where $[SO_4^{2-}]°$ is the sulfate concentration at the surface.

Murray *et al.* (1978) applied this model to data from sediment cores taken from Saanich Inlet of British Columbia (Figure 5.38). Sedimentation rate, ω, was determined using ^{210}Pb (see Chapter 8) to be about 1 cm/yr, the factor α was independently estimated to be 0.5, with average porosity of 0.927. The value of D was taken to be $2.6 \times 10^{-6} cm^2/sec$. They fit an exponential curve of the form $c = a\,e^{-bx}$ to the data and found $a = 26.6$ and $b = 0.184$. From this they determined the rate constant to be $6.1 \times 10^{-9} sec^{-1}$, and the initial concentration of metabolizable organic matter to be 380 mM/cm^3 total sediment. The latter was somewhat larger than the value determined from the profile of total organic carbon in the core. To explain the discrepancy, the authors suggested that methane is produced below the depth where sulfate is depleted. Methane then diffuses upward and is oxidized by sulfate-reducing bacteria.
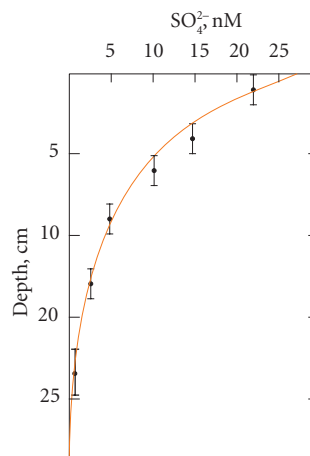

Figure 5.38   Dissolved sulfate concentrations in sediments from the Saanich Inlet. Data are shown as open circles with error bars. Curve is fitted using eqn. 5.161 and parameters given in the text. From Murray *et al.* (1978). With permission from Elsevier.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

Aagaard, P. and Helgeson, H.C. 1982. Thermodynamic and kinetic constraints on reaction rates among minerals and aqueous solutions, I. Theoretical considerations. *American Journal of Science*, 282: 237–85.

Albarède, F. 1995. *Introduction to Geochemical Modeling*. Cambridge, Cambridge University Press.

Anderson, D.E. 1981. Diffusion in electrolyte mixtures, in *Reviews in Mineralogy, Volume 8: Kinetics in Geochemical Processes* (eds A. Lasaga and R. Kirkpatrick), pp. 211–60. Washington, Mineralogical Society of America.

Berner, R.A. 1980. *Early Diagenesis*. Princeton, Princeton University Press.

Berner, R.A. 1981. Kinetics of weathering and diagenesis, in *Reviews in Mineralogy, Volume 8: Kinetics in Geochemical Processes* (eds A. Lasaga and R. Kirkpatrick), pp. 111–34. Washington, Mineralogical Society of America.

Blum, A. and Lasaga, A. 1988. Role of surface speciation in the low-temperature dissolution of minerals. *Nature*, 331: 431–3.

Blum, A. and Lasaga, A. 1991. The role of surface speciation in the dissolution of albite. *Geochimica et Cosmochimica Acta*, 55: 2193–201.

Broecker, W.S. and Oversby, V.M. 1971. *Chemical Equilibria in the Earth*, Chapter 5. New York, McGraw-Hill.

Carlson, W.D. 1980. *Experimental Studies of Metamorphic Petrogenesis*, PhD thesis, UCLA, Los Angeles.

Casey, W.H. and Bunker, B. 1990. The leaching of mineral and glass surfaces during dissolution, in *Reviews in Mineralogy, Volume 23: Mineral–Water Interface Geochemistry* (eds M. Hochella and A. White), pp. 397–426. Washington, Mineralogical Society of America.

Chermak, J.A. and Rimstidt, J.D. 1990. The hydrothermal transformation rate of kaolinite to muscovite/illite. *Geochimica et Cosmochimica Acta*, 54: 2979–90.

Chou, L. and Wollast, R. 1985. Steady-state kinetics and dissolution mechanisms of albite. *American Journal of Science*, 285: 965–93.

Crank, J. 1975. *The Mathematics of Diffusion*, 2nd edn. Oxford, Clarendon Press.

Dempster, T.J. 1985. Garnet zoning and metamorphism of the Barrovian type area, *Scotland. Contributions to Mineralogy and Petrology*, 89: 30–8.

Fisher, G.W. 1978. Rate laws in metamorphism. *Geochimica et Cosmochimica Acta*, 42: 1035–50.

Ganor, J., Mogollon, J.L. and Lasaga, A.C. 1995. The effect of pH on kaolinite dissolution rates and on activation energy. *Geochimica et Cosmochimica Acta*, 59: 1037–52.

Guy, C. and J. Schott. 1989. Multisite surface reaction versus transport control during the hydrolysis of a complex oxide. *Chemical Geology*, 78: 181–204.

Heinrich, W., Metz, P. and Gottshalk, M. 1989. Experimental investigation of the kinetics of the reaction 1 tremolite + 11 dolomite $\rightleftharpoons$ 8 fosterite + 13 calcite + 9CO$_2$ + 1 H$_2$O. *Contributions to Mineralogy and Petrology*, 102: 163–73.

Henderson, P. 1986. *Inorganic Geochemistry*. Oxford, Pergamon Press.

Hochella, M. and White, A. (ed.) 1990. *Mineral–Water Interface Geochemistry: Reviews in Mineralogy, Volume 23*. Washington, Mineralogical Society of America.

Hofmann, A.W., 1980. Diffusion in natural silicate melts, a critical review, in *Physics of Magmatic Processes* (ed. R.B. Hargraves). Princeton, Princeton University Press.

Kerrick, D.M., Lasaga, A.C. and Raeburn, S.P. 1991. Kinetics of heterogeneous reactions, in *Contact Metamorphism*, vol. 26 (ed. D.M. Kerrick), pp. 583–722. Washington, Mineralogical Society of America.

Kirkaldy, J. S. and Young, D.J. 1985. *Diffusion in the Condensed State*. London, Institute of Metals.

Kirkpatrick, R.J. 1981. Kinetics of crystallization of igneous rocks, in *Reviews in Mineralogy, Volume 8: Kinetics in Geochemical Processes* (eds A. Lasaga and R. Kirkpatrick), pp. 321–98. Washington, Mineralogical Society of America.

Laidler, K.J. 1987. *Chemical Kinetics*. New York, Harper Collins.

Lasaga, A.C. 1981a. Rate laws of chemical reactions, in *Reviews in Mineralogy, Volume 8: Kinetics in Geochemical Processes* (eds A. Lasaga and R. Kirkpatrick), pp. 1–68. Washington, Mineralogical Society of America.

Lasaga, A.C. 1981b. Transition state theory, in *Kinetics of Geochemical Processes*, *Reviews in Mineralogy 8* (eds A.C. Lasaga and R.J. Kirkpatrick), pp. 135–70. Washington, Mineralogical Society of America.

Lasaga, A.C. 1997. *Kinetic Theory in the Earth Sciences*. Princeton NJ, Princeton University Press.

Lasaga, A.C. and Kirkpatrick, R.J. (eds) 1981. *Reviews in Mineralogy, Volume 8: Kinetics in Geochemical Processes*. Washington, Mineralogical Society of America.

Lasaga, A.C., Soler, J.M., Burch, T.E. and Nagy, K.L. 1994. Chemical weathering rate laws and global geochemical cycles. *Geochimica et Cosmochimica Acta*, 58: 2361–86.

Lennie, A.R. and Vaughan, D.J. 1992. Kinetics of the marcasite-pyrite transformation: an infrared study. *American Mineralogist*, 77: 1166–71.

Liang, Y., Richter, F.M. and Chamberlin, L. 1997. Diffusion in silicate melts: III. Empirical models for multicomponent diffusion. *Geochimica Cosmochimica Acta*, 61: 5295–312.

McLean, D. 1965. The science of metamorphism in metals, in *Controls of Metamorphism* (eds W.S. Pitcher and G.W. Flinn), pp. 103–18. Edinburgh, Oliver and Boyd.

Morioka, M. and Nagasawa, H. 1990. *Ionic diffusion in olivine*, in *Advances in Physical Geochemistry, Volume 8, Diffusion, Atomic Ordering, and Mass Transport* (ed. J. Ganguly), pp. 176–97. New York, Springer-Verlag.

Murphy, W.M., Oelkers, E.H. and Lichtner, P.C. 1989. Surface reaction versus diffusion control of mineral dissolution and growth rates in geochemical processes. *Chem. Geol.* 78: 357–80.

Murray, J.W., Grundmanis, V. and Smethie, W.M. 1978. Interstital water chemistry in the sediments of Saanich Inlet. *Geochimica et Cosmochimica Acta*, 42: 1011–26.

Oxburgh, R., Drever, J.I. and Sun, T.-Y. 1994. Mechanism of plagioclase dissolution in acid solution at 25°C. *Geochimica et Cosmochimica Acta*, 58: 661–70.

Parks, G.A., 1990. Surface energy and adsorption at mineral/water interfaces: an introduction, in *Reviews in Mineralogy, Volume 23: Mineral–Water Interface Geochemistry* (eds M. Hochella and A. White), pp. 133–75. Washington, Mineralogical Society of America.

Pearson, D.G., Davies, G.R. and Nixon, P.H. 1995. Orogenic ultramafic rocks of UHP (diamond facies) origin, in *Ultrahigh Pressure Metamorphism* (eds R.G. Coleman and X. Wang), pp. 456–510. Cambridge, Cambridge University Press.

Schott, J., Berner, R.A. and Sjöberg, E.L. 1981. Mechanism of pyroxene and amphibole weathering – I. Experimental studies of iron-free minerals. *Geochimica et Cosmochimica Acta*, 45: 2123–35.

Sposito, G., 1989. *The Chemistry of Soils*. New York, Oxford University Press.

Stumm, W. (ed.) 1990. *Aquatic Chemical Kinetics: Reaction Rates of Processes in Natural Waters*. New York, Wiley-Interscience.

Stumm, W. and Wollast, R. 1990. Coordination chemistry of weathering: kinetics of the surface-controlled dissolution of oxide minerals. *Reviews in Geophysics*, 28: 53.

Toramaru, A. 1991. Model of nucleation and growth of crystals in cooling magmas. *Contributions to Mineralogy and Petrology*, 108: 106–17.

Tyrell, H.J.V. and Harris, K.R. 1984. *Diffusion in Liquids*. London, Butterworths.

Watson, E.B. 1982. Basalt contamination by continental crust: some experiments and models. *Contributions to Mineralogy and Petrology*, 80: 73–87.

Wehrli, R. and Stumm, W. 1988. Oxygenation of vanadyl(IV): Effect of coordinated surface hydroxyl groups and OH⁻. *Langmuir* 4: 753–8.

Wehrli, B., Sulzberger, B. and Stumm, W. 1989. Redox processes catalyzed by hydrous oxide surfaces. *Chem. Geol.* 78: 167–79.

Wollast, R. and Chou, L. 1992. Surface reactions during the early stages of weathering of albite. *Geochimica et Cosmochimica Acta*, 56: 3113–21.

Wood, B.J. and Walther, J.V. 1983. Rates of hydrothermal reactions. *Science*, 222: 413–15.

Zhang, Y. and Cherniak, D. (eds) 2010. *Diffusion in Minerals and Melts*. Washington, Mineralogical Society of America.

Zhong, S. and Mucci, A. 1993. Calcite precipitation in seawater using a constant addition technique: a new overall reaction kinetic expression. *Geochimica et Cosmochimica Acta*, 57: 1409–17.
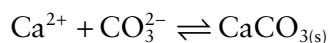
PROBLEMS

1. (a) Assuming that the precipitation of calcite from aqueous solution occurs only through the reaction:

$$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_{3(s)}$$
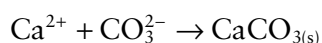
and that this reaction is *elementary*, write an equation for the rate of calcite precipitation.

   (b) Assuming that the reaction above is reversible, i.e.:

$$Ca^{2+} + CO_3^{2-} \rightleftharpoons CaCO_{3(s)}$$

and still assuming that it is *elementary*, write an equation for the dependence of *net* rate of calcite precipitation on concentration and free energy change of reaction.

2. Zhong and Mucci (1993) found that at constant concentration of dissolved Ca^{2+} ($[Ca^{2+}] \approx$ 10.5 mmol/kg), the rate of calcite precipitation in seawater obeyed the following rate law:

$$\mathfrak{R} = K_f[CO_3^{2-}]^3 - k_-$$

where $K_f = k_+(a_{Ca^{2+}})^n \gamma_{CO_3}^3 = 10^{3.5}$ and $k_- = 0.29$ (R is in units of μmol m^{-2} h^{-1}).

   (a) Is this rate law consistent with the mechanism of calcite precipitation in seawater being the elementary one described in problem 1 above, or with a more complex reaction mechanism? Justify your answer.

   (b) Using this rate law, predict the rate of calcite precipitation for concentrations of CO_3^{2-} of 0.04, 0.066, and 0.3 mmol/kg.

Rates of methane-hydroxyl reaction

T, °C	k
25	6.60×10^{-15}
10	4.76×10^{-15}
0	3.76×10^{-15}
−10	2.93×10^{-15}
−25	1.93×10^{-15}

3. Oxidation of methane in the atmosphere occurs through a number of mechanisms, including reaction with the hydroxyl radical:

$$OH + CH_4 \rightleftharpoons H_2O + CH_3$$
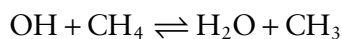
The rate of this reaction for a series of temperatures is shown in the adjacent table. Based on these data, estimate the activation energy and frequency factor for this reaction. (*HINT: Try using linear regression.*)

4. Schott *et al.* (1981) found that dependence on pH of the rate of dissolution of enstatite could be expressed as:

Rate of enstatite dissolution

pH	Rate moles Si/g-sec
1	2.75×10^{-10}
2	7.08×10^{-11}
6	2.82×10^{-13}

$$\mathfrak{R} = k a_{H^+}^n$$

where k shows a typical Arrhenius temperature dependence.

(a)   Reaction rates were measured at a series of pH values at constant temperature (22°C). These data are shown in the adjacent table. Using these data, estimate values of k and n for this temperature (*HINT: Try using linear regression.*)

T °C	Rate moles Si/g-sec
20	3.72×10^{-13}
50	2.34×10^{-12}
60	4.07×10^{-12}
75	8.13×10^{-12}

(b)   Reaction rates were also determined at various temperatures at constant pH (6). Using these data, estimate the activation energy and frequency factor for the rate constant.

(c)   Using your results from (a) and (b), estimate the rate of reaction (in moles Si released per sec per gram enstatite) at pH 4 and 30°C.

5. Marcasite and pyrite are polymorphs of FeS_2. Though pyrite has a lower ΔG_f than marcasite, the latter often forms metastably. Lennie and Vaughan (1992) found that the kinetics of the marcasite to pyrite transformation follows a simple first-order rate law:

$$-\frac{d\alpha}{dt} = k\alpha$$

where α is the volume fraction of marcasite and k has the usual Arrhenius temperature dependence with $A = 2.76 \times 10^{17} \sec^{-1}$ and $E_A = 253\,kJ/mol$. Assuming a system consisting initially of pure marcasite, calculate the time required for one half of the marcasite to convert to pyrite (i.e., $\alpha = 0.5$) at 300°C and 350°C.

6. If ΔG is the free energy of reaction for the reaction:

$$A + BC \rightarrow AC + B$$
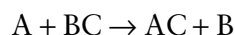
and assuming (1) this is an elementary reaction, (2) ideal behavior, and (3) it is a reversible reaction, show that the ratio of the forward and reverse rates of the reaction is:
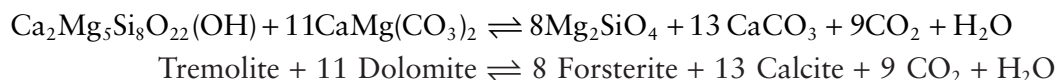
$$\frac{\mathfrak{R}_+}{\mathfrak{R}_-} = e^{-\Delta G/RT} \qquad\qquad (5.55\_1)$$

(*HINT: Start with eqn. 5.41.*)

7. On a temperature–pressure diagram, draw a line such that the time required for complete conversion of a 1 mm aragonite crystal to calcite will be complete within 10^5 years. Assume

spherically symmetric growth of calcite from a single nucleus in the center. Use the thermodynamic data in Table 2.2 and $\Delta G^* = 184\,kJ$ (see Example 5.4).

8. Using the data given in Example 5.5 for the reaction:

$$Ca_2Mg_5Si_8O_{22}(OH) + 11CaMg(CO_3)_2 \rightleftharpoons 8Mg_2SiO_4 + 13\,CaCO_3 + 9CO_2 + H_2O$$

$$\text{Tremolite} + 11\ \text{Dolomite} \rightleftharpoons 8\ \text{Forsterite} + 13\ \text{Calcite} + 9\ CO_2 + H_2O$$

make a plot of the relative volume of dolomite (V_{Do}/V_{Do0}) as a function of time assuming an initial temperature of 620°C (the equilibrium temperature) and a heating rate of 0.1°C per year. (*HINT:* Because the reaction is fast, the overall temperature change will be small, so you may assume that T (i.e. absolute temperature) is constant. However, because the temperature is close to the equilibrium temperature, the change in the temperature overstep, ΔT, will be significant. Approximate ΔG as $\Delta S \Delta T$ (as in Example 5.5) and express ΔT as a function of time, $\Delta T = R_H t$ where R_H is the heating rate, then integrate.)

9. The transformation of kaolinite to illite (muscovite) may be written as:

$$K^+ + 1.5Al_2Si_2O_5(OH)_4 \rightleftharpoons H^+ + KAl_3Si_3O_{10}(OH)_2 + 1.5H_2O$$
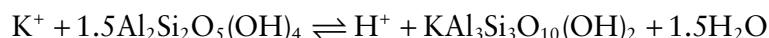
Chermack and Rimstidt (1990) determined that the forward rate of reaction was:

$$-\frac{d[K^+]}{dt} = k_+[K^+]$$

Forward and reverse rate constants for the reaction were determined to be:

$$\ln k_+ = 12.90 - 1.87 \times 10^4/T \quad \text{and} \quad \ln k_- = 6.03 - 1.21 \times 10^4/T$$

(a) What are the activation energies for the forward and reverse reactions?
(b) What is the equilibrium constant for this reaction at 275°C ?
(c) Make a plot of $\log \Re_{net}$ vs. $\log ([H^+]/[K^+])$ at 250°C, assuming a K^+ concentration of $2.0 \times 10^{-6}\,M$, ideal solution, that muscovite and kaolinite are pure phases, and that the forward and reverse reactions are elementary.

10. Using the data in Table 5.2, determine along which crystallographic axis Sr diffuses fastest in diopside at 1000°C.

11. Using the data in Example 5.8, calculate the diffusion flux for Mg and Fe in garnet.

12. A remarkable feature of sediments recording the Cretaceous–Tertiary Boundary is an enrichment in iridium (Ir) at the boundary, which is often marked by a boundary clay. Imagine a boundary clay 5 cm thick that initially has a uniform Ir concentration of 20 ppb. Assume that sediments above and below the boundary clay contain negligible Ir. If the detection limit for Ir is 2 ppb, how thick would the Ir-enriched layer be after 60 million years if the diffusion coefficient for Ir is $10^{-15}\,cm^2/sec$?

13. Show that the partial molar surface area, a, of a cube is $4v/r$ where v is the partial molar volume and r is the length of a side.

14. Assuming a surface free energy of $10^{-4}\,J/cm^2$, $\bar{V} = 101\,cc/mol$, $\Delta H_m = 54.84\,kJ/mol$, and $T_m = 1118°C$, what is the critical radius for a spherical albite crystal growing in a pure albite

melt that has been undercooled by 10°, 20°, and 30°C? Make a plot of ΔG_{tot} as a function of crystal radius for each of these temperatures. (*HINT*: your scale should span only 10 or 20 use microns.)

15. Crystal growth and dissolution are reactions that involve both diffusion and surface reactions occurring in series (i.e., a component of a growing crystal must first be delivered to the surface, then incorporated into the growing crystal). Either of these processes can be the rate-limiting step at 25°C. Diffusion in aqueous solutions typically has an activation energy of 20 kJ/mol, whereas surface reactions in aqueous solution typically have activation energies of 60–80 kJ/mol. Assuming the rates of diffusion and surface reaction for growth of a certain mineral from aqueous solution are approximately equal at 25°C, will diffusion or surface reaction be rate-limiting at 200°C?

16. Some anaerobic bacteria can utilize Mn^{4+} to oxidize organic matter. The reaction may be represented as:

$$2MnO_2(s) + CH_2O + H_2O \rightleftharpoons 2Mn^{2+} + CO_2 + 4OH^-$$
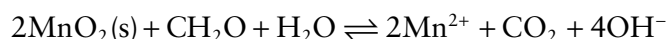
In its oxidized form, Mn is highly insoluble and effectively immobile in sediment. However, in its reduced form, Mn is soluble and mobile. Imagine that at a depth of 50 cm in actively depositing marine sediments, conditions become sufficiently reducing so that the reaction above occurs. Furthermore, assume that reaction is such that a constant concentration of 0.02 mM of Mn^{2+} is maintained at this depth and below. Above this depth, Mn^{2+} is oxidized and precipitated through reactions such as:

$$Mn^{2+} + 2OH^- + \frac{1}{2}O_2 \rightleftharpoons MnO_2(s) + H_2O$$
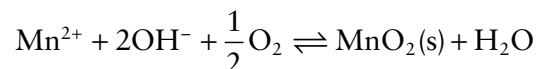
Assuming: (1) that the rate of the above reaction may be written as:

$$-\frac{d[Mn^{2+}]}{dt} = k[Mn^{2+}]$$

(2) k for this reaction is $10^{-8} sec^{-1}$, (3) the concentration of Mn^{2+} at the sediment–water interface is 0 and that diffusion from below is the sole source of Mn^{2+} between 0 and 50 cm, (4) D is 5×10^{-6} cm/sec, (5) a sedimentation rate of 1 cm/yr, (6) there is no advection, compaction, or bioturbation, and (7) a porosity of 0.85, make a plot of the concentration of dissolved Mn^{2+} vs. depth at steady state.

17. Diamond is remarkably stable at the surface of the Earth. Pearson *et al.* (1995) estimated that to convert 1 cc of diamond to graphite at 0.1 MPa and 1000°C would require 1 billion years, but only a million years would be required at 1200°C. From the difference in these rates, estimate the activation energy for the diamond–graphite transition.

Chapter 6

Aquatic chemistry

6.1 INTRODUCTION

Water continually transforms the surface of the Earth, through interaction with the solid surface and transport of dissolved and suspended matter. Beyond that, water is essential to life and central to human activity. Thus as a society, we are naturally very concerned with water quality, which in essence means water chemistry. Aquatic chemistry is therefore the principal concern of many geochemists.

In this chapter, we learn how the tools of thermodynamics and kinetics are applied to water and its dissolved constituents. We develop methods, based on the fundamental thermodynamic tools already introduced, for predicting the species present in water at equilibrium. We then examine the interaction of solutions with solids through precipitation, dissolution, and adsorption.

Most reactions in aqueous solutions can be placed in one of the following categories:
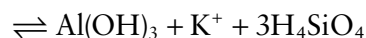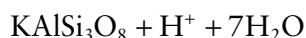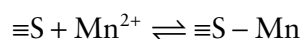
- Acid–base, e.g., dissociation of carbonic acid:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$
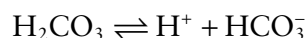
- Complexation, e.g., hydrolysis of mercury:

$$Hg^{2+} + H_2O \rightleftharpoons Hg(OH)^+ + H^+$$
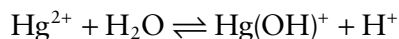
- Dissolution/precipitation, e.g., dissolution of orthoclase:

$$KAlSi_3O_8 + H^+ + 7H_2O$$
$$\rightleftharpoons Al(OH)_3 + K^+ + 3H_4SiO_4$$

- Adsorption/desorption, e.g., adsorption of Mn on a clay surface:

$$\equiv S + Mn^{2+} \rightleftharpoons \equiv S - Mn$$

(where we are using $\equiv S$ to indicate the surface of the clay).

6.2 ACID–BASE REACTIONS

The hydrogen and hydroxide ions are often participants in all the foregoing reactions. As a result, many of these reactions are pH-dependent. In order to characterize the state of an aqueous solution, that is, to determine how much $CaCO_3$ a solution will dissolve, the complexation state of metal ions, or the redox state of Mn, the first step is usually to determine pH. On a larger scale, weathering of rock and precipitation of sediments depend critically on pH. Thus pH is sometimes called the *master variable* in aquatic systems. We note in passing that while pH represents the hydrogen ion, or proton concentration, the hydroxide ion concentration is easily calculated from pH since the proton and hydroxide concentrations are related by the dissociation constant for water by:

$$K_W = a_{H^+} a_{OH^-} \qquad (6.1)$$

The value of K_W, like all equilibrium constants, depends upon temperature, but is 10^{-14} at 25°C.

Arrhenius defined an *acid* as a substance that upon solution in water releases free protons. He defined a *base* is a substance that releases hydroxide ions in solution. These are useful definitions in most cases. However, chemists generally prefer the definition of Brønstead, who defined acid and base as proton donors and proton acceptors respectively. The strength of an acid or base is measured by its tendency to donate or accept protons. The dissociation constant for an acid or base is the quantitative measure of this tendency and thus is a good indication of its strength. For example, dissociation of HCl:

$$HCl \rightleftharpoons H^+ + Cl^-$$
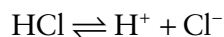
has a dissociation constant:

$$K_{HCl} = \frac{a_{H^+} a_{Cl^-}}{a_{HCl}} = 10^3$$

HCl is a strong acid because only about 3% of the HCl molecules added will remain undissociated. The equilibrium constant for dissociation of hydrogen sulfide:
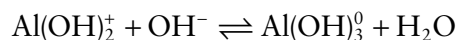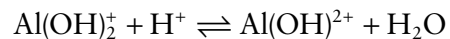
$$H_2S \rightleftharpoons H^+ + HS^-$$

is:

$$K_{H_2S} = \frac{a_{H^+} a_{HS^-}}{a_{H_2S}} = 10^{-7.1}$$

Thus H_2S is a weak acid because very few of the H_2S molecules actually dissociate except at high pH.

Metal hydroxides can either donate or accept protons, depending upon pH. For example, we can represent this in the case of aluminum as:

$$Al(OH)_2^+ + H^+ \rightleftharpoons Al(OH)^{2+} + H_2O$$

$$Al(OH)_2^+ + OH^- \rightleftharpoons Al(OH)_3^0 + H_2O$$

Compounds that can either accept or donate protons are said to be *amphoteric.*

Metals dissolved in water are always surrounded by solvation shells. The positive charges of the hydrogens in the surrounding water molecules are to some extent repelled by the positive charge of the metal ion. For this reason, water molecules in the solvation shell are more likely to dissociate and give up a proton more readily than other water molecules. Thus the concentration of such species will affect pH.

Most protons released by an acid will complex with water molecules to form hydronium ions, H_3O^+ or even $H_5O_2^+$. However, in almost all cases we need not concern ourselves with this and can treat the H^+ ion as if it were a free species. Thus we will use $[H^+]$ to indicate the concentration of $H^+ + H_3O^+ + H_5O_2^+ + \ldots$

6.2.1 Proton accounting, charge balance, and conservation equations

6.2.1.1 Proton accounting

Knowing the pH of an aqueous system is the key to understanding it and predicting its behavior. This requires a system of accounting for the H^+ and OH^- in the system. There are several approaches to doing this. One such approach is the *proton balance equation* (e.g., Pankow, 1991). In this system, both H^+ and OH^- are considered components of the system, and the proton balance equation is written such that *the concentration of all species whose genesis through reaction with water caused the production of OH^- are written on one side, and the concentration of all species whose genesis through reaction with water caused the production of H^+ are written on the other side*. Because water dissociates to form one H^+ and one OH^-, $[H^+]$ always appears on the left side and OH^- always appears on the right side of the proton balance equation. The proton balance equation for pure water is thus:

$$[H^+] = [OH^-] \qquad (6.2)*$$

Thus in pure water the concentrations of H^+ and OH^- are equal.

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*Be careful not to confuse algebraic expressions, written with an equal sign, such as the proton balance equation, with chemical reactions, written with the reaction symbol, $\rightleftharpoons$, or similar. In this case, it is obvious that this is not a balanced chemical reaction, but that will not always be the case.

Now, consider the example of a nitric acid solution. H^+ will be generated both by dissociation of water and dissociation of nitric acid:
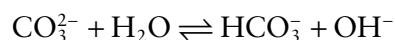
$$HNO_3 \rightleftharpoons H^+ + NO_3^-$$
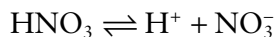
Since one NO_3^- ion is generated for every H^+, the proton balance equation becomes:

$$[H^+] = [OH^-] + [NO_3^-] \qquad (6.3)$$

Next consider a solution of calcium carbonate. We specify the calcium and carbonate ions as components. Hydrogen ions may be generated by hydrolysis of calcium:
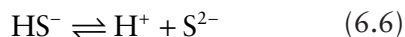
$$Ca^{2+} + H_2O \rightleftharpoons H^+ + Ca(OH)^+$$
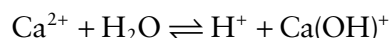
and hydroxide ions may be generated by:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

The proton balance equation for this reaction is:

$$[H^+] + [HCO_3^-] = [OH^-] + [Ca(OH)^+] \quad (6.4)$$

Now consider a solution of a *diprotonic* acid such as H_2S. H_2S can undergo two dissociation reactions:

$$H_2S \rightleftharpoons H^+ + HS^- \qquad (6.5)$$
$$HS^- \rightleftharpoons H^+ + S^{2-} \qquad (6.6)$$

For every HS^- ion produced by dissociation of H_2S, one H^+ ion would have been produced. For every S^{2-} ion, however, $2H^+$ would have been produced, one from the first dissociation and one from the second. The proton balance equation is thus:

$$[H^+] = [OH^-] + [HS^-] + 2[S^{2-}] \qquad (6.7)$$

An alternative approach to the proton balance equation is the *TOTH proton mole balance equation* used by Morel and Hering (1993). In this system, *H^+ and H_2O are always chosen as components* of the system but OH^- is not. The species OH^- is the algebraic sum of H_2O less H^+:
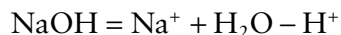
$$OH^- = H_2O - H^+ \qquad (6.8)$$

An implication of this selection of components is that when an acid, such as HCl, is present, we choose the conjugate anion as the component, so that the acid HCl is formed from components:

$$HCl = Cl^- + H^+$$

For bases, such as NaOH, we choose the conjugate cation as a component. The base, NaOH, is formed from components as follows:

$$NaOH = Na^+ + H_2O - H^+$$

Because aquatic chemistry almost always deals with dilute solutions, the concentration of H_2O may be considered fixed at a mole fraction of 1, or 55.4 M. Thus in the Morel and Hering system, H_2O is made an *implicit* component, that is, its presence is assumed but not written, so that eqn. 6.8 becomes:

$$OH^- = -H^+ \qquad (6.9)$$

The variable TOTH is the total amount of component H^+, rather than the total of species H^+. Every species containing the component H^+ contributes positively to *TOTH* while every species formed by subtracting component H^+ contributes negatively to *TOTH*. Because we create the species OH^- by subtracting component H^+ from component H_2O, the total of component H^+ for pure water will be:

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

Thus *TOTH* in this case is the difference between the concentrations of H^+ and OH^-. Of course, in pure water, $[H^+] = [OH^-]$, so *TOTH* = 0.

Now let's consider our example of the $CaCO_3$ solution. In addition to H^+ and H_2O, we choose Ca^{2+} and CO_3^{2-} as components. In the proton mole balance equation, HCO_3^- counts positively (since $HCO_3^- = CO_3^{2-} + H^+$) and $CaOH^+$ (since $CaOH^+ = Ca^{2+} + H_2O - H^+$) negatively:

$$TOTH = [H^+] + [HCO_3^-] - [OH^-] - [Ca(OH)^+] \quad (6.10)$$

Comparing eqns. 6.10 and 6.4, we see that the *TOTH* is equal to the difference between the left and right hand sides of the proton balance equation, and that in this case *TOTH* = 0. This makes sense, because, having added neither $[H^+]$ nor $[OH^-]$ to the solution,

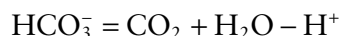the total of the component H the solution contains should be 0.

Now consider the dissolution of CO_2 in water to form carbonic acid:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (6.11)$$
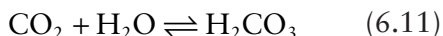
Under the right conditions of pH, this carbonic acid will dissociate to form bicarbonate ion:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (6.12)$$
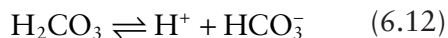
If we choose CO_2 as our component, bicarbonate ion would be made from components CO_2, H_2O, and H^+:

$$HCO_3^- = CO_2 + H_2O - H^+$$

Thus in the *TOTH* proton mole balance equation, bicarbonate ion would count negatively, so *TOTH* is:

$$TOTH = [H^+] - [OH^-] - [HCO_3^-] \quad (6.13)$$

Alternatively, had we defined CO_3^{2-} as a component, then species HCO_3^- is formed by the components:

$$HCO_3^- = H^+ + CO_3^{2-}$$

In this case, the proton mole balance equation is:

$$TOTH = [H^+] - [OH^-] + [HCO_3^-] \quad (6.13a)$$

Here we see that *TOTH* depends on how we define our components.

6.2.1.2   Conservation equations

A further constraint on the composition of a system is provided by *mass balance*. Acid–base reactions will not affect the total concentration of a substance. Thus regardless of reactions 6.5 and 6.6, and any other complexation reactions, such as

$$Pb^{2+} + S^{2-} \rightleftharpoons PbS_{aq}$$
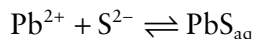
the total concentration of sulfide remains constant. Thus we may write:

$$\Sigma S = [H_2S] + [HS^-] + [S^{2-}] + [PbS_{aq}] + \ldots$$

We can write one mass balance, or *conservation*, equation for each component in solu-

tion. Of course for components such as Na that form only one species, Na^+ in this case, the mass balance equation is trivial. Mass balance equations are useful for those components forming more than one species.

While the charge balance constraint is an absolute one and always holds, mass balance equations can be trickier because other processes, such as redox, precipitation, and adsorption, can affect the concentration of a species. We sometimes get around this problem by writing the mass balance equation for an element, since an elemental concentration is not changed by redox processes. We might also define our system such that it is closed to get around the other problems. Despite these restrictions, mass balance often provides a useful additional constraint on a system.

6.2.1.3   Charge balance

As we saw in Chapter 3, solutions are electrically neutral; that is, the number of positive and negative charges must balance:

$$\boxed{\sum_i m_i z_i = 0} \qquad (6.14)$$

where m is the number of moles of ionic species i and z is the charge of species i. Equation 6.14 is known as the *charge balance equation* and is identical to eqn. 3.99. This equation provides an important constraint on the composition of a system. Notice that in some cases, the proton balance and charge balance equations are identical (e.g., eqns. 6.2 and 6.7).

For each acid–base reaction, an equilibrium constant expression may be written. By manipulating these equilibrium constant expressions as well proton balance, charge balance, and mass balance equations, it is possible to predict the pH of any solution. In natural systems where there are many species present, however, solving these equations can be a complex task indeed. An important step in their solution is to decide which reactions have an insignificant effect on pH and neglect them.

6.2.2   The carbonate system

We now turn our attention to carbonate. Water at the surface of the Earth inevitably contains dissolved CO_2, either as a result of

equilibration with the atmosphere or because of respiration by organisms. CO_2 reacts with water to form *carbonic acid*:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \qquad (6.15)$$
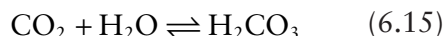
Some of the carbonic acid dissociates to form bicarbonate and hydrogen ions:

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \qquad (6.16)$$

Some of the bicarbonate will dissociate to an additional hydrogen ion and a carbonate ion:

$$HCO_3^- \rightleftharpoons H^+ + CO_3^{2-} \qquad (6.17)$$

We can write three equilibrium constant expressions for these reactions:

$$K_{sp} = \frac{a_{H_2CO_3}}{f_{CO_2}} \qquad (6.18)$$

$$K_1 = \frac{a_{H^+} a_{HCO_3^-}}{a_{H_2CO_3}} \qquad (6.19)$$

$$K_2 = \frac{a_{H^+} a_{CO_3^{2-}}}{a_{HCO_3^-}} \qquad (6.20)$$

The equilibrium constants for these reactions are given in Table 6.1 as a function of temperature.

In the above series of reactions, we have simplified things somewhat and have assumed that dissolved CO_2 reacts completely with water to form H_2CO_3. This is actually not the case, and much of the dissolved CO_2 will actually be present as distinct molecular species, $CO_{2(aq)}$. Thus reaction 6.15 actually consists of the two reactions:

$$CO_{2(g)} \rightleftharpoons CO_{2(aq)} \qquad (6.15a)$$

$$CO_{2(aq)} + H_2O \rightleftharpoons H_2CO_3 \qquad (6.15b)$$
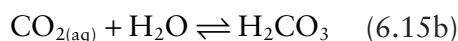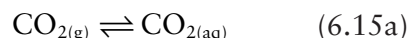
The equilibrium for the second reaction favors $CO_{2(aq)}$. However, it is analytically difficult to distinguish between the species $CO_{2(aq)}$ and H_2CO_3. For this reason, $CO_{2(aq)}$ is often combined with H_2CO_3 when representing the aqueous species. The combined total concentration of $CO_{2(aq)} + H_2CO_3$ is sometimes written as $H_2CO_3^*$. We will write it simply as H_2CO_3.

The importance of the carbonate system is that by dissociating and providing hydrogen ions to solution, or associating and taking up free hydrogen ions, *it controls the pH of many natural waters*. Example 6.2 shows that pure water in equilibrium with atmospheric CO_2 will be slightly acidic. The production of free H^+ ions as a result of the solution of CO_2 and dissociation of carbonic acid plays an extremely important role in weathering.

Table 6.1 Equilibrium constants for the carbonate system. After Plummer and Busenberg (1982). With permission from Elsevier.

T (°C)	pKCO₂[‡]	pK₁	pK₂	pK$_{cal}$	pK$_{arag}$	pK$_{CaHCO_3^+}$[*]	pK$_{CaCO_3^0}$[†]
0	1.11	6.58	10.63	8.38	8.22	−0.82	−3.13
5	1.19	6.52	10.55	8.39	8.24	−0.90	−3.13
10	1.27	6.46	10.49	8.41	8.26	−0.97	−3.13
15	1.34	6.42	10.43	8.43	8.28	−1.02	−3.15
20	1.41	6.38	10.38	8.45	8.31	−1.07	−3.18
25	1.47	6.35	10.33	8.48	8.34	−1.11	−3.22
30	1.52	6.33	10.29	8.51	8.37	−1.14	−3.27
45	1.67	6.29	10.20	8.62	8.49	−1.19	−3.45
60	1.78	6.29	10.14	8.76	8.64	−1.23	−3.65
80	1.90	6.34	10.13	8.99	8.88	−1.28	−3.92
90	1.94	6.38	10.14	9.12	9.02	−1.31	−4.05

[*]$K_{CaHCO_3^+} = a_{CaHCO_3^+}/(a_{Ca^{2+}} a_{HCO_3^-})$

[†]$K_{CaCO_3^0} = a_{CaCO_3^0}/(a_{Ca^{2+}} a_{CO_3^{2-}})$

[‡]Pressure in units of bars.

Example 6.1   Proton, mass, and charge balance equations for Na_2CO_3 solution

Write the proton, proton mass balance, charge balance, and carbonate conservation equations for a solution prepared by dissolving Na_2CO_3 in water. Assume that $NaCO_3$ dissociates completely and that the system is closed.

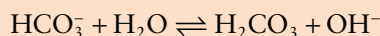*Answer:* We begin with the proton balance equation. From the dissociation of water we have:

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

In addition to this, hydroxide ions will also be generated by reaction between CO_3^{2-} and water:

$$CO_3^{2-} + H_2O \rightleftharpoons HCO_3^- + OH^-$$

and

$$HCO_3^- + H_2O \rightleftharpoons H_2CO_3 + OH^-$$
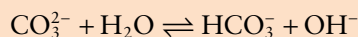
Since for each HCO_3^- formed, one OH^- must have formed and for each H_2CO_3 present, two OH^- must have formed, the proton balance equation is:

$$[H^+] + [HCO_3^-] + 2[H_2CO_3] = [OH^-] \tag{6.21}$$

Choosing CO_2 and sodium ions as components (in addition to H^+ and H_2O), the three carbonate species are made from components as follows:

$$H_2CO_3 = H_2O + CO_2$$

$$HCO_3^- = H_2O + CO_2 - H^+$$

$$CO_3^{2-} = H_2O + CO_2 - 2H^+$$
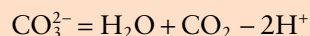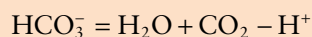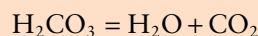
In this case, the proton mole balance equation is:

$$TOTH = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \tag{6.22}$$

The charge balance equation is:

$$[H^+] + [Na^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \tag{6.23}$$

The conservation equation for carbonate species is:

$$\Sigma CO_3 = [CO_3^{2-}] + [HCO_3^-] + [H_2CO_3] \tag{6.24}$$

Since the dissolution of Na_2CO_3 produces two moles of Na^+ for every mole of carbonate species, we may also write:

$$[Na^+] = 2\Sigma CO_3 = 2([CO_3^{2-}] + [HCO_3^-] + [H_2CO_3])$$

Ground waters may not be in equilibrium with the atmosphere, but will nonetheless contain some dissolved CO_2 (see Example 6.3). Because of respiration of organisms in soil (mainly plant roots and bacteria) through which they pass before penetrating deeper, ground waters often contain much more CO_2 than water in equilibrium with the atmosphere. In addition, calcite and other carbonates are extremely common minerals in soils and in sedimentary, metamorphic, and altered igneous rocks. Ground waters will tend to

Example 6.2   pH of water in equilibrium with the atmosphere

What is the pH of water in equilibrium with the atmospheric CO_2 at 25°C, assuming ideal behavior and no other dissolved solids or gases present? The partial pressure of CO_2 in the atmosphere is 3.9×10^{-4}.

Answer: In this case, the proton balance and charge balance equations are identical:

$$[H^+] = [OH^-] + [HCO_3^-] + 2[CO_3^{2-}] \qquad (6.25)$$

We might guess that the pH of this solution will be less than 7 (i.e., $[H^+] > 10^{-7}$). Under these circumstances, the concentrations of the hydroxyl and carbonate ions will be much lower than those of the hydrogen and bicarbonate ions. Assuming we can neglect them, our equation then becomes simply:

$$[H^+] \cong [HCO_3^-] \qquad (6.25a)$$

We can combine eqns. 6.18 and 6.19 to obtain an expression for bicarbonate ion in terms of the partial pressure of CO_2:

$$[HCO_3^-] = (K_1 K_{CO_2} P_{CO_2}) / [H^+]$$

Substituting this into 6.25a and rearranging, we have:

$$[H^+]^2 \cong K_1 K_{CO_2} P_{CO_2} \qquad (6.26)$$

Taking the negative log of this expression and again rearranging, we obtain:

$$pH \cong \frac{-\log K_1 - \log K_{CO_2} - \log P_{CO_2}}{2}$$

Substituting values from Table 6.1, we calculate pH = 5.61. Looking at Figure 6.1, we can be assured that our assumption that carbonate and hydroxyl ion abundances are valid. Indeed, an exact solution using the Solver in Excel™ differs from the approximate one by less than 0.0001 pH units.

approach equilibrium with calcite by either dissolving it or precipitating it:

$$CaCO_3 \rightleftharpoons Ca^{2+} + CO_3^{2-} \qquad (6.27)$$
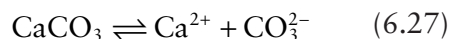
Carbonate ions produced in this way will associate with hydrogen ions to form bicarbonate as in reaction 6.17, increasing the pH of the solution. Water containing high concentrations of calcium (and magnesium) carbonate is referred to as "hard water"; such waters are generally somewhat alkaline.

Now suppose we have a known activity of all carbonate species in solution, say for example 10^{-2}:

$$a_{H_2CO_3} + a_{HCO_3^-} + a_{CO_3^{2-}} = \Sigma CO_2 = 10^{-2} \qquad (6.28)$$

From this, and the dissociation constants, we can calculate the amount of each species

present as a function of pH and temperature. For example, we can use the equilibrium constant expressions to obtain substitutions for the carbonic acid and carbonate ion activities in eqn. 6.28 that are functions of bicarbonate ion activity and pH. We then solve eqn. 6.28 to obtain an expression for the activity of the bicarbonate ion as a function of total CO_2 and hydrogen ion activity:

$$a_{HCO_3^-} = \frac{\Sigma CO_2}{(a_{H^+}/K_1)+1+(K_2/a_{H^+})} \quad (6.29)$$

Similar equations may be found for carbonic acid and carbonate ion. Carrying out these calculations at various pH values, we can construct the graph shown in Figure 6.1. In this figure, we see that carbonic acid is the dominant species at low pH, bicarbonate at intermediate pH, and carbonate at high pH.

6.2.2.1 Equivalence points

Particularly simple relationships occur when the activities of two species are equal. The pH where this occurs, known as an equivalence point, is determined by eqns. 6.19 and 6.20. For example, the point where carbonic acid concentration
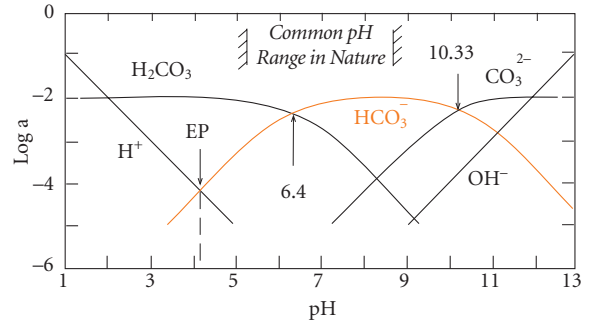

Figure 6.1 Activities of different species in the carbonate system as a function of pH, assuming $\Sigma CO_2 = 10^{-2}$. From Drever (1988).

equals bicarbonate concentration can be determined by rearranging eqn. 6.19:

$$\frac{a_{HCO_3^-}}{a_{H_2CO_3}} = \frac{K_1}{a_{H^+}} = 1 \quad (6.30a)$$

and therefore:

$$a_{H^+} = K_1 = 10^{-6.35} \quad (6.30b)$$

Example 6.3 pH of a solution with fixed total carbonate concentration

Groundwater moving through soil into a deep aquifer acquires a total dissolved CO_2 concentration of 10^{-2} M. Assuming the water does not exchange with surrounding rock, ideal behavior, and no other dissolved solids or gases, what is the pH of the water?

Answer: In this case, our charge and proton balance equations are the same as in Example 6.2, i.e., eqn. 6.25. Since the solution does not exchange with surrounding rock, it can be considered a closed system and we can write the following mass balance equation:

$$\Sigma CO_2 = [H_2CO_3]+[HCO_3^-]+[CO_3^{2-}] = 10^{-2} \quad (6.31)$$

Simultaneously solving the change balance and mass balance equations, and using equilibrium constant expressions to eliminate carbonate and OH species, we obtain:

$$[H^+]^4 + K_1[H^+]^3 + \{K_2K_1 - K_W - K_1\Sigma CO_2\}[H^{2+}] - \{K_w + 2K_2\Sigma CO_2\}K_1[H^+] - K_2K_1K_W = 0$$

We might again guess that the concentration of the carbonate ion will be very low, and that we can therefore neglect all terms in which K_2 occurs. We might also guess that pH will be acidic so that $[H^+] \gg [OH^-]$, and therefore that we can neglect terms containing K_W. Our equation becomes:

$$K_1^{-1}[H^+]^2 + [H^+] = \Sigma CO_2$$

Solving this quadratic, we find that pH = 4.18.

The point labeled EP on Figure 6.1 is called the *CO₂ equivalence point*. At this point, the concentration of the carbonate ion is extremely low, and there is exactly enough H⁺ to convert all HCO_3^- to H_2CO_3. From the perspective of the proton balance, then, the HCO_3^- concentration is equivalent to the same concentration of H_2CO_3. In a similar way, the point where the carbonic acid and carbonate ion concentrations are equal is called the *bicarbonate equivalence point*, and that where bicarbonate and hydroxyl concentrations are equal is called the *carbonate equivalence point*.

The exact concentrations of carbonate species depend on total carbonate concentration as well as the concentration of other ions in solution. Thus the distribution shown in Figure 6.1 is unique to the conditions specified ($\Sigma CO_2 = 10^{-2}$, no other ions present). Nevertheless, the distribution will be qualitatively similar for other conditions.

6.2.3   Conservative and non-conservative ions

We can divide dissolved ions into *conservative* and *non-conservative* ones. The conservative ions are those whose concentrations are not affected by changes in pH, temperature, and pressure, *assuming no precipitation or dissolution*. In natural waters, the principal conservative ions are Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, SO_4^{2-} and NO_3^-. These ions are conservative because they are fully dissociated from their conjugate acids and bases over the normal range of pH of natural waters. Non-conservative ions are those that will undergo association and dissociation reactions in this pH range. These include the proton, hydroxyl, and carbonate species as well as $B(OH)_4^-$, $H_3SiO_4^-$, HS^-, NH_4OH, phosphate species, and many organic anions. Virtually all the non-conservative species are anions, the two principle exceptions being H^+ and NH_4OH (which dissociates to form NH_4^+ at low pH). Variations in the concentrations of non-conservative ions result from reactions between them, and these reactions can occur in the absence of precipitation or dissolution. For example, reaction of the carbonate and hydrogen ion to form bicarbonate will affect the concentrations of all three ions. Of course, if the system is at equilibrium, this reaction will not occur in the absence of an external disturbance, such as a change in temperature.

6.2.4   Total alkalinity and carbonate alkalinity

Alkalinity is a measure of acid-neutralizing capacity of a solution and is defined as the sum of the concentration (in equivalents) of bases that are titratable with strong acid. Mathematically, *we define alkalinity as the negative of TOTH when the components are the principal species of the solution at the CO₂ equivalence point*. The *acidity* can be defined as the negative of alkalinity, and hence equal to *TOTH*.

As a first example, let's consider a solution containing a fixed total dissolved concentration of $CaCO_3$. At the CO₂ equivalence point, H_2CO_3 is the principal carbonate species, so we choose our components as H^+, H_2O, CO_2, and Ca^{2+}. (Since we always choose water as a component, we do not want to choose H_2CO_3 as a component, because it contains the component H_2O and hence is not fully independent. Instead, we choose CO_2 as the carbonate component in this case). Species H_2CO_3, HCO_3^- and CO_3^{2-} are made by combining these components as follows:

$$H_2CO_3 = H_2O + CO_2$$
$$HCO_3^- = H_2O + CO_2 - H^+$$
$$CO_3^{2-} = H_2O + CO_2 - 2H^+$$
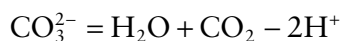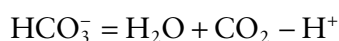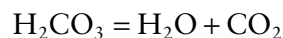
The proton mole balance equation is then:

$$TOTH = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \tag{6.32}$$

The alkalinity is then:

$$Alk = -TOTH = -[H^+] + [HCO_3^-] + 2[CO_3^{2-}] + [OH^-] \tag{6.33}$$

This sum, $-[H^+] + [HCO_3^-] + 2[CO_3^{2-}] - [OH^-]$, is called the *carbonate alkalinity*. In this example, carbonate alkalinity and alkalinity are equal since there are no other ions in solution. To avoid confusion with carbonate alkalinity, alkalinity is sometimes called *total alkalinity* (see Example 6.4).

An analytical definition of alkalinity is that it is the quantity of acid that must be added to the solution to bring the pH to the CO₂ equivalence point.

We can also express alkalinity in terms of conservative and non-conservative ions. The charge balance equation, eqn. 6.14, could be written as:

Example 6.4   The tableau method of Morel and Hering

Write an expression for the alkalinity of a solution containing $H_3SiO_4^-$, H_4SiO_4, $B(OH)_3$, $B(OH)_4^-$, H_2S, HS^-, $H_2PO_4^-$, HPO_4^{2-}, H_2CO_3, HCO_3^-, and CO_3^{2-}, as well, of course, as OH^- and H^+.

Tableau							
	H^+	H_2O	CO_2	$H_2PO_4^-$	H_4SiO_4	$B(OH)_3$	H_2S
H^+	1						
OH^-	−1	1					
H_2CO_3		1	1				
HCO_3^-	−1	1	1				
CO_3^{2-}	−2	1	1				
HPO_4^{2-}	−1			1			
$H_2PO_4^-$				1			
$H_3SiO_4^-$	−1				1		
H_4SiO_4					1		
$B(OH)_4^-$	−1	1				1	
$B(OH)_3$						1	
H_2S							1
HS^-	−1						1

Answer: The alkalinity will be the negative of *TOT*H *when the components are the principal species of tile solution at the CO₂ equivalence point*, so the real problem is just choosing components and defining our species in terms of these. At the CO_2 equivalence point, the principal species will be H_4SiO_4, $B(OH)_3$, H_2S, $H_2PO_4^-$, and H_2CO_3. The problem now is simply defining the species in terms of components. Morel and Hering (1993) proposed a method of setting up a *tableau*, a table with *the components listed across the top and the species listed vertically*. Entries in the table are just the stoichiometric coefficients used to define each species in terms of its components. In this case, the tableau will look like that shown above. The first column of the tableau shows us what the coefficients will be in our *TOT*H equation. Our expression for alkalinity will thus be:

$$Alk = -TOTH = -\{[H^+] - [OH^-] - [HCO_3^-] - 2[CO_3^{2-}] - [HPO_4^{2-}] - [H_3SiO_4^-] - [B(OH)_4^-] - [HS^-]\}$$
(6.34)

$$\Sigma_{\text{cations (in equivalents)}} - \Sigma_{\text{anions (in equivalents)}} = 0 \quad (6.35)$$

This can then be expanded to:

$$\Sigma_{\text{conserv. cations}} - \Sigma_{\text{conserv. anions}} + \Sigma_{\text{non-conserv. cations}}$$
$$- \Sigma_{\text{non-conserv. anions}} = 0$$

(all in units of equivalents).[*] Rearranging, we have:

$$\Sigma_{\text{conserv. cations}} - \Sigma_{\text{conserv. anions}} = -\Sigma_{\text{non-conserv. cations}}$$
$$+ \Sigma_{\text{non-conserv. anions}}$$
(6.36)

[*] One *equivalent* of a species is defined as the number of moles multiplied by the charge of the species. Thus one equivalent of CO_3^{2-} is equal to 0.5 moles of CO_3^{2-}, but one equivalent of Cl^- is equal to 1 mole of Cl^-. For an acid or base, an equivalent is the number moles of the substance divided by the number of hydrogen or hydroxide ions that can be potentially produced by dissociation of the substance. Thus there are 2 equivalents per mole of H_2CO_3, but 1 equivalent per mole of Na(OH).

The right hand side of eqn. 6.36 is equal to the *alkalinity*. Hence we may write:

$$Alk = \Sigma_{\text{conserv. cations}} - \Sigma_{\text{conserv. anions}}$$
$$= -\Sigma_{\text{non-conserv. cations}} + \Sigma_{\text{non-conserv. anions}} \quad (6.37)$$

This equation emphasizes an important point. The difference of the sum of conservative anions and cations is clearly a conservative property, i.e., they cannot be changed except by the addition or removal of components. Since alkalinity is equal to this difference, alkalinity is also a conservative quantity (i.e., independent of pH, pressure and temperature). *Thus total alkalinity is conservative, even though concentrations of individual species are not.*

6.2.4.1   Alkalinity determination and titration curves

If the concentrations of all major conservative ions in a solution are known, the alkalinity can be simply calculated from eqn. 6.37. It is often useful, however, to determine this independently. This is done, as the definition of alkalinity suggests, through titration. Titration is the process of progressively adding a strong acid or base to a solution until a specified pH, known as an end-point, is reached. In the case of the determination of alkalinity, this end-point is the CO_2 equivalence point.

Consider a solution containing a certain concentration of sodium bicarbonate (Na_2CO_3). Because the carbonate ion can act as a proton acceptor, $NaCO_3$ is a base. We can determine both the alkalinity and the total carbonate concentration of this solution by titrating with a strong acid, such as HCl. Let's examine the chemistry behind this procedure.

For clarity, we make several simplifying assumptions. First, we assume ideal behavior. Second, we assume the system is closed, so that all components are conserved, except for $[H^+]$ and $[Cl^-]$, which we progressively add. Third, we assume that the volume of our Na_2CO_3 solution is sufficiently large and our HCl sufficiently concentrated that there is no significant dilution of the original solution. Finally, we assume both Na_2CO_3 and HCl dissociate completely.

The charge balance equation during the titration is:

$$[Na^+] + [H^+] = [Cl^-] + [HCO_3^-] + 2[CO_3^{2-}]$$
$$+ [OH^-] \quad (6.38)$$

Since the Cl^- concentration is conservative, it will be equal to the total amount of HCl added. Into eqn. 6.38, we can substitute the following:

$$[HCO_3^-] = \frac{K_1[H_2CO_3]}{[H^+]} \quad (6.39a)$$

$$[CO_3^{2-}] = \frac{K_1K_2[H_2CO_3]}{[H^+]^2} \quad (6.39b)$$

and

$$[OH^-] = \frac{K_W}{[H^+]} \quad (6.39c)$$

Doing so and rearranging yields:

$$[Cl^-] = [Na^+] + [H^+] - \frac{K_1[H_2CO_3]}{[H^+]}$$
$$- \frac{K_1K_2[H_2CO_3]}{[H^+]^2} - \frac{K_W}{[H^+]} \quad (6.40)$$

We may also write a conservation equation for carbonate species, which is the same as eqn. 6.24 in Example 6.1. Substituting eqns. 6.39a and 6.39b into 6.24 and rearranging, we have:

$$[H_2CO_3] = \frac{\Sigma CO_2}{1 + \dfrac{K_1}{[H^+]} + \dfrac{K_1K_2}{[H^+]^2}} \quad (6.41)$$

Substituting this expression into eqn. 6.40, we obtain:

$$[Cl^-] = [Na^+] + [H^+]$$
$$- \frac{\Sigma CO_2}{[H^+] + K_1 + K_1K_2/[H^+]}\left\{K_1 - \frac{K_1K_2}{[H^+]}\right\}$$
$$- \frac{K_W}{[H^+]} \quad (6.42)$$

From stoichiometry, we also know that $\Sigma CO_2 = 2[Na^+]$. From this equation we can construct a plot showing how many moles of HCl we must add to achieve a certain pH. We can also use eqn. 6.39 and similar ones
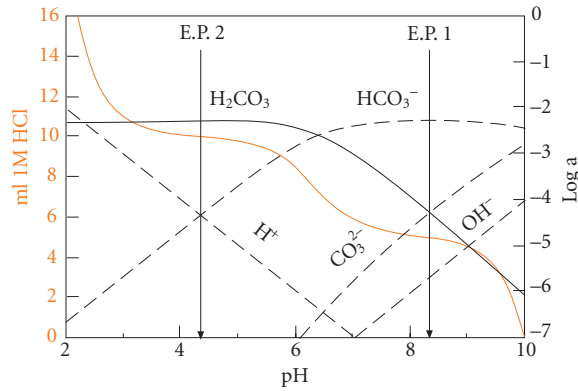
Figure 6.2 Titration curve (solid red line) for a one liter 0.005 M Na_2CO_3 solution titrated with 1 M HCl. The left axis shows the number of ml of HCl to be added to obtain a given pH. Also shown are the concentrations of carbonate species, H+, and OH- (dashed black lines, right axis gives scale). EP1 is the bicarbonate equivalence point, EP2 is the CO_2 equivalence point.

expressing the bicarbonate and carbonate ions as functions of pH to plot the change in the carbonate speciation during the titration. Figure 6.2 shows such a plot for a 0.005 M Na_2CO_3 solution. There are two regions where pH changes rapidly with small additions of HCl. These are the two end-points of the titration. Comparing the titration curve with the speciation curves, we see that the two end-points correspond to the CO_2 and bicarbonate equivalence points.

An analytical definition of alkalinity is its *acid neutralizing capacity when the end-point of the titration is the CO_2 equivalence point* (Morel and Hering, 1993). We had previously defined alkalinity as the negative of *TOT*H when the principal components are those at the CO_2 equivalence point. Let's now show that these definitions are equivalent.

Our *TOT*H expression, written in terms of components at the CO_2 equivalence point, is identical to 6.32:

$$TOTH = [H^+] - [HCO_3^-] - 2[HCO_3^-] - [OH^-] \tag{6.32}$$

and the charge balance equation (before any HCl is added) is:

$$[Na^+] + [H^+] = [HCO_3^-] + 2[CO_3^{2-}] + [OH^-]$$

Combining the two we have:

$$TOTH = -[Na^+]$$

Since the alkalinity is the negative of *TOT*H, it follows that (before the addition of HCl):

$$Alk = [Na^+] \tag{6.43}$$

We obtain exactly the same result from equation 6.37. It is easy to show that after titrating to the CO_2 equivalence point, the alkalinity is 0. The change in alkalinity is thus equal to the number of equivalents, or moles, of H⁺ we have added to the solution. Since at the end-point, $[H^+] = [HCO_3^-]$ and the concentrations of CO_3^{2-} and OH⁻ are negligible, our charge balance equation, 6.38, reduces to:

$$[Na^+] \simeq [Cl^-]$$

Comparing this with eqn. 6.42, we see that the alkalinity is equal to the amount of HCl added. In the example in Figure 6.2, the equivalence point occurs after the addition of 10 ml of 1 M HCl, or a total of 0.01 moles of Cl⁻. (Notice that since small additions of acid result in large changes in pH at the end-points, we do not have to determine pH particularly accurately during the titration for an accurate determination of alkalinity.) So the alkalinity is 0.01 equivalents. This is exactly the answer we obtain from eqn. 6.41 for 1 liter of 0.005 M Na_2CO_3, since there are 2 moles of Na⁺ for each mole of Na_2CO_3.

By assuming that the concentration of H⁺ contributes negligibly to charge balance, it is also easily shown (Problem 2) that at the bicarbonate equivalence point:

$$\Sigma CO_2 = [Cl^-] + [OH^+] \tag{6.44}$$

Thus total carbonate is obtained by titrating to the bicarbonate equivalence point (knowing the pH of the end-point allows us to determine the ΣCO_2 exactly; however neglecting the [OH⁻] term in eqn. 6.44 results in only a 1% error in the example shown). In Figure 6.2, this occurs after the addition of 5 ml 1 M HCl.

6.2.5 Buffer intensity

The carbonate system is a good example of a pH *buffer*. We define the *buffer intensity* of a solution as the inverse of change in pH per amount of strong base (or acid) added:

$$\beta \equiv \frac{dC_B}{dpH} = -\frac{dC_A}{dpH} \tag{6.45}$$

where C_B and C_A are the concentrations, in equivalents, of strong base or acid respectively. The greater the buffer capacity of a solution, the less change in its pH as an acid or base is added. The buffer capacity of a solution can be calculated by differentiation of the equation relating base (or acid) concentration to pH, as is illustrated in Example 6.5.

A pH buffer acts to control pH within a narrow range as H^+ ions are added or removed from solution by other reactions. To understand how this works, imagine a solution containing carbonic acid, CO_3^{2-}, HCO_3^-, and H^+ ions in equilibrium concentrations. Now imagine that additional H^+ ions are added (for example, by addition of rainwater containing HNO_3). In order for the right-hand side of eqn. 6.19 to remain equal to K_1 despite an increase in the activity of H^+ (which it must at constant temperature and pressure), the bicarbonate activity must decrease and the carbonic acid activity increase. It is apparent then that reaction 6.16 must be driven to the left, taking free hydrogen ions from solution, hence driving the pH back toward its original value. Similarly, reaction 6.17, the dissociation of bicarbonate, will also be driven to the left, increasing the bicarbonate concentration and decreasing the hydrogen and carbonate ion concentrations.

The buffer capacity of the carbonate system depends strongly on pH and also on the concentration of the carbonate species and the concentration of other ions in solution. In pure water containing no other ions and only

carbonate in amounts in equilibrium with the atmosphere, the buffering capacity is negligible near neutral pH, as is shown in Example 6.6. Natural solutions, however, can have substantial buffering capacity. Figure 6.3
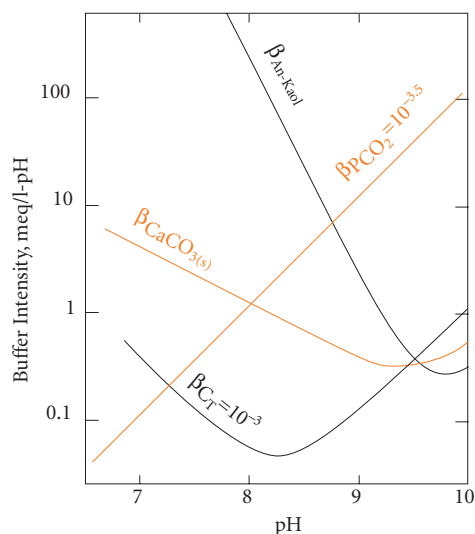

Figure 6.3   Buffer intensity as a function of pH for several ideal natural systems: β_{C_T} fixed total dissolved CO_2, $\beta_{P_{CO_2}}$ water in equilibrium with atmospheric CO_2, $\beta_{CaCO_{3(s)}}$ water in equilibrium with calcite, and $\beta_{An\text{-}Kaol.}$ water in equilibrium with anorthite and kaolinite. After Stumm and Morgan (1996). With permission from John Wiley & Sons.

Example 6.5   Calculating the alkalinity of spring water

Calculate the alkalinity of spring water from Thonon, France, whose analysis is given at right (this is the same analysis an in Problem 10 of Chapter 3.

Anions	mM	Cations	mM
HCO_3^-	5.436	Ca^{2+}	2.475
SO_4^{2-}	0.146	Mg^{2+}	0.663
NO_3^-	0.226	K^+	0.036
Cl^-	0.231	Na^+	0.223

Answer: We can use eqn. 6.37 to calculate alkalinity. All the ions listed here are conservative with the exception of HCO_3^-. To calculate alkalinity, we firet need to convert the molar concentrations to equivalents; we do so by multiplying the concentration of each species by its charge. We find the sum of conservative anion concentrations to be 0.749 meq (milliequivalents), and that of the conservative cation concentrations to be 6.535 meq. The alkalinity is the difference, 5.786 meq.

Example 6.6   Calculating buffer intensity

How will pH change for given addition of a strong base such as NaOH for a solution of pure water in equlibrium with atmospheric CO_2? Calculate the buffer intensity of this solution as a function of pH. Assume that NaOH completely dissociates and behavior is ideal.

Answer: We want to begin with the charge balance equation in this case because it relates the two quantities of interest, $[Na^+]$ and $[H^+]$. The charge balance equation is the same as in Exapmle 6.1:

$$[Na^+]+[H^+]=[OH^-]+[HCO_3^-]+2[CO_3^{2-}] \tag{6.23}$$

Since Na^+ is a conservative ion, its concentration will depend only upon the amount of NaOH added, so that $C_B = [Na^+]$. Substituting this into eqn. 6.14 and rearranging, we have:

$$C_B = [OH^-]+[HCO_3^-]+2[CO_3^{2-}]-[H^+] \tag{6.46}$$

We can now use the equilibrium constant relations to substitute for the first three terms of the right-hand side of 6.46 and obtain:

$$C_B = \frac{K_W+K_1K_{sp}P_{CO_2}}{[H^+]}+2\frac{K_2K_1K_{sp}P_{CO_2}}{[H^+]^2}-[H^+]$$

Using the relation $pH = -\log[H^+]$ to replace $[H^+]$ in this equation with pH, we have:

$$C_B = \frac{K_W+K_1K_{sp}P_{CO_2}}{10^{-pH}}+2\frac{K_2K_1K_{sp}P_{CO_2}}{10^{-2pH}}-10^{-pH}$$

Now differentiating with respect to pH, we obtain:

$$\frac{dC_B}{dpH} = \beta = \ln 10\{(K_w+K_1K_{sp}P_{CO_2})10^{pH}+4K_2K_1K_{sp}P_{CO_2}10^{2pH}+10^{-pH}\} \tag{6.47}$$

Figure 6.4 shows a plot of this equation using the values in Table 6.1. Buffer intensity is negligible in neutral to slightly acidic conditions, but increases rapidly with pH.
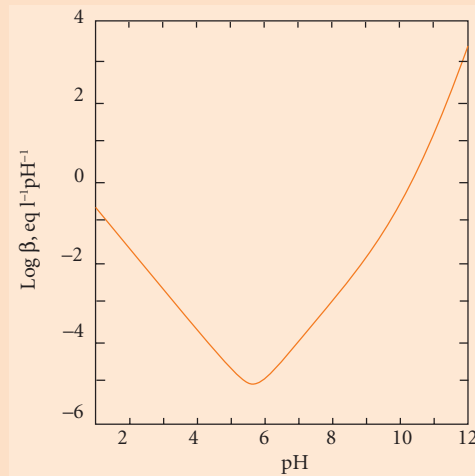

Figure 6.4   Buffer capacity of a carbonate solution in equilibrium with atmospheric CO_2.