

1 Introduction

Geochemistry, as the name suggests, is the bridge between geology and chemistry and, thus, in essence encompasses the study of all chemical aspects of the Earth and their interpretation utilizing the principles of chemistry.

Rankama and Sahama (1950)

1.1 Units of measurement

A unit of measurement is a definite magnitude of a physical quantity, defined and adopted by convention and/or by law, that is used as a standard or measurement of the same physical quantity. Any other value of the physical quantity can be expressed as a simple multiple of the unit of measurement.

The original metric system of measurement was adopted in France in 1791. Over the years it developed into two somewhat different systems of metric units: (a) the *MKS system*, based on the meter, kilogram, and second for length, mass, and time, respectively; and (b) the *CGS system* (which was introduced formally by the British Association for the Advancement of Science in 1874), based on the centimeter, gram, and second. There are other traditional differences between the two systems, for example, in the measurements of electric and magnetic fields. The recurring need for conversion from units in one of the two systems to units of the other, however, defeated the metric ideal of a universal measuring system, and a choice had to be made between the two systems for international usage.

In 1954, the Tenth General Conference on Weights and Measures adopted the meter, kilogram, second, ampere, degree Kelvin, and candela as the basic units for all international weights and measures. Soon afterwards, in 1960, the Eleventh General Conference adopted the name *International System of Units* (abbreviated to *SI* from the French “Système

International d’Unités”) for this collection of units. The “degree Kelvin” was renamed the “kelvin” in 1967.

1.1.1 The SI system of units

In the SI system, the modern form of the MKS system, there are seven base units from which all other units of measurement can be derived (Table 1.1). The International Union of Pure and Applied Chemistry (IUPAC) has recommended the use of SI units in all scientific communications. This is certainly desirable from the perspective of standardization of data, but a lot of the available chemical data were collected prior to 1960 and thus are not necessarily in SI units. It is therefore necessary for geochemists to be familiar with both SI and non-SI units. Equivalence between SI and non-SI units, and some of the commonly used physical constants are given in Appendix 1.

Most chemists, physicists, and engineers now use SI system of units, but the use of CGS (centimeter–gram–second) and other non-SI units is still widespread in geologic literature. In this book we will use SI units, but with two exceptions. As pointed out by Powell (1978) and Nordstrom and Munoz (1994), the SI unit pascal (Pa) is unwieldy for reporting geological pressures. For example, many geochemical measurements have been done at 1 atmosphere (atm) ambient pressure (the pressure exerted by the atmosphere at sea level), which translates into 101,325 pascals or 1.01 megapascals

2 Introduction

Table 1.1 The SI base units and examples of SI derived units.

SI base units			Examples of SI derived units			
Physical quantity	Name	Symbol	Physical quantity	Name	Symbol	Definition in terms of the SI base units
Length	Meter	m	Force	Newton	N	m kg s^{-2}
Mass	Kilogram	kg	Pressure	Pascal	Pa	$\text{m}^{-1} \text{kg s}^{-2} = \text{Nm}^{-2}$
Time	Second	s	Energy, work, heat	Joule	J	$\text{m}^2 \text{kg s}^{-2} = \text{Nm}$
Temperature	Kelvin	K	Electric charge	Coulomb	C	sA
Amount of substance	Mole	mol	Electric potential difference	Volt	V	$\text{m}^2 \text{kg s}^{-3} \text{A}^{-1}$
Electric current	Ampere	A	Volume	Liter	L	$\text{m}^3 10^{-3}$
Luminous intensity	Candela	cd	Electric conductance	Siemens	S	$\text{m}^{-2} \text{kg}^{-1} \text{s}^3 \text{A}^2$

Newton=the force that will accelerate a mass of 1 kg by 1 m s^{-2} .
Pascal=the pressure exerted when a force of 1 N acts uniformly over an area of 1 m^2 .
Joule=work done when a force of 1 N produces a displacement of 1 m in the direction of the force.

(Mpa), a rather cumbersome number to use. Most geochemists prefer to use bar as the unit of pressure, which can easily be converted into pascals ($1 \text{ bar} = 10^5 \text{ pascals}$ or 0.1 MPa) and which is close enough to pressure expressed in atmosphere ($1 \text{ bar} = 0.987 \text{ atm}$) for the difference to be ignored in most cases without introducing significant error. A similar problem exists in the use of the SI unit joule (J), instead of the more familiar non-SI unit calorie (cal). The calorie, defined as the quantity of heat required to raise 1 gram (g) of water from 14.5 to 15.5°C , has a physical meaning that is easy to understand. Moreover, tables of thermodynamic data, especially the older ones, use calories instead of joules. Thus, we may use calories in the calculations and report the final results in joules ($1 \text{ cal} = 4.184 \text{ J}$).

The familiar scale of temperature is the Celsius scale ($^\circ\text{C}$), which is based on two reference points for temperature: the *ice point*, the temperature at which ice is in equilibrium with liquid water at 1 atm pressure; and the *steam point*, the temperature at which steam is in equilibrium with liquid water at 1 atm pressure. The Celsius scale arbitrarily assigns a temperature of zero to the ice point and a temperature of 100 to the steam point. The SI unit of temperature is kelvin (K), which is the temperature used in all thermodynamic calculations. If pressure–temperature ($^\circ\text{C}$) plots at different volumes are constructed for any gas, the extrapolated lines all intersect at a point representing zero pressure at a temperature around -273°C (Fig. 1.1). This temperature, which is not physically attainable (although it has been approached very closely), is called the *absolute zero of temperature*. It is the temperature at which the molecules of a gas have no translational, rotational, or vibrational motion and therefore no thermal energy. The temperature scale with absolute zero as the starting point is the *kelvin temperature scale* and the unit of temperature on this scale is kelvin (K, not $^\circ\text{K}$), so named after Lord Kelvin who proposed it in 1848. The kelvin unit of temperature is defined as the $1/273.16$ fraction of the so-called *triple point*

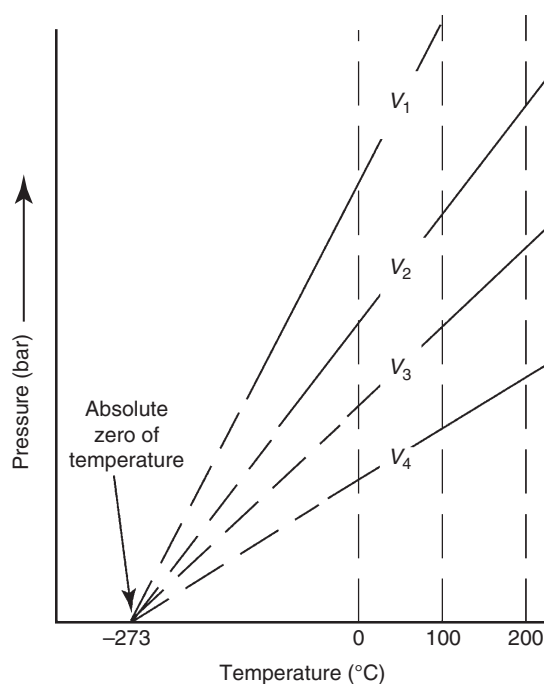


Fig. 1.1 The definition of absolute zero of temperature. The lines V_1 – V_4 show the variation of different volumes of a gas as a function of temperature and pressure. When extrapolated, the lines intersect at a point representing zero pressure at a temperature around -273°C . This temperature, which is not physically attainable, is called the absolute zero of temperature.

for H_2O (the temperature at which ice, liquid water, and steam coexist in equilibrium at 1 atm pressure), which is 0.01 K greater than the ice point. Thus, the ice point, which is defined as 0°C , corresponds to 273.15 K (see Fig. 4.3) and the relationship between kelvin and Celsius scales of temperature is given by:

$$T (\text{K}) = t (^\circ\text{C}) + 273.15 \quad (1.1)$$

Evidently, the steam point (100°C) corresponds to 373.15 K. It follows from equation (1.1) that the degree Celsius is equal in magnitude to the kelvin, which in turn implies that the numerical value of a given temperature difference or temperature interval is the same whether it is expressed in the unit degree Celsius (°C) or in the unit kelvin. (In the USA, temperatures are often measured in the Fahrenheit scale (F). The expression relating temperatures in the Celsius and Fahrenheit scales is: $F=9/5^{\circ}\text{C}+32.$)

1.1.2 Concentration units for solutions

Concentrations of solutes (dissolved substances) in solutions (solids, liquids, or gases) are commonly expressed either as mass concentrations (parts per million, or milligrams per liter, or equivalent weights per liter) or as molar concentrations (*molality*, *molarity*, or *mole fraction*; Table 1.2).

To obtain the number of moles (abbreviated *mol*) of a substance, the amount of the substance (in grams) is divided by its gram-molecular weight; to obtain the mole fraction of a substance, the number of moles of the substance is divided by the total number of moles in the solution (see section 2.2 for further elaboration). For example, the mole fraction of NaCl (gram-molecular weight=58.44) in a solution of 100 g of NaCl in 2 kg of H₂O (gram-molecular weight=18.0) can be calculated as follows:

Number of moles of NaCl=100/58.44=1.7112
 Number of moles of H₂O=2 (1000)/18.0=111.1111
 Total number of moles in the solution=1.7112 + 111.1111
 = 112.8223
 Mole fraction of NaCl in solution=1.7112 /112.8223=0.0152

Note that the mole fraction of a pure substance (solid, liquid, or gas) is unity.

The concentration units mg/L and ppm, as well as molality and molarity, are related through the density of the solution (ρ):

$$\text{concentration (ppm)} = \frac{\text{concentration of solute (g L}^{-1}\text{)}}{\rho \text{ (g mL}^{-1}\text{)}} \quad (1.2)$$

$$m = M \left(\frac{\text{weight of solution (g)}}{\text{weight of solution (g) - total weight of solutes (g)}} \right) \left(\frac{1}{\rho \text{ (g mL}^{-1}\text{)}} \right) \quad (1.3)$$

Concentrations expressed in molality or mole fraction have the advantage that their values are independent of temperature and pressure; molarity, on the other hand, is dependent on the volume of the solution, which varies with temperature and pressure. The advantage of using molarity is that it is often easier to measure the volume of a liquid than its weight. For dilute aqueous solutions at 25°C, however, the density of the solution is very close to that of pure water, $\rho=(1 \text{ kg})/(1 \text{ L})$, so that little error is introduced if the difference between mg/L and ppm or molality and molarity is ignored for such a solution.

The strength of an acid or a base is commonly expressed in terms of *normality*, the number of equivalent weights of the acid or base per liter of the solution, the *equivalent weight* being defined as the gram-molecular weight per number of Hs or OHs in the formula unit. For example, the equivalent weight of H₂SO₄ (gram-molecular weight=98) is 98/2=49, and the normality of a solution of 45 g of H₂SO₄ in 2 L of solution is 45/(49×2)=0.46.

1.2 The Geologic Time Scale

Discussions of events require a timeframe for reference. The Geologic Time Scale provides such a reference for past geologic events. Forerunners of the current version of the time scale were developed in small increments during the 19th century, long before the advent of radiometric dating, using techniques applicable to determining the relative order of events. These techniques are based on the principles of *original horizontality* (sediments are deposited in horizontal layers), *superposition* (in a normal sequence of sedimentary rocks or lava flows, the layer above is younger than the layer below), and *faunal succession* (fossil assemblages occur in rocks in a definite and determinable order). Although the time scale evolved haphazardly, with units being added or modified in different parts of the world at different times, it has been organized into a universally accepted workable scheme of classification of geologic time.

The Geologic Time Scale spans the entire interval from the birth of the Earth ($t=4.55 \text{ Ga}$, i.e., 4.55 billion years before the present) to the present ($t=0$), and is broken up into a hierarchical set of relative time units based on the occurrence of distinguishing geologic events. Generally accepted divisions for increasingly smaller units of time are *eon*, *era*, *period*, and *epoch* (Fig. 1.2). Different spans of time on the time scale are usually delimited by major tectonic or paleontological events

Table 1.2 Concentration units for a solute.

Concentration unit	Definition
Milligrams per liter (mg/L)	Mass of solute (mg) / volume of solution (L)
Parts per million (ppm)	Mass of solute (mg) / mass of solution (kg)
Mole fraction (X)	Moles of solute / total moles of solution ¹
Molarity (M)	Moles of solute / volume of solution (L)
Molality (m)	Moles of solute / mass of solvent (kg)
Normality (N)	Equivalent weight of solute (g) / volume of solution (L)

¹Moles of a substance=weight of the substance (g)/gram-molecular weight of the substance.

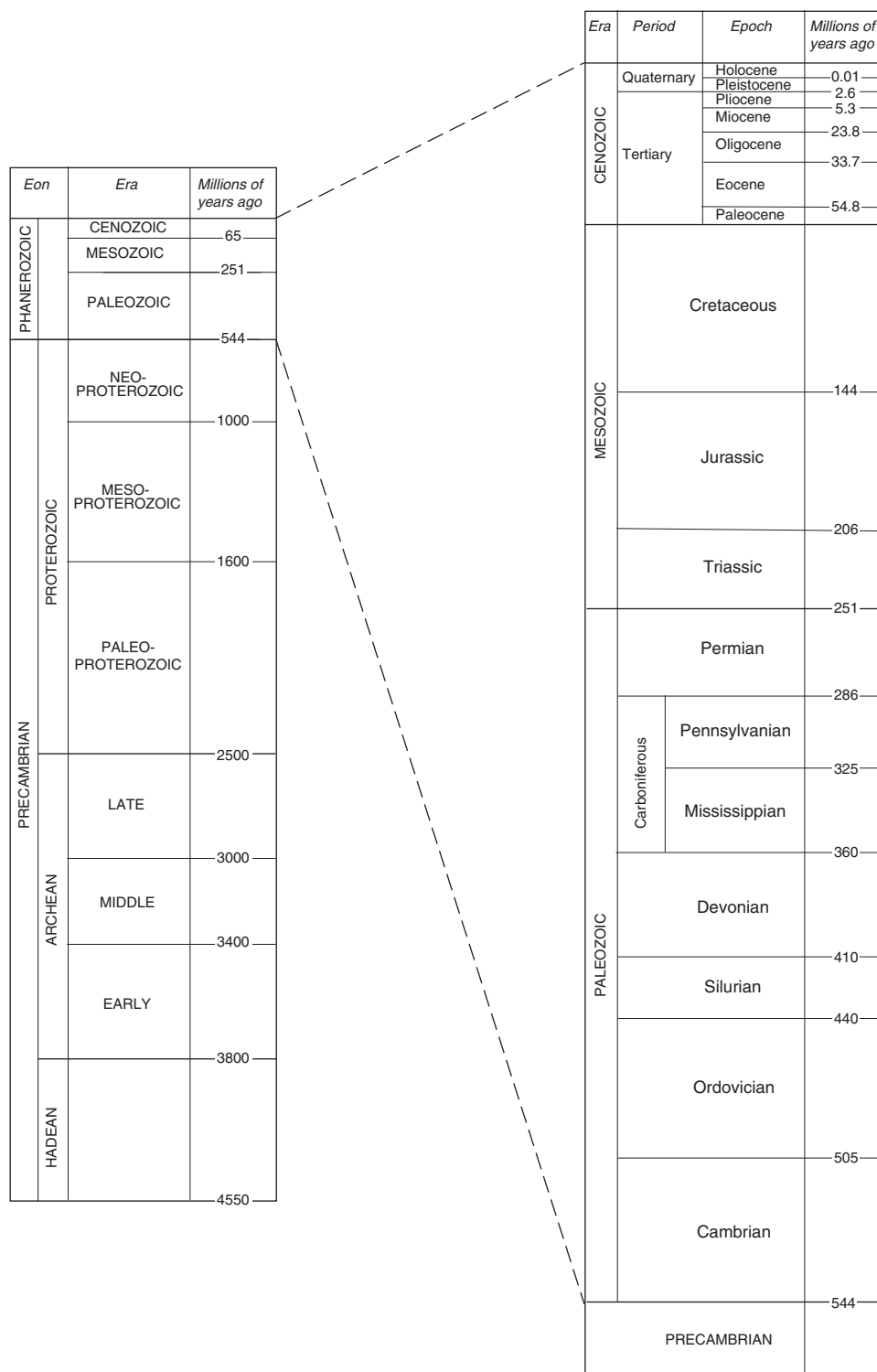


Fig. 1.2 The Geologic Time Scale. The age of the Earth, based on the age of meteorites, is 4.55 ± 0.05 Ga according to Patterson (1956) and 4.55–4.57 Ga according to Allègre *et al.* (1995).

such as orogenesis (mountain-building activity) or mass extinctions. For example, the Cretaceous–Tertiary boundary is defined by a major mass extinction event that marked the disappearance of dinosaurs and many marine species.

Absolute dates for the boundaries between the divisions were added later on, after the development of techniques for dating rocks using radioactive isotopes (see Chapter 10). The time scale shown in Fig. 1.2 includes these dates, producing an integrated

geologic time scale. Time units that are older than the Cambrian Period (that is, units in the Precambrian Eon) pre-date reliable fossil records and are defined by absolute dates.

1.3 Recapitulation

Terms and concepts

Absolute zero of temperature
 Celsius scale (temperature)
 CGS system of units
 Eon
 Epoch
 Era
 Equivalent weight
 Fahrenheit scale (temperature)
 Faunal succession
 Geologic Time Scale
 Fahrenheit scale (temperature)
 Geologic time scale
 Gram-molecular weight
 Kelvin scale (temperature)
 Mass concentration
 Mass extinction
 MKS system of units
 Molality
 Molarity
 Mole
 Mole fraction
 Original horizontality
 Period
 SI units
 Superposition

Computation techniques

- Conversion of SI units to non-SI units.
- Conversion of °C to °F and K.
- Calculations of number of moles, mole fraction, molarity, molality, ppm.

1.4 Questions

Gram atomic weights: H=1.0; C=12.01; O=16.00; Na=22.99; Al=26.98; Si=28.09; S=32.07; Cl=35.45; K=39.10; Ca=40.08.

1. The gas constant, R , has the value $1.987 \text{ cal K}^{-1} \text{ mol}^{-1}$. Show that

$$R = 8.317 \text{ Joules K}^{-1} \text{ mol}^{-1} = 8.317 \times 10^7 \text{ ergs K}^{-1} \text{ mol}^{-1} \\ = 83.176 \text{ cm}^3 \text{ bar K}^{-1} \text{ mol}^{-1}$$

2. Show that (a) $1 \text{ calorie bar}^{-1} = 41.84 \text{ cm}^3$, and (b) $1 \text{ m}^3 = 1 \text{ joule pascal}^{-1}$
3. What is the molarity of one molal NaCl solution (at 25°C and 1 bar)? Density of the NaCl solution (at 25°C and 1 bar) is 1.0405 kg L^{-1} .
4. What are the mole fractions of $\text{C}_2\text{H}_5\text{OH}$ (ethanol) and H_2O (water) in a solution prepared by mixing 70.0 g of ethanol with 30.0 g of water?
5. What are the mole fractions of $\text{C}_2\text{H}_5\text{OH}$ (ethanol) and H_2O (water) in a solution prepared by mixing 70.0 mL of ethanol with 30.0 mL of water at 25°C ? The density of ethanol is 0.789 g mL^{-1} , and that of water is 1.00 g mL^{-1} .
6. When dissolved in water, NaCl dissociates into Na^+ and Cl^- ions ($\text{NaCl} = \text{Na}^+ + \text{Cl}^-$). What is the molality of Na^+ in a solution of 1.35 g of NaCl dissolved in 2.4 kg of water? What is the concentration of Na^+ the solution in ppm?
7. The density of an aqueous solution containing 12.5 g K_2SO_4 in 100.00 g solution is 1.083 g mL^{-1} . Calculate the concentration of K_2SO_4 in the solution in terms of molality and molarity. What is the mole fraction of the solvent in the solution?
8. The ideal chemical formula of the mineral albite is $\text{NaAlSi}_3\text{O}_8$. How many moles of $\text{NaAlSi}_3\text{O}_8$ do 5 g of the mineral contain? How many moles of Si?
9. A solution made by dissolving 16.0 g of CaCl_2 in 64.0 g of water has a density of 1.180 g mL^{-1} at 25°C . Express the concentration of Ca in the solution in terms of molality and molarity.