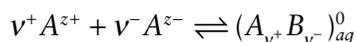


sphere ion pair (also called an outer sphere complex) is said to have formed. If water molecules are excluded from the space between the ions, an *inner sphere ion pair* (or complex) is said to have formed.

For some purposes, ion pairs can be treated as distinct species having a charge equal to the algebraic sum of the charge of the ions involved. These can be included, for example, in calculation of ionic strength to obtain a somewhat more accurate estimate of activities. On the other hand, ion pairs, including neutral ones, can be highly dipolar and may behave as charge-separated ions.

Ion associations affect activities in two ways. First, associated ions are less likely to participate in reactions, thus reducing the activity of the ions involved. Second, ion association reduces the ionic strength of the solution, and hence reduces the extent of electrostatic interactions among ions. This has the effect of increasing activity. To understand the first effect, consider the case where a certain fraction of the free ions re-associates to form ion pairs:



where the superscript 0 indicates neutrality and the subscript *aq* a dissolved aqueous species. A salt that only partially dissociates in solution is called a weak electrolyte. Let α be the fraction of the ions that associate to form ion pairs or complexes. The associate of this fraction of ions as ion pairs will be thermodynamically equivalent to that fraction of the substance not dissociating to begin with. The fraction of free ions is then $1 - \alpha$. Equation 4.83 becomes:

$$m^+ = (1 - \alpha)v^+ m \quad \text{and} \quad m^- = (1 - \alpha)v^- m \quad (4.99)$$

where m is the molality of the solute. We can rewrite eqn. 4.77 as:

$$a_{\pm} = \left[(\gamma_+ m_+)^{v^+} (\gamma_- m_-)^{v^-} \right]^{1/v} \quad (4.100)$$

Substituting 4.99 into 4.100 and rearranging, we obtain:

$$a_{\pm} = \left(\gamma_+^{v^+} \gamma_-^{v^-} \right)^{1/v} \left\{ [(1 - \alpha)v^+ m]^{v^+} [(1 - \alpha)v^- m]^{v^-} \right\}^{1/v}$$

A little more rearranging and we have:

$$a_{\pm} = \left(\gamma_+^{v^+} \gamma_-^{v^-} \right)^{1/v} \left\{ [(1 - \alpha)m]^{(v^+ + v^-)} (v^+)^{v^+} (v^-)^{v^-} \right\}^{1/v}$$

Finally, since $v = v^+ + v^-$, we obtain:

$$a_{\pm} = \left(\gamma_+^{v^+} \gamma_-^{v^-} \right)^{1/v} (1 - \alpha)m \left\{ (v^+)^{v^+} (v^-)^{v^-} \right\}^{1/v} \quad (4.101)$$

We can recognize the last term as m_{\pm} . Since $a_{\pm} = \gamma_{\pm} m_{\pm}$, we see that the mean ionic activity coefficient will be

$$\gamma_{\pm} = (1 - \alpha) \left(\gamma_+^{v^+} \gamma_-^{v^-} \right)^{1/v} \quad (4.102)$$

for an incompletely dissociated electrolyte. Thus the mean ion activity coefficients are reduced by a factor of $1 - \alpha$. Provided we have appropriate stability constants for the ion pairs or complexes, α can be calculated and an appropriate correction applied.

Now consider a CaSO_4 solution of which some fraction of the Ca^{2+} and SO_4^{2-} ions, α , associate to form CaSO_4^0 . The ionic strength of this solution would be

$$I = \frac{(1 - \alpha)}{2} (4m_{\text{Ca}^{2+}} + 4m_{\text{SO}_4^{2-}})$$

Thus the ionic strength is reduced by a factor of $1 - \alpha$ as well.

Ion pairs and complexes need not be neutral species (AlCl_2^+ , for example). When they are not, they will contribute to ionic strength. A general expression for ionic strength taking account of ion associations must include charged ion pairs and complexes:

$$I = \frac{1}{2} \left[\sum_i (1 - \alpha_i) m_i z_i^2 + \sum_n c_n z_n^2 \right] \quad (4.103)$$

where α_i is the fraction of each ion involved in ion associations, c_n is the concentration of each ion pair or complex, and z_n is its charge. We could use this result directly in the Debye-Hückel equation to make an improved estimate of ionic strength, and hence of the single ion activity coefficient.

Figure 4.29 illustrates the effect of ion pair formation for a hypothetical CaCl_2 solution in which some fraction of the ions combine to form ion pairs. The fraction of Ca^{2+} ions

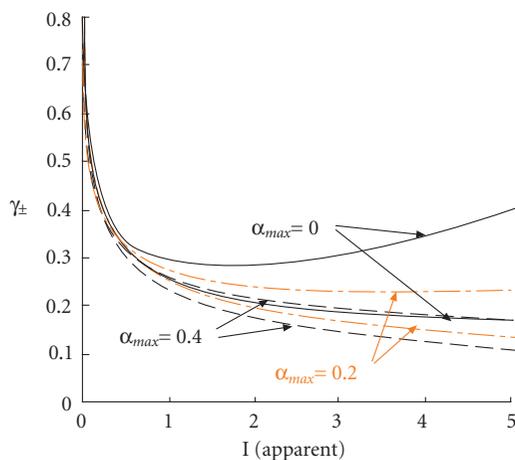


Figure 4.29 Effects of ion association on the activity coefficient. Mean ion activity coefficient of CaCl_2 for varying extents of ion association. Fraction of Ca^{2+} ions forming CaCl^- was assumed to increase linearly with ionic strength up to a maximum value (α_{\max}) at $I = 5$ m. Solid line shows electrostatic term (Debye–Hückel) after correction for ion association, dashed line shows the combined electrostatic and solvation term.

forming CaCl^- was assumed to increase linearly with ionic strength up to the maximum value shown.

If the formation of ion pairs depends on the ratio of thermal to electrostatic energy, we might expect that ion pair formation will decrease with temperature. However, the relative permittivity of water decreases with temperature, allowing increased electrostatic interaction between ions, and this effect dominates over the increased thermal energy of ions. As a result, the extent of ion association increases with temperature. Increasing pressure, on the other hand, favors dissociation of ions.

4.7.2.4 Alternative expressions for activity coefficients

There have been a number of attempts to develop working equations that account for all the effects on activity coefficients at high ionic strength. Many of these are ultimately based on the specific ion interaction theory of

Table 4.5 Truesdell–Jones parameters. From Truesdell and Jones (1974).

Ion	\hat{a}	b
Na^+	4.0	0.075
K^+	3.5	0.015
Mg^{2+}	5.5	0.20
Ca^{2+}	5.0	0.165
Cl^-	3.5	0.015
SO_4^{2-}	5.0	-0.04
CO_3^{2-}	5.4	0
HCO_3^-	5.4	0

Brønsted (1922). Brønsted proposed an equation of the form:

$$\log \gamma_i = \alpha m^{1/2} + \beta_i m \quad (4.104)$$

where α is a constant that is independent of the solute ions and β is the “specific ion interaction parameter” and is different for each ionic species. Guggenheim (1935) replaced the first term on the right with a simplified form of the Debye–Hückel equation and the second term with the summation of ion-ion interaction parameters:

$$\log \gamma_i = \frac{-z_i^2 A \sqrt{I}}{1 + \sqrt{I}} + 2 \sum_k \beta_{i,k} m_k \quad (4.105)$$

where $\beta_{i,k}$ is a parameter describing the interactions between ions i and k . For natural waters with many species, the Guggenheim equation becomes complex. Also starting from Debye–Hückel, Truesdell and Jones (1974) proposed the following simpler equation:

$$\log \gamma_i = \frac{-z_i^2 A \sqrt{I}}{1 + B \hat{a}_i \sqrt{I}} + b_i I \quad (4.106)$$

The first term on the right is identical in form to Debye–Hückel; the second term is similar to the Brønsted specific ion interaction term. Truesdell and Jones determined parameters \hat{a} and b empirically. Table 4.5 lists these parameters for some common ions (see Example 4.7). Figure 4.30 compares mean activity coefficient of calculated with the

Example 4.7 Activity coefficients in a brine

The following concentrations were measured in a shield brine from Sudbury, Canada, at 22°C. Calculate the activity coefficients of these species using the Truesdell–Jones equation.

Species	Conc. g/kg
Na	18.9
K	0.43
Ca	63.8
Mg	0.078
SO ₄	0.223
HCO ₃	0.042
Cl	162.7

Answer: Our first task is to convert g/kg to molal concentrations. We do this by dividing by molecular weight. Next, we need to calculate ionic strength (eqn. 3.75), which we find to be 5.9 m. Calculation of activity coefficients is then straightforward using eqn. 4.106 and the parameters in Tables 3.2 and 4.5. Finally, we apply a correction for the decreased concentration of water (eqn. 4.95). Our final spreadsheet is now shown.

	%o	m	z	\hat{a}_{TJ}	B_TJ	log (gamma)	ganma	gamma corr
Na	18.9	0.822	1	5	0.165	0.728	5.341	4.741
K	0.43	0.017	1	3.5	0.015	-0.238	0.579	0.514
Ca	63.8	1.595	2	5	0.165	-0.017	0.963	0.855
Mg	0.078	0.003	2	5.5	0.2	0.264	1.836	1.630
SO ₄	0.223	0.002	2	5	-0.04	-1.229	0.059	0.052
HCO ₃	0.058	0.001	1	5.4	0	-0.233	0.585	0.519
Cl	162.7	4.590	1	3.5	0.015	-0.238	0.579	0.514
	m	7.030	A	0.5092				
	I	5.913	B	0.3283				

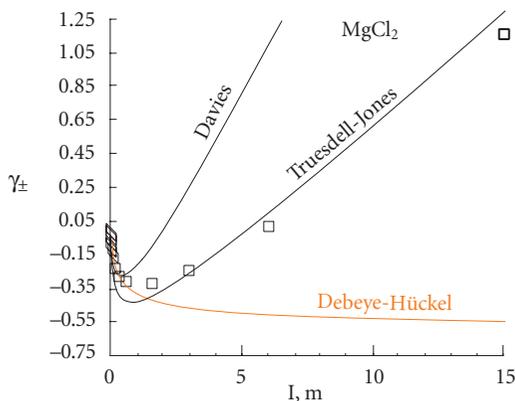


Figure 4.30 Measured mean ionic activity coefficients in MgCl₂ solution as a function of ionic strength, compared with values calculated from the Debye–Hückel, Davies and Truesdell–Jones equations.

Debye–Hückel, Davies, and Truesdell–Jones equations with the actual measured values. Generally, the Truesdell–Jones equations fit these observations very well. This is not always the case, however. The fit for Na₂CO₃, for example, is little better than for Debye–Hückel.

Other equations include those developed by Pitzer (1979) and the National Bureau of Standards. While these equations are generally more accurate than the above, their complexity places them beyond the scope of this book. The interested reader is referred to any of several texts on geochemical thermodynamics that treat them (Nordstrom and Munoz, 1986; Fletcher, 1993; Anderson and Crerar, 1993) as well as the original literature.

REFERENCES AND SUGGESTIONS FOR FURTHER READING

- Anderson, G.M. and Crerar, D.A. 1993. *Thermodynamics in Geochemistry*. New York, Oxford University Press.
- Anderson, J.L., Barth, A.P., Wooden, J.L. and Mazdab, F. 2008. Thermometers and thermobarometers in granitic systems. *Reviews in Mineralogy and Geochemistry*, 69: 121–42.
- Anderson, J.L. and Smith, D.R. 1995. The effects of temperature and f_{O_2} on the Al-in-hornblende barometer. *American Mineralogist*, 80: 549–59.
- Blundy, J. and Cashman, K. 2008. Petrologic reconstruction of magmatic system variables and processes. *Reviews in Mineralogy and Geochemistry*, 69: 179–239.
- Bohlen, S.R. and Lindsley, D.H. 1987. Thermometry and barometry of igneous and metamorphic rocks. *Annual Review of Earth and Planetary Sciences*, 15: 397–420.
- Bohlen, S.R., Wall, V.J. and Boettcher, A.L. 1983. Experimental investigations and geological applications of equilibria in the system FeO-TiO₂-Al₂O₃-SiO₂-H₂O. *American Mineralogist*, 68: 1049–58.
- Bohlen, S.R., Dollase, W.A. and Wall, V.J. 1986. Calibration and application of spinel equilibria in the system FeO-Al₂O₃-SiO₂. *Journal of Petrology*, 27: 1143–56.
- Bottinga, Y. and D. Weill. 1972. The viscosity of magmatic silicate liquids: a model for calculation. *American Journal of Science*, 272: 438–75.
- Boyd, F.R. 1973. A pyroxene geotherm. *Geochimica Cosmochimica Acta*, 37: 2533–46.
- Bradley, R.S. 1962. Thermodynamic calculations on phase equilibria involving fused salts. Part II. Solid solutions and applications to the olivines. *American Journal of Science*, 260: 550–54.
- Brey, G.P. and Köhler, T. 1990. Geothermobarometry in four-phase lherzolites II. New thermobarometers, and practical assessment of existing thermobarometers. *Journal of Petrology*, 31: 1353–78.
- Brey, G.P., Bulatov, V.K. and Girnig, A.V. (2008) Geobarometry for peridotites: Experiments in simple and natural systems from 6 to 10 GPa. *Journal of Petrology*, 49: 3–24.
- Brønsted, J.N. 1922. Studies on solubility, IV. The principle of specific interaction of ions. *Journal of the American Chemical Society*, 44: 877–98.
- Buddington, A.F. and Lindsley, D.H. 1964. Iron-titanium oxide minerals and synthetic equivalents. *Journal of Petrology*, 5: 310–57.
- Carmichael, I.S.E. and Eugster, H.P. (eds) 1987. *Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts (Reviews in Mineralogy, vol. 17)*. Washington, Mineralogical Society of America.
- Connolly, J.A.D. 1989. Multivariable phase diagrams: An algorithm based on generalized thermodynamics. *American Journal of Science*, 290: 666–718.
- Essene, E. 1989. The current status of thermobarometry in metamorphic rocks, in *The Evolution of Metamorphic Belts* (eds J.S. Daly, R.A. Cliff and B.W.D. Yardley), pp. 1–44. London: Blackwell Scientific.
- Ferry, J.M. and Spear, F.S. 1978. Experimental calibration of the partitioning of Fe and Mg between biotite and garnet. *Contributions to Mineralogy and Petrology*, 25: 871–93.
- Ferry, J. and Watson, E. 2007. New thermodynamic models and revised calibrations for the Ti-in-zircon and Zr-in-rutile thermometers. *Contributions to Mineralogy and Petrology*, 154: 429–37.
- Fletcher, P. 1993. *Chemical Thermodynamics for Earth Scientists*. Essex, Longman Scientific and Technical.
- Garrels, R.M. and Christ, C.L. 1965. *Solutions, Minerals, and Equilibria*. New York, Harper and Row.
- Gasparik, T. 1984a. Two-pyroxene thermobarometry with new experimental data in the system CaO-MgO-Al₂O₃-SiO₂. *Contributions to Mineralogy and Petrology*, 87: 87–97.
- Gasparik, T. 1984b. Experimental study of subsolidus phase relations and mixing properties of pyroxene and plagioclase in the system CaO-Al₂O₃-SiO₂. *Geochimica Cosmochimica Acta*, 48: 2537–45.
- Ghent, E.D. 1976. Plagioclase-garnet-Al₂O₃-quartz: a potential geobarometer-geothermometer. *American Mineralogist*, 61: 710–14.
- Ghiorso, M.S. 1987. Modelling magmatic systems: Thermodynamic relations., in *Thermodynamic Modelling of Geological Materials: Minerals, Fluids, and Melts* (eds I.S.E. Carmichael and H.P. Eugster), pp. 443–65. Washington, Mineralogical Society of America.
- Ghiorso, M.S., Carmichael, I.S.E., Rivers, M.L. and Sack, R.O. 1983. The Gibbs free energy of mixing of natural silicate liquids; an expanded regular solution approximation for the calculation of magmatic intensive variables. *Contributions to Mineralogy and Petrology*, 84: 107–45.
- Ghiorso, M.S. & Evans, B.W. 2008. Thermodynamics of rhombohedral oxide solid solutions and a revision of the Fe-Ti two-oxide geothermometer and oxygen-barometer. *American Journal of Science*, 308: 957–1039.
- Ghiorso, M.S., Hirshmann, M.M. and Sack, R.O. 1994. New software models thermodynamics of magmatic systems. *EOS* 75: 571–76.
- Ghiorso, M.S., Hirshmann, M.M., Reiners, P.W. and Kress, V.C. 2002. The pMELTS: a revision of MELTS for improved calculation of phase relations and major element partitioning related to partial melting of the mantle to 3 GPa. *Geochem. Geophys. Geosyst.*, 3: 2001GC000217.

- Ghiorso, M.S. and Sack, R.O. 1995. Chemical mass transfer in magmatic processes IV. A revised and internally consistent thermodynamic model for the interpolation and extrapolation of liquid-solid equilibria in magmatic systems at elevated temperatures and pressures. *Contributions to Mineralogy and Petrology*, 119: 197–212.
- Goldsmith, J.R. and Newton, R.C. 1969. P-T-X relations in the system $\text{CaCO}_3\text{-MgCO}_3$ at high temperatures and pressures. *American Journal of Science*, 267A: 160–90.
- Grover, J. 1977. Chemical mixing in multicomponent solutions: An introduction to the use of Margules and other thermodynamic excess functions to represent non-ideal behavior, in *Thermodynamics in Geology* (ed. D.G. Fraser), pp. 67–97. Dordrecht, D. Reidel.
- Guggenheim, E.A. 1935. The specific thermodynamic properties of aqueous solutions of strong electrolytes. *Philosophical Magazine*, 19: 588.
- Helgeson, H.C. 1969. Thermodynamics of hydrothermal systems at elevated temperatures and pressures. *American Journal of Science*, 267: 729–804.
- Helgeson, H.C. and Kirkham, D.H. 1974. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures, Debye-Hückel parameters for activity coefficients and relative partial molar quantities. *American Journal of Science*, 274: 1199–261.
- Helgeson, H.C., Kirkham, D.H. and Flowers, G.C. 1981. Theoretical predictions of the thermodynamic behavior of electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molar and standard and relative partial molar properties to 600°C and 5 kbar. *American Journal of Science*, 281: 1249–316.
- Holdaway, M.J. 1971. Stability of andalusite and the aluminum silicate phase diagram. *American Journal of Science*, 271: 97–131.
- Holland, T. and Blundy, J. 1994. Non-ideal interactions in calcic amphiboles and their bearing on amphibole-plagioclase thermometry. *Contributions to Mineralogy and Petrology*, 116: 433–47.
- Holland, T.J.B., Navrotsky, A. and Newton, R.C. 1979. Thermodynamic parameters of $\text{CaMgSi}_2\text{O}_6\text{-Mg}_2\text{Si}_2\text{O}_6$ pyroxenes based on regular solution and cooperative disordering models. *Contributions to Mineralogy and Petrology*, 69: 337–44.
- Johannes, W. and Puhani, D. 1971. The calcite-aragonite equilibrium reinvestigated. *Contributions to Mineralogy and Petrology*, 31: 28–38.
- Koziol, A.M. and Newton, R.C. 1988. Redetermination of the garnet breakdown reaction and improvement of the plagioclase-garnet- Al_2O_3 -quartz geobarometer. *American Mineralogist*, 73: 216–23.
- Kudo, A.M. & Weill, D.F. 1970. An igneous plagioclase thermometer. *Contributions to Mineralogy and Petrology*, 25: 52–65.
- Marcus, Y., 1985. *Ion Solvation*. John Wiley & Sons, Chichester.
- Morel, F.M.M. and Hering, J.G. 1993. *Principles and Applications of Aquatic Chemistry*. New York, John Wiley and Sons.
- Navrotsky, A. 1994. *Physics and Chemistry of Earth Materials*. Cambridge, Cambridge University Press.
- Nicholls, J. and Russell, J.K. 1990. *Modern Methods in Igneous Petrology, Reviews in Mineralogy*, vol. 24. Washington, Mineralogical Society of America.
- Nielsen, R.L. and Dungan, M.A. 1983. Low pressure mineral-melt equilibria in natural anhydrous mafic systems. *Contributions to Mineralogy and Petrology*, 84: 310–26.
- Nordstrom, D.K. and Munoz, J.L. 1986. *Geochemical Thermodynamics*. Palo Alto: Blackwell Scientific.
- Pitzer, K.S. 1979. Theory: ion interaction approach, in *Activity Coefficients in Electrolytes* (ed. R.M. Pytkowicz), pp. 157–208. Boca Raton, CRC Press.
- Powell, R. and Holland, T.J.B. 2008. On thermobarometry. *Journal of Metamorphic Petrology*, 26: 155–79. doi: 10.1111/j.1525-1314.2007.00756.x, 2008.
- Putirka, K. 2005. Igneous thermometers and barometers based on plagioclase + liquid equilibria: tests of some existing models and new calibrations. *American Mineralogist*, 90: 336–46.
- Putirka, K.D. 2008. Thermometers and barometers for volcanic systems. *Reviews in Mineralogy and Geochemistry*, 69: 61–120.
- Rankenburg, K., Lassiter, J.C. and Brey, G. 2004. Origin of megacrysts in volcanic rocks of the Cameroon volcanic chain – constraints on magma genesis and crustal contamination. *Contributions to Mineralogy and Petrology*, 147: 129–44.
- Richardson, S.M. and McSween, H.Y. 1989. *Geochemistry: Pathways and Processes*. New York, Prentice Hall.
- Robinson, R.A. and Stokes, R.H. 1959. *Electrolyte Solutions*. London, Butterworths.
- Roeder, P.L. and Emslie, R.F. 1970. Olivine-liquid equilibrium. *Contributions to Mineralogy and Petrology*, 29: 275–289.
- Spencer, K. and Lindsley, D.H. 1981. A solution model for coexisting iron-titanium oxides. *American Mineralogist*, 66: 1189–201.

- Stebbins, J.F., Carmichael, I.S.E. and Weill, D.F. 1983. The high temperature liquid and glass heat contents and the heats of fusion of diopside, albite, sanidine and nepheline. *American Mineralogist*, 68: 717–30.
- Thompson, J.B. 1967. Thermodynamic properties of simple solutions, in *Researches in Geochemistry*, vol. 2 (ed. P.H. Abelson). New York, John Wiley and Sons.
- Thompson, J.B. and Waldbaum, D.R. 1969. Mixing properties of sanidine crystalline solutions: III. Calculations based on two-phase data. *American Mineralogist*, 54: 811–38.
- Toplis, M.J. 2005. The thermodynamics of iron and magnesium partitioning between olivine and liquid: criteria for assessing and predicting equilibrium in natural and experimental systems. *Contributions to Mineralogy and Petrology*, 149: 22–39.
- Truesdell, A.H. and Jones, B.F. 1974. WATEQ, a computer program for calculating chemical equilibria in natural waters. *Journal of Research of the US Geological Survey*, 2: 233–48.
- Wood, B.J. 1987. Thermodynamics of multicomponent systems containing several solutions, in *Thermodynamic Modeling of Geological Materials: Minerals, Fluids and Melts* (eds. I.S.E. Carmichael and H.P. Eugster), pp. 71–96. Washington, Mineralogical Society of America.
- Wood, B.J. and Banno, S. 1973. Garnet-orthopyroxene and orthopyroxene-clinopyroxene relationships in simple and complex systems. *Contributions to Mineralogy and Petrology*, 42: 109–24.

PROBLEMS

1. Kyanite, andalusite, and sillimanite (all polymorphs of Al_2SiO_5) are all in equilibrium at 500°C and 376 MPa . Use this information and the table to construct an approximate temperature–pressure phase diagram for the system kyanite-sillimanite-andalusite. Assume ΔV and ΔS are independent of temperature and pressure. Label each field with the phase present.

ϕ	\bar{V} (cm^3)	S (J/K-mol)
Kyanite	44.09	242.30
Andalusite	51.53	251.37
Sillimanite	49.90	253.05

2. Show that: $\bar{G}_{excess} = (W_{G_1}X_2 + W_{G_2}X_1)X_1X_2$ may be written as a four-term power expansion, i.e.:

$$\bar{G}_{ex} = A + BX_2 + CX_2^2 + DX_2^3$$

3. Construct \bar{G} - X diagrams for a regular solution with $W = 12\text{ kJ}$ (W is the interaction parameter in a non-ideal solution) at 100°C temperature intervals from 200 to 700°C . Sketch the corresponding phase diagram.
4. Interaction parameters for the enstatite–diopside solid solution have been determined as follows: $W_{\text{H-En}} = 34.0\text{ kJ/mol}$, $W_{\text{H-Di}} = 24.74\text{ kJ/mol}$ (assume W_V and W_S are 0).
 - (a) Use the asymmetric solution model to calculate ΔG_{real} as a function of X_2 (let diopside be component 2) curves for this system at 100 K temperature intervals from 1000 K to 1500 K . Label your curves.
 - (b) What is the maximum mole fraction of diopside that can dissolve in enstatite in this temperature range?
 - (c) Sketch the corresponding T - X phase diagram.
5. Sketch \bar{G} - X diagrams for 1600°C , 1500°C , 1300°C , and 1250°C for the system diopside–anorthite (Figure 4.8). Draw tangents connecting the equilibrium liquids and solids.

6. Suppose you conduct a 1 atm melting experiment on a plagioclase crystal. Predict the mole fractions of anorthite in the liquid and solid phases at a temperature of 1425°C. Assume both the liquid and solid behave as ideal solutions. Albite melts at 1118°C, anorthite at 1553°C. ΔH_m for albite is 54.84 kJ/mol; ΔH_m for anorthite is 123.1 kJ/mol.
7. Given the following two analyses of basaltic glass and coexisting olivine phenocrysts, determine the K_D for the $\text{MgO} \rightleftharpoons \text{FeO}$ exchange reaction, and calculate the temperatures at which the olivine crystallized using both MgO and FeO. Assume Fe_2O_3 to be 10 mole % of total iron (the analysis includes only the total iron, calculated as FeO; you need to calculate from this the amount of FeO by subtracting an appropriate amount to be assigned as Fe_2O_3). Note that the mole % Fo in olivine is equivalent to the mole % Mg or MgO. (*HINT: you will need to calculate the mole fraction of MgO and FeO in the liquid.*)

Sample glass (liquid) composition	TR3D-1 (wt % oxide)	DS-D8A (wt % oxide)
SiO ₂	50.32	49.83
Al ₂ O ₃	14.05	14.09
ΣFe as FeO	11.49	11.42
MgO	7.27	7.74
CaO	11.49	10.96
Na ₂ O	2.3	2.38
K ₂ O	0.10	0.13
MnO	0.17	0.20
TiO ₂	1.46	1.55
Olivine		
Mole % Fo (= mole % Mg)	79	81

8. Starting from equations 4.54, 4.56 and 4.18, use the fundamental relationships between free energy, entropy, enthalpy, and the equilibrium constant to derive the temperature dependence of the titanomagnetite–ilmenite exchange (eqn. 4.57).
9. Determine the temperature and oxygen fugacity of equilibration for the following set of coexisting iron-titanium oxides in lavas from the Azores:

	Titanomagnetite s.s. phase mole % magnetite	Ilmenite s.s. phase mole % hematite
G-4 groundmass	29.0	10.3
SJ-8 phenocrysts	41.9	13.0
SM-28 microphenocrysts	54.5	7.0
T-8 groundmass	33.7	8.1
F-29 microphenocrysts	36.2	6.0

Make a plot of f_{O_2} vs. temperature using your results and compare with Figure 3.22. What buffer do the data fall near?

10. Average mid-ocean ridge basalt (MORB) has the composition in the table to the right. Use the “web applet” version of MELTS (<http://melts.ofm-research.org/index.html>) to answer the following questions.
- (a) At a pressure of 500 bars and $f_{\text{O}_2} = \text{FMQ-1}$, what is the liquidus temperature of this magma?

- (b) If this magma cools and undergoes fractional crystallization of solid phases to a temperature of 1100°C, what would be the composition of the remaining magma? What fraction of liquid would remain?
- (c) If instead the oxygen fugacity were FMQ+1, what would be the composition of the remaining magma at 1100°C? How much liquid would remain?

Oxide	Weight percent
SiO ₂	50.37
TiO ₂	1.44
Al ₂ O ₃	15.38
Fe ₂ O ₃	1.10
FeO	8.94
MnO	1.10
MgO	7.92
CaO	11.51
Na ₂ O	2.70
K ₂ O	0.18
P ₂ O ₅	0.15
H ₂ O	0.15

11. For a melt having a composition, in wt %, of:

SiO ₂	58.12%	TiO ₂	0.92%
Al ₂ O ₃	16.47%	Fe ₂ O ₃	1.82%
MgO	5.62%	FeO	9.94%
CaO	7.11%		

use the Ghiorso regular solution model and the interaction parameters in Table 4.3 to:

- (a) calculate the \bar{G}_{ex} and $\Delta\bar{G}_{\text{mixing}}$ for this composition at 1300°C.
 (b) calculate the activity of Si₄O₈ at this temperature.
12. An analysis of an oil field brine from Mississippi with a temperature of 150°C is shown here. Calculate the *activities* of these species at that temperature using the Truesdell–Jones equation.

Problem 12

	Conc g/kg
Na ⁺	63.00
K ⁺	6.15
Mg ²⁺	2.77
Ca ²⁺	44.6
Cl ⁻	200.4
SO ₄ ²⁻	0.13
HCO ₃ ⁻	0.03

13. Show that for a strong electrolyte, i.e., one in which dissociation is complete and:

$$m_- = \nu_- m \text{ and } m_+ = \nu_+ m$$

where m is the molality of the solute component $A_{v_+}B_{v_-}$, that:

$$m_{\pm} = m(v_+^{v_+} v_-^{v_-})^{1/v}$$

where $v = v_+ + v_-$.

I, m	γ_{\pm} observed
0.001	
0.003	0.887
0.006	0.847
0.01	
0.015	0.78
0.03	0.716
0.06	0.644
0.1	
0.15	0.541
0.3	0.462
0.6	0.385
1	
1.5	0.292
3	0.229
6	0.182

- Mean ionic activity coefficients were measured for the following solutions at an ionic strength of 3: $\gamma_{\text{KCl}} = 0.569$, $\gamma_{\text{NaCl}} = 0.734$, $\gamma_{\text{Na}_2\text{CO}_3} = 0.229$. Assuming $\gamma_{\text{Cl}^-} = \gamma_{\text{K}^+} = \gamma_{\pm\text{KCl}}$, what is the activity coefficient of CO_3^{2-} ?
- Calculate the electrostatic, γ_{elect} , and solvation, γ_{solv} , contributions to the mean ionic activity coefficient of MgCl_2 at concentrations of 0.0033, 0.01, 0.033, 0.05, 0.1, 0.33, 0.5, and 1 using the Debye–Hückel (eqn. 3.74) and Robinson and Stokes (eqn. 4.95) equations, respectively. Plot your results, as well as $\gamma_{\text{elect+solv}} = \gamma_{\text{elect}} \gamma_{\text{solv}}$ as a function of ionic strength (i.e., a plot similar to Figure 4.27).
- Calculate the mean ionic activity coefficient for NaCO_3 using the Debye–Hückel and Truesdell–Jones equations and compare your results with the observed values shown here. Overall, which fits the data better?

Chapter 5

Kinetics: the pace of things

5.1 INTRODUCTION

Thermodynamics concerns itself with the distribution of components among the various phases and species of a system at equilibrium. *Kinetics* concerns itself with the *path* the system takes in achieving equilibrium. Thermodynamics allows us to predict the equilibrium state of a system. Kinetics, on the other hand, tells us how and how fast equilibrium will be attained. Although thermodynamics is a macroscopic science, we found it often useful to consider the microscopic viewpoint in developing thermodynamics models. Because kinetics concerns itself with the path a system takes, what we will call *reaction mechanisms*, the microscopic perspective becomes essential, and we will very often make use of it.

Our everyday experience tells one very important thing about reaction kinetics: they are generally slow at low temperature and become faster at higher temperature. For example, sugar dissolves much more rapidly in hot tea than it does in ice tea. Good instructions for making ice tea might then incorporate this knowledge of kinetics and include the instruction to be sure to dissolve the sugar in the hot tea before pouring it over ice. Because of this temperature dependence of reaction rates, low-temperature geochemical systems are often not in equilibrium. A good example might be clastic sediments, which consist of a variety of phases. Some of these phases are in equilibrium with each other and with porewater, but most are not. Another example of this disequilibrium is the oceans.

The surface waters of the oceans are everywhere oversaturated with respect to calcite, yet calcite precipitates from seawater only through biological activity. At a depth of 2500 m, the ocean is undersaturated with calcite, yet calcite shells of micro-organisms persist in sediments deposited at these depths (though they do dissolve at greater depths). Thus, great care must be used in applying thermodynamics to such systems. Even in the best of circumstances, thermodynamics will provide only a limited understanding of low-temperature geochemical systems. A more complete understanding requires the application of kinetic theory. Indeed, for such systems, kinetics is the deciding factor controlling their state and evolution. Even in metamorphic systems, with temperatures in the range of 300–700°C, kinetics factors are crucially important in determining their final states.

High-temperature geochemical systems, such as magmas, are more likely to be in equilibrium, and thermodynamics provides a reasonable understanding of these systems. However, even at high temperatures, kinetic factors remain important and can inhibit equilibrium. One obvious example of disequilibrium at high temperature is the formation of volcanic glasses. Thermodynamics predicts that magmas should crystallize as they cool. But where cooling is rapid enough, this does not occur. Glasses, which in many ways are simply extremely viscous liquids, form instead.

It is perhaps ironic that it is kinetic factors, and a failure to achieve equilibrium, that in the end allow us to use thermodynamics to

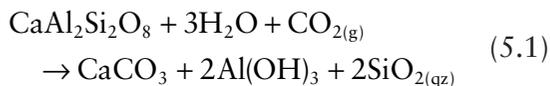
make statements about the Earth's interior. As we pointed out in the preceding chapter, if equilibrium were always achieved, the only rocks we could collect at the surface of the Earth (which is, after all, the only place we can collect them) would consist of quartz, clays, serpentine, and so on; their petrology would tell us nothing about their igneous or metamorphic histories. Fortunately, kinetic factors allow the original minerals and textures of gneisses, peridotites, and lavas to be preserved for our study.

The foregoing might suggest that kinetics and thermodynamics are entirely unrelated subjects, and further, that what we have learned about thermodynamics is of little use in many instances. This is certainly not the case. As we shall see, transition state theory provides a very strong link between kinetics and thermodynamics. What we have learned about thermodynamics will prove very useful in our brief study of kinetics. Furthermore, chemical systems are always governed by a combination of thermodynamics and kinetics, so a full understanding of the Earth requires the use of both thermodynamic and kinetics tools. The goal of this chapter is to add the latter to our geochemical toolbox.

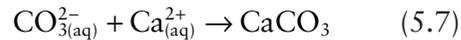
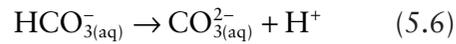
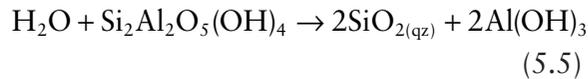
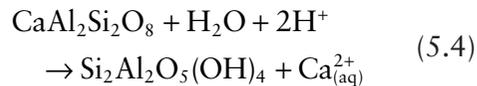
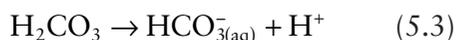
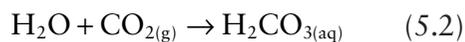
5.2 REACTION KINETICS

5.2.1 Elementary and overall reactions

In thermodynamics, we found that the equilibrium state of a system is entirely independent of the path taken to reach that state. The goal of kinetics is a description of the manner in which the equilibrium state is achieved. This description is inherently path-dependent. Consider, for example, the weathering of anorthite. We can write an *overall* reaction for this process as:



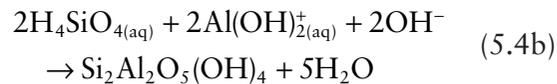
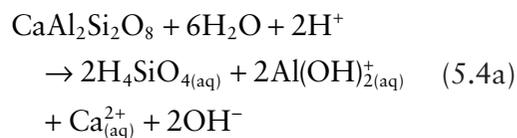
In nature, however, this process will involve several intermediate steps. These intermediate steps can include:



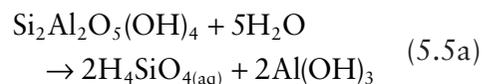
In thermodynamics, eqn. 5.1 is a perfectly adequate description of the reaction. In kinetics, a description of an *overall* reaction, such as 5.1, requires knowledge of the path taken, that is, a knowledge of the steps involved. Reactions 5.2 through 5.7 thus describe the overall reaction 5.1. Reactions 5.2, 5.3, and 5.6 are *elementary reactions* in that they involve only one step and the reaction as written describes what occurs on the microscopic level. The remaining reactions are not elementary in that they each consist of a number of more elementary steps.

5.2.2 Reaction mechanisms

Reaction 5.4 describes the breakdown of anorthite to form kaolinite plus a free calcium ion. This reaction involves profound structural changes in the solid phase that are not described by eqn. 5.4. A full kinetic description of 5.4 will require some knowledge of the steps involved in these structural changes. One possibility is that all components are in solution at an intermediate state:



Reaction 5.5, the breakdown of kaolinite to quartz and gibbsite, could involve SiO_2 dissolving, subsequently precipitating as opaline silica, and later transforming to quartz:



The description of an overall reaction in terms of elementary reactions is called the *reaction mechanism*. The rates of truly elementary reactions are path-independent because there is only one possible path. In this sense, elementary reactions are somewhat analogous to state functions in thermodynamics. Clearly then, an important step in any kinetic study is determination of the reaction mechanism, that is, to describe the process in terms of elementary reactions. As we shall see, there may be more than one possible path for an overall reaction, and several paths may be simultaneously involved. Kinetics can only provide an accurate description of a process if all these paths are known.

5.2.3 Reaction rates

Consider a reaction such as the precipitation of dolomite from a solution. We can describe this as:



We *define* the *rate* of this reaction, \mathfrak{R} , as the rate at which dolomite is produced:

$$\mathfrak{R} \equiv \frac{d[\text{CaMg}(\text{CO}_3)_2]}{dt}$$

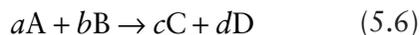
Clearly, if dolomite is to be formed, CO_3^{2-} must be consumed in this reaction twice as fast as Ca or Mg. For every mole of Ca or Mg consumed, exactly two moles of CO_3^{2-} will also be consumed and one mole of dolomite produced. This being the case, we could equally well express the reaction rate as:

$$\mathfrak{R} = -\frac{1}{2} \frac{d[\text{CO}_3^{2-}]}{dt}$$

or

$$\mathfrak{R} = -\frac{d[\text{Ca}^{2+}]}{dt} = -\frac{d[\text{Mg}^{2+}]}{dt}$$

We can now formulate the general rule. For any reaction such as:



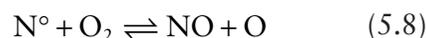
The *reaction rate*, \mathfrak{R} , is defined as the change in composition of the reaction mixture with time:

$$\mathfrak{R} \equiv -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \quad (5.7)$$

The brackets denote the concentrations of the species and the negative sign indicates that reactants are consumed as the reaction proceeds. Thus *the rate of a reaction is simply the rate at which a reactant is consumed or product produced* divided by its stoichiometric coefficient.

5.2.3.1 The reaction rate for an elementary reaction: composition dependence

Reaction rates will, in general, depend on the concentration of the reactant. To understand this, consider the reaction:



This reaction between free nitrogen atoms and oxygen molecules occurs in the stratosphere (where N° is produced by high-energy collisions involving N_2) and contributes to the production of nitrous oxide. Let's assume that reaction 5.8 is an adequate description of this reaction. In other words, we are assuming that 5.8 is an elementary reaction, and the reaction mechanism for the production of NO from nitrogen and oxygen gas is collision of a N° molecule and O_2 molecule. For the reaction to occur, the nitrogen and oxygen molecules must collide with enough kinetic energy that the mutual repulsion of the electron clouds is overcome and the electrons can be redistributed into new covalent orbits. The repulsive force represents an energy barrier, E_B , which will prevent low-energy nitrogen and oxygen atoms from reacting. Figure 5.1 illustrates this point. The reaction rate will therefore depend on (1) the number of collisions per unit time, and (2) the fraction of N and O molecules having energy greater than the barrier energy.

Let's first consider the number of collisions per unit time. In order for a "collision" to occur, the electron clouds must overlap, that is, they must approach within $(r_N + r_{\text{O}_2})$, where r_N and r_{O_2} are the radii of the nitrogen and oxygen molecules. To make things simple, imagine the oxygen to be fixed and the nitrogen in motion. In other words, our reference frame will be that of the oxygen molecules. We can imagine the nitrogen sweeping out a cross-section with radius $(r_N + r_{\text{O}_2})$ as it travels. If the nitrogen is travelling at velocity v , in

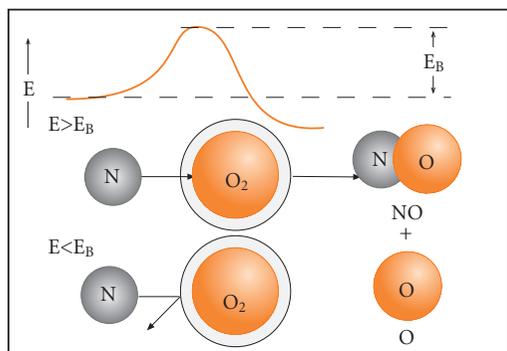


Figure 5.1 A nitrogen atom approaching an oxygen molecule must have enough kinetic energy to pass through the region where it is repelled by electrostatic repulsion of the electron cloud of the oxygen. Otherwise, it will not approach closely enough so that its electrons can combine with those of oxygen.

time t it will sweep out a cylindrical volume (Figure 5.2):

$$V = v\pi(r_N + r_{O_2})^2 t \quad (5.9)$$

Whether a collision occurs will depend on whether the *center* of an oxygen molecule falls within this volume (Figure 5.2). The number of collisions that will occur in this time will be:

$$C = n_O v \pi (r_N + r_{O_2})^2 t \quad (5.10)$$

where n_O is the number of oxygen molecules per unit volume. The number of collisions per unit time is then simply:

$$\frac{C}{t} = n_O v \pi (r_N + r_{O_2})^2 \quad (5.11)$$

If there are n_N nitrogen atoms and the average velocity between nitrogen and oxygen molecules is \bar{v} , then the number of collisions per unit time is:

$$\dot{c} = n_N n_O \bar{v} \pi (r_N + r_{O_2})^2 \quad (5.12)$$

If we let $k = \bar{v} \pi (r_N + r_{O_2})^2$

then the rate at which collisions occur is:

$$\dot{c} = k n_N n_{O_2} \quad (5.13)$$

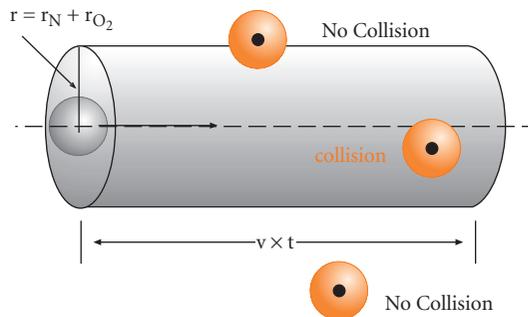


Figure 5.2 A nitrogen atom will sweep out a volume $V = v\pi(r_N + r_{O_2})^2 t$ in time t . Whether a collision occurs will depend on whether the center (indicated by black dot) of an oxygen atom falls within this volume.

Thus we see that the reaction rate in this case will depend on the concentration of nitrogen, oxygen and a constant that depends on the nature of the reactants. This is a general result.

5.2.3.2 The reaction rate for an elementary reaction: temperature dependence

We now need to estimate the fraction of nitrogen and oxygen atoms having at least the barrier energy, E_B . For simplicity, we will assume that oxygen and nitrogen molecules have an identical energy distribution. The Boltzmann distribution law, which we encountered in Section 2.8.4.1 (eqn. 2.84), can be written to express the average number of molecules having energy level ε_i as:

$$n_i = A e^{-\varepsilon_i/kT} \quad (5.14)$$

where k is Boltzmann's constant and A is a constant (comparing with equation 2.84, we see that $A = n/Q$ where n is the total number of molecules in the system and Q is the *partition function*). In plain English, this equation tells us that the number of molecules in some energy level i decreases exponentially as the energy of that level increases (Figure 2.9). We want to know the number of molecules with energy greater than E_B . In this case we are dealing with translational energy. The quantum spacings between translational energy levels are so small that they essentially form a continuum, allowing us to integrate eqn. 5.14.

Fortunately for us, the integration of 5.14 from $\varepsilon = E_B$ to infinity has a simple solution:

$$A \int_{E_B}^{\infty} e^{-\varepsilon_i/kT} d\varepsilon = AkT e^{-E_B/kT} \quad (5.15)$$

The *fraction* of molecules with energy greater than E_B is just:

$$\frac{A \int_{E_B}^{\infty} e^{-\varepsilon_i/kT} d\varepsilon}{A \int_0^{\infty} e^{-\varepsilon_i/kT} d\varepsilon} = \frac{AkT e^{-E_B/kT}}{AkT} = e^{-E_B/kT} \quad (5.16)$$

The rate of reaction will be the rate of collision times the fraction of molecules having energy greater than E_B :

$$\mathfrak{R} = n_N n_O \bar{v} \pi (r_N + r_{O_2})^2 e^{-E_B/kT} \quad (5.17)$$

Now we just need to find a value for velocity. The average velocity can be calculated from the Maxwell-Boltzmann Law,* which gives the distribution of velocities of molecules in a gas. Doing so, we find that the average velocity is:

$$\bar{v} = \sqrt{\frac{8kT}{\pi\mu}} \quad (5.18)$$

where μ is the reduced mass, $\mu = m_N m_{O_2} / (m_N + m_{O_2})$. Substituting 5.18 into 5.17, our equation for the reaction rate is:

$$\mathfrak{R} = n_N n_O \pi (r_N + r_{O_2})^2 \sqrt{\frac{8kT}{\pi\mu}} e^{-E_B/kT} \quad (5.19)$$

Redefining k as:

$$k = \pi (r_N + r_{O_2})^2 \sqrt{\frac{8kT}{\pi\mu}} e^{-E_B/kT} \quad (5.20)$$

our reaction rate equation is:

$$\mathfrak{R} = k n_N n_{O_2} \quad (5.21)$$

Thus the reaction rate in this case depends on the concentration of nitrogen and oxygen and a constant k , called the *rate constant*,[†] which depends upon temperature, properties of the reactants, and the barrier energy.

In a more rigorous analysis we would have to take into consideration atoms and molecules not being spherically symmetric and that, as a result, some orientations of the molecules are more likely to result in reaction than others. In addition, a head-on collision is more likely to result in reaction than a glancing blow, so the collision cross-section will be less than $\pi(r_N + r_{O_2})^2$. These factors can, however, be accounted for by multiplying by a constant, called a *steric factor*, so the form of our equation, and the temperature dependence, would not be affected. Values of steric factors for various reactions range over many orders of magnitude and can be quite small. In rare circumstances, they can be greater than 1 (implying an effective collision cross-section greater than the combined atomic radii).

Temperature occurs in two places in eqn. 5.22; however, the square-root dependence is slight compared to the exponential one. For example, consider a temperature change of 300 K to 325 K. For a reaction with an activation energy of 25 kJ, the exponential temperature dependence results an increase in reaction rate of more than a factor of 2, whereas the square root dependence increases the reaction rate by only 4%. Hence the temperature dependence can be essentially expressed as:

$$k \propto e^{-E_B/kT} \ddagger$$

The temperature dependence of the rate constant is most often written as:

$$\boxed{k = A e^{-E_B/kT}} \quad (5.22)$$

* So-called because Maxwell proposed it and Boltzmann proved it rigorously.

† To distinguish the rate constant, k , from Boltzmann's constant, k , we will always write the former in lower-case italics and the latter in roman typeface.

‡ This form of the temperature dependence of reaction rate was first proposed by Jacobus H. Van't Hoff (1852–1911), who deduced it by analogy to eqn. 3.96, the *Van't Hoff equation*. Van't Hoff was born in Rotterdam and in 1878 was appointed professor of geology, mineralogy, and chemistry at the University of Amsterdam. In 1896 he moved to the University of Berlin, where he remained for the rest of his life. He won the Nobel Prize for Chemistry in 1901.

which is the important *Arrhenius relation*.^{*} It expresses the rate constant in terms of the barrier, or *activation*, energy (also often written as E_A or E^*), and A , a proportionality constant sometimes called the *frequency factor* (because it depends on the frequency of collisions), and temperature. (We can replace k , Boltzmann's constant with R , the gas constant, if we deal in moles rather than atoms.)

The temperature dependence of the rate constant is illustrated in Figure 5.3. We see that the reaction rate falls off by a factor of 10^2 as temperature is decreased from 500 to 200 K. This confirms our everyday experience that reaction rates are extremely temperature-dependent. Table 5.1 lists some examples of activation energies for geochemical reactions.

The pre-exponential factor, A , is often assumed to be independent of temperature. Comparison of eqn. 5.22 with 5.21 shows, however, that it need not be. In the case of an elementary gas phase reaction, we would

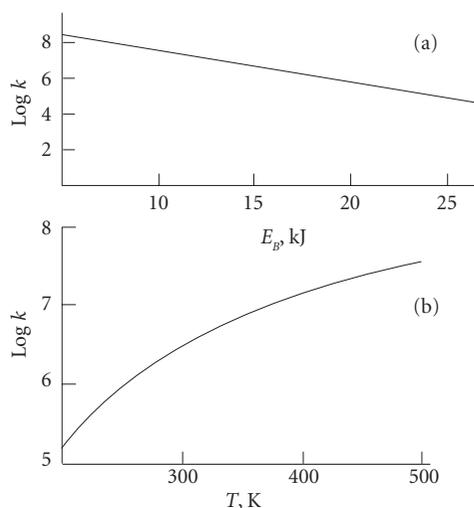


Figure 5.3 (a) Relative change in the reaction rate as a function of activation energy at 300 K. (b) Change in the reaction rate for the same as a function of temperature with an activation energy of 15 kJ.

Table 5.1 Activation energies of some geochemical reactions.

Reaction	E_A kJ/mol
$\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2 \rightarrow 3\text{MgSiO}_3 + \text{SiO}_2 + \text{H}_2\text{O}$	371.8
$\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{CaCO}_3 + \text{CO}_2$	225.0
$2\text{CaCO}_3 + \text{Mg}^{2+} \rightarrow (\text{CaMg})\text{CO}_3 + \text{Ca}^{2+}$	117.1
$\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O} + \text{SiO}_2 \rightarrow \text{NaAlSi}_3\text{O}_8 + \text{H}_2\text{O}$	106.3
$\text{C}_2\text{H}_4 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$	102.8
$\text{CaF}_2 \rightarrow \text{Ca}^{2+} + 2\text{F}^-$	73.0
$\text{MgSiO}_3 + 2\text{H}^+ + \text{H}_2\text{O} \rightarrow \text{Mg}^{2+} + \text{H}_4\text{SiO}_4$	49.0
$\text{SiO}_2(\text{qz}) + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_4$	40.6
$\text{SiO}_2(\text{am}) + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{SiO}_4$	35.8
$\text{H}_2\text{SiO}_4 \rightarrow \text{SiO}_2(\text{qz}) + 2\text{H}_2\text{O}$	28.4
$\text{Mg}_2\text{SiO}_4 + 4\text{H}^+ \rightarrow 2\text{Mg}^{2+} + \text{H}_2\text{SiO}_4$	21.7
$\text{CaCO}_3 \rightarrow \text{Ca}^{2+} + \text{CO}_3^{2-}$	20.1
$\text{O} + \text{O}_3 \rightarrow 2\text{O}_2$	13.4

^{*} Named for Svante August Arrhenius (1859–1927) because Arrhenius provided the theoretical justification for Van't Hoff's proposal. Arrhenius's PhD dissertation, completed in 1884 at the University of Uppsala in Sweden, was rated fourth class by the committee of examiners, implying great things were not expected of him. The old boys must have been a little surprised 19 years later when Arrhenius won the Nobel Prize for chemistry. Among Arrhenius's other contributions were the ionic theory of electrolyte solutions and the greenhouse theory of climate: that the CO_2 concentration in the atmosphere could be an important control on global temperature, and that anthropogenic burning of fossil fuel could lead to global warming.

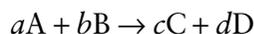
predict a dependence on the square root of temperature. Other kinds of reactions show other kinds of temperature dependencies of the frequency factor, however. A more accurate expression of temperature dependence of the reaction rate is:

$$k = AT^n e^{-E_B/kT} \quad (5.23)$$

where the exponent n can be any number. Nevertheless, the temperature dependence of the frequency factor is usually small and it can often be safely neglected, as in our example above.

5.2.3.3 A general form of the rate equation

In general, the rate of a reaction such as:



can be expressed as:

$$\mathfrak{R} = k a_A^{n_A} a_B^{n_B} a_C^{n_C} a_D^{n_D} \quad (5.24)^*$$

where k is the *rate constant* and a_A , etc. are activities (we will often use the simplifying assumption of ideality and replace these by concentrations). The exponents n_A , n_B , and so on, can be any number, including zero. The sum of the exponents n_A , n_B , . . . is the *order of the reaction*. In general, the value of the exponents must be determined experimentally, though their values can be predicted if the reaction mechanism is known, as we saw in the above example.

Just as the mole fraction was the unit of choice for thermodynamics, *moles per volume, or moles per area in the case of reactions taking place on surfaces, is the unit of choice for kinetics*. Thus wherever more than one phase is involved, one concentration should be expressed in moles per unit area or volume.

There are several simplifications of eqn. 5.24 for *elementary reactions*. First, the rate of reaction is independent of the concentration of the products, so the exponents of the products will be 0. Indeed, *one of the criteria for an elementary reaction is that the product does not influence the reaction rate*. Second,

the values of the exponents for the reactants are the stoichiometric coefficients of the reactant species. Thus if the reaction can be written in terms of a series of elementary reactions, then the exponents for the rate equation can be deduced from those of the component elementary reactions. For elementary reactions, the order of reaction will be equal to the sum of the stoichiometric coefficients of the reactants. For complex reactions, however, the order of reaction must be deduced, either experimentally, or from the component elementary reactions.

A further simplification may be made where one of the reactants is in sufficient abundance that its concentration is not affected by the progress of the reaction of interest. For instance, the hydration of CO_2 through:



The rate of this reaction will be:

$$-\frac{d[\text{CO}_2]}{dt} = k[\text{CO}_2][\text{H}_2\text{O}]$$

which is a second-order reaction. However, in aqueous solution, H_2O will always be present in great excess over CO_2 and its abundance will not be significantly changed by this reaction. This allows us to treat the reaction as if it were first order and to define a *pseudo-first order* rate constant, k^* , as:

$$k^* = k[\text{H}_2\text{O}]$$

Since $[\text{H}_2\text{O}]$ is constant, it follows that k^* is as well. The reaction rate can then be written as:

$$-\frac{d[\text{CO}_2]}{dt} = k^*[\text{CO}_2]$$

In Examples 5.1 and 5.2 we have used just such a *pseudo-first order* rate constant.

5.2.4 Rates of complex reactions

Deciding whether a reaction is elementary is not always straightforward. Consider the reaction:

* Don't confuse this equation, which expresses the way in which reaction rates depend on concentrations, with eqn. 5.7, which is the definition of the reaction rate.

Example 5.1 Rate of hydration of $\text{CO}_{2(\text{aq})}$

The rate for the hydration of CO_2 (i.e., $\text{CO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$) has been found to follow the first-order rate law:

$$-\frac{d[\text{CO}_{2(\text{aq})}]}{dt} = k[\text{CO}_{2(\text{aq})}] \quad (5.25)$$

At 25°C , k has been determined to be 0.014 sec^{-1} . Make a graph showing how the concentration of CO_2 will change with time as the reaction proceeds, assuming an equilibrium (i.e., final) CO_2 concentration of 0.

Answer: Since we are not given the absolute concentrations, we cannot determine the absolute change. We can, however, determine relative change. To do so, we just integrate 5.25:

$$-\int \frac{d[\text{CO}_{2(\text{aq})}]}{[\text{CO}_{2(\text{aq})}]} = k \int_0^t dt$$

With some rearranging, we obtain:

$$\frac{[\text{CO}_{2(\text{aq})}]}{[\text{CO}_{2(\text{aq})}]_0} = e^{-kt} \quad (5.26)$$

Figure 5.4 shows our result. It is apparent that this is a fast reaction. We can assume that equilibrium will prevail on most time-scales of interest to us.

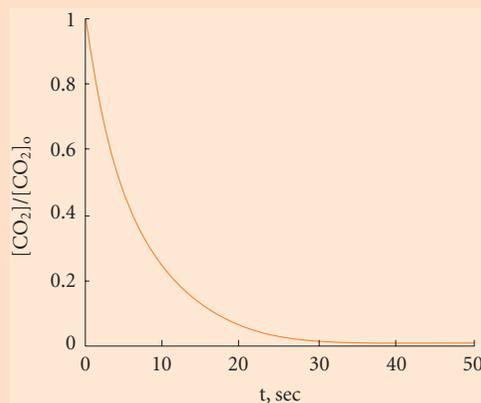
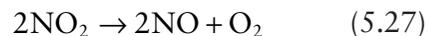


Figure 5.4. Progress in the reaction $\text{CO}_{2(\text{aq})} + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3$ with time, as measured by decrease in $[\text{CO}_2]$.



$$-\frac{d[\text{NO}_2]}{dt} = 2k[\text{NO}_2]^2$$

On a microscopic basis, we might describe this reaction as the collision of two NO_2 molecules to form two NO molecules and an O_2 molecule. Since no intermediate steps occur, this would appear to be an elementary reaction. The rate equation for this reaction has been experimentally determined to be:

This has the predicted form for an elementary reaction of second order; thus experiment confirms that reaction 5.27 is elementary.

Now consider the reaction: $2\text{O}_3 \rightarrow 3\text{O}_2$

We might reason that this reaction requires only the collision of two ozone molecules

with no intermediate products and that the reaction is therefore primary. However, the experimentally determined rate law is:

$$\frac{1}{3} \frac{d[\text{O}_2]}{dt} = -\frac{1}{2} \frac{d[\text{O}_3]}{dt} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} \quad (5.28)$$

Since the rate depends on the concentration of the product, the reaction is not elementary and must involve intermediate steps.

5.2.4.1 Chain reactions and branching

Many overall reactions involve a series of sequential elementary reactions, or steps, each

Example 5.2 Oxidation of ferrous iron

Given the adjacent equilibrium and pseudo-first order rate constants for the oxidation of three species of ferrous iron (Fe^{2+} , $\text{Fe}(\text{OH})^+$, and $\text{Fe}(\text{OH})_2$) to ferric iron in the adjacent table, calculate the overall rate of oxidation of ferrous iron at pH 2, 6, and 8, assuming a total Fe^{2+} concentration of 10^{-6} M.

Answer: The overall oxidation rate can be written as:

$$\frac{d\Sigma\text{Fe}^{2+}}{dt} = k_1[\text{Fe}^{2+}] + k_2[\text{FeOH}^+] + k_3[\text{Fe}(\text{OH})_2] \quad (5.29)$$

Equilibrium constants	
Reaction	pK
$\text{Fe}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})^+ + \text{H}^+$	4.5
$\text{Fe}(\text{OH})^+ + \text{H}_2\text{O} \rightleftharpoons \text{Fe}(\text{OH})_2 + \text{H}^+$	7.4

Oxidation rate constants	
Fe ²⁺ Species	k(s ⁻¹)
Fe ²⁺	7.9×10^{-6}
FeOH ⁺	25
Fe(OH) ₂	7.9×10^6

Thus to calculate the rate, we will have to calculate concentrations of the various species. These are given by:

$$[\text{FeOH}^+] = K_1 \frac{[\text{Fe}^{2+}]}{[\text{H}^+]} \quad \text{and} \quad [\text{Fe}(\text{OH})_2] = K_2 \frac{[\text{Fe}^{2+}]}{[\text{H}^+]^2}$$

Substitute these expressions we have:

$$\frac{d\Sigma\text{Fe}^{2+}}{dt} = [\text{Fe}^{2+}] \left(k_1 + \frac{k_2 K_1}{[\text{H}^+]} + \frac{k_3 K_2}{[\text{H}^+]^2} \right) \quad (5.30)$$

Since the total Fe^{2+} is the same at all three pHs, the concentration of the Fe^{2+} ion must vary. So we need to calculate the concentration of ionic Fe^{2+} at these pHs. The total Fe^{2+} is:

$$\Sigma\text{Fe}^{2+} = [\text{Fe}^{2+}] + [\text{FeOH}^+] + [\text{Fe}(\text{OH})_2]$$

or:

$$\Sigma\text{Fe}^{2+} = [\text{Fe}^{2+}] \left(1 + \frac{K_1}{[\text{H}^+]} + \frac{K_2}{[\text{H}^+]^2} \right)$$

so that:

$$[\text{Fe}^{2+}] = \frac{\Sigma\text{Fe}^{2+}}{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_2}{[\text{H}^+]^2}}$$

We can now calculate the rates. Substituting appropriate values into eqn. 5.30, we find the rate is 0.0031 M sec⁻¹ at pH 2, 0.9371 M sec⁻¹ at pH 4 and 7.89 M sec⁻¹ at pH 8. Thus the combination of the different rate constants and the pH dependency of the Fe speciation results in a very strong pH dependence of the oxidation rate.

of which must be completed before a subsequent reaction can occur. Such reactions are termed *chain reactions*. It is also possible that the path of an overall reaction may include two or more alternative elementary reactions, or sequences of elementary reactions, that occur simultaneously. These alternative paths are called *branches*. The combustion of hydrogen is a good example because it is a chain reaction involving several branches.

Experiments have shown that the reaction rate for the combustion of hydrogen is not simply:

$$\frac{d[\text{H}_2\text{O}]}{dt} = k[\text{H}_2]^2[\text{O}_2] \quad (5.31)$$

and therefore $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$ is not an elementary reaction. If it were an elementary reaction, eqn. 5.31 predicts that its rate should continuously decrease through the course of the reaction (provided temperature is held constant!) since the reactants will be consumed and their concentrations will decrease. In actuality the rate of this reaction can increase rapidly, sometimes catastrophically (even at constant temperature), as it proceeds. Evidently, the reaction mechanism is more complex. Indeed, it appears to involve several steps. The final step of this reaction is:

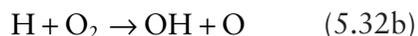


This is an elementary reaction, depending only on the concentration of the two reactants. However, one of the reactants, OH, and one of the products, H, are not among the original constituents of the gas. Rather, they are created by intermediate steps. Species that do not appear in the overall reaction are termed *reactive intermediates*.

The first step in the combustion of hydrogen is breakup of the hydrogen molecule, forming highly reactive atomic H:



The next step is reaction of the atomic hydrogen with an oxygen molecule:

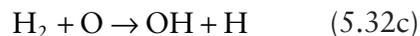


Reactions 5.32a and 5.32b are an example of a *chain reaction*.

Since 5.32 is an elementary reaction, the reaction rate can be written as:

$$\frac{d[\text{H}_2\text{O}]}{dt} = k[\text{OH}][\text{H}_2]$$

This is also the rate of the overall reaction. Thus the overall reaction will depend on the availability of OH. What makes the combustion of hydrogen particularly interesting is that there are several ways in which OH may be created. Reaction 5.32b is one way. The monatomic oxygen created in this reaction, however, provides two alternative mechanisms for the creation of the OH complex:

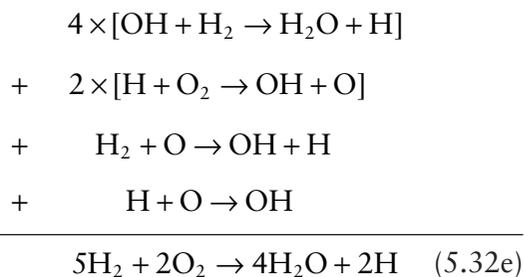


and



Reactions 5.32b through 5.32d represent alternative reaction paths or *branches*. Notice that the final step also provides an alternative mechanism, or branch, for the production of monatomic hydrogen.

The branching that occurs provides the potential for a “runaway” or explosive reaction. This is apparent if we simply sum reactions 5.32 and 5.32b through 5.32d:



Each cycle of these reactions produces four water molecules plus two hydrogens. Since the rate of the overall reaction, i.e., the production of water, depends on [OH], which in turn depends on [H], the reaction will accelerate with time. (Actually, the combustion of hydrogen is a *very* complex reaction. When all the elementary reactions are written down, including the reverse reactions and reactions with the container wall, they fill an entire page. Interestingly, it displays this runaway behavior only under certain combinations of T, P, and container size and shape. The latter dependence results from reactions with, or catalyzed by, the container wall. Under certain conditions, it will become steady state; i.e., the creation and consumption of water balance to produce a constant concentration of water.)

5.2.4.2 Rate-determining step

It often happens that the reaction rate of a chain, or sequential, reaction, is controlled by

a single step that is very much slower than the other steps. For example, how quickly you can buy a pencil at the campus bookstore on the first day of class will probably be controlled entirely by how quickly you can get through the checkout line. Such a step is called the *rate-determining step*. Once the rate of this step is determined, the rates of all other steps are essentially irrelevant.

Now consider a reaction that can occur through two branches. For example,



The reaction rate is then:

$$\frac{d[A]}{dt} = -(k_1 + k_2)[A] \quad (5.33)$$

If one path is very much faster than the other, then the fastest of the two will always be taken. Thus for branched reactions, the fastest branch determines the reaction mechanism. Mathematically, we may say that if $k_1 \gg k_2$ then $(k_1 + k_2) \approx k_1$ and therefore:

$$\frac{d[A]}{dt} \approx -k_1[A]$$

In our analogy above, if an express checkout is available, you would certainly take it. In this case, the slowness of the regular checkout line becomes irrelevant for determining how quickly you can buy your pencil. To sum up, we may say that when reactions occur *in series*, then *the slowest reaction is the rate-determining step*. When *parallel*, or branched, reaction paths of very different speeds are available, then only *the fastest path is of interest*.

5.2.5 Steady state and equilibrium

Many geochemical systems are steady-state ones, that is, time-invariant systems, or approximately so. The equilibrium state is also a steady state, but not all steady-state systems are necessarily equilibrium ones. We may say then that steady state is a necessary, but not sufficient, condition for *equilibrium*. Let's consider how a system will approach the steady state and equilibrium.

Consider the elementary reaction: $A \rightarrow B$

Suppose that this reaction does not entirely consume A, but reaches a steady state where the concentration of A is $[A]_s$, the subscript s

denoting the steady state. In this case, we can express the reaction rate as:

$$\frac{d[A]}{dt} \approx k([A]_s - [A]) \quad (5.34)$$

where $[A]_s$ is the steady state concentration of A. The reaction rate is 0 when $[A] = [A]_s$.

To see how the concentration will vary before steady state is achieved, we integrate eqn. 5.34:

$$\ln\left(\frac{[A]_s - [A]}{[A]_s - [A]^\circ}\right) = -kt$$

where $[A]^\circ$ is the initial concentration of A. This may be written as:

$$\frac{[A]_s - [A]}{[A]_s - [A]^\circ} = e^{-kt} \quad (5.35)$$

The denominator is a constant (for a given set of initial conditions), so we can rewrite eqn. 5.35 as:

$$[A]_s - [A] = Ce^{-kt}$$

The excess concentration of A, i.e., $[A] - [A]_s$ declines as e^{-t} , so that steady state is approached asymptotically. An effective steady state will be achieved when $t \gg 1/k$. As in Example 5.1, the reaction rate decreases exponentially with time, i.e.:

$$\frac{d[A]}{dt} = kCe^{-kt}$$

Now suppose that in addition to the reaction: $A \rightarrow B$, the reaction $B \rightarrow A$ also occurs and that both are first-order elementary reactions. The rates of reaction will be:

$$\frac{d[A]}{dt} = -k_+[A] + k_-[B] \quad (5.36)$$

Here we are using k_+ for the rate constant of the forward reaction and k_- for the rate constant of the reverse reaction. Assuming the system is closed and that no other processes affect the concentrations of A and B, then:

$$[A] + [B] = \Sigma AB$$

where ΣAB is the total of A and B and is a constant. Equation 5.36 can therefore be written as: