6. What is a standard solution? How is it prepared?
7. What are the requirements of a primary standard?
8. Why should a primary standard have a high formula weight?

Problems

WEIGHT/MOLE CALCULATIONS

9. Calculate the grams of substance required to prepare the following solutions: (a) 250 mL of 5.00% (wt/vol) $NaNO_3$; (b) 500 mL of 1.00% (wt/vol) NH_4NO_3, (c) 1000 mL of 10.0% (wt/vol) $AgNO_3$.
10. What is the wt/vol % of the solute in each of the following solutions? (a) 52.3 g Na_2SO_4/L, (b) 275 g KBr in 500 mL, (c) 3.65 g SO_2 in 200 mL.
11. Calculate the formula weights of the following substances: (a) $BaCl_2 \cdot 2H_2O$, (b) $KHC_2O_4 \cdot H_2C_2O_4$, (c) $Ag_2Cr_2O_7$, (d) $Ca_3(PO_4)_2$.
12. Calculate the number of millimoles contained in 500 mg of each of the following substances: (a) $BaCrO_4$, (b) $CHCl_3$, (c) $KIO_3 \cdot HIO_3$, (d) $MgNH_4PO_4$, (e) $Mg_2P_2O_7$, (f) $FeSO_4 \cdot C_2H_4(NH_3)_2SO_4 \cdot 4H_2O$.
13. Calculate the number of grams of each of the substances in Problem 11 that would have to be dissolved and diluted to 100 mL to prepare a 0.200 *M* solution.
14. Calculate the number of milligrams of each of the following substances you would have to weigh out in order to prepare the listed solutions: (a) 1.00 L of 1.00 *M* NaCl, (b) 0.500 L of 0.200 *M* sucrose ($C_{12}H_{22}O_{11}$), (c) 10.0 mL of 0.500 *M* sucrose, (d) 0.0100 L of 0.200 *M* Na_2SO_4, (e) 250 mL of 0.500 *M* KOH, (f) 250 mL of 0.900% NaCl (g/100 mL solution).
15. The chemical stockroom is supplied with the following stock solutions: 0.100 *M* HCl, 0.0200 *M* NaOH, 0.0500 *M* KOH, 10.0% HBr (wt/vol), and 5.00% Na_2CO_3 (wt/vol). What volume of stock solution would be needed to obtain the following amounts of solutes? (a) 0.0500 mol HCl, (b) 0.0100 mol NaOH, (c) 0.100 mol KOH, (d) 5.00 g HBr, (e) 4.00 g Na_2CO_3, (f) 1.00 mol HBr, (g) 0.500 mol Na_2CO_3.

MOLARITY CALCULATIONS

16. Calculate the molar concentrations of all the cations and anions in a solution prepared by mixing 10.0 mL each of the following solutions: 0.100 *M* $Mn(NO_3)_2$, 0.100 *M* KNO_3, and 0.100 *M* K_2SO_4.
17. A solution containing 10.0 mmol $CaCl_2$ is diluted to 1 L. Calculate the number of grams of $CaCl_2 \cdot 2H_2O$ per milliliter of the final solution.
18. Calculate the molarity of each of the following solations: (a) 10.0 g H_2SO_4 in 250 mL of solution, (b) 6.00 g NaOH in 500 mL of solution, (c) 25.0 g $AgNO_3$ in 1.00 L of solution.
19. Calculate the number of grams in 500 mL of each of the following solutions: (a) 0.100 *M* Na_2SO_4, (b) 0.250 *M* $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, (c) 0.667 *M* $Ca(C_9H_6ON)_2$.
20. Calculate the grams of each substance required to prepare the following solutions: (a) 250 mL of 0.100 *M* KOH, (b) 1.00 L of 0.0275 *M* $K_2Cr_2O_7$, (c) 500 mL of 0.0500 *M* $CuSO_4$.
21. How many milliliters of concentration hydrochloric acid, 38.0% (wt/wt), specific gravity 1.19, are required to prepare 1 L of a 0.100 *M* solution? (Assume density and specific gravity are equal within three significant figures.)

22. Calculate the molarity of each of the following commercial acid or base solutions: (a) 70.0% $HClO_4$, specific gravity 1.668, (b) 69.0% HNO_3, specific gravity 1.409, (c) 85.0% H_3PO_4, specific gravity 1.689, (d) 99.5% $HC_2H_3O_2$ (acetic acid), specific gravity 1.051, (e) 28.0% NH_3, specific gravity 0.898. (Assume density and specific gravity are equal within three significant figures.)

PPM CALCULATIONS

23. A solution contains 6.0 μmol Na_2SO_4 in 250 mL. How many ppm sodium does it contain? Of sulfate?

24. A solution (100 mL) containing 325 ppm K^+ is analyzed by precipitating it as the tetraphenyl borate, $K(C_6H_5)_4B$, dissolving the precipitate in acetone solution, and measuring the concentration of tetraphenyl borate ion, $(C_6H_5)_4B^-$, in the solution. If the acetone solution volume is 250 mL, what is the concentration of the tetraphenyl borate in ppm?

25. Calculate the molar concentrations of 1.00-ppm solutions of each of the following. (a) $AgNO_3$, (b) $Al_2(SO_4)_3$, (c) CO_2, (d) $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$, (e) HCl, (f) $HClO_4$.

26. Calculate the ppm concentrations of 2.50×10^{-4} *M* solutions of each of the following. (a) Ca^{2+}, (b) $CaCl_2$, (c) HNO_3, (d) KCN, (e) Mn^{2+}, (f) MnO_4^-.

27. You want to prepare 1 L of a solution containing 1.00 ppm Fe^{2+}. How many grams ferrous ammonium sulfate, $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$, must be dissolved and diluted in 1 L? What would be the molarity of this solution?

28. A 0.456-g sample of an ore is analyzed for chromium and found to contain 0.560 mg Cr_2O_3. Express the concentration of Cr_2O_3 in the sample as (a) percent, (b) parts per thousand, and (c) parts per million.

29. How many grams NaCl should be weighed out to prepare 1 L of a 100-ppm solution of (a) Na^+ and (b) Cl^-?

30. You have a 250-ppm solution of K^+ as KCl. You wish to prepare from this a 0.00100 *M* solution of Cl^-. How many milliliters must be diluted to 1 L?

31. One liter of a 500-ppm solution of $KClO_3$ contains how many grams K^+?

DILUTION CALCULATIONS

32. A 12.5-mL portion of a solution is diluted to 500 mL, and its molarity is determined to be 0.125. What is the molarity of the original solution?

33. What volume of 0.50 *M* H_2SO_4 must be added to 65 mL of 0.20 *M* H_2SO_4 to give a final solution of 0.35 *M*? Assume volumes are additive.

34. How many milliliters of 0.10 *M* H_2SO_4 must be added to 50 mL of 0.10 M NaOH to give a solution that is 0.050 *M* in H_2SO_4? Assume volumes are additive.

35. You are required to prepare working standard solutions of 1.00×10^{-5}, 2.00×10^{-5}, 5.00×10^{-5}, and 1.00×10^{-4} *M* glucose from a 0.100 *M* stock solution. You have available 100-mL volumetric flasks and pipets of 1.00-, 2.00-, 5.00-, and 10.00-mL volume. Outline a procedure for preparing the working standards.

36. A 0.500-g sample is analyzed spectrophotometrically for manganese by dissolving it in acid and transferring to a 250-mL flask and diluting to volume. Three aliquots are analyzed by transferring 50-mL portions with a pipet to 500-mL Erlenmeyer flasks and reacting with an oxidizing agent, potassium peroxydisulfate, to convert the manganese to permanganate. After reaction, these are quantitatively transferred to 250-mL volumetric flasks, diluted to volume, and measured spectrophotometrically. By comparison with standards, the average concentration in the final solution is determined to be 1.25×10^{-5} *M*. What is the percent manganese in the sample?

STANDARDIZATION CALCULATIONS

37. A preparation of soda ash is known to contain 98.6% Na_2CO_3. If a 0.678-g sample requires 36.8 mL of a sulfuric acid solution for complete neutralization, what is the molarity of the sulfuric acid solution?

38. A 0.1 *M* sodium hydroxide solution is to be standardized by titrating primary standard sulfamic acid (NH_2SO_3H). What weight of sulfamic acid should be taken so that the volume of NaOH delivered from the buret is about 40 mL?

ANALYSIS CALCULATIONS

39. A sample of USP-grade citric acid ($H_3C_6H_5O_7$, three titratable protons) is analyzed by titrating with 0.1087 *M* NaOH. If a 0.2678-g sample requires 38.31 mL for titration, what is the purity of the preparation? (USP requires 99.5%.)

40. Calcium in a 200-μL serum sample is titrated with 1.87×10^{-4} *M* EDTA solution, requiring 2.47 mL. What is the calcium concentration in the blood in mg/dL?

41. A 0.372-g sample of impure $BaCl_2 \cdot 2H_2O$ is titrated with 0.100 *M* $AgNO_3$, requiring 27.2 mL. Calculate (a) the percent Cl in the sample and (b) the percent purity of the compound.

42. An iron ore is analyzed for iron content by dissolving in acid, converting the iron to Fe^{2+}, and then titrating with standard 0.0150 *M* $K_2Cr_2O_7$ solution. If 35.6 mL is required to titrate the iron in a 1.68-g ore sample, how much iron is in the sample, expressed as percent Fe_2O_3? (See Example 5.37 for the titration reaction.)

43. Calcium in a 2.00-g sample is determined by precipitating CaC_2O_4, dissolving this in acid, and titrating the oxalate with 0.0200 M $KMnO_4$. What percent of CaO is in the sample if 35.6 mL $KMnO_4$ is required for titration? (The reaction is $5H_2C_2O_4 + 2MnO_4^- + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$.)

44. A potassium permanganate solution is prepared by dissolving 4.68 g $KMnO_4$ in water and diluting to 500 mL. How many milliliters of this will react with the iron in 0.500 g of an ore containing 35.6% Fe_2O_3? (See Example 5.29 for the titration reaction.)

45. A sample contains $BaCl_2$ plus inert matter. What weight must be taken so that when the solution is titrated with 0.100 $AgNO_3$, the milliliters of titrant will be equal to the percent $BaCl_2$ in the sample?

46. A 0.250-g sample of impure $AlCl_3$ is titrated with 0.100 *M* $AgNO_3$, requiring 48.6 mL. What volume of 0.100 *M* EDTA would react with a 0.350-g sample? (EDTA reacts with Al^{3+} in a 1:1 ratio.)

47. A 425.2-mg sample of a purified monoprotic organic acid is titrated with 0.1027 *M* NaOH, requiring 28.78 mL. What is the formula weight of the acid?

48. The purity of a 0.287-g sample of $Zn(OH)_2$ is determined by titrating with a standard HCl solution, requiring 37.8 mL. The HCl solution was standardized by precipitating AgCl in a 25.0-mL aliquot and weighing (0.462 g AgCl obtained). What is the purity of the $Zn(OH)_2$?

49. A sample of pure $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ (three replaceable hydrogens) requires 46.2 mL of 0.100 *M* NaOH for titration. How many milliliters of 0.100 *M* $KMnO_4$ will the same-size sample react with? (See Problem 43 for reaction with $KMnO_4$.)

BACK-TITRATIONS

50. A 0.500-g sample containing Na_2CO_3 plus inert matter is analyzed by adding 50.0 mL of 0.100 *M* HCl, a slight excess, boiling to remove CO_2, and then back-titrating the excess acid with 0.100 *M* NaOH. If 5.6 mL NaOH is required for the back-titration, what is the percent Na_2CO_3 in the sample?

51. A hydrogen peroxide solution is analyzed by adding a slight excess of standard $KMnO_4$ solution and back-titrating the unreacted $KMnO_4$ with standard Fe^{2+} solution. A 0.587-g sample of the H_2O_2 solution is taken, 25.0 mL of 0.0215 M $KMnO_4$ is added, and the back-titration requires 5.10 mL of 0.112 *M* Fe^{2+} solution. What is the percent H_2O_2 in the sample? (See Examples 5.25 and 5.29 for the reactions.)

52. The sulfur content of a steel sample is determined by converting it to H_2S gas, absorbing the H_2S in 10.0 mL of 0.00500 *M* I_2, and then back-titrating the excess I_2 with 0.00200 *M* $Na_2S_2O_3$. If 2.6 mL $Na_2S_2O_3$ is required for the titration, how many milligrams of sulfur are contained in the sample? Reactions:

$$H_2S + I_2 \rightarrow S + 2I^- + 2H^+$$

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

TITER

53. Express the titer of a 0.100 *M* EDTA solution in mg BaO/mL.

54. Express the titer of a 0.0500 *M* $KMnO_4$ solution in mg Fe_2O_3/mL.

55. The titer of a silver nitrate solution is 22.7 mg Cl/mL. What is its titer in mg Br/mL?

EQUIVALENT WEIGHT CALCULATIONS

56. Calculate the equivalent weights of the following substances as acids or bases: (a) HCl, (b) $Ba(OH)_2$, (c) $KH(IO_3)_2$, (d) H_2SO_3, (e) $HC_2H_3O_2$ (acetic acid).

57. Calculate the molarity of a 0.250 *N* solution of each of the acids or bases in Problem 56.

EQUIVALENT WEIGHT

58. Calculate the equivalent weight of KHC_2O_4 (a) as an acid and (b) as a reducing agent in reaction with MnO_4^- ($5HC_2O_4^- + 2MnO_4^- + 11H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$).

59. Mercuric oxide, HgO, can be analyzed by reaction with iodide and then titration with an acid: $HgO + 4I^- \rightarrow HgI_4^{2-} + 2OH^-$. What is its equivalent weight?

60. Calculate the grams of one equivalent each of the following for the indicated reaction: (a) $FeSO_4$ ($Fe^{2+} \rightarrow Fe^{3+}$), (b) H_2S ($\rightarrow S^0$), (c) H_2O_2 ($\rightarrow O_2$), (d) H_2O_2 ($\rightarrow H_2O$).

61. $BaCl_2 \cdot 2H_2O$ is to be used to titrate Ag^+ to yield AgCl. How many milliequivalents are contained in 0.5000 g $BaCl_2 \cdot 2H_2O$?

NORMALITY

62. A solution is prepared by dissolving 7.82 g NaOH and 9.26 g $Ba(OH)_2$ in water and diluting to 500 mL. What is the normality of the solution as a base?

63. What weight of arsenic trioxide, As_2O_3, is required to prepare 1 L of 0.1000 *N* arsenic(III) solution (arsenic 3+ is oxidized to 5+ in redox reactions)?

64. If 2.73 g $KHC_2O_4 \cdot H_2C_2O_4$ (three ionizable protons) having 2.0% inert impurities and 1.68 g $KHC_8H_4O_4$ (one ionizable proton) are dissolved in water and diluted to 250 mL, what is the normality of the solution as an acid, assuming complete ionization?

65. A solution of $KHC_2O_4 \cdot H_2C_2O_4 \cdot 2H_2O$ (three replaceable hydrogens) is 0.200 *N* as an acid. What is its normality as reducing agent? (See Problem 43 for its reaction as a reducing agent.)

66. $Na_2C_2O_4$ and $KHC_2O_4 \cdot H_2C_2O_4$ are mixed in such a proportion by weight that the normality of the resulting solution as a reducing agent is 3.62 times the normality as an acid. What is the proportion? (See Problem 43 for its reaction as a reducing agent.)

67. What weight of $K_2Cr_2O_7$ is required to prepare 1.000 L of 0.1000 *N* solution? (In reaction, $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3} + 7H_2O$.)

CHARGE EQUIVALENT CALCULATIONS

68. A chloride concentration is reported as 300 mg/dL. What is the concentration in meq/L?

69. A calcium concentration is reported as 5.00 meq/L. What is the concentration in mg/dL?

70. A urine specimen has a chloride concentration of 150 meq/L. If we assume that the chloride is present in urine as sodium chloride, what is the concentration of NaCl in g/L?

GRAVIMETRIC CALCULATIONS

71. What weight of manganese is present in 2.58 g of Mn_3O_4?

72. Zinc is determined by precipitating and weighing as $Zn_2Fe(CN)_6$.

(a) What weight of zinc is contained in a sample that gives 0.348 g precipitate?

(b) What weight of precipitate would be formed from 0.500 g of zinc?

73. Calculate the gravimetric factors for:

Substance Sought	Substance Weighed
Mn	Mn_3O_4
Mn_2O_3	Mn_3O_4
Ag_2S	$BaSO_4$
$CuCl_2$	AgCl
MgI_2	PbI_2

Recommended References

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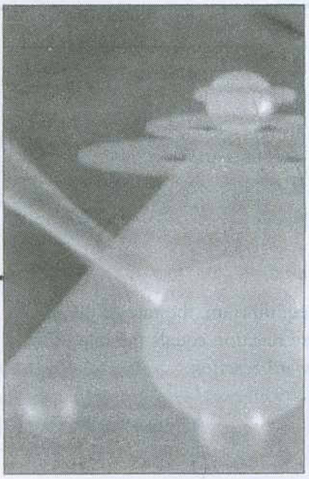

Chapter Six

GENERAL CONCEPTS OF CHEMICAL EQUILIBRIUM

"The worst form of inequality is to try to make unequal things equal."
—Aristotle

Even though chemical reactions may go far to completion, the reactions *never* go in only one direction. In fact, reactions reach an equilibrium in which the rates of reactions in both directions are equal. In this chapter we review the equilibrium concept and the equilibrium constant and describe general approaches for calculations using equilibrium constants. We discuss the activity of ionic species along with the calculation of activity coefficients. These values are required for calculations using thermodynamic equilibrium constants, that is, for the diverse ion effect, described at the end of the chapter. They are also used in potentiometric calculations (Chapter 13).

6.1 Chemical Reactions: The Rate Concept

In 1863 Guldberg and Waage described what we now call the law of mass action, which states that the rate of a chemical reaction is proportional to the "active masses" of the reacting substances present at any time. The active masses may be concentrations or pressures. Guldberg and Waage derived an equilibrium constant by defining equilibrium as the condition when the rates of the forward and reverse reactions are equal. Consider the chemical reaction

$$aA + bB \rightleftharpoons cC + dD \tag{6.1}$$

According to Guldberg and Waage, the rate of the forward reaction is equal to a constant times the concentration of each species raised to the power of the number of molecules participating in the reaction: that is,[1]

$$\text{Rate}_f = k_f[A]^a[B]^b \tag{6.2}$$

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[1] [ ] represents moles/liter and here represents the effective concentration. The effective concentration will be discussed under the diverse ion effect, when we talk about activities.

when rate$_f$ is the rate of the forward reaction and k_f is the **rate constant**, which is dependent on such factors as the temperature and the presence of catalysts. [A] and [B] represent the molar concentrations of A and B. Similarly, for the backward reaction, Guldberg and Waage wrote

$$\text{Rate}_b = k_b[\mathrm{C}]^c[\mathrm{D}]^d \tag{6.3}$$

and for a system at equilibrium, the forward and reverse rates are equal:

$$k_f[\mathrm{A}]^a[\mathrm{B}]^b = k_b[\mathrm{C}]^c[\mathrm{D}]^d \tag{6.4}$$

At equilibrium, the rate of the reverse reaction equals the rate of the forward reaction.

Rearranging these equations gives the **molar equilibrium constant** (which holds for dilute solutions) for the reaction, K:

$$\frac{[\mathrm{C}]^c[\mathrm{D}]^d}{[\mathrm{A}]^a[\mathrm{B}]^b} = \frac{k_f}{k_b} = K \tag{6.5}$$

The expression obtained here is the correct expression for the equilibrium constant, *but the method of derivation has no general validity.* This is because reaction rates actually depend on the *mechanism* of the reaction, determined by the number of colliding species, whereas the equilibrium constant expression depends only on the *stoichiometry* of the chemical reaction. The sum of the exponents in the rate constant gives the *order* of the reaction, and this may be entirely different from the stoichiometry of the reaction (see Chapter 22). An example is the rate of reduction of $S_2O_8^{2-}$ with I^-:

$$S_2O_8^{2-} + 3I^- \rightarrow 2SO_4^{2-} + I_3^-$$

The rate is actually given by $k_f[S_2O_8^{2-}][I^-]$ (a second-order reaction) and not $k_f[S_2O_8^{2-}][I^-]^3$, as might be expected from the balanced chemical reaction (a fourth-order reaction would be predicted). The only sound theoretical basis for the equilibrium constant comes from thermodynamic arguments. See Gibbs free energy in Section 6.3 for the thermodynamic computation of equilibrium constant values.

The value of K can be calculated empirically by measuring the concentrations of A, B, C, and D at equilibrium. Note that the more favorable the rate constant of the forward reaction relative to the backward reaction, the larger will be the equilibrium constant and the farther to the right the reaction will be at equilibrium.

The larger the equilibrium constant, the farther to the right is the reaction at equilibrium.

When the reaction between A and B is initiated, the rate of the forward reaction is large because the concentrations of A and B are large, whereas the backward reaction is slow because the concentrations of C and D are small (that rate is initially zero). As the reaction progresses, A and B decrease and C and D increase, so that the rate of the forward reaction diminishes while that for the backward reaction increases (Figure 6.1). Eventually, the two rates become equal, and

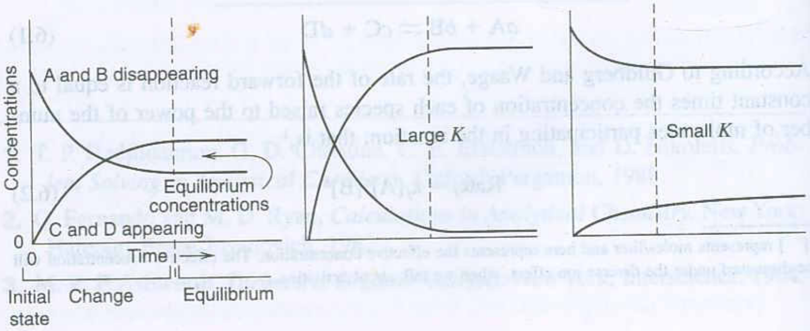


Fig. 6.1. Progress of a chemical reaction.

the system is in a state of equilibrium. At this point, the individual concentrations of A, B, C, and D remain constant (the relative values will depend on the reaction stoichiometry and how far the equilibrium lies to the right). However, the system remains in dynamic equilibrium, with the forward and backward reactions continuing at equal rates.

You will notice that the equilibrium constant expression is the ratio in which the concentrations of the products appear in the numerator and the concentrations of the reactants appear in the denominator. This is quite arbitrary, but it is the accepted convention. Hence, a large equilibrium constant indicates the equilibrium lies far to the right.

We should point out that although a particular reaction may have a rather large equilibrium constant, the reaction may proceed from *right* to *left* if sufficiently large concentrations of the *products* are initially present. Also, the equilibrium constant tells us nothing about how *fast* a reaction will proceed toward equilibrium. Some reactions, in fact, may be so slow as to be unmeasurable. The equilibrium constant merely tells us the tendency of a reaction to occur and in what direction, not whether it is fast enough to be feasible in practice. (See Chapter 22 on kinetic methods of analysis for the measurement of reaction rates and their application to analyses.)

A large equilibrium constant does not assure the reaction will proceed at an appreciable rate.

For the reaction depicted in Equation 6.1, the rate at which equilibrium approached will likely be different for either the forward or the reverse reaction. That is, if we start with a mixture of C and D, the rate at which equilibrium is approached may be much slower or faster than for the converse reaction.

6.2 Types of Equilibria

We can write equilibrium constants for many types of chemical processes. Some of these equilibria are listed in Table 6.1. The equilibria may represent dissociation (acid/base, solubility), formation of products (complexes), reactions (redox), a distribution between two phases (water and nonaqueous solvent—solvent extraction; adsorption from water onto a surface, as in chromatography, etc.). We will describe some of these equilibria below and in later chapters.

Equilibrium constants may be written for dissociations, associations, reactions, or distributions.

6.3 Gibbs Free Energy and the Equilibrium Constant

The tendency for a reaction to occur is defined thermodynamically from its change in **enthalpy** (ΔH) and **entropy** (ΔS). Enthalpy is the heat absorbed when an endothermic reaction occurs under constant pressure. When heat is given off

Table 6.1
Types of Equilibria

Equilibrium	Reaction	Equilibrium Constant
Acid–base dissociation	$HA + H_2O \rightleftharpoons H_3O^+ + A^-$	K_a, acidity constant
Solubility	$MA \rightleftharpoons M^{n+} + A^{n-}$	K_{sp}, solubility product
Complex formation	$M^{n+} + aL^{b-} \rightleftharpoons ML_a^{(n-ab)+}$	K_f, formation constant
Reduction–oxidation	$A_{red} + B_{ox} \rightleftharpoons A_{ox} + B_{red}$	K_{eq}, reaction equilibrium constant
Phase distribution	$A_{H_2O} \rightleftharpoons A_{organic}$	K_D, distribution coefficient

(exothermic reaction), ΔH is negative. Entropy is a measure of the disorder, or randomness, of a substance or system.

Everything in the universe tends toward increased disorder (increased entropy) and lower energy (lower enthalpy).

A system will always tend toward lower energy and increased randomness, that is, lower enthalpy and higher entropy. For example, a stone on a hill will tend to roll spontaneously down the hill (lower energy state), and a box of marbles ordered by color will tend to become randomly ordered when shaken. The combined effect of enthalpy and entropy is given by the **Gibbs free energy**, G:

$$G = H \quad TS \tag{6.6}$$

where T is the absolute temperature in kelvins; G is a measure of the energy of the system, and a system spontaneously tends toward lower energy states. The change in energy of a system at a constant temperature is

$$\Delta G = \Delta H - T\,\Delta S \tag{6.7}$$

A spontaneous reaction results in energy given off and a lower free energy. At equilibrium, the free energy does not change.

So a process will be *spontaneous when* ΔG *is negative*, will be spontaneous in the reverse direction when ΔG is positive, and will be at equilibrium when ΔG is zero. Hence, a reaction is favored by heat given off (negative ΔH), as in exothermic reactions, and by increased entropy (positive ΔS). Both ΔH and ΔS can be either positive or negative, and the relative magnitudes of each and the temperature will determine whether ΔG will be negative so that the reaction will be spontaneous.

Standard enthalpy H°, standard entropy S°, and standard free energy G° represent the thermodynamic quantities for one mole of a substance at standard state ($P = 1$ atm, $T = 298$ K, unit concentration). Then,

$$\Delta G^\circ = \Delta H^\circ - T\,\Delta S^\circ \tag{6.8}$$

ΔG° is related to the equilibrium constant of a reaction by

$$\boxed{K = e^{-\Delta G^\circ/RT}} \tag{6.9}$$

or

$$\boxed{\Delta G^\circ = -RT \ln K = -2.303RT \log K} \tag{6.10}$$

A large equilibrium constant results from a large negative free energy.

where R is the gas constant (8.314 J K^{-1} mol^{-1}). Hence, if we know the standard free energy of a reaction, we can calculate the equilibrium constant. Obviously, the larger ΔG° (when negative), the larger will be K. Note that while ΔG° and ΔG give information about the spontaneity of a reaction, they say nothing about the *rate* at which it will occur.

6.4 Le Châtelier's Principle

We can shift an unfavorable equilibrium by increasing the reactant concentration.

The equilibrium concentrations of reactants and products can be altered by applying stress to the system, for example, by changing the temperature, the pressure, or the concentration of one of the reactants. The effects of such changes can be predicted from **Le Châtelier's principle**, which states that when stress is applied to a system at chemical equilibrium, the equilibrium will shift in a direction that tends to relieve or counteract that stress. The effects of temperature, pressure, and concentrations on chemical equilibria are considered below.

6.5 Temperature Effects on Equilibrium Constants

As we have mentioned, temperature influences the individual rate constants for the forward and backward reactions and therefore the equilibrium constant (more correctly, temperature affects the free energy—see Equation 6.10). An increase in temperature will displace the equilibrium in the direction that results in absorbing heat, since this removes the source of the stress. So an endothermic forward reaction (which absorbs heat) will be displaced to the right, with an increase in the equilibrium constant. The reverse will be true for an exothermic forward reaction, which releases heat. The extent of the displacement will depend on the magnitude of the heat of reaction for the system.

All equilibrium constants are temperature dependent, as are the rates of reactions.

In addition to influencing the position of equilibrium, temperature has a pronounced effect on the rates of the forward and backward reactions involved in the equilibrium, and so it influences the *rate* at which equilibrium is approached. This is because the number and the energy of collisions among the reacting species increase with increasing temperature. The rates of many endothermic reactions increase about two- to threefold for every 10°C rise in temperature.

6.6 Pressure Effects on Equilibria

Pressure can have a large influence on the position of chemical equilibrium for reactions occurring in the gaseous phase. An increase in pressure favors a shift in the direction that results in a reduction in the volume of the system. But for reactions occurring in solutions, normal pressure changes have a negligible effect on the equilibrium because liquids cannot be compressed the way gases can.

For solutions, pressure effects are usually negligible.

6.7 Effect of Concentrations on Equilibria

The value of an equilibrium constant is independent of the concentrations of the reactants and products. However, the *position* of equilibrium is very definitely influenced by the concentrations. The direction of change is readily predictable from Le Châtelier's principle. Consider the reaction of iron(III) with iodide:

Changes in concentration do not affect the equilibrium constant. They *do* affect the position of the equilibrium.

$$3I^- + 2Fe^{3+} \rightleftharpoons I_3^- + 2Fe^{2+}$$

If the four components are in a state of equilibrium, as determined by the equilibrium constant, addition or removal of one of the components would cause the equilibrium to reestablish itself. For example, suppose we add more iron(II) to the solution. According to Le Châtelier's principle, the reaction will shift to the left to relieve the stress. Equilibrium will eventually be reestablished, and its position will still be defined by the same equilibrium constant.

6.8 Catalysts

Catalysts either speed up or retard the rate at which an equilibrium is attained by affecting the rates of both the forward and the backward reactions. But catalysts affect both rates to the same extent and thus have no effect on the value of an equilibrium constant.

Catalysts do not affect the equilibrium constant or the position at equilibrium.

See Chapter 22 for analytical uses of enzyme catalysts.

Catalysts are very important to the analytical chemist in a number of reactions that are normally too slow to be analytically useful. An example is the use of an osmium tetroxide catalyst to speed up the titration reaction between arsenic(III) and cerium(IV), whose equilibrium is very favorable but whose rate is normally too slow to be useful for titrations. The measurement of the change in the rate of a kinetically slow reaction in the presence of a catalyst can actually be used for determining the catalyst concentration.

6.9 Completeness of Reactions

For quantitative analysis, equilibria should be at least 99.9% to the right for precise measurements. A reaction that is 75% to the right is still a "complete" reaction.

If the equilibrium of a reaction lies sufficiently to the right that the remaining amount of the substance being determined (reacted) is too small to be measured by the measurement technique, we say the reaction has gone to completion. If the equilibrium is not so favorable, then Le Châtelier's principle may be applied to make it so. We may either increase the concentration of a reactant or decrease the concentration of a product. Production of more product may be achieved by (1) allowing a gaseous product to escape, (2) precipitating the product, (3) forming a stable ionic complex of the product in solution, or (4) preferential extraction.

It is apparent from the above discussion that Le Châtelier's principle is the dominant concept behind most chemical reactions in the real world. It is particularly important in biochemical reactions, and external factors such as temperature can have a significant effect on biological equilibria. Catalysts (enzymes) are also key players in many biological and physiological reactions, as we shall see in Chapter 22.

6.10 Equilibrium Constants for Dissociating or Combining Species—Weak Electrolytes and Precipitates

Equilibrium constants are finite when dissociations are less than 100%.

When a substance dissolves in water, it will often partially or completely dissociate or ionize. Partially dissociated electrolytes are called *weak electrolytes*, and completely dissociated ones are *strong electrolytes*. For example, acetic acid only partially ionizes in water and is therefore a weak electrolyte. But hydrochloric acid is completely ionized and thus is a strong electrolyte. (Acid dissociations in water are really proton transfer reactions: $HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^-$). Some substances completely ionize in water but have limited solubility; we call these *slightly soluble substances*. Substances may combine in solution to form a dissociable product, for example, a complex. An example is the reaction of copper(II) with ammonia to form the $Cu(NH_3)_4{}^{2+}$ species.

A weak electrolyte is only partially dissociated. A slightly soluble substance is a strong electrolyte because the portion that dissolves is totally ionized.

The dissociation of weak electrolytes or the solubility of slightly soluble substances can be quantitatively described by equilibrium constants. Equilibrium constants for completely dissolved and dissociated electrolytes are effectively infinite. Consider the dissociating species AB:

$$AB \rightleftharpoons A + B \tag{6.11}$$

The equilibrium constant for such a dissociation can be written generally as

$$\boxed{\frac{[A][B]}{[AB]} = K_{eq}} \tag{6.12}$$

The larger K_{eq}, the greater will be the dissociation. For example, the larger the equilibrium constant of an acid, the stronger will be the acid.

Some species dissociate stepwise, and an equilibrium constant can be written for each dissociation step. A compound A_2B, for example, may dissociate as follows:

$$A_2B \rightleftharpoons A + AB \qquad K_1 = \frac{[A][AB]}{[A_2B]} \tag{6.13}$$

$$AB \rightleftharpoons A + B \qquad K_2 = \frac{[A][B]}{[AB]} \tag{6.14}$$

The overall dissociation of the compound is the sum of these two equilibria:

Successive stepwise dissociation constants become smaller.

$$A_2B \rightleftharpoons 2A + B \qquad K_{eq} = \frac{[A]^2[B]}{[A_2B]} \tag{6.15}$$

If we multiply Equations 6.13 and 6.14 together, we arrive at the overall equilibrium constant:

$$K_{eq} = K_1K_2 = \frac{[A][AB]}{[A_2B]} \cdot \frac{[A][B]}{[AB]} = \frac{[A]^2[B]}{[A_2B]} \tag{6.16}$$

When chemical species dissociate in a stepwise manner like this, the successive equilibrium constants generally become progressively smaller. Note that in equilibrium calculations we always use mol/L for solution concentrations.

If a reaction is written in the reverse, the same equilibria apply, but the equilibrium constant is inverted. Thus, in the above example, for $A + B \rightleftharpoons AB$, $K_{eq(reverse)} = [AB]/([A][B]) = 1/K_{eq(forward)}$. If K_{eq} for the forward reaction is 10^5, then K_{eq} for the reverse reaction is 10^{-5}.

$K_{forward} = 1/K_{backward}$

Similar concepts apply for combining species, except, generally, the equilibrium constant will be greater than unity rather than smaller, since the reaction is favorable for forming the product (e.g., complex). We will discuss equilibrium constants for acids, complexes, and precipitates in later chapters.

6.11 Calculations Using Equilibrium Constants—How Much Is in Equilibrium?

Equilibrium constants are useful for calculating the concentrations of the various species in equilibrium, for example, the hydrogen ion concentration from the dissociation of a weak acid. In this section we present the general approach for calculations using equilibrium constants. The applications to specific equilibria are treated in later chapters dealing with these equilibria.

CHEMICAL REACTIONS

It is sometimes useful to know the concentrations of reactants and products in equilibrium in a chemical reaction. For example, we may need to know the amount of reactant for the construction of a titration curve or for calculating the potential of an electrode in the solution. These are, in fact, applications we consider in later chapters. Some example calculations will illustrate the general approach to solving equilibrium problems.

Example 6.1

The chemicals A and B react as follows to produce C and D:

$$A + B \rightleftharpoons C + D \qquad K = \frac{[C][D]}{[A][B]}$$

The equilibrium constant K has a value of 0.30. Assume 0.20 mol of A and 0.50 mol of B are dissolved in 1.00 L, and the reaction proceeds. Calculate the concentrations of reactants and products at equilibrium.

Solution

The initial concentration of A is 0.20 M and that of B is 0.50 M, while C and D are initially 0 M. After the reaction has reached equilibrium, the concentrations of A and B will be decreased and those of C and D will be increased. Let x represent the equilibrium concentration of C or the moles/liter of A and B reacting. Since we get one mole of D with each mole of C, the concentration of D will also be x. We may represent the *initial* concentration of A and B as the **analytical concentrations**, C_A and C_B. The **equilibrium concentrations** are [A] and [B]. The concentrations of A and B will each be diminished by x, that is, $[A] = C_A - x$ and $[B] = C_B - x$. So the equilibrium concentrations are

The equilibrium concentration is the initial (analytical) concentration minus the amount reacted.

	$[A]$	$[B]$	$[C]$	$[D]$
Initial	0.20	0.50	0	0
Change (x = mmol/mL reacting)	$-x$	$-x$	$+x$	$+x$
Equilibrium	$0.20 - x$	$0.50 - x$	x	x

We can substitute these values in the equilibrium constant expression and solve for x:

$$\frac{(x)(x)}{(0.20 - x)(0.50 - x)} = 0.30$$

$$x^2 = (0.10 - 0.70x + x^2)0.30$$

$$0.70x^2 + 0.21x - 0.030 = 0$$

This is a quadratic equation and can be solved algebraically for x using the quadratic formula given in Appendix B:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-0.21 \pm \sqrt{(0.21)^2 - 4(0.70)(-0.030)}}{2(0.70)}$$

$$= \frac{-0.21 \pm \sqrt{0.044 + 0.084}}{1.40} = 0.11\ M$$

$$[\mathrm{A}] = 0.20 - x = 0.09\ M$$
$$[\mathrm{B}] = 0.50 - x = 0.39\ M$$
$$[\mathrm{C}] = [\mathrm{D}] = x = 0.11\ M$$

Instead of using the quadratic equation, we may use the **method of successive approximations**. In this procedure, we will first neglect x compared to the initial concentrations to simplify calculations, and calculate an initial value of x. Then we can use this first estimate of x to subtract from C_A and C_B to give an initial estimate of the equilibrium concentration of A and B, and calculate a new x. The process is repeated until x is essentially constant.

In successive approximations, we begin by taking the analytical concentration as the equilibrium concentration, to calculate the amount reacted. Then we repeat the calculation after subtracting the calculated reacted amount, until it is constant.

First calculation
$$\frac{(x)(x)}{(0.20)(0.50)} = 0.30$$
$$x = 0.173$$

The calculations converge more quickly if we keep an extra digit throughout.

Second calculation
$$\frac{(x)(x)}{(0.20 - 0.173)(0.50 - 0.173)} = 0.30$$
$$x = 0.051$$

Third calculation
$$\frac{(x)(x)}{(0.20 - 0.051)(0.50 - 0.051)} = 0.30$$
$$x = 0.14_2$$

Fourth calculation
$$\frac{(x)(x)}{(0.20 - 0.142)(0.50 - 0.142)} = 0.30$$
$$x = 0.079$$

Fifth calculation
$$\frac{(x)(x)}{(0.20 - 0.79)(0.50 - 0.079)} = 0.30$$
$$x = 0.12_4$$

Sixth calculation
$$\frac{(x)(x)}{(0.20 - 0.124)(0.50 - 0.124)} = 0.30$$
$$x = 0.093$$

Seventh calculation
$$\frac{(x)(x)}{(0.20 - 0.093)(0.50 - 0.093)} = 0.30$$
$$x = 0.11_4$$

Eighth calculation
$$\frac{(x)(x)}{(0.20 - 0.114)(0.50 - 0.114)} = 0.30$$
$$x = 0.10_4$$

Ninth calculation
$$\frac{(x)(x)}{(0.20 - 0.100)(0.50 - 0.100)} = 0.30$$
$$x = 0.11_0$$

We will take 0.11 as the equilibrium value of x since it essentially repeated the value of the seventh calculation. Note that in these iterations, x oscillates above and below the equilibrium value. The larger x is compared to C, the larger will be the

Shorten the number of iterations by taking the average of the first two for the next.

oscillations and the more iterations that will be required to reach an equilibrium value (as in this example—not the best for this approach). There is a more efficient way of completing the iteration. Take the average of the first and second for the third iteration, which should be close to the final value (in this case, 0.11_2). One or two more iterations will tell us we have reached the equilibrium value. Try it!

……

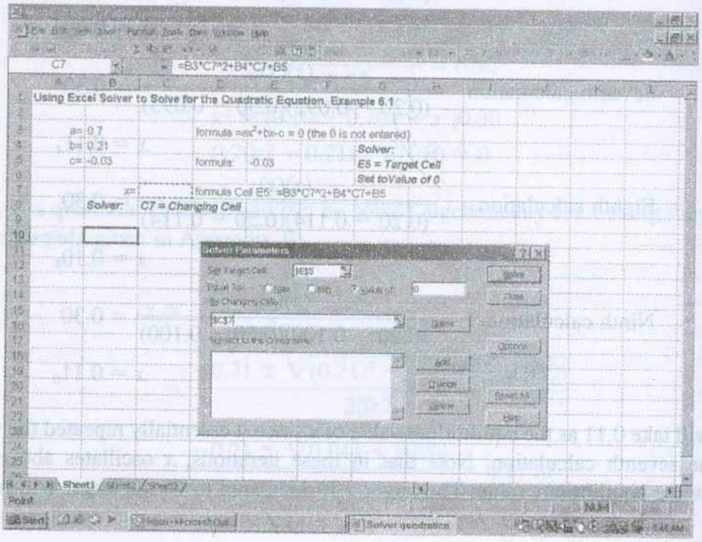
In Example 6.1, appreciable amounts of A remained, even though B was in excess, because the equilibrium constant was not very large. In fact, the equilibrium was only about halfway to the right since C and D were about the same concentration as A. In most reactions of analytical interest, the equilibrium constants are large, and the equilibrium lies far to the right. In these cases, the equilibrium concentrations of reactants that are not in excess are generally very small compared to the other concentrations. This simplifies our calculations.

EXCEL SOLVER FOR PROBLEM SOLVING—THE QUADRATIC EQUATION

Microsoft Excel has a very useful program called *Solver*. To use this program, we must first arrange an equation to give a formula equal to a known value. Solver effectively calculates the formula in reverse, by starting with the answer of the formula (the known value) and, by iteration, solving for the value or values of one or more variables in the formula that results in the correct answer. (Other spreadsheet programs have similar problem solvers.)

As previously stated, in order to apply the Solver program, we must arrange the equation to give a formula equal to a known value. This can be a value we want to minimize (as in least squares), maximize, set to zero, or any other fixed number. When we do this, the variable or variables (whose values we wish to calculate) are on one side of the formula. In Example 6.1, we arrange the equilibrium constant equation to give a formula equal to zero: $0.70x^2 + 0.21x - 0.30 = 0$. The variable is x.

The Solver program is generally found under Tools in the Excel spreadsheet. If you do not see it there, it is probably an Add-In, which you have to activate by checking the Solver Add-In box. Once you locate Solver, click on it and you will open the Solver Parameters dialogue box. The filled-in Solver dialogue box for Example 6.1 is shown here:



C7 =B3*C7^2+B4*C7+B5

Using Excel Solver to Solve for the Quadratic Equation, Example 6.1

a= 0.7 formula =ax²+bx-c = 0 (the 0 is not entered)
b= 0.21 Solver:
c= -0.03 formula: -0.03 E5 = Target Cell
Set toValue of 0
x= formula Cell E5: =B3*C7^2+B4*C7+B5
Solver: C7 = Changing Cell

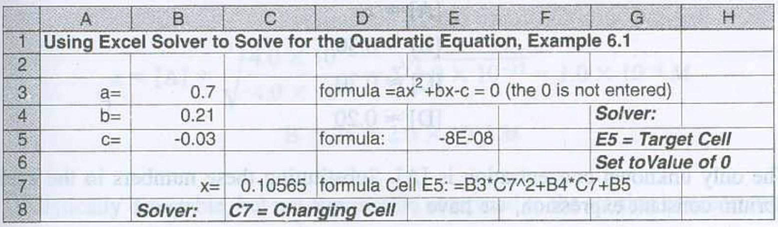
Solver Parameters
Set Target Cell: E5
Equal To: Value of: 0
By Changing Cells: C7

Three parameters need to be entered. The Set Target Cell: is where you enter the cell containing the entered formula. Entering \$ signs for the cell is optional. If you click on the cell to enter (either before or after opening Solver), they are automatically entered. The Equal To: is where you enter the value that the equation is set to (0, in this case). And By Changing Cells: is where you enter the cell or cells containing the variable or variables (*x*, in this case). If you have more than one variable cell, insert a comma between each cell entry. Since we don't know the value of the *x* cell, we may leave it empty, or we may put an estimated initial value in the cell.

For the equation we have chosen, create a spreadsheet with cells that contain the constants *a*, *b*, and *c*, that is, 0.70, 0.21, and −0.030, that will be used in the formula; the variable *x*; the formula ($0.70x^2 + 0.21x - 0.30$): =[0.70 cell]*[*x* cell]^2 + [0.21 cell]*[*x* cell] + [−0.030 cell]. Label each cell. In the spreadsheet above, the constants are in cells B3, B4, and B5. The variable *x* is in cell C7, and the formula is B3*C7^2 + B4*C7 + B4. The formula is entered in cell E5. Note that E5 shows a value of −0.03 (i.e., the value of *c*) since *x* does not yet have a value.

Click on Solver. When its parameters dialogue box appears in the spreadsheet, click on the Set Target Cell: (it should be empty, if not, delete any cell that is there), followed by clicking on cell E5 (or type E5). Do the same for By Changing Cells:, clicking on cell C7 to enter. In Equal To:, click Value of: and enter zero. You are now ready to solve the formula. But before you do, click on Options and note the Precision box, where the precision is entered as 0.000001 (10^{-6}). This number should be at least 100 times smaller than the smallest number being operated on (*a*, *b*, and *c* in this case) and the solution, *x*. This is the case for this problem, but if you should encounter problems where it is not, you should insert more zeros in the Precision number, for example, when the magnitude of the calculated answer is on the order of the entered precision (in which case, repeat the Solver calculation).

Close the Solver Options window and click on Solve and you receive a message that "Solver found a solution," and you see the answer for *x* is 0.10565:



	A	B	C	D	E	F	G	H
1	**Using Excel Solver to Solve for the Quadratic Equation, Example 6.1**							
2								
3	a=	0.7		formula =ax^2+bx-c = 0 (the 0 is not entered)				
4	b=	0.21					***Solver:***	
5	c=	-0.03		formula:	-8E-08		***E5 = Target Cell***	
6							***Set toValue of 0***	
7		x=	0.10565	formula Cell E5: =B3*C7^2+B4*C7+B5				
8		***Solver:***	***C7 = Changing Cell***					

The formula is equal to −8E-08, a very small number resulting from the iterations (essentially equal to zero).

Mathematically, the quadratic equation also always has a negative answer for *x* (which we are not interested in since it makes no chemical sense). That value of *x* can be obtained by constraining the answer to be less than zero in the Subject to the Constraints box. Click on Add. For Cell Reference, click on C7. Adjust the arrow to move to <=. In the Constraint dialogue box, type 0. Then click OK. Click on Solve, and you see the answer $x = -0.40565$ (and formula = −9E-07).

If you click on Options in the Solver dialogue box, you can set limits that may slightly alter the final result. We will use Solver on other occasions to aid in solving tedious problems.

The spreadsheet setup for Example 6.1 is given in your CD, Chapter 6. You can use it for solving other quadratic equations by inserting the appropriate *a*, *b*, *c* constants in the cells and then activating Solver to calculate *x*; insert the target cell (formula) and the changing cell (*x*).

Example 6.2

Assume that in Example 6.1 the equilibrium constant was 2.0×10^{16}. Calculate the equilibrium concentrations of A, B, C, and D.

Solution

If the equilibrium constant for a reaction is very large, *x* is very small compared to the analytical concentration, which simplifies calculations.

Since *K* is very large, the reaction of A with B will be virtually complete to the right, leaving only traces of A at equilibrium. Let *x* represent the equilibrium concentration of A. An amount of B equal to A will have reacted to form an equivalent amount of C and D (about 0.20 *M* for each). We can summarize the equilibrium concentrations as follows:

$$[\mathrm{A}] = x$$
$$[\mathrm{B}] = (0.50 - 0.20) + x = 0.30 + x$$
$$[\mathrm{C}] = 0.20 - x$$
$$[\mathrm{D}] = 0.20 - x$$

Or, looking at the equilibrium,

$$\begin{array}{ccccccc} \mathrm{A} & + & \mathrm{B} & \rightleftharpoons & \mathrm{C} & + & \mathrm{D} \\ x & & 0.30 + x & & 0.20 - x & & 0.20 - x \end{array}$$

Basically, we have said that all of A is converted to a like amount of C and D, except for a small amount *x*. Now *x* will be very small compared to 0.20 and 0.30 and can be neglected. So we can say

$$[\mathrm{A}] = x$$
$$[\mathrm{B}] \approx 0.30$$
$$[\mathrm{C}] \approx 0.20$$
$$[\mathrm{D}] \approx 0.20$$

The only unknown concentration is [A]. Substituting these numbers in the equilibrium constant expression, we have

$$\frac{(0.20)(0.20)}{(x)(0.30)} = 2.0 \times 10^{16}$$

$$x = [\mathrm{A}] = 6.7 \times 10^{-18}\ M \text{ (analytically undetectable)}$$

In this case the calculation was considerably simplified by neglecting *x* in comparison to other concentrations. If *x* should turn out to be significant compared to these concentrations, then the solution should be reworked using the quadratic formula, or the method of successive approximations starting with the first estimate of *x*. **Generally, if the value of *x* is less than about 5% of the assumed concentration, it can be neglected.** In this case, the error in *x* itself is usually 5%

Neglect *x* compared to *C* (product) if $C \leq 0.01K_{\mathrm{eq}}$ in a reaction.

or less. **This simplification will generally hold if the product concentration is less than 1% at K_{eq}, that is $\leq 0.01\ K_{eq}$.**

Example 6.3

A and B react as follows:

$$A + 2B \rightleftharpoons 2C \qquad K = \frac{[C]^2}{[A][B]^2}$$

Assume 0.10 mol of A is reacted with 0.20 mol of B in a volume of 1000 mL; $K = 1.0 \times 10^{10}$. What are the equilibrium concentrations of A, B, and C?

Solution

We have stoichiometrically equal amounts of A and B, so both are virtually all reacted, with trace amounts remaining. Let x represent the equilibrium concentration of A. At equilibrium, we have

$$\begin{array}{ccccc} A & + & 2B & \rightleftharpoons & 2C \\ x & & 2x & & 0.20 - 2x \approx 0.20 \end{array}$$

For each mole of A that either reacts or is produced, we produce or remove two moles of C, and consume or produce two moles of B. Substituting into the equilibrium constant expression,

$$\frac{(0.20)^2}{(x)(2x)^2} = 1.0 \times 10^{10}$$

$$\frac{0.040}{4x^3} = 1.0 \times 10^{10}$$

$$x = [A] = \sqrt[3]{\frac{4.0 \times 10^{-2}}{4.0 \times 10^{10}}} = \sqrt[3]{1.0 \times 10^{-12}} = 1.0 \times 10^{-4}\ M$$

$$B = 2x = 2.0 \times 10^{-4}\ M$$

(analytically detectable, but not appreciable compared to the starting concentration)

DISSOCIATION EQUILIBRIA

Calculations involving dissociating species are not much different from the example just given for chemical reactions.

Example 6.4

Calculate the equilibrium concentrations of A and B in a 0.10 M solution of a weak electrolyte AB with an equilibrium constant of 3.0×10^{-6}.

Solution

$$\mathrm{AB} \rightleftharpoons \mathrm{A} + \mathrm{B} \qquad K_{\mathrm{eq}} = \frac{[\mathrm{A}][\mathrm{B}]}{[\mathrm{AB}]}$$

Both [A] and [B] are unknown and equal. Let x represent their equilibrium concentrations. The concentration of AB at equilibrium is equal to its initial analytical concentration minus x.

$$\begin{array}{ccc} \mathrm{AB} & \rightleftharpoons \mathrm{A} & + \ \mathrm{B} \\ 0.10 - x & x & x \end{array}$$

Neglect x compared to C (analytical concentration) if $C \geq 100K_{\mathrm{eq}}$ in a dissociation.

The value of K_{eq} is quite small, so we are probably justified in neglecting x compared to 0.10. Otherwise, we will have to use a quadratic equation. Substituting into the K_{eq} expression,

$$\frac{(x)(x)}{0.10} = 3.0 \times 10^{-6}$$

$$x = [\mathrm{A}] = [\mathrm{B}] = \sqrt{3.0 \times 10^{-7}} = 5.5 \times 10^{-4}\ M$$

6.12 The Common Ion Effect—Shifting the Equilibrium

Equilibria can be markedly affected by adding one or more of the species present, as is predicted from Le Châtelier's principle. Example 6.5 illustrates this principle.

Example 6.5

Recalculate the concentration of A in Example 6.4, assuming that the solution also contains 0.20 M B.

Solution

We can represent the equilibrium concentration as follows:

	[AB]	[A]	[B]
Initial	0.10	0	0.20
Change (x = mmol/mL of AB dissociated)	$-x$	$+x$	$+x$
Equilibrium	$0.10 - x$	x	$0.20 + x$
	≈ 0.10		≈ 0.20

The value of x will be smaller now than before because of the common ion effect of B, so we can certainly neglect it compared to the initial concentrations. Substituting in the equilibrium constant expression,

$$\frac{(x)(0.20)}{(0.10)} = 3.0 \times 10^{-6}$$

$$x = 1.5 \times 10^{-6}\ M$$

The concentration of A was decreased nearly 400-fold.

The common ion effect can be used to make analytical reactions more favorable or quantitative. The adjustment of acidity, for example, is frequently used to shift equilibria. Titrations with potassium dichromate, for example, are favored in acid solution, since protons are consumed in its reactions. Titrations with iodine, a weak oxidizing agent, are usually done in slightly alkaline solution to shift the equilibrium toward completion of the reaction, for example, in titrating arsenic(III):

Adjusting the pH is a common way of shifting the equilibrium.

$$H_3AsO_3 + I_2 + H_2O \rightleftharpoons H_3AsO_4 + 2I^- + 2H^+$$

6.13 Systematic Approach to Equilibrium Calculations—How to Solve Any Equilibrium Problem

Now that some familiarity has been gained with equilibrium problems, we will consider a systematic approach for calculating equilibrium concentrations that will work with all equilibria, no matter how complex. It consists of identifying the unknown concentrations involved and *writing a set of simultaneous equations equal to the number of unknowns*. Simplifying assumptions are made with respect to relative concentrations of species (not unlike the approach we have already taken) to shorten the solving of the equations. This approach involves writing expressions for **mass balance** of species and one for **charge balance** of species as part of our equations. We will first describe how to arrive at these expressions.

MASS BALANCE EQUATIONS

The principle of mass balance is based on the law of mass conservation, and it states that the number of atoms of an element remains constant in chemical reactions because no atoms are produced or destroyed. The principle is expressed mathematically by equating the concentrations, usually in molarities. The equations for all the pertinent chemical equilibria are written, from which appropriate relations between species concentrations are written.

Example 6.6

Write the equation of mass balance for a 0.100 *M* solution of acetic acid.

Solution

The equilibria are

$$HOAc \rightleftharpoons H^+ + OAc^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

We know that the analytical concentration of acetic acid is equal to the sum of the equilibrium concentrations of all its species:

$$C_{HOAc} = [HOAc] + [OAc^-] = 0.100\ M$$

A second mass balance expression may be written for the equilibrium concentration of H^+, which is derived from both HOAc and H_2O. We obtain one H^+ for each OAc^- and one for each OH^-:

$$[H^+] = [OAc^-] + [OH^-]$$

In a mass balance, the analytical concentration is equal to the sum of the concentrations of the equilibrium species derived from the parent compound (or an appropriate multiple).

Example 6.7

Write the equations of mass balance for a 1.00×10^{-5} *M* $[Ag(NH_3)_2]Cl$ solution.

Solution

The equilibria are

$$[Ag(NH_3)_2]Cl \rightarrow Ag(NH_3)_2^+ + Cl^-$$

$$Ag(NH_3)_2^+ \rightleftharpoons Ag(NH_3)^+ + NH_3$$

$$Ag(NH_3)^+ \rightleftharpoons Ag^+ + NH_3$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

The Cl^- concentration is equal to the concentration of the salt that dissociated, that is, 1.00×10^{-5} *M*. Likewise, the sum of the concentrations of all silver species is equal to the concentration of Ag in the original salt that dissociated:

$$C_{Ag} = [Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2^+] = [Cl^-] = 1.00 \times 10^{-5}\ M$$

We have the following nitrogen-containing species:

$$NH_4^+ \quad NH_3 \quad Ag(NH_3)^+ \quad Ag(NH_3)_2^+$$

The concentration of N from the last species is twice the concentration of $Ag(NH_3)_2^+$. The total concentration of the nitrogen is twice the concentration of the original salt, since there are two NH_3 per molecule. Hence, we can write

$$C_{NH_3} = [NH_4^+] + [NH_3] + [Ag(NH_3)^+] + 2[Ag(NH_3)_2^+] = 2.00 \times 10^{-5}\ M$$

Finally, we can write

$$[OH^-] = [NH_4^+] + [H^+]$$

Some of the equilibria and the concentrations derived from them may be insignificant compared to others and may not be needed in subsequent calculations, for example, the last mass balance.

We have seen that several mass balance expressions may be written. Some may not be needed for calculations (we may have more equations that unknowns), or some may be simplified or ignored due to the small concentrations involved compared to others. This will become apparent in the equilibrium calculations below.

CHARGE BALANCE EQUATIONS

According to the **principle of electroneutrality**, all solutions are electrically neutral; that is, there is no solution containing a detectable excess of positive or negative charge because the sum of the positive charges equals the sum of negative charges. We may write a *single* charge balance equation for a given set of equilibria.

Example 6.8

Write a charge balance equation for a solution of H_2S.

Solution

The equilibria are

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{2-}$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Dissociation of H_2S gives H^+ and two anionic species, HS^- and S^{2-}, and that of water gives H^+ and OH^-. The amount of H^+ from that portion of *completely* dissociated H_2S is equal to twice the amount of S^{2-} formed, and from *partial* (first step) dissociation is equal to the amount of HS^- formed. That is, for each S^{2-} formed, there are 2 H^+; for each HS^- formed, there is 1 H^+; and for each OH^- formed, there is 1 H^+. Now, for the singly charged species, the *charge* concentration is identical to the concentration of the *species*. But for S^{2-}, the charge concentration is twice the concentration of the species, so we must multiply the S^{2-} concentration by 2 to arrive at the charge concentration from it. According to the principle of electroneutrality, positive charge concentration must equal the negative charge concentration. Hence,

$$[H^+] = 2[S^{2-}] + [HS^-] + [OH^-]$$

Note that while there may be more than one source for a given species (H^+ in this case), the total charge concentrations from all sources is always equal to the net equilibrium concentration of the species multiplied by its charge.

In a charge balance, the sum of the charge concentrations of cationic species equals the sum of charge concentrations of the anionic species in equilibrium.

The charge concentrations is equal to the molar concentration times the charge of a species.

Example 6.9

Write a charge balance expression for a solution containing KCl, $Al_2(SO_4)_3$, and KNO_3. Neglect the dissociation of water.

Solution

$$[K^+] + 3[Al^{3+}] = [Cl^-] + 2[SO_4^{2-}] + [NO_3^-]$$

Example 6.10

Write a charge balance equation for a saturated solution of CdS.

Solution

The equilibria are

$$CdS \rightleftharpoons Cd^{2+} + S^{2-}$$
$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$$

$$HS^- + H_2O \rightleftharpoons H_2S + OH^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$

Again, the charge concentration for the singly charged species (H^+, OH^-, HS^-) will be equal to the concentrations of the species. But for Cd^{2+} and S^{2-}, the charge concentration will be twice their concentrations. We must again equate the positive and negative charge concentrations.

$$2[Cd^{2+}] + [H^+] = 2[S^{2-}] + [HS^-] + [OH^-]$$

……

Example 6.11

Write a charge balance equation for Example 6.7.

Solution

$$[Ag^+] + [Ag(NH_3)^+] + [Ag(NH_3)_2{}^+] + [NH_4{}^+] + [H^+] = [Cl^-] + [OH^-]$$

Since all are singly charged species, the charge concentrations are equal to the molar concentrations.

……

EQUILIBRIUM CALCULATIONS USING THE SYSTEMATIC APPROACH—THE STEPS

In the systematic approach, a series of equations equal in number to the number of unknown species is written. These are simultaneously solved, using approximations to simplify.

We may now describe the systematic approach for calculating equilibrium concentrations in problems involving several equilibria. The basic steps can be summarized as follows:

1. Write the chemical reactions appropriate for the system.
2. Write the equilibrium constant expressions for these reactions.
3. Write all the mass balance expressions.
4. Write the charge balance expression.
5. Count the number of chemical species involved and the number of *independent* equations (from steps 2, 3, and 4). If the number of equations is greater than or equal to the number of chemical species, then a solution is possible. At this point, it is possible to proceed to an answer simply by brute (mathematical) force.
6. Make simplifying assumptions concerning the relative concentrations of chemical species. At this point you need to think like a chemist so that the *math* will be simplified.
7. Calculate the answer.
8. Check the validity of your assumptions!

Let us examine one of the examples worked before, but using this approach.

Example 6.12

Repeat the problem stated in Example 6.4 using the systematic approach outlined above.

Chemical reactions

$$AB = A + B$$

Use equilibrium constant expressions plus mass and charge balance expressions to write the equations.

Equilibrium constant expressions

$$K_{eq} = \frac{[A][B]}{[AB]} = 3.0 \times 10^{-6} \qquad (1)$$

Mass balance expressions

$$C_{AB} = [AB] + [A] = 0.10\ M \qquad (2)$$

$$[A] = [B] \qquad (3)$$

Remember that C represents the total analytical concentration of AB.

Charge balance expression

There is none because none of the species is charged.

Number of expressions versus number of unknowns

There are three unknowns ([AB], [A], and [B]) and three expressions (one equilibrium and two mass balance).

Simplifying assumptions: We want the equilibrium concentrations of A, B, and AB. Because K is small, very little AB will dissociate, so from (2):

$$[AB] = C_{AB} - [A] = 0.10 - [A] \approx 0.10\ M$$

Use the same rules as before for simplifying assumptions ($C_A \geq 100K_{eq}$ for dissociations, $C \leq 0.01K_{eq}$ for reactions).

Calculate

[AB] was found above.

[A] can be found from (1) and (3).

$$\frac{[A][B]}{0.10} = 3.0 \times 10^{-6}$$

$$[A] = \sqrt{3.0 \times 10^{-7}} = 5.5 \times 10^{-4}\ M$$

[B] can be found from (3):

$$[B] = [A] = 5.5 \times 10^{-4}\ M$$

Check

$$[AB] = 0.10 - 5.5 \times 10^{-4} = 0.10\ M \text{ (within significant figures)}$$

You see that the same answer was obtained as when the problem was worked intuitively as in Example 6.4. You may think that the systematic approach is excessively complicated and formal. For this extremely simple problem that may be a justified opinion. However, you should realize that the systematic approach will be applicable to *all* equilibrium calculations, regardless of the difficulty of the

The systematic approach is applicable to multiple equilibria.

problem. You may find problems involving multiple equilibria and/or many species to be hopelessly complicated if you use only an intuitive approach. Nevertheless, you should also realize that a good intuitive "feel" for equilibrium problems is an extremely valuable asset. You should attempt to improve your intuition concerning equilibrium problems. Such intuition comes from experience gained by working a number of problems of different varieties. As you gain experience you will be able to shorten some of the formalism of the systematic approach, and you will find it easier to make appropriate simplifying assumptions.

Example 6.13

Repeat the problem outlined in Example 6.5 using the systematic approach. Assume the charge on A is +1, the charge on B is −1, and that the extra B (0.20 *M*) comes from MB; MB is completely dissociated.

Solution

Chemical reactions

$$AB = A^+ + B^-$$

$$MB \rightarrow M^+ + B^-$$

Equilibrium expressions

$$K_{eq} = \frac{[A^+][B^-]}{[AB]} = 3.0 \times 10^{-6} \tag{1}$$

Mass balance expressions

$$C_{AB} = [AB] + [A^+] = 0.10\ M \tag{2}$$

$$[B^-] = [A^+] + [M^+] = [A^+] + 0.20\ M \tag{3}$$

Charge balance expression

$$[A^+] + [M^+] = [B^-] \tag{4}$$

Note that the charge balance is usually not needed.

Number of expressions versus number of unknowns

There are three unknowns ([AB], [A⁺], and [B⁻]; the concentration of M⁺ is known to be 0.20 *M*) and three independent expressions (one equilibrium and two mass balance; the charge balance is the same as the second mass balance).

Simplifying assumptions

(i) Because K_{eq} is small, very little AB will dissociate, so from (2).

$$[AB] = 0.10 - [A^+] \approx 0.10\ M$$

(ii) [A] ≪ [M] so from (3) or (4):

$$[B^-] = 0.20 + [A^+] \approx 0.20\ M$$

Calculate

[A] is now found from (1):

$$\frac{[A^+](0.20)}{0.10} = 3.0 \times 10^{-6}$$

$$[A^+] = 1.5 \times 10^{-6}\ M$$

Check

(i) $[AB] = 0.10 - 1.5 \times 10^{-6} = 0.10\ M$

(ii) $[B] = 0.20 + 1.5 \times 10^{-6} = 0.20\ M$

••

We will in general use the approximation approaches given in Sections 6.10 and 6.11, which actually incorporate many of the equilibria and assumptions used in the systematic approach. The use of the systematic approach for problems involving multiple equilibria is discussed in Chapter 8.

We can now write some general rules for solving chemical equilibrium problems, using the approximation approach. These rules should be applicable to acid–base dissociation, complex formation, oxidation–reduction reactions, and others. That is, all equilibria can be treated similarly.

1. Write down the equilibria involved.
2. Write the equilibrium constant expressions and the numerical values.
3. From a knowledge of the chemistry involved, let x represent the equilibrium concentration of the species that will be unknown and small compared to other equilibrium concentrations; other species of unknown and small concentrations will be multiples of this.
4. List the equilibrium concentrations of all species, adding or subtracting the appropriate multiple of x from the analytical concentration where needed.
5. Make suitable approximations by neglecting x compared to finite equilibrium concentrations. This is generally valid if the finite concentration is about $100 \times K_{eq}$ or more. Also, if the calculated x is less than approximately 5% of the finite concentration, the assumption is valid.
6. Substitute the approximate representation of individual concentration into the equilibrium constant expression and solve for x.
7. If the approximations in step 5 are invalid, use the quadratic formula to solve for x, or use the method of successive approximations.

The application of these rules will become more apparent in subsequent chapters when we deal with specific equilibria in detail.

6.14 Heterogeneous Equilibria—Solids Don't Count

Heterogeneous equilibria are slower than solution equilibria.

Equilibria in which all the components are in solution generally occur quite rapidly. If an equilibrium involves two phases, the rate of achieving equilibrium will generally be substantially slower than in the case of solutions. An example is the distribution equilibrium of an analyte between a chromatographic column (e.g., solid) and an eluent solvent. Because the equilibrium time is infinite, the rate of elution of the analyte down the chromatographic column must be slow enough for equilibrium to be achieved. The dissolution of a solid or formation of a precipitate will not be instantaneous.

The "concentration" of a solid or pure liquid is unity.

Another way in which heterogeneous equilibria differ from homogeneous equilibria is the manner in which the different constituents offset the equilibrium. Guldberg and Waage showed that when a solid is a component of a reversible chemical process, its active mass can be considered constant, regardless of how much of the solid is present. That is, adding more solid does not bring about a shift in the equilibrium. So the expression for the equilibrium constant need not contain any concentration terms for substances present as solids. That is, the standard state of a solid is taken as that of the solid itself, or unity. Thus, for the equilibrium

$$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$$

we write that

$$K_{eq} = [Ca^{2+}][F^-]^2$$

The same is true for pure liquids (undissolved) in equilibrium, such as mercury. The standard state of water is taken as unity in dilute *aqueous solutions*, and water does not appear in equilibrium constant expressions.

6.15 Activity and Activity Coefficients—Concentration Is Not the Whole Story

The "effective concentration" of an ion is decreased by shielding it with other "inert" ions, and it represents the activity of the ion.

Generally, the presence of diverse salts (not containing ions common to the equilibrium involved) will cause an increase in dissociation of a weak electrolyte or in the solubility of a precipitate. Cations attract anions, and vice versa, and so the cations of the analyte attract anions of the diverse electrolyte and the anions of the analyte attract the cations. The attraction of the ions of the equilibrium reaction by the dissolved electrolyte effectively shields them, *deceasing their effective concentration* and shifting the equilibrium. As the charge on either the diverse salt or the ions of the equilibrium reaction is increased, the diverse salt effect generally increases. This effect on the equilibrium is not predicted by Le Châtelier's principle; but if you think in terms of the effective concentrations being changed, it is analogous in some ways to the common ion effect.

Activities are important in potentiometric measurements. See Chapter 13.

This "effective concentration" of an ion in the presence of an electrolyte is called the **activity** of the ion. Activity can be used to describe quantitatively the effects of salts on equilibrium constants (see the diverse salt effect below). Activity is also important in potentiometric measurements (see Chapter 13). In this section we describe how to estimate activity.

THE ACTIVITY COEFFICIENT

The **activity** of an ion a_i is defined by

$$\boxed{a_i = C_i f_i} \tag{6.17}$$

where C_i is the concentration of the ion i and f_i is its **activity coefficient**. The concentration is usually expressed as molarity, and the activity has the same units as the concentration. The activity coefficient is dimensionless, but numerical values for activity coefficients do depend on the choice of standard state. The activity coefficient varies with the total number of ions in the solution and with their charge, and it is a correction for interionic attraction. *In dilute solution, less than 10^{-4} M, the activity coefficient of a simple electrolyte is near unity*, and activity is approximately equal to the concentration. As the concentration of an electrolyte increases, or as an extraneous salt is added, the activity coefficient generally decreases, and the activity becomes less than the concentration.

IONIC STRENGTH

From the above discussion, we can see that the activity coefficient is a function of the total electrolyte concentration of the solution. The **ionic strength** is a measure of total electrolyte concentration and is defined by

For ionic strengths less than 10^{-4}, activity coefficients are near unity.

$$\boxed{\mu = \tfrac{1}{2}\sum C_i Z_i^2} \tag{6.18}$$

where μ is the ionic strength and Z_i is the charge on each individual ion. All cations and anions present in solution are included in the calculation. Obviously, for each positive charge there will be a negative charge.

Example 6.14

Calculate the ionic strength of a 0.2 *M* solution of KNO_3 and a 0.2 *M* solution of K_2SO_4.

Solution

For KNO_3,

$$\mu = \frac{C_{K^+}Z_{K^+}^2 + C_{NO_3^-}Z_{NO_3^-}^2}{2}$$

$$[K^+] = 0.2\ M \qquad [NO_3^-] = 0.2\ M$$

$$\mu = \frac{0.2 \times (1)^2 + 0.2 \times (1)^2}{2} = 0.2$$

For K_2SO_4,

$$\mu = \frac{C_{K^+}Z_{K^+}^2 + C_{SO_4^{2-}}Z_{SO_4^{2-}}^2}{2}$$

$$[K^+] = 0.4\ M \qquad [SO_4^{2-}] = 0.2\ M$$

So, $$\mu = \frac{0.4 \times (1)^2 + 0.2 \times (2)^2}{2} = 0.6$$

Note that due to the doubly charged SO_4^{2-}, the ionic strength of the K_2SO_4 is three times that of the KNO_3.

Higher charged ions contribute more to the ionic strength.

If more than one salt is present, then the ionic strength is calculated from the total concentration and charges of all the different ions. For any given electrolyte, the ionic strength will be proportional to the concentration. Strong acids that are completely ionized are treated in the same manner as salts. If the acids are partially ionized, then the concentration of the ionized species must be estimated from the ionization constant before the ionic strength is computed. Very weak acids can usually be considered to be nonionized and do not contribute to the ionic strength.

Example 6.15

Calculate the ionic strength of a solution consisting of 0.30 *M* NaCl and 0.20 *M* Na_2SO_4.

$$\mu = \frac{C_{N^+}Z^2_{Na^+} + C_{Cl^-}Z^2_{Cl^-} + C_{SO_4{}^{2-}}Z^2_{SO_4{}^{2-}}}{2}$$

$$= \frac{0.70 \times (1)^2 + 0.30 \times (1)^2 + 0.20 \times (2)^2}{2}$$

$$= 0.90$$

CALCULATION OF ACTIVITY COEFFICIENTS

In 1923, Debye and Hückel derived a theoretical expression for calculating activity coefficients. The equation, known as the **Debye–Hückel equation**, is

This equation applies for ionic strengths up to 0.2.

$$\boxed{-\log f_i = \frac{0.51Z_i^2\sqrt{\mu}}{1 + 0.33\alpha_i\sqrt{\mu}}} \qquad (6.19)$$

The estimation of the ion size parameter places a limit on the accuracy of the calculated activity coefficient.

The numbers 0.51 and 0.33 are constants for water at 25°C, and the former includes the $-\frac{3}{2}$ power of both the dielectric constant of the solvent and the absolute temperature; α_i is the **ion size parameter**, which is the effective diameter of the hydrated ion in angstrom units, Å. An angstrom is 100 picometers (pm, 10^{-10} meter). A limitation of the Debye–Hückel equation is the accuracy to which α_i can be evaluated. For many singly charged ions, α_i is generally about 3 Å, and for practical purposes Equation 6.19 simplifies to

This equation may be used for ionic strengths less than 0.01.

$$\boxed{-\log f_i = \frac{0.51Z_i^2\sqrt{\mu}}{1 + \sqrt{\mu}}} \qquad (6.20)$$

See Ref. 9 for a tabulation of α_i values.

For common multiply charged ions, α_i may become as large as 11 Å. But at ionic strengths less than 0.01, the second term of the denominator becomes small with respect to 1, so uncertainties in α_i become relatively unimportant, and Equation 6.20 can be applied at ionic strengths of 0.01 or less. Equation 6.19 can be applied up to ionic strengths of about 0.2. Ref. 9 at the end of the chapter lists values for α_i for different ions and also includes a table of calculated activity coefficients, using Equation 6.19, at ionic strengths ranging from 0.0005 to 0.1. The CD for Chapter 6 contains a list of ion size parameters for some common ions taken from this reference.

Example 6.16

Calculate the activity coefficients for K^+ and $SO_4{}^{2-}$ in a 0.0020 *M* solution of potassium sulfate.

Solution

The ionic strength is 0.0060, so we can apply Equation 6.20:

$$-\log f_{K^+} = \frac{0.51(1)^2\sqrt{0.0060}}{1+\sqrt{0.0060}} = 0.037$$

$$f_{K^+} = 10^{-0.037} = 10^{-1} \times 10^{0.963} = 0.918$$

$$-\log f_{SO_4^{2-}} = \frac{0.51(2)^2\sqrt{0.0060}}{1+\sqrt{0.0060}} = 0.14_7$$

$$f_{SO_4^{2-}} = 10^{-0.14_7} = 10^{-1} \times 10^{0.85_3} = 0.71_3$$

……

Example 6.17

Calculate the activity coefficients for K^+ and SO_4^{2-} in a 0.020 *M* solution of potassium sulfate.

Solution

The ionic strength is 0.060, so we would use Equation 6.19. From Ref. 9, we find that $\alpha_{K^+} = 3$ Å and $\alpha_{SO_4^{2-}} = 4.0$ Å. For K^+, we can use Equation 6.20:

$$-\log f_{K^+} = \frac{0.51(1)^2\sqrt{0.060}}{1+\sqrt{0.060}} = 0.10_1$$

$$f_{K^+} = 10^{-0.101} = 10^{-1} \times 10^{0.899} = 0.79_4$$

For SO_4^{2-}, use Equation 6.19:

$$-\log f_{SO_4^{2-}} = \frac{0.51(2)^2\sqrt{0.060}}{1+0.33\times 4.0\sqrt{0.060}} = 0.37_8$$

$$f_{SO_4^{2-}} = 10^{-1} \times 10^{0.62_2} = 0.41_9$$

This latter compares with a calculated value of 0.39_6 using Equation 6.20. Note the decrease in the activity coefficients compared to 0.002 *M* K_2SO_4, especially for the SO_4^{2-} ion.

……

Spreadsheets for calculating activity coefficients using Equations 6.19 and 6.20 are given in the CD for Chapter 6.

For higher ionic strengths, a number of empirical equations have been developed. Perhaps one of the more useful is the **Davies modification** (see Ref. 8):

$$\boxed{-\log f_i = 0.51Z_i^2\left(\frac{\sqrt{\mu}}{1+\sqrt{\mu}} - 0.3\,\mu\right)} \qquad (6.21)$$

Use this equation for ionic strengths of 0.2–0.5. It gives increasing activity coefficients compared to the Debye–Hückel equation.

It is valid up to ionic strengths of about 0.5.

A 0.01 *M* solution of HCl prepared in 8 *M* NaCl has an activity about 100 times that in water! Its pH is actually 0.0. See F. E. Critchfield and J. B. Johnson, *Anal. Chem.*, **30**, (1958) 1247 and G. D. Christian, *CRC Crit. Rev. in Anal. Chem.*, **5**(2) (1975) 119–153.

At very high electrolyte concentrations, activity coefficients may actually increase and become greater than unity. This is because the activity of the solvent, water, is decreased and solvated ionic species become partially desolvated. This increases their reactivity and hence their activity. Note that Equation 6.21 actually "corrects" the value of f_i to a larger value as *M* increases.

We can draw some general conclusions about the estimation of activity coefficients.

The greater the charge on diverse ions, the greater their effect on the activity.

The activity of nonelectrolytes is the same as the concentration, up to ionic strengths of 1.

1. The activity coefficients of ions of a given charge type are approximately the same in solutions of a given ionic strength, and this activity coefficient is the same regardless of their individual concentrations.
2. The behavior of ions become less ideal as the charge type increases, resulting in less confidence in calculated activity coefficients.
3. The calculated activity coefficient of an ion in a mixed electrolyte solution will be less accurate than in a single-electrolyte solution.
4. The activity coefficients of nonelectrolytes (uncharged molecules) can generally be considered equal to unity in ionic strengths up to 0.1, and deviations from this approximation are only moderate in ionic strengths as high as 1. Undissociated acids, HA, are nonelectrolytes whose activity coefficients can be taken as unity.

6.16 The Diverse Ion Effect: The Thermodynamic Equilibrium Constant and Activity Coefficients

We mentioned at the beginning of the last section on activity that the presence of diverse salts will generally increase the dissociation of weak electrolytes due to a shielding (or decrease in the activity) of the ionic species produced upon dissociation. We can quantitatively predict the extent of the effect on the equilibrium by taking into account the activities of the species in the equilibrium.

Thermodynamic equilibrium constants hold at all ionic strengths.

In our consideration of equilibrium constants thus far, we have assumed no diverse ion effect, that is, an ionic strength of zero and an activity coefficient of 1. Equilibrium constants should more exactly be expressed in terms of activities rather than concentrations. Consider the dissociation of AB. The **thermodynamic equilibrium constant** (i.e., the equilibrium constant extrapolated to the case of infinite dilution) K°_{eq} is

$$\boxed{K^\circ_{\text{eq}} = \frac{a_{\text{A}} \cdot a_{\text{B}}}{a_{\text{AB}}} = \frac{[\text{A}]f_{\text{A}} \cdot [\text{B}]f_{\text{B}}}{[\text{AB}]f_{\text{AB}}}} \qquad (6.22)$$

Since the **concentration equilibrium constant** $K_{\text{eq}} = [\text{A}][\text{B}]/[\text{AB}]$, then

$$\boxed{K^\circ_{\text{eq}} = K_{\text{eq}} \frac{f_{\text{A}} \cdot f_{\text{B}}}{f_{\text{AB}}}} \qquad (6.23)$$

or

$$\boxed{K_{eq} = K^\circ_{eq}\frac{f_{AB}}{f_A \cdot f_B}} \qquad (6.24)$$

The numerical value of K°_{eq} holds for all activities. $K_{eq} = K^\circ_{eq}$ at zero ionic strength, but at appreciable ionic strengths, a value for K_{eq} must be calculated for each ionic strength using Equation 6.24. The equilibrium constants listed in Appendix C are for zero ionic strength; that is, they are really thermodynamic equilibrium constants. (Experimental K_{eq} values are available at different ionic strengths and can be used for equilibrium calculations at the listed ionic strength, using molar concentrations without having to calculate activity coefficients.)

Concentration equilibrium constants must be corrected for ionic strength.

Example 6.18

The weak electrolyte AB dissociates to A^+ and B^-, with a thermodynamic equilibrium constant K°_{eq} of 2×10^{-8} (a) Calculate the molar equilibrium constant K_{eq}. (b) Calculate the percent dissociation of a $1.0 \times 10^{-4}\ M$ solution of AB in water and in the presence of a diverse salt of ionic strength 0.1, if the activity coefficients of A^+ and B^- are 0.6 and 0.7, respectively, at $\mu = 0.1$.

Solution

(a)

$$AB \rightleftharpoons A^+ + B^-$$

$$K_{eq} = \frac{[A^+][B^-]}{[AB]}$$

$$K^\circ_{eq} = \frac{a_{A^+} \cdot a_{B^-}}{a_{AB}} = \frac{[A^+]f_{A^+} \cdot [B^-]f_{B^-}}{[AB]f_{AB}}$$

The activity coefficient of a neutral species is unity, so

$$K^\circ_{eq} = \frac{[A^+][B^-]}{[AB]} \cdot f_{A^+} \cdot f_{B^-} = K_{eq} f_{A^+} \cdot f_{B^-}$$

$$K_{eq} = \frac{K^\circ_{eq}}{f_{A^+} \cdot f_{B^-}} = \frac{2 \times 10^{-8}}{(0.6)(0.7)} = 5 \times 10^{-8}$$

(b)

$$\begin{array}{ccccc} AB & \rightleftharpoons & A^+ & + & B^- \\ 1 \times 10^{-4} - x & & x & & x \end{array}$$

In water, $f_{A^+} = f_{B^-} \approx 1$ (since $\mu < 10^{-4}$), $x \ll 10^{-4}$

$$\frac{[A^+][B^-]}{[AB]} = 2 \times 10^{-8}$$

$$\frac{(x)(x)}{1.0 \times 10^{-4}} = 2 \times 10^{-8}$$

$$x = 1_4 \times 10^{-6}\ M$$

$$\%\ \text{dissociated} = \frac{1_4 \times 10^{-6}\ M}{1.0 \times 10^{-4}\ M} \times 100\% = 1_4\%$$

For 0.1 *M* salt,

$$\frac{[A^+][B^-]}{[AB]} = 5 \times 10^{-8}$$

$$\frac{(x)(x)}{1.0 \times 10^{-4}} = 5 \times 10^{-8}$$

$$x = 2_2 \times 10^{-6}$$

$$\% \text{ dissociated} = \frac{2_2 \times 10^{-6}}{1.0 \times 10^{-4}} \times 100\% = 2_2\%$$

which represents a 57% increase in dissociation.

……

We will generally ignore diverse salt effects.

Calculations using the diverse ion effect are illustrated in Chapter 7 for acid dissociation and in Chapter 10 for precipitate solubilities. For illustrative purposes throughout this book, we will in general neglect the diverse ion effects on equilibria. In most cases, we are interested in *relative* changes in equilibrium concentrations, and the neglect of activities will not change our arguments.

Learning Objectives

WHAT ARE SOME OF THE KEY THINGS WE LEARNED FROM THIS CHAPTER?

- The equilibrium constant (key equations: 6.12, 6.15), p. 194
- Calculation of equilibrium concentrations, p. 195
- Using Excel Solver to solve the quadratic equation, p. 198
- The systematic approach to equilibrium calculations: mass balance and charge balance equations, p. 203
- Activity and activity coefficients (key equation: 6.19), p. 210
- Thermodynamic equilibrium constants (key equation: 6.22), p. 214

Problems

EQUILIBRIUM CALCULATIONS

1. A and B react as follows: $A + B \rightleftharpoons C + D$. The equilibrium constant is 2.0×10^3. If 0.30 mol of A and 0.80 mol of B are mixed in 1 L, what are the concentrations of A, B, C, and D after reaction?

2. A and B react as follows: $A + B \rightleftharpoons 2C$. The equilibrium constant is 5.0×10^6. If 0.40 mol of A and 0.70 mol of B are mixed in 1 L, what are the concentrations of A, B, and C after reaction?

3. The dissociation constant for salicylic acid, $C_6H_4(OH)COOH$, is 1.0×10^{-3}. Calculate the percent dissociation of a 1.0×10^{-3} *M* solution. There is one dissociable proton. (See also Excel Problem 25 below.)

4. The dissociation constant for hydrocyanic acid, HCN, is 7.2×10^{-10}. Calculate the percent dissociation of a 1.0×10^{-3} *M* solution.

5. Calculate the percent dissociation of the salicylic acid in Problem 3 if the solution also contained 1.0×10^{-2} *M* sodium salicylate (the salt of salicylic acid).

6. Hydrogen sulfide, H_2S, dissociates stepwise, with dissociation constants of 9.1×10^{-8} and 1.2×10^{-15}, respectively. Write the overall dissociation reaction and the overall equilibrium constant.

7. Fe^{2+} and $Cr_2O_7^{2-}$ react as follows: $6Fe^{2+} + Cr_2O_7^{2-} + 14H^+ \rightleftharpoons 6\,Fe^{3+} + 2Cr^{3+} + 7H_2O$. The equilibrium constant for the reaction is 1×10^{57}. Calculate the equilibrium concentrations of the iron and chromium species if 10 mL each of 0.02 *M* $K_2Cr_2O_7$ in 1.14 *M* HCl and 0.12 *M* $FeSO_4$ in 1.14 *M* HCl are reacted.

SYSTEMATIC APPROACH TO EQUILIBRIUM CALCULATIONS

8. Write charge balance expressions for (a) a saturated solution of Bi_2S_3; (b) a solution of Na_2S.

9. Write the equations of mass balance and electroneutrality for a 0.100 *M* $[Cd(NH_3)_4]Cl_2$ solution.

10. Prove the following relations using the principles of electroneutrality and mass balance:

(a) $[NO_2^-] = [H^+] - [OH^-]$ for 0.2 *M* HNO_2 solution

(b) $[CH_3COOH] = 0.2 - [H^+] + [OH^-]$ for 0.2 *M* CH_3COOH solution

(c) $[H_2C_2O_4] = 0.1 - [H^+] + [OH^-] - [C_2O_4^{2-}]$ for 0.1 *M* $H_2C_2O_4$ solution

(d) $[HCN] = [OH^-] - [H^+]$ for 0.1 *M* KCN solution

(e) $[H_2PO_4^-] = \dfrac{[OH^-] - [H^+] - [HPO_4^{2-}] - 3[H_3PO_4]}{2}$ for 0.1 *M* Na_3PO_4 solution.

(f) $[HSO_4^-] = 0.2 - [H^+] - [OH^-]$ for 0.1 *M* H_2SO_4 solution (assume that the dissociation of H_2SO_4 to H^+ and HSO_4^- is quantitative).

11. Write equations of mass balance for an aqueous saturated solution of BaF_2 containing the species F^-, HF, HF_2^-, and Ba^{2+}.

12. Write an equation of mass balance for an aqueous solution of $Ba_3(PO_4)_2$.

13. Calculate the pH of a 0.100 *M* solution of acetic acid using the charge/mass balance approach.

IONIC STRENGTH

14. Calculate the ionic strengths of the following solutions: (a) 0.30 *M* NaCl; (b) 0.30 *M* Na_2SO_4; (c) 0.30 *M* NaCl and 0.20 *M* K_2SO_4; (d) 0.20 *M* $Al_2(SO_4)_3$ and 0.10 *M* Na_2SO_4.

15. Calculate the ionic strengths of the following solutions: (a) 0.20 *M* $ZnSO_4$; (b) 0.40 *M* $MgCl_2$; (c) 0.50 *M* $LaCl_3$; (d) 1.0 *M* $K_2Cr_2O_7$; (e) 1.0 *M* $Tl(NO_3)_3$ + 1.0 *M* $Pb(NO_3)_2$.

ACTIVITY

16. Calculate the activity coefficients of the sodium and chloride ions for a 0.00100 *M* solution of NaCl.

17. Calculate the activity coefficients of each ion in a solution containing 0.0020 *M* Na_2SO_4 and 0.0010 *M* $Al_2(SO_4)_3$.

18. Calculate the activity of the NO_3^- ion in a solution of 0.0020 *M* KNO_3.

19. Calculate the activity of the CrO_4^{2-} ion in a 0.020 *M* solution of Na_2CrO_4.

THERMODYNAMIC EQUILIBRIUM CONSTANTS

20. Write thermodynamic equilibrium constant expressions for the following:

(a) $HCN \rightleftharpoons H^+ + CN^-$

(b) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

21. Calculate the pH of a solution of 5.0×10^{-3} M benzoic acid (a) in water and (b) in the presence of 0.05 M K_2SO_4.

EXCEL EXERCISES

22. Without reference to the CD, write a spreadsheet program for calculating activity coefficients using Equation 6.20. Then compare it with the one on the CD. Do a calculation with both to check the accuracy.

23. Calculate the activity coefficients for K^+ and SO_4^{2-} in Example 6.16 using the CD spreadsheet for Equation 6.20. Compare your results with the manually calculated values in the example.

24. Calculate the activity coefficients in Example 6.17 using the CD spreadsheets for Equations 6.19 and 6.20. Compare your results with the manually calculated values in the example.

25. Use Excel Solver to calculate the concentration, x, in Problem 3 above. (The problem requires use of the quadratic equation.)

26. Solve Problems 16 to 19 above using Excel.

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Chapter Seven

ACID–BASE EQUILIBRIA

> *"There are three side effects of acid. Enhanced long term memory, decreased short term memory, and I forget the third."*
> —Timothy Leary

The acidity or basicity of a solution is frequently an important factor in chemical reactions. The use of buffers of a given pH to maintain the solution pH at a desired level is very important. In addition, fundamental acid–base equilibria are important in understanding acid–base titrations and the effects of acids on chemical species and reactions, for example, the effects of complexation or precipitation. In Chapter 6, we described the fundamental concept of equilibrium constants. In this chapter, we consider in more detail various acid–base equilibrium calculations, including *weak acids* and *bases*, hydrolysis of *salts of weak acids and bases*, buffers, polyprotic acids and their salts, and *physiological buffers*. Acid–base theories and the basic pH concept are reviewed first.

7.1 Acid–Base Theories—Not All Are Created Equal

Several acid–base theories have been proposed to explain or classify acidic and basic properties of substances. You are probably most familiar with the **Arrhenius theory**, which is applicable only to water. Other theories are more general and are applicable to other solvents. We describe the common acid–base theories here.

The Arrhenius theory is restricted to aqueous solutions. See *J. Am. Chem. Soc.*, **36** (1912) 353 for his personal observations of the difficulty Arrhenius had in the acceptance of his theory.

ARRHENIUS THEORY—H^+ AND OH^-

Arrhenius, as a graduate student, introduced a radical theory in 1894 (for which he received the Nobel Prize) that an **acid** is any substance that ionizes (partially or completely) in water to give *hydrogen ions* (which associate with the solvent to give hydronium ions, H_3O^+):

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

A **base** ionizes in water to give *hydroxyl ions*. Weak (partially ionized) bases generally ionize as follows:

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

while strong bases such as metal hydroxides (e.g., NaOH) dissociate as

$$M(OH)_n \rightarrow M^{n+} + nOH^-$$

This theory is obviously restricted to water as the solvent.

THEORY OF SOLVENT SYSTEMS—SOLVENT CATIONS AND ANIONS

Franklin's theory is similar to the Arrhenius theory but is applicable also to other ionizable solvents.

In 1905, Franklin introduced the solvent system concept of acids and bases. This theory recognizes the ionization of a solvent to give a cation and an anion; for example, $2H_2O \rightleftharpoons H_3O^+ + OH^-$ or $2NH_3 \rightleftharpoons NH_4^+ + NH_2^-$. An **acid** is defined as a solute that yields the *cation of the solvent* while a **base** is a solute that yields the *anion of the solvent*. Thus, NH_4Cl is a strong acid in liquid ammonia (similar to HCl in water: $HCl + H_2O \rightarrow H_3O^+ + Cl^-$) while $NaNH_2$ is a strong base in ammonia (similar to NaOH in water); both of these compounds ionize to give the solvent cation and anion, respectively. Ethanol ionizes as follows: $2C_2H_5OH \rightleftharpoons C_2H_5OH_2^+ + C_2H_5O^-$. Hence, sodium ethoxide, $NaOC_2H_5$, is a strong base in this solvent.

BRØNSTED–LOWRY THEORY—TAKING AND GIVING PROTONS

The Brønsted–Lowry theory assumes a transfer of protons from an acid to a base, i.e., conjugate pairs.

The theory of solvent systems is suitable for ionizable solvents, but it is not applicable to acid–base reactions in nonionizable solvents such as benzene or dioxane. In 1923, Brønsted and Lowry separately described what is now known as the **Brønsted–Lowry** theory. This theory states that an **acid** is any substance that can *donate a proton*, and a **base** is any substance that can *accept a proton*. Thus, we can write a "half-reaction"

$$\boxed{\text{Acid} = H^+ + \text{base}} \qquad (7.1)$$

The acid and base of a half-reaction are called **conjugate pairs**. Free protons do not exist in solution, and there must be a proton acceptor (base) before a proton donor (acid) will release its proton. That is, there must be a combination of two half-reactions. Some acid–base reactions in different solvents are illustrated in Table 7.1. In the first example, acetate ion is the conjugate base of acetic acid and ammonium ion is the conjugate acid of ammonia. The first four examples represent ionization of an acid or a base in a solvent, while the others represent a neutralization reaction between an acid and a base in the solvent.

Table 7.1

Brønsted Acid–Base Reactions

Solvent	$Acid_1$	+	$Base_2$	→	$Acid_2$	+	$Base_1$
NH_3 (liq.)	HOAc		NH_3		NH_4^+		OAc^-
H_2O	HCl		H_2O		H_3O^+		Cl^-
H_2O	NH_4^+		H_2O		H_3O^+		NH_3
H_2O	H_2O		OAc^-		HOAc		OH^-
H_2O	HCO_3^-		OH^-		H_2O		CO_3^{2-}
C_2H_5OH	NH_4^+		$C_2H_5O^-$		C_2H_5OH		NH_3
C_6H_6	H picrate		$C_6H_5NH_2$		$C_6H_5NH_3^+$		picrate$^-$

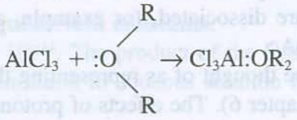
It is apparent from the above definition that a substance cannot act as an acid unless a base is present to accept the protons. Thus, acids will undergo complete or partial ionization in basic solvents such as water, liquid ammonia, or ethanol, depending on the basicity of the solvent and the strength of the acid. But in neutral or "inert" solvents, ionization is insignificant. However, ionization in the solvent is not a prerequisite for an acid–base reaction, as in the last example in the table, where picric acid reacts with aniline.

LEWIS THEORY—TAKING AND GIVING ELECTRONS

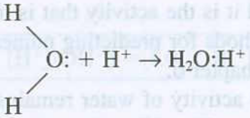
Also in 1923, G. N. Lewis introduced the electronic theory of acids and bases. In the **Lewis** theory, an acid is a substance that can accept an electron pair and a base is a substance that can donate an electron pair. The latter frequently contains an oxygen or a nitrogen as the electron donor. Thus, nonhydrogen-containing substances are included as acids. Examples of acid–base reactions in the Lewis theory are as follows:

The Lewis theory assumes a donation (sharing) of electrons from a base to an acid.

$$H^+ \text{ (solvated)} + :NH_3 \rightarrow H:NH_3^+$$



$$AlCl_3 + :O(R)_2 \rightarrow Cl_3Al:OR_2$$



$$H_2O: + H^+ \rightarrow H_2O:H^+$$

$$H^+ + :OH^- \rightarrow H:OH$$

In the second example, aluminum chloride is an acid and ether is a base.

7.2 Acid–Base Equilibria in Water

We see from the above that when an acid or base is dissolved in water, it will dissociate, or **ionize**, the amount of ionization being dependent on the strength of the acid. A "strong" electrolyte is completely dissociated, while a "weak" electrolyte is partially dissociated. Table 7.2 lists some common electrolytes, some strong and some weak. Other weak acids and bases are listed in Appendix C.

Table 7.2
Some Strong Electrolytes and Some Weak Electrolytes

Strong	Weak
HCl	$HC_2H_3O_2$ (acetic acid)
$HClO_4$	NH_3
H_2SO_4[a]	C_6H_5OH (phenol)
HNO_3	$HCHO_2$ (formic acid)
NaOH	$C_6H_5NH_2$ (aniline)
$NaC_2H_3O_2$	

[a] The first proton is completely ionized in dilute solution, but the second proton is partially ionized ($K_i = 10^{-2}$).

Hydrochloric acid is a strong acid, and its ionization is complete:

$$HCl + H_2O \rightarrow H_3O^+ + Cl^- \tag{7.2}$$

An equilibrium constant for Equation 7.2 would have a value of infinity. The proton H^+ exists in water as a hydrated ion, the **hydronium ion**, H_3O^+. Higher hydrates probably exist, particularly $H_9O_4^+$. The hydronium ion is written as H_3O^+ for convenience and to emphasize Brønsted behavior.

Acetic acid[1] is a weak acid, which ionizes only partially (a few percent):

$$HOAc + H_2O \rightleftharpoons H_3O^+ + OAc^- \tag{7.3}$$

We can write an **equilibrium constant** for this reaction:

$$K_a^\circ = \frac{a_{H_3O^+} \cdot a_{OAc^-}}{a_{HOAc} \cdot a_{H_2O}} \tag{7.4}$$

where K_a° is the **thermodynamic acidity constant** (see Section 6.16) and a is the **activity** of the indicated species. Salt cations or anions may also partially react with water after they are dissociated, for example, acetate ion from dissociated acetate salt, to give HOAc.

The activity can be thought of as representing the effective concentration of an ion (described in Chapter 6). The effects of protons in reactions are often governed by their activities, and it is the activity that is measured by the widely used pH meter (Chapter 13). Methods for predicting numerical values of activity coefficients were described in Chapter 6.

In dilute solutions, the activity of water remains essentially constant, and is taken as unity at standard state. Therefore, Equation 7.4 can be written as

$$K_a^\circ = \frac{a_{H_3O^+} \cdot a_{OAc^-}}{a_{HOAc}} \tag{7.5}$$

Autoprotolysis is the self-ionization of a solvent to give a cation and anion, e.g., $2CH_3OH \rightleftharpoons CH_3OH_2^+ + CH_3O^-$.

Pure water ionizes slightly, or undergoes **autoprotolysis**:

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \tag{7.6}$$

The equilibrium constant for this is

$$K_w^\circ = \frac{a_{H_3O^+} \cdot a_{OH^-}}{a_{H_2O}^2} \tag{7.7}$$

Again, the activity of water is constant in dilute solutions (its concentration is essentially constant at ~55.3 M), so

$$K_w^\circ = a_{H_3O^+} \cdot a_{OH^-} \tag{7.8}$$

where K_w° is the **thermodynamic autoprotolysis**, or **self-ionization, constant**.

We will use H^+ in place of H_3O^+, for simplification. Also, molar concentrations will generally be used instead of activities.

Calculations are simplified if we neglect activity coefficients. This simplification results in only slight errors for dilute solutions, and we shall use molar concentrations in all our calculations. This will satisfactorily illustrate the equilibria involved. Most of the solutions we will be concerned with are rather dilute, and we will frequently be interested in relative changes in pH (and large ones) in which

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[1] We shall use the symbol OAc^- to represent the acetate ion $CH_3—\overset{\overset{\displaystyle O}{\|}}{C}—O^-$

case small errors are insignificant. We will simplify our expressions by using H^+ in place of H_3O^+. This is not inconsistent since the waters of solvation associated with other ions or molecules (e.g., metal ions) are not generally written and H_3O^+ is not an entirely accurate representation of the species present anyway.

Molar concentration will be represented by square brackets [ ] around the species. Simplified equations for the above reactions are

$$HCl \rightarrow H^+ + Cl^- \tag{7.9}$$

$$HOAc \rightleftharpoons H^+ + OAc^- \tag{7.10}$$

$$\boxed{K_a = \frac{[H^+][OAc^-]}{[HOAc]}} \tag{7.11}$$

$$H_2O \rightleftharpoons H^+ + OH^- \tag{7.12}$$

$$\boxed{K_w = [H^+][OH^-]} \tag{7.13}$$

K_a and K_w are the **molar equilibrium constants.**

At 25°C, $K_w = 1.0 \times 10^{-14}$. The product of the hydrogen ion concentration and the hydroxyl ion concentration in aqueous solution is *always* equal to 1.0×10^{-14} at room temperature:

$$\boxed{[H^+][OH^-] = 1.0 \times 10^{-14}} \tag{7.14}$$

Chemists (and especially students!) are lucky that nature made K_w an even unit number at room temperature. Imagine doing pH calculations with a K_w like 2.39×10^{-13}. However, see Section 7.4 where you indeed must (for other temperatures).

In pure water, then, the concentrations of these two species are equal since there are no other sources of H^+ or OH^- except H_2O dissociation:

$$[H^+] = [OH^-]$$

Therefore,

$$[H^+][H^+] = 1.0 \times 10^{-14}$$

$$[H^+] = 1.0 \times 10^{-7}\,M \equiv [OH^-]$$

If an acid is added to water, we can calculate the hydroxyl ion concentration if we know the hydrogen ion concentration from the acid. *Except when the hydrogen ion concentration from the acid is very small, 10^{-6}* M *or less, any contribution to $[H^+]$ from the ionization of water can be neglected.*

Example 7.1

A 1.0×10^{-3} *M* solution of hydrochloric acid is prepared. What is the hydroxyl ion concentration?

Solution

Since hydrochloric acid is a strong electrolyte and is completely ionized, the H^+ concentration is 1.0×10^{-3} *M*. Thus,

$$(1.0 \times 10^{-3})[OH^-] = 1.0 \times 10^{-14}$$

$$[OH^-] = 1.0 \times 10^{-11}\,M$$

7.3 The pH Scale

pScales are used to compress a range of numbers over several decades in magnitude.

The concentration of H^+ or OH^- in aqueous solution can vary over extremely wide ranges, from 1 *M* or greater to 10^{-14} *M* or less. To construct a plot of H^+ concentration against some variable would be very difficult if the concentration changed from, say, 10^{-1} *M* to 10^{-13} *M*. This range is common in a titration. It is more convenient to compress the acidity scale by placing it on a logarithm basis. The **pH** of a solution was defined by Sørenson as

$$\boxed{pH = -\log[H^+]} \qquad (7.15)$$

pH is really $-\log a_{H^+}$. This is what a pH meter (glass electrode) measures—see Chapter 13.

The minus sign is used because most of the concentrations encountered are less than 1 *M*, and so this designation gives a positive number. (More strictly, pH is now defined as $-\log a_{H^+}$, but we will use the simpler definition of Equation 7.15.) In general, **pAnything = −log Anything**, and this method of notation will be used later for other numbers that can vary by large amounts, or are very large or small (e.g., equilibrium constants).

Example 7.2

Calculate the pH of a 2.0×10^{-3} *M* solution of HCl.

Solution

HCl is completely ionized, so

$$[H^+] = 2.0 \times 10^{-3}\ M$$

$$pH = -\log(2.0 \times 10^{-3}) = 3 - \log 2.0 = 3 - 0.30 = 2.70$$

A similar definition is made for the hydroxyl ion concentration:

$$\boxed{pOH = -\log[OH^-]} \qquad (7.16)$$

A 1 *M* HCl solution has a pH of 0 and pOH of 14. A 1 *M* NaOH solution has a pH of 14 and a pOH of 0.

Equation 7.13 can be used to calculate the hydroxyl ion concentration if the hydrogen ion concentration is known, and vice versa. The equation in logarithm form for a more direct calculation of pH or pOH is

$$-\log K_w = -\log[H^+][OH^-] = -\log[H^+] - \log[OH^-] \qquad (7.17)$$

$$\boxed{pK_w = pH + pOH} \qquad (7.18)$$

At 25°C,

$$\boxed{14.00 = pH + pOH} \qquad (7.19)$$

Example 7.3

Calculate the pOH and the pH of a 5.0×10^{-2} *M* solution of NaOH.

Solution

$$[OH^-] = 5.0 \times 10^{-2}\ M$$

$$pOH = -\log(5.0 \times 10^{-2}) = 2 - \log 5.0 = 2 - 0.70 = 1.30$$

$$pH + 1.30 = 14.00$$

$$pH = 12.70$$

or

$$[H^+] = \frac{1.0 \times 10^{-14}}{5.0 \times 10^{-2}} = 2.0 \times 10^{-13}\ M$$

$$pH = -\log(2.0 \times 10^{-13}) = 13 - \log 2.0 = 13 - 0.30 = 12.70$$

Example 7.4

Calculate the pH of a solution prepared by mixing 2.0 mL of a strong acid solution of pH 3.00 and 3.0 mL of a strong base of pH 10.00.

Keep track of millimoles!

Solution

$$[H^+] \text{ of acid solution} = 1.0 \times 10^{-3}\ M$$

$$\text{mmol } H^+ = 1.0 \times 10^{-3}\ M \times 2.0\ \text{mL} = 2.0 \times 10^{-3}\ \text{mmol}$$

$$pOH \text{ of base solution} = 14.00 - 10.00 = 4.00$$

$$[OH^-] = 1.0 \times 10^{-4}\ M$$

$$\text{mmol } OH^- = 1.0 \times 10^{-4}\ M \times 3.0\ \text{mL} = 3.0 \times 10^{-4}\ \text{mmol}$$

There is an excess of acid.

$$\text{mmol } H^+ = 0.0020 - 0.0003 = 0.0017\ \text{mmol}$$

$$[H^+] = 0.0017\ \text{mmol}/5.0\ \text{mL} = 3.4 \times 10^{-4}\ M$$

$$pH = -\log 3.4 \times 10^{-4} = 4 - 0.53 = 3.47$$

Example 7.5

The pH of a solution is 9.67. Calculate the hydrogen ion concentration in the solution.

Solution

$$-\log[H^+] = 9.67$$

$$[H^+] = 10^{-9.67} = 10^{-10} \times 10^{0.33}$$

$$[H^+] = 2.1 \times 10^{-10}\ M$$

$[H^+] = 10^{-pH}$.

When $[H^+] = [OH^-]$, then a solution is said to be **neutral**. If $[H^+] > [OH^-]$, then the solution is **acidic**. And if $[H^+] < [OH^-]$, the solution is **alkaline**. The hydrogen ion and hydroxyl ion concentrations in pure water at 25°C are each 10^{-7} *M*, and the pH of water is 7. A pH of 7 is therefore neutral. Values of pH that are greater than this are alkaline, and pH values less than this are acidic. The reverse is true of pOH values. A pOH of 7 is also neutral. Note that the product of $[H^+]$ and $[OH^-]$ is always 10^{-14} at 25°C, and the sum of pH and pOH is always 14. If the temperature is other than 25°C, then K_w is different from 1.00×10^{-14}, and a neutral solution will have other than 10^{-7} *M* H^+ and OH^- (see below).

A 10 *M* HCl solution should have a pH of −1 and pOH of 15.

Students are often under the illusion that it is impossible to have a **negative pH**. There is no theoretical basis for this. A negative pH only means that the hydrogen ion concentration is greater than 1 *M*. In actual practice, a negative pH is uncommon because of two reasons. First, even strong acids may become partially undissociated at high concentrations. For example, 100% H_2SO_4 is so weakly dissociated that it can be stored in iron containers; more dilute H_2SO_4 solutions would contain sufficient protons from dissociation to attack and dissolve the iron. The second reason has to do with the *activity*, which we have chosen to neglect for dilute solutions. Since pH is really $-\log a_{H^+}$ (this is what a pH meter reading is a measure of), a solution that is 1.1 *M* in H^+ may actually have a positive pH because the activity of the H^+ is less than 1.0 *M*.[2] This is because at these high concentrations, the activity coefficient is less than unity (although at still higher concentrations the activity coefficient may become greater than unity—see Chapter 6). Nevertheless, there is mathematically no basis for not having a negative pH (or a negative pOH), although it may be rare in analytical solutions encountered.

The pH of 10^{-9} *M* HCl is *not* 9!

If the concentration of an acid or base is much less than 10^{-7} *M*, then its contribution to the acidity or basicity will be negligible compared with the contribution from water. The pH of a 10^{-8} *M* sodium hydroxide solution would therefore not differ significantly from 7. If the concentration of the acid or base is around 10^{-7} *M*, then its contribution is not negligible and neither is that from water; hence the sum of the two contributions must be taken.

Example 7.6

Calculate the pH and pOH of a 1.0×10^{-7} *M* solution of HCl.

Solution

Equilibria:

$$HCl \rightarrow H^+ + Cl^-$$
$$H_2O \rightleftharpoons H^+ + OH^-$$
$$[H^+][OH^-] = 1.0 \times 10^{-14}$$
$$[H^+]_{H_2O\ diss.} = [OH^-]_{H_2O\ diss.} = x$$

Since the hydrogen ions contributed from the ionization of water are not negligible compared to the HCl added,

$$[H^+] = C_{HCl} + [H^+]_{H_2O\ diss.}$$

---

[2] As will be seen in Chapter 13, it is also difficult to *measure* the pH of a solution having a negative pH or pOH because high concentrations of acids or bases tend to introduce an error in the measurement by adding a significant and unknown liquid-junction potential in the measurements.

Then,

$$([H^+]_{HCl} + x)(x) = 1.0 \times 10^{-14}$$

$$(1.00 \times 10^{-7} + x)(x) = 1.0 \times 10^{-14}$$

$$x^2 + 1.00 \times 10^{-7}\,x - 1.0 \times 10^{-14} = 0$$

Using the quadratic equation to solve [see Appendix B and the use of Excel Solver (Section 6.11)],

$$x = \frac{-1.00 \times 10^{-7} \pm \sqrt{1.0 \times 10^{-14} + 4(1.0 \times 10^{-14})}}{2} = 6.2 \times 10^{-8}\ M$$

Therefore, the *total* H^+ concentration $= (1.00 \times 10^{-7} + 6.2 \times 10^{-8}) = 1.62 \times 10^{-7}\ M$:

$$\text{pH} = -\log 1.62 \times 10^{-7} = 7 - 0.21 = 6.79$$

$$\text{pOH} = 14.00 - 6.79 = 7.21$$

or, since $[OH^-] = x$,

$$\text{pOH} = -\log(6.2 \times 10^{-8}) = 8 - 0.79 = 7.21$$

Note that, owing to the presence of the added H^+, the ionization of water is suppressed by 38% by the common ion effect (Le Châtelier's principle). At higher acid (or base) concentrations, the suppression is even greater and the contribution from the water becomes negligible. This contribution can be considered negligible if the concentration of protons or hydroxyl ions from an acid or base is *10^{-6} M or greater.*

We usually neglect the contribution of water to the acidity in the presence of an acid since its ionization is suppressed in the presence of the acid.

The calculation in this example is more academic than practical because *carbon dioxide from the air dissolved in water exceeds these concentrations*. Since carbon dioxide in water forms an acid, extreme care would have to be taken to remove and keep this from the water, to have a solution of $10^{-7}\ M$ acid.

7.4 pH at Elevated Temperatures: Blood pH

It is a convenient fact of nature for students and chemists who deal with acidity calculations and pH scales in aqueous solutions at room temperature that K_w is an integral number. At 100°C, for example, $K_w = 5.5 \times 10^{-13}$, and a *neutral solution* has

$$[H^+] = [OH^-] = \sqrt{5.5 \times 10^{-13}} = 7.4 \times 10^{-7}\ M$$

$$\text{pH} = \text{pOH} = 6.13$$

$$\text{p}K_w = 12.26 = \text{pH} + \text{pOH}$$

Not all measurements or interpretations are done at room temperature, however, and the temperature dependence of K_w must be taken into account (recall from Chapter 6 that equilibrium constants are temperature dependent). An important example is the pH of the body. The pH of blood at body temperature (37°C) is 7.35 to 7.45. This value represents a slightly more alkaline solution relative to neutral water than the same value would be at room temperature. At 37°C, $K_w = 2.5 \times 10^{-14}$ and $\text{p}K_w = 13.60$. The pH (and pOH) of a neutral solution is $13.60/2 = 6.80$. The hydrogen ion (and hydroxide ion) concentration is $\sqrt{2.5 \times 10^{-14}} =$

A neutral solution has pH < 7 above room temperature.

1.6×10^{-7} *M*. Since a neutral blood solution at 37°C would have pH 6.8, a blood pH of 7.4 is more alkaline at 37°C by 0.2 pH units than it would be at 25°C. This is important when one considers that a change of 0.3 pH units in the body is extreme.

The hydrochloric acid concentration in the stomach is about 0.1 to 0.02 *M*. Since $\text{pH} = -\log [\text{H}^+]$, the pH at 0.02 *M* would be 1.7. It will be the same *regardless of the temperature* since the hydrogen ion concentration is the same (neglecting solvent volume changes), and the same pH would be measured at either temperature. But, while the pOH would be $14.0 - 1.7 = 12.3$ at 25°C, it is $13.6 - 1.7 = 11.9$ at 37°C.

The pH of blood must be measured at body temperature to accurately reflect the status of blood buffers.

Not only does the temperature affect the ionization of water in the body and therefore change the pH of a neutral solution, it also affects the ionization constants of the acids and bases from which the buffer systems in the body are derived. As we shall see later in the chapter, this influences the pH of the buffers, and so a blood pH of 7.4 measured at 37°C will not be the same when measured at room temperature, in contrast to the stomach pH, whose value was determined by the concentration of a strong acid. For this reason, measurement of blood pH for diagnostic purposes is generally done at 37°C (see Chapter 13). (Neglecting changes in equilibrium constants of the blood buffer systems, the measured pH would be the same at 25 or 37°C—remembering to readjust the acidity scale at 37°C—but this is purely academic since the equilibrium constants do indeed change.)

7.5 Weak Acids and Bases—What Is the pH?

We have limited our calculations so far to strong acids and bases in which ionization is assumed to be complete. Since the concentration of H^+ or OH^- is determined readily from the concentration of the acid or base, the calculations are straightforward. As seen in Equation 7.3, weak acids (or bases) are only partially ionized. While mineral (inorganic) acids and bases such as HCl, $HClO_4$, HNO_3, and NaOH are strong electrolytes that are totally ionized in water, most organic acids and bases, as found in clinical applications, are weak.

The ionization constant can be used to calculate the amount ionized and, from this, the pH. The acidity constant for acetic acid at 25°C is 1.75×10^{-5}:

$$\frac{[\text{H}^+][\text{OAc}^-]}{[\text{HOAc}]} = 1.75 \times 10^{-5} \qquad (7.20)$$

When acetic acid ionizes, it dissociates to equal portions of H^+ and OAc^- by such an amount that the computation on the left side of Equation 7.20 will always be equal to 1.75×10^{-5}:

$$\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^- \qquad (7.21)$$

If the original concentration of acetic acid is *C* and the concentration of ionized acetic acid species (H^+ and OAc^-) is *x*, then the final concentration for each species at equilibrium is given by

$$\begin{array}{ccccc} \text{HOAc} & \rightleftharpoons & \text{H}^+ & + & \text{OAc}^- \\ (C - x) & & x & & x \end{array} \qquad (7.22)$$

Example 7.7

Calculate the pH and pOH of a $1.00 \times 10^{-3}\ M$ solution of acetic acid.

Solution

$$\text{HOAc} \rightleftharpoons \text{H}^+ + \text{OAc}^-$$

The concentrations of the various species are as follows:

	$[HOAc]$	$[H^+]$	$[OAc^-]$
Initial	1.00×10^{-3}	0	0
Change (x = mmol/mL HOAc ionized)	$-x$	$+x$	$+x$
Equilibrium	$1.00 \times 10^{-3} - x$	x	x

From Equation 7.20

$$\frac{(x)(x)}{1.00 \times 10^{-3} - x} = 1.75 \times 10^{-5}$$

The solution is that of a quadratic equation. If less than about 10 or 15% of the acid is ionized, the expression may be simplified by neglecting x compared with C ($10^{-3}\ M$ in this case). This is an arbitrary (and not very demanding) criterion. The simplification applies if *K_a is smaller than about 0.01C*, that is, smaller than 10^{-4} at $C = 0.01\ M$, 10^{-3} at $C = 0.1\ M$, and so forth. Under these conditions, the error in calculation is 5% or less (results come out too high), and within the probable accuracy of the equilibrium constant. Our calculation simplifies to

If $C_{\text{HA}} > 100K_a$, x can be neglected compared to C_{HA}.

$$\frac{x^2}{1.00 \times 10^{-3}} = 1.75 \times 10^{-15}$$

$$x = 1.32 \times 10^{-4}\ M \equiv [\text{H}^+]$$

Therefore,

$$\text{pH} = -\log 1.32 \times 10^{-4} = 4 - \log 1.32 = 4 - 0.12 = 3.88$$

$$\text{pOH} = 14.00 - 3.88 = 10.12$$

The simplification in the calculation is not serious, particularly since equilibrium constants are often not known to a high degree of accuracy (frequently no better than ±10%). In the above example, solution of the quadratic equation results in $[\text{H}^+] = 1.26 \times 10^{-4}\ M$ (5% less) and pH = 3.90. This pH is within 0.02 unit of that calculated using the simplification, which is near the limit of accuracy to which pH measurements can be made, and almost certainly as close a calculation as is justified in view of the experimental errors in K_a or K_b values and the fact that we are using concentrations rather than activities in the calculations. In our calculations, we also neglected the contribution of hydrogen ions from the ionization of water (which was obviously justified); this is generally permissible except for very dilute ($<10^{-6}\ M$) or very weak ($K_a < 10^{-12}$) acids.

The absolute accuracy of pH measurements is no better than 0.02 pH units. See Chapter 13.

Similar equations and calculations hold for weak bases.

Example 7.8

The basicity constant K_b for ammonia is 1.75×10^{-5} at 25°C. (It is only coincidental that this is equal to K_a for acetic acid.) Calculate the pH and pOH for a 1.00×10^{-3} M solution of ammonia.

Solution

$$\begin{array}{cccc} NH_3 + H_2O & \rightleftharpoons & NH_4^+ & + \; OH^- \\ (1.00 \times 10^{-3} - x) & & x & x \end{array}$$

$$\frac{[NH_4^+][OH^-]}{[NH_3]} = 1.75 \times 10^{-5}$$

The same rule applies for the approximation applied for a weak acid. Thus,

$$\frac{(x)(x)}{1.00 \times 10^{-3}} = 1.75 \times 10^{-5}$$

$$x = 1.32 \times 10^{-4}\ M = [OH^-]$$

$$pOH = -\log 1.32 \times 10^{-4} = 3.88$$

$$pH = 14.00 - 3.88 = 10.12$$

7.6 Salts of Weak Acids and Bases—They Aren't Neutral

The hydrolysis of OAc^- is no different than the "ionization" of NH_3 in Example 7.8.

The salt of a weak acid, for example, NaOAc, is a strong electrolyte, like (almost) all salts, and completely ionizes. In addition, the anion of the salt of a weak acid is a **Brønsted base**, which will accept protons. It partially hydrolyzes in water (a Brønsted acid) to form hydroxide ion and the corresponding undissociated acid. For example,

$$OAc^- + H_2O \rightleftharpoons HOAc + OH^- \tag{7.23}$$

The HOAc here is undissociated and therefore does not contribute to the pH. This ionization is also known as **hydrolysis** of the salt ion. Because it hydrolyzes, sodium acetate is a weak base (the conjugate base of acetic acid). The ionization constant for Equation 7.23 is equal to the basicity constant of the salt. The weaker the conjugate acid, the stronger the conjugate base, that is, the more strongly the salt will combine with a proton, as from the water, to shift the ionization in Equation 7.23 to the right. *Equilibria for these Brønsted bases are treated identically to the weak bases we have just considered.* We can write an equilibrium constant:

$$K_H = K_b = \frac{[HOAc][OH^-]}{[OAc^-]} \tag{7.24}$$

K_H is called the **hydrolysis constant** of the salt and is the same as the basicity constant. We will use K_b to emphasize that these salts are treated the same as for any other weak base.

The value of K_b can be calculated from K_a of acetic acid and K_w if we multiply both the numerator and denominator by $[H^+]$:

$$K_b = \frac{[\mathrm{HOAc}][\mathrm{OH^-}]}{[\mathrm{OAc^-}]} \cdot \frac{[\mathrm{H^+}]}{[\mathrm{H^+}]} \tag{7.25}$$

The quantity inside the dashed line is K_w and the remainder is $1/K_a$. Hence,

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10} \tag{7.26}$$

We see from the small K_b that the acetate ion is quite a weak base with only a small fraction of ionization. *The product of* K_a *of any weak acid and* K_b *of its conjugate base is always equal to* K_w:

$$\boxed{K_a K_b = K_w} \tag{7.27}$$

For any salt of a weak acid HA that hydrolyzes in water,

$$A^- + H_2O \rightleftharpoons HA + OH^- \tag{7.28}$$

$$\boxed{\frac{[\mathrm{HA}][\mathrm{OH^-}]}{[\mathrm{A^-}]} = \frac{K_w}{K_a} = K_b} \tag{7.29}$$

The pH of such a salt (a Brønsted base) is calculated in the same manner as for any other weak base. When the salt hydrolyzes, it forms an equal amount of HA and OH^-. If the original concentration of A^- is C_{A^-}, then

$$\underset{(C_{A^-} - x)}{A^-} + H_2O \rightleftharpoons \underset{x}{HA} + \underset{x}{OH^-} \tag{7.30}$$

The quantity x can be neglected compared to C_{A^-} if $C_{A^-} > 100K_b$, which will generally be the case for such weakly ionized bases.

We can solve for the OH^- concentration using Equation 7.29:

$$\frac{[\mathrm{OH^-}][\mathrm{OH^-}]}{C_{A^-}} = \frac{K_w}{K_a} = K_b \tag{7.31}$$

Compare this with the algebraic setup in Example 7.8. They are identical:

$$\boxed{[\mathrm{OH^-}] = \sqrt{\frac{K_w}{K_a} \cdot C_{A^-}} = \sqrt{K_b \cdot C_{A^-}}} \tag{7.32}$$

This equation holds only if $C_{A^-} > 100K_b$, and x can be neglected compared to C_{A^-}. If this is not the case, then the quadratic formula must be solved as for other bases in this situation.

Example 7.9

Calculate the pH of a 0.10 *M* solution of sodium acetate.

Solution

Compare this base "ionization" with that of NH_3, Example 7.8.

Write the equilibria

$$NaOAc \rightarrow Na^+ + OAc^- \text{ (ionization)}$$
$$OAc^- + H_2O \rightleftharpoons HOAc + OH^- \text{ (hydrolysis)}$$

Write the equilibrium constant

$$\frac{[HOAc][OH^-]}{[OAc^-]} = K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Let x represent the concentration of HOAc and OH^- at equilibrium. Then, at equilibrium,

$$[HOAc] = [OH^-] = x$$
$$[OAc^-] = C_{OAc^-} - x = 0.10 - x$$

Since $C_{OAc^-} \gg K_b$, neglect x compared to C_{OAc^-}. Then,

$$\frac{(x)(x)}{0.10} = 5.7 \times 10^{-10}$$
$$x = \sqrt{5.7 \times 10^{-10} \times 0.10} = 7.6 \times 10^{-6}\ M$$

Compare this last step with Equation 7.32. Also, compare the entire setup and solution with those in Example 7.8. The HOAc formed is undissociated and does not contribute to the pH:

$$[OH^-] = 7.6 \times 10^{-6}\ M$$
$$[H^+] = \frac{1.0 \times 10^{-14}}{7.6 \times 10^{-6}} = 1.3 \times 10^{-9}\ M$$
$$pH = -\log 1.3 \times 10^{-9} = 9 - 0.11 = 8.89$$

Similar equations can be derived for the cations of salts of weak bases (the salts are completely dissociated). These are **Brønsted acids** and ionize (hydrolyze) in water:

$$BH^+ + H_2O \rightleftharpoons B + H_3O^+ \tag{7.33}$$

The B is undissociated and does not contribute to the pH. The acidity constant is

$$K_H = K_a = \frac{[B][H_3O^+]}{[BH^+]} \tag{7.34}$$

The acidity constant (hydrolysis constant) can be derived by multiplying the numerator and denominator by [OH⁻]:

$$K_a = \frac{[\mathrm{B}]\boxed{[\mathrm{H_3O^+}]\quad[\mathrm{OH^-}]}}{[\mathrm{BH^+}]\quad[\mathrm{OH^-}]} \tag{7.35}$$

Again, the quantity inside the dashed lines is K_w, while the remainder is $1/K_b$. Therefore,

$$\boxed{\frac{[\mathrm{B}][\mathrm{H_3O^+}]}{[\mathrm{BH^+}]} = \frac{K_w}{K_b} = K_a} \tag{7.36}$$

and for NH_4^+,

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10} \tag{7.37}$$

We could, of course, have derived K_a from Equation 7.27. It is again coincidence that the numerical value of K_a for NH_4^+ equals K_b for OAc^-.

The salt of a weak base ionizes to form equal amounts of B and H_3O^+ (H^+ if we disregard hydronium ion formation as was done previously). We can therefore solve for the hydrogen ion concentration (by assuming $C_{BH^+} > 100\,K_a$):

$$\frac{[\mathrm{H^+}][\mathrm{H^+}]}{C_{\mathrm{BH^+}}} = \frac{K_w}{K_b} = K_a \tag{7.38}$$

$$\boxed{[\mathrm{H^+}] = \sqrt{\frac{K_w}{K_b} \cdot C_{\mathrm{BH^+}}} = \sqrt{K_a \cdot C_{\mathrm{BH^+}}}} \tag{7.39}$$

Again, this equation only holds if $C_{BH^+} > 100K_a$. Otherwise, the quadratic formula must be solved.

Example 7.10

Calculate the pH of a 0.25 *M* solution of ammonium chloride.

Solution

Write the equilibria

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \quad \text{(ionization)}$$
$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+ \quad \text{(hydrolysis)}$$
$$(NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+)$$

Write the equilibrium constant

$$\frac{[\mathrm{NH_4OH}][\mathrm{H^+}]}{[\mathrm{NH_4^+}]} = K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.75 \times 10^{-5}} = 5.7 \times 10^{-10}$$

Let x represent the concentration of $[\mathrm{NH_4OH}]$ and $[\mathrm{H^+}]$ at equilibrium. Then, at equilibrium,

$$[\mathrm{NH_4OH}] = [\mathrm{H^+}] = x$$
$$[\mathrm{NH_4^+}] = C_{\mathrm{NH_4^+}} - x = 0.25 - x$$

Since $C_{\mathrm{NH_4^+}} \gg K_a$, neglect x compared to $C_{\mathrm{NH_4^+}}$. Then,

$$\frac{(x)(x)}{0.25} = 5.7 \times 10^{-10}$$

$$x = \sqrt{5.7 \times 10^{-10} \times 0.25} = 1.2 \times 10^{-5}\ M$$

Compare this last step with Equation 7.39. Also, compare the entire setup and solution with those in Example 7.7. The $\mathrm{NH_4OH}$ formed is undissociated and does not contribute to the pH:

$$[\mathrm{H^+}] = 1.2 \times 10^{-5}\ M$$

$$\mathrm{pH} = -\log(1.2 \times 10^{-5}) = 5 - 0.08 = 4.92$$

……

7.7 Buffers—Keeping the pH Constant (or Nearly So)

A **buffer** is defined as a solution that resists change in pH when a small amount of an acid or base is added or when the solution is diluted. This is very useful for maintaining the pH for a reaction at an optimum value. A buffer solution consists of a mixture of a weak acid and its conjugate base or a weak base and its conjugate acid at predetermined concentrations or ratios. That is, we have a mixture of a weak acid and its salt or a weak base and its salt. Consider an acetic acid–acetate buffer. The acid equilibrium that governs this system is

$$\mathrm{HOAc} \rightleftharpoons \mathrm{H^+} + \mathrm{OAc^-}$$

But now, since we have added a supply of acetate ions to the system (e.g., from sodium acetate), the hydrogen ion concentration is no longer equal to the acetate ion concentration. The hydrogen ion concentration is

$$[\mathrm{H^+}] = K_a \frac{[\mathrm{HOAc}]}{[\mathrm{OAc^-}]} \tag{7.40}$$

Taking the negative logarithm of each side of this equation, we have

$$-\log[\mathrm{H^+}] = -\log K_a - \log \frac{[\mathrm{HOAc}]}{[\mathrm{OAc^-}]} \tag{7.41}$$

$$\mathrm{pH} = \mathrm{p}K_a - \log \frac{[\mathrm{HOAc}]}{[\mathrm{OAc^-}]} \tag{7.42}$$

Upon inverting the last log term, it becomes positive:

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{OAc^-}]}{[\mathrm{HOAc}]} \tag{7.43}$$