



INTRODUCTION TO

Geochemistry

Principles and Applications

KULA C. MISRA

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ATOMIC WEIGHTS OF THE ELEMENTS

<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>	<i>Element</i>	<i>Symbol</i>	<i>Atomic Number</i>	<i>Atomic Weight</i>
Actinium	Ac	89	r	Mercury	Hg	80	200.59
Aluminum	Al	13	26.98	Molybdenum	Mo	42	95.94
Americium	Am	95	r	Neodymium	Nd	60	144.24
Antimony	Sb	51	121.76	Neon	Ne	10	20.18
Argon	Ar	18	39.95	Neptunium	Np	93	r
Arsenic	As	33	74.92	Nickel	Ni	28	58.69
Astatine	At	85	r	Niobium	Nb	41	92.91
Barium	Ba	56	137.33	Nitrogen	N	7	14.01
Berkelium	Bk	97	r	Nobelium	No	102	259.10
Beryllium	Be	4	9.01	Osmium	Os	76	190.23
Bismuth	Bi	83	208.98	Oxygen	O	8	16.00
Boron	B	5	10.81	Palladium	Pd	46	106.40
Bromine	Br	35	79.90	Phosphorus	P	15	30.97
Cadmium	Cd	48	112.4	Platinum	Pt	78	195.08
Calcium	Ca	20	40.08	Plutonium	Pu	94	r
Californium	Cf	98	r	Polonium	Po	84	r
Carbon	C	6	12.01	Potassium	K	19	39.10
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.91
Cesium	Cs	55	132.91	Promethium	Pm	61	r
Chlorine	Cl	17	35.45	Protactinium	Pa	91	231.04
Chromium	Cr	24	52.00	Radium	Ra	88	r
Cobalt	Co	27	58.93	Radon	Rn	86	r
Copper	Cu	29	63.55	Rhenium	Re	75	186.21
Curium	Cm	96	r	Rhodium	Rh	45	102.90
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99	r	Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.36
Europium	Eu	63	151.96	Scandium	Sc	21	44.96
Fermium	Fm	100	r	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.09
Francium	Fr	87	r	Silver	Ag	47	107.87
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.99
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.61	Sulfur	S	16	32.07
Gold	Au	79	196.97	Tantalum	Ta	73	180.95
Hafnium	Hf	72	178.49	Technetium	Tc	43	r
Helium	He	2	4.00	Tellurium	Te	52	127.60
Holmium	Ho	67	164.93	Terbium	Tb	65	158.93
Hydrogen	H	1	1.01	Thallium	Tl	81	204.38
Indium	In	49	114.82	Thorium	Th	90	232.04
Iodine	I	53	126.90	Thulium	Tm	69	168.93
Iridium	Ir	77	192.22	Tin	Sn	50	118.71
Iron	Fe	26	55.85	Titanium	Ti	22	47.87
Krypton	Kr	36	38.80	Tungsten	W	74	183.84
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lead	Pb	82	207.2	Vanadium	V	23	50.94
Lithium	Li	3	6.94	Xenon	Xe	54	131.29
Lutetium	Lu	71	174.97	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.31	Yttrium	Y	39	88.91
Manganese	Mn	25	54.94	Zinc	Zn	30	65.39
Mendelevium	Md	101	258.10	Zirconium	Zr	40	91.22

r = radioactive, no stable isotopes. Source of data: *CRC Handbook of Chemistry and Physics*, 81st ed. (2000)

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Principles and Applications

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Preface

Geochemistry deals essentially with the processes and consequences of distribution of elements in minerals and rocks in different physical-chemical environments and, as such, permeates all branches of geology to varying degrees. An adequate background in geochemistry is, therefore, an imperative for earth science students. This book is an attempt to cater to that need. It covers a wide variety of topics, ranging from atomic structures that determine the chemical behavior of elements to modern biogeochemical cycles that control the global-scale distribution of elements. It is intended to serve as a text for an introductory undergraduate/graduate level course in geochemistry, and it should also provide the necessary background for more advanced courses in mineralogy, petrology, and geochemistry.

The organization of the book is logical and quite different from the geochemistry texts in the market. Excluding the "Introduction", the 12 chapters of the book are divided into four interrelated parts. Part I (Crystal Chemistry – Chapters 2 and 3) provides a brief review of the electronic structure of atoms and of different kinds of chemical bonds. Part II (Chemical Reactions – Chapters 4 through 9) discusses the thermodynamic basis of chemical reactions involving phases of constant and variable composition, including reactions relevant to aqueous systems and reactions useful for geothermometry and geobarometry. A substantial portion of the chapter on oxidation–reduction reactions (Chapter 8) is devoted to a discussion of the role of bacteria in such reactions. The last chapter of Part II is a brief introduction to the kinetic aspects of chemical reactions. Part III (Isotope Geochemistry – Chapters 10 and 11) introduces the

students to radiogenic and stable isotopes, and their applications to geologic problems, ranging from dating of rocks and minerals to the interpretation of an anoxic atmosphere during the Hadean and Archean eras. Part IV (The Earth Supersystem - Chapters 12 and 13) is an overview of the origin and evolution of the solid Earth (core, mantle, and crust), and of the atmosphere and hydrosphere. A brief discussion of some important biogeochemical cycles provides a capstone to the introductory course.

The treatment in this book recognizes the welcome fact that geochemistry has become increasingly more quantitative, and assumes that the students have taken the usual selection of elementary courses in earth sciences, chemistry, and mathematics. Nevertheless, most relevant chemical concepts and mathematical relations are developed from first principles. It is my experience that the derivation of an equation enhances the appreciation for its applications and limitations. To maintain the flow of the text, however, some derivations and tangential material are separated from the text in the form of "boxes." Supplementary data and explanations are presented in 10 appendixes.

Quantitative aspects of geochemistry are emphasized throughout the book to the extent they are, in my judgment, appropriate at an introductory level.

Each chapter in the book contains many solved examples illustrating the application of geochemistry to real-life geological and environmental problems. At the end of each chapter is a list of computational techniques the students are expected to have learned and a set of questions to reinforce the importance of solving problems. It is an integral part of the learning process that the students solve every one of these problems. To help the students in this endeavor, answers to selected problems are included as an appendix (Appendix 10).

I owe a debt of gratitude to all my peers who took the time to review selected parts of the manuscript: D. Sherman, University of Bristol; D.G. Pearson, Durham University; Hilary Downes, University College (London); Harry McSween, Jr., University of Tennessee (Knoxville); and Harold Rowe, University of Texas (Arlington). Their constructive critiques resulted in significant improvement of the book, but I take full responsibility for all shortcomings of the book. Thanks are also due to many of my colleagues in the Department of Earth and Planetary Sciences, University of Tennessee – Christopher Fedo, Robert Hatcher, Linda Kah, Theodore Labotka, Colin Sumrall, and Lawrence Taylor – who in course of many discussions patiently shared with me their expertise on selected topics covered in the book. I am particularly grateful to Harry McSween for many prolonged discussions regarding the origin and early history of the Earth, and to Ian Francis, Senior Commissioning Editor, Earth and Environmental Sciences, Wiley-Blackwell Publishers, for his sustained encouragement throughout this endeavor. I am also indebted to the many publishers and individuals who have kindly allowed me to include copyrighted figures in the book. Lastly, and most importantly, this book could not have been completed without the patience of my wife, children, and grandchildren, who had to endure my preoccupation with the book for long stretches.

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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

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.

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 (Mpa), a rather cumbersome number to use. Most geochemists prefer to use bar as the unit of pressure, which can easily be

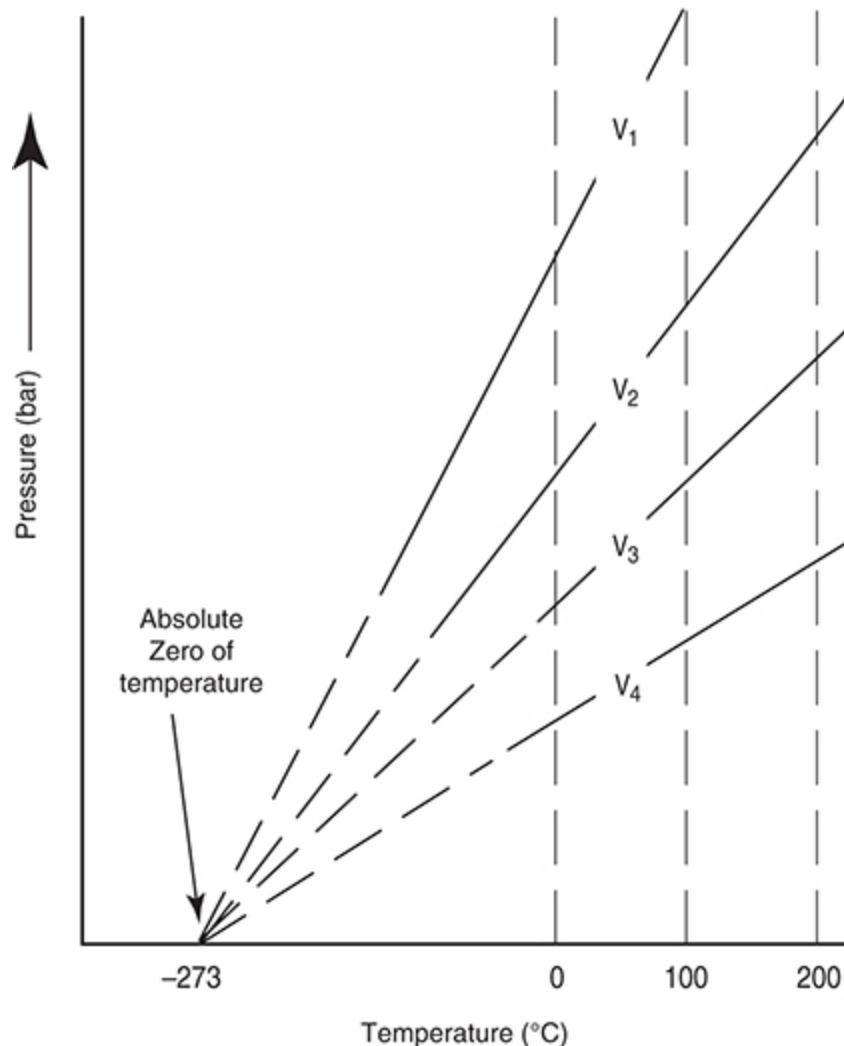
converted into pascals ($1 \text{ bar} = 10^5 \text{ pascals}$ or 0.1 MPa) and which is close enough to pressure expressed in atmosphere ($1 \text{ bar} = 0.987 \text{ atm}$) for the difference to be ignored in most cases without introducing significant error. A similar problem exists in the use of the 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*

for H₂O (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:

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

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.



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](#)).

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.

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):

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

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

(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 $45/(49 \times 2) = 0.46$.

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 ($t = 4.55$ 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 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.

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).

