

# 1 Introduction and Overview

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Geochemists study chemical processes on and in the Earth as well as meteorites and samples from the other planetary bodies. In geochemical kinetics, chemical kinetic principles are applied to Earth sciences. Many theories in geochemical kinetics are from chemical kinetics, but the unique nature of Earth sciences, especially the inference of geological history, requires development of theories that are specific for geochemical kinetics.

Although classical *thermodynamics* provides a powerful tool for understanding the equilibrium state (end point) of a chemical process, it is *kinetics* that elucidates the timescale, steps, and paths to approach the equilibrium state. For example, thermodynamics tells us that diamond is not stable at room temperature and pressure, but kinetics and experience tell us that diamond persists at room temperature and pressure for billions of years. Transition from diamond to graphite or oxidation of diamond to carbon dioxide is extremely slow at room temperature and pressure. Another example is the existence of light elements. According to thermodynamics, if the universe were to reach equilibrium, there would be no light elements such as H, C, and O (and hence no life) because they should react to form Fe. The fact is (fortunately) that an equilibrium state would never be reached. Hence, one may say that thermodynamics determines the direction and equilibrium state of a reaction or process, but only at the mercy of kinetics. Thermodynamics is sometimes a good approximation, but kinetics rules in many cases. Therefore, it is critical to understand kinetics.

Chemists have been studying kinetics for a long time, but early geochemists mostly applied thermodynamics to terrestrial chemical processes because long geologic times (and high temperatures in many cases) presumably would allow

many reactions to reach equilibrium. However, it became evident that many processes could not be understood in terms of equilibrium thermodynamics alone. The need to apply kinetics in geochemistry led to numerous papers, monographs, and books. The Carnegie Institution of Washington sponsored a conference on geochemical transport and kinetics (Hofmann et al., 1974). The Mineralogical Society of America organized a short course on the kinetics of geochemical processes (Lasaga and Kirkpatrick, 1981). The series *Advances in Physical Geochemistry* covers many aspects of kinetics, especially in Volumes 2, 3, 4, and 8 (Saxena, 1982, 1983; Thompson and Rubie, 1985; Ganguly, 1991). The early diagenesis books by Berner (1980) and Boudreau (1997) included much kinetics. Lasaga (1998) published a tome on *Kinetic Theory in the Earth Sciences*. Many chemical kinetics textbooks are also available.

Chemical reactions may be classified by the number of phases involved in the reaction. If the reaction takes place inside one single phase, it is said to be a *homogeneous reaction*. Otherwise, it is a *heterogeneous reaction*. For homogeneous reactions, there are no surface effects and *mass transfer* usually does not play a role. Heterogeneous reactions, on the other hand, often involve surface effects, formation of new phases (*nucleation*), and mass transfer (*diffusion* and *convection*). Hence, the theories for the kinetics of homogeneous and heterogeneous reactions are different and are treated in different sections.

All geochemical methods and tools (such as the isochron method in geochronology) inferring time and rate are based on kinetics. Applications of geochemical kinetics to geology may be classified into two categories. One category may be referred to as *forward problems*, in which one starts with the initial conditions and tries to understand the subsequent reaction progress. This is an important goal to geochemists who aim to understand the kinetics of geological processes, such as reaction kinetics in aqueous solutions, the kinetics of magma crystallization, bubble growth during volcanic eruptions, weathering rate and mechanisms, and metamorphic reaction rate and mechanisms. The second category of applications may be called *inverse problems*, in which one starts from the end products (rocks) and tries to infer the past. This second category is unique in geology, and is particularly important to geochemists who aim to infer the age, thermal history, and initial conditions from the rock assemblage (that is, treating a rock as a history book).

One specific application in the first category is to estimate the time required for a reaction to reach equilibrium in nature. If equilibrium is assumed in modeling a geochemical process, it is important to know the limitations (e.g., the timescale for the assumption to be valid). For example, in acid–base reactions, the reaction is rapid and the timescale to reach equilibrium is much less than one second. Hence, pH measurement of natural waters is usually meaningful and can be used to estimate species concentrations of various pH-related reactions. However, in redox reactions, the reaction is often slow and it may take days or years to reach equilibrium. Therefore, pe (or Eh) measurement of natural waters may not mean

much, and each half-reaction may result in a distinct  $p_e$  value (negative of base-10 logarithm of electron activity).

Another application in the first category is for experimentalists investigating equilibrium processes (such as the determination of equilibrium constants) to evaluate whether equilibrium is reached. The experimental duration must be long enough to reach equilibrium. To estimate the required experimental duration to insure that equilibrium is reached, one needs to have a rough idea of the kinetics of the reaction to be studied. Or experiments of various durations can be conducted to evaluate the attainment of equilibrium.

A specific example of applications in the second category is the dating of rocks. Age determination is an inverse problem of radioactive decay, which is a first-order reaction (described later). Because radioactive decay follows a specific law relating concentration and time, and the decay rate is independent of temperature and pressure, the extent of decay is a measure of time passed since the radioactive element is entrapped in a crystal, hence its age. In addition to the age, the initial conditions (such as initial isotopic ratios) may also be inferred, which is another example of inverse problems.

A second example of applications in the second category is to estimate cooling history of a rock given the mineral assemblage with abundances and compositions. For example, the presence of glass in a rock or the retention of a high-temperature polymorph such as sanidine in a rock means that it cooled down rapidly. With quantitative understanding of the rate of chemical reactions or diffusion, it is possible to quantify the cooling rate, as well as the rate for a subducted slab to return to the surface, by studying the mineral assemblage, such as (i) the core and rim composition as well as the compositional gradient of each mineral, and (ii) the intracrystalline elemental distribution.

This chapter provides a general discussion of kinetics versus thermodynamics, chemical kinetics versus geochemical kinetics, and an overview of the basics of various kinetic processes and applications. Subsequent chapters will provide in-depth development of theories and applications of specific subjects. The purpose of the overview in this chapter is to provide the big picture of the whole field before in-depth exploration of the topics. Furthermore, this chapter is a stand-alone chapter that may be used in a general geochemistry course to introduce kinetics to students.

## 1.1 Thermodynamics versus Kinetics

Thermodynamics is a powerful tool. It states that at constant temperature and pressure, the system always moves to a state of lower *Gibbs free energy*. Equilibrium is achieved when the lowest Gibbs free energy of the system is attained. Given an initial state, thermodynamics can predict the direction of a chemical reaction, and the maximum extent of the reaction. Macroscopically, reactions

opposite to the predicted direction cannot happen spontaneously. Hence, thermodynamics is widely applied to predict yields in chemical industry and to understand reactions in nature. For example, at 25°C, if the pH of an aqueous solution is 5 (meaning that  $H^+$  activity is  $10^{-5}$  M), we know that the  $OH^-$  activity of the solution must be  $10^{-9}$  M.

However, thermodynamics is not enough. It cannot predict the time to reach equilibrium, or even whether the equilibrium state will ever be reached. Some equilibria may never be reached (and we also hope so). For example, if the universe reached equilibrium, there would be no light elements such as hydrogen, helium, lithium, beryllium, and boron, because they would react to form Fe. It is the high activation energy for these reactions that prevents them from happening. Some equilibria take such a long time that practically it can be said that the reaction is not happening, such as homogenization of a zoned crystal at room temperature. Other equilibria take place slowly, such as weathering of rocks under surface conditions. Some equilibria are rapidly reached, such as acid–base reactions in water.

Consider, for another example, a diamond ring. Thermodynamically the diamond crystal is unstable, and should convert to graphite, or react with oxygen in air to become carbon dioxide. Graphite in itself is also unstable in air and should burn in air to become carbon dioxide. Nonetheless, kinetically the reaction is very slow because of the strong C–C bonds in diamond and graphite. Breaking these bonds requires high *activation energy* (this concept is explored in detail later) and does not happen at room temperature, except in the presence of a strong oxidant. Or one could also say that the reaction is extremely slow at room temperatures, and, for practical purposes, it can be regarded that “a diamond is forever.”

A beauty of thermodynamics is that it is not concerned with the detailed processes, and its predictions are independent of such details. Thermodynamics predicts the extent of a reaction when equilibrium is reached, but it does not address or care about reaction mechanism, i.e., how the reaction proceeds. For example, thermodynamics predicts that falling tree leaves would decompose and, in the presence of air, eventually end up as mostly  $CO_2$  and  $H_2O$ . The decomposition could proceed under dry conditions, or under wet conditions, or in the presence of bacteria, or in a pile of tree leaves that might lead to fire. The reaction paths and kinetics would be very different under these various conditions. Because thermodynamics does not deal with the processes of reactions, it cannot provide insight on reaction mechanisms.

In a similar manner, in thermodynamics, often it is not necessary to know the detailed or actual species of a component. For example, in thermodynamic treatment, dissolved  $CO_2$  in water is often treated as  $H_2CO_3(aq)$ , although most of the dissolved  $CO_2(aq)$  is in the form of molecular  $CO_2(aq)$  and only about 0.2–0.3% of dissolved  $CO_2(aq)$  is in the form of  $H_2CO_3(aq)$ . Another example is for dissolved  $SiO_2$  in water. In thermodynamic treatment,  $SiO_2(aq)$  is commonly

used for  $\text{H}_4\text{SiO}_4(\text{aq})$  or other species of dissolved  $\text{SiO}_2(\text{aq})$ . As long as consistency is maintained, assuming the wrong species would not cause error in thermodynamic treatment. However, in kinetics, knowing speciation is crucial.

An equilibrium Earth would be extremely boring (e.g., there would be no life, no oxygen in the air, no plate tectonics, etc). Disequilibrium is what makes the world so diverse and interesting. Hence, kinetics may also be regarded, especially by kineticists, as our friends. Without kinetic barriers, there would be no geochemists to study kinetics or science because all human beings, and in fact all life forms, “should burst into flames!” Some geochemists have a more positive attitude and understand that “geochemists never die, but merely reach equilibrium” (Lasaga, 1998).

The goals of geochemical kinetics are to understand (i) the reaction rate and how long it would take to reach equilibrium for a specific reaction or system, (ii) atomistic mechanisms for a reaction to proceed, and (iii) the history (such as age and cooling rate) of rocks based on reaction extents.

The kinetics of a reaction is inherently much more difficult to investigate than the equilibrium state of the reaction. The first step in studying the kinetics of a reaction is to know and stoichiometrically balance the reaction, and to understand the thermodynamics. If the reaction cannot even be written down and balanced, then it's premature to study the kinetics (this may sound trivial but there are authors who try to model the kinetics of undefined reactions). Equilibrium and kinetics can be studied together. For example, one may carry out a series of experiments at different durations, and examine how the reaction reaches equilibrium. This time series would provide information on both equilibrium and kinetics of the reaction. In addition to the macroscopic (or thermodynamic) understanding, reaction kinetics also requires an understanding at the molecular or atomic level. A reaction may be accomplished by several steps or through several paths. It may involve intermediate species that are neither reactants nor products. Catalysts can change reaction path and, hence, reaction rates. The equilibrium state is independent of these steps, paths, intermediate species, and/or catalysts, but the reaction rate may depend on all these. Hence, a seemingly simple reaction may have complicated reaction rate laws.

Understanding the kinetics of reactions can be rewarding. First, knowing reaction rates allows prediction of how quickly reactions reach equilibrium. To a thermodynamicist, this is the most important application. For example, when a reaction is used as a *geothermometer*, it is important to master the kinetics of the reaction so that the limitations and the meaning of the inferred temperature in these applications are understood. Second, since the rate of a reaction depends on the detailed path or mechanism of the reaction, insight into the reaction at the molecular level can be gained. Third, quantification of reaction rates and their dependence or lack of dependence on temperature allows geochemists to infer the age, thermal history, and initial conditions of the system. This class of applications is probably the most important to Earth scientists.

## 1.2 Chemical Kinetics versus Geochemical Kinetics

The scope of kinetics includes (i) the rates and mechanisms of homogeneous chemical reactions (reactions that occur in one single phase, such as ionic and molecular reactions in aqueous solutions, radioactive decay, many reactions in silicate melts, and cation distribution reactions in minerals), (ii) diffusion (owing to random motion of particles) and convection (both are parts of mass transport; diffusion is often referred to as kinetics and convection and other motions are often referred to as dynamics), and (iii) the kinetics of phase transformations and heterogeneous reactions (including nucleation, crystal growth, crystal dissolution, and bubble growth).

Geochemical kinetics can be viewed as applications of chemical kinetics to Earth sciences. Geochemists have borrowed many theories and concepts from chemists. Although fundamentally similar to chemical kinetics, geochemical kinetics distinguishes itself from chemical kinetics in at least the following ways:

(1) Chemists mostly try to understand the processes that would happen under a given set of conditions (such as temperature, pressure, and initial conditions), which may be termed *forward problems*. Geochemists are interested in the forward problems, but also *inverse problems* from the product (usually a rock) to infer the initial conditions and history, including the age, the peak temperature and pressure, the temperature–pressure history, and the initial isotopic ratio or mineral composition. If the extent of a reaction depends on time but not on temperature and pressure (such as radioactive decay and growth), then the reaction can be used to infer the age (geochronology). If the extent of a reaction depends on time and temperature (such as a chemical reaction, or the diffusive loss of a radiogenic daughter), then the reaction may be used as a geothermometer and cooling rate indicator (geospeedometer). If the extent of a reaction depends on pressure, then that reaction may be used as a geobarometer. (Because chemical reaction rate usually does not depend strongly on pressure, few decompression rate indicators are developed.) In other words, the inverse problems in geochemical kinetics include geochronology based on radioactive decay and radiogenic growth, thermochronology based on radiogenic growth and diffusive loss, and geospeedometry based on temperature-dependent reaction rates.

(2) Chemists mostly deal with kinetics under isothermal conditions. However, due to the nature of many geological problems, geochemists often must deal with kinetics of reactions and diffusion during cooling. Furthermore, the inverse problems (thermochronology and geospeedometry) also require an understanding of kinetic problems during cooling. The investigation of reactions and diffusion during cooling led to kinetic concepts such as apparent equilibrium temperature, closure temperature, and apparent age, which are unique to geochemistry. Dealing with kinetics under cooling also requires more complicated mathematics and numerical simulations.

(3) The goal of chemical kinetics is to understand principles using laboratory and theoretical tools. Hence, chemists often use the simplest reactions for experimental and theoretical work to elucidate the principles. Geochemists investigate natural kinetic processes in the atmosphere, rivers, oceans, weathering surfaces, magma, and rocks, as well as processes crossing the boundaries of various systems, and, hence, must deal with complicated reactions and processes. Although experimental studies are often necessary, experimental work is motivated by and designed to address a geological problem. Because geological problems are complicated, such applications often involve approximations and assumptions so that a simple model of the complicated system is developed. One has to understand kinetics as well as the geological problem to make the right approximations and assumptions.

(4) Chemical kinetic textbooks mainly deal with kinetics of homogeneous reactions to elucidate the principles of kinetics. Some chemical kinetics texts are entirely on homogeneous reactions. Because most geochemical reactions are heterogeneous reactions and because geochemists need to treat realistic reactions in nature, geochemical kinetic textbooks must treat heterogeneous reactions more thoroughly.

In short, geochemical kineticists do not have the luxury of chemical kineticists and must deal with real-world and more complicated systems. Geochemists developed the theories and concepts to deal with inverse kinetic problems, reaction kinetics during cooling, and other geologically relevant questions. These new scopes, especially the inverse theories, reflect the special need of Earth sciences, and make geochemical kinetics much more than merely chemical kinetic theories applied to Earth sciences.

### 1.3 Kinetics of Homogeneous Reactions

A homogeneous reaction is a reaction inside a single phase, that is, all reactants and products as well as intermediate species involved in the reaction are part of a single phase. The phase itself may be homogeneous, but does not have to be so. For example, there may be concentration gradients in the phase. Homogeneous reactions are defined relative to heterogeneous reactions, meaning reactions involving two or more phases. The following are some examples of homogeneous reactions, and how to distinguish homogeneous versus heterogeneous reactions.

(1) *Radioactive decay*. Two examples are



Even though the above reactions are at the level of nuclei, in the notation adopted in this book, each nuclide is treated as a neutral atomic species including

both the nucleus and the full number of electrons. Hence, electrons that eventually would become part of the atom do not appear separately in the products or reactants. Furthermore, emission of  $\gamma$ -rays or other forms of energy does not appear because it is a form of energy, and it is understood that a reaction will always be accompanied by energy changes.

In the above radioactive decays, a parent nuclide shakes itself to become another nuclide or two nuclides. A unidirectional arrow indicates that there is no reverse reaction; or if there is any reverse reaction, it is not considered. He produced by the homogeneous reaction (radioactive decay) may subsequently escape into another phase, which would be another kinetic process.

(2) *Other nuclear reactions.* The Sun is powered by *nuclear hydrogen burning* in the Sun's core:



This might be said to be the most important reaction in the solar system because energy from this reaction powers the Sun, lights up the planets, warms the Earth's surface, and nourishes life on the Earth. This is a complicated reaction, with several pathways to accomplish it, and each pathway involving several steps.

(3) *Chemical reactions in the gas phase.* One reaction is the *chemical hydrogen burning*:



Another reaction is ozone decomposition reaction:



This reaction and the ozone production reaction determine the ozone level in the stratosphere. Note that in geochemistry, for accurate notation, a reaction species is in general followed by the phase the species is in. The advantage of this notation will be clear later when multiple phases are involved.

Another example of gas-phase reaction is the oxidation of the toxic gas CO (released when there is incomplete burning of natural gas or coal) by oxygen in air:



The two-directional arrow  $\rightleftharpoons$  indicates that there is reverse reaction. The final product will satisfy the equilibrium constant  $K_6 = f_{\text{CO}_2}^2 / [f_{\text{CO}}^2 f_{\text{O}_2}] = \exp(-20.72 + 67,997/T)$  (obtained using data in Robie and Hemingway, 1995), where  $T$  is temperature in kelvins and the subscript 6 means that it is for Reaction 1-6. At room temperature and pressure, the equilibrium constant is large (about  $10^{45}$ ), and, hence, the reaction goes all the way to  $\text{CO}_2$ . At higher temperatures, the equilibrium constant decreases. At higher pressures, the equilibrium constant increases. This reaction is important for experimental geochemists because they

vary the ratio of CO gas (often the minor gas) to CO<sub>2</sub> gas (often the major gas) in a gas-mixing furnace to generate the desired  $f_{O_2}$  at high temperatures, with  $f_{O_2} = \frac{CO_2}{CO_2 + CO} = \frac{1}{1 + K_6}$ . Reversible reactions such as Reaction 1-6 may be viewed as two reactions moving in opposite directions. The forward reaction goes from the left-hand side to the right-hand side, and will be referred to as Reaction 1-6f. The backward reaction goes from the right-hand side to the left-hand side, and will be referred to as Reaction 1-6b. That is, Reactions 1-6f and 1-6b are as follows:



(4) *Chemical reactions in an aqueous solution.* One example is



CO<sub>2</sub>(aq) means dissolved CO<sub>2</sub> in the aqueous solution. The following reaction



is different and is not a homogeneous reaction because CO<sub>2</sub> is in the gas phase. By comparing Reactions 1-7 and 1-8, the importance of denoting the phases is clear.

An aqueous solution contains many ionic species and one can write numerous reactions in it. A fundamental chemical reaction in all aqueous solutions is the ionization of water:

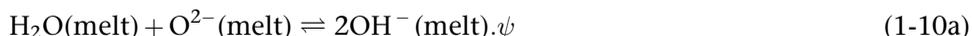


The above reaction can also be written as  $H_2O(\text{aq}) \rightleftharpoons H^+(\text{aq}) + OH^-(\text{aq})$ , depending on how one views the proton species in water. More aqueous reactions can be found in Table 1-1a.

(5) *Chemical reactions in silicate melts.* One example is



In the above reaction, H<sub>2</sub>O(melt) is molecular H<sub>2</sub>O dissolved in the melt, O(melt) is a bridging oxygen in the melt, and OH(melt) is a hydroxyl group in the melt. The charges are ignored but the oxidation state for each species is understood in the context. The above reaction may also be written as



Chemists may prefer the notation of Reaction 1-10a, and cry over the notation of Reaction 1-10 because the charges are not indicated. However, in geochemistry, often O<sup>2-</sup>(melt) is used to indicate a free oxygen ion (i.e., oxygen ion not bonded to Si<sup>4+</sup> ion) in melt, O<sup>-</sup>(melt) is used to indicate nonbridging oxygen (oxygen ion bonded to only one Si<sup>4+</sup> ion), and O(melt) is used to indicate bridging oxygen

(oxygen ion in between two  $\text{Si}^{4+}$  ions, as Si–O–Si). Reaction 1-10 may also be written more specifically as

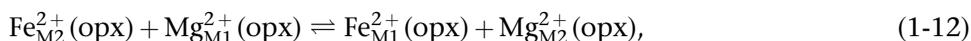


Another homogeneous reaction in silicate melt is the silicon speciation reaction:



where  $\text{Q}_n$  means that a  $\text{SiO}_4^{4-}$  tetrahedral unit in which  $n$  oxygen anions are bridging oxygens.

(6) *Chemical reactions in a mineral.* One example is the Mg–Fe order–disorder reaction in an orthopyroxene (opx) crystal:

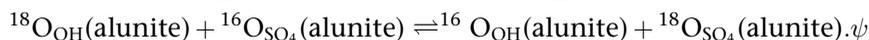
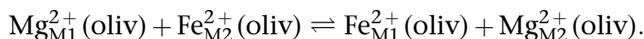
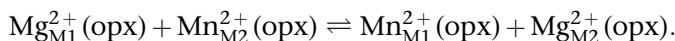


where M1 and M2 are two octahedral crystalline sites with slightly different size and symmetry, and  $\text{Fe}_{\text{M2}}^{2+}(\text{opx})$  means  $\text{Fe}^{2+}$  in M2 site of opx. The  $\text{Mg}^{2+}$  prefers the M1 site and  $\text{Fe}^{2+}$  prefers the M2 site. Hence, the forward reaction is the disordering reaction, and the backward reaction is the ordering reaction. Another way to write the above chemical reaction is



where  $\text{FeMgSi}_2\text{O}_6(\text{opx})$  means that Fe is in M2 site (that is, the first element in the formula is in M2 site) and Mg is in M1 site.

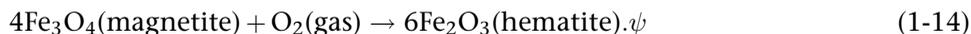
There are many other order–disorder reactions in minerals, for example,



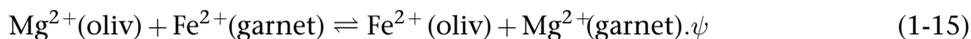
(7) *Heterogeneous reactions.* Many reactions encountered in geology are not homogeneous reactions, but are heterogeneous reactions. For example, phase transition from diamond to graphite is not a homogeneous reaction but a heterogeneous reaction:



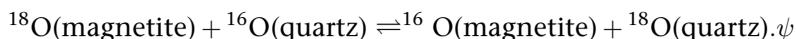
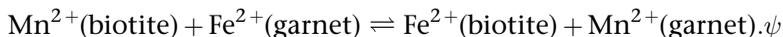
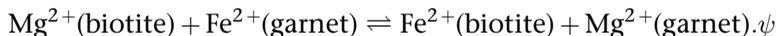
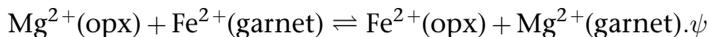
Oxidation of magnetite to hematite is also a heterogeneous reaction:



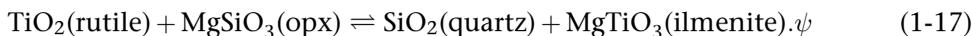
Fe–Mg exchange between two minerals is another heterogeneous reaction:



There are many other exchange reactions between two minerals, for example,



Two more heterogeneous reactions are as follows:



The dissolution of a mineral in water or in a silicate melt is also a heterogeneous reaction. Heterogeneous reactions will be discussed separately from homogeneous reactions.

For the kinetics of a reaction, it is critical to know the rough time to reach equilibrium. Often the term “mean reaction time,” or “reaction timescale,” or “relaxation timescale” is used. These terms all mean the same, the time it takes for the reactant concentration to change from the initial value to  $1/e$  toward the final (equilibrium) value. For unidirectional reactions, half-life is often used to characterize the time to reach the final state, and it means the time for the reactant concentration to decrease to half of the initial value. For some reactions or processes, these times are short, meaning that the equilibrium state is easy to reach. Examples of rapid reactions include  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$  (timescale  $\leq 67 \mu\text{s}$  at 298 K), or the decay of  $^6\text{He}$  (half-life 0.8 s) to  $^6\text{Li}$ . For some reactions or processes, the equilibrium state takes a very long time to reach. For example,  $^{26}\text{Al}$  decays to  $^{26}\text{Mg}$  with a half-life of 730,000 years, and  $^{144}\text{Nd}$  decays to  $^{140}\text{Ce}$  with a half-life of 2100 trillion years. Converting  $^1\text{H}$  to  $^4\text{He}$  does not happen at all at room temperature, but can occur at extreme temperatures in the core of the Sun.

### 1.3.1 Reaction progress parameter $\xi$

Consider the forward reaction of Reaction 1-10f,  $\text{H}_2\text{O}(\text{melt}) + \text{O}(\text{melt}) \rightarrow 2\text{OH}(\text{melt})$ . To describe the reaction rate, one can use the concentration of any of the species involved in the reaction, such as  $d[\text{H}_2\text{O}]/dt$ ,  $d[\text{O}]/dt$ , and  $d[\text{OH}]/dt$ , where brackets mean concentration in the melt (e.g., mol/L). Because in this case the reaction is going to the right-hand side,  $d[\text{OH}]/dt$  is positive, and  $d[\text{H}_2\text{O}]/dt$  and  $d[\text{O}]/dt$  are negative. Furthermore, the absolute value of  $d[\text{OH}]/dt$  and that of  $d[\text{H}_2\text{O}]/dt$  differ by a factor of 2, because one mole of  $\text{H}_2\text{O}$  reacts with one mole of network O to form two moles of OH in the melt. In general, we can write that  $d[\text{OH}]/dt = -2d[\text{H}_2\text{O}]/dt = -2d[\text{O}]/dt$ . In other words,  $(\frac{1}{2}) d[\text{OH}]/dt = -d[\text{H}_2\text{O}]/dt = -d[\text{O}]/dt$ .

Without a standard definition of reaction progress, one would have to be specific about which species is used in describing the reaction rate. To standardize

the description and to avoid confusion, a standard reaction progress parameter  $\xi$  is defined as

$$\frac{d\xi}{dt} \equiv \frac{d[\text{OH}]}{2dt} \equiv \frac{-d[\text{H}_2\text{O}]}{dt} \equiv \frac{-d[\text{O}]}{dt}, \quad (1-18)$$

$$\xi|_{t=0} = 0, \quad (1-19)$$

where the stoichiometric coefficients 2 and 1 are in the denominator, and a negative sign accompanies the reaction rate of the reactants. By this definition,  $\xi$  is positive if the reaction goes to the right-hand side. If the reaction goes to the left-hand side, the above treatment also works, but  $\xi$  would be negative. That is, if  $\xi$  is found to be negative, or  $d\xi/dt$  is found to be negative, then the reaction goes to the left-hand side. The species concentrations are related to  $\xi$  as follows:

$$[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_0 - \xi, \quad (1-20)$$

$$[\text{O}] = [\text{O}]_0 - \xi, \quad (1-21)$$

$$[\text{OH}] = [\text{OH}]_0 + 2\xi, \quad (1-22)$$

where the subscript "0" means at the initial time. Hence, after solving for  $\xi$ , the concentration evolution of all species can be obtained.

### 1.3.2 Elementary versus overall reactions

If a reaction is a one-step reaction, that is, if it occurs on the molecular level as it is written, then the reaction is called an *elementary reaction*. In an elementary reaction, either the particles collide to produce the product, or a single particle shakes itself to become something different. For example, Reactions 1-1 and 1-2 occur at the atomic scale as they are written. That is, a parent nuclide shakes itself to become a more stable daughter nuclide (or two daughter nuclides).

If a reaction is not an elementary reaction, i.e., if the reaction does not occur at the molecular level as it is written, then it is called an *overall reaction*. An overall reaction may be accomplished by two or more steps or paths and/or with participation of intermediate species. For example, nuclear hydrogen burning Reaction 1-3,  $4^1\text{H} \rightarrow ^4\text{He}$ , is an overall reaction, not an elementary reaction. There are several paths to accomplish the reaction, with every path still an overall reaction accomplished by three or more steps. One path is called a *PP I chain* and involves the following steps:



Each of the above three reactions is an elementary reaction. During the first step, two  $^1\text{H}$  nuclides collide to form one  $^2\text{H}$  (in the process, one proton plus one electron become a neutron). In the second step, one  $^2\text{H}$  collides with  $^1\text{H}$  to form

one  ${}^3\text{He}$ . In the third step, two  ${}^3\text{He}$  collide to form one  ${}^4\text{He}$  and two  ${}^1\text{H}$ .  ${}^2\text{H}$  and  ${}^3\text{He}$  are intermediate species, which are produced and consumed. The net result is  $4{}^1\text{H} \rightarrow {}^4\text{He}$  (which can be obtained by 2 times the first step, plus 2 times the second step, plus the third step), releasing 26.73 MeV energy. In the presence of carbon, a second path to accomplish nuclear hydrogen burning is through the *CNO cycle* (carbon–nitrogen–oxygen cycle). This cycle involves the following steps:



The net result by adding up all the above reactions is four  ${}^1\text{H}$  reacting to form a  ${}^4\text{He}$ . The  ${}^{12}\text{C}$  is first used for reaction and then returned unchanged. Hence,  ${}^{12}\text{C}$  acts as a *catalyst*, a substance that helps a reaction to take place without itself being consumed.

Note that in the above notation, nuclear reactions are written in the same format as chemical reactions. Physicists would include extra information in writing these reactions such as energy released or required, e.g., as  $\gamma$ -particles or neutrinos. If needed, energy information is given separately as shown above. (Sometimes, the energy required is explicitly included to highlight that the reaction would not be possible without energy input, such as photochemical reactions.) Furthermore, because physicists treat  ${}^1\text{H}$  as the nucleus of a hydrogen atom (i.e., without the electron), they also include the electron or positron released or required. In this book,  ${}^1\text{H}$  means a hydrogen atom (i.e., including the electron). Hence, electrons (which are part of an atom) and positrons (which would annihilate electrons) are not needed.

Reaction 1-5,  $2\text{O}_3(\text{gas}) \rightarrow 3\text{O}_2(\text{gas})$ , is an overall reaction. Both Reactions 1-6f and 1-6b,  $2\text{CO}(\text{gas}) + \text{O}_2(\text{gas}) \rightleftharpoons 2\text{CO}_2(\text{gas})$ , are also overall reactions. Both Reactions 1-9f and 1-9b are elementary reactions. Whether a reaction is an elementary reaction or an overall reaction can only be determined experimentally, and cannot be determined by simply looking at the reaction. Many simple gas-phase reactions in the atmosphere involve intermediate radicals and, hence, are complicated overall reactions.

### 1.3.3 Molecularity of a reaction

The *molecularity* of an elementary reaction refers to the number of particles in the reactants (left-hand side). If the molecularity is 1, the elementary reaction is said

to be unimolecular. If the molecularity is 2, the elementary reaction is said to be bimolecular. If the molecularity is 3, the elementary reaction is said to be trimolecular (or termolecular). No example is known for higher molecularities because it is basically impossible for 4 particles to collide simultaneously.

For example, the molecularity is 1 for radioactive decay reactions (1-1) and (1-2). The molecularity of the forward reaction does not have to be the same as that of the backward reaction.

Although elementary reactions and overall reactions can only be distinguished in the laboratory, a few simple guidelines can be used to guess. If the number of particles of the reaction is 4 or more, it is an overall reaction. If the number of particles is 3, then most likely the reaction is an overall reaction because there are only a limited number of trimolecular reactions. Almost all elementary reactions have molecularities of 1 or 2. However, the reverse is not true. For example, Reaction 1-5,  $2\text{O}_3(\text{gas}) \rightarrow 3\text{O}_2(\text{gas})$ , has a “molecularity” of 2 but is not an elementary reaction.

In thermodynamics, a reaction can be multiplied by a constant factor without changing the meaning of the reaction. However, in kinetics, an elementary reaction is written according to how the reaction proceeds, and cannot be multiplied by a constant. For example, if Reaction 1-7,  $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$ , is multiplied by 2, thermodynamic treatment stays the same, but kinetically the forward reaction would have a molecularity of 4, and is different from Reaction 1-7f.

### 1.3.4 Reaction rate law, rate constant, and order of a reaction

The reaction rate law is an empirical relation on how the reaction rate depends on the various species concentrations. For example, for the following reaction,



the experimentally determined reaction rate law is

$$d\xi/dt = k_{32}[\text{H}_2][\text{I}_2], \quad (1-33)$$

where  $k_{32}$  is a constant called the reaction rate constant or reaction rate coefficient. It depends on temperature as  $k_{32} = \exp(25.99 - 20,620/T) \text{ L mol}^{-1} \text{ s}^{-1}$  in the temperature range of 400–800 K (Baulch et al., 1981, p. 521; Kerr and Drew, 1987, p. 209).

For another reaction,



although it looks simple and similar to Reaction 1-32, the experimentally determined reaction rate law is very different and contains two constants ( $k_{34}$  and  $k'_{34}$ ):

$$\frac{d\xi}{dt} = \frac{k_{34}[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'_{34} \frac{[\text{HBr}]}{[\text{Br}_2]}}, \quad (1-35)$$

with  $k_{34} = \exp(30.24 - 20,883/T)$  and  $k'_{34} = (275/T) \exp(990/T)$  (Baulch et al., 1981, pp. 348–423).

Another simple reaction with a complicated reaction rate law is Reaction 1-5,  $2\text{O}_3(\text{gas}) \rightarrow 3\text{O}_2(\text{gas})$ , which may be accomplished thermally or by photochemical means. The reaction rate law for the thermal decomposition of ozone is  $d\xi/dt = k_5[\text{O}_3]^2/[\text{O}_2]$  when  $[\text{O}_2]$  is very high, and is  $d\xi/dt = k'_5[\text{O}_3]$  when  $[\text{O}_2]$  is low.

For an unknown reaction, the reaction law cannot be written down simply by looking at the reaction equation. Instead, experimental study must be carried out on how the reaction rate depends on the concentration of each species. For elementary reactions, the reaction rate follows the law of mass action and can be written by looking at the reaction. If the following reaction is an elementary reaction



then the reaction rate law (i.e., the law of mass action) is

$$d\xi/dt = k[\text{A}]^\alpha [\text{B}]^\beta, \quad (1-37)$$

where  $k$  is the reaction rate constant. The value of  $k$  depends on the specific reaction and on temperature. The overall order of the reaction is  $\alpha + \beta$ . The order of the reaction with respect to species A is  $\alpha$ . The order of the reaction with respect to species B is  $\beta$ . If the concentration of one species does not vary at all (e.g., concentration of  $\text{H}_2\text{O}$  in a dilute aqueous solution), the concentration raised to some power becomes part of the reaction rate constant. A reaction does not have to have an order. For example, Reaction 1-34 does not have an order.

In summary, when a reaction is said to be an elementary reaction, the reaction rate law has been experimentally investigated and found to follow the above rate law. One special case is single-step radioactive decay reactions, which are elementary reactions and do not require further experimental confirmation of the reaction rate law. For other reactions, no matter how simple the reaction may be, without experimental confirmation, one cannot say a priori that it is an elementary reaction and cannot write down the reaction rate law, as shown by the complicated reaction rate law of Reaction 1-34. On the other hand, if the reaction rate law of Reaction 1-36 is found to be Equation 1-37, Reaction 1-36 may or may not be an elementary reaction. For example, Reaction 1-32 is not an elementary reaction even though the simple reaction law is consistent with an elementary reaction (Bamford and Tipper, 1972, p. 206).

The rate law for the radioactive decay of  $^{87}\text{Rb}$  (Reaction 1-1),  $^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$ , is

$$d\xi/dt = k_1 [^{87}\text{Rb}], \quad (1-38)$$

which is equivalent to the familiar expression of

$$d[{}^{87}\text{Rb}]/dt = -\lambda_{87}[{}^{87}\text{Rb}], \quad (1-39)$$

with  $k_1 = \lambda_{87}$ . Rate constants for radioactive decay are special in that they do not vary with temperature or pressure or chemical environment (an exception to this rule is found for decay by electron capture). The rate law for other radioactive decay systems can be written down similarly.

The rate law for Reaction 1-7f,  $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$ , follows that of an elementary reaction (but Lewis and Glaser (2003) presented a quantum mechanical study that suggests the reaction is not elementary):

$$d\xi/dt = k_{7f}[\text{CO}_2], \quad (1-40)$$

where  $[\text{CO}_2]$  is the concentration of dissolved  $\text{CO}_2$  in the aqueous solution, and  $k_{7f}$  is the forward reaction rate constant ( $k_{7b}$  will denote the backward reaction rate constant). The concentration of  $\text{H}_2\text{O}$  does not appear because it is a constant and is absorbed into  $k_{7f}$ . That is, Reaction 1-7f has a molecularity of 2 but an order of 1. Hence, even for elementary reactions, the molecularity of a reaction does not have to be the same as the order of the reaction. When the molecularity is not the same as the order of a reaction because the concentration of one or two species is kept constant either due to the concentration of the species is high or because the concentration of the species is buffered, the reaction order is also referred to as pseudo-order. Therefore, one may also say that Reaction 1-7f is a pseudo-first-order reaction. The rate law for the backward reaction (Reaction 1-7b) is

$$d\xi/dt = k_{7b}[\text{H}_2\text{CO}_3]. \psi \quad (1-41)$$

Elementary reaction  $2\text{H}_2\text{O}(\text{aq}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$  (Reaction 1-9f) is a zeroth-order reaction (or pseudo-zeroth-order reaction):

$$d\xi/dt = k_{9f}, \quad (1-42)$$

because  $[\text{H}_2\text{O}]^2$  is a constant absorbed into  $k_{9f}$ . This is another example in which the molecularity (2) is not the same as the order (0) of a reaction. Another pseudo-zeroth-order reaction is the decomposition of  $\text{PH}_3$  on hot tungsten at high pressures (which is a heterogeneous reaction but has a simple order);  $\text{PH}_3$  decomposes at a constant rate until its disappearance.

The backward reaction (Reaction 1-9b) is, on the other hand, a second-order reaction with the following rate law:

$$d\xi/dt = k_{9b}[\text{H}_3\text{O}^+][\text{OH}^-]. \psi \quad (1-43)$$

The units of the reaction rate constant depend on the order of reaction. The units can be determined by knowing that the left-hand side must have a unit

**Table 1-1a Reaction rate coefficients for some chemical reactions in aqueous solutions**

Reaction	<i>T</i> (K)	Order	<i>k<sub>f</sub></i>	<i>k<sub>b</sub></i>	<i>K</i>	Ref.
$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^{-}$	298	0; 2	$10^{-2.85}$	$10^{11.15}$	$10^{-14.00}$	1
$\text{D}_2\text{O} \rightleftharpoons \text{D}^+ + \text{OD}^{-}$	298	0; 2	$\sim 10^{-3.79}$	$10^{10.92}$	$\sim 10^{-14.71}$	2
$\text{H}_3\text{O}^+ + \text{NH}_3 \rightarrow \text{NH}_4^+ + \text{H}_2\text{O}$	293	2; 1	$10^{10.63}$	$10^{1.37}$	$10^{9.26}$	2
$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$	298	1; 1	0.043	15	$10^{-2.54}$	3
$\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3$	273	1; 1	0.002			4
$\text{H}_2\text{CO}_3 \rightleftharpoons \text{H}^+ + \text{HCO}_3^-$	298	1; 2	$10^{6.9}$	$10^{10.67}$	$10^{-3.77}$	3, 5
$\text{HCO}_3^- \rightleftharpoons \text{CO}_2 + \text{OH}^{-}$	298	1; 2	$10^{-4.00}$	$10^{3.65}$	$10^{-7.65}$	3, 5
$\text{HCO}_3^- \rightleftharpoons \text{H}^+ + \text{CO}_3^{2-}$	298	1; 2			$10^{-10.33}$	5
$\text{HCO}_3^- + \text{OH}^- \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O}$	293	2; 1	$\sim 10^{9.8}$	$\sim 10^{6.1}$	$10^{3.67}$	3
$\text{H}_2\text{CO}_3 + \text{OH}^- \rightleftharpoons \text{HCO}_3^- + \text{H}_2\text{O}$	298	2; 1			$10^{10.23}$	
${}^{56}\text{Fe}^{2+} + {}^{55}\text{Fe}^{3+} \rightarrow$ ${}^{56}\text{Fe}^{3+} + {}^{55}\text{Fe}^{2+}$		2; 2	0.87	0.87	1.000x	4
${}^{56}\text{Fe}^{2+} + {}^{55}\text{FeCl}^{2+} \rightarrow$ ${}^{56}\text{FeCl}^{2+} + {}^{55}\text{Fe}^{2+}$		2; 2	5.4	5.4	1.000x	4

*Note.* Units of *k* and *K* are customary with concentrations in M and time in s. In the “Order” column the first number indicates the reaction order of the forward reaction, and the second number for the backward reaction.

*References.* 1, Laidler (1987, p. 39); 2, Pilling and Seakins (1995, p. 169); 3, Bamford and Tipper (1972, p. 284); 4, Lasaga and Kirkpatrick (1981, p. 23, p. 12); 5, Drever (1997, p. 42).

of concentration (in M) per unit time (in s), or  $\text{Ms}^{-1}$ . Hence, the units of *k* are  $\text{Ms}^{-1}$  for zeroth-order reactions,  $\text{s}^{-1}$  for first-order reactions,  $\text{M}^{-1}\text{s}^{-1}$  (or  $\text{L mol}^{-1}\text{s}^{-1}$ ) for second-order reactions, etc. For reactions in silicate melt or mineral, the concentration may be given by mole fractions that are dimensionless; then the unit of *k* would always be  $\text{s}^{-1}$ . Table 1-1 lists the values of *k* for some reactions.

For overall reactions, the reaction rate law cannot be written down by simply looking at the reaction, but has to be determined from experimental studies. (Whether a reaction is elementary must be determined experimentally, which means that reaction rate laws for all chemical reactions must be experimentally determined.) The reaction rate law may take complicated forms, which might mean that the order of the reaction is not defined.

**Table 1-1b Reaction rate coefficients for some gas-phase reactions**

Reaction	$T$ (K)	Order	$k_f$ (L mol <sup>-1</sup> s <sup>-1</sup> )	$k_b$ (L mol <sup>-1</sup> s <sup>-1</sup> )	Ref.
$H_2 + I_2 \rightleftharpoons 2HI$	400–800	2; 2	$\exp(26.00 - 20,620/T)$	$\exp(23.97 - 22,020/T)$	1
$NO + O_3 \rightarrow$ $NO_2 + O_2$	283–442	2	$\exp(21.67 - 1598/T)$		1
$NO_2 + O_3 \rightarrow$ $NO_3 + O_2$	230–360	2	$\exp(18.10 - 2450/T)$		1

*Note.* Notation as in Table 1-1a.

*References.* 1, Kerr and Drew (1987, pp. 209–212).

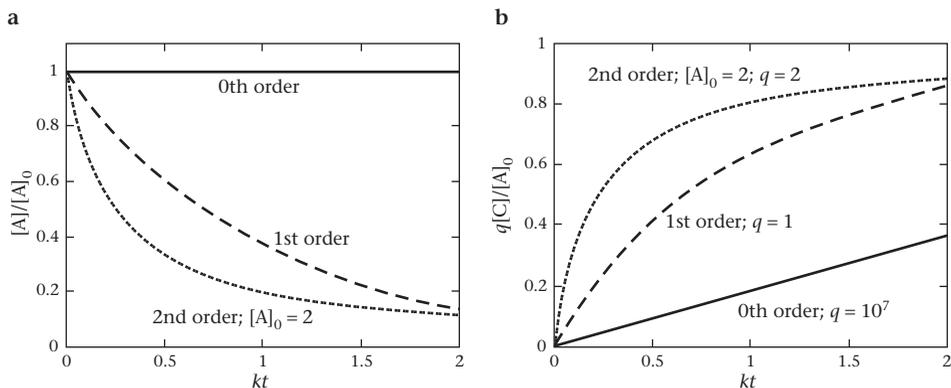
**Table 1-1c Reaction rate coefficients for some solid-phase reactions**

Reaction	$T$ (°C)	Order	$k_f$ (s <sup>-1</sup> )	$k_b$ (s <sup>-1</sup> )	$K$	Ref.
$H_2O(\text{ice}) \rightleftharpoons H^+(\text{ice}) + OH^-(\text{ice})$	263	0; 2		$10^{12.93}$		1
$Fe^{(M2)}(\text{opx}) + Mg^{(M1)}(\text{opx}) \rightleftharpoons$ $Fe^{(M1)}(\text{opx}) + Mg^{(M2)}(\text{opx})$	800	2, 2	$10^{-3.1}$	$10^{-2.4}$	0.189	2

*Note.* Notation as in Table 1-1a. Unit of concentration is mole fraction.

*References.* 1, Pilling and Seakins (1995, p. 169); 2, Data are for an opx with  $Fe/(Fe + Mg) = 0.011$  (Wang et al., 2005).

Strictly speaking, the concepts of elementary versus overall reactions, reaction rate law, and orders of a reaction apply only to homogeneous reactions. For heterogeneous reactions, the reaction rate is often discussed in terms of interface reaction and mass transfer. Hence, the order of a heterogeneous reaction, such as Reaction 1-8,  $CO_2(\text{gas}) + H_2O(\text{aq}) \rightarrow H_2CO_3(\text{aq})$ , or Reaction 1-14,  $4Fe_3O_4$  (magnetite) +  $O_2(\text{gas}) \rightarrow 6Fe_2O_3$  (hematite), or the dissolution of a mineral in water, may be meaningless. (For part of the heterogeneous reaction process, the interface reaction, it may be possible to define the order.) There are other ways to describe the overall rates of heterogeneous reactions. For example, if a mineral dissolves at a constant rate (which could be due to convection for a falling mineral in water or in a well-stirred solution, or due to slow interface reaction rate), it may be called a linear dissolution law, and should not be called a zeroth-order nor pseudo-zeroth-order reaction. If the dissolution distance is proportional



**Figure 1-1** Comparison of (a) reactant and (b) product concentration evolution for zeroth-order, first-order, and the first type of second-order reactions. The horizontal axis is  $kt$ , and the vertical axis is normalized reactant concentration in (a) and normalized product concentration multiplied by a parameter  $q$  so that the comparison can be more clearly seen in (b).

to square root of time, then it may be called a parabolic reaction law (not a  $\frac{1}{2}$ -order reaction), which usually implies diffusion control.

### 1.3.5 Concentration evolution for reactions of different orders

Only unidirectional elementary reactions are considered in this overview chapter because these reactions are relatively simple to treat. More complicated homogeneous reactions are discussed in Chapter 2.

#### 1.3.5.1 Zeroth-order reactions

An example of a zeroth-order reaction is Reaction 1-9f,  $2\text{H}_2\text{O}(\text{aq}) \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq})$ . For zeroth-order reactions, the concentrations of the reactants do not vary (which is why they are zeroth-order reactions). Use the reaction rate progress parameter  $\xi$ . Then

$$d\xi/dt = k_{9f} \cdot \psi \tag{1-44}$$

The unit of  $k_{9f}$  is  $\text{Ms}^{-1}$ . Integration of the above leads to  $\xi = k_{9f}t$ . That is,  $[\text{H}_3\text{O}^+] = [\text{H}_3\text{O}^+]_0 + k_{9f}t$ , and  $[\text{OH}^-] = [\text{OH}^-]_0 + k_{9f}t$ , where subscript 0 means the initial concentration. The concentration of the reactant stays the same,  $[\text{H}_2\text{O}] = [\text{H}_2\text{O}]_0 - 2k_{9f}t \approx [\text{H}_2\text{O}]_0$  (Figure 1-1). The concentration of each of the products increases linearly with time (Figure 1-1). Because of the backward reaction (Reaction 1-9b),  $\text{H}_3\text{O}^+(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow 2\text{H}_2\text{O}(\text{aq})$ , the linear concentration increase would not continue for long. The concentration evolution for this reversible reaction is discussed in Chapter 2.

### 1.3.5.2 First-order reactions

There are many examples of first-order reactions. The most often encountered in geochemistry is the radioactive decay of an unstable nuclide. For example, the rate law for the decay of  $^{147}\text{Sm}$  (Reaction 1-2) can be written as

$$d\xi/dt = k_2[^{147}\text{Sm}] = k_2([^{147}\text{Sm}]_0 - \xi). \quad (1-45)$$

That is,  $d\xi/[^{147}\text{Sm}]_0 - \xi = k_2 dt$ . The unit of  $k_2$  (i.e.,  $\lambda_{147}$ ) is  $\text{s}^{-1}$ . Remember that  $\xi|_{t=0} = 0$  by the definition of  $\xi$ . Integration leads to

$$\ln([^{147}\text{Sm}]_0 - \xi) - \ln[^{147}\text{Sm}]_0 = -k_2 \cdot t$$

That is,  $([^{147}\text{Sm}]_0 - \xi)/[^{147}\text{Sm}]_0 = \exp(-k_2 t)$ . Hence,

$$\xi = [^{147}\text{Sm}]_0 \{1 - \exp(-k_2 t)\}. \quad (1-46)$$

Written in terms of species concentrations,

$$[^{147}\text{Sm}] = [^{147}\text{Sm}]_0 - \xi = [^{147}\text{Sm}]_0 \exp(-k_2 t), \quad (1-47a)$$

$$[^{143}\text{Nd}] = [^{143}\text{Nd}]_0 + [^{147}\text{Sm}]_0 \{1 - \exp(-k_2 t)\}, \quad (1-47b)$$

$$[^{143}\text{Nd}] = [^{143}\text{Nd}]_0 + [^{147}\text{Sm}]_0 \{\exp(k_2 t) - 1\}, \quad (1-47c)$$

$$[^4\text{He}] = [^4\text{He}]_0 + \xi = [^4\text{He}]_0 + [^{147}\text{Sm}]_0 \{\exp(k_2 t) - 1\}. \quad (1-47d)$$

The concentration of the radioactive nuclide (reactant, such as  $^{147}\text{Sm}$ ) decreases exponentially, which is referred to as *radioactive decay*. The concentration of the daughter nuclides (products, including  $^{143}\text{Nd}$  and  $^4\text{He}$ ) grows, which is referred to as *radiogenic growth*. Note the difference between Equations 1-47b and 1-47c. In the former equation, the concentration of  $^{143}\text{Nd}$  at time  $t$  is expressed as a function of the initial  $^{147}\text{Sm}$  concentration. Hence, from the initial state, one can calculate how the  $^{143}\text{Nd}$  concentration would evolve. In the latter equation, the concentration of  $^{143}\text{Nd}$  at time  $t$  is expressed as a function of the  $^{147}\text{Sm}$  concentration also at time  $t$ . Let's now define time  $t$  as the present time. Then  $[^{143}\text{Nd}]$  is related to the present amount of  $^{147}\text{Sm}$ , the age (time since  $^{147}\text{Sm}$  and  $^{143}\text{Nd}$  were fractionated), and the initial amount of  $^{143}\text{Nd}$ . Therefore, Equation 1-47b represents forward calculation, and Equation 1-47c represents an *inverse problem* to obtain either the age, or the initial concentration, or both. Equation 1-47d assumes that there are no other  $\alpha$ -decay nuclides. However, U and Th are usually present in a rock or mineral, and their contribution to  $^4\text{He}$  usually dominates and must be added to Equation 1-47d.

Similarly, for Reaction 1-1, the concentration evolution with time can be written as

$$[^{87}\text{Rb}] = [^{87}\text{Rb}]_0 \exp(-k_1 t), \quad (1-48a)$$

$$[^{87}\text{Sr}] = [^{87}\text{Sr}]_0 + [^{87}\text{Rb}]_0\{1 - \exp(-k_1t)\}, \quad (1-48b)$$

$$[^{87}\text{Sr}] = [^{87}\text{Sr}]_0 + [^{87}\text{Rb}]\{\exp(k_1t) - 1\}, \quad (1-48c)$$

where  $k_1 = \lambda_{87}$ .

The most important geologic applications of radioactive decay and radiogenic growth are to determine the age of materials and events, in a branch of geochemistry called *geochronology*. Unlike the *forward problems* of calculating the concentration evolution with time given the initial conditions, in geochronology, the age and the initial conditions are inferred from what can be observed today. These inverse problems are especially important in geology. Equations of type Equation 1-47a to 1-47d are the basic equations for dating. For example, in  $^{14}\text{C}$  dating, an equation of type Equation 1-47a is used. For  $^{40}\text{K}$ - $^{40}\text{Ar}$  dating, it is often assumed that  $[^{40}\text{Ar}]_0$  is known (often assumed to be zero) and hence age can be determined.

To use Equation 1-47c for dating, one has to overcome the difficulty that there are two unknowns, the initial amount of  $^{143}\text{Nd}$  and the age. With this in mind, the most powerful method in dating, the *isochron method*, is derived. To obtain the *isochron* equation, one divides Equation 1-47c by the stable isotope of the product (such as  $^{144}\text{Nd}$ ):

$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right) = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_0 + \left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}}\right) (e^{k_2t} - 1), \quad (1-49)$$

where  $(^{143}\text{Nd}/^{144}\text{Nd})$ ,  $(^{147}\text{Sm}/^{144}\text{Nd})$ ,  $(^4\text{He}/^3\text{He})$ , and  $(^{147}\text{Sm}/^3\text{He})$  are present-day ratios that can be measured. Equation 1-49 is referred to as an *isochron equation*, which is the most important equation in isotope geochronology. Its application is as follows. A rock usually contains several minerals. If they formed at the same time (hence isochron, where *iso* means same and *chron* means time), which excludes inherited minerals in a sedimentary or metamorphic rock, and if they have the same initial isotopic ratio  $(^{143}\text{Nd}/^{144}\text{Nd})_0$ , then a plot of  $y = (^{143}\text{Nd}/^{144}\text{Nd})$  versus  $x = (^{147}\text{Sm}/^{144}\text{Nd})$  would yield a straight line. The slope of the straight line is  $(e^{k_2t} - 1)$  and the intercept is  $(^{143}\text{Nd}/^{144}\text{Nd})_0$ . From the slope, the age  $t$  can be calculated. From the intercept, the initial isotopic ratio is inferred. Comparison of Equations 1-47c and 1-49 reveals the importance of dividing by  $^{144}\text{Nd}$ : different minerals formed from a common source (such as a melt) would rarely have the same  $[^{143}\text{Nd}]_0$  concentration, but they would have the same isotopic ratio  $(^{143}\text{Nd}/^{144}\text{Nd})_0$ . Hence, Equation 1-47c would not yield a straight line (because the “intercept” is not a constant), but Equation 1-49 would yield a straight line. The use of radioactive decay and radiogenic growth in geochronology and thermochronology is covered more extensively in Chapter 5.

A good example of a first-order (pseudo-first-order) chemical reaction is the hydration of  $\text{CO}_2$  to form carbonic acid, Reaction 1-7f,  $\text{CO}_2(\text{aq}) + \text{H}_2\text{O}(\text{aq}) \rightarrow \text{H}_2\text{CO}_3(\text{aq})$ . Because this is a reversible reaction, the concentration evolution is considered in Chapter 2.

### 1.3.5.3 Second-order reactions

Most elementary reactions are second-order reactions. There are two types of second-order reactions:  $2A \rightarrow C$  and  $A + B \rightarrow C$ . The first type (special case) of second-order reactions is



The reaction rate law is

$$d\xi/dt = k[A]^2 = k([A]_0 - 2\xi)^2. \psi \quad (1-51)$$

The solution can be found as follows:

$$d\xi/([A]_0 - 2\xi)^2 = k dt. \psi \quad (1-51a)$$

Then

$$-d([A]_0 - 2\xi)/([A]_0 - 2\xi)^2 = 2k dt. \psi \quad (1-51b)$$

Then

$$1/([A]_0 - 2\xi) - 1/[A]_0 = 2kt. \psi \quad (1-51c)$$

That is

$$1/[A] - 1/[A]_0 = 2kt. \psi \quad (1-52)$$

Or

$$[A] = [A]_0/(1 + 2k[A]_0t). \psi \quad (1-53)$$

The concentration of the reactant varies with time hyperbolically.

The second type (general case) of second-order reactions is



The reaction rate law is

$$d\xi/dt = k[A][B] = k([A]_0 - \xi)([B]_0 - \xi). \psi \quad (1-55)$$

If  $[A]_0 = [B]_0$ , The solution is the same as Equation 1-53. For  $[A]_0 \neq [B]_0$ , the solution can be found as follows:

$$d\xi/\{([A]_0 - \xi)([B]_0 - \xi)\} = k dt. \psi \quad (1-56)$$

$$u d\xi/([A]_0 - \xi) - u d\xi/([B]_0 - \xi) = k dt, \quad \text{where } u = 1/([B]_0 - [A]_0). \psi$$

$$u \ln \{([A]_0 - \xi)/[A]_0\} - u \ln \{([B]_0 - \xi)/[B]_0\} = -kt. \psi$$

$$\ln\{([A]_0 - \xi)/[A]_0\} - \ln\{([B]_0 - \xi)/[B]_0\} = -k([B]_0 - [A]_0)t$$

$$\xi = [A]_0[B]_0(q - 1)/(q[A]_0 - [B]_0), \quad \text{where } q = \exp\{-k([B]_0 - [A]_0)t\}. \psi \quad (1-57)$$

Figure 1-1 compares the concentration evolution with time for zeroth-, first-, and the first type of second-order reactions. Table 1-2 lists the solutions for concentration evolution of most elementary reactions.

### 1.3.5.4 Half-lives and mean reaction times

A simple way to characterize the rate of a reaction is the time it takes for the concentration to change from the initial value to halfway between the initial and final (equilibrium). This time is called the *half-life* of the reaction. The half-life is often denoted as  $t_{1/2}$ . The longer the half-life, the slower the reaction. The half-life is best applied to a first-order reaction (especially radioactive decay), for which the half-life is independent of the initial concentration. For example, using the decay of  $^{147}\text{Sm}$  as an example,  $[^{147}\text{Sm}] = [^{147}\text{Sm}]_0 \exp(-kt)$  (derived above). Now, by definition,

$$[^{147}\text{Sm}] = [^{147}\text{Sm}]_0/2 \text{ at } t = t_{1/2}.$$

That is,

$$[^{147}\text{Sm}]_0/2 = [^{147}\text{Sm}]_0 \exp(-kt_{1/2}).$$

Solving  $t_{1/2}$ , we obtain

$$t_{1/2} = (\ln 2)/k. \quad (1-58)$$

For reactions with a different order, the half-life depends on the initial concentrations. For example, for a second-order reaction,  $2A \rightarrow \text{product}$ , with  $d[A]/dt = -2k[A]^2$ , then

$$t_{1/2} = 1/(2k[A]_0). \quad (1-59)$$

That is, the higher the initial concentration, the shorter the half-life! This counterintuitive result is due to the reaction rate being proportional to the square of the concentration, meaning that the rate increases more rapidly than the concentration itself. Nonetheless, for  $[A]$  to reach 0.01 M, it takes a longer time starting from 0.2 M than starting from 0.1 M by the extra time for  $[A]$  to attain from 0.2 to 0.1 M. The half-lives of various reactions are listed in Table 1-2.

The *mean reaction time* or *reaction timescale* (also called *relaxation timescale*; relaxation denotes the return of a system to equilibrium) is another characteristic time for a reaction. Roughly, the mean reaction time is the time it takes for the concentration to change from the initial value to  $1/e$  toward the final (equilibrium) value. The mean reaction time is often denoted as  $\tau$  (or  $\tau_r$  where subscript “r” stands for reaction). The rigorous definition of  $\tau$  is through the following equation (Scherer, 1986; Zhang, 1994):

$$\frac{d\xi}{dt} = \frac{\xi_\infty - \xi}{\tau}, \quad (1-60)$$

**Table 1-2 Concentration evolution and half-life for elementary reactions**

Order	Type of reaction	Reaction rate law	Expression of $\xi(t)$	Linear plot	Half-life ( $t_{1/2}$ ) and mean reaction time ( $\tau$ )
0	$A \rightarrow C$	$d\xi/dt = k$	$\xi = kt$ $A = A_0 - kt \approx A_0$ $C = C_0 + kt$	$C = C_0 + kt$	$t_{1/2} = \frac{A_0}{2k}; \tau = A/k$
1	$A \rightarrow C$	$d\xi/dt = kA$	$\xi = A_0(1 - e^{-kt});$ $A = A_0e^{-kt}$ $C = C_0 + A_0(1 - e^{-kt})$ $A = \frac{A_0}{1 + 2kA_0t}$	$\ln A = \ln A_0 - kt$	$t_{1/2} = \frac{\ln 2}{k}; \tau = 1/k$
2	$2A \rightarrow C$	$d\xi/dt = kA^2$ $-dA/dt = 2kA^2$	$A = \frac{A_0}{1 + 2kA_0t}$	$1/A = 1/A_0 + 2kt$	$t_{1/2} = \frac{1}{2kA_0};$ $\tau = 1/(2kA)$
2	$A + B \rightarrow C$	$d\xi/dt = kAB$	If $A_0 \neq B_0$ , then $\xi = \frac{A_0B_0(q-1)}{(qA_0 - B_0)}$ where $q = e^{-k(B_0 - A_0)t}$ . $A_0 = A_0 - \xi; B = B_0 - \xi$ If $A_0 = B_0$ , then $A = B = \frac{B_0}{1 + kB_0t}$	$\ln \frac{A}{B} = \ln \frac{A_0}{B_0} + (A_0 - B_0)kt$ If $A_0 = B_0$ , then $1/A = 1/B = 1/B_0 + kt$	If $A_0 = B_0$ , then $t_{1/2} = 1/(kA_0);$ if $A_0 < B_0$ , then; $t_{1/2} = 1/(kB_0)$ for A; if $A_0 > B_0$ , then $t_{1/2} = 1/(kA_0)$ for B
3	$3A \rightarrow C$	$d\xi/dt = kA^3$ $-dA/dt = 3kA^3$		$\frac{1}{A^2} = \frac{1}{A_0^2} + 6kt$	$t_{1/2} = \frac{1}{2kA_0^2}; \tau = 1/(3kA^2)$
3	$2A + B \rightarrow C$	$d\xi/dt = kA^2B$ $-dA/dt = 2kA^2B$	If $A_0 \neq 2B_0$ , then $kt(A_0 - 2B_0) = \left(\frac{1}{A_0} - \frac{1}{A}\right) + \ln \frac{AB_0}{A_0B}$	$\frac{1}{A^2} = \frac{1}{A_0^2} + 6kt$	
3	$A + B + C \rightarrow$	$d\xi/dt = kABC$			
$n$	$nA \rightarrow C$	$d\xi/dt = kA^n$ $-dA/dt = nA^n$	$\frac{1}{A^{n-1}} = \frac{1}{A_0^{n-1}} + n(n-1)kt$ $n \neq 0, 1$	$\frac{1}{A^{n-1}} = \frac{1}{A_0^{n-1}} + n(n-1)kt$ $n \neq 0, 1$	$t_{1/2} = \frac{2^{n-1} - 1}{n(n-1)kA_0^{n-1}}$ $n \neq 0, 1$

A, B, and C denote the species, and  $A, B$ , and  $C$  (italicized) denote the concentration of the species (i.e.,  $A = [A]$ ). Subscript "0" denotes the initial concentration.  $\xi$  is the reaction progress parameter and  $k$  is the rate constant.

where  $\xi$  is the reaction rate progress parameter,  $\xi_\infty$  is the value of  $\xi$  at  $t = \infty$  (i.e., as the reaction reaches completion or equilibrium). An equivalent definition is  $\tau = -dt/d \ln|\xi - \xi_\infty|$ . The longer the mean reaction time, the slower the reaction is. By this definition, the mean reaction time may vary as the reaction goes on. Because the mean reaction time is defined using the reaction rate, the rate law can be directly compared with the definition of  $\tau$  so as to find  $\tau$ . Hence, even though the definition is more complicated than the half-life, obtaining the mean reaction time is often simpler. For a first-order reaction,  $\tau$  is independent of the initial concentration. Still using the decay of  $^{147}\text{Sm}$  as an example,

$$d\xi/dt = -d[^{147}\text{Sm}]/dt = \lambda_{147}[^{147}\text{Sm}].\psi$$

Because  $\xi_\infty = [^{147}\text{Sm}]_0$  and  $\xi = [^{147}\text{Sm}]_0 - [^{147}\text{Sm}]$ , we have  $(\xi_\infty - \xi) = [^{147}\text{Sm}]$ . Hence,

$$d\xi/dt = \lambda_{147}(\xi_\infty - \xi).\psi \quad (1-61)$$

By definition  $d\xi/dt = (\xi_\infty - \xi)/\tau$ ; therefore,

$$\tau = 1/\lambda_{147}.\psi \quad (1-62)$$

The above simple formula is one of the reasons why some authors prefer the use of the mean reaction time (or relaxation timescale) instead of the half-life. The mean reaction time is longer than the half-life.

For a second-order reaction, the mean reaction time is not so simple. For example, for reaction  $2A \rightarrow \text{product}$ ,  $d\xi/dt = k[A]^2$ . Because  $\xi_\infty = [A]_0/2$ , and  $\xi = ([A]_0 - [A])/2$ , then  $(\xi_\infty - \xi) = [A]/2$ . Therefore,  $d\xi/dt = k[A]^2 = [A]/(2\tau)$ . Simplification leads to

$$\tau = 1/(2k[A]).\psi \quad (1-63)$$

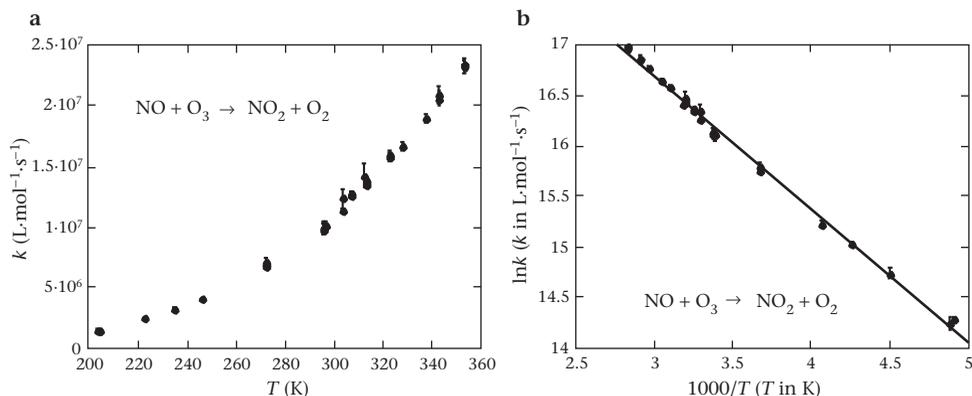
The mean reaction time during a reaction varies as the concentration varies if the reaction is not a first-order reaction. Expressions of mean reaction time of various types of reactions are listed in Table 1-2. In practice, half-lives are often used in treating radioactive decay reactions, and mean reaction times are often used in treating reversible chemical reactions.

### **1.3.6 Dependence of reaction rate constant on temperature; Arrhenius equation**

Experimental data show that the reaction rate constant depends on temperature, and often in the following form:

$$k = A \exp[-E/(RT)], \quad (1-64)$$

where  $k$  is the reaction rate constant for a reaction,  $T$  is temperature (always in kelvins),  $R$  is the universal gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ ; in older books and



**Figure 1-2** Rate coefficients (Borders and Birks, 1982) for gas-phase reaction  $\text{NO} + \text{O}_3 = \text{NO}_2 + \text{O}_2$ . Two data points with large errors are excluded. (a)  $k$  versus  $T$ ; (b)  $\ln k$  versus  $1000/T$  to linearize the plot.

journal articles, the value  $1.9872 \text{ cal mol}^{-1} \text{ K}^{-1}$  is used),  $E$  is called the activation energy (in J or cal), and  $A$  is called the preexponential parameter (for lack of a better name) and is also the value of  $k$  as  $T$  approaches  $\infty$ . The relation was first discovered by the Swedish chemist Svante August Arrhenius (1859–1927), and hence bears the name *Arrhenius equation*. Because the activation energy  $E$  and the gas constant  $R$  often occur together as  $E/R$  (which has the dimension of temperature),  $(E/R)$  is often grouped together in this book, and the Arrhenius equation is hence in the form of  $k = A \exp(-B/T)$ .

Given the Arrhenius equation for a reaction, i.e., given the preexponential factor  $A$  and the activation energy  $E$  as well as the applicable temperature range,  $k$  can be found at any temperature within the range. The calculation is not complicated but one must (i) maintain consistency between units, and (ii) be especially careful about the unit of temperature (which must be converted to kelvins).

On the other hand, given experimental data of  $k$  versus  $T$  at several temperatures (either you made the measurements or there are literature data), one can use the data to obtain the Arrhenius equation by regression. Then the Arrhenius equation can be used for both interpolation (which is usually reliable) and extrapolation. Caution must be exercised for extrapolation because if an equation is extrapolated too far outside the data coverage (in this case, the temperature range), the error might be greatly amplified, and the activation energy  $E$  might change with temperature (see Figure 1-17 in a later section; see also Lasaga, 1998).

**Example 1.1** If  $E = 250 \text{ kJ/mol}$ ,  $A = 10^{10} \text{ s}^{-1}$ , and the applicable temperature range is 270 to 1000 K, find  $k$  at  $500^\circ\text{C}$ .

**Solution:** First, convert temperature to Kelvin scale:  $T = 773.15$  K. Because it is within the range of 270 to 1000 K, the formula  $k = A \exp[-E/(RT)]$  can be used. Use  $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$ . To make sure all units are consistent,  $E$  must be in J/mol (instead of kJ/mol). That is,  $E = 250,000 \text{ J/mol}$ . Using the formula, one finds that  $k = 1.288 \times 10^{-7} \text{ s}^{-1} = 4.065 \text{ yr}^{-1}$ .

For the purpose of viewing data and for regression, the Arrhenius equation is often rewritten in the following form:

$$\ln k = \ln A + [-E/(RT)]. \quad (1-65)$$

By letting  $y = \ln k$ ,  $x = 1/T$ , constant  $\ln A = a$ , and constant  $(-E/R) = b$ , then the above equation becomes

$$y = a + bx. \quad (1-66)$$

Hence, the exponential Arrhenius equation has been transformed to a linear equation. Figure 1-2 shows kinetic data in  $k$  versus  $T$  (Figure 1-2a) and in  $\ln k$  versus  $1/T$  (Figure 1-2b). Actually,  $1000/T$  instead of  $1/T$  is often used so that the numbers on the horizontal axis are of order 1, which is the same relation except now the slope is  $0.001E/R$ . Because the linear relation is so much simpler and more visual, geochemists and many other scientists love linear equations because data can be visually examined for any deviation or scatter from a linear trend. Hence, they take extra effort to transform a relation to a linear equation. As will be seen later, many other equations encountered in geochemistry are also transformed into linear equations.

**Linear regression** Given experimental data  $(x_i, y_i)$ , where  $i = 1, 2, \dots, n$ , fitting the data to an equation, such as  $y = a + bx$ , where  $a$  and  $b$  are parameters to be obtained by fitting, is not as trivial as one might first think. By plotting the data, one can always draw by hand a straight line that fits the data. Nowadays with help from graphing or spreadsheet programs, the task is simple if one does not want to pay much attention to data uncertainties. However, experimental data always have uncertainties. For example, every temperature measurement may have some error, or there may be temperature fluctuations during an experiment, and each estimate of the reaction rate coefficient may have a large error. Furthermore, the error for one experiment may differ from that of another. To treat errors in a rigorous fashion, more advanced linear regression algorithms must be used (see below).

For a given data set of  $(x_i, y_i)$ , where  $i = 1, 2, \dots, n$ , the simplest non-eyeball fit of the data, which is usually what graphing programs and spreadsheet programs use, can be obtained as follows. First calculate the average of  $x_i$ 's and  $y_i$ 's (the averages are denoted as  $\bar{x}$  and  $\bar{y}$ ):

$$\bar{x} = (x_1 + x_2 + \cdots + x_n)/n \equiv \sum_{i=1}^n x_i/n, \quad (1-67)$$

$$\bar{y} = \sum_{i=1}^n y_i/n. \quad (1-68)$$

Then  $a$  and  $b$  can be calculated:

$$b = \frac{\sum_{i=1}^n (x_i - \bar{x})(y_i - \bar{y})}{\sum_{i=1}^n (x_i - \bar{x})^2}, \quad (1-69a)$$

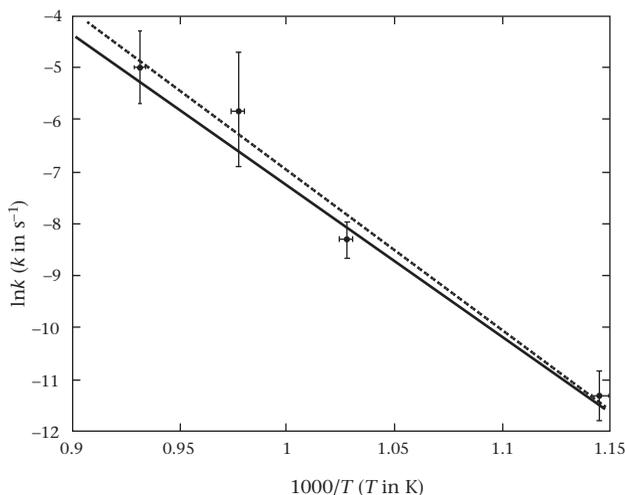
$$a = \bar{y} - b\bar{x}. \quad (1-69b)$$

In the above simple fit, the implicit assumptions are that (i)  $x_i$  values have no errors, and (ii) all  $y_i$  values have identical error. The above fit cannot account for different errors in  $y_i$ , nor errors in  $x_i$ , nor correlations in the errors. Therefore, data with high accuracy would not be emphasized as they deserve, and data with large uncertainty would not be deemphasized. To account for data uncertainties, more advanced programs must be used, and the best is by York (1969). Most radiogenic isotope geochemists use such a program for fitting isochrons, but other geochemists do not necessarily do that. If a program treats all errors perfectly and the fit equation is  $y = a + bx$ , and  $x$  is switched with  $y$  and the data are refitted, the equation would be exactly  $x = (y - a)/b = -a/b + (1/b)y$ .

**Example 1.2** The following data are from Besancon (1981) for Fe–Mg disordering reaction between M1 and M2 sites of an orthopyroxene. The errors are estimated from the number of experimental data points for each determination and whether there are enough points between the initial state and the final equilibrium state.

$T$ (K)	$k$ ( $s^{-1}$ )	$1000/T$	$\ln k$
$873 \pm 3$	$1.24 \times 10^{-5} \times 1.6$	$1.1453 \pm 0.0039$	$-11.30 \pm 0.47$
$973 \pm 3$	$2.45 \times 10^{-4} \times 1.4$	$1.0276 \pm 0.0032$	$-8.31 \pm 0.34$
$1023 \pm 3$	$0.00295 \times 3$	$0.9774 \pm 0.0029$	$-5.83 \pm 1.10$
$1073 \pm 3$	$0.00677 \times 2$	$0.9318 \pm 0.0026$	$-5.00 \pm 0.69$

**Solution:** If simple linear least-squares fitting is used, the result is  $\ln k = 23.576 - 30,559/T$  (dashed line in Figure 1-3). If York's linear least-squares fitting program is used, the resulting equation is  $\ln k = 21.762 - 29.029/T$  (solid line in Figure 1-3). The more advanced fit emphasizes and passes through data with smaller error bars, as expected.



**Figure 1-3** Comparison of simple least-squares fitting (dashed line) versus weighted least-squares fitting (solid line) that accounts for all individual errors and correlations. The data are Fe–Mg disordering rate coefficients in an orthopyroxene from Besancon (1981). Errors are estimated from the paper. The equation of the dashed line is  $y = 23.576 - 30.559x$ . The equation of the solid line is  $y = 21.762 - 29.029x$ . The solid line goes through the data point with the smallest error within its errors, but the simple fit does not.

### 1.3.7 Nonisothermal reaction kinetics

Except for radioactive decays, other reaction rate coefficients depend on temperature. Hence, for nonisothermal reaction with temperature history of  $T(t)$ , the reaction rate coefficient is a function of time  $k(T(t)) = k(t)$ . The concentration evolution as a function of time would differ from that of isothermal reactions. For unidirectional elementary reactions, it is not difficult to find how the concentration would evolve with time as long as the temperature history and hence the function of  $k(t)$  is known. To illustrate the method of treatment, use Reaction  $2A \rightarrow C$  as an example. The reaction rate law is (Equation 1-51)

$$d\xi/dt = k[A]^2 = k([A]_0 - 2\xi)^2,$$

where  $x|_{t=0} = 0$  and  $k$  is a function of  $t$ . Rearranging the above leads to

$$d\xi/(k dt) = ([A]_0 - 2\xi)^2, \quad (1-70a)$$

Define

$$\alpha = \int_0^t k dt. \psi \quad (1-70b)$$

Hence,  $\alpha|_{t=0} = 0$ , and  $d\alpha = k dt$ . Therefore, Equation 1-70a becomes

$$d\xi/(d\alpha) = ([A]_0 - 2\xi)^2. \psi \quad (1-70c)$$

The above equation is equivalent to Equation 1-51 by making  $\alpha$  equivalent to  $kt$ . Hence, the solution can be obtained similar to Equation 1-53 as follows:

$$[A] = [A]_0 / (1 + 2[A]_0 \alpha) \quad (1-70d)$$

In general, for unidirectional elementary reactions, it is easy to handle non-isothermal reaction kinetics. The solutions listed in Table 1-2 for the concentration evolution of elementary reactions can be readily extended to nonisothermal reactions by replacing  $kt$  with  $\alpha = \int k dt$ . The concepts of half-life and mean reaction time are not useful anymore for nonisothermal reactions.

The most often encountered thermal history by geologists is continuous cooling from a high temperature to room temperature (such as cooling of volcanic rocks, plutonic rocks, and metamorphic rocks). One of the many ways to approximate the cooling history is as follows:

$$T = T_0 / (1 + t/\tau_c) \quad (1-70e)$$

where  $T_0$  is the initial temperature and  $\tau_c$  is the time for temperature to cool from the initial temperature to half of the initial temperature. (Other temperature versus time functions are discussed in later chapters.) Because  $k$  depends on temperature as  $A \exp[-E/(RT)]$ , the dependence of  $k$  on time may be expressed as follows:

$$K = A \exp[-E(1 + t/\tau_c)/(RT_0)] = A \exp[-E/(RT_0)] \exp[-Et/\tau_c RT_0] \quad (1-70f)$$

Let  $k_0 = A \exp[-E/(RT_0)]$ , meaning the initial value of the rate coefficient, and  $\tau = \tau_c(RT_0/E)$ . Then the expression of  $k$  becomes

$$k = k_0 e^{-t/\tau} \quad (1-70f)$$

That is,  $k$  decreases with time exponentially with a timescale of  $\tau$ . Therefore,  $\alpha$  can be found to be

$$\alpha = \int_0^t k dt = k_0 \tau (1 - e^{-t/\tau}) \quad (1-70g)$$

If the reaction occurs at high temperature, but the rate at room temperature is negligible (i.e., negligible reaction even for 4 billion years), the integration can be carried out to  $t = \infty$ , leading to

$$\alpha = k_0 \tau \quad (1-70h)$$

Therefore, under the conditions of continuous cooling and negligible reaction rate at room temperatures, the degree of the reaction is equivalent to that at the high temperature  $T_0$  (where the rate coefficient is  $k_0$ ) for a finite duration of  $\tau = \tau_c(RT_0/E)$ . An example of calculations is shown below.

**Example 1.3** For a first-order reaction  $A \rightarrow B$ ,  $k = \exp(-6.00 - 25,000/T) \text{ s}^{-1}$ . Suppose the temperature history is given by  $T = 1400/(1 + t/1000)$ , where  $T$  is in K and  $t$  is in years. The initial concentration of A is  $[A]_0 = 0.1 \text{ mol/L}$ . Find the final concentration of A after cooling to room temperature.

*Solution:* The initial temperature  $T_0 = 1400 \text{ K}$ . The rate coefficient at  $T_0$  can be found to be

$$k_0 = \exp(-6.00 - 25,000/T_0) \text{ s}^{-1} = 4.35 \times 10^{-11} \text{ s}^{-1} = 0.00137 \text{ yr}^{-1}.$$

The cooling timescale  $\tau_c = 1000$  years. The activation energy is  $25,000R$ . Hence, the timescale for  $k$  to decrease is

$$\tau = 1000 \cdot 1400/25,000 = 56 \text{ years}.$$

Hence,

$$\alpha = k_0 \tau = 0.077.$$

From Table 1-2, replacing  $kt$  by  $\alpha$ , it can be found that the concentration

$$[A] = [A]_0 e^{-\alpha} = 0.1 \times 0.926 = 0.0926 \text{ mol/L}.$$

This concludes the solution.

Additionally, we can also estimate whether the reaction at room temperature is significant. At  $298 \text{ K}$ ,  $k = \exp(-6.00 - 25,000/298) \text{ s}^{-1} = 9.1 \times 10^{-40} \text{ s}^{-1} = 2.88 \times 10^{-32} \text{ yr}^{-1}$ . Even if the sample has been at this temperature for the whole age of the Earth,  $kt$  would be of the order  $1.3 \times 10^{-22}$ , and  $e^{-kt} = 1$ . The extent of the reaction at room temperature is negligible.

The above analyses show that it is fairly easy to deal with temperature variation for unidirectional elementary reaction kinetics containing only one reaction rate coefficient. Analyses similar to the above will be encountered often and are very useful. However, if readers get the impression that it is easy to treat temperature variation in kinetics in geology, they would be wrong. Most reactions in geology are complicated, either because they go both directions to approach equilibrium, or because there are two or more paths or steps. Therefore, there are two or more reaction rate coefficients involved. Because the coefficients almost never have the same activation energy, the above method would not simplify the reaction kinetic equations enough to obtain simple analytical solutions.

### 1.3.8 More complicated homogeneous reactions

A *reversible reaction* can go both forward and backward, depending on the initial concentrations of the species. Most chemical reactions are reversible. For example, Reactions 1-6 to 1-12 are all reversible.

A *chain reaction* is accomplished by several sequential steps. Chain reactions are also known as consecutive reactions or sequential reactions. For a chain reaction,

the slowest step is the rate-limiting step. For example, the decay of  $^{238}\text{U}$  to  $^{206}\text{Pb}$  is a chain reaction. Nuclear hydrogen burning by the PP I chain process is also a chain reaction.

If a reaction can be accomplished by two or more paths, the paths are called *parallel paths* and the reaction is called a *parallel reaction*. The overall reaction rate is the sum of the rates of all the reaction paths. The fastest reaction path is the rate-determining path. For nuclear hydrogen burning, the PP I chain is one path, the PP II chain is another path, and the CNO cycle is yet another path.

A *branch reaction* is when the reactants may form different products. It is similar to a parallel reaction in that there are different paths, but unlike a parallel reaction in that the different paths lead to different products for a branch reaction but to the same product (eventually) for a parallel reaction. For example,  $^{40}\text{K}$  undergoes a branch reaction, one branch to  $^{40}\text{Ar}$  and the other to  $^{40}\text{Ca}$ .

For bimolecular second-order reactions and for trimolecular reactions, if the reaction rate is very high compared to the rate to bring particles together by diffusion (for gas-phase and liquid-phase reactions), or if diffusion is slow compared to the reaction rate (for homogenous reaction in a glass or mineral), or if the concentrations of the reactants are very low, then the reaction may be limited by diffusion, and is called an *encounter-controlled reaction*.

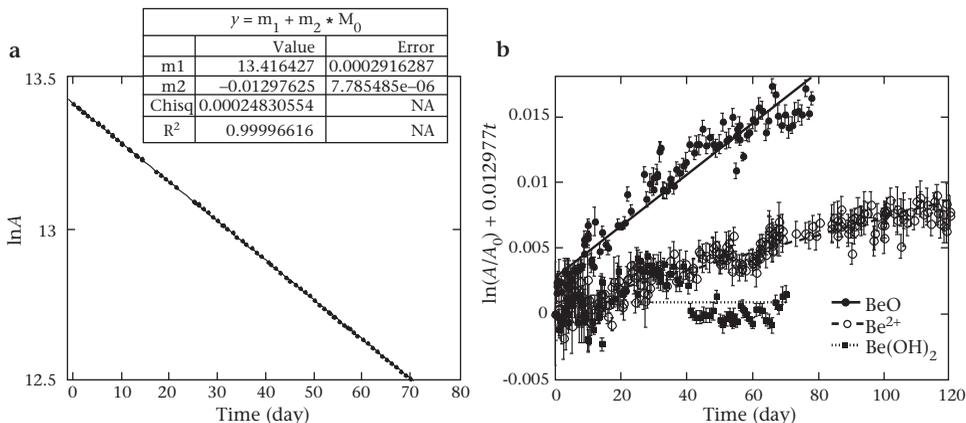
An example of branch reactions is discussed in Section 1.7.2. The quantitative treatment of the kinetics of other reactions is complicated, and is the subject of Chapter 2.

### **1.3.9 Determination of reaction rate laws, rate constants, and mechanisms**

Reaction rate laws are determined experimentally. For reactions known to be elementary reactions, it is necessary to experimentally determine the rate constant. For other reactions that may or may not be elementary, it is necessary to experimentally determine the reaction rate law and the rate constant. If the reaction rate law conforms to that of an elementary reaction, i.e., for reaction  $\alpha\text{A} + \beta\text{B} \rightarrow \text{products}$ , the reaction rate law is  $d\xi/dt = k[\text{A}]^\alpha[\text{B}]^\beta$ , then the reaction is considered consistent with an elementary reaction, but other information to confirm that no other steps occur is necessary to demonstrate that a reaction is elementary. It is possible that a reaction has the “right” reaction rate law, but is shown later to be nonelementary based on other information.

#### **1.3.9.1 Determination of the reaction rate constant**

$^7\text{Be}$  is the lightest nuclide that decays by electron capture and hence is the best nuclide to demonstrate whether or not the decay constant for electron capture depends on the chemical environment and pressure. (The decay constants for  $\alpha$ -decay and  $\beta$ -decay through emission of an electron or a positron from the



**Figure 1-4** (a) Logarithm of the activity of  $^7\text{Be}$  (counts per minute) in  $\text{Be}(\text{OH})_2$  versus time to demonstrate that the decay is a first-order reaction and that the decay constant is  $0.012977 \text{ day}^{-1}$  (or half-life is 53.41 days). Error is about the size of the points. (b)  $\ln(A/A_0) + 0.012977t$  versus  $t$  to compare the decay constant of  $^7\text{Be}$  in different compounds. The error bars are at the  $2\sigma$  level. The data indicate that the decay constant of  $^7\text{Be}$  depends on the chemical environment. Data from Huh (1999).

nucleus do not depend on temperature, pressure and chemical environment because these are processes inside the nucleus. The decay constant for  $\beta$ -decay through electron capture may depend on these factors because they may affect the behavior of K-shell electrons and, hence, their probability to be captured.) Because the variation of decay constant for electron capture may impact on the accuracy of the  $^{40}\text{K}$ - $^{40}\text{Ar}$  dating method, the accurate determination of the decay constant of  $^7\text{Be}$  is of special interest. Huh (1999) determined the rate constant for the decay of  $^7\text{Be}$  to  $^7\text{Li}$ . The reaction is known to be a first-order reaction with the rate law of  $d[{}^7\text{Be}]/dt = -k[{}^7\text{Be}]$ , where  $[{}^7\text{Be}]$  can be the concentration of  $^7\text{Be}$ , or the activity of  $^7\text{Be}$ , or the total number of  $^7\text{Be}$  atoms. Hence, the task is to determine the value of decay constant  $k$ . Huh (1999) measured the variation of  $^7\text{Be}$  activity (proportional to concentration) with time. The data can be fit by the exponential decay equation similar to Equation 1-47a:

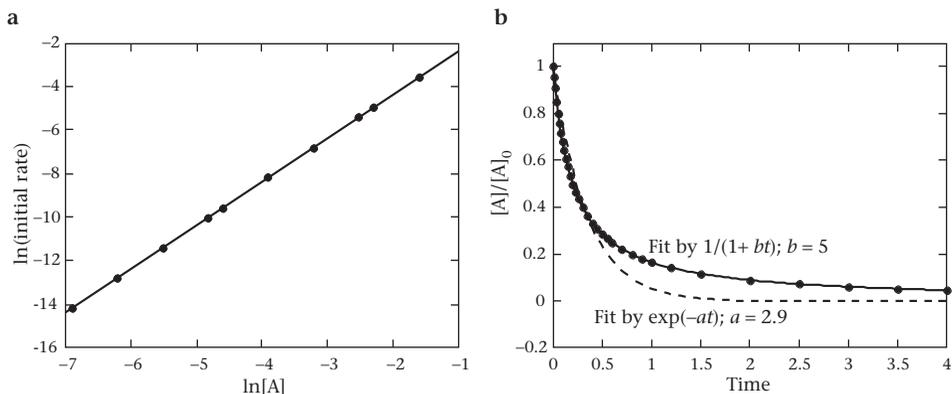
$$[{}^7\text{Be}] = [{}^7\text{Be}]_0 e^{-\lambda t},$$

or

$$A = A_0 e^{-\lambda t},$$

where  $A$  is activity of  $^7\text{Be}$  and equals  $\lambda[{}^7\text{Be}]$ . Figure 1-4a shows the decay data in the compound  $\text{Be}(\text{OH})_2$  plotted as  $\ln A$  versus  $t$ . The decay constant of  $^7\text{Be}$  in  $\text{Be}(\text{OH})_2$  is found to be  $0.012977 \text{ day}^{-1}$ .

To examine whether there are small differences in the decay constant of  $^7\text{Be}$  in different compounds, Figure 1-4b plots  $\ln(A/A_0) + 0.012977t$  versus  $t$  for  $^7\text{Be}$  decay in  $\text{Be}(\text{OH})_2$ ,  $\text{BeO}$ , and dissolved  $\text{Be}^{2+}$ . If the decay constant of  $^7\text{Be}$  in



**Figure 1-5** Determination of the order of hypothetical reactions with respect to species A. (a) The initial reaction rate method is used. The initial rate versus the initial concentration of A is plotted on a log–log diagram. The slope 2 is the order of the reaction with respect to A. The intercept is related to  $k$ . (b) The concentration evolution method is used. Because the exponential function (dashed curve) does not fit the data (points) well, the order is not 1. The solution for the second-order reaction equation (solid curve) fits the data well. Hence, the order of the reaction is 2.

$\text{Be}(\text{OH})_2$  were the same as that in other compounds, they would all follow the same horizontal trend within error. Figure 1-4b shows that  $\ln(A/A_0) + 0.012977t$  versus  $t$  follows different trend for different compounds, indicating that the decay constant of  $^7\text{Be}$  depends on the kind of compound Be is in. The variation of the decay constant amounts to about 1.5%. Tossell (2002) raised doubt about the experimental results based on calculated electron density of Be in various compounds, but the reliability of the theoretical calculation has not been verified.

### 1.3.9.2 Determination of the reaction rate law

For a reaction  $\alpha A + \beta B \rightarrow \text{products}$ , to determine the reaction rate law, one often-used method is to vary the concentration of one species at a time and keep the concentration of the other species constant. This requires that each of the reactants (A and B) can be prepared in the pure form, and that the concentration can be varied freely and independently of the other species. For example, one may first fix the concentration of B at very high concentration (such as 1 M), and vary the concentration of A at low concentration levels but with a large concentration range (such as 0.001–0.01 M). A large range of concentration for A is necessary to develop an accurate reaction rate law. During the reaction, the concentration of B may be regarded as constant. The order of the reaction with respect to A can be determined using either of the following methods:

(1) *Initial rate method*. If the initial production rate of the product can be determined directly as a function of the initial concentration of A, such as  $\text{rate} \propto [\text{A}]^n$ ,

one finds the order of the reaction with respect to A to be  $n$ . Practically, this can be done by plotting  $\ln(\text{initial rate})$  versus  $\ln[A]$ , and the slope would be  $n$ , the order of the reaction. If the relation is not linear (which means the order is not defined), or if the slope is not an integer, then the reaction is not an elementary reaction. This method is called the initial rate method. Figure 1-5a shows an example of determining the order of a reaction using the initial rate method.

(2) *Concentration evolution method.* If the rate cannot be directly measured, but the concentration evolution of A as a function of time can be measured, then the order of the reaction can be compared with theoretical solutions (Table 1-2). For example, if  $[A] = [A]_0 - kt$ , i.e., if  $[A]$  decreases linearly with  $t$ , then the order with respect to A is zero. If  $[A]/[A]_0 = \exp(-kt)$ , i.e., if  $\ln[A]$  is linear to  $t$ , then the order with respect to A is 1. If  $[A]/[A]_0 = 1/(1 + 2k[A]_0t)$ , i.e., if  $1/[A]$  is linear to  $t$ , then the order with respect to A is 2. Figure 1-5b shows an example of determining the order of a reaction using the concentration evolution method.

After obtaining the order of the reaction with respect to A, one can fix the concentration of A at a very high concentration, and examine the order of the reaction with respect to B. In this way the complete reaction rate law can be developed.

The above methods of investigating the order of the reaction with respect to each species independently, although simple and practical for many reactions (such as atmospheric reactions and aqueous reactions) studied by chemists and geochemists, is often difficult to apply to homogeneous reactions in a silicate melt or mineral because the concentration of each species may not be varied freely and independently. This will become clear later when the kinetics for the Fe–Mg order–disorder reaction in orthopyroxene and the interconversion reaction between molecular  $\text{H}_2\text{O}$  and OH groups in silicate melt are discussed.

For very rapid reactions such as the ionization of  $\text{H}_2\text{O}$ , it is difficult to determine the rate constants using conventional methods. One often-used method is the relaxation method. The system is initially at equilibrium under a given set of conditions. The conditions are then suddenly changed so that the system is no longer at equilibrium. The system then relaxes to a new equilibrium state. The speed of relaxation is measured, usually by spectrophotometry, and the rate constants can be obtained. One technique to change the conditions is to increase temperature suddenly by the rapid discharge from a capacitor. This technique is called temperature-jump technique.

### 1.3.9.3 Reaction mechanisms

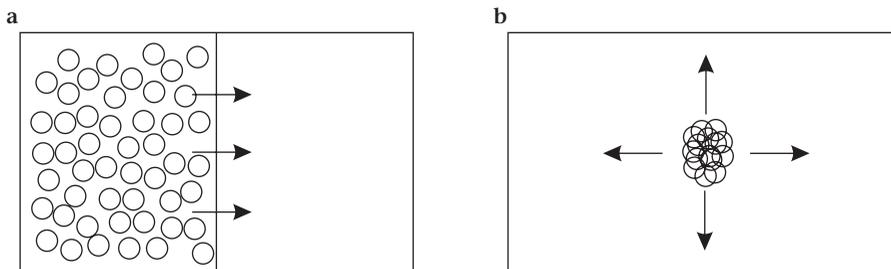
After obtaining the reaction rate law, if it does not conform to an elementary reaction, then the next step is to try to understand the reaction mechanism, i.e., to write down the steps of elementary reactions to accomplish the overall reaction. This task is complicated and requires experience. Establishing the mechanism for a homogeneous reaction is, in general, more like arguing a case in court, than a

mathematical proof. A few general rules are as follows. First, elementary reactions are usually *monomolecular* or *bimolecular*. Only very rarely are they *termolecular*. Secondly, rate constants for elementary reactions increase with temperature roughly according to Arrhenius law, i.e., the activation energy  $E$  is positive and not a strong function of temperature. Thirdly, it might be necessary to examine whether the reaction rate is affected by light, whether there are color changes or other indications that might point to the formation of some intermediate species, etc. It is from synthesizing all the experimental observations that a reaction mechanism may emerge. The proposed mechanism should have testable consequences, such as measurable intermediate species, which can be investigated further to verify or reject the proposed mechanism.

## 1.4 Mass and Heat Transfer

The physical transport of mass from one position to another plays a significant to dominant role in many kinetic processes. For example, a zoned crystal becomes homogeneous through diffusion, and magma erupts through fluid flow. Diffusion and fluid flow are two ways to accomplish the physical transport of masses, referred to as mass transfer. Besides pure mass transfer problems, mass transfer also plays an important role in many heterogeneous reactions (reactions involving two or more phases). The following are some examples of mass transfer problems encountered in geology:

- Homogenization of a zoned crystal through diffusion
- The change of melt inclusion composition by diffusion through the host mineral
- Diffusive loss of Ar from a mineral, affecting age determination (closure temperature)
- Diffusive exchange of isotopes, affecting age determination (closure temperature)
- Diffusive exchange of isotopes, affecting temperature determination (thermometry)
- Diffusion in a temperature gradient (Soret diffusion)
- Exchange of components between phases (heterogeneous reactions)
- Spinodal decomposition of a phase into two phases (heterogeneous reactions)
- Mass transfer during bubble growth in volcanic eruptions (heterogeneous reactions)



**Figure 1-6** Two examples of random motion of particles, which will lead to net flux (a) to the right-hand side, and (b) from the center to all directions.

- The transport of pollutant in river or in ground water: both diffusion and flow
- Mass transfer during crystal growth or dissolution (heterogeneous reactions)

In this section, we focus on diffusive mass transfer. The mathematical description of mass transfer is similar to that of heat transfer. Furthermore, heat transfer may also play a role in heterogeneous reactions such as crystal growth and melting. Heat transfer, therefore, will be discussed together with mass transfer and examples may be taken from either mass transfer or heat transfer.

### 1.4.1 Diffusion

Diffusion is due to random particle motion in a phase. The random motion leads to a net mass flux when the concentration of a component is not uniform (more strictly speaking, when the chemical potential is not uniform). Hence, a zoned crystal can be homogenized through diffusion. Some examples of diffusion are shown in Figure 1-6.

The phenomenological law that describes diffusion is

$$\mathbf{J} = -D \partial C / \partial x, \quad (1-71)$$

where  $\mathbf{J}$  is the diffusive flux,  $D$  is the diffusion coefficient (also referred to as diffusivity),  $C$  is the concentration,  $x$  is distance,  $\partial C / \partial x$  is the concentration gradient (a vector), and the negative sign means that the direction of diffusive flux is opposite to the direction of concentration gradient (i.e., diffusive flux goes from high to low concentration, but the gradient is from low to high concentration). The above equation was first proposed by the German physiologist Adolf Fick (1829–1901) and hence bears the name *Fick's law* (sometimes called *Fick's first law*). The unit of  $D$  is length<sup>2</sup>/time, such as m<sup>2</sup>/s, mm<sup>2</sup>/s, and μm<sup>2</sup>/s (1 μm<sup>2</sup>/s = 10<sup>-6</sup> mm<sup>2</sup>/s = 10<sup>-12</sup> m<sup>2</sup>/s). The value of the diffusion coefficient is a

**Table 1-3a Diffusion coefficients in aqueous solutions**

Dissolved gas molecules	$D$ ( $\text{m}^2/\text{s}$ ) at $25^\circ\text{C}$	Ions	$D$ ( $\text{m}^2/\text{s}$ ) at $25^\circ\text{C}$
Ar	$2.00 \times 10^{-9}$	$\text{H}^{+\leftrightarrow}$	$9.1 \times 10^{-9}$
Air	$2.00 \times 10^{-9}$	$\text{Li}^{+\leftrightarrow}$	$1.0 \times 10^{-9}$
$\text{CO}_2$	$1.92 \times 10^{-9}$	$\text{Na}^{+\leftrightarrow}$	$1.3 - 10^{-9}$
CO	$2.03 \times 10^{-9}$	$\text{OH}^{-\leftrightarrow}$	$5.2 \times 10^{-9}$
He	$6.28 \times 10^{-9}$	$\text{Cl}^{-\leftrightarrow}$	$2.0 \times 10^{-9}$
$\text{N}_2$	$1.88 \times 10^{-9}$	$\text{Br}^{-\leftrightarrow}$	$2.1 \times 10^{-9}$
$\text{O}_2$	$2.10 \times 10^{-9}$		

*Note.* Molecular diffusivities from Cussler (1997, p. 112); ionic diffusivities from Pilling and Seakins (1995, p. 148).

characterization of the “rate” of diffusion and, hence, is very important in quantifying diffusion. Many experimental studies have been carried out to determine diffusivity. Typical values of diffusion coefficients are as follows:

- In gas,  $D$  is large, about  $10 \text{ mm}^2/\text{s}$  in air at 298 K;
- In aqueous solution,  $D$  is small, about  $10^{-3} \text{ mm}^2/\text{s}$  in water at 298 K;
- In silicate melts,  $D$  is small, about  $10^{-5} \text{ mm}^2/\text{s}$  at 1600 K;
- In a solid,  $D$  is very small, about  $10^{-11} \text{ mm}^2/\text{s}$  in silicate mineral at 1600 K.

Diffusion coefficients of some ionic and molecular species are listed in Table 1–3. The diffusivities in Table 1–3 are molecular, ionic, or atomic diffusivities due to the random motion of particles excited by thermal energy. If a system is disturbed randomly, such as fish swimming in a lake, wave motion, boating, as well as other random disturbances, then mass transport may also be described by diffusion (*eddy diffusion*) on a scale larger than each perturbation, but the diffusivity may be significantly larger. If not much activity happens in water, eddy diffusivity (or turbulent diffusivity) would be only slightly higher than molecular diffusivity. In seawater, vertical turbulent diffusivity is about  $10^{-5} \text{ m}^2/\text{s}$  (e.g., Gregg et al., 2003), 4 orders of magnitude greater than molecular diffusivity. If the water is a main waterway for shipping, eddy diffusivity can be many orders of greater. For example, eddy diffusivity may be as high as  $70 \text{ m}^2/\text{s}$ . This and other concepts of diffusion, such as *self-diffusion*, *tracer diffusion*, *chemical diffusion*, *grain boundary diffusion*, and *effective diffusion through a porous medium*, are examined in Chapter 3.

**Table 1-3b  $^{18}\text{O}$  diffusion coefficients in some minerals under hydrothermal conditions ( $P_{\text{H}_2\text{O}} = 100 \text{ MPa}$ )**

Mineral	Direction	$D \text{ (m}^2\text{/s)}$	$T \text{ range (K)}$	$D \text{ along other directions}$
Albite	Bulk	$\exp(-29.10-10,719/T)$	623–1073	
Anorthite	Bulk	$\exp(-25.00-13,184/T)$	623–1073	
Orthoclase	Bulk	$\exp(-26.12-12,882/T)$	623–1073	
Almandine	Isotropic	$\exp(-18.93-36,202/T)$	1073–1273	
Apatite	//c	$\exp(-18.53-24,658/T)$	823–1473	$\perp\text{c}$ 3 orders slower
Biotite	$\perp\text{c}$	$\exp(-20.82-17,110/T)$	773–1073	//c 4 orders slower
Muscovite	$\perp\text{c}$	$\exp(-18.68-19,626/T)$	785–973	//c 4 orders slower
Phlogopite	$\perp\text{c}$	$\exp(-18.08-21,135/T)$	873–1173	//c 4 orders slower
Calcite	Bulk	$\exp(-18.78-24,658/T)$	673–1073	
Diopside	//c	$\exp(-22.62-27,174/T)$	973–1523	$\perp\text{c}$ 2 orders slower
Hornblende	//c	$\exp(-25.33-20,632/T)$	923–1073	$\perp\text{c}$ 1 to 1.3 orders slower
Richterite	//c	$\exp(-17.32-28,684/T)$	923–1073	
Tremolite	//c	$\exp(-26.94-19,626/T)$	923–1073	
Magnetite	Isotropic	$\exp(-21.77-22,645/T)$	773–1073	
Quartz( $\alpha$ )	//c	$\exp(-3.96-34,158/T)$	773–823	$\perp\text{c}$ 2 orders slower
Quartz( $\beta$ )	//c	$\exp(-23.94-17,079/T)$	873–1073	$\perp\text{c}$ 2 orders slower

Reference: Brady (1995).

Note. The direction of diffusion is the direction of fastest diffusion.

Although the diffusion coefficient is related to the diffusion “rate,” it is difficult to define a single diffusion “rate” during diffusion because the diffusion distance is proportional not to duration, but to the square root of duration:

$$x \propto t^{1/2} \cdot \psi \quad (1-72)$$

**Table 1-3c Ar diffusion coefficients in some minerals**

Mineral	Orientation	Shape model	T range (K)	$D$ (m <sup>2</sup> /s)	$T_c$ (K)
Hornblende	Powder	Sphere	773–1173	$\exp(-12.94-32,257/T)$	770
Phlogopite	Powder	Cylinder	873–1173	$\exp(-9.50-29,106/T)$	646
Biotite	Powder	Cylinder	873–1023	$\exp(-11.77-23,694/T)$	554
Orthoclase	Powder	Sphere	773–1073	$\exp(-13.48-21,685/T)$	529

*Note.* The closure temperature  $T_c$  (see later discussion) depends on grain size and cooling rate; here it is calculated for a radius of 0.1 mm and a cooling rate of 5 K/Myr (Brady, 1995). Cylinder shape model means that the grains are treated as infinitely long cylinders with diffusion along the cross section (in the plane  $\perp c$ ).

The diffusion coefficient increases rapidly with temperature. The dependence of diffusivity on temperature also follows the Arrhenius relation,

$$D = Ae^{-E/(RT)}, \quad (1-73)$$

where  $A$  is the preexponential factor and equals the value of  $D$  as  $T$  approaches  $\infty$ ,  $E$  is the activation energy, and  $R$  is the universal gas constant.

Fick's first law relates the diffusive flux to the concentration gradient but does not provide an equation to solve for the evolution of concentration. In general, diffusion treats problems in which the concentration of a component or species may change with both spatial position and time, i.e.,  $C = C(x, t)$ , where  $x$  describes the position along one direction. Therefore, a differential equation for  $C(x, t)$  must include differentials with respect to both  $t$  and  $x$ . That is, a partial differential equation is necessary to describe how  $C$  would vary with  $x$  and  $t$ . It can be shown that under simple conditions, the flux equation and mass conservation can be transformed to the following equation:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1-74)$$

where  $C$  is a function of  $x$  and  $t$ , and  $D$  is assumed to be independent of  $C$ . This equation is called the *diffusion equation*, and is also referred to as Fick's second law. The mathematics of diffusion is complicated and is discussed in Chapter 3. In this section, some results are presented and explained but not derived.

From the diffusion equation, it can be seen that if  $\partial^2 C / \partial x^2 = 0$ , then  $\partial C / \partial t = 0$ , meaning that the concentration at the position would not vary with time. Hence, if the initial concentration is uniform, the concentration would not change with time. If the initial concentration profile is linear and the concentrations at the two ends are not changed from linear distribution, because

$\partial^2 C / \partial x^2 = 0$  for a linear profile, the concentration profile would remain as a linear profile. A linear profile is often the steady state for a diffusion-controlled profile.

Some examples of concentration evolution (Crank, 1975) are shown and explained below. These are all often-encountered problems in diffusion. The purpose of the examples and the qualitative discussion is to help readers develop familiarity and gain experience in treating diffusion in a qualitative fashion.

#### 1.4.1.1 Point-source diffusion

Initially, a substance is concentrated at one point along a straight line that extends to infinity to both sides. For convenience, the position of the point is defined as  $x = 0$ . One real-world problem is the spill of toxic substance into a narrow lake. This problem is called the one-dimensional (or 1-D) point-source problem. With time, the substance would diffuse out and be diluted. The concentration variation as a function of time is shown in Figure 1-7a. The mathematical description of the concentration of the substance as a function of  $x$  and  $t$  is

$$C = \frac{M}{(4\pi Dt)^{1/2}} e^{-x^2/4Dt}, \quad (1-75)$$

where  $M$  is the total initial mass at the point source. For the unit of  $C$  to be mass/volume, the unit of  $M$  must be mass/area (such as  $\text{kg}/\text{m}^2$ ). Therefore, even though this is a 1-D diffusion problem, one must know the cross-section area of the spill (and the cross-section area is assumed to be constant for 1-D diffusion) so that mass per unit area of the cross section can be calculated. The concentration at the center ( $x = 0$ ) is  $C = M/(4\pi Dt)^{1/2}$ . That is, the center concentration is infinity at zero time, and decreases as  $(t)^{-1/2}$ .

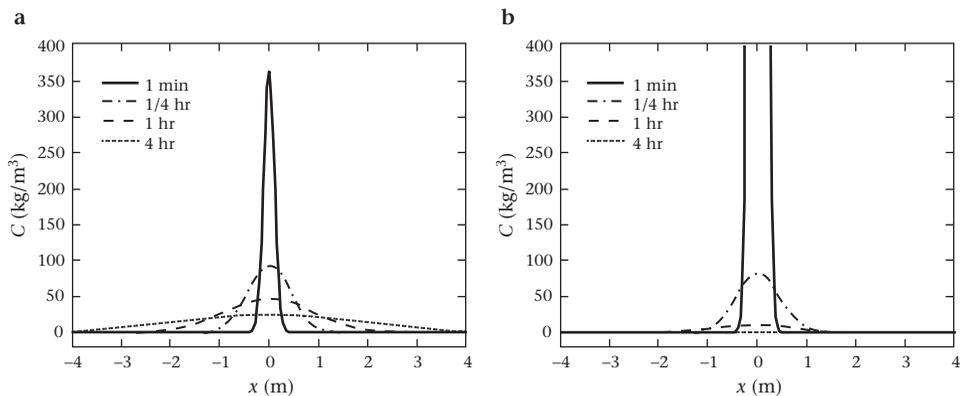
If a substance is initially concentrated at one point and then diffuses into three dimensions (along a spherical radius  $r$ ) such as Figure 1-6b, then,

$$C = \frac{M}{(4\pi Dt)^{3/2}} e^{-r^2/4Dt}, \quad (1-76)$$

where  $M$  is the total initial mass (in kg) at the point source. The concentration variation along  $r$  is shown in Figure 1-7b. This problem is called the three-dimensional (or 3-D) point-source problem. The dispersion of the mass is more rapid compared to 1-D point-source diffusion.

#### 1.4.1.2 Half-space diffusion

One example of half-space diffusion is the cooling of an oceanic plate. The oceanic plate when created at the mid-ocean ridge is hot, with a roughly uniform temperature of about 1600 K. It is cooled at the surface (quenched by ocean water) as it moves away from the ocean ridge. For simplicity, ignore complexities



**Figure 1-7** Evolution of concentration profiles for (a) one-dimensional point-source diffusion and (b) 3-D point-source diffusion. This calculation is made for  $M = 100 \text{ kg/m}^2$ , and  $D_{\text{eddy}} = 10^{-4} \text{ m}^2/\text{s}$  (eddy diffusivity). In the 3-D case,  $C$  was much higher at the center at smaller times because initial mass distribution was at a point instead of a plane; but at greater times, the concentration dissipates much more rapidly.

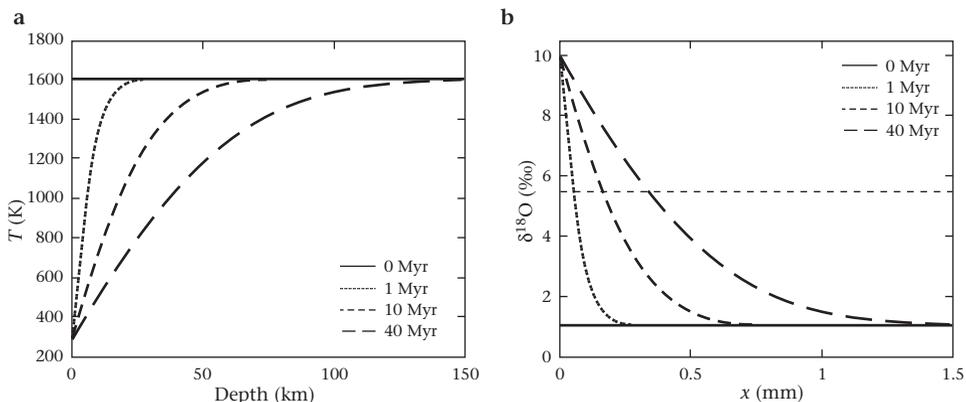
such as the intrusion of sheeted dikes, crystallization of the magma, and hydrothermal circulation. The surface temperature may be regarded as constant at ocean floor temperature (about 275 K). The plate thickness may be regarded as infinite. This problem with uniform initial temperature and a constant surface temperature is referred to as the (1-D) half-space diffusion problem. The evolution of temperature with time is diagrammed in Figure 1-8a. The low surface temperature gradually propagates into the interior of the oceanic plate.

Another example of half-space diffusion problem is as follows. A thin-crystal wafer initially contains some  $^{40}\text{Ar}$  (e.g., due to decay of  $^{40}\text{K}$ ). When the crystal is heated up (metamorphism),  $^{40}\text{Ar}$  will diffuse out and the surface concentration of  $^{40}\text{Ar}$  is zero. If the temperature is constant and, hence, the diffusivity is constant, the problem is also a half-space diffusion problem.

A third example is as follows. Initially a crystal has a uniform  $\delta^{18}\text{O}$ . Then the crystal is in contact with a fluid with a higher  $\delta^{18}\text{O}$ . Ignore the dissolution of the crystal in the fluid (e.g., the fluid is already saturated with the crystal). Then  $^{18}\text{O}$  would diffuse into the crystal. Because fluid is a large reservoir and mass transport in the fluid is rapid,  $\delta^{18}\text{O}$  at the crystal surface would be maintained constant. Hence, this is again a half-space diffusion problem with uniform initial concentration and constant surface concentration. The evolution of  $\delta^{18}\text{O}$  with time is shown in Figure 1-8b.

### 1.4.1.3 Diffusion couple

If two samples of different composition are placed together in contact, then diffusion will occur to bridge the compositional difference and homogenize the



**Figure 1-8** Heat and mass diffusion in a semi-infinite medium in which the diffusion profile propagates according to square root of time. (a) The evolution of temperature profile of oceanic plate. The initial temperature is 1600 K. The surface temperature (at depth = 0) is 275 K. Heat diffusivity is  $1 \text{ mm}^2/\text{s}$ . (b) The evolution of  $\delta^{18}\text{O}$  profile in a mineral. Initial  $\delta^{18}\text{O}$  in the mineral is 1‰. The surface  $\delta^{18}\text{O}$  is 10‰.  $D = 10^{-22} \text{ m}^2/\text{s}$ .

two samples. The concentration evolution is plotted in Figure 1–9. The diffusion-couple profile may be regarded to consist of two profiles, one to the left ( $x < 0$ ) with a surface concentration that is the arithmetic average of the two initial concentrations, and one to the right ( $x > 0$ ), with the same surface concentration. The center composition gradually propagates into both sides.

#### 1.4.1.4 Homogenization of an oscillatory zoned crystal

Initially the concentration of a component in a crystal is a periodic function such as a sine (or cosine) function as follows:

$$C|_{t=0} = C_0 + A \sin(2\pi x/l), \quad (1-77)$$

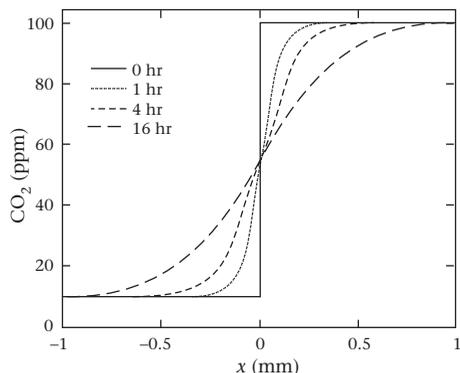
where  $A$  is the amplitude of the concentration fluctuation and  $l$  is the periodicity. As time progresses, the concentration profile would stay as a periodic function, but the amplitude would decrease with time:

$$C(x, t) = C_0 + Ae^{-4\pi^2 Dt/l^2} \sin(2\pi x/l). \quad (1-78)$$

The new amplitude is  $Ae^{-4\pi^2 Dt/l^2}$ , decreasing with time exponentially. The concentration evolution is diagrammed in Figure 1–10.

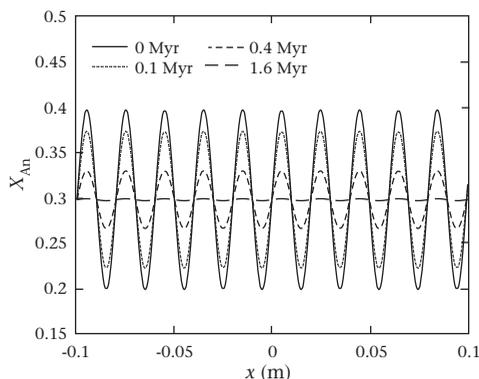
#### 1.4.1.5 Diffusion distance

The diffusion profile is a smooth profile. Even if the initial concentration distribution is not smooth, diffusion smoothes out any initial discontinuities. Therefore, there is no well-defined diffusion front (except for some special cases),



**Figure 1-9** The evolution of concentration profile in a diffusion couple of silicate melt.  $D = 1 \mu\text{m}^2/\text{s}$ . Initially, the concentration profile is a discontinuous step function. The profile then becomes smooth.

and it is difficult to define a diffusion distance. Nonetheless, as duration of diffusion increases, the diffusion profile becomes longer and its length is proportional to square root of time (Figures 1–7 to 1–10). Hence, it is useful to define a characteristic diffusion distance similar to the definition of half-life. Unfortunately, unlike the case for radioactive decay or first-order reactions where there is a unique definition of half-life, in diffusion, there is no unique definition of *characteristic diffusion distance*. Some authors define the characteristic distance as  $x_c = (Dt)^{1/2}$ , where  $x_c$  means the characteristic diffusion distance (if it would cause no confusion, the subscript “c” is often dropped from the notation). This definition roughly corresponds to the *midconcentration distance* (see definition below). Others define  $x_c = (4Dt)^{1/2}$ , and still others define  $x_c = (\pi Dt)^{1/2}$ . All formulas state that the characteristic “diffusion distance” is proportional to  $(Dt)^{1/2}$ .



**Figure 1-10** The evolution of concentration profile of an oscillatory zoned plagioclase crystal.  $D = 10^{-24} \text{m}^2/\text{s}$ . The width of each cycle is 0.02 mm. In 1.6 Myr, the crystal is nearly homogeneous.

To avoid confusion and maintain consistency, we need a unique definition of diffusion distance, similar to the concept of half-life. In this book, a midconcentration distance for diffusion ( $x_{\text{mid}}$ ) is defined. The *midconcentration distance* is the distance at which the concentration is halfway between the maximum and minimum along the profile at a specific time. For the half-space diffusion problem where  $x_{\text{mid}}$  is best defined because there is a definite surface where diffusion commences and the surface concentration is constant,

$$x_{\text{mid}} = 0.95387(Dt)^{1/2} \quad (1-79)$$

For the point source diffusion problem,

$$x_{\text{mid}} = (4Dt \ln 2)^{1/2} = 1.6651(Dt)^{1/2} \quad (1-80)$$

For a diffusion couple, the definition of  $x_{\text{mid}}$  requires some thinking because the mid-concentration of the whole diffusion couple is right at the interface, which does not move with time. This is because for a diffusion couple every side is diffusing to the other side. On the other hand, if a diffusion couple is viewed as two half-space diffusion problems with the interface concentration viewed as the fixed surface concentration, then,  $x_{\text{mid}}$  equals  $0.95387(Dt)^{1/2}$ , the same as the half-space diffusion problem.

Knowing that  $x_{\text{mid}} = \alpha(Dt)^{1/2}$ , one can also estimate the time required for diffusion to reach some depth  $x$  (that is, for the concentration at that depth to be halfway between the initial and final concentrations) using

$$t_{1/2} = x^2 / (\alpha^2 D) \quad (1-81)$$

**Example 1.4** Knowing  $D = 10^{-22} \text{ m}^2/\text{s}$ , for half-space diffusion, estimate the time for the depth of  $1 \text{ } \mu\text{m}$  to reach the midconcentration.

*Solution:* Because  $\alpha = 0.95387$  for half-space diffusion,

$$t_{1/2} = x^2 / (\alpha^2 D) = (10^{-6})^2 / (0.95387^2 \times 10^{-22}) \text{ s} = 348 \text{ yr}$$

#### 1.4.1.6 Microscopic view of diffusion

Statistically, diffusion can be viewed as random walk of atoms or molecules. Consider diffusion in an isotropic crystal, such as Mg and Mn exchange in spinel for a case in which the only concentration gradient is along the  $x$  direction. Consider now two adjacent lattice planes (left and right) at distance  $l$  apart. If the jumping distance of Mg is  $l$  and the frequency of Mg ions jumping away from the original position is  $f$ , then the number of Mg ions jumping from left to right is  $\frac{1}{6} n_L f dt$ , and the number of Mg ions jumping from right to left is  $\frac{1}{6} n_R f dt$ , where  $n_L$  and  $n_R$  are the number of Mg ions per unit area on the left-hand side plane and on the right-hand side plane. The factor  $\frac{1}{6}$  in the expressions is due to the fact that every ion jump can be decomposed to motion in six directions on three

orthogonal axes (left, right, up, down, front, back), and we are considering only one direction (from left to right or from right to left). The jumping frequency  $f$  is assumed to be the same from left to right or from right to left, i.e., random walk is assumed. Therefore, the net flux from the left plane to the right plane is

$$\mathbf{J} = \frac{1}{6}(n_L - n_R)f \cdot \psi \quad (1-82a)$$

Since  $n_L = lC_L$  and  $n_R = lC_R$ , where  $C_L$  and  $C_R$  are the concentrations of Mg on the two planes, then

$$\mathbf{J} = \frac{1}{6}l(C_L - C_R)f \cdot \psi \quad (1-82b)$$

Now because

$$C_L - C_R = -l \frac{\partial C}{\partial x} \quad (1-82c)$$

we have

$$\mathbf{J} = -\frac{1}{6}l^2 f \frac{\partial C}{\partial x} \cdot \psi \quad (1-82d)$$

Comparing this with Fick's law (Equation 1-71), we have

$$D = \frac{1}{6}l^2 f \cdot \psi \quad (1-82e)$$

Thus, microscopically, the diffusion coefficient may be interpreted as one-sixth of the jumping distance squared times the overall jumping frequency. Since  $l$  is of the order  $3 \times 10^{-10}$  m (interatomic distance in a lattice), the jumping frequency can be roughly estimated from  $D$ . For  $D \approx 10^{-17}$  m<sup>2</sup>/s such as Mg diffusion in spinel at 1400°C, the jumping frequency is  $6D/l^2 \sim 700$  per second. Because ion jumping requires a site to accept the ion, the jumping frequency in solids depends on the concentration of vacancies and other defects. In liquids, the jumping frequency depends on the flexibility of the liquid structure, and is hence related to viscosity.

For an anisotropic crystal, jumping frequencies in different directions may not be the same, and, hence,  $D$  along each crystallographic direction may be different. The relation between  $D$  and jumping frequency may be written as follows:

$$D_i = l_i^2 f_i, \quad (1-82f)$$

where  $D_i$  is diffusivity along a crystallographic direction  $i$ ,  $l_i$  is the jumping distance along the direction, and  $f_i$  is the jumping frequency along the direction.

### 1.4.2 Convection

Diffusion is one mode of mass transfer. If the phase is fluid or if the temperature is high for the solid to show fluid behavior, there is a second way to transfer mass,

which is fluid flow, sometimes referred to as convection, or convective mass transfer, or advection, depending on the authors and the problems at hand. (More strictly, especially in meteorology, advection means horizontal motion of gas and convection means vertical motion. However, the distinction is not always made.) There is mass flux due to fluid flow. In the case of unidirectional laminar flow along the  $x$  direction, the concentration variation as a function of  $x$  and  $t$  can be related through the following partial differential equation:

$$\frac{\partial C}{\partial t} = -u \frac{\partial C}{\partial x}, \quad (1-83)$$

where  $u$  is the flow rate along the  $x$ -direction. Because diffusion is always present, the full equation in the presence of flow is called the convective diffusion equation and is as follows:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - u \frac{\partial C}{\partial x}, \quad (1-84)$$

Convection enhances mass transfer. The general convective diffusion equation is not trivial to solve and will be dealt with later.

## 1.5 Kinetics of Heterogeneous Reactions

There are a variety of heterogeneous reactions. Most reactions encountered by geologists are heterogeneous reactions. The kinetic aspects of various heterogeneous reactions have been reviewed by a number of authors (Kirkpatrick, 1975, 1981; Berner, 1978). Heterogeneous reactions may be classified as at least three different types.

(1) The first and the simplest type is *component exchange* between phases without growth or dissolution of either phase. Examples include oxygen isotope exchange between two minerals, and  $\text{Fe}^{2+}$ - $\text{Mg}^{2+}$  exchange between olivine and garnet or between olivine and melt. This is essentially a diffusion problem.

(2) The second type is *simple phase transitions* in which one phase transforms into another of identical composition, e.g., diamond  $\rightarrow$  graphite, quartz  $\rightarrow$  coesite, and water  $\rightarrow$  ice. This type sounds simple, but it involves most steps of heterogeneous reactions, including nucleation, interface reaction, and coarsening.

(3) The third and the most common type is *complex phase transformations*, including the following: (i) some components in a phase combine to form a new phase (e.g.,  $\text{H}_2\text{O}$  exsolution from a magma to drive a volcanic eruption; the precipitation of calcite from an aqueous solution,  $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow$  calcite; the condensation of corundum from solar nebular gas; and the crystallization of olivine from a basaltic magma), (ii) one phase decomposes into several phases (e.g., spinodal decomposition, or albite  $\rightarrow$  jadeite + quartz), (iii) several phases combine into one phase (e.g., melting at the eutectic point, or jadeite + ←

(continued)

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