by a drift in consecutively measured values or by the change in the measured value resulting from a change in experimental technique.

The second class of errors, *random errors*, or *accidental errors*, is indicated by fluctuations in successive measurements. These random variations are due to small errors beyond the control of the observer. For example, if a barometer is read several times in succession, the values read from the vernier will be found to fluctuate about a mean value. Strictly speaking, we can never measure the true value of any quantity but only an approximation to it. The purpose of the statistical treatment of experimental data is to determine the most probable value of a measured quantity and to estimate its reliability.

The error of a measurement is the difference between the observed value and the true value of the quantity. If the error is small compared to the magnitude of the measured quantity, the measurement is said to be *accurate*. The statement of the accuracy of a result, therefore, implies that the true value is known. Since the true value is generally unknown, the mean of the series of determinations is used, and the differences between the observed values and the mean are referred to as *residuals*. If the residuals are small compared to the magnitude of the measured quantity, the measurement is said to be *precise*. A precise measurement is not necessarily an accurate measurement, but an accurate measurement must be a precise measurement. Small random errors occur more frequently than large ones, and for many experimental measurements the error distribution may be adequately represented by the Gaussian function, or "error function,"

$$y_x = \frac{h}{\sqrt{\pi}} e^{-h^2x^2} \tag{1}$$

where y_x is the probability of observing a value differing from the mean by x. If the precision constant h has a large value, the probability decreases very rapidly from its maximum at $x = 0$ to very small values, so that the probability of making large errors is very small. If h is small, the probability curve falls off very slowly and larger errors occur more frequently. It may be shown that if the set of residuals of a series of measurements follows Eq. (1), the arithmetic mean is the best approximation to the true value of the quantity measured.

Estimation of Experimental Errors. In order to determine the precision of a measurement, it is necessary to repeat the measurement a number of times in order to find how much the values scatter about the mean. In many cases, however—and this is particularly true for experiments in the physical-chemistry laboratory, where time is limited—it is necessary to *estimate* the precision of a measurement. No fixed values can be given for the precisions of various types of measurements because the precision depends upon the apparatus, the conditions under which it is used, and upon the carefulness of the operator. Therefore it is necessary to develop an awareness to various sources of error in order to make reliable estimates.

In the measurement of weight in the laboratory, the precision may vary over a wide range. An ordinary analytical balance may be used to obtain weights to ±0.1 mg, but the precision will depend upon the sensitivity of the balance and the way in which it is used as well as the quality of the weights. Large objects may be weighed on a trip balance with a precision of ±0.1 g.

In the measurement of volume the precision will depend upon whether volumetric flasks, pipettes, or burettes are used and on the size of the volume to be measured. The National Bureau of Standards tolerances for volumetric equipment are given in textbooks on quantitative analysis. In brief, a 25-ml volumetric flask (to contain) should be reliable to 0.03 ml, or 0.12 per cent, and a liter volumetric flask to 0.5 ml, or 0.05 per cent. A 10-ml transfer pipette should be reliable to 0.01 ml, or 0.1 per cent, and a 2-ml pipette to 0.006 ml, or 0.3 per cent. Of course, the accuracy of a volume required to reach an end point in a titration depends upon the sharpness of the end point as well as the accuracy of the burette.

In the measurement of pressure an ordinary laboratory barometer can be read to ±0.2 mm, and the pressure should be accurate within this uncertainty after the necessary corrections have been made (see Appendix). On the other hand, the pressure obtained with a simple mercury manometer without a special reading device will be uncertain by about ±1 mm.

The uncertainty in a measurement of temperature will be quite different if the temperature is measured with a good mercury-in-glass thermometer near room temperature or by use of a thermocouple at a high temperature. In calculating the percentage error in the temperature it must be remembered that it is the uncertainty of the value which is used in the calculation which is significant. Thus, an uncertainty of 1° at 25° would not cause a 4 per cent error in a calculation of molecular weight from the ideal-gas law, but a 0.3 per cent error. In other types of experiments it is the change in temperature which is significant rather than the absolute temperature, and so it is important to estimate the precision with which this difference can be measured.

In other cases, a scale can be read to a greater precision than is warranted by other factors in the experimental arrangement. For example, if a low-sensitivity galvanometer is employed for detection of the null point in a potentiometric circuit, it may be observed that the potentiometer slide-wire can be adjusted several divisions before a detectable movement of the galvanometer occurs. In this case, the precision is determined by the galvanometer rather than the graduated slide-wire.

Influence of Experimental Errors on the Final Result. A final physical-chemical result is usually obtained by combining the results of different kinds of measurements. The accuracy of any final result is influenced by the accuracy of the measurements of the several quantities involved. If it happens that one of the quantities involved is subject to a much greater error than the others, it will have the preponderant effect in determining the accuracy of the final result. For example, in the determination of molecular weight from the elevation of the boiling point (Exp. 13), the solvent and solute can be weighed more accurately than the boiling-point elevation can be determined. If, however, the relative errors in the various measured quantities are of the same order of magnitude, the errors introduced by all the measured quantities must be considered. In trying to improve the accuracy of a given experimental determination it is important to emphasize improvement of the least accurate measurement.

A simple and useful method for calculating the error in a final result is to calculate the maximum error which would be obtained if the errors in all the measured quantities had their maximum values and were in such directions that all affected the final result in the same direction. It is unlikely that the errors will combine in this way as there is usually some compensation of errors, but it is useful to know the maximum value an error could have in an unfavorable case. When the errors are small (that is, a few per cent or less), the following methods based on differential calculus are convenient.

Addition and Subtraction. If a final result u is the sum of measured quantities x and y

$$u = x + y$$
$$du = dx + dy$$

In terms of finite increments,

$$\Delta u = \Delta x + \Delta y \qquad (2)$$

Thus, if the error in measuring x is Δx and the error in measuring y is Δy, the maximum error in u is $\Delta x + \Delta y$. For example, a chemical compound is weighed in a weighing bottle weighing 27.021 ± 0.001 g. If the weight of the compound plus weighing bottle is 27.141 ± 0.001 g, the maximum uncertainty in the weight of the compound is indicated by writing 0.120 ± 0.002 g. Thus, the maximum error in the final result is about 2 parts per 100 although the weighings were made to about 4 parts per 100,000. Note that Δx and Δy have been taken as positive quantities.

Stated in words, the rule is: *The maximum error in a sum or difference is equal to the sum of the* absolute values *of the maximum errors in the measured quantities.*

Multiplication and Division. If a final result u is the product of two measured quantities x and y

$$\begin{aligned} u &= xy \\ du &= x\,dy + y\,dx \\ \frac{du}{u} &= \frac{dy}{y} + \frac{dx}{x} \end{aligned}$$

If the errors in x and y are small, the error Δu in u may be calculated from

$$\frac{\Delta u}{u} = \frac{\Delta x}{x} + \frac{\Delta y}{y} \tag{3}$$

For example, if a rectangular area is 10.0 ± 0.1 cm long and 5.0 ± 0.1 cm wide, the maximum error in the area may be calculated from

$$\begin{aligned} \frac{\Delta A}{50} &= \frac{0.1}{10.0} + \frac{0.1}{5.0} \\ \Delta A &= 1.5\text{ cm}^2 \end{aligned}$$

The student may readily satisfy himself that Eq. (3) also applies if $u = x/y$. In the case of calculations involving multiplication and division, it is convenient to talk about errors in terms of percentage errors, and Eq. (3) may be written as

$$\frac{\Delta u}{u}100 = \frac{\Delta x}{x}100 + \frac{\Delta y}{y}100 \tag{4}$$

Stated in words, the rule is: *The maximum percentage error in a product or quotient is equal to the sum of the* percentage errors *in the measured quantities.* This rule is accurate only when the percentage errors are small.

Logarithms. If a final result is the logarithm of a measured quantity

$$
\begin{aligned}
u &= \ln x \\
du &= \frac{dx}{x} \\
\Delta u &= \frac{\Delta x}{x}
\end{aligned}
\tag{5}
$$

Thus, the error in the final result is equal to the fractional error, $\Delta x/x$, in the measured quantity if this error is small.

In the case of more complicated calculations, it is convenient to calculate the maximum percentage error by differentiating the expression by which the final result is obtained and substituting the measured quantities and their experimental errors in such a way as to cause all the errors to accumulate in the most unfavorable way. In making such a calculation, it is frequently advisable to take the natural logarithm of the equation before differentiating. For example, the parachor P of benzene is to be calculated from

$$P = \frac{M}{d}\gamma^{1/4} \tag{6}$$

where M = molecular weight = (78.11 ± 0.01) g mole^{-1}
d = density = (0.879 ± 0.001) g cm^{-3}
γ = surface tension = (28.8 ± 0.2) dynes cm^{-1}

The value of the parachor is 205.8, and the maximum error may be calculated as follows:

$$
\begin{aligned}
\ln P &= \ln M - \ln d + \tfrac{1}{4}\ln \gamma \\
\frac{dP}{P} &= \frac{dM}{M} - \frac{d(d)}{d} + \frac{1}{4}\frac{d\gamma}{\gamma}
\end{aligned}
$$

In calculating the error ΔP all positive signs are used.

$$
\begin{aligned}
\frac{\Delta P}{P} &= \frac{\Delta M}{M} + \frac{\Delta d}{d} + \frac{1}{4}\frac{\Delta\gamma}{\gamma} \\
&= \frac{0.01}{78.11} + \frac{0.001}{0.879} + \frac{0.2}{(4)(28.8)} \\
&= 0.0029 \\
\Delta P &= (0.0029)(205.8) = 0.60
\end{aligned}
\tag{7}
$$

To indicate this uncertainty the final result is written 205.8 ± 0.6.

Other Methods for Representing Errors. When a large number of observations are made, the error may be indicated in a more precise way. The following terms are frequently used:

1. *Average Error.* The average error is simply the average of the deviations from the mean value. If the deviation (without sign) of a single observation is d, then the average error a is

$$a = \pm \frac{\Sigma(d)}{n} \tag{8}$$

where n is the number of observations.

2. *Standard Deviation.* The standard deviation is defined by the following equation:

$$\delta = \pm \sqrt{\frac{\Sigma(d)^2}{n-1}} \tag{9}$$

3. *Probable Error.* The probable error p is the error such that the number of errors greater than p is equal to the number of errors which are less than p. The probable error of a single observation is

$$p = \pm 0.6745 \sqrt{\frac{\Sigma(d)^2}{n-1}} \tag{10}$$

The indeterminate error in the mean is equal to the corresponding error in a single observation divided by $\sqrt{n}$. Thus, the larger the number of consecutive measurements, the nearer the average value is likely to lie to the true value. Since the error in the mean decreases as $1/\sqrt{n}$, the point is soon reached when the increase in precision obtainable from more measurements does not justify the expenditure of the time and labor required.

The probable error in a final result may be calculated if the probable errors in the various measured quantities are known. Such a calculation is a little more complicated than the calculation of the maximum error described in the preceding section. If y is a function of the independent variables x, z, w, . . . , it may be shown that the probable error p in y is

$$p = \pm \sqrt{\left(\frac{\partial y}{\partial x}\right)^2 r_x^2 + \left(\frac{\partial y}{\partial z}\right)^2 r_z^2 + \left(\frac{\partial y}{\partial w}\right)^2 r_w^2 + \cdots} \tag{11}$$

where r_x is the probable error in x, etc. For example, the volume of a sphere is given by $V = (4/3)\pi\rho^3$ where ρ is the radius of the sphere. If the average of several determinations of the radius of the sphere is 1.21 cm and the probable error in the determination of the radius is ±0.01 cm, the probable error in the volume calculated is

$$p = \pm 4\pi\rho^2 r_\rho = \pm 4\pi(1.21)^2\, 0.01 = \pm 0.18 \text{ cm}^3$$

so that the calculated volume should be written 7.41 ± 0.18 cm^3, or more properly 7.4 ± 0.2 cm^3.

Equation 11 may be used to show that the probable error of the sum or difference of two quantities A and B, respectively, affected with probable errors $\pm a$ and $\pm b$, is

$$p = \pm \sqrt{a^2 + b^2} \tag{12}$$

In the case of a multiplication, the probable error of the product of two quantities A and B is

$$p = \pm \sqrt{(Ab)^2 + (Ba)^2} \tag{13}$$

The probable error of the quotient B/A of two quantities A and B is

$$p = \pm \frac{1}{A} \sqrt{b^2 + \frac{B^2a^2}{A^2}} \tag{14}$$

The calculation of the probable error in more complex functions is described in books on the treatment of experimental data.

TABLE 1. NUMBER OF COUNTS OBTAINED IN 120 SEC USING A GEIGER-MULLER COUNTER
(Average count = 537)

Trial	Count	Deviation from average	Trial	Count	Deviation from average
1	552	+15	26	534	− 3
2	510	−27	27	521	−16
3	542	+ 5	28	539	+ 2
4	559	+22	29	508	−29
5	547	+10	30	519	−18
6	569	+32	31	532	− 5
7	513	−24	32	528	− 9
8	524	−13	33	590	+67
9	544	+ 7	34	540	+ 3
10	546	+ 9	35	517	−20
11	581	+44	36	504	−33
12	516	−21	37	538	+ 1
13	519	−18	38	525	−12
14	567	+30	39	533	− 4
15	530	+ 7	40	578	+41
16	551	+14	41	562	+25
17	514	−23	42	525	−12
18	586	+49	43	526	−11
19	540	+ 3	44	521	−16
20	551	+14	45	556	+19
21	524	−13	46	551	+14
22	544	+ 7	47	523	−14
23	531	− 6	48	549	+12
24	519	−18	49	583	+46
25	534	− 3	50	534	− 3

Random Errors. The determination of the average emission rate of a radioactive sample offers an example of random errors which are subject to mathematical treatment. The actual rate of emission of ionizing radiation is continually fluctuating because of the random nature of the disintegration process so that the number of counts recorded by a Geiger-Müller counter during equal time intervals with the same radioactive sample will be randomly distributed about an average value. This is illustrated in Table 1, which gives the number of counts obtained in successive intervals of 120 sec for a sample of uranyl nitrate. For reasons to be mentioned later, the mean value is generally taken as the most probable value for the quantity being measured. In this case, the average number is 537 counts, and the deviations of the individual values from the average are given in column 3. These deviations may be referred to as residuals or errors. It is seen that 25 of the values are larger than the average and 25 are smaller, and it may be noted that values which depart widely from the mean occur less frequently than those for which the deviation is small.

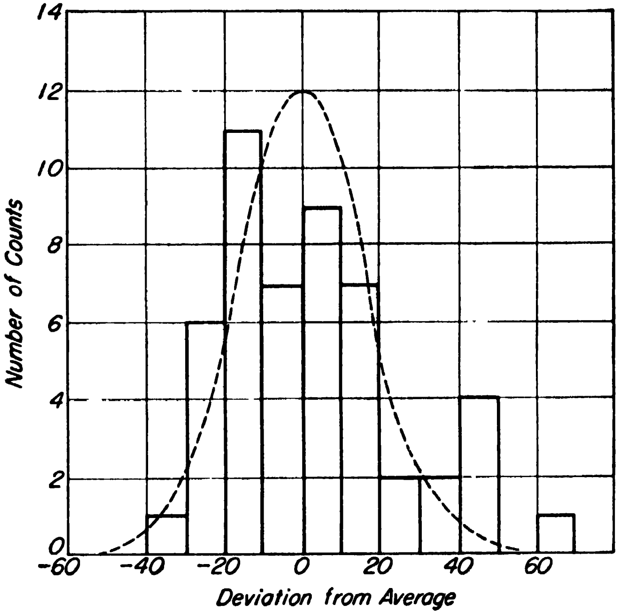

FIG. 80. Frequency of errors in the determination of radioactivity, using a Geiger-Müller counter.

The frequency of errors of a given magnitude is given by the graph in Fig. 80, in which the number of deviations having values between 0 and 9, 10 and 19, 20 and 29, etc., is plotted versus the deviation. Such a graph is referred to as a frequency-distribution curve. If a much larger number of measurements was made, the distribution would approach that represented by the dashed curve, which is the result which would theoretically be obtained from an infinite number of trials. (The scale of the ordinate is arbitrary.)

In the case of radioactive counting, the probability of a given count may be calculated from Poisson's equation,[1] but in many other cases it is not possible to predict in advance the exact distribution law followed. For the great majority of experimental measurements, however, the error distribution may be adequately represented by the Gaussian function, or "error function," which is given by Eq. (1).

Equation (1) is referred to as a *normalized* distribution function, since the coefficient is such that the probability of x lying between $x = -\infty$ and $x = +\infty$ is unity. For large numbers of counts, the frequency distribution may be adequately represented by the Gaussian function, and the dashed line in Fig. 80 represents the probability distribution which would be obtained for an infinitely great number of trials. The probable percentage error in a given determination of radioactivity depends upon the total number of counts and may be predicted[2] from a consideration of the laws of probability. Table 2 gives the probable percentage error and the nine-tenths error for various total numbers of counts. The probable error is the error which is exceeded 50 times in 100 trials, and the nine-tenths error is the error which is exceeded 10 times in 100 trials, on the average.

TABLE 2. THE ERROR OF COUNTING DETERMINATIONS

Total counts	Probable error, per cent	Nine-tenths error, per cent
100	7.8	16
1,000	2.2	5.1
10,000	0.7	1.6
100,000	0.23	0.5

SIGNIFICANT FIGURES

The accuracy of a measurement should be indicated by the number of significant figures used in recording its magnitude, and care must be exercised that too many significant figures are not used.

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[1] Rasetti, "Elements of Nuclear Physics," pp. 32-35, Prentice-Hall, Inc., New York (1936).

[2] Strong, "Procedures in Experimental Physics," p. 298, Prentice-Hall, Inc., New York (1939).

In calculations performed by longhand multiplication or a calculating machine, more figures are obtained than are significant, and the final result must be rounded off in accordance with the experimental uncertainty. Most of the multiplications and divisions required for work in the physical-chemistry laboratory may be made with a slide rule. The significant figures of a number include all the certain digits and the first (and first only) doubtful digit of that number. If no statement of accuracy accompanies an experimental result, it is assumed that the last digit may be uncertain by 2 or 3. Thus, if the experimentally determined molecular weight of carbon dioxide is given as 44.0, it would indicate that the most probable value for the molecular weight lies between about 43.7 and 44.3. If the experimental value is given as 44.00, it would indicate that the most probable value for the molecular weight lies between 43.97 and 44.03. The statement of an experimental result is incomplete unless the uncertainty in the value is indicated.

The digit 0 requires special consideration, since zeros to the left of the decimal point are not necessarily significant in regard to accuracy. For example, a volume of water measured in a 2-liter graduate might be recorded as 1,800 ml. Since such graduates are graduated every 20 ml, the last zero is not significant, and this fact could be indicated by writing the result as 1.80×10^3 ml. Zeros preceding the numbers in a decimal fraction are not significant. Thus, in the number 0.0000053 there are only two significant figures. In the case of very large or very small numbers it is convenient to use exponential notation, and so the preceding number could be written 5.3×10^{-6}.

REPRESENTATION OF DATA

There are three principal methods by which experimental data may be represented: tables, graphs, and equations.

Tabular Representation. Tables may be divided into three classes: qualitative, statistical, and functional tables. A *statistical* table, as its name implies, is one which lists statistical facts. Thus a table in the "World Almanac" which lists countries with a series of columns for population, area, national income, and the like is a statistical table, as is Table 1, Exp. 7. Such tables are fairly common in scientific work, but for the purposes of physical chemistry the functional table is of primary importance.

In the *functional* table, corresponding values of an independent variable x and a dependent variable y are listed side by side. As in all tables, every functional table should have a title which is clear and complete, yet brief, and each column of the table should have a heading giving the name and the unit of the quantity listed. The choice of the independent variable is to some extent arbitrary, but it should be a simple one, such as time, temperature, distance, etc. One should usually choose rounded values of the independent variable in order of increasing values, with successive values differing by a constant amount. The dependent variable is preferably given in terms of smoothed data. Numerical items are arranged so that the decimal points are vertically aligned in each column. The rules governing significant figures (page 330) should be observed.

There are several ways of obtaining smoothed data, the most common one being to plot the primary data, draw a representative smooth curve, and read information directly from the curve at desired points. The equation of the curve may also be found (page 335), and data may be computed from the equation at any desired value of the independent variable.

TABLE 3. THE VAPOR PRESSURE OF ACETONE AS A FUNCTION OF TEMPERATURE, ILLUSTRATING DIFFERENT MEANS OF SMOOTHING DATA

t, °C	(1) p, cm Hg From curve, Fig. 81a	(2) p, cm Hg From straight line, Fig. 81b	(3) p, cm Hg From Eq. (15) with $m = -1.662$, $b = 6.929$
5	8.91	9.02	8.98
10	11.39	11.6	11.47
15	14.50	14.1	14.49
20	18.17	18.2	18.16
25	22.53	22.8	22.67
30	28.00	28.0	27.98
35	34.57	34.3	34.28
40	42.09	42.0	41.82
45	50.76	50.9	50.64
50	61.07	61.5	61.09
55	72.30	73.8	73.40

These principles are illustrated in Table 3. Data represented are from a student's determination of the vapor pressure of acetone as a function of the temperature. In column 1 are listed data read directly from the curve of p versus T (Fig. 81a). The graph as originally prepared was of large scale and permitted readings to four significant figures. In column 2 are data obtained from the straight-line graph of Fig. 81b, which is plotted from the same experimental data. The scale of this graph did not permit reading beyond three significant figures. In column 3 are data computed from the equation

$$\log p = m\left(\frac{1}{T}\right) + b \tag{15}$$

where the constants have been evaluated by the method of least squares (page 339).

Actually none of these methods yields smoothed data of the highest possible quality in this particular case for the following reasons:

1. *From p versus T Curve.* Although the curve drawn for p as a function of T is the best approximation to the correct functional form, the decision as to how the curve should fit the points will be in slight error if the estimation is done purely by eye.

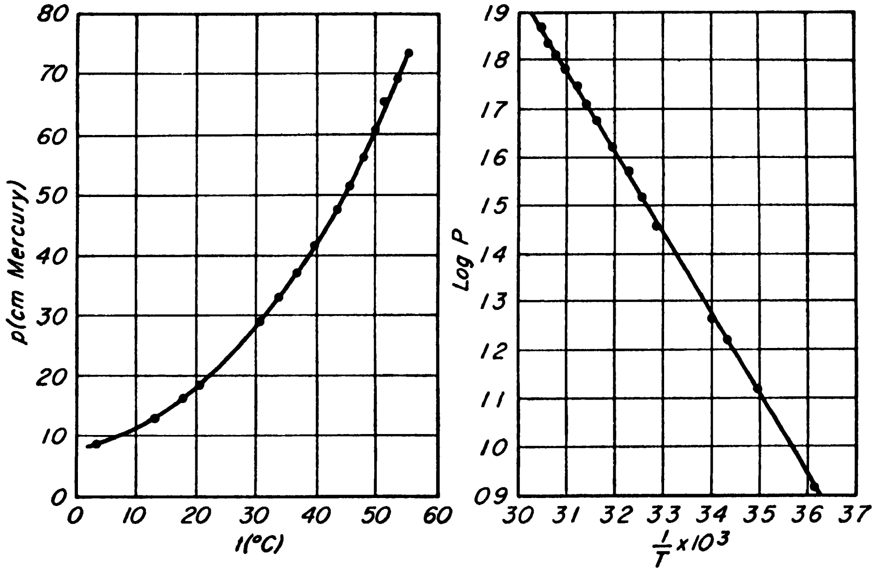

FIG. 81. (a) The vapor pressure of acetone as a function of temperature; (b) plot of log p versus $1/T$ for acetone.

2. *From Eq.* (15) *with Constants Determined by Least Squares.* This would be the last word in data smoothing if log p versus $1/T$ were actually a straight line. The best line through the points does, however, have a slight curvature. If the precision of the data was not quite so good, it is unlikely that the curvature could be assigned with certainty.

If a three-constant equation of the form

$$\log p = m(1/T) + a \log T + b$$

or better, $\log p = [A/(T + C)] + B$, were used in place of Eq. (15), the least-squares method, or even an approximate method, for evaluating the constants would yield smoothed data of very high quality. However, the labor of computation would be increased greatly.

3. *Directly from the Straight Line of Fig.* 81*b*. This is the usual procedure, yet it involves the errors encountered in both the other methods.

Other topics concerned with functional tables, including several methods of smoothing data by arbitrary numerical procedures, and the problems of interpolation and extrapolation are treated fully by Worthing and Geffner.[1]

Representation of Data by Graphs. Graphs have many advantages which favor their use in representing data. One of the most important of these advantages is that a graph may reveal maxima, minima, inflection points, or other significant features in data which might be overlooked in a tabular or formula representation. Furthermore, direct differentiation may be performed by drawing tangents to a curve, and integration may be accomplished by determining the area under a curve; in many cases these operations would otherwise be tedious or impractical.

The steps to be followed in preparing a satisfactory graph have been extensively treated and illustrated with numerous examples by Worthing and Geffner.[2] We shall summarize here only some of the more important points.

1. *Choosing the Graph Paper.* Ordinary rectangular coordinate paper is satisfactory for a large majority of purposes. Semilogarithmic paper is convenient when one of the coordinates is to be the logarithm of an observed variable (Exp. 9). If both coordinates are to be logarithms of variables, log-log paper may be used (Exp. 44). Where an unknown functional relation is involved, these types of paper are sometimes used because it is found by trial and error that they yield a closer approximation to a straight line than does rectangular coordinate paper. Another special-purpose paper which has triangular coordinates is used in Exp. 21.

It is practically always worth the extra expense to obtain high-quality paper made by a reputable manufacturer. Translucent paper is available for tracing or blueprinting. If the graph is to be reproduced in print, it is well to remember that blue coordinate lines will not show up; main coordinate lines may be traced over with India ink for satisfactory reproduction.

2. *Choosing the Coordinate Scales.* Five rules are listed by Worthing and Geffner. They are not altogether inflexible, and in case of doubt common sense should prevail.

Rule 1. The scale for the independent variable should be plotted along the X-axis (abscissa).

Rule 2. The scales should be so chosen that the coordinates of any point on the plot may be determined quickly and easily.

Rule 3. The scales should be numbered so that the resultant curve is as extensive as the sheet permits, provided that the uncertainties of meas-

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[1] *Op. cit.*, Chap. I.

[2] *Ibid.*, Chap. II.

urement are not made thereby to correspond to more than one or two of the smallest divisions.

Rule 4. Other things being equal, the variables should be chosen to give a resultant plot which approaches as nearly as practicable to a straight line.

Rule 5. Scales should be chosen such that the curve will, to the extent possible, have a geometrical slope approximating unity.

3. *Labeling the Coordinate Scales.* Main coordinate lines (or alternate ones) are labeled with the values they represent. The name of the quantity represented is given along each axis, together with the units in which it is measured.

4. *Plotting the Data.* Each point should be surrounded by a suitable symbol, such as a circle. If at all practicable, it is customary to have the size of the symbol correspond approximately to the precision of the determination.

It frequently happens that several curves are to be plotted on the same sheet of graph paper. This is the customary manner in which a third variable is treated on a two-dimensional graph. When this is done a different type of symbol should be used for each set of data.

One should not carry the above considerations to the extreme. It is possible to have such a hodgepodge of points and curves that fundamental relations are obscured.

5. *Fitting a Curve to the Plotted Points.* If sufficient points are available and the functional relation between the two variables is well defined, a smooth curve is drawn through the points. These conditions prevail in practically all physical-chemical work. French curves, splines, or other devices should be used for maximum smoothness, unless a straight line is being graphed. Generally speaking, inflections or discontinuities will be absent; however, if such irregularities are greater than the experimental error, one must not ignore them. An inflection in the cooling curve of a molten alloy (Exp. 22) indicates the freezing point.

The curve should pass as close as reasonably possible to all the plotted points, though it need not pass through any single one. There is a natural tendency to overestimate the importance of the end points; often these are the least accurate points on the graph.

6. *Preparing a Descriptive Caption.* This should include a more or less complete description of what the graph is intended to show. The caption is usually included in an open region directly on the graph paper unless it is to be reproduced for printing. If the data have been taken from the work of another, the source should be acknowledged.

Representation of Data by Equations. In order to obtain the maximum usefulness from a set of experimental data, it is frequently desirable to express the data by a mathematical equation. An advantage of this method is that data are represented in a compact fashion and in a form which is convenient for differentiation, integration, or interpolation. Frequently the form of the relationship between the dependent and independent variable is known, and it is desired to determine the values of the coefficients in the equation, since these coefficients correspond to physical quantities. Common examples of such equations follow:

Vapor-pressure equation:

$$\log p = \frac{-L}{2.3R}\frac{1}{T} + \text{constant} \qquad \text{(Exp. 9)}$$

Beer-Lambert law:

$$\log \frac{I}{I_0} = -acb \qquad \text{(Exp. 4)}$$

Langmuir adsorption equation:

$$\frac{c}{x/m} = \frac{1}{\alpha} + \frac{\beta}{\alpha}c \qquad \text{(Exp. 41)}$$

First-order reaction-rate equation:

$$\log c = \frac{-kt}{2.3} + \text{constant} \qquad \text{(Exp. 26)}$$

Radioactive decay law:

$$\log \frac{N_t}{N_0} = -\frac{0.693t}{t_{1/2}2.3} \qquad \text{(Exp. 54)}$$

In many cases the form of the relation between the independent and dependent variables is unknown and must be determined. This may be done by plotting the data and comparing the shape with that for known functions.[1] Frequently the functional relationship is such that a straight-line graph may be obtained by changing the coordinates. For example, in the case of the Langmuir adsorption equation, a plot of amount adsorbed, x/m, versus concentration c is a curved line, while a plot of $c/(x/m)$ versus c yields a straight line. When the data or some function of the data can be plotted as a straight line, the constants can be determined simply from the slope and intercept. In many cases where a straight line is not obtained it is best to use a power series of the type

$$y = a + bx + cx^2 + dx^3 + \cdots$$

with as many empirical constants as necessary to represent the data.

Three methods for the evaluation of the constants in a linear equation will be discussed. In order of increasing degree of objectivity, these

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[1] Graphs of a wide variety of functions are given in Worthing and Geffner, *op. cit.*, p. 57.

methods are (1) graphical method, (2) method of averages, (3) method of least squares.

1. *Graphical Method.* This method is especially useful for the determination of the constants in a linear equation. If a given equation is not linear with respect to the variable, it may frequently be arranged in a linear form by making a simple substitution. For example, in the case of the vapor-pressure equation given above, the linear equation

$$y = mx + b$$

is obtained by substituting $\log p = y$, $1/T = x$, $m = -L/2.3R$, and $b = \text{constant}$. Thus, when $\log p$ is plotted versus $1/T$, a straight line is obtained if this equation is correct. A plot of student data for the vapor pressure of acetone determined by the Ramsay-Young method is shown in Fig. 81*b*. The best straight line is drawn "through" these points with a transparent straightedge. The slope m of the line is calculated from the coordinates x_1,y_1 and x_2,y_2 of two points on the line:

$$m = \frac{y_2 - y_1}{x_2 - x_1}$$

These points are not selected from the original data and are taken as far apart as possible. The constant b is equal to the intercept on the Y-axis for $x = 0$. In this case, it is more convenient to calculate b from the slope m and the coordinates of one of the points on the line:

$$b = y_1 - mx_1$$

The values of m and b calculated graphically from Fig. 81*b* are

$$m = -1.662$$
$$b = 6.929$$

2. *Method of Averages.* The constants in a linear equation may be calculated from only two pairs of values for the variables. In general, more than two pairs of values are available, and different values for the constants will be obtained when different experimental points are used in the calculation. One method for determining the constants by using all the experimental data is the method of averages. This method is based on the assumption that the correct values of the constants m and b are those which make the sum of the residuals equal zero. The residuals v_i are the differences between the values of y calculated from the empirical equation and the experimentally determined values y_i. In the case we are discussing, the residuals are

$$v_i = mx_i + b - y_i \tag{16}$$

This assumption gives only one condition on the constants, and so it is further assumed that if there are r constants, the residuals may be divided into r groups and $\Sigma v_i = 0$ for each group. The groups are chosen to contain nearly the same number of experimental values, but it should be noted that different methods of choosing the groups will lead to different values for the constants. If the number of residuals in a group is k, the summation of Eq. (16) yields

$$\sum_1^k v_i = m\sum_1^k x_i + kb - \sum_1^k y_i = 0$$

If the data in Table 4 are divided into two groups (1 to 7) and (8 to 15), the two equations are

$$\begin{aligned} 23.715m + 7b - 9.089 &= 0 \\ 24.886m + 8b - 14.061 &= 0 \end{aligned}$$

The values of m and b calculated from these simultaneous equations are

$$\begin{aligned} m &= -1.6571 \\ b &= 6.9125 \end{aligned}$$

The values of the residuals calculated from Eq. (16) by using these constants and the values obtained experimentally are given in Table 4 to indicate the precision with which the data are represented.

TABLE 4. APPLICATION OF A LINEAR EQUATION TO EXPERIMENTAL DATA

	$\frac{1}{T} \times 10^3$ x	log p y	x^2	xy	Residuals $(mx_i + b - y_i) \times 10^3$ Graphical method	Method of averages	Method of least squares
1	3.614	0.920	13.06100	3.324880	+5	+4	+2
2	3.493	1.121	12.20105	3.915653	+5	+3	+2
3	3.434	1.221	11.79236	4.192914	+3	+1	0
4	3.405	1.271	11.59402	4.327755	+1	−1	−2
5	3.288	1.463	10.80944	4.810344	+4	+1	0
6	3.255	1.522	10.59502	4.954110	−1	−3	−4
7	3.226	1.571	10.40708	5.068046	−1	−4	−4
8	3.194	1.623	10.20164	5.183862	0	−3	−3
9	3.160	1.679	9.98560	5.305640	0	−3	−3
10	3.140	1.711	9.85960	5.372540	+1	−2	−1
11	3.117	1.749	9.71569	5.451633	+2	−2	−1
12	3.095	1.783	9.56902	5.518385	+4	+1	+1
13	3.076	1.814	9.46178	5.579864	+5	+1	+2
14	3.060	1.838	9.36360	5.624280	+7	+4	+4
15	3.044	1.864	9.26594	5.674016	+8	+4	+4
Σ	48.601	23.150	157.89433	74.303922			

3. *Method of Least Squares.* The methods already described give different values of the constants depending upon the judgment of the investigator. The method of least squares has the advantage of giving a unique set of values for the constants, and the values of y calculated by using the constants determined by this method are the most probable values of the observations, it being assumed that the residuals follow the Gaussian law of error. The principle of least squares asserts that the best representative curve is that for which the sum of the squares of the residuals v_i is a minimum. In the case of the equation which we have been discussing, this sum is

$$S = \sum_{i=1}^{n} (x_i m + b - y_i)^2$$

$$= m^2 \sum_1^n x_i^2 + 2bm \sum_1^n x_i - 2m \sum_1^n x_i y_i + nb^2 - 2b \sum_1^n y_i + \sum_1^n y_i^2$$

The necessary conditions for a minimum are

$$\frac{\partial S}{\partial m} = 0 = 2m \sum_1^n x_i^2 + 2b \sum_1^n x_i - 2 \sum_1^n y_i x_i$$

$$\frac{\partial S}{\partial b} = 0 = 2m \sum_1^n x_i + 2b(n) - 2 \sum_1^n y_i$$

These two equations may be solved simultaneously for m and b to yield

$$m = \frac{(n)\Sigma y_i x_i - \Sigma x_i \Sigma y_i}{(n)\Sigma x_i^2 - (\Sigma x_i)^2}$$

$$b = \frac{\Sigma x_i^2 \Sigma y_i - \Sigma x_i \Sigma x_i y_i}{(n)\Sigma x_i^2 - (\Sigma x_i)^2}$$

where the summations are to be carried out from 1 to n. Thus, in order to compute the constants by this method, it is necessary to calculate Σx_i, Σy_i, Σx_i^2, and $\Sigma x_i y_i$ as shown in Table 4. The calculations are carried out with more figures than the number of significant figures in the experimental data because the experimental values are assumed to be exact for purposes of the calculation.

The values of m and b obtained are

$$m = -1.6601$$
$$b = 6.9221$$

and the values of the residuals are given in the last column of Table 4 for comparison with those obtained by the other methods. Calculations by the least-squares method are time-consuming and are, therefore, carried out only for the most precise data.

The student is referred to books on mathematics for the application of this method to equations with three or more variables.[1]

ERROR PROBLEMS

(1) The molecular weight (M) of an ideal gas may be calculated from the gas law

$$pv = \frac{g}{M} RT$$

where p = pressure, atm
v = volume, liters
g = weight, g
T = absolute temperature
R = gas constant, 0.08206 liter-atm deg^{-1} mole^{-1}

In an experiment with CH_4 a student obtains the following values and estimates the indicated maximum errors:

$p = 735 \pm 1$ mm
$v = 210 \pm 2$ ml
$g = 137 \pm 2$ mg
$T = 25° \pm 1°C$

Calculate the molecular weight and the maximum error resulting from these uncertainties assuming CH_4 follows the ideal-gas law exactly.

(2) The relationship between the intensity (I) of light transmitted through a solution, the incident intensity (I_0), the length (b, cm) of the absorbing path, and the concentration of the solution (c, moles/liter) is known as the Beer-Lambert law and may be written

$$\log (I_0/I) = acb$$

where a is the absorbancy index.

A solution of a dye containing 5.00×10^{-4} moles liter^{-1} transmits 8 per cent of light of a certain wavelength through a 1-cm cell. The uncertainty in the reading is ±1 per cent in transmission. The sample is diluted accurately by a factor of 2 and the measurement repeated. The following data are obtained in this way:

$c \times 10^4$	*% Transmission*
5.00	8 ± 1
2.50	27 ± 1
1.25	53 ± 1
0.625	73 ± 1

Calculate a and its maximum uncertainty for each solution.

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[1] Sokolnikoff and Sokolnikoff, "Higher Mathematics for Engineers and Physicists," 2d ed., McGraw-Hill Book Company, Inc., New York (1941).

(3) A student determines the heat capacity of a calorimeter bomb by burning benzoic acid, which has a heat of combustion of 6,315 cal g^{-1}. The pellet of benzoic acid weighed 0.5478 ± 0.0003 g. Also 0.020 ± 0.0003 g of wire with a heat of combustion of 1,600 cal g^{-1} is burned. The calorimeter contained 1875 ± 2 g of water. The measured temperature rise was 1.57 ± 0.01°C. Calculate the heat capacity, x, of the bomb by using the following equation.

$$x = \frac{6{,}315G + 1{,}600g}{t} - 0.999W$$

where G = grams of benzoic acid
g = grams of wire
t = observed temperature rise
W = grams of water in the calorimeter

What is the maximum error in the heat capacity of the bomb due to the errors in the various measurements?

(4) The relative viscosity (η_1/η_2) of a liquid may be calculated from the time (t_1) required for a given volume to flow through the capillary of a viscometer using

$$\frac{\eta_1}{\eta_2} = \frac{d_1t_1}{d_2t_2}$$

where t_2 = flow time for the reference liquid (water)
d_1,d_2 = densities for the liquid and water, respectively

If at 25°, $d_2 = 0.99707$ g cm^{-3} and $t_2 = 45.1 \pm 0.4$ sec, calculate η_1/η_2 and the maximum uncertainty in this value for a liquid for which $d_1 = 0.897 \pm 0.003$ and $t_1 = 36.4 \pm 0.4$ sec.

(5) The molecular weight (M) of a solute may be calculated from the elevation of the boiling point (ΔT_b) for a solution containing g grams of solute in G grams of solvent using the equation

$$M = \frac{1{,}000K_bg}{G\Delta T_b}$$

where K_b is a constant characteristic of the solvent.

In an experiment in which the molecular weight of napthalene in benzene is to be determined, it is found that the reading of the Beckmann thermometer for boiling benzene is 2.975 ± 0.005°, and for a solution containing 1.054 ± 0.001 g of napthalene in 87.0 ± 0.1 g of benzene the reading is 3.210 ± 0.005°. This type of thermometer does not show degrees above the freezing point of water and is only useful in determining temperature differences. Calculate M and the maximum uncertainty introduced by these estimated errors. (Given: $K_b = 2.53$.)

CHAPTER 18

PHYSICAL PROPERTIES OF GASES

Volume by Displacement. A measured quantity of gas may be introduced into a system by displacing it with a measured quantity of liquid, in a flask provided with a two-holed rubber stopper. In an alternative method, the gas may be drawn over by running out a measured volume of liquid. The gas must be insoluble in the liquid. Mercury is the best liquid for most purposes, but it is too heavy for large volumes, and water, oil, nitrobenzene, and sulfuric acid have been used. Some of these liquids have a negligible vapor pressure, but a correction is necessary in the case of water. The temperature of the incoming liquid must be the same as that of the vessel.

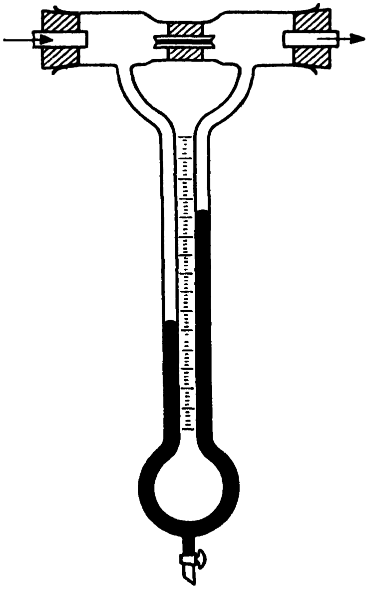

FIG. 82. Flowmeter.

Large volumes of gas are measured conveniently with commercial gas meters, in which cups or vanes rotate in a closed chamber containing a liquid at the bottom. The number of revolutions is recorded on one or more circular scales. The meters are calibrated with known volumes of gas.

Flowmeters. The rate of flow of a gas is conveniently measured with a flowmeter, as illustrated in Fig. 82. The difference in pressure on the two sides of a capillary tube, as indicated by the manometer, is a measure of the rate of flow of gas through the flowmeter. The flowmeter is calibrated at several different rates of flow, and a smooth curve is drawn showing the rate of flow as a function of the difference in levels (Fig. 83).

A convenient flow meter is available which is made entirely of Pyrex glass. A graduated tube is mounted vertically in a larger concentric tube, and the displacement of the liquid due to the passage of gas is read directly on the tube. The rate of flow is nearly a straight-line function of the scale reading, and the rate of flow corresponding to any reading of the scale may be interpolated with accuracy. The factors involved in the theory and use of the flowmeter have been discussed by Benton.[1]

In calibrating a flowmeter, air or other gas is passed through the flowmeter by a displacement method, while the liquid used in the manometer is maintained continuously at a constant setting. The time taken for a given volume to pass through is determined accurately with a stop watch. Capillary tubes of different bores may be used for different velocity ranges.

Another type of flowmeter is finding use in the measurement of the flow of both gases and liquids. A vertical tube provided with a linear scale has a larger internal diameter at the top than at the bottom. When gas rushes upward through this tube, it carries a small float upward. The greater the flow of gas or liquid, the higher the float rises, but at the greater rates of flow, the area of the annular ring between the float and the containing tube becomes larger. These factors are so balanced that the height of the float is a linear function of the rate of flow. The Flowrator,[2] or Rotameter[3] diagramed in Fig. 84 is a convenient meter of this type. Laboratory kits with interchangeable sets of metering tubes and

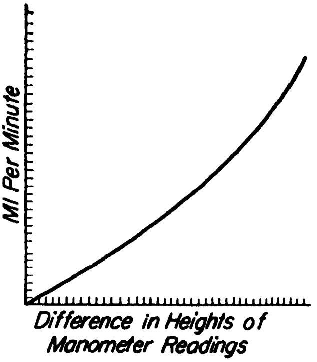

FIG. 83. Calibration curve for flowmeter.

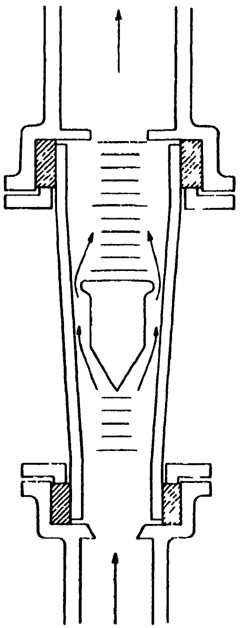

FIG. 84. Rotameter or Flowrator for measuring the rate of flow of gases or liquids.

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[1] *Ind. Eng. Chem.*, **11**, 623 (1919).

[2] Fischer and Porter Co., Hatboro, Pa.

[3] Brooks Rotameter Co., Lansdale, Pa.

floats of different sizes are available with capacities from 0.06 to 220 ml of liquid water per minute. The meters can be used for fluids other than water and air, with the help of standard corrections depending on the density of the fluid and the float and on viscosity and pressure.[4]

Manometers. The closed-end manometer is readily made from a U tube and a wooden meter stick. A steel or brass scale is necessary when an accuracy greater than 0.2 mm is required. The glass tube, of Pyrex, should not be less than 1 cm in diameter for accurate measurements. It is essential to use pure mercury (Chap. 26) and to boil out all occluded air by inverting the U tube, connecting to a vacuum pump, and heating gently and cautiously with a moving flame throughout the length of the mercury to remove any trapped air between the mercury and the wall.

At a definite gas pressure, the height of mercury changes with the density of the mercury, and it is necessary to refer the manometer readings to 0°C as a standard temperature. At room temperature, the barometer usually reads 2 or 3 mm too high. A table of corrections is given in the Appendix which applies to a barometer having a glass tube and a brass scale.

A mirror on the scale helps to avoid parallax, the eye and its image forming a straight line across the top of the meniscus. More accurate readings can be taken with a reliable cathetometer. Short manometers recording pressures of 10 cm and less are used in vacuum distillations. Open-end manometers are easier to make than the closed-end manometer just described, because they do not have to be boiled out. They give the difference in pressure between the vessel and the atmosphere, and the absolute value of the pressure is obtained by subtracting this reading from (or adding to it) the barometer reading. They require one more reading than the closed-end, or vacuum, manometers. The closed-end manometers are superior, for they are quite independent of barometric fluctuations. Mercury is usually used as the liquid, but any nonvolatile liquid may be used if it is not too viscous and if its density is known. The

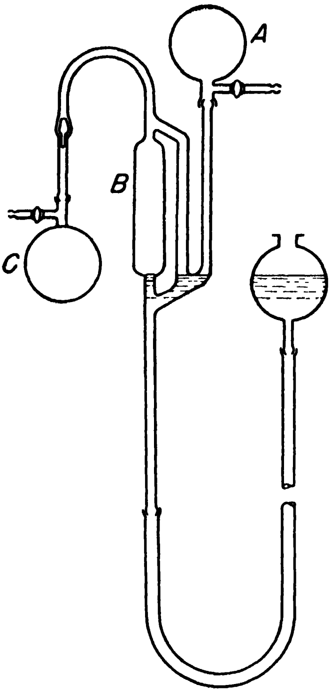

FIG. 85. Toepler pump.

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[4] Fischer and Porter Co., Hatboro, Pa., Flowrator Nomograph Bull. 60.

manometer readings are converted into the equivalent millimeters of mercury from a knowledge of the densities. Paraffin oil, nitrobenzene, bromonaphthalene, water, or other liquid may be used for small pressure differences.

Pumps. Several types of vacuum pumps and certain vacuum techniques are described in Exp. 58.

The Toepler pump is used for transferring gas from one vessel to another under reduced pressure. It operates by alternately raising and lowering a mercury level as shown in Fig. 85. Each time the mercury level is lowered the gas from *A* expands into *B*, and each time it is raised the gas is forced from *B* into *C* or out into the room. The height of the mercury tube must be greater than the barometer height, or the mercury level may be raised by applying compressed air to the top of the mercury in the reservoir, thus permitting the reservoir to be just below the pump.

CHAPTER 19

OPTICOCHEMICAL MEASUREMENTS

Many types of analyses may be made by optical methods. These methods have the advantage that they are rapid and sensitive and leave the sample unchanged. Also, the optical tools are popular as instruments of physical chemistry in the determination of the structure, size, and shape of both ordinary and large molecules in solution or of colloidal particles in suspension.

SPECTROMETRY[1]

For work in the infrared, photographic plates specially sensitized with dyes (Exp. 50) may be used up to nearly 10,000 A or 1 μ. At longer wavelengths a spectrometer-thermopile assembly must be used. The thermopile responds equally to all wavelengths, but it is less sensitive than the photographic plate or the photoelectric cell. For sources of radiation, solid filaments, stable in the air, are rendered incandescent by electricity. "Nernst glowers," or "globars," are most frequently used. The optical parts are made of various materials, depending on the range of the spectrum to be covered- glass up to 1.5 to 2.0 μ, quartz to 4 μ, rock-salt crystals (NaCl) to 15 μ, and potassium bromide crystals to 25 μ.[2] Gratings can be used for dispersion at all wavelengths.

Several elaborate instruments with mechanical recording of absorption spectra may now be purchased, and a broad new field of infrared measurements is thus opened up.

The principle of an infrared spectrometer is illustrated in Fig. 86. The prism is mounted on a plate, which can be rotated by means of a drum provided with a scale of wavelengths. Quantitative measurements of absorption are made by measuring the amount of energy that falls on the thermopile. The interrupted beam produces a pulsating current which

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[1] Mellon, "Analytical Absorption Spectroscopy," John Wiley & Sons, Inc., New York (1950); Brode, "Chemical Spectroscopy," John Wiley & Sons, Inc., New York (1947).

[2] Large prisms and plates of NaCl, KBr, AgCl, and other salts are made from artificially grown crystals by the Harshaw Chemical Co., Cleveland, Ohio.

can be amplified. References may be consulted for the technique of infrared spectrometry.[1]

There is a wide variety of instruments suitable for use in the visible and ultraviolet regions, among them simple (glass) prism spectroscopes, simple (quartz) prism spectrographs, multiple-prism assemblies for both instruments, grating spectrographs, etc.[2] The description of the use of a spectrograph is given in Exp. 51.

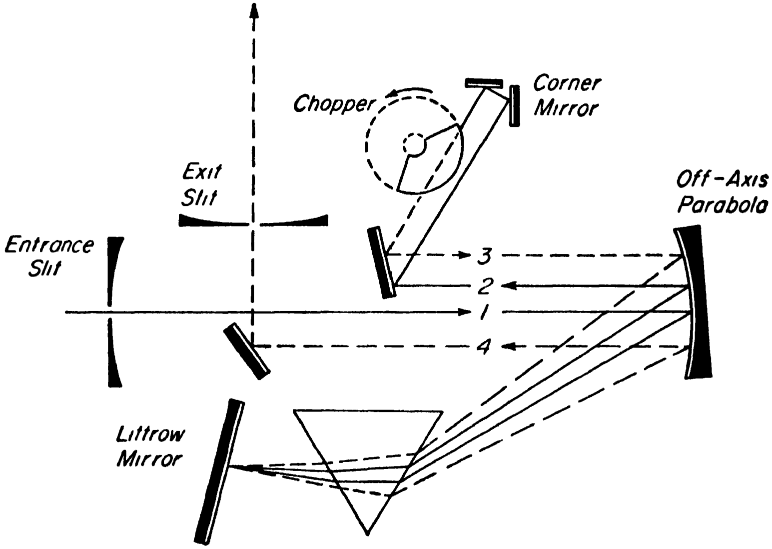

FIG. 86. Infrared spectrophotometer.

The spectrophotometer is an instrument for comparing intensities at different wavelengths, as contrasted with a colorimeter operating at one or relatively few wavelengths. An example of a prism spectrophotometer for use in the visible and ultraviolet is illustrated in Fig. 87. The main parts involved are a dispersing system, optical path to include cell with solution or solvent, and arrangement for comparison at the various wavelengths of the light intensities transmitted by the solution and solvent.

Spectrophotometers are used in many ways. They serve in quantitative analysis to measure the concentration of certain cations, anions,

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[1] Barnes, Gore, Liddel, and Williams, "Infrared Spectroscopy," Reinhold Publishing Corporation, New York (1944); Harley and Wiberley, "Instrumental Analysis," John Wiley & Sons, Inc., New York (1954); Williams, *Rev. Sci. Instr.*, **19**, 135 (1948); Wright, *Ind. Eng. Chem., Anal. Ed.*, **13**, 1 (1941).

[2] Excellent descriptions of these instruments are to be found in Gibb, "Optical Methods of Chemical Analysis," McGraw-Hill Book Company, Inc., New York (1942); Harrison, Lord, and Loofbourow, "Practical Spectroscopy," Prentice-Hall, Inc., New York (1948): West *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Interscience Publishers, Inc., New York (1949).

organic groups, etc.; for vitamin assays; to measure pH, dissociation reactions, and reaction rates; and to give information about molecular structure. Most of these applications depend on the use of the Beer-Lambert law. Spectrophotometers are also used for fluorometric measurements in which the sample is irradiated with ultraviolet light and the intensity of fluorescent light is measured.

Recording spectrophotometers have been an important recent development. These instruments automatically plot percentage transmission or absorbancy versus wavelength in the range 220 to about 1,000 mμ. A correction is made automatically for the blank cell which is placed in the instrument.

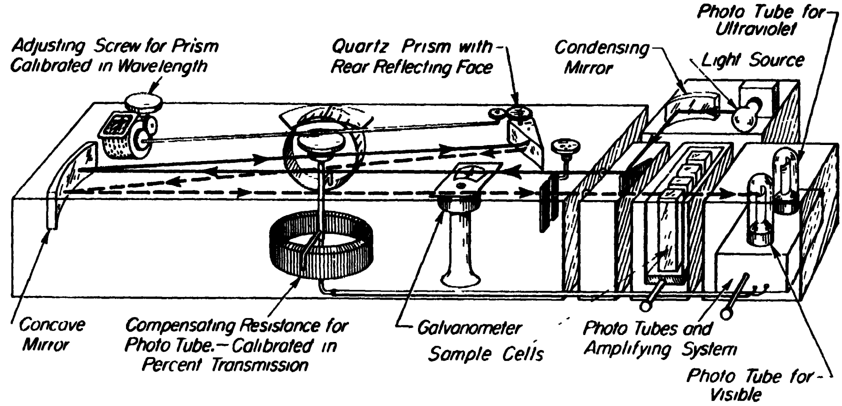

FIG. 87. Beckman spectrophotometer for visible and ultraviolet regions.

LIGHT SCATTERING

The measurement of the intensity of light scattered by a turbid suspension is used in some cases to determine concentration. Instruments for this purpose are called nephelometers and have been described by Gibb.[1]

Some light is scattered even by a pure liquid because it is inhomogeneous on a microscopic scale. The scattering by a solution is greater because of local differences in refractive index due to fluctuations in concentration of solute. The study of the intensity of light scattered by a solution of a high polymer or protein may be used to determine the molecular weight and shape of these molecules.[2] In the case of molecules having dimensions comparable to the wavelength of light or greater, measurements of light scattered at several angles are required; thus the

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[1] *Op. cit.*

[2] Debye, *J. Phys. & Colloid Chem.*, **51**, 18 (1947); Zimm, *J. Chem. Phys.*, **16**, 1099 (1948); West, *op. cit.*; Bender, *J. Chem. Educ.*, **29**, 15 (1952).

apparatus is arranged so that the photomultiplier detector may be placed at several angles.[1] The principle of operation of the apparatus is illustrated by Fig. 88.

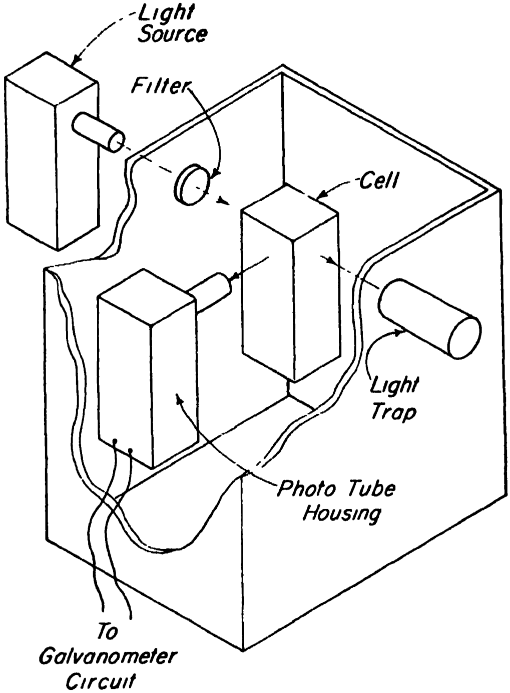

FIG. 88. Light-scattering apparatus.

REFRACTOMETRY[2]

The principles of refractometry and the construction of the Abbe and immersion refractometers have been described in Exp. 3.

The compensator (or Amici prism), which makes possible the use of white light in the Abbe and immersion refractometers, consists of two direct-vision prisms in the telescope barrel which can be rotated in opposite directions. The direct-vision prisms are made to give dispersion, with a minimum of deviation, by cementing a dense prism of flint glass between two prisms of crown glass. If the first direct-vision prism spreads out the light into a spectrum, and if the second prism is set at the same angle, the dispersion is doubled. However, if the prism is rotated

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[1] Stein and Doty, *J. Am. Chem. Soc.*, **68**, 159 (1946); Debye, *J. Applied Phys.*, **17**, 392 (1946); Zimm, *op. cit.*

[2] Bauer and Fajans *in* Weissberger (ed.): *op. cit.*, 2d ed , Vol. I, Part II (1949).

through 180°, as shown in Fig. 5, the second prism will subject the dispersed beam to an opposite dispersion, thus reproducing white light. The prism of the refractometer itself also produces dispersion, the amount depending on the refractive index of the liquid. The extent to which the prisms of the compensator must be rotated in order to offset the dispersion of the refractometer liquid and produce white light must be determined each time by trial. The reading on the compensator drum is a measure of the dispersion of the liquid.

The Pulfrich refractometer is perhaps the oldest and the most accurate. It requires a sodium or mercury lamp or other source of monochromatic light because it does not have a compensating Amici prism. The horizontal beam of monochromatic light goes through a cup of liquid cemented to the top of the prism and is refracted through an angle which is measured directly by rotating the eyepiece until it picks up the colored line of light, directly coincident with the point of intersection of the cross hairs. The angle of refraction is read directly in degrees on a circular scale, using a vernier and lens.

The zero setting of the instrument is obtained by holding a small light at arm's length in front of the small square window near the eyepiece and turning the graduated circular scale until the image of the cross hairs reflected from the face of the main prism coincides with the cross hairs themselves. This window has a right-angled prism which directs a light beam on to the prism surface from which it is reflected back into the eyepiece. The zero setting is subtracted from the reading of the angle of refraction.

The refractive index n_λ at each wavelength λ is calculated by means of the formula

$$n_\lambda = \sqrt{N_\lambda^2 - \sin^2 i}$$

where N_λ = refractive index of the glass prism against air for the wavelength of light used

$\sin i$ = sine of the angle of emergence i measured on the circular scale

The values of N_λ are furnished with the Pulfrich instrument, usually for the blue (4358 A), green (5460 A), and yellow (5780 A) lines of the mercury arc.

The cup of the Pulfrich refractometer is cemented to the prism. For organic liquids, fish glue may be used. Still better is a concentrated gelatin solution containing potassium dichromate, which is exposed to bright sunlight after setting in place. When aqueous solutions are used the glass cup must be attached with Canada balsam or other waterproof cement. A smaller metal cup with circulating thermostated water sets into the cup of liquid.

The Abbe refractometer is checked by placing against the upper prism a plate glass of known refractive index supplied with the instrument. The two surfaces are held together with a drop of liquid having a higher index of refraction, e.g., α-bromonaphthalene. If the refractometer does not give the proper reading, it is adjusted by means of the small screw at the back of the telescope. The immersion refractometer is checked with distilled water. If the shadow edge does not fall at 15.0 for 17.5°C or at 13.25 for 25°C, adjustment is made by means of a screw inside the micrometer drum. *Adjustments of this kind on expensive instruments should be made only by authorized persons.*

The Pulfrich and the immersion refractometers may be provided with interchangeable prisms which extend the range to different refractive indices. The immersion refractometer is provided with a small metal cap with a glass bottom which fits over the prism and permits measurements to be made with small amounts of liquid.

The refractive index of liquids changes considerably with temperature, and temperature control to 0.1 or 0.2° is necessary. The refractive index of glass against air changes also, but to a considerably smaller extent. For example, in the Pulfrich refractometer, the refractive index of the prism is given for 20°, and an increase of 3° gives an increase in the refractive-index calculations of about 1 in the fifth decimal place. This temperature correction for the glass may be neglected in ordinary work at room temperature.

Small differences in refractive index may be determined with great accuracy by using an interferometer. A beam of monochromatic light is split into two parts which traverse different tubes and combine again to give interference bands. An adjustable plate is included in one path and turned until the two sets of interference bands are made to match. The interferometer can be applied to the analysis either of gases or of liquids.[1]

MICROSCOPY[2]

The resolving power (R.P.) of a microscope is a measure of its capacity to reproduce minute details of the structure of the object in the image. It is directly proportional to a quantity called the numerical aperture (N.A.), and inversely proportional to the wavelength λ of the light employed.

$$\text{R.P.} = \frac{\text{N.A.}}{\lambda}$$

This formula is valid only for central illumination; if sufficiently oblique illumination is used, the resolving power may be almost doubled. The

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[1] Williams, "Applications of Interferometry," Methuen & Co., Ltd., London (1930).

[2] Jelley *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part I (1949).

resolving power also increases with an increase in the refractive index of the medium intervening between the front lens of the objective and the cover glass over the specimen. Thus, by using water-immersion and oil-immersion lenses, the resolving power can be further increased.

Eyepieces equipped with a measuring scale are known as micrometer eyepieces. Such eyepieces are very useful in connection with the ultramicroscope. The scale may be calibrated in absolute units by means of a stage micrometer, which is viewed in the same manner as any object would be. The scale must be calibrated for each objective used. The filar micrometer is almost indispensable for measurements of small lengths.

Binocular microscopes are advantageous from several points of view—they give a correct stereoscopic image, they prevent fatigue in prolonged studies, and with a properly constructed camera very satisfactory stereophotomicrographs can be made.

A useful modification of the light microscope is the phase microscope of Zernicke, of Saylor, and of Jupnik.[1] It enhances the contrast of the image which is observed, making possible an observation of sections too thin or too transparent for the conventional techniques. It is also valuable in the microscopic determination of refractive index.

Microscopes for use in the chemical laboratory should be provided with polarizing and analyzing Nicol prisms. Very important information is often secured by examinations of substances in polarized light. Special microscopes known as chemical microscopes are available, having such prisms and other useful accessories.

The Ultramicroscope. Any particle having a diameter less than 120μ cannot be observed directly with a microscope. However, smaller particles having refractive indices appreciably different from the solvent can be caused to reflect light. The ultramicroscope is an instrument in which the particles are very strongly illuminated, and they are observed with a microscope so that as much light as possible from each particle is received in the eye. As illustrated in Fig. 89, light from a strong source *A* is focused by means of a lens *L* on the slit *S*, which is so constructed that it may have either a horizontal or vertical position with respect to the base. The light is again focused on the cell *C*, which contains the diluted colloid, by means of a lens *L′* and an objective *O*. An ordinary microscope *M* is used to observe the light scattered by the particles of the colloid. This is essentially the ultramicroscope described by Siedentopf and Zsigmondy[2] and is commonly known as the slit ultramicroscope.

Siedentopf gives four factors that control the efficiency of the ultramicroscope:

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[1] *Chem. Eng. News*, **26**, 1907 (1948).

[2] *Ann. Physik* (4), **10**, 1 (1903).

1. The source of light should be as strong as possible.
2. The aperture of the illuminating system and of the system used for observing the particles should be as high as possible.
3. There must be high contrast between the particles and their background.
4. The light scattering of the particles should be high.

In order to obtain higher intensities of illumination, a number of dark-field condensers have been designed. Prominent among these are the paraboloid[1] and cardioid[2] dark-field condensers of Siedentopf and the dark-field condenser of Jentzsch.[3]

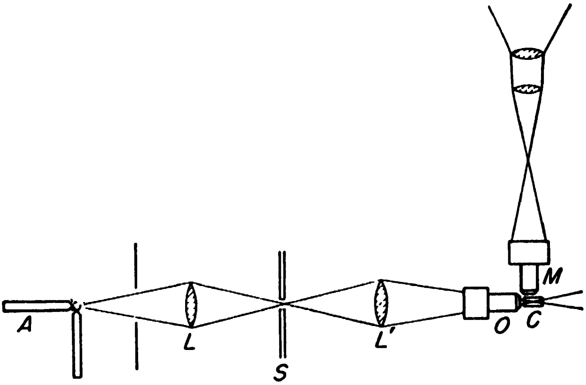

FIG. 89. Principle of the ultramicroscope.

The use of the dark-field condensers to which reference has been made is not, however, without disadvantages. With them, it is practically impossible to tell anything about the shape or orientation of the particles, because in these condensers light enters from all sides. In the so-called azimuth diaphragm condenser, designed by Szegvari,[4] only light from two diametrically opposite directions can enter the cell, so that it is possible to change the direction of the light in the cell by simply turning the diaphragm about its axis.

The Electron Microscope. The limiting factor in the resolution of small objects by the optical microscope is the wavelength of the light. The details of material under examination cannot be seen if they are smaller than the wavelength of the light used in the observation. A beam of monoenergetic electrons can exhibit interference effects characteristic

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[1] Siedentopf, *Z. wiss. Mikroskop.*, **24**, 104 (1907).

[2] Siedentopf, *Verhandl. deut. physik. Ges.*, **12**, 1 (1910).

[3] *Verhandl. deut. physik. Ges.*, **12**, 975, 992 (1910).

[4] *Z. physik. Chem.*, **112**, 277 (1924).

of a wave motion with a wavelength λ of

$$\lambda = \frac{300hc}{Ve}$$

where V = accelerating potential, volts
e = electron charge, esu
h = Planck's constant
c = velocity of light

It is readily calculated that a beam of electrons can have a wavelength of a fraction of an angstrom unit, as against 4000 to 8000 A for the wavelength of visible light. Moreover, the electron beam can be bent by an electrostatic or an electromagnetic field so that it can be focused by simple adjustment of current and voltage. These principles have been applied to make electron microscopes,[1] and many excellent pictures have been taken with them. Bacteria, fine powders such as carbon black, fibers, and many things of biological interest have been examined with much greater magnification than was previously possible, and new details have been revealed.

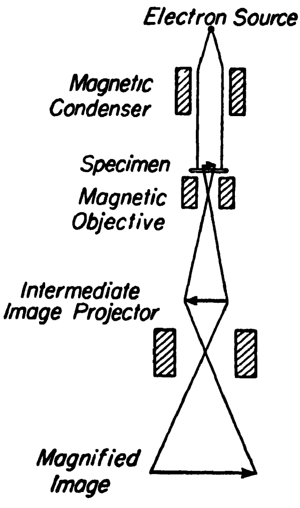

FIG. 90. Principle of the electron microscope.

The principle of the electron microscope is shown in Fig. 90. Electrons are produced as in radio tubes, accelerated by fields of 30,000 to 100,000 volts, and focused with magnetic fields as indicated. The object is placed on a thin nitrocellulose film, which is fairly transparent to the beam and shows no structure of its own. The electrons pass through and are focused on a fluorescent plate, where the image is viewed by eye. The electrons are scattered by the denser parts of the object, but the transparent parts of the object show up more brightly. A photographic plate is then substituted for the fluorescent screen, and a short exposure gives a satisfactory picture.

OPTICAL SYSTEMS FOR STUDY OF MOVING AND DIFFUSING BOUNDARIES

To observe the changes in boundary position and breadth which take place in electrophoresis, diffusion, sedimentation-velocity, and chro-

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[1] Zworykin *et al.*, "Electron Optics and the Electron Microscope," John Wiley & Sons, Inc., New York (1945); Meyers, "Electron Optics," Chapman & Hall, Ltd., London (1939); Hamm *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part III (1954).

matography experiments, optical methods are indispensable. The light-absorption method was developed to a reasonable degree of precision by Svedberg and associates[1] to give concentration as a function of distance in an optical cell, but it is now obsolete.

It has been replaced by the refraction and interference methods, which give not concentration, but concentration gradient (more strictly refractive-index gradient), as a function of distance in the cell. The classical one is the scale method of Lamm, which is quite accurate but somewhat tedious in use. There have come into use other refractive methods, based upon the schlieren effect, the methods having been devised by Wiener, Svensson, Philpot, and Longsworth.[2] The cylindrical-lens schlieren optical system is illustrated in Fig. 91. This method makes use of the bending of light by the refractive-index gradient between two solutions of different composition, and hence of different refractive index, and of the fact that the angular deflection of the light is directly proportional to the magnitude of the gradient. An image of the horizontal illuminated slit A is focused by means of a large lens (schlieren lens) B on a diagonal slit in the focal plane D of the schlieren lens. The cylindrical lens F with its axis vertical is focused on the inclined slit and on the photographic plate G. The camera lens E focuses the cell C on the photographic plate. The presence of the cylindrical lens does not alter the vertical coordinates of a point in the photograph of the cell, but in conjunction with the diagonal slit may displace the ray of light horizontally across the optical axis if it has been bent downward by a refractive-index gradient. This lateral displacement is directly proportional to the refractive-index gradient in

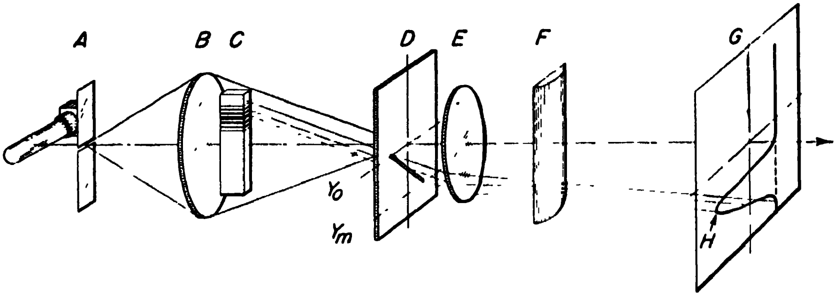

FIG. 91. Schlieren optical system for observing and photographing refractive-index gradients.

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[1] Svedberg and Rinde, *J. Am. Chem. Soc.*, **46**, 2677 (1924); Tiselius and Gross, *Kolloid-Z.*, **66**, 11 (1934).

[2] Wiener, *Ann. Physik*, **49**, 105 (1893); Svensson, *Kolloid-Z.*, **87**, 181 (1939); Philpot, *Nature*, **141**, 283 (1938); Longsworth, *J. Am. Chem. Soc.*, **61**, 529 (1939); *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

the cell at the level at which the light ray passed through, so that the photograph obtained is a plot of refractive-index gradient versus position in the cell.

If the liquid in the cell is homogeneous, all the light passing through it is concentrated in the normal slit image of Y_0 and is focused on the photographic plate by the camera lens to form the vertical base line of the pattern. With a boundary between two solutions of different refractive index in the cell, the light through the layer having the maximum gradient is deflected to Y_m. These rays pass through the inclined slit to the right of the optical axis and are therefore passed to the left by the cylindrical lens to form the peak of the pattern at H. Other rays through regions in which the refractive-index gradients are less intersect the diagonal slit at positions between the normal slit image and Y_m and form points in the refractive-index-gradient plot on the photographic plate. The plot of refractive index versus vertical height in the cell may be obtained by integration of the refractive-index-gradient curve.

Still more accurate optical systems for the study of moving and diffusing boundaries depend upon several interference phenomena. The rigorous quantitative use of the Gouy interference effect[1] was the pioneering effort in this direction.

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[1] Kegeles and Gosting, *J. Am. Chem. Soc.*, **69**, 2516 (1947); Coulson, Cox, Ogston, and Philpot, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948); Gosting and Onsager, *J. Am. Chem. Soc.*, **74**, 6066 (1952).

CHAPTER 20

THERMAL MEASUREMENTS

THERMOMETRY[1]

The International Temperature Scale. Although the constant-volume hydrogen thermometer is the standard on which the centigrade and absolute scales are based, such a thermometer is inconvenient to use except as an ultimate standard. For this reason the Seventh General Conference on Weights and Measures in 1927 established the international temperature scale as a reliable secondary standard for general use in the laboratory. It is defined by several fixed points (Table 1), and means for interpolating between the fixed points are provided.

TABLE 1. FIXED POINTS OF THE INTERNATIONAL TEMPERATURE SCALE
[All at 1 atm pressure (760 mm Hg)]

Substance	Designation	Temperature, °C
Oxygen	Boiling point	−182 97
Water (air-saturated)	Freezing point	0 000
Water	Boiling point	100 000
Sulfur	Boiling point	441 60
Antimony	Freezing point	630 50
Silver . .	Freezing point	960 5
Gold	Freezing point	1063

From the ice point to 660° the international centigrade temperature is computed from the resistance R_t of a standard platinum resistance thermometer by means of the equation

$$R_t = R_0(1 + At + Bt^2) \tag{1}$$

The constants R_0, A, and B are determined by calibration at the ice, steam, and sulfur points. From −190° to the ice point a platinum

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[1] A standard reference book on this subject is "Temperature—Its Measurement and Control in Science and Industry," Reinhold Publishing Corporation, New York (1941). It includes 125 papers presented at a symposium. See also Griffiths, "Methods of Measuring Temperature," Charles Griffin & Co., Ltd., London (1947).

resistance thermometer is also used, with a modified interpolation formula:

$$R_t = R_0[1 + At + Bt^2 + C(t - 100)t^3] \qquad (2)$$

R_0, A, and B are the same as before, and C is determined by measurement at the oxygen point.

From 660 to 1063° the temperature is computed from the electromotive force E of a standard platinum versus platinum-rhodium thermocouple by means of the equation

$$E = a + bt + ct^2 \qquad (3)$$

where a, b, and c are obtained from measurements at the antimony point, silver point, and gold point.

Above the gold point an optical method, based on the Wien formula for black-body radiation, is used.

The international temperature scale assures laboratories throughout the world of an accurate and readily reproducible basis of temperature measurement. It should be pointed out, however, that the fixed points are subject to such changes as are occasioned by materials of higher purity or more refined experimental techniques in gas thermometry.

Mercury Thermometers. The mercury thermometer is the simplest and most widely used instrument for measuring temperature. Mercury is particularly suitable because it has a very uniform coefficient of expansion, it does not wet glass, it is easily purified, and the thermometer is easily read. At atmospheric pressure it remains liquid from −40 to +357°C.

Thermometers of various grades and ranges are available, including (*a*) 0 to 100, 250, and 360°, graduated in degrees for general purposes; (*b*) sets of thermometers from −40 to +400°, each having a range of 50° and graduated to 0.1°; (*c*) 18 to 28°, graduated to 0.01°, or 17 to 31°, graduated to 0.02°, for calorimetric work; (*d*) −0.5 to +0.5°, graduated to 0.01° for freezing-point lowering; (*e*) Beckmann-type thermometers with adjustable range, graduated to 0.01°; (*f*) high-temperature thermometers, in which special combustion glasses or quartz are used with nitrogen or argon under pressure to extend the upper temperature limit as high as 750°C.

The graduations should extend a little beyond the nominal limits, and a high-grade thermometer of any range should have an ice point for standardization if actual temperatures are to be measured. If only differences in temperature are required, the ice point is not necessary. The thermometer is usually used in a vertical position.

Reading. Exposed stem, parallax, and sticking mercury constitute three important sources of error in the reading of thermometers.

Thermometers are usually calibrated for total immersion of the mercury, and a correction is necessary when part of the stem is exposed. The thermometer will read too low if the air surrounding the stem is colder than the bath in which the bulb is immersed, and too high if the air is warmer. A second thermometer is placed near the exposed stem, and the stem correction S is given by the formula

$$S = 0.00016n(t' - t)$$

where n = length of exposed mercury column in terms of scale degrees
t' = temperature of bath
t = average temperature of emergent stem

The factor 0.00016 is suitable for the glass used in most thermometers.

It should be emphasized that stem corrections are not accurate, and for very high or very low temperatures a considerable error may be introduced. It is better to avoid the exposed stem by improving the experimental conditions.

Parallax may cause an erroneous reading, depending upon the extent to which the eye is below or above the level of the top of the mercury thread. It may be eliminated completely by reading the thermometer from a distance with a cathetometer (telescope and cross hair), and it may be reduced considerably by carefully regulating the position of the eye. Special thermometer lenses sliding along the stem are helpful.

A thermometer should be read whenever possible with a rising thread rather than a falling thread, and in either case it is necessary in accurate work to tap the thermometer gently before reading, to prevent sticking.

Standardization. In the simplest method, the thermometer is compared with a standard thermometer, for which purpose a thermometer certified by the National Bureau of Standards is useful. The two thermometers are set side by side in a thermostat, vapor bath, or large, well-stirred body of liquid. The National Bureau of Standards thermometer is immersed nearly to the top of the thread, and the other thermometer is immersed to the depth at which it is to be used. The true temperature as given by the standard thermometer is obtained by adding or subtracting the correction indicated on the National Bureau of Standards certificate, after correction for a possible change in the ice point (see below).

An illustration of the correction follows: A standardized thermometer wholly immersed in the vapor of a boiling liquid registered 80.05°, and the National Bureau of Standards correction was −0.02°. The correct temperature of the vapor was then 80.03°. A second thermometer, under the same conditions, gave a reading of 79.91°. The second thermometer read too low by 0.12°, and therefore 0.12° should be added to any temperature in the region of 80° read on this particular thermometer.

The ice point is always taken before a standardization, and it should check with the ice point given on the certificate, if the corrections as given in the certificate are to apply. In case the ice point does not check, a constant adjustment of all the corrections is necessary. For example, in the thermometer described above, the ice point was −0.01°. If after long aging the ice point should read −0.02° instead of −0.01°, all the corrections given in the table would also be too low by 0.01°, and each should have 0.01° added.

In taking the ice point of a thermometer, it is necessary to have the ice very finely divided and intimately distributed throughout the whole bath. A large layer of water is not allowed to accumulate, and the spaces between the pieces of ice must be filled with water, not air. For ordinary work, finely shaved, close-packed ice in distilled water makes a satisfactory ice bath. For precision work, the recommendations of White[1] should be followed.

Fixed boiling points, freezing points, or transition temperatures of pure materials are also used for standardizing thermometers (Table 1). Calibration against a platinum resistance thermometer certified by the National Bureau of Standards is the best method.

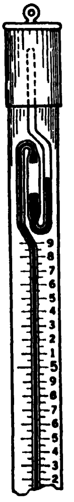

FIG. 92. Beckmann thermometer.

The standardization of a mercury-in-glass thermometer should be rechecked frequently at one point, usually the ice point. Slow permanent changes in the glass result in changes in the volume of the bulb. Furthermore, temporary changes in the bulb volume are likely to result from heating; the bulb may not regain its original volume for several days.

Beckmann Thermometer. A Beckmann thermometer is shown in Fig. 92. This instrument reads directly to 0.01° and can be estimated to 0.001°. Its range is only 5 or 6°, but it can be set for any temperature by adjusting the mercury in the reservoir at the top of the scale. The thermometer is warmed until sufficient mercury has been driven over into the reservoir, and it is then given a sharp tap with the hand to break the thread at the entrance to the reservoir.

The thread is broken when the temperature is a little above the desired temperature, because a certain amount of cooling is necessary to bring the mercury back on the scale.

If the mercury is below the scale, mercury must be brought in from the reservoir at the top. The thermometer is warmed until mercury flows into the reservoir, and it is inverted so that the mercury connects

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[1] *J. Am. Chem. Soc.*, **46**, 2418 (1924).

with the mercury in the reservoir. The thermometer is then turned back into an upright position, very cautiously, and allowed to cool slowly. When the mercury is a little above the desired temperature, the thread is broken as before with a sharp tap. The flow of mercury through the long tube is slow, and time must be allowed for the attainment of equilibrium before the thread is broken. In some thermometers an auxiliary scale is provided for the reservoir, to assist in rapid setting.

Scale divisions on Beckmann thermometers are not exactly equivalent in all temperature ranges. Tables of correction factors for different ranges have been published.[1]

Other Liquid Thermometers. If thallium is added to mercury to give an 8.5 per cent solution, the amalgam can be cooled to −60° before freezing. Liquid pentane can be used down to liquid-air temperatures, and toluene can be used to −100°, which is below the temperature of carbon dioxide snow. Alcohol is not used for high-grade thermometers because its thermal expansion is not sufficiently uniform at all temperatures.

Bimetallic Thermometers. In this type of thermometer the temperature is indicated on a dial by a pointer actuated by the differential expansion of a bimetallic strip. They are usually accurate to only about 1 per cent, but their ruggedness and easily read scale make them very useful where high accuracy is not important.

Gas Thermometers. Gas thermometers are inconvenient to use for any purpose other than ultimate standardization. For such purposes the experimental arrangement and the calculations are quite complex.[2]

Resistance Thermometers. The electrical resistance of a wire increases in a regular manner as the temperature rises, and since the resistance of a wire can be measured with great precision, this measurement offers an accurate method for determining temperatures.

Platinum wire is usually used because of its chemical inertness and its high resistance. It must be of the highest grade, carefully purified, and annealed by heating to redness with an electric current. It is annealed again at a lower temperature after winding.

The wire is wound on mica supports in such a way that the metal is subjected to as slight a strain as possible when the thermometer is heated or cooled. Usually the coil is enclosed in a sealed glass or quartz tube; when it is desired to minimize the lag of the thermometer, the coil is enclosed in a flattened metal case. Platinum resistance thermometers

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[1] For detailed discussion, see Busse *in* "Temperature—Its Measurement and Control in Science and Industry," p. 228.

[2] See, for example, the following papers in "Temperature—Its Measurement and Control in Science and Industry," Keyes, p. 45; Roebuck and Murell, p. 60; Cragoe, p. 89.

are usually manufactured with a resistance of 25.5 or 2.55 ohms at 0°, so that the resistance will change by about 0.1 or 0.01 ohm deg^{-1}, respectively.

In accurate resistance thermometry, it is essential that the resistance from which the temperature is computed be that of the thermometer element itself and contain no contribution from the leads. This is accomplished by using a four-lead thermometer and a suitable bridge, in which the lead resistance is effectively eliminated by a switching arrangement. In Fig. 93, r_1 and r_2 are equal ratio arms, C, c, T, and t are the four leads, X is the thermometer resistance, and R_a and R_b are the resistances required to balance the bridge in the two arrangements. It is evident that $R_a + C = X + T$ and $R_b + T = X + C$. Hence, $X = (R_a + R_b)/2$.

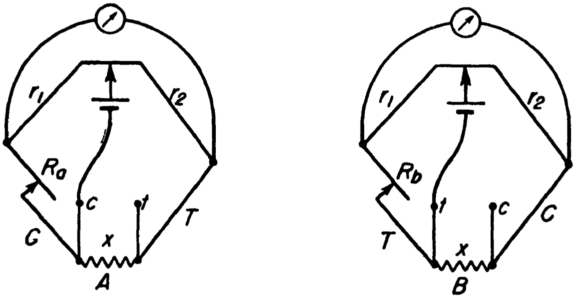

FIG. 93. Circuit diagram illustrating resistance measurements of a four-lead thermometer.

If temperatures are to be determined to a precision of ±0.001°, it is necessary to employ a carefully calibrated bridge in which the resistance of the contacts between decades has been eliminated.[1]

For computing temperatures from observed resistances, the equation

$$t = \frac{100(R_t - R_0)}{R_{100} - R_0} + \delta\left(\frac{t}{100} - 1\right)\frac{t}{100} \tag{4}$$

is more convenient than Eq. (1). The constants R_0, $R_{100} - R_0$ (the "fundamental interval"), and δ are determined by calibration at the ice, steam, and sulfur points. This calibration is performed by the National Bureau of Standards for a reasonable charge. The value of t is calculated from R by successive approximations, a process which is not difficult owing to the relatively small value of δ. Convenient tables for converting platinum resistance values to degrees centigrade have been published.[2]

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[1] For a discussion of this point and other factors in precision resistance thermometry, see Mueller *in* "Temperature—Its Measurement and Control in Science and Industry," p. 162, and "Resistance Thermometers," Leeds and Northrup Co., Philadelphia, Pa.

[2] Werner and Frazer, *Rev. Sci. Instr.*, **23**, 163 (1952).

A carefully constructed and standardized platinum resistance thermometer is preeminent in the field of thermometry for its reliability in both accuracy and precision over long periods of time. Other resistance thermometers can be made of nickel, copper,[1] Hytemco,[2] and other metals and alloys in cases where extreme accuracy is subordinate to economy and ease of construction.

The resistance of a thermometer may also be determined by comparing, by means of a potentiometer, the potential drop across the thermometer with that across a standard resistor in series with the resistance thermometer and a source of applied potential.

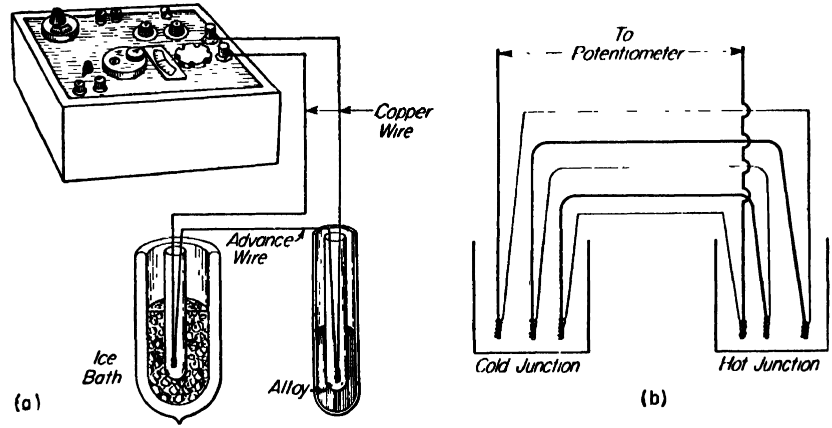

FIG. 94. (*a*) Use of the thermocouple in alloy-cooling-curve studies; (*b*) a three-junction thermel.

Resistance thermometers can also be made of nonmetallic materials, in which the resistance *decreases* very sharply as the temperature increases. Such thermometers are called "thermistors." They permit the use of a less accurate bridge for temperature measurement and are suitable for small temperature *differences*.

Thermocouples.[3] In a closed circuit of dissimilar metals, a current is generated when the junctions are at different temperatures. A simple thermocouple is shown in Fig. 94, together with a multiple-junction assembly which is called a *thermel*. The heavy line represents one metal, and the lighter line represents the other.

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[1] Maier, *J. Phys. Chem.*, **34**, 2860 (1930).

[2] Hytemco is an alloy with an exceptionally high temperature coefficient of resistance; it is manufactured by the Driver-Harris Co., Harrison, N.J.

[3] For a comprehensive discussion, see Roeser *in* "Temperature—Its Measurement and Control in Science and Industry," p. 180.

In Fig. 94 the use of the thermocouple in determining the freezing curves of alloys is illustrated. The potentiometer shown is a commercial instrument of moderate precision made expressly for use with thermocouples.

The common types of thermocouples and their important characteristics are illustrated in Table 2. Extended tables of electromotive force as a function of temperature for the different types are found in many of the standard handbooks.

Copper and constantan (Advance) may be soldered together by using rosin or other noncorrosive flux, but the other metals are welded together in an oxygas flame or in an electric arc. The two wires are twisted together for a short distance, held in an insulated clamp, and connected to one pole of the electric circuit (110 volts). An insulated carbon rod is connected through a suitable resistance (15 ohms) to the other electrode. The rod is touched to the end of the thermocouple and pulled away slightly, giving an electric arc. As soon as the two wires are welded together, the electrode is pulled farther away to stop the arc.

TABLE 2. TYPES OF THERMOCOUPLES

Type	Usual temperature range, °C	Maximum temperature, °C (for short periods)	Millivolts per degree at room temperature
Copper-constantan[a]	0–350	600	0 0428
Iron-constantan[a]	−200–750	1000	0 0540
Chromel-P Alumel[b]	−200 1200	1350	0 0110
Platinum to platinum 10 per cent rhodium	0–1450	1700	0 0064

[a] Constantan is a general name given to a group of copper-nickel alloys. It can be obtained under the trade name Advance from the Driver-Harris Co., Harrison, N J., or from pyrometer manufacturers.

[b] Chromel-P and Alumel are high-nickel alloys obtainable from the Hoskins Manufacturing Co., Detroit, Mich., or from pyrometer manufacturers.

For room temperature, insulation of cloth or enamel is sufficient; for high temperatures, wire can be obtained with Fiberglas insulation, or separate sleeving of the latter can be obtained. Porcelain tubes are also widely used. It is essential to protect the wires carefully from corrosion; in furnaces, long gas-tight tubes of glass, porcelain, or quartz are used. In working with solutions at room temperatures, the thermocouple is usually encased in a thin glass tube, frequently filled with oil to give better thermal contact. When several junctions are used, the exposed junctions come at higher and higher levels in the encasing tube to prevent short-circuiting.

For precision work, the wire must be carefully selected and tested.

Full particulars for making and using these thermoelectric thermometers are given by White[1] and by Adams.[2] They can be made sensitive to 0.00001°.

A thermoelectric thermometer is used either with a potentiometer or with a millivoltmeter or galvanometer. The former is necessary in precision work, but the latter is so much more convenient that it is used in industrial work. In the latter case, the current rather than the electromotive force is measured, and an error is introduced because the change in current with temperature is due not only to the thermocouple electromotive force but also to the change in resistance of the wires. To minimize this error, large wires are used, so that the changeable resistance of the thermocouple is small in comparison with the fixed resistance of the galvanometer. Galvanometer or millivoltmeter scales may be calibrated directly in terms of degrees. The resistance of the thermocouple should be about equal to the critical-damping resistance of the galvanometer.

Thermocouples are used extensively in many industrial operations. Recording potentiometers are commonly employed where a permanent record of temperature at all times is desired. Instruments are available which will record as many as 16 temperatures as a function of time on a single strip of paper.

For accurate work the potentiometer is specially designed to avoid spurious thermal electromotive forces or leakage. Reversing switches are particularly useful in this work. The White potentiometer,[3] Wenner potentiometer,[4] and microvolt potentiometer[5] are specially designed for use with thermocouples.

The cold junction is usually set into cracked ice in a vacuum-jacketed bottle, but in crude work at high temperatures it is sometimes left at room temperature. A fluctuation in the temperature of the cold end is, of course, just as effective as a fluctuation in the furnace; the meter reading depends on the difference in temperature between the two junctions.

Thermocouples are calibrated with fixed temperatures, of which the most common are melting ice, 0°; boiling water, 100° (barometer correction); the transition temperature of sodium sulfate, 32.38°; boiling sulfur, 444.6°; melting lead, cadmium, tin, zinc, gold, and palladium.

Optical Pyrometers.[6] The operation of optical pyrometers depends on the fact that the radiation emitted by a hot body is a function of the

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[1] *J. Am. Chem. Soc.*, **36**, 2292 (1914).

[2] *J. Am. Chem. Soc.*, **37**, 481 (1915); International Critical Tables, Vol. I, p. 57, McGraw-Hill Book Company, Inc., New York (1926).

[3] Leeds and Northrup, catalogue E-33A (1940), Philadelphia, Pa.

[4] Leeds and Northrup, catalogue (1938).

[5] Rubicon Company, Bull. 270, Philadelphia, Pa.

[6] Symposium, Optical and Radiation Pyrometry, *in* "Temperature—Its Measurement and Control in Science and Industry," p. 1115ff.

temperature. They are very easy to use and are popular in industrial control operations. They are about the only instruments that can be used for the measurement of very high temperatures. They are not suitable for temperatures below 500 or 600°, because the radiation is not sufficiently intense.

Several types are available, but the disappearing-filament type shown in Fig. 95 is one of the simplest and most practical.

The furnace, crucible, or other hot object is viewed through the telescope. An electric-light bulb with a carbon filament is placed in the optical system so that the observer sees the filament across the field. A variable resistance changes the current through the lamp. The wire appears bright on a darker field when the wire is hotter than the hot object, and it appears dark on a light field when it is colder. When the two temperatures are exactly the same, the filament seems to disappear and the whole field becomes uniform. A red screen is used, and for very high temperatures the brightness of the radiation from the furnace is reduced with a thicker screen. The current required to make the filament disappear is noted on the milliammeter, and the corresponding temperature is obtained by reference to a table supplied by the manufacturers for use with the lamp.

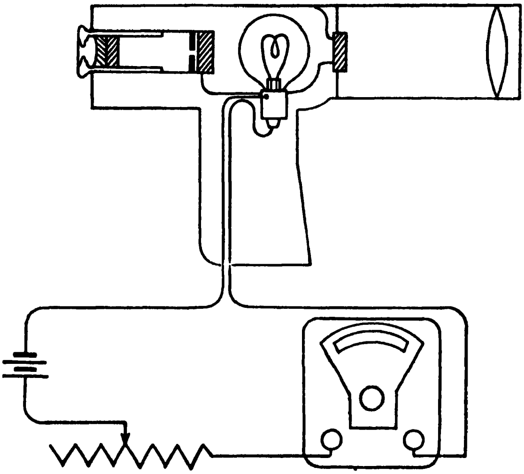

FIG. 95. Radiation pyrometer of the disappearing-filament type.

The table is prepared by calibrating the lamp at known temperatures, reading the milliammeter when the rheostat is so adjusted as to make the filament disappear. A few readings are sufficient, the rest being obtained by interpolation. The temperature of the furnace may be determined with a thermocouple or resistance thermometer. The melting points of antimony, silver, and gold may be used for calibration temperatures.

The furnace should be nearly closed and viewed through a small opening so as to give true black-body radiation. If an open strip of metal is viewed, the calculated temperature may be considerably too low. Empirical corrections for radiation from platinum and various other metals have been worked out.

CALORIMETRY

Calorimetric measurements, several examples of which are treated in Exps. 6 to 8, form an important part of experimental physical chemistry. A comprehensive survey of this field has been given by Sturtevant.[1] The specific details of the equipment and procedures employed in accurate work depend upon the particular type of measurement being made. Representative references on typical calorimetric problems include the following: heats of combustion (general;[2] liquids;[3] gases[4]); heat capacities of solutions;[5] heats of dilution;[6] heats of hydrogenation;[7] heat capacity of liquids;[8] heats of vaporization;[9] heat capacity of gases;[10] ice calorimeter;[11] low-temperature-heat-capacity, heat-of-fusion, etc., measurements.[12]

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[1] Sturtevant *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Chap. 14, Interscience Publishers, Inc., New York (1949).

[2] Coops *et al.*, *Rec. trav. chim.*, **66**, 113–176 (1947) (in English); Dickinson, *Natl. Bur. Standards* (*U.S.*) *Bull.* **11**, 189 (1915); Jessup and Green, *J. Research Natl. Bur. Standards*, **13**, 469 (1934).

[3] Prosen and Rossini, *J. Research Natl. Bur. Standards*, **27**, 289 (1941).

[4] Prosen, Maron, and Rossini, *J. Research Natl. Bur. Standards*, **42**, 269 (1949).

[5] Gucker, Ayres, and Rubin, *J. Am. Chem. Soc.*, **58**, 2118 (1936).

[6] Gucker, Pickard, and Planck, *J. Am. Chem. Soc.*, **61**, 459 (1939); Sturtevant, *J. Phys. Chem.*, **45**, 127 (1941).

[7] Kistiakowsky, Romeyn, Ruhoff, Smith, and Vaughan, *J. Am. Chem. Soc.*, **57**, 65 (1935).

[8] Osborne and Ginnings, *J. Research Natl. Bur. Standards*, **39**, 453 (1947).

[9] *Ibid.*; Waddington, Todd, and Huffman, *J. Am. Chem. Soc.*, **69**, 22 (1947).

[10] Masi and Petkof, *J. Research Natl. Bur. Standards*, **48**, 179 (1952); Waddington, Todd, and Huffman, *J. Am. Chem. Soc.*, **69**, 22 (1947).

[11] Ginnings and Corruccini, *J. Research Natl. Bur. Standards*, **38**, 583 (1947).

[12] Aston and Eidenoff, *J. Am. Chem. Soc.*, **61**, 1533 (1939); Huffman, *Chem. Revs.*, **40**, 1 (1947); Ruehrwein and Huffman, *J. Am. Chem. Soc.*, **65**, 1620 (1943); Waddington, Todd, and Huffman, *J. Am. Chem. Soc.*, **69**, 22 (1947).

CHAPTER 21

PHYSICAL PROPERTIES OF LIQUIDS AND SOLUTIONS

DETERMINATION OF THE BOILING POINT[1]

The boiling point of a liquid is a characteristic property which is often useful for purposes of identification and for the determination of purity. The boiling point is usually taken as the temperature which is established on the bulb of a thermometer on which a thin layer of the condensed liquid coexists with the vapor. Boiling liquids are generally superheated by the heating device used, and any boiling liquid is superheated because it boils under the pressure at the surface plus the hydrostatic pressure at the level in the liquid at which the temperature is measured. Special ebulliometers[2] are required for the measurement of the boiling temperature of a liquid or of a solution. In the case of a pure liquid, the true boiling and condensation temperatures are equal.

If certain precautions are observed, the boiling point of a pure liquid may be determined in an ordinary distilling flask. The thermometer should be short so that the whole column of mercury is surrounded by the vapor, or else a rather unsatisfactory stem correction is necessary (page 359). The thermometer bulb should be near the outlet tube so that it registers the temperature of the exit vapors. The boiling should not be so violent as to cause spray to reach the thermometer bulb or so rapid as to build up a pressure in the flask appreciably greater than atmospheric pressure. To avoid splashing, the flask should not be over half full.

One of the greatest sources of error comes from overheating the neck of the flask and heating the thermometer bulb by radiation. A large gas flame is particularly bad in this respect. A small gas flame without wire gauze or sand bath is better. It is a good plan to heat the distilling flask in a beaker of hot water (or oil, at higher temperatures) to a temperature only slightly above the boiling point of the liquid, as determined with an ordinary thermometer in the water bath. A thin-walled cylin-

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[1] This subject has been reviewed by Swietoslawski and Anderson *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part I, Chap. 4, Interscience Publishers, Inc., New York (1949).

[2] Swietoslawski, "Ebulliometry," Chemical Publishing Company, Inc., Brooklyn, N.Y. (1937).

drical tube placed in the vapor between the thermometer and the flask is sometimes used to minimize radiation.

Overheating may be minimized by using an electric heating mantle covered with glass cloth or by using a heating coil immersed in the boiling liquid. The vapor rises from the electrically heated liquid and passes over into a side tube, completely enveloping the thermometer, which is suspended on a platinum wire attached to a glass hook on the stopper. A trap at the bottom may be used to return the liquid to the boiling flask. If the thermometer is completely within the vapor, a proper thermometer reading is ensured. Both stoppers may be made of glass if corks or rubber stoppers need be avoided.

This design gives good circulation of the liquid and allows the heating to be carried on until only a small volume of liquid remains. The heating coil of bare platinum wire is sealed through long glass tubes which pass down through the stopper of the flask. Copper wires leading to the source of current are welded to the platinum wires before the latter are sealed in glass.

Superheating. The liquid should boil smoothly and steadily, but in some cases there is a tendency for the liquid to become heated above its boiling point. Superheating may be greatly reduced by any means of trapping small air bubbles in the liquid. Small chips of unglazed porcelain with air enclosed in the pores, or pieces of platinum or platinized platinum, are effective. The smoothest boiling is obtained with the internal electric heating coil described above.

Distilling flasks covered with sintered glass powder are effective in preventing bumping.[1] Some of the same glass of which the flask is made is ground in a mortar and moved around inside while the flask is heated in a blast lamp to its softening temperature. Again, the surface may be coated with silica by evaporating a dilute solution of sodium silicate, heating to dull-red heat, cooling, and treating with dilute hydrochloric acid and rinsing.[2]

Bumping is particularly apt to be troublesome under reduced pressure, and it may be advisable to have a small stream of air bubbling through the liquid. A tube is inserted in the stopper, with its lower end drawn out into a capillary extending into the liquid. Its upper end is closed by a rubber tube and an adjustable pinchcock to control the rate of bubbling.

If only a small amount of liquid is available, the boiling point may be determined by the method of Smith and Menzies.[3] The liquid is placed in an inverted bulb, which is fastened to the bulb of a thermometer and immersed in a bath of water or other transparent liquid which is immisci-

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[1] Morton, *Ind. Eng. Chem., Anal. Ed.*, **6**, 384 (1934).

[2] Swietoslawski, *J. Chem. Educ.*, **5**, 469 (1928).

[3] *J. Am. Chem. Soc.*, **32**, 879 (1910).

ble with the liquid being studied. The temperature is raised gradually, and when the boiling point is reached, a stream of bubbles issues from the bulb.

Ebulliometers. An ebulliometer is a special apparatus for the measurement of the boiling temperature of a liquid or of a solution. With a differential ebulliometer the boiling and condensation temperatures may be measured simultaneously. This apparatus may also be used for the determination of the degree of purity of liquid substances, of the molecular weight of a nonvolatile solute, or of the pressure coefficient of the boiling point.

Another differential boiling-point apparatus is described by Menzies and Wright.[1] A narrow graduated tube is closed at one end and bent up to give a U tube, with the closed arm about 2 cm long and the other about 12 cm long. It is partly filled with water or other liquid, sealed off at the ends, and placed vertically in a flask. There is thus an air pocket in the short arm and another one at the top of the long arm. A vapor pump pours the boiling solution over the pocket in the lower arm, whereas the pocket at the top of the long arm is surrounded only by vapor. Measured changes in the level of the enclosed liquid enable one to calculate the differences in vapor pressure of this liquid, and from the differences in vapor pressure, the corresponding differences in temperature can be calculated. This temperature difference then is equal to the difference in temperature between the solution boiling in the flask and its vapor. At 35° a difference in level of 1 mm of water corresponds to 0.0313°, and at 100° it corresponds to 0.0026°.

MEASUREMENT OF VAPOR PRESSURE

The measurement of vapor pressure is closely related to the measurement of boiling point, so that it is difficult to make a distinction between these two types of measurements. If the boiling point is determined at a series of pressures, the vapor-pressure -temperature relation is obtained. This is the essence of the so-called dynamic method, which is especially important. Three other general methods, some of which may be adapted as differential methods, will be described briefly.

Dynamic Method. The dynamic method of Ramsay and Young is illustrated by Exp. 9.

The construction of apparatus used at the National Bureau of Standards is described by Willingham and coworkers.[2] This apparatus consists of an electrically heated boiler, a vapor space with a vertical reen-

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[1] *J. Am. Chem. Soc.*, **43**, 2314 (1921).

[2] Willingham, Taylor, Pignocco, and Rossini, *J. Research Natl. Bur. Standards*, **35**, 219 (1945).

trant tube containing a platinum resistance thermometer, and a condenser. The pressure is controlled by an automatic device actuated by electrical contacts sealed through the barometer tube.

Special apparatus has been designed for the study of binary solutions.[1]

Static Method. In the simplest method the liquid is contained in a bulb connected with a mercury manometer and a vacuum pump. The greatest source of error lies in the presence of air or other permanent gases which have been dissolved by the liquid or trapped by the mercury. Enough liquid is evaporated with the pump to sweep out all the gases. The evacuation is repeated until further evacuation gives no lowering of the vapor pressure. The whole apparatus should be thermostated. The method has been used by many investigators.

The isoteniscope of Menzies[2] is useful for the determination of vapor pressure of a liquid or a solution.

Differential static methods have been developed by Frazer and Lovelace[3] and by Menzies.[4]

Gas-saturation Method (Transpiration Method). In this method a measured volume of air or other inert gas is saturated by passing it through the liquid at a definite temperature. The quantity of liquid vaporized is obtained from the loss in weight of the liquid, or by removal of the vapor from the gas stream in weighed absorbing tubes. Assuming Dalton's law of partial pressures and the ideal-gas law, the partial pressure of the vapor, p, is calculated by the formula

$$p = \frac{g}{Mv} RT$$

where R = gas constant
T = absolute temperature
v = total volume of gas (including air and vapor) containing g grams of vapor of molecular weight M

When v is expressed in liters and p in atmospheres, R is expressed in liter-atm deg^{-1} mole^{-1}. In case the vapor pressure is very low, it can be neglected in comparison with the atmospheric pressure in calculating the volume of the gas.

If a gas is passed first through pure solvent and then through a solution, the vapor pressure of the solution can be calculated from the

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[1] Scatchard, Raymond, and Gilman, *J. Am. Chem. Soc.*, **60**, 1275 (1938); Scatchard and Raymond, *J. Am. Chem. Soc.*, **60**, 1278 (1938); Scatchard, Wood, and Mochel, *J. Am. Chem. Soc.*, **61**, 2306 (1939); *ibid.*, **62**, 712 (1940); Othmer and Josefowitz, *Anal. Chem.*, **39**, 1175 (1947); Othmer and Morley, *Ind. Eng. Chem.*, **38**, 751 (1946); Thomson *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part I (1949).

[2] Smith and Menzies, *J. Am. Chem. Soc.*, **32**, 1412 (1910).

[3] Frazer, Lovelace, *et al.*, *J. Am. Chem. Soc.*, **45**, 2930 (1923).

[4] *J. Am. Chem. Soc.*, **33**, 1615 (1911).

vapor pressure of pure solvent, the total pressure at each saturator, and the gain in weight of each absorber, thus eliminating the need of measuring the volume of the gas.

Premature condensation must be avoided if the vapor is to be absorbed and weighed, and at higher temperatures the saturator, absorption tubes, and connecting tubes are all immersed in the thermostat. It is essential to saturate completely the air or other gas with the vapor of the liquid; but, on the other hand, there must be no stoppage in the apparatus which might build up a changing or an unknown hydrostatic pressure. If the air is passed through the saturator so slowly that a still slower rate gives no greater vapor pressure, it may be concluded that the air is completely saturated. The air-saturation method has been used in precision researches by Washburn[1] for the determination of vapor pressures of aqueous solutions and has been further developed by more recent workers.[2] When both components of a solution are volatile, it is necessary to have a suitable means for analyzing the condensed vapor. A physic method such as refractometry or a chemical method such as titration may be used.

Isopiestic Method. This method depends upon the fact that if vessels containing two different solutions are placed side by side in a closed space, vapor will distill from the solution of higher vapor pressure and condense in the one having the lower vapor pressure. At equilibrium the vapor pressures of the two solutions are equal. The solutions are then analyzed to determine their concentrations, and if the vapor pressure of one of the solutions is known from other absolute measurements, the vapor pressure of the other is determined.

It is important that the vessels be in good thermal contact. This is usually achieved by using metal cups which fit snugly into holes bored in a large copper block. This block fits into a stainless-steel vessel with a cover and a lead gasket, so that the whole system can be evacuated and rotated in a large thermostat kept constant nearly to 0.001°. After 24 hr, the little cups are covered and weighed. They are replaced in the vessel, the covers removed, and the determinations repeated again after 24 hr or until there is no further change in weight.

Robinson and Sinclair[3] compared the activities of water in solutions of inorganic halides with those in solutions of potassium chloride at different concentrations. Scatchard, Hamer, and Wood[4] determined the activities of water in solutions of potassium chloride, sulfuric acid, sucrose, urea,

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[1] Washburn and Heuse, *J. Am. Chem. Soc.*, **37**, 309 (1915).

[2] Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927); Pearce and Eckstrom, *J. Am. Chem. Soc.*, **59**, 2689 (1937); Bechtold and Newton, *J. Am. Chem. Soc.*, **62**, 1390 (1940).

[3] *J. Am. Chem. Soc.*, **56**, 1830 (1934).

[4] *J. Am. Chem. Soc.*, **60**, 3061 (1938).

and glycerol as compared with solutions of sodium chloride. The results are very accurate and permit a check on the several different methods that have been used for the determination of the activity of water in solution. Owen and Cooke[1] used the method to carry out a series of vapor-pressure measurements with electrolyte mixtures.

FRACTIONAL DISTILLATION[2]

The separation of two liquids by distillation and the determination of the number of theoretical plates for laboratory fractionating columns have been described in Exp. 15. In addition to the number of theoretical plates, there are a number of factors, such as feed rate and operating holdup, to be considered in selecting or designing fractionating columns. The feed rate of the column is defined as the rate of entry of vapor into the bottom of the column, and, depending upon the design of the column, a certain feed rate may not be exceeded without flooding the packing. It is desirable to use as high a feed rate as possible so that a given distillation may be accomplished in the shortest possible time. The operating holdup of a column is the volume of vapor and liquid in the column under operating conditions. It is desirable that the column have a small holdup so that a minimum amount of liquid is held in the column at any time. It may be shown[3] that the sharpness of separation obtainable in a batch distillation is approximately a linear function of the ratio of charge to holdup. Thus, decreasing the holdup relative to the charge enables a sharper separation to be obtained with the same number of theoretical plates and the same total distillation time. Actually high feed rate and small holdup are not easily obtained in the same column and must be balanced against each other.

A number of different types of fractionating columns have been devised in an effort to improve the contact between the liquid and the ascending vapor. The ideal packing offers uniformly distributed interstices, a large surface for contact, and enough free space for a desirable feed rate. Too large packing has a small area for contact and a tendency to channel, while too small packing allows insufficient feed rate. If the ratio of

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[1] *J. Am. Chem. Soc.*, **59**, 2273 (1937).

[2] For further material the following references are recommended: Robinson and Gilliland, "The Elements of Fractional Distillation," 4th ed., McGraw-Hill Book Company, Inc., New York (1950); Morton, "Laboratory Techniques in Organic Chemistry," Chap. IV, McGraw-Hill Book Company, Inc., New York (1938); Carney, "Laboratory Fractional Distillation," The Macmillan Company, New York (1949); Ward, Review of the Literature on the Construction, Testing, and Operation of Laboratory Fractionating Columns, *U.S. Bur. Mines, Tech. Paper*, **600** (1939): Glasebrook and Williams *in* Weissberger (ed.): *op. cit.*, Vol. IV (1951).

[3] Rose, Welshans, and Long, *Ind. Eng. Chem.*, **32**, 673 (1940).

column diameter to the diameter of the individual packing units is greater than 8:1 and the ratio of column height to column diameter is greater than 15:1, the tendency to channel will be slight.

A fractionating column is most efficient when its operation is adiabatic throughout its length. An insulating jacket, a vacuum jacket, or an electrically heated jacket may be used. If an electrically heated jacket is used, it is important to keep the column somewhat hotter at the bottom than at the top.

Two types of still heads may be used to control the reflux ratio: (*a*) liquid-dividing heads and (*b*) vapor-dividing heads. Vapor-dividing heads have the advantage that the reflux ratio may be controlled more precisely. Automatic devices may be used with both types to control reflux ratios conveniently.

High-vacuum Distillation. With the development of efficient vacuum pumps (see Exp. 58), high-vacuum distillation of material of low volatility has become a common commercial and laboratory operation. This method has the advantage that high-molecular-weight organic molecules, such as vitamins, sterols, and synthetic polymers, which cannot be distilled at their normal boiling points without decomposition, may be distilled unharmed. Hickman[1] and others have developed new tools and special techniques for such distillations. When vacuum distillations are carried out with the usual flask–condenser–receiver–vacuum-pump apparatus, it is found that reducing the pressure in the receiver below about 5 mm Hg produces little increase in the rate of distillation or lowering of the temperature of the distillation. This is because of the resistance to the flow of the vapor exerted by the neck and side arm of the distillation flask. In order to avoid this difficulty and to increase the amount of vapor which actually reaches the condenser, the condenser must be placed quite close to the surface where evaporation is taking place. If the distance of transfer is comparable with the mean free path of the vapor molecules, it is known as *molecular* distillation.

There are important differences in principle between ordinary distillation and molecular distillation. In ordinary distillation, molecules from the vapor reenter the surface and tend to produce equilibrium between liquid and vapor phase. Under these conditions the quantities of the various constituents distilling are proportional to their partial pressures. In molecular distillation, on the other hand, molecules do not reenter the liquid phase and there is no equilibrium between liquid and vapor. The separation achieved depends only upon the differences in rates of evaporation of the various components.

The differences in the ordinary and molecular distillation processes lead to important differences in apparatus design. In molecular distillation it

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[1] Hickman, *Chem. Revs.*, **34**, 51 (1944); *Am. Scientist*, **33**, 205 (1945).

is clear that there is no generation of vapor bubbles below the surface because the vapor would have to exert a pressure of the order of a millimeter of mercury, while at the temperature of the distillation, the vapor pressure is actually less than 0.001 mm. It is important, therefore, for the liquid film to be thin and the surface constantly changed. This has been achieved by the falling-film still, in which a thin film of liquid flows down over the heater, and by the centrifugal still, in which a thin film of solution is spun out over the surface of a shallow conical evaporator which is rotated at a high speed. Another reason for using a very thin film is to reduce thermal decomposition by subjecting the sensitive organic compounds to a high temperature for only a very short time. In a centrifugal still, the liquid is heated for less than a tenth of a second. Thus thermal decomposition is greatly reduced by carrying out the distillation at a low pressure and by allowing only short exposure to the elevated temperature.

The measurement of the temperature of the vapor is not practical in short-path distillation, but information can be gained by distilling a number of known substances at different temperatures and plotting a curve of material condensed against temperature. In this way the relative temperature at which an unknown material comes over can be determined by reference to some known material.[1] These separations may be made very conveniently with a series of pilot dyes[2] of different volatilities which condense to give a colored deposit.

DENSITY[3]

Density measurements find numerous applications in physical chemistry. The method used depends upon the accuracy required. Precise density methods may be used to trace stable isotopes such as D, C^{13}, N^{15}, and O^{18}.

Densities of liquids are most frequently expressed in grams per milliliter. Since the milliliter is defined as one one-thousandth of the volume of 1 kg of pure, ordinary water at its temperature of maximum density (3.98°C), the density in grams per milliliter is the ratio of the absolute density of the liquid at t°C to the absolute density of water of 3.98° and is frequently represented by d_4^t.

The densities of liquids may be determined by measurement of the

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[1] Embree, *Ind. Eng. Chem.*, **29**, 975 (1937).

[2] Hickman, *Ind. Eng. Chem.*, **29**, 968, 1107 (1937).

[3] Discussions of experimental methods for the determination of density are to be found in Bauer *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part I, pp. 253–296; Reilly and Rae, "Physico-chemical Methods," 5th ed., Vol. 1, pp. 577–608, 609–628, D. Van Nostrand Company, Inc., New York (1953).

weight of liquid occupying a known volume (pycnometric methods) and by buoyancy methods based on Archimedes' principle.

Pycnometers. Pycnometers are vessels with capillary necks in which a definite volume of liquid is weighed. The volume is determined by weighing the vessel filled with water at a definite temperature. A table giving the density of water as a function of temperature is given in the Appendix. Two types of pycnometers are illustrated by Fig. 25.

In order to obtain fifth-place accuracy in density determinations, a number of precautions must be observed. The weights should be checked against each other to obtain their relative values. It is not necessary to compare the set with a certified standard mass. One of the largest errors is often due to the adsorption of an uncertain amount of moisture by the glass, and it is necessary to wipe the pycnometer with a damp cloth and allow it to stand in the balance case for several minutes before weighing. A similar pycnometer of approximately the same volume may be used to advantage as a counterpoise.

In order to obtain the true weight of the liquid in the pycnometer, it is necessary to correct for the buoyancy of the air. The volume occupied by the glass of the pycnometer can be left out of the calculation if the tare has very nearly the same weight and density. The true (vacuum-corrected) weight W_0 is calculated from the equation

$$W_0 = W\left(1 + \frac{D_{\text{air}}}{D_s} - \frac{D_{\text{air}}}{8.5}\right)$$

where W = apparent weight given by brass weights
D_{air} = density of the air
D_s = density of substance being weighed

In the present case D_s is the density of the liquid in the pycnometer. For fifth-place accuracy the density of the weights may be assumed to be 8.5 g/ml even when the small-denomination weights are made of material of different density. The density of the air may usually be taken to be 0.0012 g/ml, but for accurate work the variation of the density of air due to changes in room temperature, barometric pressure, and relative humidity must be considered. If the temperature (t°C), barometric pressure (P millimeters of mercury), and the relative humidity (H, in per cent) are measured at the time of the weighing, the density of air may be calculated from the equation

$$D_{\text{air}} = \frac{0.001293}{1 + 0.00367t}\,\frac{(P - k)}{760}$$

where $k = 0.0038HP^t_{H_2O}$
$P^t_{H_2O}$ = vapor pressure of water, mm of mercury at t°C

In the case of volatile liquids, it is necessary to correct for the weight of the saturated vapor enclosed in the pycnometer.

For determining the density of a solid, a pycnometer with a wide mouth that will admit the solid is necessary. The ordinary type is a small bottle with a ground-glass stopper through which is bored a fine capillary.

The bottle is filled with water, and the stopper is inserted firmly, after which it is placed in a thermostat. The excess liquid is wiped off, and the pycnometer is dried and weighed. The pycnometer is weighed empty and again with the solid. After filling with water (plus the solid), it is weighed again, and all the data are then available for calculating the weight and volume of the solid and its density. In case the solid is soluble in water, some other inert liquid is used, and the density of the liquid is determined also.

The greatest source of error in determining the density of a solid is the adsorption of air by the solid. For this reason, the pycnometer containing the solid and some liquid is set in a larger bottle, which is connected to a vacuum pump, and evacuated until all air bubbles have ceased rising from the solid; then the pycnometer is filled completely.

Buoyancy Methods. *Hydrometer.* The specific gravity of a liquid may be most easily determined with an ordinary hydrometer. Hydrometers may be purchased in sets that cover a wide range of densities, each hydrometer retaining a high sensitivity over a limited range. They find extensive use in industrial operations and in making up solutions of definite concentration, and particularly in testing storage batteries.

Westphal Balance. The Westphal balance is more accurate than the hydrometer. It depends on the principle of Archimedes, according to which the buoyant effect is directly proportional to the weight of the liquid displaced. The sinker is suspended in pure water, with the unit weight in position, and a threaded counterpoise is turned until the pointer reads zero on the scale. The sinker is then dried and suspended in the liquid whose density is to be measured. The smaller weights are set at the proper places on the scale so as to restore the point of balance. Some balances are constructed with three riders, corresponding to 0.1, 0.01, and 0.001, and the scale is divided into 10 equal parts. The position on the scale gives the numerical value for each rider; e.g., if the 0.1 rider is at 9, the 0.01 at 8, and the 0.001 at 7, the specific gravity is 0.987.

The temperature is read directly on a thermometer which is enclosed in the sinker. A very fine platinum wire is used for suspending the sinker; the surface-tension effect on this wire is negligible for ordinary work, but for accurate work it may prove to be a source of error. The wire should be immersed to the same depth for each measurement.

The same principle of weighing a sinker which is suspended in a liquid is used in the chainomatic balance, shown in Fig. 96. With this more elaborate instrument, densities may be determined quickly with an accuracy of 1 part in 10,000. The value of the instrument is increased by the introduction of an electric heating coil and switch, to maintain the liquid at a definite temperature.

Floating Equilibrium. The objection to the wire projecting through the surface of the liquid in the case of the Westphal balance can be eliminated by having a bulb so carefully adjusted that it neither sinks nor rises in the liquid.

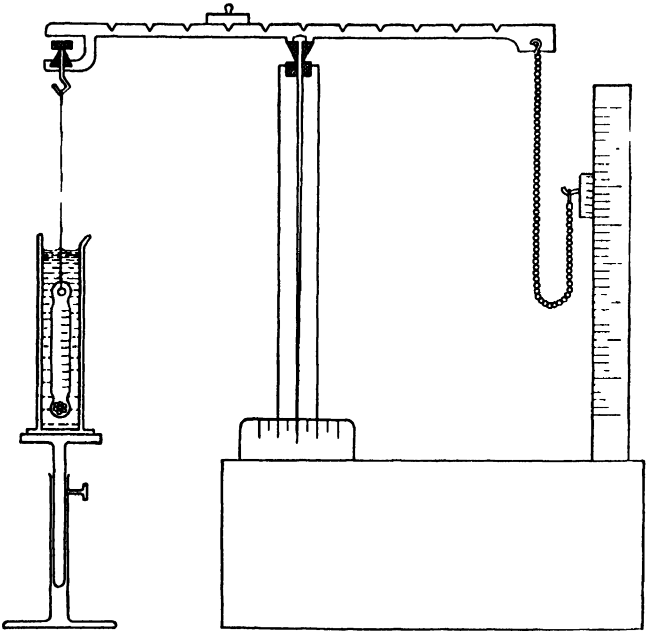

FIG. 96. Chainomatic balance for determining the density of liquids.

Lamb and Lee[1] obtained accurate results by placing a piece of iron in the float and measuring the strength of the electromagnetic field that was necessary to keep the bulb in a position of equilibrium without sinking or rising.

Richards and Shipley[2] adjusted the temperature until the sinker reached a point of equilibrium, and thus obtained high precision.

Lewis and MacDonald[3] used this method for measuring the density of water enriched in D_2O.

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[1] *J. Am. Chem. Soc.*, **35**, 1666 (1913); *cf.* also Jones and Hall, *J. Am. Chem. Soc.*, **59**, 258 (1937).

[2] *J. Am. Chem. Soc.*, **36**, 1 (1914); Richards and Harris, *J. Am. Chem. Soc.*, **38**, 1000 (1916).

[3] *J. Chem. Phys.*, **1**, 341 (1933).

Gilfillan[1] adjusted the hydrostatic pressure on the liquid with a mercury column until equilibrium of the bulb was obtained. He calibrated the apparatus with dilute potassium chloride solutions of known densities.

The density of solids can be determined in a somewhat similar way by mixing two liquids of different density until the solid neither rises nor sinks. The system must be evacuated to remove air from the solid. A heavy liquid like methylene iodide is mixed with a light liquid like benzene, and the density of the final mixture is determined with a pycnometer. The density of the liquid is the same as the density of the solid with which it is in floating equilibrium.

This method has been used by Hutchinson and Johnston[2] for the accurate determination of the density of lithium fluoride. The necessary precautions have been described, and the determinations were sufficiently accurate to follow the concentration of lithium isotopes[3] by electrolysis.

Falling Drop. The falling-drop method of Barbour and Hamilton[4] is especially useful when only small quantities of solution are available. This method is sufficiently sensitive to be useful for determining the concentration of deuterium oxide in water. The method consists in measuring the velocity of fall of a drop of water through a nonmiscible liquid of known density, usually *o*-fluorotoluene.[5] The density of a water drop may be calculated to 1 to 2 parts per million by using Stokes' law.

VISCOMETRY[6]

The Ostwald viscometer has been improved by Bingham.[7] The liquid is forced through a capillary with compressed air maintained at constant pressure. There are marks at the top and bottom of the bulb, and the time required for the liquid to flow first up and then down is recorded. An improved viscometer described by Ubbelohde[8] eliminates errors due to

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[1] *J. Am. Chem. Soc.*, **56,** 406 (1934).

[2] *J. Am. Chem. Soc.*, **62,** 3165 (1940).

[3] Johnson and Hutchinson, *J. Chem. Phys.*, **8,** 869 (1940).

[4] *Am. J. Physiol.*, **69,** 654 (1924); *J. Biol. Chem.*, **69,** 625 (1926).

[5] Keston, Rittenberg, and Schoenheimer, *J. Biol. Chem.*, **122,** 227 (1937).

[6] The general subject of viscometry is discussed by Hatchek, "The Viscosity of Liquids," George Bell & Sons, Ltd., London (1928); Barr, "Viscometry," Oxford University Press, New York (1931); Philippoff, "Viscositat der Kolloide," Steinkopff, Dresden and Leipzig (1942); Blair, "A Survey of General and Applied Rheology," Pitman Publishing Corp., New York (1944); McGoury and Mark *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part I (1949).

[7] "Fluidity and Plasticity," p. 76, McGraw-Hill Book Company, Inc., New York (1922).

[8] *Ind. Eng. Chem., Anal. Ed.*, **9,** 85 (1937).

surface tension and is not as sensitive to deviations from the exact vertical position as is the Ostwald viscometer.

In using an Ostwald viscometer, it is necessary to apply a kinetic-energy correction if the flow times of the solvent and solution being studied are very different. This source of error is due to the fact that not all the potential energy of the liquid is converted to thermal energy by viscous friction but some remains as kinetic energy of the liquid leaving the capillary. The corrected form of Poiseuille's equation is

$$\eta = \frac{\pi p r^4}{8(l + \lambda)V} t - \frac{m d V}{8\pi(l + \lambda)t} \tag{1}$$

where V = volume of liquid passing through capillary in time t
λ = small end correction of magnitude of several diameters of capillary
m = small constant, usually about 1.12

and the significance of the other symbols is the same as in Exp. 11. This equation may be simplified by writing

$$\eta = Adt - \frac{Bd}{t} \tag{2}$$

where A and B are apparatus constants. These constants may be determined by employing two or more liquids of accurately known viscosity. The kinetic-energy correction may also be calculated from the approximate dimensions of the apparatus. Neglecting second-order correction terms, the corrected relative viscosity is given by

$$\frac{\eta}{\eta_0} = \frac{dt}{d_0 t_0}\left[1 + k\left(\frac{1}{t_0^2} - \frac{1}{t^2}\right)\right] \tag{3}$$

where the subscript zeros denote solvent and $k = mV^2/\pi^2 hgr^4$. The kinetic-energy correction is also discussed by Kaaschow.[1]

The use of automatic timing for the transit of the meniscus of the liquid in the capillary tube, by means of a photoelectric cell, has been developed to a high degree of perfection by Jones and Talley[2] and by Riley and Seymour.[3] Details of the necessary assembly have been given by these investigators in articles in which they also analyze sources of error in the use of viscometers.

The rotating-cylinder, or Couette-type, viscometer, in which is measured the torque that is required to rotate a cylinder at a given rate of speed in the solution, has certain advantages over the capillary-tube type.

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[1] *Ind. Eng. Chem., Anal. Ed.*, **10**, 35 (1938).

[2] *Physics*, **4**, 215 (1933); *J. Am. Chem. Soc.*, **55**, 624 (1933).

[3] *Ind. Eng. Chem., Anal. Ed.*, **18**, 387 (1946).

A source of error in a capillary-tube type of viscometer arises from the fact that the shearing stress exerted on the liquid is not uniform but varies with the distance from the center of the capillary. This effect is not important if the viscosity of the liquid is independent of the shearing stress (Newtonian liquid), but in the case of non-Newtonian liquids, the viscosity obtained is an average value which depends on the dimensions of the instrument and the relation between viscosity and shearing stress. In the rotating-cylinder viscometer, this difficulty may be avoided.

One of the simplest methods for determining viscosity depends upon the determination of the velocity of a sphere falling through the liquid when it has reached a uniform velocity. This is based on Stokes' law relating the viscosity of the liquid to the frictional force which acts on a moving sphere. It is necessary to apply corrections for the influence on the velocity of the wall of the tube and the bottom of the tube. For a small sphere of radius r falling axially through a viscous liquid in a cylindrical tube, the complete expression[1] is

$$\frac{1}{t}\left(1 + 2.4\,\frac{r}{R}\right)\left(1 + 3.3\,\frac{r}{h}\right) = 2gr^2\left(\frac{d_1 - d_2}{9\eta}\right) \tag{4}$$

where R = radius of cylinder
h = height of liquid
g = acceleration due to earth's gravitational field
d_1 = density of sphere
d_2 = density of liquid

In measurements with spheres due to equal radius in tubes of the same dimensions

$$\eta = K(d_1 - d_2)t$$

The tube constant may be evaluated experimentally by measuring the time of fall through a liquid whose density and viscosity are known or may be calculated from Eq. (4). In determining relative viscosities, the tube constant cancels:

$$\frac{\eta}{\eta_s} = \frac{(d_1 - d_2)\,t}{(d_1 - d_s)\,t_s} \tag{5}$$

The subscript s refers to the standard liquid. The sphere is discharged slowly into the tube, a few centimeters below the surface, through a glass tube slightly larger than the sphere; 1.5 mm is a suitable diameter for the sphere, and 20 cm is a satisfactory height for fall. The vessel should have a diameter at least ten times that of the sphere. A steel ball such as those used in ball bearings makes an excellent ball for the experiment,

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[1] Reilly and Rae, *op. cit.*, p. 677.

because it is almost truly spherical. It must be free from air bubbles as it leaves the discharge tube.

The determination of absolute viscosities is rather difficult. It requires careful measurements of the apparatus, including the length and radius of the capillary, and some rather uncertain corrections. Further details concerning absolute measurements are given by Thorpe and Rodger[1] and by Bingham, Schlesinger, and Coleman.[2]

Viscosity has been studied at very high pressures.[3]

SURFACE TENSION[4]

When the surface tension of a liquid is to be determined, one should choose the particular method which will give the best results with the least effort. The realms of utility for the four methods are outlined as follows:

1. *Single liquids.*
   - *a. Capillary rise:* For highest accuracy, but not rapid.
   - *b. Ring method:* Very fast and reasonably accurate if suitable apparatus is available. Can be used for interfacial tension.
   - *c. Drop weight:* Best general method for both surface and interfacial tensions if both accuracy and speed are considered. Can be used with very small quantities of liquid.
   - *d. Bubble pressure:* A moderately good method. Best for very viscous liquids.
2. *Solutions.*
   - *a. Drop weight:* Best method for surface and interfacial tension if long time effects are not involved.
   - *b. Ring method:* Excellent for surface tension, even if time effects are involved.
   - *c. Drop shape:* Excellent for the study of time effects.

DIFFUSION

An important transport process is that of molecular diffusion in solution, with any difference in concentration being reduced by a spontaneous transfer of matter. It is caused by the Brownian motion of the dissolved molecules.

The flow of matter is defined as the amount of material which in unit time passes through a unit area of plane perpendicular to the direction of flow. It is the product of a concentration and a velocity. Thus, if the

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[1] *Phil. Trans.*, **A185**, 397 (1894).

[2] *J. Am. Chem. Soc.*, **38**, 27 (1916); Hyde, *Proc. Roy. Soc.* (*London*), **A97**, 240 (1920).

[3] Bridgman, "The Physics of High Pressures," George Bell & Sons, Ltd., London (1931).

[4] The measurement of surface tension has been reviewed by Harkins *in* Weissberger (ed.): *op. cit.*, Vol. I; Adam, "Physics and Chemistry of Surfaces," Oxford University Press, New York (1942); Reilly and Rae, *op. cit.*, pp. 629–659.

concentration is expressed in moles per cubic centimeter and the distance of displacement is, given in centimeters, then the flow J is measured in moles $\mathrm{cm}^{-2}\,\mathrm{sec}^{-1}$.

The diffusion coefficient D is defined by two laws of Fick.[1] They are

$$J = -D\frac{\partial c}{\partial x} \tag{1}$$

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{2}$$

The coefficient which is defined by these equations is often referred to as a constant. This is only approximately true, and the study of the variation of D with concentration gives useful information.

The diffusion of molecules in liquid media has been the subject of a number of reviews.[2] There are several types of experiment.

1. **Free Diffusion.** In this method, which is based on the second law of Fick, an initially sharp boundary is formed between the solution and the solvent with the more dense phase in the bottom of the diffusion cell. The cell should be tall enough so that the composition at the bottom and at the top of the column remains unchanged during the period of observation. The gradual blurring of the boundary may be followed by a number of methods. In early work, samples of solution were taken from various levels in the cell and their concentrations used to calculate the diffusion coefficient. In some cases, it is possible to determine the concentration at every level in the diffusion cell by means of quantitative light-absorption measurements. The most generally applicable and accurate methods for the determination of the diffusion coefficient are optical methods which depend upon the fact that light is deflected upon passing through a refractive-index gradient such as that established in a diffusion column. In the Lamm[3] scale method, the displacements of lines in the photograph of a linear scale placed behind the diffusion cell are measured with a microcomparator. The schlieren method, in which a plot of refractive-index gradient versus position in the cell is obtained directly, is described in Chap. 19. The diffusion coefficient may be calculated from the shape of the curve by several methods.

Interference methods developed by Kegeles and Gosting,[4] Longsworth,[5]

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[1] Fick, *Pogg. Ann.*, **94**, 59 (1855).

[2] Williams and Cady, *Chem. Revs.*, **14**, 171 (1934); Neurath, *Chem. Revs.*, **30**, 257 (1942); Harned, *Chem. Revs.*, **40**, 462 (1947); Geddes *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part I, pp. 551–619 (1949); Gosting, *Adv. Protein Chem.*, **11** (1957).

[3] *Arkiv Kemi., Mineral. Geol.*, **17B**, No. 13 (1943).

[4] *J. Am. Chem. Soc.*, **69**, 2516 (1947); Gosting, Hanson, Kegeles, and Morris. *Rev. Sci. Instr.*, **20**, 209 (1949).

[5] *J. Am. Chem. Soc.*, **74**, 4155 (1952); **75**, 5705 (1953).

and Coulson *et al.*[1] yield more accurate diffusion coefficients than any of the above methods.

A number of cells have been designed for the purpose of forming a sharp initial boundary between solution and solvent.[2]

2. **Restricted Diffusion.** Harned[3] has used a conductivity method for the determination of concentration changes of salts in a diffusion cell. In this method, the difference in the conductances of the solution as measured between pairs of electrodes at the bottom and at the top of the cell is utilized in the calculation of the diffusion coefficient. This method is limited to the study of electrolytes, and an experimental precision of 0.1 per cent may be obtained at concentrations less than 0.01 *N*.

3. **Steady-state Diffusion.** In this method the first law of Fick serves as the means for the computation of the result. Diffusion takes place through a region in which the concentration gradient is independent of time. An example of this method is the porous-plate method of Northrop and Anson.[4] One form of the diffusion cell consists of a bell-shaped glass vessel, closed at the narrow top end by a stopcock, and at the wide bottom end by a sealed-in sintered-glass disk. The cell is filled with a solution and is immersed in a beaker of water just touching its surface. Various sizes have been used, varying from 10 to 200 ml capacity. Diffusion is allowed to proceed until the concentrations in the pores of the sintered-glass disk are those for a "steady state," which generally requires several hours. When steady-state concentrations have been attained, the cell is placed in contact with a fresh sample of solvent, and diffusion is allowed to proceed for a suitable length of time. From concentrations determined after various times in aliquots of solution and solvent, the diffusion coefficient may be calculated. It is necessary to calibrate the cell by an experiment with a substance of known diffusion coefficient. The advantage of this method is that it is useful for determining the diffusion coefficients of radioisotopes or biologically active substances in dilutions so low that optical methods cannot be used. In such experiments very careful control of temperature is required to prevent thermal convection.[5]

Micro methods for use with colored materials have been developed by Fürth[6] and Nistler.[7]

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[1] Coulson, Cox, Ogston, and Philpot, *Proc. Roy. Soc.* (*London*), **A192**, 382 (1948).

[2] Loughborough and Stamm, *J. Phys. Chem.*, **40**, 1113 (1936); Claesson, *Nature*, **158**, 834 (1946).

[3] *Loc. cit.*

[4] *J. Gen. Physiol.*, **12**, 543 (1929); Clack, *Proc. Phys. Soc.* (*London*), **36**, 313 (1924).

[5] Mouquin and Cathcart, *J. Am. Chem. Soc.*, **57**, 1791 (1935).

[6] *Kolloid-Z.*, **41**, 300 (1927).

[7] *Kolloidchem. Beih.*, **28**, 296 (1929).

OSMOTIC PRESSURE[1]

The simplest device for demonstrating osmosis is an inverted thistle tube with a cellophane membrane stretched across its mouth. When the tube is filled with a solution and placed in pure water, water molecules pass through the membrane into the solution. The hydrostatic pressure developed in the tube is a measure of the osmotic pressure, but equilibrium is reached slowly. If the meniscus in the vertical tube is adjusted initially to approximately the correct height, so that equilibrium is reached more rapidly, rough determinations of osmotic pressure may be made even with this simple apparatus.

Osmotic-pressure determinations may be divided into two classes according to the molecular weight of the solute. If the membrane is permeable only to solvent molecules, the so-called "total osmotic pressure" is obtained. In the case of solutions which contain solutes of both low and very high molecular weight, the total osmotic pressure would be due to both classes of solute molecules. However, if the osmotic-pressure determination is carried out with a membrane permeable to both solvent molecules and low-molecular-weight solute molecules, the osmotic pressure measured is due only to the large molecules and is referred to as "colloid osmotic pressure."

In the case of solutes of molecular weight less than 10,000, the great difficulties encountered in the preparation of membranes impermeable to solute molecules preclude the general use of the osmometric method. In the apparatus of Frazer and Myrick,[2] a porous clay cup contains an electrolytically deposited membrane of copper ferrocyanide which allows the passage of solvent but not of the low-molecular-weight solute. This clay cup, containing the solvent, is surrounded by a strong bronze cylinder containing the solution and the connection to the manometer. To measure the pressure, an electrical-resistance gauge or a water interferometer may be used in place of the customary mercury manometer. With this apparatus Frazer and his coworkers have measured osmotic pressures up to 273 atm.

Osmotic pressure may be successfully used to determine the molecular weights of macromolecules, such as high polymers, proteins, and polysaccharides. A simple calculation will show that an osmotic pressure of 1 mm of water corresponds to a freezing-point depression of roughly 0.0001°C. Such a freezing-point depression might be caused by a minute

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[1] A general review of this subject is given by Wagner *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part I, Chap. 11 (1949).

[2] *J. Am. Chem. Soc.*, **38**, 1907 (1916); Frazer and Lotz, *J. Am. Chem. Soc.*, **43**, 2501 (1921).

trace of salt in a protein solution, while the salt would not significantly affect the osmotic pressure of the isoelectric protein measured with a membrane permeable to small ions and water molecules.

Osmotic-pressure measurements may be carried out by dynamic or static methods. In the dynamic method,[1] the rate of movement of the meniscus in the capillary tube is measured at a number of heights and used to obtain the equilibrium height, whereas in the static method, the equilibrium height is determined directly. The construction of a standard type of static osmometer for high-polymer work is illustrated in Fig. 97.[2] The cell consists of two stainless-steel plates clamped together with the membrane between the plates. The faces of the two plates are machined with a set of concentric cuts 2 mm wide and 2 mm deep. The solution is placed in one half-cell and the solvent in the other, and the membrane simultaneously acts as a gasket. With valves 1 and 2 closed and valve stem 3 removed, solution is poured into the left-hand tube, while solvent is simultaneously poured into the right one, so that the liquid level rises at about the same rate on both sides of the membrane. Valve 3 is then inserted and closed, and valve 1 is opened to drop the meniscus in the solution standpipe to its desired position. The left meniscus is maintained at constant height while the rate of approach of the right meniscus to its equilibrium position is determined from both

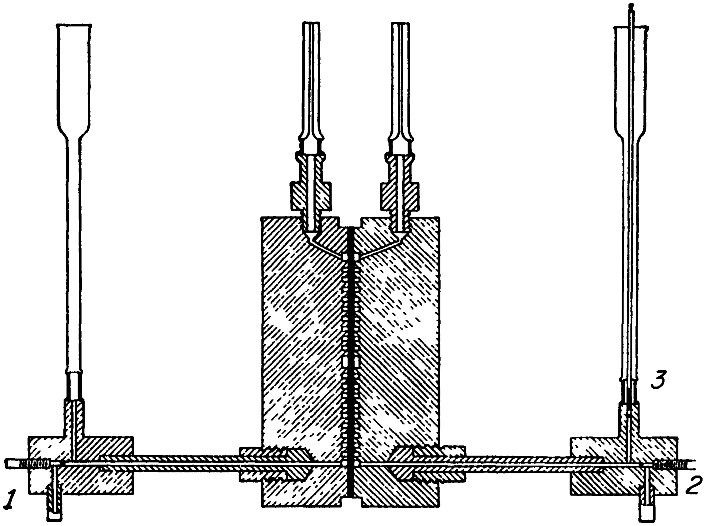

Fig. 97. Static osmometer.

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[1] Montanna and Jilk, *J. Phys. Chem.*, **45**, 1374 (1941).

[2] Fuoss and Mead, *J. Phys. Chem.*, **47**, 59 (1943); Flory, *J. Am. Chem. Soc.*, **65**, 374 (1943).

the high-pressure and low-pressure sides. Smaller glass osmometers[1] are also widely used.

Semipermeable membranes for use with polymer solutions are generally prepared by treating cellophane with 3 per cent sodium hydroxide or by denitrating collodion (cellulose nitrate), using ammonium polysulfide.

Because of the nonideality of polymer solutions, it is necessary to extrapolate osmotic-pressure measurements at several concentrations to infinite dilution in order to calculate the molecular weight. A plot of p/c versus c is quite linear in the low-concentration range and is used for the extrapolation.

A number of osmometers have been designed especially for protein work.[2] In these osmometers the protein solution is contained in a bag of collodion or regenerated cellulose (such as Visking sausage casing) and the pressure measured by means of a toluene manometer.

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[1] Zimm and Myerson, *J. Am. Chem. Soc.*, **68**, 911 (1946); Schulz, *Z. physik. Chem.*, **A176**, 317 (1936); *ibid.*, **B52**, 1 (1942).

[2] Bull, *J. Am. Chem. Soc.*, **68**, 742 (1946); Scatchard, Batchelder, and Brown, *J. Am. Chem. Soc*, **68**, 2320 (1946).

CHAPTER 22

ELECTRICAL MEASUREMENTS

A wide variety of electrical measurements are met with in physical chemistry. These include measurements of the electromotive forces of electrochemical cells, thermocouples, and thermopiles, measurements of resistance in the determination of electrolytic conductance and of temperature, the measurement of quantity of electricity in the determination of transference numbers and ionic mobilities and of electrical energy in calorimetry, and measurements of dielectric constant.

The absolute electrical units are based upon the fundamental mechanical units of mass, length, and time by the use of accepted principles of electromagnetism. These units are maintained, as were the international units used before 1948, by groups of standard resistors and of standard cells. The international ohm and volt are slightly larger than the corresponding absolute units. The conversion factors for adjusting values of standards in this country are as follows:[1]

1 int ohm = 1.000495 abs ohms
1 int volt = 1.00033 abs volts
1 int amp = 0.999835 abs amp
1 int coulomb = 0.999835 abs coulomb
1 int henry = 1.000495 abs henrys
1 int farad = 0.999505 abs farad
1 int watt = 1.000165 abs watts
1 int joule = 1.000165 abs joules

GALVANOMETERS

The D'Arsonval galvanometer consists of a rectangular coil of wire suspended from a fine wire in the field of a permanent magnet. The bottom part of the coil is made steady by a loosely coiled metallic spring which also serves as a lead. The current in the moving coil flows perpendicular to the lines of magnetic force, producing a torque on the coil. The coil turns until the restoring moment due to the twist in the spring is

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[1] *Natl. Bur. Standards Circ.*, **C459** (1947).

just equal to the torque due to the current. The motion of the coil is observed and magnified by means of a beam of light reflected from a small mirror mounted on the coil. A wide variety of galvanometers is available to provide the sensitivity, period, and ruggedness desired. The current sensitivity of a galvanometer is defined as the current in microamperes required in the galvanometer coil to produce a standard deflection, usually 1 mm on a scale placed perpendicular to the reflected light beam at a distance of 1 m. Sometimes the sensitivity is expressed in microvolts, which is the electromotive force which produces the standard deflection when it is introduced into the series circuit consisting of the galvanometer and its external critical-damping resistance. The microvolt sensitivity is, therefore, the product of the microampere sensitivity and the sum of the galvanometer resistance and its external critical-damping resistance. The sensitivity of a galvanometer is less frequently given in terms of the ballistic sensitivity, which is the quantity of electricity which must be discharged through a galvanometer in a time which is short compared to its free period to produce the standard deflection.

The period of a galvanometer is the time in seconds required for one complete undamped oscillation of the galvanometer. In most galvanometer applications, a period as short as possible, consistent with other necessary requirements, is desired. Short periodicity conserves the time of the observer and makes possible precision of measurement of fluctuating phenomena that would otherwise be unobtainable. For other measurements, such as ballistic measurements, long periods are desirable to facilitate reading.

For most applications it is desirable to damp a galvanometer so that the final reading is obtained without oscillation. A critically damped galvanometer reaches its final reading without oscillation and in the shortest possible time. It is customary to take the period of a critically damped galvanometer as equal to its undamped period, for although the critically damped period is theoretically infinite, practically a critically damped deflection is within about 1.5 per cent of its final position in the undamped periodic time. If the resistance of the external circuit is too small, the galvanometer will be overdamped; that is, the coil will rotate too slowly. In this case, more resistance is added in series. If the resistance of the external circuit is too great, the galvanometer will be underdamped, and critical damping is achieved by addition of a lower resistance in parallel.

For the most satisfactory operation of a galvanometer, one should select an instrument whose external critical-damping resistance is slightly lower than the resistance presented to the galvanometer by the circuit with which it is to be employed. An ordinary laboratory has use for low-resistance galvanometers (20 to 100 ohms) for thermopile work and calorimetry and for high-resistance galvanometers (over 1,000 ohms) for measurements of electromotive force. In an a-c galvanometer, sensitivity and period are important, but critical-damping resistance as such is of less significance because proper damping also depends on capacitance and inductance.

Portable box-type galvanometers are extensively employed in research. These galvanometers are taut-suspension moving-coil instruments with built-in lamps and scales, as illustrated in Fig. 98. The light beam traverses the case five times after reflection from the moving mirror, thus considerably increasing the sensitivity. Such galvanometers are commonly available with sensitivities down to 2.5 μvolts mm^{-1} and 0.005 μamp mm^{-1}.

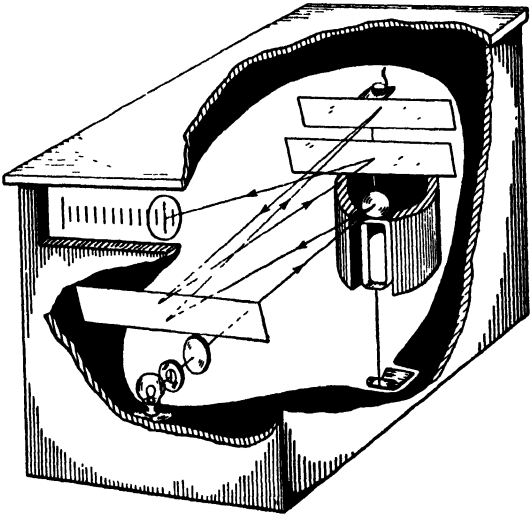

FIG. 98. Portable galvanometer using multiple reflections.

For greater sensitivity, galvanometers with more delicate suspensions must be used. These galvanometers must be carefully leveled and mounted on vibrationless supports.[1] The beam of light from a small lamp is focused on a scale at 1 m distance, by means of a focusing mirror or a long-focus lens attached to the glass window of the galvanometer. High-sensitivity galvanometers are commonly available with sensitivities down to 0.1 μvolt mm^{-1} or 0.0001 μamp mm^{-1}.

If a sensitivity much greater than 10^{-8} amp or 10^{-7} volts mm^{-1} is required with a low critical-damping resistance, it is necessary to use a special type of galvanometer or some type of amplification. Very small

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[1] The design of vibrationless supports has been discussed by Strong, "Procedures in Experimental Physics," pp. 328, 590, Prentice-Hall, Inc., New York (1939).

direct currents, as from thermopiles, may be amplified by vacuum-tube circuits if the current is subjected to mechanical interruption. Such methods are especially useful in infrared spectroscopy and have been reviewed by Williams.[1]

Another type of amplified galvanometer is the photoelectric galvanometer, which consists of a taut-suspension galvanometer and a double-cathode photocell in a balanced bridge circuit. In the null position, the galvanometer light beam illuminates both photocell cathodes equally, under which condition the photocell constitutes a balanced bridge with zero potential difference across the photocell cathodes. Displacement of the light beam produces a signal in the photocell circuit whose magnitude and polarity are determined by the magnitude and polarity of the electromotive force applied to the galvanometer terminals. This method has been useful in amplifying thermopile currents.[2]

Ammeters and voltmeters are essentially portable galvanometers of low sensitivity. The ammeters for registering current are of very low resistance and are connected in series in the circuit. Voltmeters, for measuring the potential between two points in a circuit, on the other hand, are connected in parallel with the circuit, and their resistance must be so high that only a small fraction of the current flows through them. For example, if a meter with which the full-scale deflection is obtained with 1 milliamp is to be used as a 10-volt voltmeter, a series resistance S must be added. If the resistance of the meter is R, $R + S = 10/0.001$, and the resistance to be placed in series so that the meter will show a full-scale deflection for 10 volts is $(10/0.001) - R$. Similarly, the series resistance required to use the milliammeter as a 100-volt voltmeter is $(100/0.001) - R$. High-grade commercial ammeters and voltmeters are guaranteed to be correctly graduated to as close as ¼ per cent of the full-scale reading, but cheaper instruments are generally accurate only to about 2 per cent of the full-scale reading, irrespective of the actual reading.

MEASUREMENT OF ELECTROMOTIVE FORCE

Potentiometers. The principle of the potentiometer has been discussed in Exp. 34. Since the galvanometer acts only as a null-point indicator, the accuracy of measurement depends only on the accuracy of the standard-cell voltage and the accuracy of the resistance coils, provided that the galvanometer is sufficiently sensitive and the resistance of the circuit is not too great. Since the resistance coils can be manufactured with exceedingly high precision, the accuracy of the method depends

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[1] *Rev. Sci. Instr.*, **19**, 135 (1948).

[2] Gershinowitz and Wilson, *J. Chem. Phys.*, **6**, 197 (1938); Mortimer, Blodgett, and Daniels, *J. Am. Chem. Soc.*, **69**, 822 (1947).

principally on the constancy of the standard-cell voltage. Potentiometers for research purposes are designed in such a way that it is possible to check the potentiometer against the standard cell without disturbing the setting of the resistances in the measuring circuit. This is illustrated in Fig. 99. Fixed connections for the standard cell span a definite portion of the circuit *OB*, across which the fall in potential is adjusted to be equal to the voltage of the standard cell by varying *R*. By means of a double-pole double-throw switch, either the standard cell or the unknown emf can be put in the circuit through the galvanometer. In making the first trial balance, the galvanometer key 1 is used, so as to include a high resistance in the galvanometer circuit and prevent a large current from flowing through the standard cell. When the potential drop of the potentiometer and the electromotive force of the unknown cell or standard are nearly balanced, key 3 is pressed to obtain maximum galvanometer sensitivity. When the total resistance of the unknown cell is comparatively small, such as 100 ohms, a potential difference of, say, 0.0001 volt between the potential drop in the slide-wire and the electromotive force of the unknown cell can cause sufficient current to flow through the galvanometer to produce a deflection. However, if the resistance of the unknown cell is, say, 5 megohms, the current through the circuit due to 0.0001 volt is only $0.0001/(5 \times 10^6)$, or 2×10^{-11} amp, which is too small to turn the coil of an ordinary galvanometer. In such a case, it is necessary to use an electrometer or vacuum-tube voltmeter.

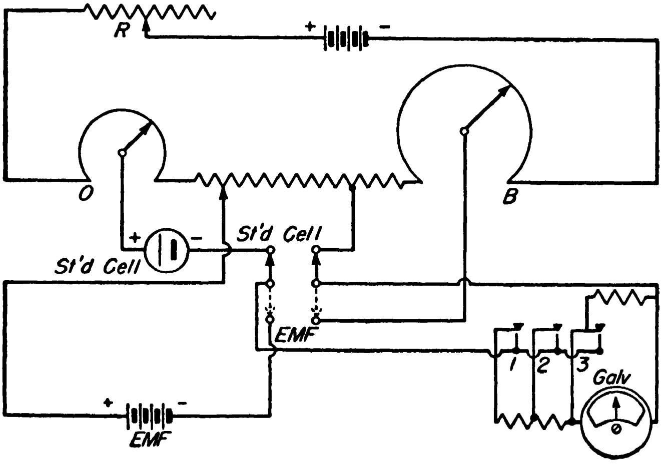

FIG. 99. Potentiometer circuit

Special potentiometers have been designed for thermocouple work. These include the Wenner potentiometer[1] and the White potentiometer.

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[1] Behr, *Rev. Sci. Instr.*, **3**, 109 (1932).

Double potentiometers of the White type are particularly useful in calorimetry where it is desired to measure, practically simultaneously, two temperatures which are appreciably different, without resetting dials.

Recording Potentiometers. It is possible to buy a recording potentiometer which performs the operations of balancing against an applied potential automatically and standardizing itself by balancing against the standard cell at regular intervals. The automatic balancing mechanism replaces the galvanometer in the usual potentiometer circuit. This mechanism consists of an amplifier which drives a motor whose direction and speed depend upon the polarity and voltage of the unbalance. The motor moves the contact on the potentiometer slide-wire, and the attached pen makes a trace on the moving chart.

In selecting a recording potentiometer for a particular application several factors have to be considered. The potential required to give a full-scale displacement may range from a few millivolts to several volts. The pen speed, that is, the time required for the pen to go across the full scale to a new balance point, may range from a second to a minute. For measurements requiring higher speed, recording galvanometers in which a beam of light reflected from a galvanometer mirror strikes moving photographic paper may be used. Also the trace on a cathode-ray oscillograph may be photographed. The rate with which the paper moves under the pen of a recording potentiometer may range from 1 to 1,000 in. hr^{-1}. The input impedance of recording potentiometers is generally in the range of 1,000 ohms except in special types.

The precision of recording potentiometers at any point on the chart is about 0.3 per cent of the full-scale voltage. Since so many measurements may be reduced to a measurement of voltage, recording potentiometers can be used in a wide variety of applications. They can be fitted with mercury switches or microswitches which can operate heaters or motors at certain definite potentials.

More specific information may be obtained from the manufacturers.[1]

Standard Cells. The electromotive force of the Weston cell in the new absolute system is 1.0186 abs volts at 20°. This cell is set up in an air-tight H-shaped vessel, with platinum wires sealed through the bottoms for connection with the electrodes, as shown in Fig. 100. The positive electrode consists of pure mercury, which is covered by a thick paste of mercurous sulfate and a small quantity of cadmium sulfate. The negative electrode is a cadmium amalgam containing 12.5 per cent of cadmium. On the top of the solidified amalgam and the mercurous sulfate paste are placed some rather large and clear cadmium sulfate crystals; then the cell is filled with a saturated solution of cadmium sulfate. The ends of the tubes are closed, allowing sufficient air space for thermal expansion.

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[1] Leeds and Northrup Co. and the Minneapolis-Honeywell Regulator Co., etc.

The materials must be thoroughly purified. The temperature coefficient of the cell is small, so that the electromotive force may be given with accuracy sufficient for most purposes by the expression

$$E_t = E_{20} - 0.0000406(t - 20)$$

In actual laboratory measurements the unsaturated cadmium cell is more commonly used than the Weston cell. This cell contains a solution of cadmium sulfate saturated at 4° and has the advantage that the temperature coefficient (0.00001 volt deg^{-1}) is less than for the saturated cell. The voltage of the unsaturated cadmium cell varies between 1.01856 and 1.01910 int volts. The following precautions should be taken in using standard cells: (*a*) The cell should not be exposed to temperatures below 4°C nor above 40°C. (*b*) Abrupt changes of temperature should be avoided because they may produce temporary variations of several hundredths of 1 per cent in the electromotive force. (*c*) All parts of the cell should be at the same temperature. (*d*) Current in excess of 0.0001 amp should never pass through the cell. (*e*) The electromotive force of the cell should be redetermined at intervals of a year or two.

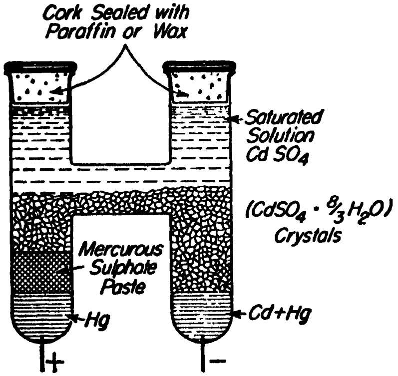

FIG. 100. Weston normal cell.

Standard Electrodes. The cells whose electromotive forces are to be determined may be considered to be made up of two electrodes, one an indicator and the other a reference electrode. The calomel electrodes and the silver–silver chloride electrode are the most commonly used reference electrodes.

There are three types of calomel electrodes in common use, depending upon the concentration of the potassium chloride solution used: 0.1 *N*, *N*, or saturated. The electromotive forces at 25° and temperature coefficients of the three calomel electrodes are as follows:[1]

Hg, Hg_2Cl_2(s); KCl (0.1 *N*) $E = -0.3338 + 0.00007(t - 25)$
Hg, Hg_2Cl_2(s); KCl (1.0 *N*) $E = -0.2800 + 0.00024(t - 25)$
Hg, Hg_2Cl_2(s); KCl (sat) $E = -0.2415 + 0.00076(t - 25)$

Commercially available saturated calomel cells such as that illustrated in Fig. 40 are especially convenient for work in the physical-chemistry laboratory.

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[1] Hamer, *Trans. Electrochem. Soc.*, **72**, 45 (1937).

The calomel electrode may be prepared as follows: The electrode consists of a test tube with a side arm bent down at right angles and fitted with a ground-glass plug which serves as a salt bridge, the current being carried by the thin liquid film between the wall of the tube and the plug. It is preferable to have the tube made of Pyrex and the plug of soft glass. If the plug is cooled before insertion into the tube, it will become firmly fixed upon subsequent warming to room temperature. This type of junction has a high resistance and requires the use of a high-resistance galvanometer (approximately 1,000 ohms) in the potentiometer circuit. A junction of this type should be kept immersed in potassium chloride solution when not in use so that the liquid film will not dry out. An alternative method of reducing diffusion at the junction involves constricting the end of the bridge arm to a tip, which contains solidified agar. This connecting bridge has a much lower resistance than the type with a ground-glass joint. Better still is a simple connecting salt bridge with sintered glass at the ends.[1]

The glass vessels are cleaned and rinsed thoroughly, using distilled water for the latter operation. The calomel paste is made by grinding calomel in a mortar with purified mercury and potassium chloride solution of the concentrations indicated above (depending on the type of electrode to be used). A few milliliters of redistilled mercury is placed in the tube and is covered with calomel paste to a depth of approximately 1 cm. The tube and the bridge are then filled with potassium chloride solution of the desired concentration, and an electrode consisting of a platinum wire fused to a copper wire, which is sealed in a glass tube mounted in a stopper, is placed in the pool of mercury.

In all precise electromotive-force work, oxygen must be carefully excluded from the cell. This may be done by bubbling purified nitrogen through the solutions in the cell for a period of time. Tank nitrogen is readily freed from small amounts of oxygen by passing over heated copper turnings. The effluent nitrogen is bubbled first through distilled water and then into the solutions in order to avoid excessive evaporation from the latter. Another type of purification system is described by van Brunt.[2]

MEASUREMENT OF ELECTROLYTIC CONDUCTANCE[3]

Alternating-current Wheatstone Bridge. The measurement of electrolytic conductance using the Wheatstone bridge has been described in

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[1] Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **13**, 393 (1941).

[2] Van Brunt, *J. Am. Chem. Soc.*, **36**, 1448 (1914).

[3] Robinson and Stokes, "Electrolyte Solutions," p. 87, Academic Press, Inc., New York (1955).

Exp. 29. Alternating current must be used to prevent electrical polarization of the electrodes, and this introduces a number of problems not present in d-c bridge measurements. A simple Wheatstone bridge for measurements of resistance with direct current is illustrated in Fig. 31. Resistance R_3 is adjusted to bring points A and B to the same potential, as indicated by the absence of a galvanometer deflection when the tap switch is closed. If a d-c source is used, only pure resistances are involved, and when A and B are at the same potential,

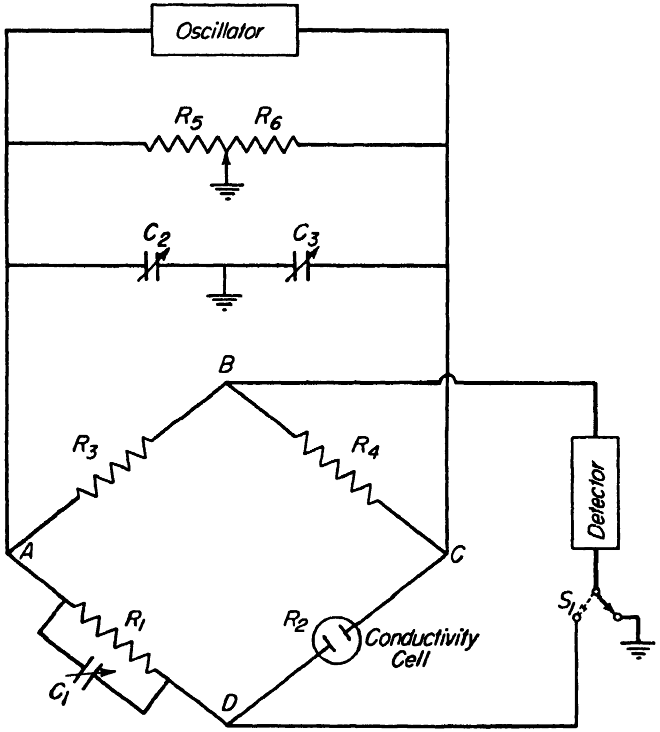

FIG. 101. Alternating-current bridge circuit.

$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

If an alternating source of current is used, it is necessary to balance the reactances in the circuit as well as the resistances. For example, in the a-c bridge circuit illustrated in Fig. 101 the conductivity cell has both capacitance and resistance. A variable condenser C_1 is placed across resistance R_1. When the capacitance of C_1 is made equal to that of the conductivity cell, D and B will be at the same potential if the various pure resistances satisfy the above relation. If D and B are not at ground potential, however, current can flow through the detector or earphones to the ground via distributed capacity. In precise measurements, it is necessary to provide means for adjusting points D and B to ground potential. The most common circuit for this purpose is referred to as a Wagner earthing device. As illustrated in Fig. 101, this device consists of adjustable resistances (R_5 and R_6) and capacitances (C_2 and C_3) between A and ground and between C and ground. After adjusting the bridge to the minimum signal of the detector or earphones, the switch S_1 is closed to the grounded position, and the resistances and capacitances of the Wagner earthing device are adjusted to the minimum signal of the detector. In this way, point B is brought to ground potential. It should be noted that since alternating current is used, the potentials of C and A vary sinusoidally with time, one being above ground potential while the other is below ground potential. Finally, the main-bridge balance is readjusted with the detector in the original position.

The source of power is usually some form of vacuum-tube oscillator like that described on page 427. Such an oscillator may be designed to give a pure-sine-wave current so that the current in one direction exactly offsets that in the other. The microphone hummer is an inexpensive and, at the same time, very satisfactory source of alternating current for less precise measurements. The frequency is maintained at a constant value by the vibration of an electrically driven tuning fork which actuates the microphone. The magnet that keeps the fork in vibration is supplied from the secondary of a transformer which is operated by the current through the microphone. At audio frequencies a telephone headset may be used as a detector, but to attain the best results, an amplifier must be used since the bridge current should be maintained at the lowest possible value in order to avoid heating effects in the conductivity cell. This is achieved by limiting the voltage input from the oscillator to less than 10 volts.

Edelson and Fuoss[1] have given the specifications for the construction of a portable audio-frequency conductance bridge. They discuss the use of an oscilloscope for obtaining the balance points.[1,2] This method is more sensitive and indicates the resistance and capacitance balance separately.

The theory and design of a-c bridges for measuring the conductance of electrolytic solutions have been discussed by Jones and Josephs[3] and by Shedlovsky.[4]

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[1] *J. Chem. Educ.*, **27**, 610 (1950).

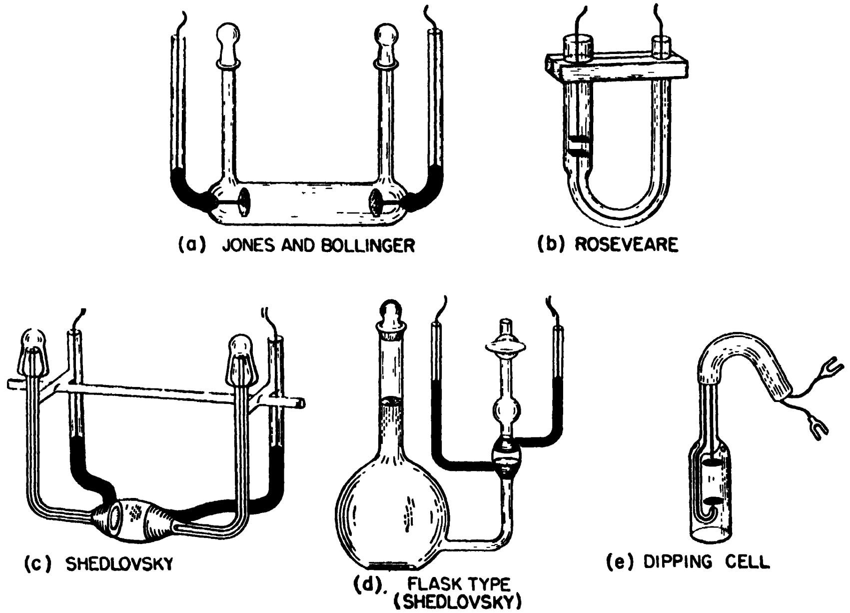
[2] Jones, Mysels, and Juda, *J. Am. Chem. Soc.*, **62**, 2919 (1940).

[3] *J. Am. Chem. Soc.*, **50**, 1049 (1928).

[4] *J. Am. Chem. Soc.*, **52**, 1793 (1930).

The construction of bridges for high-precision work (accuracy of 0.02 per cent or better) has been discussed by Dike[1] and Luder.[2]

The resistance coils of the Wheatstone bridge must be wound non-inductively, i.e., the wire is doubled back in the middle and the two parts of the wire with current going in opposite directions are side by side. Coils can be constructed in this way so that the difference between d-c and 20,000-cycle a-c resistances is less than 0.01 per cent.



(a) JONES AND BOLLINGER (b) ROSEVEARE

(c) SHEDLOVSKY (d). FLASK TYPE (SHEDLOVSKY) (e) DIPPING CELL

FIG. 102. Conductivity cells.

Electrolytic conductance may also be measured with direct current using nonpolarizable electrodes.[3] This method is capable of quite precise results, but it is applicable only to those electrolytes for which nonpolarizable electrodes are available.

Conductivity Cells. A number of forms of conductivity cells are shown in Fig. 102. The cells are usually constructed of highly insoluble glass, such as Jena 16III or Pyrex, or of quartz. The platinum electrodes should be heavy and well anchored, so that the cell constant will not change when the cell is used frequently. The conductivity cell for a given measurement should be chosen with an appropriate cell constant, so that the resistance will not fall far below 1,000 ohms, where excessive polarization

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[1] *Rev. Sci. Instr.*, **2**, 379 (1931).

[2] *J. Am. Chem. Soc.*, **62**, 89 (1940).

[3] Andrews and Martin, *J. Am. Chem. Soc.*, **60**, 871 (1938); Shiff and Gordon, *J. Chem. Phys.*, **16**, 336 (1948).

difficulties are encountered with the usual apparatus, or above 10,000 to 30,000 ohms, where errors due to insulation leakage are encountered. For solutions of low conductance, the electrodes should be large and close together. For solutions of high conductance, the electrodes should be smaller and farther apart. If very high resistances, such as that of distilled water, must be measured, it is advisable to shunt the cell with a known high resistance R_s (10,000 ohms, for instance) and then to compute the cell resistance R_c from the resistance of the parallel combination, using the parallel-circuit equation

$$\frac{1}{R} = \frac{1}{R_c} + \frac{1}{R_s}$$

Jones and Bollinger[1] have shown that in many cells which have been commonly used the filling tubes are relatively close to the electrode leads, so that disturbing parasitic currents can flow through capacitance-resistance paths, and these can produce variations in cell constant with resistance. The cell designed by Jones and Bollinger is shown in Fig. 102*a*. The Roseveare cell, Fig. 102*b*, with the corners of the thin platinum plates welded in the glass, is easy to make. In measuring the conductivity of solutions which show any tendency to foam, it is desirable to use a cell with conical electrodes (Shedlovsky, Fig. 102*c*) through which the electrolyte is flowed into the cell. The flask-type cell shown in Fig. 102*d* is useful for preparing and measuring the conductivities of very dilute solutions without risk of contamination from atmospheric or other impurities.[2] The dipping-type cell, Fig. 102*e*, is not suitable for precise measurements but is often convenient for practical measurements. A Freas-type conductivity cell is illustrated in Fig. 31*a*.

Polarization may be practically eliminated by using a pure-sine-wave alternating current of moderate frequency and by coating the electrodes with platinum black. The electrodes can be platinized by immersing them in a solution containing 3 g of platinic chloride and 0.02 g of lead acetate in 100 ml of water and connecting them to two dry cells connected in series. The current is regulated by means of a rheostat so that only a small amount of gas is evolved. After the electrodes are coated with platinum black, they are removed from the solution and thoroughly washed with distilled water. Any traces of chlorine adsorbed from the plating solution may be removed by continuing the electrolysis, with the same connections, in a dilute solution of sulfuric acid. In precise measurements of electrical conductance, it is especially important to test for the possibility of polarization.[3] Polarization has the effect of increasing

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[1] *J. Am. Chem. Soc.*, **53**, 411 (1931).

[2] Shedlovsky, *J. Am. Chem. Soc.*, **54**, 1411 (1932).

[3] Jones and Bollinger, *J. Am. Chem. Soc.*, **57**, 280 (1935).

the measured resistance and, in general, is less important at higher frequencies.

A cell with platinized electrodes should always be filled with distilled water when stored.

For work in very dilute solutions, which has become of great theoretical importance, the platinized surface must be dispensed with because it is so difficult to rinse out the last traces of electrolyte from it. Bright platinum electrodes are used, but since some polarization results it is necessary to make measurements at several frequencies and to extrapolate the values to infinite frequency.

Conductance of Potassium Chloride Solutions. In a very careful and exacting research, Jones and Bradshaw[1] have redetermined the electrical conductance of standard potassium chloride solutions for use in the calibration of conductance cells. The results of the work are summarized in Table 1. The values given in this table do not include the conductance due to water, which must be added and should be less than $L_{H_2O} = 10^{-6}$ ohm^{-1} cm^{-1} in work with dilute solutions. The potassium chloride should be fused in an atmosphere of nitrogen to drive out water, and in the case of salts which are deliquescent it is necessary to use a Richards bottling apparatus[2] to avoid exposure to air.

TABLE 1. SPECIFIC CONDUCTANCE OF STANDARD POTASSIUM CHLORIDE SOLUTIONS

Grams of potassium chloride per 1,000 g of solution in vacuum	Specific conductance, ohms^{-1} cm^{-1}		
	0°C	18°C	25°C
71.1352	0.06517_6[a]	0.09783_8	0.1134_2
7.41913	0.007137_9	0.011166_7	0.012856_0
0.745263	0.0007736_4	0.0012205_2	0.0014087_7

[a] The lowering of the last figure indicates that this figure is uncertain.

Conductance Water. In all conductance measurements made in aqueous solution it is necessary to have very pure water. Distillation in a seasoned glass vessel and condenser with ground-glass joints or with a block-tin condenser can give water with a specific conductance of about 1×10^{-6} ohm^{-1} cm^{-1} if a little potassium permanganate is added to the flask. If such a distillation is carried out in air, the water is saturated with the carbon dioxide of the air (0.04 per cent). Some of the dissolved carbon dioxide can be removed to give a higher resistance by bubbling carbon dioxide-free air through the water.

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[1] *J. Am. Chem. Soc.*, **55**, 1780 (1933).

[2] Richards and Parker, *Proc. Am. Acad. Arts Sci.*, **32**, 59 (1896).

It is interesting to note that Kohlrausch and Heydweiller[1] reported the preparation of purified water with a specific conductance at 18° of only 0.043×10^{-6} ohm^{-1} cm^{-1}.

Conductance water for laboratory use may be prepared on a large scale by redistilling distilled water and condensing in a block-tin condenser. By condensing the water at relatively high temperatures, the absorption of carbon dioxide is reduced.

MEASUREMENT OF CURRENT AND QUANTITY OF ELECTRICITY

The most direct method for the measurement of quantity of electricity involves the use of a coulometer, as, for example, a silver coulometer in which silver is plated on a platinum crucible from a silver nitrate solution. Other coulometers have been used in which iodine is liberated from a potassium iodide solution and titrated with standard sodium thiosulfate solution, copper is deposited from an acidified copper sulfate solution, or water is decomposed and the volume of gas evolved is measured.

The most accurate and convenient method for the determination of a steady current is to measure the potential drop across a standard resistance through which the current flows, as illustrated later on page 402. The current is calculated by Ohm's law. When accurate resistors are required in the laboratory, calibrated resistors of the National Bureau of Standards type[2] should be used. These resistors are constructed of selected manganin wire and are immersed in oil. The limit of error is 0.01 per cent for wattage dissipation up to 0.1 watt and 0.04 per cent up to 1.0 watt. Since the limit of error on a good standard resistance is 0.01 per cent and the potential may be determined versus a standard cell for which the electromotive force is known to 0.01 per cent, the current may be calculated with considerable accuracy. For accurate measurements of current in transference or electrical-heating experiments, it is desirable to have rather constant current. This may be accomplished by means of a mechanical[3] or an electronic[4] current regulator.

MEASUREMENT OF ELECTRICAL ENERGY

The input of electrical energy in calorimetry can be measured very accurately, more accurately in many cases than is justified by the other

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[1] Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," 2d ed., Teubner Verlagsgesellschaft, Leipzig (1916).

[2] Rosa, *J. Research Natl. Bur. Standards*, **4**, 121 (1912).

[3] Longsworth and MacInnes, *J. Opt. Soc. Amer.*, **19**, 50 (1929).

[4] Le Roy and Gordon, *J. Chem. Phys.*, **6**, 398 (1938); Bender and Lewis, *J. Chem. Educ.*, **24**, 454 (1947).

errors in the measurement. The general arrangement is indicated in Fig. 103.

The energy in joules dissipated by the heating coil *H* is obtained by multiplying the potential drop across the coil in volts by the current in amperes and the time in seconds. The current is measured by determining the potential drop across a known resistance *R* placed in series. The current and voltage drop are maintained constant by manual control throughout the experiment.

The heating coil is made of manganin or other wire having a low temperature coefficient of resistance. It may be wound on mica, insulated between two mica sheets, and encased in a silver or copper sheath, or made by winding resistance wire on a threaded tube of anodized aluminum.

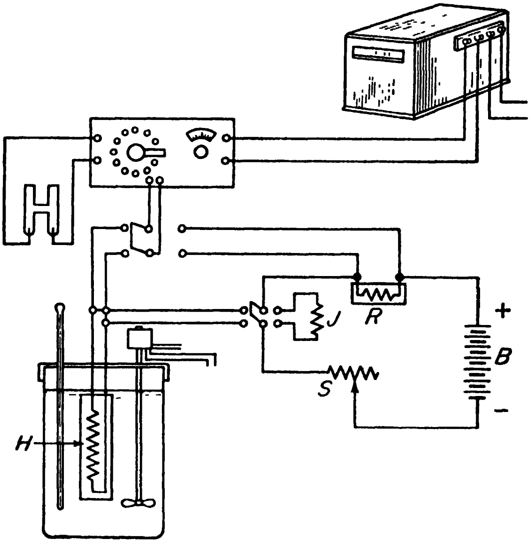

FIG. 103. Measurement of electrical energy in calorimetry.

The current is supplied by steady storage batteries *B* in good condition. The standard resistance *R* consists of uncovered manganin or constantan wire or other alloy having a negligible temperature coefficient of resistance. It is immersed in oil to keep the temperature nearly constant, and it should be proved that the current used in the experiment does not raise the temperature of the wire sufficiently to change its resistance. Any excessive heating effect may be reduced by using wire of larger diameter and greater length. The resistance of *R* should be chosen so that the potential drop across it may be conveniently measured with the potentiometer.

The potentiometer is used to measure the potential drop across the heater or across the standard resistance. It is not permissible to use a voltmeter, because the voltmeter itself carries some current and acts as a shunt around the resistance which is being measured. A voltmeter may be used, however, in a compensation method, if it is used with a galvanometer.

The double-pole double-throw switch is used to connect the potentiometer either to the heating coil or to the standard resistance. It must be of good quality, with perfect contacts and no electrical leakage across the base.

The current is kept constant by continuous adjustment of the rheostats. It is important to have the contacts of the rheostat in good condition. They should be rubbed with emery paper frequently and coated with petroleum jelly. Two rheostats are convenient, one for coarse adjustments and one for fine adjustments.

If plenty of batteries are available, it is well to use a large number and bring the current down with a high resistance. In this way, any slight change in the resistance of the circuit has a slight effect on the current. The circuit is closed by throwing the upper double-pole double-throw switch to the left. Before starting a determination, the lower switch is thrown to the right for several minutes so that the current will flow through a resistance which is approximately equal to the resistance of the heating coil. In this way the battery reaches a steady condition before the experiment is started. If the switch is thrown immediately to the left from the position of open circuit, the battery voltage drops rather rapidly at first and renders difficult the control of the current at a constant amperage. The calculation is simplified and the accuracy is increased if the current is kept constant throughout the experiment.

The time of passage of the current is determined with a stop watch or an electric clock or timer. If the time, as measured with a stop watch, is the least accurate factor, a chronometer may be used, or the time may be increased by decreasing the rate of heating. Stop watches used for such work should be checked frequently, as they are likely to get out of order.

For precision work an equipotential shield is provided to eliminate stray currents. All the instruments are set on a piece of sheet metal, which is grounded, and under every insulator is placed a grounded metal shield.

MEASUREMENT OF TRANSFERENCE NUMBERS AND IONIC MOBILITIES[1]

The moving-boundary method[2] for the determination of transference numbers and ionic mobilities has largely replaced the earlier Hittorf method. This has happened because the velocity of a moving boundary

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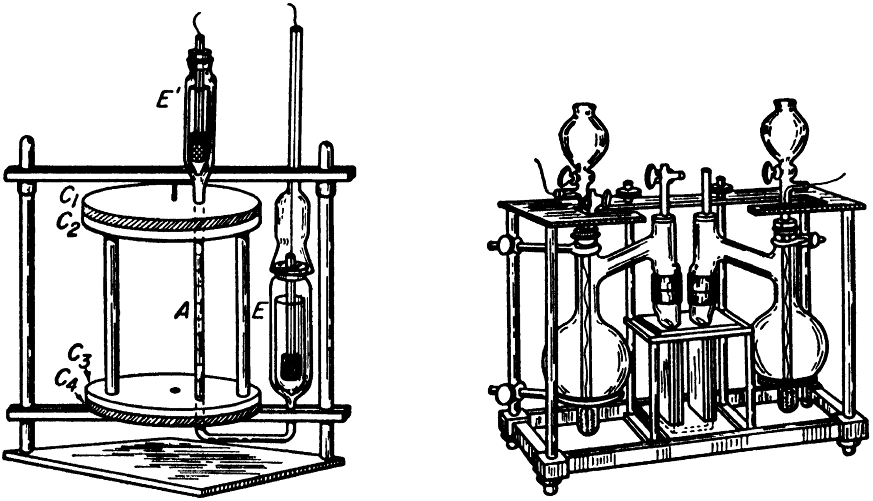
[1] Robinson and Stokes, *op. cit.*, p. 99.

[2] MacInnes and Longsworth, *Chem. Revs.*, **11**, 171 (1932).

may be measured considerably more accurately (to ±0.02 per cent) than the change in concentration of an ion in an electrode chamber of the Hittorf apparatus. The moving-boundary method also has the advantage that it may be applied to mixtures of ions, particularly proteins. In the moving-boundary apparatus used in Exp. 31, the anode was made of metallic cadmium so that the solution following the moving boundary was cadmium chloride. In general, it is desirable to be able to use other salts as following electrolyte, and so there is the problem of forming an initially sharp boundary between the leading electrolyte and following electrolyte. This is best achieved by the shearing mechanism invented by MacInnes and Brighton.[1] The construction of the modern apparatus is shown in Fig. 104*a*. Heavy glass plates C_1, C_2, C_3, and C_4 are ground so that C_1 and C_2, and C_3 and C_4, fit well together and rotate on each other. The moving-boundary tube *A* is mounted in C_2 and C_3. The silver–silver chloride electrodes E' and E are attached to C_1 and C_4. Electrode chambers are required to prevent products of the electrode reaction from reaching the moving-boundary cell. If the boundary is to be a rising boundary, it is formed at C_3-C_4 as follows: Electrode vessel *E* and the tube connecting it to C_4 are filled with the indicator electrolyte; the glass plates C_1 and C_2 are clamped firmly together, and C_3 is rotated with respect to C_4 so that initially the tube *A* does not connect to electrode *E*. Tube *A* and E' are then filled with the leading electrolyte.



(a) (b)

FIG. 104. (*a*) Moving-boundary apparatus; (*b*) electrophoretic cell and electrodes

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[1] *J. Am. Chem. Soc.*, **47**, 994 (1925).

Electrode E' is shut to the atmosphere, and A is rotated into juxtaposition with the hole in C_4, connecting E. Upon application of the current, the sharp boundary formed by this method moves up tube A. The time required for the boundary to move between graduations on A is determined. Since it is not practical to use coulometers for the measurement of current, it is desirable to hold the current constant by one of the devices mentioned on page 422 and to use a potentiometer and an accurately known resistance to measure the current.

It is necessary to apply a correction for the volume change due to the electrode reaction and to the migration of ions into and out of the region between the moving boundary and the closed electrode.[1]

If neither the indicator nor leading electrolyte contains colored ions, it is necessary to locate the boundary by the difference in refractive index of the two solutions. In the case of sharp boundaries, this may be done by focusing a lens on the boundary while placing an illuminated slit behind and somewhat below the boundary. If the refractive-index gradients are not sharp, as in the case of moving protein boundaries, more complicated optical methods must be used for the determination of boundary velocity. One such method is the schlieren optical system which is described in Chap. 19.

Electrophoresis of Proteins. The electrophoretic mobility of a protein is determined by the moving-boundary method.

Before an electrophoresis experiment by the moving-boundary method is performed, the protein solution must be dialyzed in cellophane tubing against a buffer of the desired pH and ionic strength until equilibrium is reached. Simple forms of electrophoresis apparatus have been used for a long time, but it was not until Tiselius of the University of Uppsala announced his improvements in the apparatus in 1937[2] that electrophoresis became a practical and precise tool for studying high-molecular-weight electrolytes and their naturally occurring mixtures, such as plasma. The modern electrophoresis apparatus has been described in a number of review articles.[3] Important features of this apparatus are the low-temperature thermostat and the schlieren optical system. The electrophoresis of proteins is generally carried out at a temperature of 1 to 4°C, because near the temperature of maximum density of the buffer the heating in the cell produced by the current does not produce a significant

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[1] Longsworth, *J. Am. Chem. Soc.*, **65**, 1755 (1943); Longsworth and MacInnes, *J. Am. Chem. Soc.*, **62**, 705 (1940).

[2] Tiselius, *Trans. Faraday Soc.*, **33**, 524 (1937).

[3] Longsworth, *Chem. Revs.*, **30**, 323 (1942); MacInnes and Longsworth *in* Alexander: "Colloid Chemistry," Vol. 5, p. 387, Reinhold Publishing Corporation (1946); Alberty, *J. Chem. Educ.*, **25**, 426, 619 (1948); Alberty *in* Neurath and Bailey: "The Proteins," Vol. I, Part A, Academic Press, Inc., New York (1953).

density variation across the cell, and convection is avoided. A diagram of the electrophoretic cell and electrodes is shown in Fig. 104*b*. The limbs of the U-shaped cell in the center are rectangular in cross section (3 by 25 mm) and 9 cm long. The cell is built in three sections which may be displaced relative to one another to facilitate the formation of sharp boundaries. The electrode vessels, which are filled with buffer, are designed to prevent products of the electrode reaction from reaching the moving protein boundaries. The electrodes consist of silver wire coated with silver chloride and are immersed in a strong salt solution, which is added through the separatory funnels.

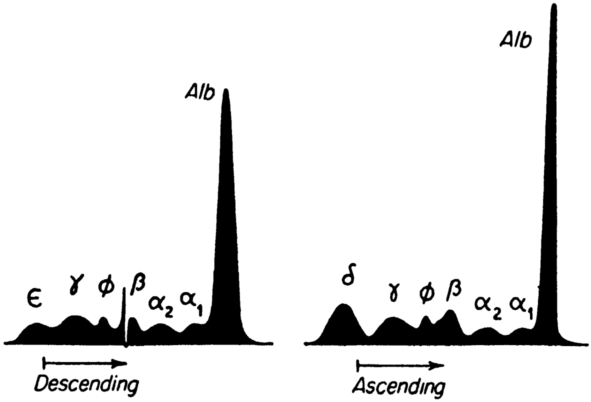

FIG. 105. Electrophoretic pattern of human plasma.

In the electrophoresis of a mixture of proteins, a series of moving boundaries representing the constituents of the solution is obtained upon passage of the current. In the photograph obtained with the schlieren optical system (Chap. 19), each boundary appears as a peak, as illustrated by the electrophoretic pattern of human plasma shown in Fig. 105.

In addition to the α-, β-, and γ-globulins, there is albumin, which makes up over half of normal human plasma, and fibrinogen ϕ. The δ and ϵ boundaries which remain near the initial boundary position do not represent protein components as originally supposed, so they are ignored in obtaining the analysis.[1] The velocity of each boundary may be used to calculate the electrophoretic mobility of the corresponding protein component, and the areas under the various peaks in the schlieren pattern are directly proportional to the changes in refractive index across the various boundaries, so that the relative amounts of the various proteins in the mixture may be calculated. The deviations of protein electrophoresis experiments from ideality and the assumptions involved in

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[1] Longsworth and MacInnes, *J. Am. Chem. Soc.*, **62**, 705 (1940).

making the analysis have been described by Longsworth,[1] Svensson,[2] and Dole.[3]

Diethylbarbiturate buffer of 0.10 ionic strength has been found experimentally to give the clearest resolution of plasma into its components. The pH ranges for commonly used buffers are given in Table 2. The pK values ($-\log K$) indicate the pH of maximum buffering capacity at 25°.

TABLE 2. BUFFERS FOR ELECTROPHORESIS

Buffer pair	pK	pH range
Glycine–hydrochloric acid	2.4	1.0–4.0
Acetic acid–sodium acetate	4.7	4.0–5.5
Cacodylic acid–sodium cacodylate	6.6	5.5–7.5
Diethylbarbituric acid–sodium diethylbarbiturate	7.9	7.5–9.0
Glycine–sodium hydroxide ...	9.7	9.0–11.0

The electrophoresis apparatus is also useful for the separation of proteins or other electrolytes which are otherwise difficult to obtain in a purified state. Samples may be removed from the electrophoresis cell after electrophoresis, or even during the experiment, by immersing a fine capillary in the cell and slowly withdrawing a sample with a syringe.[4] A separation method depending upon simultaneous electrophoresis and convection has been used for the separation of proteins.[5]

MEASUREMENT OF CAPACITANCE

Capacity measurements are required in the study of the dielectric properties of substances, as illustrated, for example, by the determination of dipole moments of polar molecules. Two important methods for making capacitance measurements, the resonance and heterodyne-beat methods, have already been discussed in connection with Exps. 40 and 41. A third method of great importance for measurements on solutions having an appreciable conductance, such as aqueous or alcoholic solutions of proteins, involves the use of the impedance bridge.

The steady current flowing in a d-c circuit depends upon the magnitude of the applied potential and the resistance of the circuit. In the case of alternating current, the equilibrium current is limited by the circuit

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[1] *J. Am. Chem. Soc.*, **67**, 1109 (1945); *J. Phys. Colloid Chem.*, **51**, 171 (1947).

[2] *Arkiv. Kemi., Mineral. Geol.*, **22A** (10), 1 (1946).

[3] *J. Am. Chem. Soc.*, **67**, 1119 (1945).

[4] Tiselius, *op. cit.*, p. 524 (1937); Blix, Tiselius, and Svensson, *J. Biol. Chem.*, **137**, 485 (1941).

[5] Nielsen and Kirkwood, *J. Am. Chem. Soc.*, **68**, 181 (1946).

impedance Z, which depends not only on the circuit resistance R but also on the reactance X, which arises from the capacitance and inductance in the circuit. The reactance, and hence the impedance, is a function of the frequency of the current. The phase relationships between the currents and voltages in the various branches of an a-c circuit depend also upon the reactances of the components involved.

The impedance bridge is a four-terminal network of the type shown in Fig. 106*a* in which the arms are impedances, which will, in general, consist of some combination of resistance, capacitance, and inductance. The familiar Wheatstone bridge is a particular type of impedance bridge where all four arms are pure resistances; in a-c bridge operation this represents a limiting condition only, as indicated below. Two common forms of impedance bridge are shown in Figs. 106*b* and *c*, together with a statement of the conditions which are satisfied at bridge balance, i.e., zero voltage across the detector. These conditions are obtained from the requirements that the voltages appearing at the two points across which the detector is connected (measured relative to some common reference point) must be equal both in magnitude and in phase when the bridge is balanced. The frequency of the applied voltage may or may not enter explicitly into the balance equations; when it does, as in the Wien bridge, the bridge may be used for frequency measurements in terms of known standards of impedance.

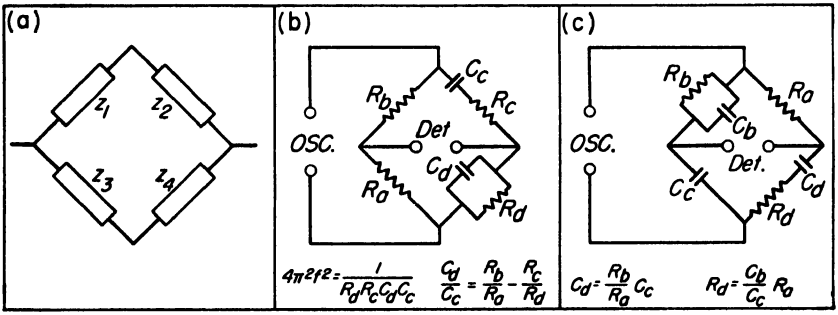

FIG. 106. (*a*) Generalized representation of impedance bridge; (*b*) Wien impedance bridge; (*c*) Schering impedance bridge.

Capacitance measurements with the impedance bridge are usually made by the substitution method. In the parallel-substitution method, a standard capacitor is connected in the bridge circuit in parallel with the unknown capacitor, and the bridge is balanced. The unknown capacitor is then removed, and the bridge again balanced by resetting the standard capacitor. The change in capacitance of the standard required to reestablish balance is then equal to the capacitance of the unknown plus any changes in lead capacitances or other stray-capacitance effects involved. The series-substitution method may also be employed. Because of these lead capacities, etc., it is desirable where possible to use a variable-capacitance cell for the measurement of dielectric constants, as described under Exp. 40, since high accuracy is thereby achieved.

It is customary to think of resistances, capacitances, and inductances as separately realizable entities. In actual practice, however, it is impossible to construct a pure resistance, capacitance, or inductance. Any circuit element is an impedance in which one contribution may predominate but in which all three appear. As the operating frequency increases, this fact becomes more and more important. In Fig. 107 are given the schematic representations of capacitance, inductance, and resistance, showing to a first approximation how each of these circuit elements behaves in an a-c circuit.

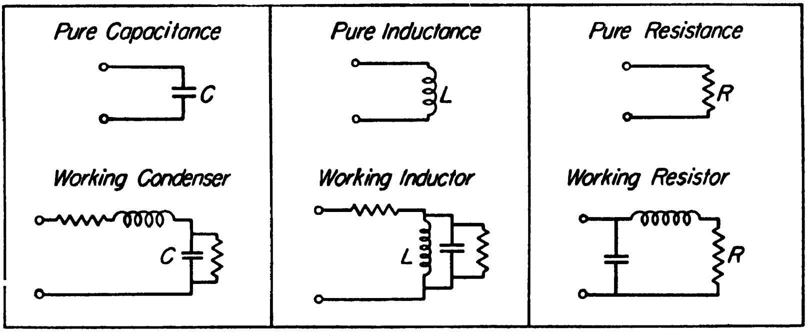

FIG. 107. Schematic representation of working circuit elements.

Careful attention to proper shielding and grounding of the bridge is required in order to prevent the environment, including the operator, from influencing the performance of the bridge. Successful work, particularly at high frequencies, requires a sound understanding of the theory of a-c bridge circuits, which is treated comprehensively by Hague[1] and Hartshorn,[2] and a good background of practical experience in the field.

The power source for the bridge must have adequate frequency stability and power output. At audio frequencies the resistance-capacitance-coupled oscillator mentioned above is a versatile and reliable unit. At radio frequencies crystal-controlled oscillators or stable variable-frequency oscillators of several types are available. Suitable power sources in practically any frequency range are available from commercial manu-

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[1] "Alternating Current Bridge Methods," 5th ed., Sir Isaac Pitman & Sons, Ltd., London (1945).

[2] "Radio-frequency Measurements by Bridge and Resonance Methods," John Wiley & Sons, Inc., New York (1941).

facturers, such as General Radio Co., Boonton Radio Corp., Hewlitt-Packard Co., etc.

Electronic circuits make it possible to produce a detector of sufficient sensitivity to make available the maximum precision of modern bridges. It is generally advisable to employ a detector circuit which will respond preferentially to the particular frequency for which the results are desired. The detector usually consists of an amplifier where the input is derived from the bridge and whose output is fed for indication into a vacuum-tube voltmeter. The impedance of the detector should be high, of course, but this requirement is easily satisfied by the vacuum-tube detector. At audio frequencies earphones or an amplifier-earphone combination may be employed. At radio frequencies a radio receiver equipped to receive continuous wave signals may also be used.

The Schering bridge has been used extensively by Fuoss[1] in studies of the dielectric behavior of plastics. Oncley[2] and Shaw[3] have described bridge circuits based on the use of the Type 516-C radiofrequency bridge previously manufactured by the General Radio Co. This unit has been superceded by the Type 916-A bridge. This same company produces a Type 821-A Twin-T Impedance Measuring Circuit which has been used by Smyth and associates.[4] The frequency range covered by this circuit extends from 460 kilocycles to 40 megacycles. Types of cells suitable for use in this work are described by these authors, and by Elliott and Williams,[5] Albright,[6] and Ferry and Oncley.[7]

The development of experimental methods for work in the microwave region, i.e., at the extremely high frequencies of the order of 10^{10} cycles/sec, has made available important data on the dielectric behavior of substances under conditions not accessible previously in experimental work. The technique and equipment employed in such work have been described by Roberts and von Hippel[8] and by Collie, Hasted, and Ritson.[9]

[1] *J. Am. Chem. Soc.*, **59,** 1703 (1937), and succeeding papers.

[2] *J. Am. Chem. Soc.*, **60,** 1115 (1938).

[3] *J. Chem. Phys.*, **10,** 609 (1942).

[4] Conner, Clarke, and Smyth, *J. Am. Chem. Soc.*, **64,** 1379 (1942).

[5] *J. Am. Chem. Soc.*, **61,** 718 (1939).

[6] *J. Am. Chem. Soc.*, **59,** 2098 (1937).

[7] *J. Am. Chem. Soc.*, **63,** 272 (1941).

[8] *J. Applied Phys.*, **17,** 610 (1946).

[9] *Proc. Phys. Soc. (London)*, **73,** 71 (1948).

CHAPTER 23

ELECTRONICS

One of the most important developments in experimental physical chemistry in recent years has been the increased application of electronic methods in the solution of problems of control and measurement; a sound working knowledge of electronics is thus of great value to the experimental scientist. It is our present purpose to discuss some of the important points concerned from a qualitative point of view. A thorough treatment of the principles involved is available in such texts as those of Reich,[1] Terman,[2] and Eastman;[3] an introduction to experimental work in electronics of particular value to chemists has been provided by Müller, Garman, and Droz.[4] Current developments in the field are reported in *Electronics* magazine and in the *Review of Scientific Instruments* and in the technical literature issued by manufacturers of electronic components.

Thermionic Emission and the Space Charge. A metallic conductor is characterized by the presence within it of electrons which are so loosely bound that they can move about with relative freedom, but which under ordinary circumstances cannot escape from the metal because they do not possess enough energy to break through the potential barrier at the surface. As the temperature of the conductor is raised, however, the average kinetic energy of these free electrons is increased and eventually becomes large enough so that electrons can escape from the metal into the space around it. This phenomenon is termed *thermionic emission.*

If a given metallic conductor is heated in a vacuum, electrons are emitted by it at a rate which depends upon its temperature. As the electron density in the space around the emitter increases, forces arise which oppose the net transfer of additional electrons from the emitter,

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[1] Reich, "Theory and Applications of Electron Tubes," 2d ed., McGraw-Hill Book Company, Inc., New York (1944).

[2] Terman, "Radio Engineers' Handbook," McGraw-Hill Book Company, Inc., New York (1943); "Radio Engineering," 3d ed., McGraw-Hill Book Company, Inc., New York (1947).

[3] Eastman, "Fundamentals of Vacuum Tubes," 3d ed., McGraw-Hill Book Company, Inc., New York (1949).

[4] Muller, Garman, and Droz, "Experimental Electronics," Prentice-Hall, Inc., New York (1945).

and a dynamic equilibrium is established with a definite electron density in the space around the emitter. The cloud of electrons so produced around the emitter is termed the *space charge.*

The operation of most electron tubes depends upon thermionic emission, but electrons may be released from metal electrodes in a vacuum tube by other methods as well. If a high-velocity electron strikes the electrode, one or more electrons within the metal may be given enough energy to escape; this effect is referred to as *secondary emission.* In the *photoelectric* effect, the energy required to permit electron emission is obtained by the absorption of light quanta of suitable frequency. Electrons may also be extracted from metals by the action of very strong electric fields, as in gas-filled tubes.

ELECTRON TUBES

An electron tube consists of a number of electrodes mounted in an envelope of glass or metal, which is usually highly evacuated but which, for specific applications, may contain a suitable gas at low pressure. One electrode, the *cathode*, supplies the electrons required for the operation of the tube. In the high-vacuum tubes and in most gas-filled tubes, the electrons are produced by thermionic emission. The cathode may be of the filamentary type, i.e., a wire heated directly by the passage of an electric current, or of the indirectly heated type, in which the electron-emitting material is placed on the outside surface of a sleeve which is heated by radiation and conduction from a filament placed within it. The indirectly heated cathode has the obvious advantage that all points of the emitting surface are always at the same potential, which is not true of the filamentary type.

The other electrodes serve to collect the electrons passing through the tube or to control their flow. Most of the collecting is done by one electrode in particular, which is called the *plate.* The control electrodes are usually referred to as *grids.* The schematic representation of these tube elements and other electronic components is shown in Fig. 108, and some useful additional information is given in the Appendix. An excellent text on vacuum tubes proper as distinct from applications has been made available by Spangenberg.[1]

The Diode and Rectification. The diode is the simplest electron tube and contains two electrodes, a cathode and a plate. When the cathode is heated to its operating temperature, the space charge considered above is produced around it. If the plate is maintained at a potential positive with respect to the cathode, electrons will be drawn to it from the space charge, where the electron density will be maintained by a net transfer

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[1] "Vacuum Tubes," McGraw-Hill Book Company, Inc., New York (1948).

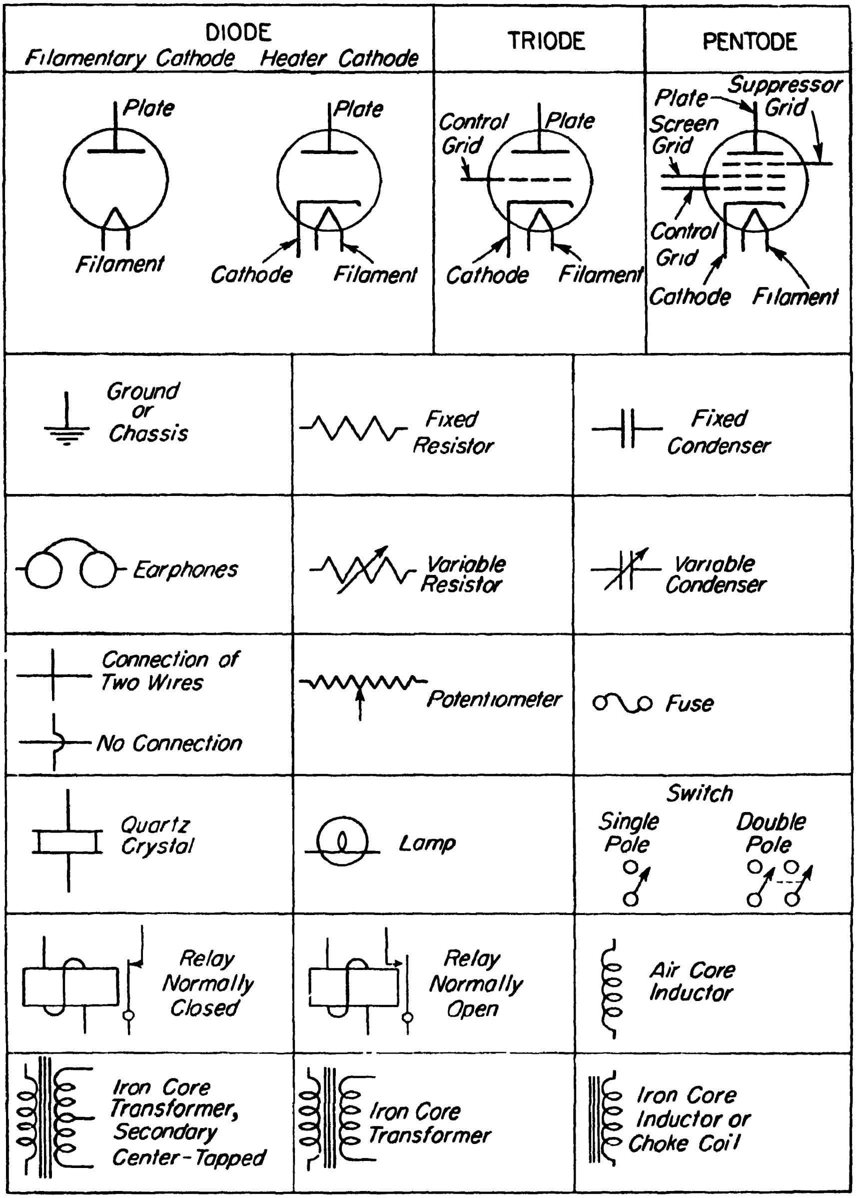

FIG. 108. Schematic representation of circuit components.

of electrons from the hot cathode. When the plate is negative with respect to the cathode, no electrons will be attracted to it. The diode thus provides a means of controlling the direction of flow of an electric current.

This property is applied in the conversion of alternating current to direct current, a process called rectification. The basic circuit employed is shown in Fig. 109*a*. Let an alternating voltage E_{AB} be impressed across the input terminals. During one half-cycle of the applied voltage, the plate will be positive with respect to the cathode, and current will flow through the tube and through the series load resistor R, producing a potential drop E_o across it. The magnitude of the current flowing depends on the magnitude of the impressed voltage E_{AB}, so that E_o will vary during this half-cycle as shown in Fig. 109*b*. During the other half of the cycle, the plate is negative with respect to the cathode; no current flows through the tube, and the potential drop E_o across the load resistor R is zero. For an obvious reason this circuit is called a half-wave-rectifier circuit. The maximum value of E_o is less than the crest value of E_{AB} because of the potential drop between the cathode and plate required to keep the electrons moving through the tube.

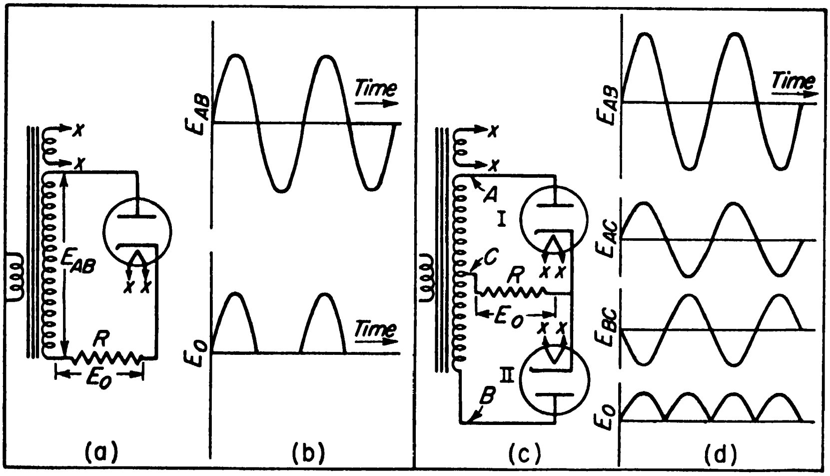

FIG. 109. Diode rectification and voltage wave forms. (*a*) and (*b*) Half-wave-rectifier circuit; (*c*) and (*d*) full-wave-rectifier circuit.

Both halves of the a-c wave may be utilized by employing two diodes in the circuit of Fig. 109*c*. In this case the secondary winding of the power transformer is tapped at its mid-point C, which is connected through a load resistor R to the cathodes of the two diodes; during the half-cycle of the applied alternating voltage in which point A is positive with respect to C, point B will be negative with respect to C, and only diode I will conduct, producing a current through R. During the next half-cycle, B will be positive and A negative with respect to C, and only diode II will conduct, producing a current which flows through R *in the same direction* as that of the previous half-cycle. The output voltage E_o across the load resistor R of this *full-wave-rectifier circuit* then takes the form shown in Fig. 109*d*. The conversion of this pulsating voltage to obtain a steady d-c potential is discussed below under Power Supplies.

The diode illustrates the fundamental property of electron tubes in general of permitting current flow in one direction only. If the potential of the diode plate is held constant, then the current flowing through the tube will also remain constant. The most important applications of electron tubes result from the control of the magnitude of the tube current which is made possible by the introduction of additional electrodes.

The Triode and Amplification. The triode contains, in addition to a cathode and a plate, a third electrode called the *control grid* (or merely *grid*), which ordinarily consists of a wire helix surrounding the cathode and extending its full length. As is shown in Fig. 110, the grid is much closer to the cathode than is the plate.

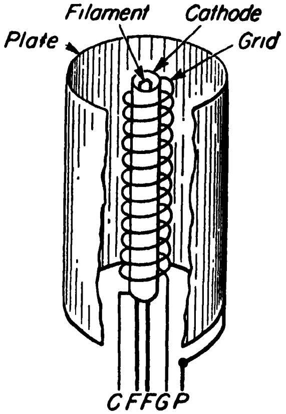

FIG. 110. Electrode arrangement of triode.

The force acting on the electrons of the space charge in the triode depends upon the potentials of both the grid and the plate; because it is closer to the cathode, the grid exerts the greater influence upon the flow of current through the tube. For a given plate voltage, as the grid bias is increased, i.e., as the grid is made more negative with respect to the cathode, the plate current is decreased; a decrease in grid bias results in an increase in the current flowing to the plate. A quantitative expression of these relationships is found in the *characteristic curves* for the particular tube under consideration, such as those given in Fig. 111 for the 6J5, a common triode. It is seen that the control grid acts like a valve which controls the flow of electrons to the plate.

The triode is normally operated with the grid slightly negative with respect to the cathode. Under these conditions, the current flowing from the cathode to the grid will be very small, although it will not be zero. (Some of the electrons emitted by the cathode possess fairly high energies and so are able to travel to the grid in spite of its negative potential; positive ions resulting from residual gas in the tube will travel to the grid; thermionic emission of electrons from the grid may take place if the grid becomes hot, etc.) The small grid current means that very little power must be expended in the grid circuit to control the potential of the grid and hence to control the relatively much larger power in the plate circuit.

Amplification is made possible with the triode by connecting a suitable load impedance, such as a resistance, in series with the plate of the tube,

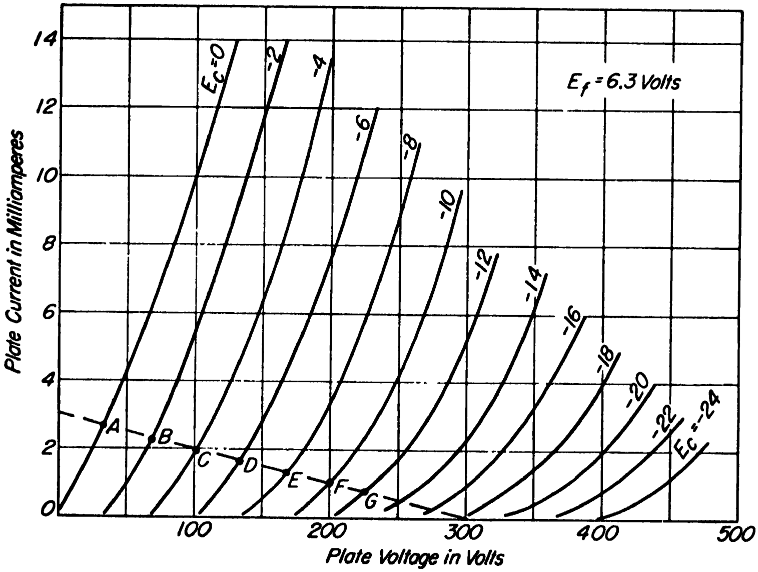

FIG. 111. Characteristic curves for the 6J5 triode. Broken line is load line for plate load resistor of 100,000 ohms, plate supply voltage 300 volts.

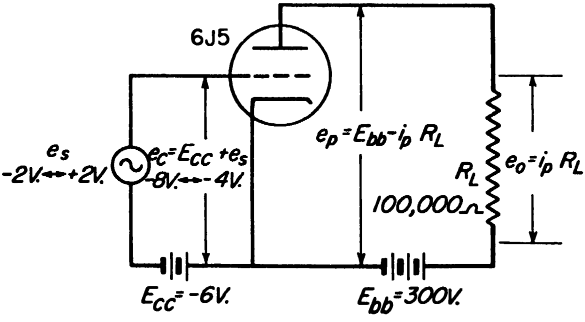

FIG. 112. Circuit diagram for simple triode amplifier stage.

as shown in Fig. 112. The plate current of the tube then must flow through this resistance, across which is produced a potential drop which will change whenever the plate current changes. When an alternating voltage source e_s is connected in the grid circuit, the grid potential will vary with the time, causing the plate current and hence the potential drop e_o across the load resistor R_L to vary with the time. The variation in e_o is greater than the variation e_s of the grid potential which causes it, so that amplification of the signal voltage is accomplished.

The performance of the tube in amplification can be characterized quantitatively by use of the curves of Fig. 111. It must be noted that the plate voltage of the triode will not be constant when it is acting as an amplifier, because of the variation of the potential drop across the load resistor. For a given value of grid bias, the plate voltage will have the value which produces a plate current such that the sum of the plate voltage and the potential drop across the load resistor, $e_o = i_pR_L$, is equal to the plate supply voltage.

For the circuit of Fig. 112, when the alternating signal voltage e_s is zero, the grid bias is -6 volts. Reference to Fig. 111 shows that the plate current will then be 1.65 milliamp, corresponding to a plate voltage e_p of 135 volts and a drop e_o across the load resistor of 165 volts, for the required total of 300 volts. During the half-cycle when e_s is positive, the grid bias will be decreased, yielding a higher plate current and lower plate voltage; the minimum value of grid bias is -4 volts, for which the plate current is found to be 1.98 milliamp, $e_p = 102$ volts, and $e_o = 198$ volts. The maximum grid bias is -8 volts, for which $i_p = 1.33$ milliamp, $e_p = 167$ volts, and $e_o = 133$ volts. The corresponding data for various grid-bias values are summarized in Table 1.

TABLE 1. CURRENT-VOLTAGE RELATIONSHIPS FOR AMPLIFIER CIRCUIT OF FIG. 112

Point on Fig. 111	Grid voltage e_c	Plate current i_p, milliamp	Plate voltage e_p	$e_o = i_pR_L$
A	0	2 66	34	266
B	− 2	2.32	68	232
C	− 4	1.98	102	198
D	− 6	1 65	135	165
E	− 8	1.33	167	133
F	−10	1.01	199	101
G	−12	0.70	230	70

The points *A*, *B*, etc., represent the intersections with the various characteristic curves of a straight line called the "load line," which gives the plate voltage of the tube as a function of the plate current. This line which has the equation $e_p = E_{bb} - i_pR_L$ is shown in Fig. 111. It thus is the straight line drawn from the plate supply voltage point on the voltage axis ($i_p = 0$, $e_p = E_{bb}$) to the current axis at the point ($e_p = 0$, $i_p = E_{bb}/R_L$). The quantity E_{bb}/R_L represents the current which would flow through the load resistor if the whole supply voltage were impressed across it.

Figure 113 shows how the plot of plate current i_p versus the grid voltage e_c, called the dynamic transfer characteristic, is used to determine the form of the output voltage e_o from that of the signal voltage, e_s. If the wave form of the output voltage is to be the same as that of the input voltage, i.e., if distortionless amplification is to be obtained, the dynamic transfer characteristic must be a straight line. In the case at hand, it is seen that the amplification will be nearly distortionless and that the change in grid voltage from -8 to -4 volts produces a change in the voltage across R_L of 65 volts, a sixteenfold voltage amplification.

The amplification that can be obtained with the triode is limited in practice by interelectrode-capacitance effects, among which the plate-to-grid capacitance is of primary importance. That is, the plate and grid act as the two conductors of a condenser with a vacuum dielectric; the capacitance involved here is not large, of the order of 3 or 4 $\mu\mu$f usually, but it is large enough to cause instability and otherwise impair the performance of the tube as an amplifier at high frequencies or at high levels of amplification. In addition, the change of plate voltage with plate current in the triode amplifier reduces its effectiveness. As the grid bias decreases with an increase in signal voltage, the plate voltage decreases; this plate-voltage change opposes the change in plate current caused by the grid and thereby reduces the effective amplification. To eliminate these difficulties, the pentode, or five-electrode electron tube, was developed.

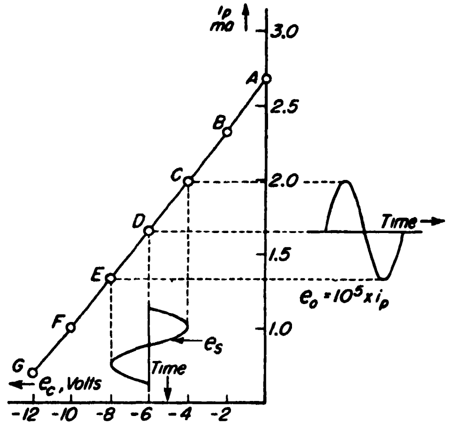

FIG. 113. Dynamic transfer characteristic for the 6J5 triode with 100,000-ohm plate load resistor.

The Pentode. The two additional electrodes of the pentode are grids which are placed between the control grid and the plate. The one nearest the control grid, called the *screen grid*, is maintained at a constant potential positive with respect to the cathode and acts as an electrostatic shield, which may reduce the plate-to-grid capacitance to a value as low as 0.005 $\mu\mu$f. Because of the shielding action of the screen grid, the plate voltage has relatively little effect except at low plate voltages in determining the plate current, which is principally controlled by the control-grid and screen-grid potentials. The screen grid also acts as a collector of electrons, but because its effective area is much smaller than that of the plate, this screen-grid current is small compared to the plate current under normal operating conditions.

The fifth electrode in the pentode is called the *suppressor grid* and is located between the screen grid and the plate. It is generally operated at cathode potential, and its function is to create a potential distribution between the screen grid and the plate which will cause secondary electrons emitted from the plate to return to the plate. If the suppressor grid were not provided, the secondary electrons would go in part to the screen grid, with a resultant deleterious effect on the performance of the tube. Secondary emission takes place at the plate of the triode also, of course, but in that case the secondary electrons have no place to go except back to the plate.

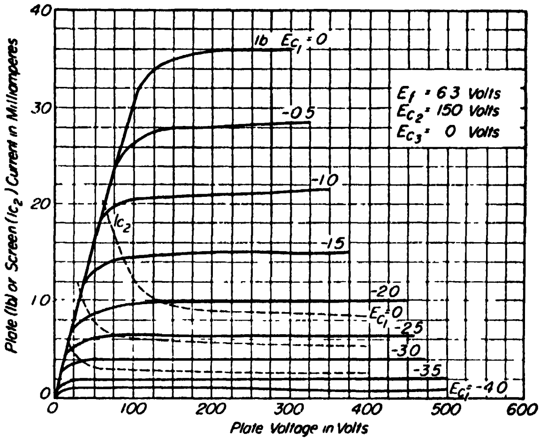

FIG. 114. Characteristic curves for the 6AC7 pentode. Effect of plate voltage and control-grid bias on plate current for constant screen- and suppressor-grid potentials.

Characteristic curves for a typical pentode are shown in Fig. 114. The pentode is probably the type of electron tube in most extensive use. It permits high-voltage amplification at both low and high frequencies and is usually characterized by a lower control-grid current than a triode with the same power-handling capacity.

POWER SUPPLIES

In the various circuits considered in this chapter, the source of d-c power has been represented as a battery. In certain applications or in portable self-powered equipment, battery power sources are useful in providing a constant voltage, but in general an electronic d-c power supply operated by alternating current is desired.

Full-wave Rectifier. A typical circuit employed for this purpose is given in Fig. 115. It is based on the full-wave-rectifier circuit of Fig. 109, the initial output of which is a pulsating voltage which is the equivalent of a steady d-c voltage plus an alternating component called the *ripple voltage.* In this case, the main component of the ripple voltage is of the frequency of 120 cycles/sec. For the reduction of the ripple voltage in the output voltage, there are employed one or more filter stages of the type shown, which is called an L-section, or choke-input, filter. The iron-core inductance, or *choke* coil, of each stage offers a high impedance to alternating current but a much lower resistance to direct current. The condenser, on the other hand, offers a comparatively low impedance to alternating current, while permitting no passage of direct current. By use of a suitable number of stages, the ripple voltage may be reduced as far as desired; in noncritical applications such as relay circuits, etc., only one filter stage is necessary.

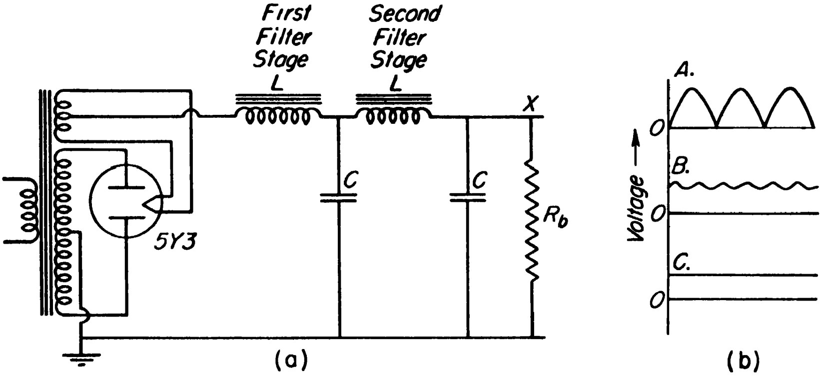

FIG. 115. (*a*) Direct-current power-supply circuit; (*b*) voltage wave forms in d-c power-supply circuit. *A*, output with no filter stage, *B*, output with one filter stage, *C*, output with two filter stages.

The chokes should always be placed in the lead which is *not* grounded, which is usually (but not necessarily) the positive lead. There is considerable capacitance between the secondary of the power transformer and its primary, one side of which is grounded. This capacitance to ground will by-pass some a-c ripple around the chokes if they are put in the grounded side of the filter. In order for the filter to function effectively, the current through it must not fall below a minimum value. The bleeder resistor R_b provides this minimum current flow and also serves to permit the condensers to discharge rapidly when the power supply is turned off, a safety factor of importance.

The tube illustrated is called a full-wave rectifier and corresponds to two diodes in a single envelope with a common filamentary cathode. The output voltage at X depends upon the secondary voltage of the transformer and upon the current furnished by the rectifier, which determines the potential drops across the tube and the chokes. The output voltage of the circuit will then vary with fluctuations in the line voltage across the transformer primary and with the current drawn by the load. This undesirable feature may be eliminated by the addition of a voltage-regulating section, the possible types of which are described in standard references.[1]

Dry-disc Rectifiers. When large direct currents are required at low voltages, the so-called dry-disc rectifiers are used. In Fig. 116 is shown the construction of a typical unit of this type, whose operation depends upon the discovery that when two suitable plates are placed in contact, electron flow can take place readily in one direction but only with difficulty in the other direction. For this reason the process is referred to as contact rectification. Suitable combinations of plates for this purpose include:

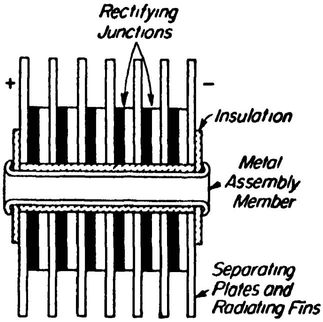

FIG. 116. Construction of a dry-disc rectifier.

1. Copper–copper oxide. The oxide is present as a coating on the copper. Electrons flow freely from the copper to the copper oxide but with difficulty in the reverse direction.
2. Selenium-alloy base plate. An aluminum base plate is coated with selenium over which an alloy is sprayed. Electrons flow readily from alloy to selenium but not in the reverse direction.
3. Magnesium–copper sulfide. The copper sulfide is present as a coating on copper. Electrons flow freely from the magnesium to the copper sulfide but not in the reverse direction.

Dry-disc rectifiers are compact, silent, dependable, and rugged and have a high current capacity. Each type of disc assembly has a characteristic reverse voltage rating, which represents the maximum voltage for which an adequate rectifying action is maintained. Where a voltage output greater than the reverse voltage rating is required, two or more units are used in series as shown in Fig. 116. The ripple voltage in the rectifier output is removed by use of filters as described above.

Alternating-current Voltage Regulators. The ordinary 110-volt 60-cycle a-c line voltage is subject to fluctuations arising primarily from the changing load on the line. Regulating units of several kinds are available for providing a constant-voltage output at the line frequency. In one type,[2] the output power is not drawn directly from the line but rather from a resonant circuit, the voltage across which tends to remain con-

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[1] Reich, *op. cit.*; Terman, *op. cit.*

[2] Chute, "Electronics in Industry," p. 437, McGraw-Hill Book Company, Inc., New York (1946).

stant despite fluctuations in the line feeding it. In another type, the output voltage is derived from an autotransformer, the primary voltage of which is changed as required to produce regulation by feedback from an electronic circuit actuated by fluctuations in the output voltage.

The main point to consider in the selection of an a-c voltage regulator is the nature of the load to be supplied. The design of some regulators is such that a constant-voltage output will be obtained only if the load has a specified value. Others, such as the electronically controlled type, give a constant voltage for wide variations in load and hence are more versatile.

Constant Current Supply. When it is desired to maintain a constant d-c current through a changing resistive load, as in Exp. 31, the circuit of Fig. 117 may be employed. Its operation is seen to depend upon the fact that the plate current of the pentode tube is nearly independent of the plate voltage when the control-grid and screen-grid potentials are constant, provided that the plate voltage never drops too low. As the resistance in the plate circuit increases, the potential drop across it increases and the plate voltage of the tube decreases. The resulting change in plate current depends upon the specific properties of the pentode employed. For small currents, the 6AC7 tube specified is very satisfactory. The magnitude of the plate current is controlled by adjusting the grid bias of the tube. Since the 6AC7 plate current changes rapidly with its grid bias, use of a battery to obtain a constant bias voltage is necessary.

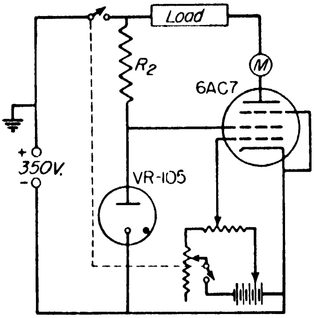

FIG. 117. Circuit diagram for constant current supply.

Constancy of screen-grid voltage is assured by use of the special tube shown, the VR-105, which is called a voltage-regulator tube.[1] This type of tube contains a cold cathode of large area, an anode of small area, and a gas, such as argon, at low pressure. It is found that such a tube is characterized by a practically constant potential drop from cathode to anode and a constant current density at the cathode provided that the current lies within limits specified by the manufacturer. If the voltage across the series combination of R_2 and the tube changes, the current through the tube will change but the potential drop across it will not, because the area covered by the discharge at the cathode will simply change as required to maintain a constant current density. The total change in voltage appears across R_2, where it will not affect the pentode screen potential. The resistor R_2 must be large enough to restrict the maximum

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[1] Reich, *op. cit.*

current through the VR tube to a safe value, or the voltage-regulating property of the tube will be lost.

MISCELLANEOUS ELECTRONIC CIRCUITS

Vacuum-tube Relay. A current of the order of at least 6 milliamp is required for the operation of the usual electromagnetically actuated relay. It is often desired to operate such a relay by means of a control device which either cannot produce a current of this magnitude, such as a phototube, or with which such a current would produce undesirable effects. In this latter category falls the ordinary mercury thermoregulator, the flow of current through which may result in fouling of the capillary due to arcing at the mercury-air interface as contact is made or broken at the control point. The ability of the vacuum tube to control a large amount of power through the expenditure of a small amount of power permits a straightforward solution of the problem.

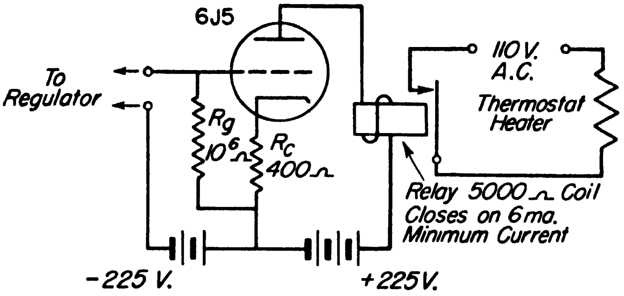
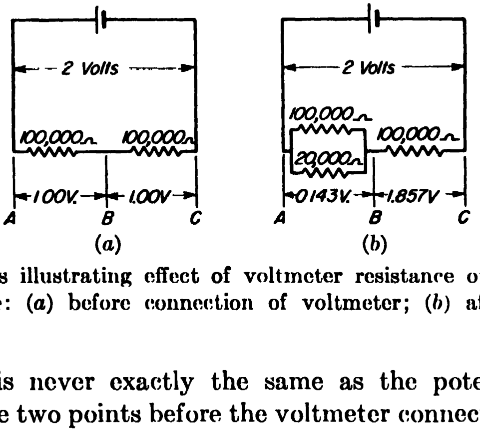


Fig. 118. Vacuum-tube relay circuit.

In Fig. 118 is given a typical vacuum-tube relay circuit employed in thermostat regulation. When the regulator contacts are open, the bias on the tube is maintained by the flow of plate current through the cathode resistor R_c. Reference to Fig. 111 shows that the grid bias will be approximately −4 volts, the plate current 10 milliamp, the plate voltage 170 volts, and the potential drop across the relay coil 50 volts. (Ten milliamperes flowing through the 400-ohm cathode resistor produces a potential drop of 4 volts.) The relay contacts will hence be closed, and current will flow through the thermostat heater until the regulator contacts are closed by expansion of the mercury. When this occurs, a potential drop of 22.5 volts is produced across the resistor R_g; the grid bias is thus changed to −22.5 volts, and the plate current of the tube is reduced to zero. (When there is no current flowing through R_c, the potential drop across it is also zero.) The relay contacts are thus opened, and the heating current is turned off. It is to be noted that the maximum current flowing through the mercury interface of the regulator is only 22.5×10^{-6} amp, a value which can be reduced still further, if required, by adjustment of the circuit parameters or use of a different tube. The larger R_g is, the smaller is the current that flows in the regulator circuit; the maximum value of R_g for a particular tube is limited by the possibility of grid current flow as indicated above. It is not possible to omit R_g, because in such a case the grid is left floating when the regulator contacts are open, and the performance of the tube becomes erratic.

Vacuum-tube Voltmeters. The measurement of d-c voltages arising in very high resistance systems cannot be carried out by the use of conventional electromagnetic voltmeters or potentiometric techniques. A voltmeter will show the potential difference existing across its terminals, but this value is never exactly the same as the potential difference between the same two points before the voltmeter connections were made and often is markedly different from it. For example, consider the simple case illustrated in Fig. 119. It is desired to measure the potential drop between the points A and B, the value of which is obviously 1 volt. A voltmeter giving a full-scale deflection for 1 volt will have an internal resistance which will normally be 1,000 ohms or less, but which may be as high as 20,000 ohms. If a meter of this latter type is connected across AB, it will read 0.143 volt, because the resistance between A and B has been changed to 16,666 ohms. It is obvious, then, that when the resistance of the voltmeter is not large compared with that of the source whose potential is being measured, a large error will result. It is necessary to employ a measuring instrument which itself draws negligible power from the source under measurement in order to obtain an accurate result.



(a) (b)

FIG. 119. Diagrams illustrating effect of voltmeter resistance on measurement of potential difference: (a) before connection of voltmeter; (b) after connection of voltmeter.

The potentiometric method is often recommended as one which permits a d-c potential measurement to be made without drawing any current from the source. This condition holds, of course, when the potentiometer is exactly balanced against the source, but in order to determine when balance is achieved it is necessary that enough current flow through the source to actuate the balance-detecting galvanometer (compare Fig. 37). The precision with which the balance can be established depends upon the sensitivity of the galvanometer and upon the resistance of the galvanometer circuit, which is determined by the resistance in the source as well as that contributed by the potentiometer proper. Suppose a potentiometer is used to measure the potential across *AB* of Fig. 119. Let us suppose that a galvanometer giving a deflection of 0.005 μamp mm^{-1} is employed (this type of galvanometer is regularly used in practical work), and that a galvanometer deflection of 0.2 mm can be reliably distinguished from zero deflection. The minimum uncertainty in the potential measurement is then that potential required to produce a current of 0.001 μamp (10^{-9} amp), through a resistance somewhat greater than 100,000 ohms, or 0.1 millivolt. The measurement could then be carried out with an accuracy of the order of 0.1 per cent.

In many cases, as with a glass-electrode system for pH measurements, it is desired to measure a potential difference of the order of a volt arising in a source whose resistance may be 10^8 ohms or more, with a desired accuracy of the order of 1 millivolt. If this were to be accomplished with a potentiometer, it would be necessary to use a galvanometer with which a current of 10^{-11} amp could be reliably distinguished from zero current, a procedure which is not practical. Even higher-resistance sources are involved in other cases, as when a very small current is measured by determination of the potential drop it produces in flowing through a very high resistance. There is also the problem of measuring a-c potentials in systems of high resistance, a problem of extreme importance in experimental work of some types.

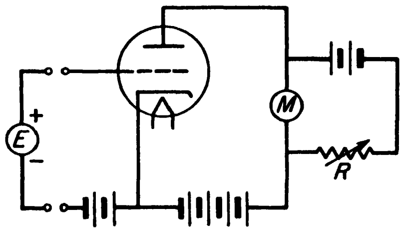


FIG. 120. Basic d-c vacuum-tube–voltmeter circuit. *E* represents potential difference to be measured.

It has previously been pointed out that very little power must be expended in the grid circuit of an electron tube in order to control its plate current. This property of the tube is the basis of the design of the vacuum-tube voltmeter, the basic circuit for which is shown in Fig. 120. The grid bias of the triode is adjusted to a convenient operating value when the input terminals are short-circuited. The resistance *R*, which must be large compared with that of the meter, is adjusted to make the meter in the plate circuit read zero; in this fashion a sensitive meter may be used to yield increased accuracy in the measurement of *changes* in the plate current of the tube. The unknown voltage is then connected across the input terminals; the increase in plate current of the tube is a measure of the unknown voltage. The meter is calibrated by use of known voltages.

The input resistance of the vacuum-tube voltmeter, i.e., the resistance it offers to the source, is extremely high, because the only current that has to flow through the source is the grid current of the triode. This current will be very small when the grid is negative with respect to the cathode; its specific magnitude will depend upon the particular tube used and the actual operating conditions. With selected standard tubes, an input resistance of the order of hundreds of megohms may be obtained, and with special tubes even higher values are possible. Naturally, in practice the circuits employed are considerably elaborated over that of Fig. 120. Amplification of small voltages may be provided and inverse feedback incorporated to improve stability of operation and linearity of response.

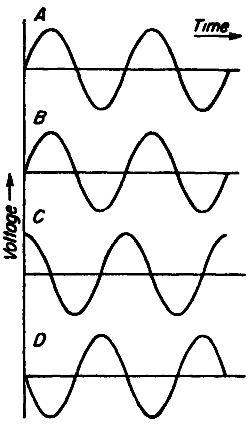


FIG. 121. Phase relationships for alternating voltages.

The accuracy of the vacuum-tube voltmeter is of the order of 2 per cent for the measurement of d-c voltages of moderate magnitudes. This accuracy may seem low compared with that of standard potentiometric measurements, but it is to be remembered that the vacuum-tube voltmeter makes practical measurements which often cannot be made in any other way.

Phase of Alternating Voltages. Two alternating voltages are said to be *in phase* if they pass through corresponding points of their respective cycles at the same time, as, e.g., voltages A and B of Fig. 121. Since one cycle of the sine wave $E = A \sin \theta$ is equivalent to 360°, or 2π radians, voltages A and C are said to be 90° *out of phase*, while A and D are 180° out of phase. A is said to lead C by 90° and D by 180°. The general expression for a sine-wave voltage of frequency f is

$$E = A \sin (2\pi ft + \delta)$$

where A determines the maximum amplitude of the voltage, and δ determines the value of the voltage at the time $t = 0$. The quantity δ is called the *phase angle* and is usually expressed in degrees.

Feedback. The term *feedback* refers to the process of deriving from the output of an amplifier stage a voltage E_f, called the *feedback voltage*, and applying it in series with the grid signal of the same or an earlier stage. The result of this process depends upon the phase of the feedback voltage relative to that of the grid signal. If the two voltages are 180° out of phase, *inverse*, or *negative*, *feedback* results. If they are in phase, *positive*, or *regenerative, feedback* results. Inverse feedback is sometimes referred to as *degenerative feedback.*

Inverse feedback is illustrated in the circuit of Fig. 122. The input signal E_i is applied in series with the fraction $r_2/(r_1 + r_2)$ of the output voltage E_o of the amplifier stage. Since the plate voltage of an electron tube with a resistive plate load is decreased by an increase in grid voltage, the output voltage E_o is 180° out of phase with the input voltage. The feedback voltage $E_f = [r_2/(r_1 + r_2)]E_o$ is then 180° out of phase with E_i; the net grid excitation of the amplifier is reduced, and its amplification is reduced. At the same time the distortion of the input wave by the amplifier is reduced, and the stability of the amplifier is increased.

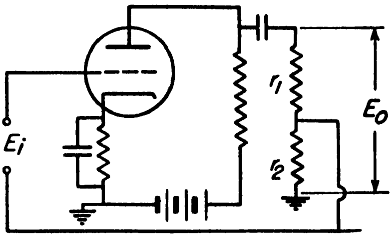


FIG. 122. Amplifier stage illustrating inverse feedback.

Positive feedback is to be avoided in amplifiers but is fundamental to the operation of some types of oscillators, as described below.

Vacuum-tube Oscillator. An oscillator circuit is one which can be used to convert d-c power into a-c power. Of greatest importance are the so-called feedback oscillators, in which the grid excitation for an amplifier is derived by diverting, or "feeding back," part of the amplifier output into the grid circuit. Let us assume that the application of a voltage E_s to the input of the amplifier produces the amplified output voltage E_o. This amplified output voltage may be applied to a suitable network to obtain a voltage E_f, which may be used to replace E_s provided that E_f and E_s are equal in phase as well as in magnitude. It is then possible to dispense with E_s entirely, the circuit generating its own excitation voltage. The amplifier must obviously be able to deliver at least enough power to make up any power losses in the grid circuit. In practice, it is not necessary to supply the initial grid excitation E_s; when the circuit is properly arranged, any random variation in plate current is rapidly amplified until the oscillation reaches the full magnitude permitted by the circuit constants.

In Fig. 123 is given the schematic representation of the operating principle of an excellent audio-frequency oscillator.[1] The output voltage of the amplifier is impressed across a coupling network as shown. The magnitude and phase of the voltage across the output terminals depend upon the amplification of which the amplifier is capable and upon the frequency f of the current. It may be shown[2] that the amplifier must be able to produce at least a threefold voltage amplification of an input

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[1] Terman, Buss, Hewlett, and Cahill, *Proc. IRE*, **27**, 649 (1939).

[2] Reich, *op. cit.*

signal without phase distortion and that the frequency of oscillation is given by the expression

$$f = \frac{1}{2\pi R_1 C_1}$$

where R_1 is in ohms, C_1 in farads, and f in cycles per second.

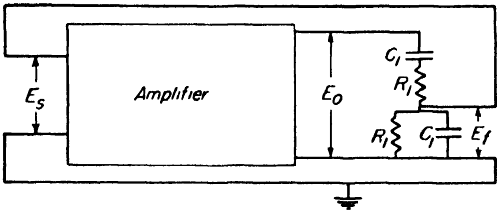

FIG. 123. Schematic representation of the principle of operation of the resistance-capacitance-coupled oscillator.

The a-c power produced by the circuit other than that required for grid-excitation purposes is, in principle, available for other uses. The performance of the oscillator is affected by withdrawal of appreciable power from it, however; hence in critical applications the oscillator proper is used only to control a power amplifier which delivers the required power to the load.

Other methods may be employed to obtain the feedback required in this type of oscillator circuit, but the basic principle of operation, the feeding back of part of the output of an amplifier to provide its grid excitation, remains the same.

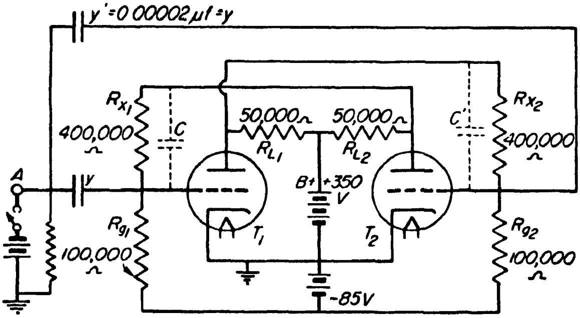

FIG. 124. Eccles-Jordan trigger circuit.

Eccles-Jordan Trigger Circuit. When two triodes are connected as in the circuit of Fig. 124, it will be found that current will flow through only one tube at a time, because the flow of current in one tube T_1 automatically produces a grid bias on the other tube T_2, which prevents it from conducting. The useful property of this circuit arises from the fact that it is possible to produce an abrupt interchange of the roles of the two tubes, i.e., to make T_2 conduct instead of T_1, by applying a voltage pulse simultaneously to the grids of the two tubes. This property makes the circuit useful for pulse-counting purposes. That this is so may be verified by determining the circuit behavior for the values of the circuit parameters given in Fig. 124, starting with the assumption that T_1 is conducting and T_2 is not conducting.

The grid bias of T_1 is obviously equal to -85 volts plus the potential drop across the resistor R_{g_1}. Since there is no current flowing through T_2, the potential drop across R_{g_1} is given by

$$\begin{aligned} E_{R_{g_1}} &= (350 + 85) \text{ volts} \times \frac{100{,}000 \text{ ohms}}{100{,}000 + 400{,}000 + 50{,}000 \text{ ohms}} \\ &= 79.2 \text{ volts} \end{aligned}$$

The grid bias of T_1 is then equal to -5.8 volts; its plate voltage and plate current i_{p_1} must now be determined. The potential drops across R_{g_2}, R_{x_2}, and R_{L_1} must add up to 435 volts, since these three resistors are connected in series across the 435-volt total voltage supply. If the current flowing through R_{g_2} and R_{x_2} is i_{c_2}, the current flowing through R_{L_1} is $i_{c_2} + i_{p_1}$, and

$$100{,}000 i_{c_2} + 400{,}000 i_{c_2} + 50{,}000(i_{p_1} + i_{c_2}) = 435 \text{ volts}$$

The additional information required for the determination of the values of the two unknowns i_{p_1} and i_{c_2} is provided by the characteristic curves for the 6C5 triode, since the plate voltage for T_1 is $350 - 50{,}000\ (i_{p_1} + i_{c_2})$ volts, and the grid bias of the tube has been determined to be -5.8 volts. It is found that i_{p_1} is 3.4 milliamp and i_{c_2} is 0.5 milliamp, corresponding to a plate voltage of 155 volts for T_1 and a drop of 195 volts across R_{L_1}. These results may be verified by reference to Fig. 111, as the characteristic curves for the 6J5 are practically identical with those for the 6C5 in the region concerned. Since i_{c_2} is 0.5 milliamp, the potential drop across R_{g_2} is 50 volts. The grid bias of T_2 is therefore -35 volts, a value for which the tube cannot conduct, substantiating our previous assumption to this effect. The foregoing calculation shows that T_2 cannot conduct if T_1 is conducting, because the flow of the plate current through the plate load resistor of T_1 automatically produces a grid bias on T_2 which prevents it from conducting.

When the switch is open, the point A is at ground potential. If the switch is closed, A becomes negative with respect to ground, and electrons will be repelled from the condensers y and y' until the potential drops across them have been increased by 10 volts. The electrons from condenser y' flow through R_{x_2} and R_{L_1} to B^+ and in so doing cause a momentary increase in the grid bias of T_2, which cannot be made less conducting. The electrons flowing out of condenser y flow through R_{x_1} and R_{L_1} and hence cause a decrease in the potential drop across R_{g_1}, increasing the grid bias on T_1 and making it less conducting; as a result, the plate current of T_1 decreases, the potential drop across R_{L_1} decreases, and the potential drop across R_{g_2} therefore increases, making the grid bias smaller and rendering the tube T_2 conducting. (Owing to the amplifying properties of the triode, the decrease in the grid bias on T_2 resulting from the decrease in the potential drop across R_{L_1} more than offsets the increase in grid bias due to the electron flow from y'.) As T_2 begins to conduct, the drop across R_{L_2} increases, which increases the grid bias on T_1 still further, and the process continues until T_1 is nonconducting and T_2 alone conducts.

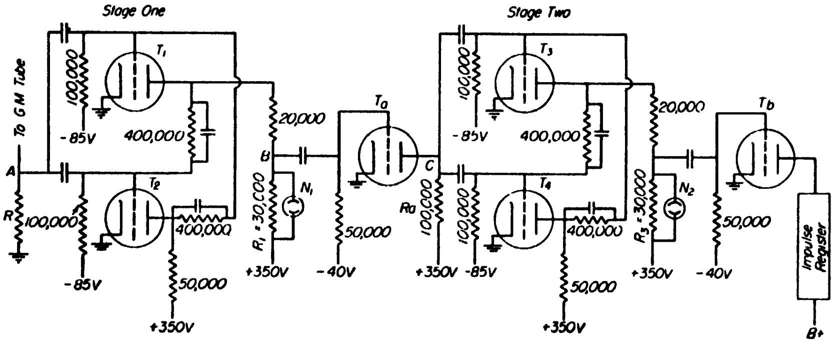

FIG. 125. Scale-of-four counting circuit based on Eccles-Jordan trigger circuit.

If now the switch is opened, the point A is returned to ground potential, and a condenser-discharging current flows into y through R_{g_1}, momentarily decreasing the bias of T_2. T_1 then begins to conduct, and the circuit "triggers" again, returning T_1 to the conducting state and T_2 to the nonconducting state. Because this triggering action is positive and rapid, the Eccles-Jordan circuit finds application in the scaling units employed for counting the pulses from Geiger-Müller tubes. With such sharp pulses the condensers c and c' are used to eliminate the influence of the interelectrode capacitances in the triodes on the action of the circuit.

Pulse-counting or Scaling Circuit. A typical scaling circuit[1] based on the Eccles-Jordan trigger circuit is shown in Fig. 125. It is seen to consist of two stages, or trigger pairs, of the type just considered, connected by an in-between-stage tube whose function is indicated below. In addition, small neon lamps have been placed across a portion of the plate resistor of one tube of each pair to indicate which tube is conducting. These tubes give a visible indication but draw practically no current.

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[1] Lifschutz and Lawson, *Rev. Sci. Instr.*, **9**, 83 (1938).

Let us suppose that the tubes T_2 and T_4 are initially in the conducting state. Both neon lights will then be out, since no current will be flowing through the resistors R_1 and R_3. (This condition may be achieved, for example, by grounding the grids of T_2 and T_4 momentarily.) Let an avalanche of electrons from the Geiger-Müller tube flow through the resistor R to ground. The point A will be abruptly driven negative, and a negative pulse will be applied to the grids of T_1 and T_2; i.e., the grid bias of each tube will be momentarily increased. As explained above, this will cause the first stage to trigger; T_2 will be cut off, and T_1 will conduct. When T_1 is not conducting, there is no potential drop across R_1, and the neon lamp N_1 is out. When T_1 abruptly is made to conduct, the flow of plate current through R_1 creates a potential drop which lights N_1, while the resulting abrupt decrease in potential at point B sends a negative pulse to the grid of T_a. Since T_a is normally nonconducting anyway, this momentary increase in its grid bias has no effect on T_a, and hence there is no effect on stage 2, where T_4 continues to conduct, with T_3 nonconducting. The first pulse from the Geiger-Müller tube then makes T_1 conduct, lighting N_1, cuts T_2 off, and has no other effect.

Let a second pulse come from the Geiger-Müller tube. Stage 1 will again be triggered; T_2 will conduct, and T_1 will be cut off. When the plate current of T_1 is cut off, N_1 will go out, and the potential at point B will rise abruptly, causing a positive pulse at the grid of T_a, which is thereby momentarily rendered conducting. The resulting momentary flow of plate current through the plate resistor R_a causes an abrupt decrease of potential at point C. This in turn causes a negative pulse at the grids of T_4 and T_3, thus triggering the second stage so that T_4 is cut off and T_3 conducts, lighting neon lamp N_2 and sending a negative pulse to T_b, which is unaffected. The second pulse thus turns off N_1, turns on N_2, and has no further effects.

The third pulse will again trigger stage 1; T_1 is again made conducting, N_1 lights up, and a negative pulse is applied to the gird of T_a. Since T_a is unaffected by a negative pulse, stage 2 is not affected by the third pulse, and N_2 also remains on.

A fourth pulse will trigger stage 1, turning N_1 off and applying a positive pulse to the grid of T_a. This in turn applies a negative pulse to the grids of T_3 and T_4. The second stage triggers also; N_2 is turned off, and a positive pulse is applied to the grid of T_b. This results in a momentary flow of plate current through T_b and hence through the coil of the electromagnetically actuated mechanical impulse register, which records one count. The fifth pulse will then light N_1, the sixth will light N_2 and turn off N_1, etc.

Because the counter is actuated only by every fourth pulse, this circuit is referred to as a scale-of-four counting circuit. In practical work, a scale-of-64 circuit is ordinarily used, for which six stages are required instead of the two considered above. The operation of the circuit is similar to the above, but 64 pulses at the input are required to actuate the mechanical register.

The Cathode-ray Oscilloscope. The essential element of the cathode-ray oscilloscope is the oscilloscope tube, whose structure is shown in Fig. 126. It contains an electron gun, which produces a beam of electrons that is directed upon a fluorescent screen at the opposite end of the tube, and deflecting plates,[1] to which voltages may be applied to displace the beam from its equilibrium position. As the beam moves, its path is traced out on the fluorescent screen, where it may be observed or photographed. The electron gun consists of a thermionic emitting cathode, a grid, and two anodes. The grid controls the electron density of the beam and to a lesser extent influences the focusing of the beam by the two anodes which accelerate the electrons toward the screen. The final velocity with which the electrons leave the gun depends upon the potential of the second anode. The intensity of the image is changed by changing the grid voltage, while adjustment of the beam focus is accomplished by changing the potential of the focusing anode. The diaphragms in the electrodes help to keep the beam sharp.

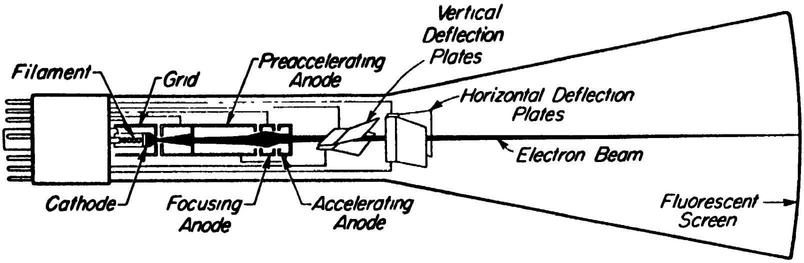

FIG. 126. Electrode arrangement of cathode-ray oscilloscope tube

The two sets of deflecting plates in the tube are arranged so that one causes a horizontal deflection of the beam, and hence of the fluorescent spot produced on the screen, and the other a vertical deflection. Because appreciable voltages must be impressed across the plates to produce a large displacement of the beam, amplifiers are provided in the instrument to amplify suitably the actual input voltages. When alternating voltages are applied simultaneously to the two plates, the position of the spot at any time represents the vector sum of the instantaneous values of the voltages applied to the two sets of plates. Because the screen is phosphorescent as well as fluorescent, the motion of the spot produces a line

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[1] Magnetic deflection can also be employed, but in practically all laboratory instruments electrostatic deflection is used.

pattern on the screen, the nature of which depends on the wave shapes, amplitudes, and phase relation of the two voltages.

A major application of the cathode-ray oscilloscope is in showing the appearance of a voltage as a function of the time. For this purpose the beam is periodically swept horizontally across the screen at a uniform rate to a point of maximum displacement, from which it returns practically instantaneously to its zero position; the frequency of this action is termed the *sweep frequency*, and the special type of voltage wave applied to the horizontal plates to produce it is provided by a special variable-frequency oscillator incorporated in the instrument. The unknown voltage is applied to the vertical-deflection plates. If the frequency of the sweep voltage is adjusted to equality with that of the unknown, the pattern on the screen will represent one cycle of the unknown voltage.

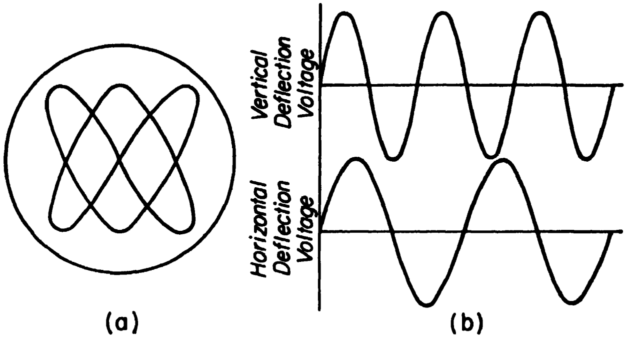

FIG. 127. Typical Lissajous pattern in frequency comparison with the cathode-ray oscilloscope

The oscilloscope is also useful for the comparison of the frequencies of two voltages. The two voltages are applied simultaneously to the two sets of deflection plates. If the ratio of the frequencies is a rational number, a closed pattern called a Lissajous figure will result, and from its form the frequency ratio can be determined. Usually an unknown frequency is determined by comparing it with the output of a standard calibrated variable-frequency oscillator, the frequency of which is adjusted until a simple Lissajous pattern is obtained. In Fig. 127 is shown the Lissajous pattern for a frequency ratio of 3:2, the voltage applied to the vertical plates being of the higher frequency.

The phase of two sinusoidal voltages of the same frequency can also be determined. The two signals are applied to the two sets of deflection plates. The vertical and horizontal amplifiers are adjusted as required to give equal deflections for the two signals, if the latter are not equal in amplitude. If the two voltages are in phase, the pattern will be a straight line making an angle of 45° with the horizontal. If the voltages are 90° out of phase, the pattern is a circle. For other phase angles the pattern is an ellipse. Even if one voltage is not sinusoidal, the patterns may be analyzed, though with greater difficulty.

Very little power is taken from the voltage sources under investigation with the cathode-ray oscilloscope, a major advantage. Connecting the input of a typical oscilloscope across the source is equivalent to connecting across it a parallel combination of a 2,000,000-ohm resistance and a 30-$\mu\mu$f condenser (exclusive of lead effects). The input circuits of most oscilloscopes are designed to transmit only a-c voltages, so that d-c voltages can be investigated only in those cases in which terminals are provided to make possible direct connections to the deflection plates.

SAFETY PRECAUTIONS

It is particularly important that the safety factor be kept firmly in mind in working on or with electronic circuits, since the hazards involved in any electrical work where high voltages may be present are considerable. A current of as little as 15 milliamp has been known to be fatal, and although such shocks usually are produced by higher-voltage sources, the ordinary 110-volt a-c line voltage has been known to be sufficient. The resistance offered by the *dry* human skin is usually around 40,000 ohms, but when the skin is moist, particularly as a result of perspiration, the skin resistance is much lower. It is also to be noted that the figure of 110 volts represents the root-mean-square value of the alternating voltage wave, and the peak voltage in the cycle is over 150 volts. The 220-volt a-c lines must be accorded even greater respect.

Direct-current voltages are also very dangerous. A particular source of trouble arises when, owing to faulty circuit design, no path has been provided for the discharge of high-voltage condensers after the main power switch has been turned off. A good-quality condenser will retain its charge for quite a time if the only discharge path is by slow leakage of current between the terminals. A bleeder resistor across the condenser may be employed to eliminate this difficulty, although in high-power work it is preferable to employ a relay, operated by the main power switch, which automatically short-circuits the high-voltage condensers when the power is turned off. It is a sound practice to check the voltage across any high-voltage condensers before working around them, as a general precaution.

It is desirable to employ double-pole switches in a-c or d-c power lines. One side of the 110-volt a-c line is usually at ground potential; if a non-polarized plug is used, with a single-pole switch in the line there is an even chance that one terminal of the load will be live when the main power switch is off, unless, of course, a transformer is used between line and load. A 220-volt line may be grounded at the midpoint of the main transformer, so that there is always an alternating potential of 110 volts rms between each terminal and ground. In supplying 110-volt a-c power to a building, the power is sometimes brought in on such a line; two sets of 110-volt outlets are obtained by taking, respectively, the two sides of the 220-volt line versus ground. The two live wires from different outlets can then have a potential difference of 220 volts alternating current between them.

Safety in electronics or other electrical work is essentially a matter of common sense and alertness. Alterations of circuits should be carried out only with the primary power source disconnected. In measuring voltages, etc., properly insulated test leads must be used. Of fundamental importance, of couse, is a good understanding of the circuits involved.

Time Measurements. Accurate time-interval measurements can be made with an electric timer driven by a synchronous motor, for which the rate of rotation of the armature is directly proportional to the power frequency. The primary intrinsic source of uncertainty in measurements made by this method is fluctuation of the frequency of the a-c supply from the 110-volt power line, since the timer can obviously read correctly only for a constant specified frequency, 60 cycles in practice. The line frequency is controlled at the generator and is held on the average very close to 60 cycles, but in a particular short period may deviate appreciably from this average value. For example, the power company records for a typical day at Madison, Wis., showed a minimum instantaneous frequency of 59.94 cycles/sec and a maximum of 60.04. A comprehensive study of the timing errors associated with such frequency variations has been reported by Craig, Satterthwaite, and Wallace.[1]

These errors can be eliminated by use of a constant-frequency power supply. Units of this type, controlled by a tuning fork or a quartz-crystal master oscillator, can have a frequency stability of 1 part in 10^5 or better and are available commercially. The operating frequency can be checked by use of the standard time signals from radio station WWV (see below). The timer is turned on and off in synchronism with selected time signals from WWV. The ratio of the true length of the time interval to the elapsed time shown by the timer gives the calibration factor to be applied to all timer indications.

An electrically operated clutch is used to couple the motor shaft to the sweep-hand system of the timer. For optimum results the clutch and motor circuits should be independent so that the motor can run continuously rather than being turned on when the clutch is activated, since

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[1] *Anal. Chem.*, **20**, 255 (1948).

it takes a small but not negligible time for a synchronous motor to get up to rated speed after the voltage is applied.

The clutch action represents an additional source of error. If alternating current is used to actuate the clutch, as is commonly the case, an uncertainty of the order of 0.01 sec is introduced because the clutch can throw in only during the part of the voltage cycle when the voltage is appropriately high. Special d-c-operated high-speed clutches can be obtained to minimize this error.

If the timer is controlled manually, the reaction time of the observer sets a limit to the accuracy obtainable. Wherever possible the timer should be controlled automatically. For example, in calorimetric work a high-speed double-pole relay can be used as a pair of switches acting simultaneously in the timer and calibration heater circuits.

Time and Frequency Standards. The continuous broadcasts from WWV, the National Bureau of Standards short-wave radio station in Washington, provide accurate time and frequency standards for the calibration of scientific equipment. The principle radio frequencies transmitted are 5, 10, 15, and 25 megacycles (1 megacycle = 10^6 cycles/sec). At each of these frequencies time signals are carried as well as standard audio frequencies of 440 and 600 cycles/sec.

Each time signal is sent as a 0.005-sec pulse (5 cycles of 1,000 cycles/sec), the beginning of which marks the beginning of a second with an accuracy of one part in a million. As a reference point, no time pulse is transmitted at the start of the 59th second of each minute. These time signals are heard as clicks against the background of the audio-frequency modulation.

Starting on the hour with 600 cycles, the 440 and 600 cycles/sec modulating frequencies are broadcast in alternate 5-min periods. The audio frequencies are cut off for the last minute of each period; during this interval an announcer gives the correct Eastern Standard Time. These services are also carried at 2.5 and 25 megacycles at reduced power, and the time signals alone at 30 and 35 megacycles at very reduced power.

The radio and audio frequencies are accurate to one part in fifty million, and together with the time signals form an indispensable set of standards for scientific work.

Semiconductors. The energies of electrons in a solid are quantized. The available energy levels for the electrons come in sets or "bands" of closely spaced levels; these bands are separated by an "energy gap" or forbidden energy zone. The lowest band is generally called the valence bond band, because the energy levels concerned correspond to localized binding, and the electrons correspondingly are not free to move. An electron must acquire enough energy to move across the energy gap into the higher band in order to be able to contribute to the electrical conductivity of the solid; the higher band is hence termed the conductance band. The magnitude of the energy gap thus determines the conductivity of the material.

If the gap is very large, few electrons will be present in the conduction band at ordinary temperatures. and the solid is an insulator. For the other extreme, the good conductors, the lower part of the conduction band and the upper part of the valence bond band overlap, eliminating the energy gap. The semiconductors represent the intermediate case of a moderate energy gap. For silicon it is 1.1 electron volts, for germanium 0.7 electron volt, in contrast to the 7-electron-volt gap for diamond, an insulator. A semiconductor has a negative coefficient of resistance, because the redistribution of electrons over the possible energy levels produced by an increase in temperature increases the population of the conduction band levels.

Impurities can have very marked effects on the properties of a semiconductor. They result in the presence of additional bands, called impurity bands, which may be located just above the valence bond band or just below the conduction band. Electrons can be raised from the valence bond band to one of the unoccupied adjacent impurity band levels, or into the conduction band from a filled impurity band level below it by the expenditure of relatively little energy compared to the normal energy gap. In this way a material can exhibit semiconductor properties even though the energy gap for the pure material is very large.

This effect of impurities is deliberately exploited in modern semiconductor products by the addition of small but accurately controlled amounts of specific impurities to a highly purified basic material, either silicon or germanium. The valence shells of these atoms contain four electrons, and in the pure crystal a given atom forms four covalent bonds, in a tetrahedral arrangement, with neighboring atoms, just as in the diamond structure for carbon. In the pure state these two elements are poor conductors, their conductivity being somewhat less than one millionth of that of a typical metal.

If arsenic is added to germanium, it enters the structure by replacement of germanium atoms. The neutral arsenic atom has five electrons in the valence shell, of which only four are required in bonding to the four neighboring germanium atoms. The fifth electron is quite easily removed from the influence of the arsenic atom, and so is readily raised to the conduction band. About 0.05-electron-volt energy is required, and this amount is readily supplied by thermal agitation at room temperature. The arsenic is hence called a do*n*or impurity, and the resulting semiconductor is referred to as *n*-type germanium.

A different result is obtained by the addition of indium, for example, for which the neutral atom has three electrons in the valence shell.

When such an atom enters the germanium lattice by substitution, it forms four covalent bonds with neighboring atoms. In order to do so it must capture an electron from an adjacent germanium atom. This removal of an electron from a covalent bond creates a net positive charge referred to as a "hole." This hole does not remain localized, as exchange of electrons between atoms can permit it to move through the structure. The resulting semiconductor is called *p*-type material, and the indium an *acceptor* impurity.

In any semiconductor the motion of both electrons and holes contributes to the conductivity. In *p*-type material the conduction is mainly by holes, with electrons minority carriers. In *n*-type material the roles are reversed. Since a hole can be destroyed by combination with an electron, the hole has a finite lifetime. The general characteristics of semiconductors are treated in the reference works of Shockley[1] and Wright.[2]

The most important applications of these semiconductors involve the use of appropriate combinations of *p*- and *n*-type materials in rectifiers and in more complex units called "transistors." These new semiconductor devices can replace vacuum tubes in many circuits, and the transistor field in particular is developing at a very rapid rate. Transistor theory differs markedly from vacuum-tube theory, however; an introduction to the field has been given by Coblentz and Owens.[3]

Thermistors. Another semiconductor device of great practical utility is the *thermistor*, whose name is derived from the descriptive phrase "thermally sensitive resistor." Thermistors are made from mixtures of various metallic oxides sintered together under controlled conditions to yield a ceramiclike material which has a large negative temperature coefficient of resistance, usually of the order of 4 per cent/°C at room temperature. Oxides of manganese and nickel produce thermistors of high specific resistance which can be lowered by admixture of cobalt oxide. For a particular thermistor the resistance R, to a good approximation, is represented by the relation

$$\log R = \frac{a}{T} + b$$

where a and b are constants characteristic of the thermistor.

The combination of high specific resistance, large temperature coefficient of resistance, and good stability make thermistors particularly suitable for use in temperature control and measurement. They can be

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[1] "Electrons and Holes in Semiconductors," D. Van Nostrand Company, Inc., New York (1950).

[2] "Semi-conductors," John Wiley & Sons, Inc., New York (1950).

[3] "Transistors," McGraw-Hill Book Company, Inc., New York (1955).

sealed in glass for protection from corrosive materials, with the resultant element still small enough to give a very rapid response to a change in the temperature of its environment. The resistance changes obtained are large enough so that special Wheatstone bridges and precautions required with platinum resistance thermometers are not needed.

Thermistors are available from a number of commercial sources listed in the Buyer's Guide issue of *Electronics* magazine.

CHAPTER 24

PHOTOCHEMISTRY[1]

The first practical requirement in photochemical research is a source of light having sufficient intensity to produce a measurable reaction in a reasonable length of time. For quantitative research it is necessary to use monochromatic light and to know the intensity of the light. Perhaps the greatest difficulty in photochemical technique lies in the fact that any means of restricting the light to a narrow range of wavelengths reduces its intensity and makes the measurement of the chemical change difficult.

SOURCES OF LIGHT

Tungsten Filament. For reactions with visible light, a 200- to 1,000-watt tungsten-filament lamp is often satisfactory. If the voltage tends to fluctuate seriously, the intensity of the lamp may be maintained uniform with special transformers or electronically controlled circuits. Ribbon-filament lamps are preferred if the light is to be focused on a cell or monochromator.

For high intensities, a 70-volt lamp may be operated on a 110-volt circuit. The life of the lamp is only about 2 hr under these conditions, but the lamps are not expensive. They are sold with photographic supplies under the name "photoflood lamps."

Mercury Arc. The mercury-vapor arc in quartz is the most convenient and powerful source of light for photochemical reactions but there are only a few lines in its spectrum, and it is without effect on those reactions which require intermediate wavelengths. As shown in a later section, however, the small number of lines is advantageous in procuring monochromatic light.

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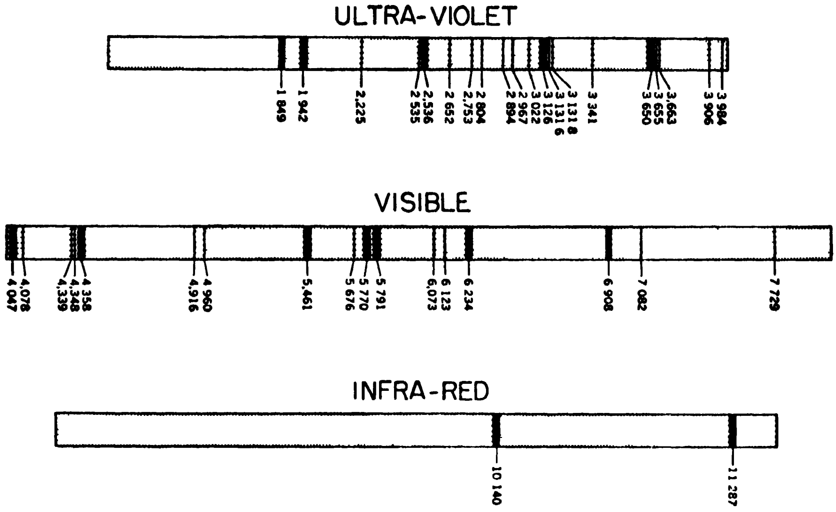
[1] General references include the following: Noyes and Boekelheide *in* Weissberger (ed.): "Technique of Organic Chemistry," Vol. II, Interscience Publishers, Inc., New York (1948); Buttolph *in* Hollaender (ed.): "Radiation Biology," Vol. II, Chap. 2, McGraw-Hill Book Company, Inc., New York (1955); Scott and Sinsheimer *in* Hollaender (ed.): "Radiation Biology," Vol. II, Chap. 4, McGraw-Hill Book Company, Inc., New York (1955); Withrow and Withrow *in* Hollaender (ed.): "Radiation Biology," Vol. III, Chap. 3, McGraw-Hill Book Company, Inc., New York (1956).

The spectrum of the mercury arc is shown in Fig. 128. The widths of the lines are proportional to the intensities.

Several types of mercury arcs are commercially available. Some intense lamps are operated at several amperes on direct current. As the lamp heats, the vapor pressure of the mercury increases, and the resistance of the lamp increases so that it is necessary to decrease the resistance of the rheostat. An ammeter is included in the circuit. After several minutes, the lamp reaches a steady condition. Care must be taken to connect the positive and the negative terminals correctly as labeled and to prevent, with suitable resistance, the passage of too large a current. *Always* in working with ultraviolet light it is important to protect the eyes with tight-fitting, effective glasses (welding glasses). Albumins in the eye may be coagulated by ultraviolet light, and the effect is cumulative.



Figures Denote Wave-Lengths in Angstroms

FIG. 128 Spectrum of the mercury arc.

The lamps are expensive, and they deteriorate with age, particularly with high currents. The life of a lamp may be increased by wiping off any dust or finger marks with a little alcohol before starting. If not removed, this material may be "burnt" into the transparent quartz surface.

Several lamps are available which operate at higher voltages on alternating current with a transformer and high reactance. The small lamps of the General Electric Type AH-5 (250 watts) are inexpensive and convenient when a very intense light is not needed. They require an inexpensive transformer.

Intense light for illuminating monochromator slits or small cells may be obtained with water-cooled capillary lamps, in which the light is concentrated in a small region.[1] The AH-6 lamp of the General Electric Company is a very intense water-cooled lamp which operates on alternating current.

"Cold" quartz lamps operating on alternating current at about 6,000 volts give about 85 per cent of all the light at the 2537 A line. They are commercially available, and a low-energy lamp is marketed as a "germicidal lamp."

Other Arcs. Light of high intensity can be obtained with an arc passing between two carbon electrodes arranged to move in a sliding frame as they are used up. The control may be effected automatically with a clock mechanism. The light is not steady, and frequent renewals are necessary, but the intensity of the blue and long ultraviolet is high. The spectrum contains many bands and a continuous background. Special-cored carbons may be purchased,[2] containing one or more salts (such as iron, strontium, nickel, and rare-earth metals), which enrich the spectrum in different regions.

The spectrum of the iron arc contains a great many lines, and the intensity in any one is not great. It is rich in the ultraviolet, and it is perhaps the most convenient source of light for reaching the regions between the mercury lines. The iron arc does not waste away as fast as the carbon arc. It is usually operated with both electrodes vertical, the upper one (of smaller diameter) being negative. A small piece of titanium steel or tungsten, floating on the top of the lower electrode, serves to keep the arc centered. The brown fumes of the iron oxide are objectionable, and the evolution of heat may cause difficulties. The iron arc is much used in spectroscopy and in the determination of absorption spectra, on account of its large number of well-defined lines.

The sodium Lab-arc operating on 110 volts alternating current is recommended when monochromatic light is needed for polarimetry or other optical measurements. The light is too weak, however, for most photochemical reactions. The lamp contains a little neon, which ionizes readily and starts the lamp. Full intensity is not reached until the arc has been operating for several minutes. The neon introduces extra lines in the spectrum, but they are weak in comparison with the sodium lines. For most work they constitute no objection, but if necessary they may be removed with the help of optical filters. A cadmium-mercury lamp is now commercially available which gives a bright red line in ad-

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[1] Daniels and Heidt, *J. Am. Chem. Soc.*, **54**, 2381 (1932).

[2] National Therapeutic Arc Carbons, National Carbon Company, Cleveland, Ohio.

dition to the mercury lines. It is useful with red optical filters for work in photosynthesis.

Copper, aluminum, and other metals may also be used as rods to give electric arcs. Quartz capillary arcs have been made, using bismuth, cadmium, lead, thallium, and zinc,[1] but they are short-lived.

The radiation emitted by the hydrogen arc[2] is nearly continuous throughout the ultraviolet when the arc is designed so that the atoms recombine rapidly to give molecular hydrogen. It is valuable for obtaining absorption spectra in the ultraviolet below the range of the tungsten lamp. It is used also for photochemical reactions in the ultraviolet.

For the shorter ultraviolet in the region of 2000 A and below, spark discharges between electrodes of aluminum, magnesium, and zinc are used. Several types have been described.[3] It is possible, though troublesome, to obtain from them intensities equal to those of the mercury lamp. Large transformers of 5 to 10 kw and 10,000 volts are used with large condensers. A blast of cooling air is directed against this spark. The noise and oxide dust are objectionable.

Flash photolysis[4] is a significant new development in which photochemical reactions are carried out with light of great intensity, caused by the momentary discharge of electricity accumulated in large condensers. These intermittent flashes between electrodes are focused onto the reacting system, and they are sufficiently intense, for example, to dissociate chlorine gas Cl_2 into colorless Cl atoms The rate of recombination of the atoms is measured with photoelectric cells which record the amount of light transmitted through the mixture of chlorine molecules and atoms. The same technique is used for studying the photodecomposition of organic molecules and the recombination rate of free radicals and atoms.

ACTIVATED INTERMEDIATES IN KINETICS

Molecules may be rendered highly reactive not only by the absorption of light but by a sudden input of energy in the form of shock waves.[5] A gas or a mixture of gases is placed under extremely high pressures on one side of a diaphragm. When the pressure is increased still further, the diaphragm ruptures and the gas moves into the low-pressure chamber with great velocity, the molecules having kinetic energy equivalent to that which they would have at very high temperatures. Gaseous

[1] Hoffman and Daniels, *J. Am. Chem. Soc.*, **54**, 4226 (1932).

[2] Noyes and Leighton, "The Photochemistry of Gases," p. 28, Reinhold Publishing Corporation (1941); Munch, *J. Am. Chem. Soc.*, **57**, 1863 (1935).

[3] Howe and Noyes, *J. Am. Chem. Soc.*, **58**, 1405 (1936).

[4] Christie, Norrish, and Porter, *Proc. Roy. Soc.* (*London*), **A216**, 152 (1952).

[5] Carrington and Davidson, *J. Phys. Chem.*, **57**, 418 (1953).

bromine molecules are broken down into bromine atoms, for example, and the new products and their rate of recombination are recorded by light absorption using a photocell and oscillograph.

New information is being obtained concerning free radicals and energy-rich intermediates which are produced by the absorption of light or by exposure to radioactivity. Again, these "hot" radicals can be made by a nuclear transformation which releases enormous energies within a molecule which contains a disintegrating atom. A "hot" atom or "hot" radical is one which has been produced with energy much in excess of the average energy of the surrounding molecules and has not yet come into thermal equilibrium with them. These hot atoms are responsible for interesting phenomena which throw light on the mechanisms of some reactions. An excellent review is given by Willard.[1]

Important progress in the study of free radicals and hot free radicals is being made by freezing them in solid materials, such as a frozen solvent, and measuring the light absorption of these immobilized units.

OPTICAL FILTERS

Glass Filters. Filters are the cheapest and most convenient means for restricting the radiation to a narrow range of frequencies. With them it is possible to isolate many of the mercury lines for photochemical investigations and to use light of different wavelengths for the photoelectric colorimeter. Although the filters absorb a considerable amount of the desired light, they absorb much more of the light in other parts of the spectrum. The transmission curves of typical Corning glass filters[2] are given in Fig. 129. The numbers on the curves refer to the manufacturer's color specification. The shaded areas and the specification numbers below the figure give the transmission of filters suitable for the lines of the mercury arc. The filters are ground to a given thickness and polished in standard sizes, 2 in. square and larger. Many of the glasses have sharp cutoffs, the shorter wavelengths at the left of the curve being absorbed.

Pyrex chemical-brand glass in a thickness of 2 mm transmits more than 60 per cent of the light at 3650 A, and Corex D glass in a thickness of 2 mm transmits more than 60 per cent of the light at 3020 A. Noviol Shade A 3-73 cuts off in the region of 4200 A; Traffic Shade Yellow 3-68 cuts off in the region of 5400 A, and H. R. Dark Red 2-59 cuts off in the region of 6200 A. Many other similar filters are available, only a few of which are shown here.

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[1] "Radiation Chemistry and Hot Atom Chemistry," Annual Reviews of Physical Chemistry, Vol. VI, Annual Reviews, Inc., Stanford, Calif. (1955).

[2] Glass Color Filters, Corning Glass Works, Corning, N.Y. (1948).

Other glass filters have specific transmission bands. Red Purple Corex 7-54 and Red Purple Ultra 7-39 have broad transmission bands in the ultraviolet; 4-67 has a broad transmission in the green, and 4-77 has transmission in the red and at two bands at 5000 and 5100 A.

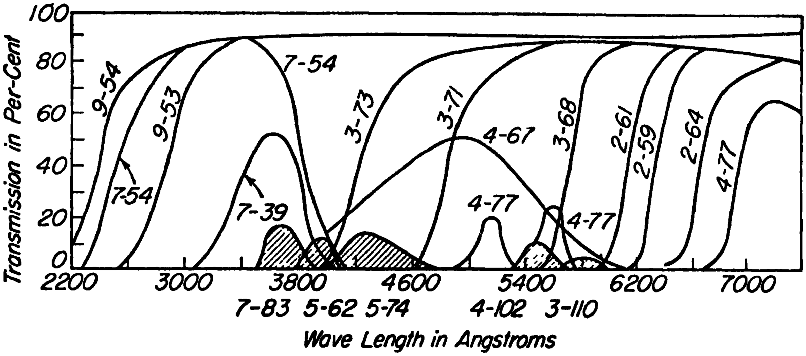

FIG. 129. Transmission curves for typical Corning glass filters.

The lines of the mercury arc can be isolated as shown by the shaded areas using the combinations of filters shown in Table 1.

TABLE 1. CORNING GLASS FILTERS FOR THE LINES OF THE MERCURY ARC

Wavelength, A	Color	Color specification number	Code numbers
3650	Ultraviolet	7-83	7380, 5860
4050	Violet	5-62	3060, 4308, 5970
4360	Blue	5-74	3389, 5113
5460	Green	4-102	3484, 5120, 4303
5780	Yellow	3-110	3480, 4303

Solutions. Several solutions and pure liquids have been used for isolating regions of the spectrum.

A molar solution of cupric chloride in a glass cell 1 cm thick transmits most of the light between 4000 and 6000 A and absorbs the remaining light. Addition of calcium chloride cuts off more of the violet light, and with sufficient calcium chloride the solution can be made to absorb all light of wavelength shorter than 4800 A.

A solution of *p*-nitrosodimethylaniline has absorption in the general region from 3800 to 4500 A.[1] When combined with a cupric chloride filter, it absorbs the visible and transmits some of the ultraviolet just below 3800 A.

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[1] Uhler and Wood, *Carnegie Inst. Wash. Pub.*, **71**, 21 (1907); Wood, *Phil. Mag.*, **5**, 257 (1903).

A concentrated solution of iodine in carbon disulfide is opaque to visible light but transmits infrared light.

Most of the filters transmit some infrared light. Glass and water absorb the longer infrared but allow a considerable portion of light in the neighborhood of 1 μ to pass through. A nearly saturated solution of copper sulfate, 2.5 or, preferably, 5 cm thick, has been used for absorbing the infrared. Such a solution absorbs large amounts of the visible light, too. Glasses which absorb much of the near infrared as well as the long infrared are now commercially available.

A set of filters for several lines of the mercury lamp has been assembled by Bowen.[1] The green line of mercury at 5460 A is isolated by a 1-cm layer of $CuCl_2 \cdot 2H_2O$ in ethanol (4.57 g per 100 ml) and a 0.5-cm layer of $CuCl_2 \cdot 2H_2O$ in acetone (1.4 g per 100 ml). Only 6.5 per cent of the green light is transmitted.

The line at 4358 A is isolated by a solution of 1 part in 10,000 of crystal violet and 4 per cent *p*-nitrotoluene in ethyl alcohol.

The line at 4047 to 4078 A is isolated with a 10-cm layer of a solution containing 0.44 g $CuSO_4 \cdot 5H_2O$ in 100 ml of 2.7 *M* NH_4OH, a 1-cm layer of a solution of 0.75 g I_2 in 100 ml of CCl_4, and a 2-cm layer of 1 g quinine hydrochloride in 100 ml of water. The iodine and quinine solutions have to be renewed frequently.

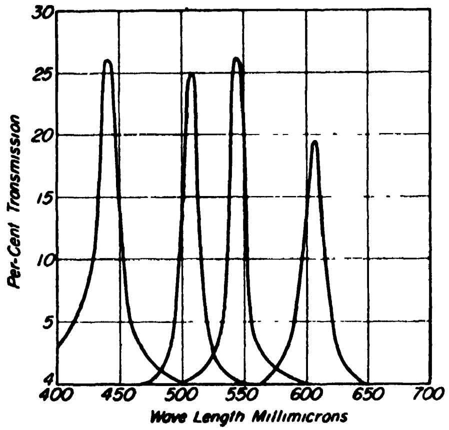

FIG. 130. Spectral transmission of four interference filters.

Interference Filters. Commercial interference filters[2] consist of thin evaporated layers of dielectric material between semitransparent metallic films on glass. A narrow range of wavelengths is transmitted, all others being reflected. Filters with a wide variety of transmission peaks (every 50 to 100 A) are available, and a few of these are illustrated in Fig. 130. These interference filters offer a convenient means for transmitting light in narrow wavelength regions, from 3400 to 10,000 A. Multilayer interference filters are prepared by evaporating 15 alternating layers of high- and low-refractive-index materials and mounting between clear glass plates. Seventy per cent transmission is possible with a half-band width of 70 A.

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[1] *J. Chem. Soc.*, **76** (1935).

[2] Farrand Optical Co., Inc., New York, N.Y.; Baird Associates, Inc., Cambridge, Mass.

MONOCHROMATORS

In general, the undesired wavelengths can be refracted to one side with a prism more effectively than they can be absorbed in a filter. A spectrometer system (Exp. 4) which is arranged to supply radiation of a narrow range of frequencies is called a *monochromator*.

If a continuous light source is used, there may be some overlapping of adjacent regions, and for this reason a discontinuous spectrum, such as that of the mercury arc, is particularly advantageous for use with the monochromator. The handicap of low intensity can be offset in part by long exposures, by using larger prisms and lenses, and by using capillary arcs of greater intensity. Energies up to 20,000 and 100,000 ergs/sec, at different wavelengths of the mercury spectrum, have been obtained with a purity of 98 per cent and more.[1] A double monochromator gives radiation of high purity.[2]

A monochromator suitable for photochemical investigations in the visible spectrum may be made from a hollow glass prism (15 cm on an edge) filled with ethyl cinnamate. This liquid has a high refractive index, and it does not deteriorate with use. Toluene may be used also. Hollow prisms may be made conveniently by cementing sheets of plastic together, but the optical quality is inferior.

Monochromators using large water prisms with quartz windows, for use in the ultraviolet, have been described by Harrison[3] and by Cannon and Rice.[4] Liquid prisms should be thermostated if it is necessary to prevent distortion of the lines.

THERMOPILES

A thermopile is made of a number of couples of unlike metals arranged in series with blackened-metal receivers attached to the junctions. The hot junctions are placed in the path of the light and the cold junctions at one side so that the light does not strike them. Radiations of all wavelengths are absorbed by the black receivers and converted into heat so that the temperature of one set of junctions is increased.

The elements are chosen so as to give a maximum thermoelectric effect with a minimum of heat conductance between the two junctions. The material should be as thin as possible, to minimize the heat capacity, without being too fragile. Bismuth-silver thermopiles are often used, but copper-constantan and platinum-tellurium elements are satisfactory.

[1] Heidt and Daniels, *J. Am. Chem. Soc.*, **54**, 2384 (1932).

[2] Forsythe and Barnes, *Rev. Sci. Instr.*, **4**, 289 (1933).

[3] *Rev. Sci. Instr.*, **5**, 149 (1934).

[4] *Rev. Sci. Instr.*, **13**, 513 (1942).

Detailed instructions for constructing thermopiles are given by Cartwright and Strong.[1] The construction of a small thermopile has been described by Beckmann and Dickinson.[2] The theory and practice of thermopile construction have been discussed critically by Leighton and Leighton.[3]

The ordinary linear thermopile is smaller than the reaction cell behind which it is placed, and it is necessary to move the thermopile over the whole area of the transmitted beam in order to obtain an average value. Large-area thermopiles which do their own integrating are convenient for photochemical investigations. The thermocouples, thoroughly insulated with glyptal lacquer, are attached with de Khotinsky cement to the back of a blackened receiver of sheet silver, 10 by 40 mm in area and 0.02 mm in thickness. The cold junctions are attached in a similar manner to another silver sheet of the same size and heat capacity which is located at the side of the entering light beam. Twenty or more thermocouples of copper and constantan (Advance) wire are connected in series. The number is chosen so as to give the critical damping resistance for the galvanometer. The junctions are soldered with pure tin, using rosin for a flux and removing all excess tin. The thermocouples and receiver are attached to a bakelite frame, which is then set into a rectangular block of aluminum or other metal. Radiation strikes the blackened receiver through a quartz window.

The thermopile is connected directly to the galvanometer, and the deflection is proportional to the current through the galvanometer, which, in turn, is proportional to the voltage generated by the difference in temperature of the junctions. The temperature difference is proportional to the energy of radiation falling on the receivers. The radiation receiver is covered with lampblack, together with a little platinum black to increase the heat conductance. The mixture is suspended in methanol containing a trace of shellac, applied to the receiver, and allowed to evaporate. The black surface is practically nonselective, converting radiation of all wavelengths directly into heat. This is the advantage over photoelectric cells, which are much more sensitive than thermopiles, but which respond only in restricted regions of the spectrum.

The thermopile should have a resistance equal to the critical-damping resistance of the galvanometer, so that a quick return to the zero reading is obtained. The galvanometer scale is arranged to slide back and forth so that it may be conveniently set at zero before each thermopile reading in order to avoid any error due to drift. The drift is caused by thermal

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[1] Strong, "Procedures in Experimental Physics," Prentice-Hall, Inc., New York (1939).

[2] *J. Am. Chem. Soc.*, **52**, 126 (1930).

[3] *J. Phys. Chem.*, **36**, 1882 (1932).

inequalities in the thermopile circuit produced by unequal or fluctuating room temperature or by air currents. Evacuation not only improves the constancy of the zero point, but it may increase the sensitivity severalfold.

Calibration. The deflection of the thermopile-galvanometer system is sufficient for comparative results, but for investigations connecting the quantity of chemical reaction with the energy absorbed (molecules per erg or per quantum), deflections are converted into absolute units. The quantity of radiation falling on the thermopile is obtained in ergs per second or in watts by calibration with a carbon filament lamp standardized at the National Bureau of Standards.[1] The apparatus is shown in Fig. 131. The standard lamp *L* is connected to storage batteries or other steady source of direct current, and the rheostat *R* is adjusted until the ammeter *M* gives an exact reading corresponding to one of the values given in the calibration table accompanying the lamp (e.g., 0.4 amp). A black screen *A*, 1 m square, is set 100 cm back of the lamp, and another one *B*, having a square hole 25 cm on a side, is set 25 cm in front of the lamp with the opening directly in front of it. The thermopile slit is mounted exactly 200 cm from the tip of the lamp. The lamp is rotated so that the two lines etched on either side of the globe are in line with the thermopile, giving the same conditions as used in the standardization. The room must be dark, free from objects that may reflect light on the thermopile *S*, and the operator must remain at a considerable distance.

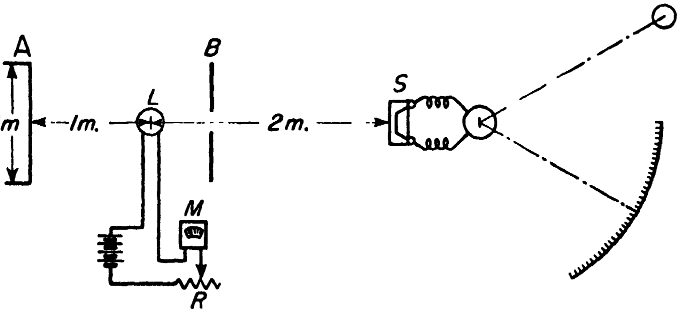

FIG. 131. Arrangement for calibration of a thermopile

The slit is narrower than the thermopile receivers, and its area must be accurately determined. If there are horizontal gaps between the receivers, a correction for the area must be made. The effective area is multiplied by the radiation in watts per square millimeter as given on the calibration sheet.

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[1] These lamps may be purchased at a nominal cost from the National Bureau of Standards. The calibration is described by Coblentz, *Natl. Bur. Standards* (*U.S.*), *Bull.*, **11**, 87 (1915).

Windows on the thermopile are necessary to prevent fluctuations in output due to temperature changes and air drafts. Glass windows are unsatisfactory if the thermopile is to be calibrated in absolute units, because glass absorbs some of the infrared radiation emitted by the carbon-filament lamp. Polished quartz windows are preferred for this purpose, and a correction is made by finding the small percentage decrease in deflection caused by interposing a second quartz plate in front of the pile. The same procedure can be used for glass windows also, but the correction is larger. Thin, transparent plastic windows may be used.

The total radiation E may be calculated from:

$$E = \frac{g}{s} atr$$

where s = galvanometer deflection with standard lamp
g = galvanometer deflection with monochromator
r = radiation from standard lamp in ergs sec^{-1} mm^{-2}, under conditions specified by the National Bureau of Standards
a = area of slit
t = time of radiation

BOLOMETERS

The bolometer is essentially a sensitive Wheatstone bridge, with two arms consisting of strips of thin platinum foil placed side by side. One of the strips is blackened, and when it is exposed to radiation its resistance is raised and the galvanometer is thrown out of balance. The increase in resistance of the foil is proportional to the rise in temperature, which in turn is proportional to the energy impinging on it. The bolometer is capable of great accuracy. Descriptions are given by Abbott.[1]

A bolometer of extreme sensitivity has been described by Milton.[2] The sensitive element is a strip of columbium nitride kept at the temperature of boiling hydrogen, at which point the compound undergoes a transition to the superconducting state. The change in resistance is enormous for a minute amount of radiant energy falling on the element.

PHOTOELECTRIC CELLS

When light of short wavelengths strikes the surface of potassium or other alkali metals (or their hydrides), electrons are emitted, and they conduct current in a photoelectric cell across the evacuated space of the

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[1] *Astrophys. J.*, **18**, 1 (1903).

[2] *Chem. Revs.*, **39**, 419 (1946).

enclosing glass vessel to a positive wire. The deflection of the galvanometer is proportional to the intensity of light when a d-c potential of 90 to 180 volts is applied. The spectral sensitivity of photoelectric cells is dependent on the particular alkali metal used, the metals of higher atomic weights being more sensitive for longer wavelengths.

One of the important uses of the commercial photoelectric cell is the automatic control of various processes by the operation of relays and accessory apparatus. The arrangement for this purpose is shown in Fig. 132. When the light intensity on the phototube cathode increases from zero, electrons are drawn through the resistor *R*. The potential drop thus produced across *R* acts to make the grid less negative with respect to the cathode. In consequence the plate current of the tube increases and the relay contacts will close when the light gets strong enough.

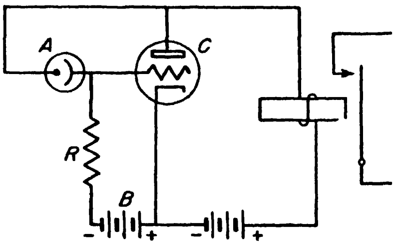

FIG. 132. Photoelectric cell and relay.

Photoelectric cells and amplifiers for laboratory work are discussed by Strong.[1]

Although the photoelectric cell is selective in its response to radiation, it can nevertheless be used in some photochemical work. The fact that it does not respond to the longer wavelengths is advantageous in certain cases. For example, if a filter is available to cut off light of shorter wavelength than that of the specified region and the photocell does not respond to light of longer wavelengths, the photocell may give an accurate measure of the light absorbed in the photochemical reaction. The photoelectric cell and galvanometer circuit may be calibrated[2] against a sensitive thermopile, using monochromatic light to which the photoelectric cell is sensitive. The thermopile in turn is calibrated with white light from a carbon lamp as described on page 449.

A photoelectric surface may be included in the Geiger-Müller chamber described on page 456, thereby giving a sensitivity much greater than that of a simple photoelectric cell.

Photomultiplier tubes are recommended for the quantitative measurement of light of very low intensity. A photomultiplier tube, which is comparatively inexpensive, contains nine electrodes placed at suitable angles in series, within the evacuated tube, with a 100-volt potential between each pair. The first electrode is coated with cesium or other material which ejects electrons when light falls on it. The photoelectrons are drawn at a 100-volt potential to a second electrode which is positively

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[1] *Op. cit.*, Chap. X.

[2] Morehead and Daniels, *J. Phys. Chem.*, **56**, 546 (1952).

charged, and each electron, when it hits, ejects several more. Each of these in turn is drawn to the third electrode, which is 100 volts more positive than the second, and when they hit they release additional electrons. This cascading effect is continued with each additional electrode so that it is possible to detect and measure extremely small amounts of light. Photomultiplier tubes are finding important use in the studies of feeble fluorescence and luminescence and in astronomy.

Barrier-layer cells, or photovoltaic cells, are available for measuring the intensity of light. At the contact between two layers of the different lattices of a semiconductor, there may be impurities which produce a positive and a negative layer. The light liberates electrons which reach an electrode and flow around a circuit and neutralize the positive vacancies in the crystal which were produced when the electrons were liberated. A copper-copper oxide surface, for example, generates a small voltage when struck by light. The reading of this voltage on a sensitive voltmeter is proportional to the intensity of light. This type of instrument is widely used for exposure meters in photography. The measurement of voltage without amplification provides a simple means of measuring the light intensity; but the barrier-layer cells are less sensitive than photocells, they have a much larger time lag, and they are subject to fatigue and some deterioration.

A single crystal of silicon has been treated with pentavalent and trivalent impurities in such a way as to produce positive and negative layers with which the Bell Telephone Laboratory has converted direct sunlight into electricity with an 11 per cent efficiency.[1]

REACTION CELLS

Flasks or open dishes may be used for qualitative work. In precision work, the cell has front and back plates of polished quartz or glass, and the cell is placed between the exit slit of the monochromator and the thermopile.

Quartz is transparent throughout the whole visible and ultraviolet range down to 2000 A. Pyrex in 2 mm thickness will transmit 10 per cent at 3000 A, whereas Corex will transmit 20 per cent at wave lengths as low as 2750 A. Vycor glass contains 96 per cent silica and is fairly transparent as low as 2500 A. All these glasses are transparent throughout the longer ultraviolet, visible, and short infrared. Window glass is suitable for visible light.

Glass cells of various sizes and shapes for holding filter solutions or chemically reacting systems may be purchased, or they may be constructed by fusing a Pyrex tube around a closely fitting circular window

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[1] Chapin, Fuller, and Pearson, *J. Applied Phys.*, **25**, 676 (1954).

cut from a polished plate of Pyrex with a revolving brass tube and emery powder. For some reactions, the cells may be made with polished-glass plates cemented to the ends of a glass tube with Tygon cement or other cement which is inert toward the solution used. When requirements for optical precision are not too great, the photoreaction cells may be made conveniently from Lucite or other plastic material sawed out to the right size and held together tightly with brass screws and a little cement. It is usually desirable to arrange the cell so that it is almost completely filled by the light beam.

Corrections for the light reflected at an interface are necessary in accurate work. The light should strike the windows at right angles, but even under these conditions about 4 per cent of the light is reflected at each quartz-air surface. The light reflected at a quartz-water or glass-water surface is practically negligible. The fraction of light reflected at right angles is given by Fresnel's formula

$$\frac{I_r}{I_i} = \left(\frac{\mu - 1}{\mu + 1}\right)^2$$

where I_r, I_i = intensity of the reflected and incident light, respectively
μ = ratio of the refractive indices of the two mediums

The light entering the inside of the empty cell is greater than that registered on the thermopile receivers, by an amount that depends on the number of quartz-air (or glass-air) surfaces through which the light passes. Sometimes the light reflected from the thermopile window passes back through the cell. The corrections are usually small, and they vary with the particular arrangement of cells and thermostat windows. Usually the corrections can be made to cancel out in gas reactions by placing an empty cell in the path of the light when a zero reading is made. The difference in energies registered on the thermopile gives the energy absorbed. In the case of solutions, the amount of light absorbed is obtained by subtracting the galvanometer reading with solution in the cell from the reading with pure solvent in the cell. It is a great convenience to have two cells exactly alike, either one of which may be slid into the path of the light.

PHOTOGRAPHY

A simple photographic emulsion of silver halide and gelatin is usefully sensitive only to the blue, violet, and near ultraviolet. The short-wavelength limit is set by absorption of the gelatin; sensitivity falls rapidly below 2500 A and is negligible below 1900 A. The long-wavelength limit is set by the absorption of the silver halide and varies from about 4300 A for pure silver chloride to 5200 A for silver bromoiodide.[1]

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[1] Mees, "The Theory of the Photographic Process," p. 962, The Macmillan Company, New York (1942).

In order to photograph radiation of wavelength less than 2000 A, it is necessary to use emulsions very low in gelatin or to sensitize an ordinary emulsion with a fluorescent coating. The low-gelatin emulsions are called Schumann plates, and directions for their preparation are given by Hopfield.[1] Improvements of the Schumann plate are made by Ilford, Ltd., and sold as Q plates.

Ordinary emulsions may be sensitized to the short ultraviolet by coating with a material which, when exposed to ultraviolet, fluoresces with emission of radiation to which the emulsion is sensitive. This method is convenient and gives good sensitivity, but the resolving power is lowered by spreading of the image. Characteristics of such plates have been described fully by Harrison.[2] The ethyl ester of dihydrocollidinedicarboxylic acid is suitable for the short ultraviolet sensitization. It may be obtained from the Eastman Kodak Company as "ultraviolet sensitizing solution, No. 3177," or the Kodak plates may be purchased with the proper fluorescent coatings.

Sensitization to wavelengths longer than those absorbed by the silver halide is produced by adding to the emulsion special dyes (optical sensitizers) which are adsorbed on the silver halide and sensitize it to the light which the dyed grains absorb. The chemistry of the dyes and the mechanism of their action are described by Mees[3] and James and Higgins.[4]

Dyes of many chemical types may act as long-wavelength sensitizers, but the most important classes are the cyanines and merocyanines. Photographic plates and films sensitive to the green (orthochromatic), to the whole visible spectrum (panchromatic), and to the infrared out to 9000 A and farther are available.[5]

Applications of photography to specific problems are described in a number of books.[6]

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[1] Hopfield and Appleyard, *J. Opt. Soc. Amer.*, **22**, 488-495 (1932).

[2] *J. Opt. Soc. Amer.*, **11**, 113 (1925).

[3] Mees, *op. cit.*, Chaps. 23-25.

[4] "Fundamentals of Photographic Theory," Chap. 11, John Wiley & Sons, Inc., New York (1948).

[5] "Photographic Plates for Scientific and Technical Use," 6th ed., Eastman Kodak Co., Rochester, N.Y. (1948); "Photographic Materials for Spectrum Analysis," Eastman Kodak Co., Rochester, N.Y.

[6] Shillaber, "Photomicrography in Theory and Practice," John Wiley & Sons, Inc., New York (1944); "Photomicrography," 14th ed., Eastman Kodak Company, Rochester, N.Y. (1944); Clark, "Photography by Infrared," 2d ed., John Wiley & Sons, Inc., New York (1946); Scott, "Photographic Evidence," Vernon Law Book Co., Kansas City, Mo. (1942); Longmore, "Medical Photography," Focal Press, London (1944); Tupholm, "Photography in Engineering," Faber & Faber, Ltd., London (1945).

CHAPTER 25

ISOTOPES AND RADIOACTIVITY[1]

Most of the elements can exist in different forms, or isotopes, each having the same atomic number and nearly the same chemical properties but having different atomic weights.

The safe handling of radioactive material and the proper disposal or storage of waste are required in any laboratory investigations using radioactive isotopes.[2] Many excellent instruments are now on the market for monitoring laboratories and personnel. Photographic film badges, pocket meters, and portable instruments for detecting and measuring, α, β, and γ rays are available.

IONIZATION CHAMBERS

Most instruments for measuring radioactivity depend on the ionization produced in a gas by α, β, or γ rays. Electrodes are placed in a space filled with the gas, and the current is measured with an electronic circuit.

When a low voltage is applied to the electrodes in the gas space, a current is produced. When the voltage is increased, the current increases because more gaseous ions are drawn to the electrodes before they have a chance to recombine. Eventually a saturation current is reached, at

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[1] General references include the following: Bale and Bonner *in* Weissberger (ed.): "Technique of Organic Chemistry," 2d ed., Vol. I, Part II, Interscience Publishers, Inc., New York (1949); Cook and Duncan, "Modern Radiochemical Practise," Oxford University Press, New York (1952); Glasstone, "Sourcebook on Atomic Energy," D. Van Nostrand Company, Inc., New York (1950); Halliday, "Introductory Nuclear Physics," John Wiley & Sons, Inc., New York (1950); Korff, "Electron and Nuclear Counters," D. Van Nostrand Company, Inc., New York (1946); Pollard and Davidson, "Applied Nuclear Physics," John Wiley & Sons, Inc., New York (1950); Wahl and Bonner, "Radioactivity Applied to Chemistry," John Wiley & Sons, Inc., New York (1951); Marinelli and Taylor *in* Hollaender (ed.): "The Measurement of Ionizing Radiations for Biological Purposes," Radiation Biology, Vol I, Part I, McGraw-Hill Book Company, Inc., New York (1955).

[2] "Safe Handling of Radioactive Isotopes," National Bureau of Standards, Superintendent of Documents, Washington; "Permissible Dose from External Sources of Ionizing Radiation," National Bureau of Standards, Superintendent of Documents, Washington; *Nucleonics*, 1 (4), 60 (1947).

which all the electrons and gas ions produced by the radioactivity are drawn to the electrodes, and the current then becomes independent of the applied voltage. The current is then directly proportional to the number of ions produced and to the amount of radioactivity. Instruments which measure this saturation current are called ionization chambers. For weak radioactivity, these currents have to be amplified greatly, and the electrical leakages around insulations and the stray currents are amplified also, thus imposing a practical limitation on the sensitivity of the instrument.

When the applied difference in potential is increased sufficiently beyond that needed to produce saturation current, the current is increased greatly, because each electron and ion can then ionize additional molecules by impact, which in turn ionize more molecules. An avalanche of electrons is produced by ionization of molecules caused by collision of the molecules with rapidly moving electrons on their way to the positive electrode. At these voltages, a considerable current pulse is registered for each ionizing radiation that comes into the gas chamber. An instrument which measures the number of individual α, β, or γ rays or neutrons in this manner is called a proportional counter.

The magnitude of the current produced by electrons and ions reaching the electrodes depends on the number of ions initially produced. For example, an α particle which produces 10,000 pairs of gas ions in the chamber will give over 330 times as much current as a cosmic ray which produces 30 pairs of ions. In the proportional counter, the voltage may be set so as to record only those impulses which are produced by ionizing radiations above a specified energy.

GEIGER-MÜLLER COUNTERS

When the voltage applied to the electrodes is increased above the so-called proportional region, the avalanche of ions produced by the initial ions becomes still greater. A tube operating at these high voltages is called a Geiger-Müller counter, and the voltage is said to be in the Geiger region. The current due to the weakly ionizing rays is magnified more than that due to the strongly ionizing rays, because the current for these strongly ionizing rays is nearly up to a maximum value.

Geiger-Müller counters[1] are widely used because of their great sensitivity, except when it is desired to distinguish between radiations of different energies. They are commercially available in many different types.

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[1] Korff, *op. cit.*; Lapp and Andrews, "Nuclear Radiation Physics," pp. 210 228, Prentice-Hall, Inc., New York (1948).

The Geiger-Müller tube consists of a central wire, positively charged, surrounded coaxially by a conducting tube, which may be made by depositing a metal inside a glass tube. It is filled with suitable gases at pressures of 100 to 200 mm, and a potential of 800 to 2,000 volts is applied.

Argon or some other easily ionizable gas is used for filling the Geiger-Müller tube, and a second gas is usually added in small amounts to act as a quenching gas. Alcohol or other polyatomic gas quenches the avalanche of current under suitable conditions, by absorbing the electrons and undergoing chemical decomposition in such a way that neither photons nor electrons are produced. In this way the avalanche of electrons is soon stopped.

Each pulse of current from the Geiger-Müller tube (or from a proportional counter) passes through a thyratron tube and actuates a mechanical device which turns a wheel and records the number of the impulses. The mechanical counters do not function properly when the radioactivity is too intense, and scaling circuits (p. 430) are available in multiples of 2 so that only every fourth, sixteenth, thirty-second, or sixty-fourth pulse is recorded on the mechanical counter. Decade scalers are also available.

The Geiger-Müller counters are made in various ways to meet special requirements. For γ rays, rather large volumes are used to give sufficient absorption. For β rays, a smaller volume is preferred, to minimize the effect of cosmic rays. Very thin windows, usually of mica, are required for soft β rays such as are emitted by radioactive carbon. In screen-wall counters the radioactive material is deposited on a coaxial tube of screen, thus giving a fairly uniform distribution of the radioactive material through the length of the tube. Thin glass is satisfactory for hard β and γ rays. The use of the Geiger-Müller counter has been described for solids and solutions in Exps. 53 and 54. Annular chambers are available with very thin metal walls with a thickness of 30 mg cm^{-2}.

The measurement of weak emitters requires special precautions on account of the self-absorption.[1] Further descriptions may be found in survey articles.[2]

COUNTING OF ALPHA PARTICLES

The counting of α particles involves special features. These particles are not very penetrating, and the material emitting the α particles must be placed inside the chamber, or the window of the Geiger-Müller counter must be extremely thin (1 mg cm^{-2} of glass or less). Alpha particles

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[1] Libby, *Anal. Chem.*, **19**, 2 (1947).

[2] Faul and Sullivan, *Nucleonics*, **4**(1), 53 (1949).

have a short range and a large amount of kinetic energy, and thus produce a great deal of ionization in a small volume.

The pulse ionization chamber used for α particles is small, with disk-shaped electrodes about 10 mm apart. The lower electrode is positive, and it holds the sample of solid material. The upper electrode is charged to about 1,250 volts negative. The positive ions formed by an α particle are drawn to the negative electrode, and the negative ions are attracted to the positive electrode, thus causing a change in voltage between the collecting electrodes. The pulse of voltage change produced is only about 200 μvolts, and it is amplified nearly a millionfold with a suitable amplifying circuit as described on page 415. Air is usually used as the gas in the ionization chamber.

The number of pulses per minute, or the number of α particles counted per minute, is known as the counting rate. The disintegration rate, often expressed in terms of the half-life, is a characteristic property of a radioisotope. The counting yield, which is defined as the ratio of the counting rate to the disintegration rate, is determined by several factors, including the *geometry factor*, which is defined as the fraction of the total number of α particles which start out in the direction of the sensitive volume of the counter. In the ideal case where the sample is mounted on a flat disk, the geometry factor is 50 per cent.

The 50 per cent geometry factor implies that half the α particles are lost because they are shot downward and absorbed in the supporting material below. However, some are scattered back and recorded in the sensitive volume of the counter. The back scattering increases with the atomic weight of the material and in the case of platinum amounts to 4 per cent, with the result that a counting yield of 52 per cent is obtained.

The counting efficiency is decreased by the short-range α particles in the material of the sample. The range of some α particles is about 4 cm in air under standard conditions, or 4.92 mg cm^{-2}, and the corresponding range in a solid is about 10 mg cm^{-2}, because the stopping power (per gram) of most solids is about one-half that of air. The sample should be very thin and uniformly spread on the counting plate.

The parallel-plate counter is so efficient that a recordable pulse is generated when only 10 per cent of the path of an α particle lies between the electrodes. The pulses are generally monitored with a cathode-ray oscilloscope.

A difficulty in the counting of α particles lies in the fact that if the particles come into the chamber too frequently, particles may be counted together as a single pulse. The pulse in an ionization chamber lasts for about 10^{-5} min, and if the pulses come at uniformly spaced intervals, many thousand could be counted. However, the α particles are emitted at random intervals, sometimes following each other within a period of less than 10^{-5} min. They will then appear on the circuit and the oscilloscope as a single pulse. Such losses in counting are called *coincidence losses*, and they increase with the counting rate of the sample, amounting in the case of the ordinary parallel-plate counter to about 0.8 per cent per thousand counts per minute. Such instruments cannot be used when the α counts are more than about 10,000 counts per minute. In order to reduce the number of counts, the geometry of the counter may be decreased by interposing screens. The sample of α-emitting solid is placed below a screenlike electrode and raised or lowered by a movable hand-adjusted support. The α particles are collimated by passing them through a long tube bored out of a large block of metal.

In another type of α counter, the geometry factor is reduced sufficiently to decrease the number of α particles overlapping and registering as a single count. The sample is placed on a support at the bottom, and the α particles spread out so that only a small fraction of them pass through a small opening directly above the sample. The α particles would be stopped by any gas, and so the chamber is provided with a very thin mica window and evacuated. After passing through the window, the particles are received on the top plate of a parallel-plate α counter. The geometry factor may be increased at will by raising the level of the sample and increasing the solid angle subtended.

In the methane proportional counter,[1] a charged wire is placed in the center of a cylindrical tube filled with continuously flowing methane at atmospheric pressure. The sample of solid is mounted inside, and the geometry factor is nearly 50 per cent.

The pulse analyzer[2] sorts out electronically the different size of pulses and measures simultaneously the number of α particles of different specified ranges, each coming from a different radioisotope.

OTHER COUNTERS

Crystal Counters. When a suitable crystal is touched firmly by electrical contacts and a potential is applied, a small current is produced.[3] When the crystal is exposed to α, β, and γ rays, electrons are dislodged, which in turn release other electrons in the crystals and produce an increased electrical current, which is then amplified. The sensitive volume of these crystal counters is small, and the response is extremely rapid. Some of them must be operated at liquid-air temperatures.

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[1] Simpson, *Phys. Rev.*, **70**, 117 (1946); MDDC 46, U.S. Atomic Energy Commission, Oak Ridge, Tenn. (1947).

[2] Ghiorso, Weissbound, and Robinson, Multichannel Pulse Analyzer, MDDC 23, U.S. Atomic Energy Commission, Oak Ridge, Tenn.

[3] Woolridge, Ahearn, and Burton, *Phys. Rev.*, **71**, 913 (1947); Curtiss and Brown, *Phys. Rev.*, **72**, 643 (1947); Hofstadter, *Nucleonics*, **4**(4), 2 (1949).

Fluorescence Counters. The α, β, and γ rays are allowed to fall on naphthalene or other transparent material which fluoresces with the emission of visible light. The intensity of light emitted is measured with a photomultiplier tube. Great sensitivity and reliability are claimed for this instrument.[1]

In counting α particles, each particle gives a flash of light which actuates a relay and counter. If the fluorescent material is very thin, the cosmic rays do not produce enough fluorescent light to be recorded, and only the α rays are recorded. Thick layers of the transparent fluorescent material, however, are very effective for γ rays and other penetrating rays; in fact, they are more effective than the gas-filled Geiger counters because they contain more material for absorption. For α counting the fluorescent material in the form of a fine powder may be sprinkled over the surface of a thin, transparent plastic sheet which has been coated with an adhesive (Scotch tape). Some of the crystals adhere, and they are placed facing downward immediately above the source of α particles.[2] DuPont Type D, ZnS- -Ag phosphor is satisfactory for the fluorescent material. Only a small amount is needed, and it may be readily renewed when it becomes contaminated with radon.

For precision work at high sensitivity, parts of the electronic circuits are refrigerated to keep the background current low. Two photomultiplier tubes may be arranged over the sample so that only if both tubes are actuated by the same flash of light will the recording mechanism operate. Stray light and electrical charges are not apt to actuate the circuit.

Scintillation liquids are available, as well as the crystals. The radioactive material can be dissolved in the liquid.

Thermoluminescent dosimeters accumulate the energy of radiation and release it as visible light when the crystalline material is heated.[3]

Neutron Counters. Neutrons have no electrical charge and accordingly are very penetrating. They are absorbed, however, by certain elements, such as boron, which undergo nuclear reaction. When a boron atom absorbs a neutron, the α particle, which is ejected at high velocity, produces ionization in the surrounding material. Neutron counters, then, are made by coating the inside wall of Geiger-Müller counters or ionization chambers with boron-containing material, so that the ejected α particles produce ionization currents as described on page 455. In another type of neutron counter, the ionization chamber contains gaseous

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[1] Allen, *Nucleonics*, **3**(1), 34 (1948); Birks, "Scintillation Counters," McGraw-Hill Book Company, Inc., New York (1953).

[2] Reed, *Nucleonics*, **7**(6), 56 (1950).

[3] Daniels, Boyd, and Saunders, *Science*, **109**, 440 (1949).

boron trifluoride instead of a boron-coated surface. Since B^{10} is the isotope of boron which gives this neutron-α-particle nuclear reaction, it is possible to make specially sensitive counters of BF_3 in which the ratio of B^{10} to B^9 has been increased by the electromagnetic separation of the isotopes.

Radioautographs. The presence and location of radioactivity can be detected with photographic plates, and the extent of the blackening of the plate gives a measure of the concentration of the activity of the material.[1] Some γ rays are too penetrating to give a large effect. Weak β rays are especially satisfactory. The location of radioactive tracers such as radiophosphorus can easily be determined in leaves and biological cells by placing the specimen over a photographic plate for a long time. The photographic method gives an accumulated effect over a long period of time (days or weeks if necessary) while the sample is being exposed to the plate.

α particles can be detected and measured in very low concentration by placing the sample (preferably as a solution which is then evaporated) on a photographic plate. Kodak Nuclear Track Plates Type NTA are the best for this purpose. If the α-emitting material is concentrated, the plate will show a darkening when developed. If the α emitters are of low concentration, α particles will leave short straight tracks, which are characteristic and which can be counted accurately with the help of a microscope or a projection lantern.

MASS SPECTROMETRY[2]

The separation of ions according to the ratio of mass to charge can be carried out with a mass spectrometer. The mass spectrometer of Nier,[3] illustrated in Fig. 133, is one of the most popular types for determining the relative abundances of different isotopes. The glass tube, containing an ion source at one end and an ion collector at the other, is evacuated with a diffusion pump. It must be heated before it is used in order to drive out traces of adsorbed water and gases. Electrons produced by a hot filament ionize molecules of any gases present. The ions produced are accelerated by a potential of from 800 to 1,000 volts, and the ion paths are bent by the field of an electromagnet (about 3,500 gausses). The ion current at the collector is amplified and recorded automatically. Mass spectrometers, commercially available,[4] are finding extensive use

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[1] Yagoda, "Radioactive Measurements with Nuclear Emulsions," John Wiley & Sons, Inc., New York (1949).

[2] Stewart *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part II, Chap. 31 (1949); Dempster, *Sci. Monthly*, **47**, 145–153 (1948).

[3] *Rev. Sci. Instr.*, **11**, 212 (1940).

[4] Consolidated Engineering Corporation, Pasadena, Calif., for example.

not only in the use of isotopes but in the analysis of mixtures of organic vapors and products of reactions.[1]

The mass spectrometer has also been used as a leak detector by attaching it to an evacuated system and passing over the surface of the system a tube from which helium gas flows. When the helium is brought near a leak, a helium-ion current is indicated by the mass spectrometer, which is set for an ion of this particular mass.

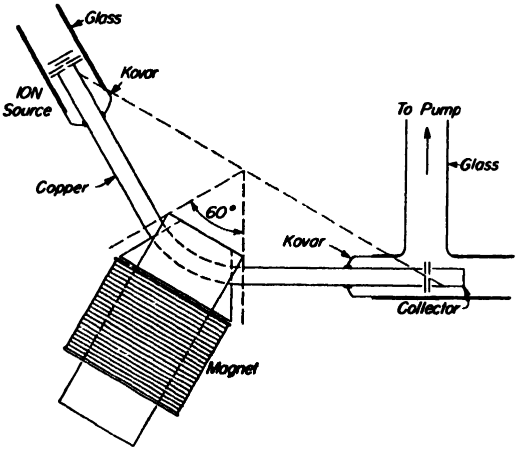

FIG 133. Nier mass spectrometer.

Analysis of mixtures of stable isotopes may frequently be made by other methods, which include (*a*) density determinations, e.g., the determination of D_2O in water, (*b*) measurement of refractive index, (*c*) measurement of thermal conductivity of gaseous mixtures, (*d*) measurement of isotope effects in molecular or atomic spectra, and (*e*) measurements of atomic weights by chemical methods.

ISOTOPES

Research involving isotopes has been greatly accelerated by the increased availability of radioisotopes and stable isotopes from the U.S. Atomic Energy Commission and the Atomic Energy Commission of Canada and other nations. A number of radioisotopes which do not occur naturally have been made available in large quantities by the operation of uranium nuclear reactors. A great variety is available at nominal prices in quantities of fractions of a millicurie to several curies. Cata-

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[1] Washburn, Wiley, and Rock, *Ind. Eng. Chem., Anal. Ed.*, **15**, 541 (1943); Inghram and Hayden, "A Handbook on Mass Spectroscopy," National Academy of Sciences, National Research Council, Washington, D.C. (1954); "Mass Spectrometry," Institute of Petroleum, London (1952).

logues, price lists, and application blanks can be obtained from the Isotopes Division, U.S. Atomic Energy Commission, Oak Ridge, Tenn. A prospective purchaser of isotopes must state that he is equipped to handle them, that his monitoring instruments are properly calibrated, that he will take adequate precautions in the handling of waste materials, and that he will accept legal responsibility for any damage from radioactivity.

Many organic and inorganic compounds are commercially available which have been synthesized with radioactive elements for use in tracer experiments.

Several excellent texts have been written on the preparation and use of isotopic tracers.[1]

Radioisotopes may be formed by (n,α), (n,p), and (n,γ) reactions in uranium nuclear reactors in which neutrons are absorbed and α particles, protons, or γ rays are emitted. Production of these isotopes involves the insertion of an element, often in the form of a chemical compound, contained in a small aluminum container, into the nuclear reactor for a few days or months. Important examples of isotopes made in this way are C^{14}, I^{131}, P^{32}, Br^{82}, and Fe^{59}.

Isotopes may be obtained also by separation from other fission products produced in a nuclear reactor.[2]

Stable nonradioactive isotopes H^2, B^{10}, O^{18}, Hg^{198}, C^{13}, and N^{15} in concentrated form are available[3] for tracer experiments in which a mass spectrometer is used to measure changes in isotope concentration.

Deuterium or heavy hydrogen is produced on a large scale by electrolysis of large quantities of water. Heavy carbon and heavy nitrogen have been produced by the thermal diffusion method in which a gas, methane, for example, is placed in a tall vertical tube through which runs an electrically heated wire. The heavier isotope tends to concentrate at the bottom.[4] From 1 mg to 1 g of a number of electromagnetically concentrated isotopes are available from the U.S. Atomic Energy Commission on a loan basis.

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[1] Bradford, "Radioisotopes in Industry," Reinhold Publishing Corporation, New York (1953); Calvin, Heidelberger, Reid, Tolbert, and Yankwich, "Isotopic Carbon," John Wiley & Sons, Inc., New York (1949); Friedlander and Kennedy, "Introduction to Radioactivity," John Wiley & Sons, Inc., New York (1955); Glasstone, *op. cit.*; Kamen, "Radioactive Tracers in Biology," 2d ed., Academic Press, Inc., New York (1951); Thode, "Isotopes," Annual Review of Physical Chemistry, Vol. 4, Stanford Annual Reviews, Inc., Stanford, Calif. (1953); United Nations Atomic Energy Commission, "International Bibliography of Atomic Energy," Vol. 2, United Nations, New York (1950); Whitehouse, "Radioactive Isotopes," Oxford University Press, New York (1953).

[2] Plutonium Project, *J. Am. Chem. Soc.*, **68**, 2411–2442 (1946).

[3] Hg^{198} from Isotopes Division, U.S. Atomic Energy Commission, Oak Ridge, Tenn.; C^{13} and N^{15} from Eastman Kodak Co., Rochester, N.Y.

[4] Taylor and Glockler, *J. Chem. Phys.*, **7**, 851 (1939).

The chemical equilibrium method developed by Urey[1] is used for C^{13} and N^{15}. The nitrogen is concentrated by the passage of ammonia gas upward through a packed tower, down which a stream of ammonium chloride solution is passing.

A number of isotopes which cannot be produced in the pile can be produced with a cyclotron. The cyclotron makes use of a much greater diversity in energy and type of nuclear bombarding projectiles, but it is difficult to obtain as large amounts as are available from the nuclear reactor.

GAMMA RADIATION

Radioactive cobalt (Co^{60}) is now available from the Atomic Energy Commission for experiments with γ rays on chemically reacting systems and radiation effects on solids and liquids. For long exposures in small spaces, the Co^{60} γ sources are more convenient than X rays. Units of 5 curies[2] and 40 curies[3] can be made without great expense and activated with a nuclear reactor at the Oak Ridge National Laboratory.

[1] Thode and Urey, *J. Chem. Phys.*, **7**, 34 (1939); Hutchison, Stewart, and Urey, *. Chem. Phys.*, **8**, 532 (1940).

[2] Saunders, Morehead, and Daniels, *J. Phys. Chem*, **75**, 3096 (1953).

[3] Firestone and Willard, *Rev. Sci. Instr*, **24**, 904 (1954).

CHAPTER 26

PURIFICATION OF MATERIALS

In many experiments, the factor which limits the accuracy of the results is the purity of the materials used rather than the refinement of the measurements. For example, nothing is gained by determining the refractive index of a liquid to five decimal places if it contains an impurity in amount sufficient to alter the refractive index in the third decimal place.

Methods. A considerable amount of technical knowledge and laboratory skill are required in the proper purification of materials for precision measurements. A knowledge of the origin of the starting material is of basic importance, since it will suggest the identity of the probable impurities and thus influence the procedure adopted. For example, benzene from petroleum sources invariably contains thiophene and other sulfur compounds. Since these contaminants are more rapidly sulfonated than benzene, they can be removed by shaking the benzene repeatedly with small portions of concentrated sulfuric acid. Another example is provided by commercial "absolute" alcohol, which usually contains traces of benzene introduced in the removal of water from the alcohol by an azeotropic distillation step (see below).

Purification procedures in general involve both chemical and physical processes. The chemical steps are specifically characteristic of the compounds involved. The physical procedures utilized will be selected most often from among the following processes.

Crystallization. One of the best methods of purification available is a series of fractional crystallization steps. The impurities present must not form solid solutions with the compound being purified. When materials with low freezing points are treated, precautions must be taken to protect them from condensing atmospheric moisture.

Fractional Distillation. This is probably the most common procedure used for the purification of liquids. A very efficient column is required when the boiling points of the impurities are close to that of the major constituent. Azeotropic solutions, because of their constant boiling points at constant pressure, have often been mistaken for pure components. It should be recognized that fractional distillation is routinely and unimaginatively used in many cases in which a better result can be obtained by fractional crystallization or other methods.

Azeotropic Distillation. Here advantage is taken of the formation of an azeotropic mixture involving an impurity to facilitate purification by fractional distillation. In the production of commercial absolute alcohol, benzene is added to the 95 per cent azeotrope of alcohol and water obtained by ordinary distillation. A ternary azeotrope of water, ethanol, and benzene can then be fractionated out to remove the water present. Further distillation removes the benzene in a binary azeotrope with ethanol.

Adsorption. The selectivity shown in adsorption processes (illustrated in Exp. 47) can result in remarkably effective separations extremely difficult to duplicate by other methods. A recent advance has been the development of vapor-phase chromatography.[1] Vapor-phase chromatography is similar to partition chromatography, the moving liquid phase being replaced by a gas phase. A column, which is usually heated, is filled with a packing such as diatomaceous earth which is moistened with a nonvolatile oil. A flow of helium gas is used to force the sample to be analyzed through the column. The rates at which various components of a mixture travel the length of the column depend upon the equilibrium of that substance between the dissolved and gas phases.

Recommendations concerning the purification of many organic liquids are given in the reference "Organic Solvents."[2] Archibald[3] describes methods for the preparation of pure inorganic compounds, and Farkas and Melville[4] have specified methods for the preparation, purification, and analysis of a number of gases.

It will commonly be found that the adequate elimination of water from a sample constitutes one of the most difficult problems in the whole purification process. The method of drying employed is determined primarily by the chemical properties of the material. If the product is not used immediately, care must be taken to prevent its recontamination by absorption of atmospheric moisture. Because of its low molecular weight, polar character, and chemical reactivity, relatively small amounts of water can be very troublesome.

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[1] James and Martin, *Biochem. J.*, **50**, 679 (1952); Ray, *J. Applied Chem.*, **4**, 21 (1954); Patton, Lewis, and Kaye, *Anal. Chem.*, **27**, 170 (1955); see also, *Chem. Eng. News*, **34**, 1692 (1956).

[2] Riddick and Toops, rev. 2d ed. of Weissberger and Proskauer's, "Organic Solvents," *in* Weissberger (ed.): "Technique of Organic Chemistry," Vol. VII, Interscience Publishers, Inc., New York (1955).

[3] "The Preparation of Pure Inorganic Substances," John Wiley & Sons, Inc., New York (1932).

[4] "Experimental Methods in Gas Reactions," Macmillan & Co., Ltd., London (1939).

Criteria of Purity. One of the best criteria available for organic compounds is the constancy of the freezing point or melting point throughout the phase transition.[1] If a liquid is impure, the impurities will become concentrated in the liquid phase as the solid separates out; the freezing point thus is gradually lowered. If the liquid phase can be treated as an ideal solution, an assumption of adequate validity in many cases, and if no solid solutions are formed, the amount of impurity can be calculated with fair accuracy from the shape of the freezing or melting curve. Since high sensitivity is required in the temperature measurements, a platinum resistance thermometer or multiple-junction thermocouple is used.

Comparison of the normal boiling point, refractive index, etc., with the accepted values for the compound concerned is often used to estimate the quality of a sample. A valuable reference tabulation of physical constants of organic compounds has been prepared by Timmermans.[2] Unfortunately the reference data available are often of inadequate accuracy; the objective evaluation of purity furnished by the freezing-point method is hence much to be preferred in critical cases.

It is important to know the identity as well as the mole fraction of impurity present, in order to judge its effect on the measurements to be made. In addition, direct determination of the important contaminants may be possible through standard analytical procedures.

For inorganic compounds spectrographic and polarographic analyses are used for testing for traces of impurities, and standard colorimetric and precipitation tests are available, also.

Water. Ordinary distilled water is sufficiently pure for most work in physical chemistry, but for some applications, such as conductance measurements, it is necessary to use specially redistilled water.

Steam is generated from a dilute alkaline permanganate solution in a quartz or heavily tinned copper boiler and is partially condensed in a quartz or block tin condenser. The escaping steam carries off gases evolved by the boiling liquid and prevents exposure of the condensate to the laboratory air. The condensate is collected in a quartz or tinned copper reservoir under air which has been treated to remove carbon dioxide, ammonia, etc. Polyethylene bottles can also be used for storage of water to prevent its contamination by dissolution of constituents of ordinary glasses.

Mercury. It is assumed that reasonably pure mercury is available as starting material. A preliminary treatment is first necessary to remove

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[1] White, *J. Phys. Chem.*, **23**, 393 (1920); Skau, *J. Phys. Chem.*, **37**, 609 (1933); Glasgow, Streiff, and Rossini, *J. Research Natl. Bur. Standards*, **35**, 355 (1945); Sturtevant *in* Weissberger (ed.): *op. cit.*, 2d ed., Vol. I, Part I, Chap. 14.

[2] "Physico-chemical Constants of Pure Organic Compounds," Elsevier Press, Inc., Houston, Tex. (1950).

oxidizable contaminants such as zinc, lead, etc. A pinhole is made at the apex of a dry filter paper cone placed in a dry funnel. Mercury is poured into the filter and collected in a glass filter flask of such a size that a layer one or two inches deep results. A 10 per cent solution of nitric acid, to which some mercurous nitrate has been added, is poured over the mercury to a depth of several inches. Into the neck of the flask is fitted a rubber stopper through which proceeds a glass tube drawn down to a diameter of about 1 mm at the lower end, which should extend well under the surface of the mercury. The side arm of the flask is connected to a water aspirator, and a slow stream of air bubbled through the mercury for several days. A filter should be placed in the air line to prevent drawing dust from the laboratory into the mercury.

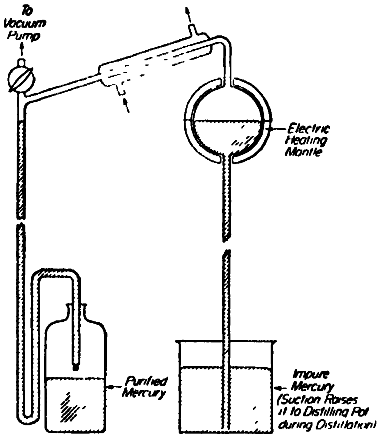

FIG. 134. Mercury still

The metal is then washed with distilled water and dried. It should again be run through a pinhole in a filter to eliminate surface scum, and then is transferred to a still and distilled under vacuum. A satisfactory still-design is shown in Fig. 134; an automatic still of this type has been described by Cannon.[1] It is preferable to check the purity of the product by spectrographic analysis, since several distillations may be required to achieve the desired result. The danger of mercury poisoning should be kept in mind in any processing of mercury.

Benzene. Reagent grade benzene is treated with concentrated sulfuric acid until it gives a negative test for thiophene with isatin. It is then washed repeatedly with water and dried first with calcium chloride, then with sodium. Fractional distillation results first in the elimination of residual water as the binary azeotrope; the product can then be collected. If extreme purity is required, slow fractional crystallization may be employed, as described by Schwab and Wichers.[2]

Ethanol. Ethanol is treated with silver oxide to remove aldehydes and distilled from calcium oxide, after long digestion, to remove water. It is very difficult to remove the last traces of water from ethanol, and the pure alcohol takes up moisture very quickly from the air.

Hydrocarbons. A large number of hydrocarbons have been purified and their physical properties studied as part of the work of Research

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[1] *J. Chem. Educ.*, **28**, 272 (1951).

[2] *J. Research Natl. Bur. Standards*, **25**, 747 (1940).

Project 44 of the American Petroleum Institute, which operated first at the National Bureau of Standards, and is now located at the Department of Chemistry of Carnegie Institute of Technology. The methods employed have been described in a series of publications.[1]

A number of hydrocarbons are available commercially from the Phillips Petroleum Company, Bartlesville, Okla., as "research-grade" products whose purity has been determined by the freezing-point method.

Sodium Chloride. Since sodium chloride has a small temperature coefficient of solubility, it cannot be easily purified by crystallization. A saturated solution of sodium chloride is treated with hydrochloric acid gas to throw out the pure salt. The hydrochloric acid gas is introduced through an inverted funnel, because a small tube is soon plugged up with the crystals. Rubber connections are attacked by hydrochloric acid, so the connections and the generating bottle are all of glass. The gas is generated by dropping concentrated hydrochloric acid, drop by drop, into concentrated sulfuric acid while shaking to avoid the formation of two layers, which might lead to an explosion.

The precipitated sodium chloride is packed into a funnel, rinsed with a minimum amount of water, and fused in a platinum dish at red heat.

Sodium Hydroxide. For most titrations with alkali, it is necessary to have the alkali free from carbonate to obtain a sharp end point. High-grade commercial sodium hydroxide may now be obtained which ordinarily needs no further purification. Sodium hydroxide solution free from carbonate is readily prepared from a saturated stock solution. The carbonate is thrown out as an insoluble precipitate by the high concentration of sodium hydroxide which exists in a saturated solution. The clear supernatant solution is drawn off with a siphon and diluted with carbon dioxide–free water to the desired concentration, at room temperature. The saturated solution is about 15 *M*, and it is kept in a bottle, the inside of which has been covered with paraffin.

Methods for the purification of other substances may be found in the literature.

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[1] *J. Research Natl. Bur. Standards*, **35**, 355–373 (1945); **37**, 141–145 (1946); **38**, 53 (1947); **39**, 321 (1947); **41**, 323 (1948); *Chem. Eng. News*, **25**, 730 (1948).

APPENDIX

PHYSICAL-CHEMICAL CONSTANTS

The following tables give the recommended values of the fundamental constants for physical chemistry as of July 1, 1951.[1] They are based upon the reanalysis and reevaluation of experimental values by DuMond and Cohen.[2]

VALUES OF THE DEFINED CONSTANTS

Standard gravity	980.665 cm $\sec^{-2}$
Standard atmosphere	1,013,250 dynes cm^{-2}
Standard millimeter of mercury pressure	$\frac{1}{760}$ atm
Calorie (thermochemical)	4.1840 joules
	4.18331 int joules
	41.2929 cm^3 atm
	0.0412917 l atm

VALUES OF THE BASIC CONSTANTS

Velocity of light	c	$(2.997902 \pm 0.000013) \times 10^{10}$ cm $\sec^{-1}$
Planck constant	h	$(6.6238 \pm 0.00027) \times 10^{-27}$ erg sec $molecule^{-1}$
Avogadro constant	N	$(6.0238 \pm 0.00016) \times 10^{23}$ molecules $mole^{-1}$
Faraday constant	F	$96{,}493 \pm 7$ coulombs $equiv^{-1}$
		23,062 cal (volt $equiv)^{-1}$
Absolute temperature of the "ice point,"[3] 0°C	$T_{0^\circ C}$	273.16 ± 0.01°K.
Pressure-volume product for 1 mole of a gas at 0° and zero pressure	$(pV)_{T_{0^\circ}}^{p=0}$	22,414.6 cm^3 atm $mole^{-1}$
		22.4140 liter atm $mole^{-1}$
		2271.16 ± 0.04 joules $mole^{-1}$

VALUES OF THE DERIVED CONSTANTS

Electronic charge	$e = \frac{F}{N}$	$(1.60186 \pm 0.000036) \times 10^{-19}$ coulomb
		1.60186×10^{-20} emu
		4.8022×10^{-10} esu
Gas constant	$R = \frac{(pV)_{T_{0^\circ}}^{p=0}}{T_{0^\circ}}$	1.9872 cal deg^{-1} $mole^{-1}$
		82.057 cm^3 atm deg^{-1} $mole^{-1}$
		0.082054 l atm deg^{-1} $mole^{-1}$
		8.3144 ± 0.00034 joules deg^{-1} $mole^{-1}$
Boltzmann constant	$k = R/N$	$(1.38026 \pm 0.000067) \times 10^{-16}$ erg deg^{-1} $molecule^{-1}$

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[1] Rossini, Gucker, Johnston, Pauling, and Vinal, *J. Am. Chem. Soc.*, **74**, 2699 (1952).

[2] DuMond and Cohen, *Phys. Rev.*, **82**, 555 (1951).

[3] It is expected that the absolute temperature of the "ice point," 0°C, will be defined by international agreement as 273.150°K. Minor changes in some of the derived constants will then be required.

VALUES OF CERTAIN AUXILIARY RELATIONS

1 second (mean solar) = 1.00273791 sidereal seconds
1 joule = 0.999835 ± 0.000052 international joule
1 ohm = 0.999505 ± 0.000015 international ohm
1 ampere = 1.000165 ± 0.000025 international amperes
1 volt = 0.999670 ± 0.000029 international volt
1 coulomb = 1.000165 ± 0.000025 international coulombs
1 watt = 0.999835 ± 0.000052 international watt
1 liter = 1,000.028 ± 0.004 cm^3

REDUCTION OF BAROMETER READINGS ON A BRASS SCALE TO 0°

$$p_0 = p - p\frac{\alpha t - \beta(t - t_s)}{1 + \alpha t}$$

p_0 = barometer reading reduced to 0°
p = observed barometer reading
t = centigrade temperature of barometer
α = 0.0001818 = mean cubical coefficient of expansion of mercury between 0 and 35°
β = linear coefficient of expansion of scale material, 18.4×10^{-6} for brass
t_s = temperature at which scale was calibrated, normally 20°C

CORRECTION TO BE SUBTRACTED FROM BAROMETER READINGS

t, °C	720 mm	730 mm	740 mm	750 mm	760 mm	770 mm	780 mm
15	1.76	1.78	1.81	1.83	1.86	1.88	1.91
16	1.88	1.90	1.93	1.96	1.98	2.01	2.03
17	1.99	2.02	2.05	2.08	2.10	2.13	2.16
18	2.11	2.14	2.17	2.20	2.23	2.26	2.29
19	2.23	2.26	2.29	2.32	2.35	2.38	2.41
20	2.34	2.38	2.41	2.44	2.47	2.51	2.54
21	2.46	2.50	2.53	2.56	2.60	2.63	2.67
22	2.58	2.61	2.65	2.69	2.72	2.76	2.79
23	2.69	2.73	2.77	2.81	2.84	2.88	2.92
24	2.81	2.85	2.89	2.93	2.97	3.01	3.05
25	2.93	2.97	3.01	3.05	3.09	3.13	3.17
26	3.04	3.09	3.13	3.17	3.21	3.26	3.30
27	3.16	3.20	3.25	3.29	3.34	3.38	3.42
28	3.28	3.32	3.37	3.41	3.46	3.51	3.55
29	3.39	3.44	3.49	3.54	3.58	3.63	3.68
30	3.51	3.56	3.61	3.66	3.71	3.75	3.80

VAPOR PRESSURE OF WATER

t, °C	p, mm Hg	t, °C	p, mm Hg	t, °C	p, mm Hg	t, °C	p, mm Hg
0	4.6	26	25.2	40	55.3	90	526.0
5	6.5	27	26.8	45	71.9	95	634.0
10	9.2	28	28.3	50	92.5	96	657.7
15	12.8	29	30.1	55	118.1	97	682.1
20	17.5	30	31.8	60	149.5	98	707.3
21	18.7	31	33.7	65	187.6	99	733.2
22	19.8	32	35.7	70	233.8	100	760.0
23	21.0	33	37 7	75	289.3	101	787.6
24	22.4	34	39 9	80	355 5	102	816.0
25	23.8	35	42.2	85	433.8	103	845.3

Density of Water in Grams per Milliliter

Degrees	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
0	0.999841	847	854	860	866	872	878	884	889	895
1	0.999900	905	909	914	918	923	927	930	934	938
2	0.999941	944	947	950	953	955	958	960	962	964
3	0.999965	967	968	969	970	971	972	972	973	973
4	0.999973	973	973	972	972	972	970	969	968	966
5	0.999965	963	961	959	957	955	952	950	947	944
6	0.999941	938	935	931	927	924	920	916	911	907
7	0.999902	898	893	888	883	877	872	866	861	855
8	0.999849	843	837	830	824	817	810	803	796	789
9	0.999781	774	766	758	751	742	734	726	717	709
10	0.999700	691	682	673	664	654	645	635	625	615
11	0.999605	595	585	574	564	553	542	531	520	509
12	0.999489	486	475	463	451	439	427	415	402	390
13	0.999377	364	352	339	326	312	299	285	272	258
14	0.999244	230	216	202	188	173	159	144	129	114
15	0.999099	084	069	054	038	023	007	*991	*975	*959
16	0.998943	926	910	893	877	860	843	826	809	792
17	0.998744	757	739	722	704	686	668	650	632	613
18	0.998595	576	558	539	520	501	482	463	444	424
19	0.998405	385	365	345	325	305	285	265	244	224
20	0.998203	183	162	141	120	099	078	056	035	013
21	0.997992	970	948	926	904	882	860	837	815	792
22	0.997770	747	724	701	678	655	632	608	585	561
23	0.997538	514	490	466	442	418	394	369	345	320
24	0.997296	271	246	221	196	171	146	120	095	069
25	0.997044	018	*992	*967	*941	*914	*888	*862	*836	*809
26	0.996783	756	729	703	676	649	621	594	567	540
27	0.996512	485	457	429	401	373	345	317	289	261
28	0.996232	204	175	147	118	089	060	031	002	*973
29	0.995994	914	885	855	826	796	766	736	706	676
30	0.995646	616	586	555	525	494	464	433	402	371

* Where values are designated with an asterisk, the first three figures are to be supplied from the zero column in the next lower row.

METHODS OF EXPRESSING CONCENTRATIONS

The concentration of a solution may be expressed in any of the following ways:

a. Percentage by weight. [Grams solute ÷ (grams solute + grams solvent)]
b. Moles per 1,000 ml of solution. ("Molar" = 1 mole in 1,000 ml of solution)
c. Moles per 1,000 g of solvent. ("Molal" = 1 mole in 1,000 g solvent)
d. Mole fraction. [Moles solute ÷ (moles solute + moles solvent)]

For technical work, (*a*) is used; (*b*) is very convenient in volumetric analysis; (*c*) is used in certain theoretical work, because the temperature variable is eliminated; and (*d*) is extensively used in theoretical work involving physical properties of solutions.

COLOR CODE CONVENTIONS FOR ELECTRONIC CIRCUIT COMPONENTS

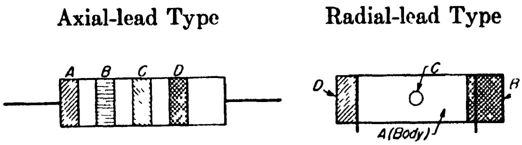
I. Resistors and Capacitors

Color code:

Color	Significant figure	Decimal multiplier	Tolerance, per cent, 1938 RMA standard	Voltage rating,[a] 1938 RMA standard
Black	0	1		
Brown	1	10	1	100
Red	2	100	2	200
Orange	3	1,000	3	300
Yellow	4	10,000	4	400
Green	5	100,000	5	500
Blue	6	1,000,000	6	600
Violet	7	10,000,000	7	700
Gray	8	100,000,000	8	800
White	9	1,000,000,000	9	900
Gold	. .	0.1	± 5	1,000
Silver	. .	0.01	±10	2,000
No color	. . .	. . . . .	±20	500

[a] Capacitors only.

Resistors:

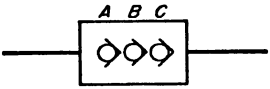

Axial-lead Type Radial-lead Type

A. First significant figure, resistance in ohms.
B. Second significant figure.
C. Decimal multiplier.
D. Tolerance.

Fixed Mica Capacitors:

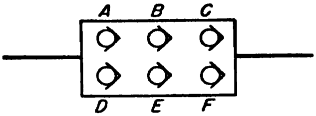
1. Radio Manufacturers Association 1938 Standard.

Three-dot Code



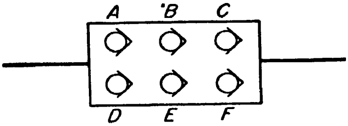
A. First significant figure.
B. Second significant figure.
C. Decimal multiplier.
500 volts, 20 per cent tolerance only.

Six-dot Code



A. First significant figure.
B. Second significant figure.
C. Third significant figure.
D. Voltage rating.
E. Tolerance.
F. Decimal multiplier.

2. American War Standard and Joint Army-Navy Code.



A. Always black (mica condenser).
B. First significant figure.
C. Second significant figure.
D. AWS or JAN characteristic.
E. Tolerance.
F. Decimal multiplier.

II. RMA Transformer Color Code

Power Transformers:

Primary—black.
High-voltage winding—red; center tap, red and yellow.
Rectifier filament winding—yellow; center tap, yellow and blue
Filament winding No. 1—green; center tap, green and yellow.
Filament winding No. 2—brown; center tap, brown and yellow.
Filament winding No. 3—slate; center tap, slate and yellow.

Audio Transformers:

Blue—plate lead.
Red—B+ lead.
Brown—second plate on push-pull.
Green—grid lead.
Black—ground lead.
Yellow—second grid on push-pull.

Intermediate Frequency Transformers:

Blue—plate lead.
Red—B+ lead.
Green—grid lead.
Black—ground (or AVC).
For center-tapped I.F. transformer, second grid is green-and-black-striped.

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