# Suggested Reading

P Hakonen and OV Lounasmaa, *Science* **265**, 1821 (1994). Describes experiments on spins in metals showing negative temperatures.

TL Hill, *An Introduction to Statistical Thermodynamics*, Addison-Wesley, 1960. The classic text for discussion of ensembles and fluctuations, and many applications of statistical mechanics.

C Kittel and H Kroemer, *Thermal Physics*, 2nd edition, WH Freeman, New York, 1980. Outstanding general text on statistical thermodynamics. Good discussion of negative temperatures.

RK Pathria, *Statistical Mechanics*, Pergamon, Oxford, 1972. Excellent advanced treatment of statistical mechanics, including a good description of fluctuations.

JR Waldram, *The Theory of Thermodynamics*, Cambridge University Press, Cambridge, 1985. Excellent discussion of fluctuations.

13 Chemical Equilibria
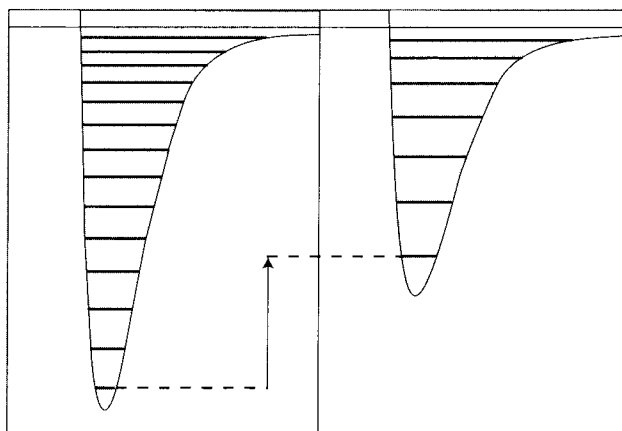
Simple Chemical Equilibria Can Be Predicted from Atomic Structures

A major goal in chemistry is to predict the equilibria of chemical reactions, the relative amounts of the reactants and products, from their atomic masses, bond lengths, moments of inertia, and their other structural properties. In this chapter, we consider reactions in the gas phase, which are simpler than reactions in liquid phases. In Chapter 16 we will consider solvation effects.

The Condition for Chemical Equilibrium

First consider the simplest equilibrium between two states, A and B,

$$A \xrightarrow{K} B. \tag{13.1}$$

Two-state equilibria include: chemical isomerization, the folding of a biopolymers from an open to a compact state, the binding of a ligand to a surface or a molecule, the condensation of a vapor to a liquid or the freezing of a liquid to a solid.

The *equilibrium constant* K is the ratio of the numbers or concentrations of particles in each of the two states at equilibrium. To make it unambiguous whether K is the ratio of the amount of A divided by the amount of B or B divided by A, the arrow in Equation (13.1) has a direction. It points to the *final*

state from the *initial state*. The terms 'initial' and 'final' have no implication about time or kinetics. They imply only which is the numerator and which is the denominator in the equilibrium constant K. With the direction shown in Equation (13.1), K is the ratio B/A. You can point the arrow in either direction. Once you choose the direction, the sign of every thermodynamic quantity is determined.

The quantity that predicts chemical equilibria is the chemical potential. For equilibria at fixed temperature and pressure, the appropriate extremum function is the Gibbs free energy: $dG = -SdT + Vdp + \mu_A dN_A + \mu_B dN_B$, where N_A and N_B are the numbers of particles in the two states, and μ_A and μ_B are their chemical potentials. At constant T and p, the condition for equilibrium is

$$dG = \mu_A dN_A + \mu_B dN_B = 0. \tag{13.2}$$

If every molecule is in either state A or B, the total number of molecules N_{total} is constant:

$$N_A + N_B = N_{\text{total}} = \text{constant} \quad \Rightarrow \quad dN_A + dN_B = 0. \tag{13.3}$$

A molecule lost as A is converted to a B molecule, so $dN_A = -dN_B$, and the condition for equilibrium Equation (13.2) can be written in terms of dN_A:

$$(\mu_A - \mu_B)dN_A = 0. \tag{13.4}$$

Equation (13.4) must hold for any non-zero variation dN_A, so the condition for equilibrium is that the chemical potentials of species A and B are the same:

$$\mu_A = \mu_B. \tag{13.5}$$

Now we want to get μ_A and μ_B from microscopic models, to predict how chemical equilibria depend on atomic structures. We need to relate each chemical potential to its partition function.

Partition Functions for Chemical Reactions

First, to simplify our notation for the rest of the chapter, we express the partition function (Equation (10.18) as q', with an added ',
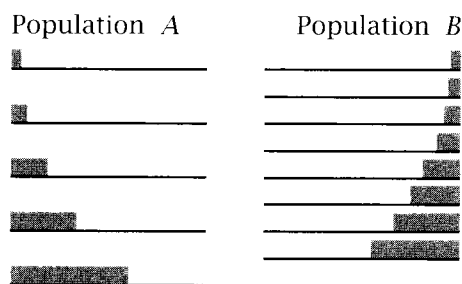
$$q' = \sum_{j=0}^{t} e^{-\varepsilon_j/kT} = e^{-\varepsilon_0/kT} + e^{-\varepsilon_1/kT} + \ldots + e^{-\varepsilon_t/kT}. \tag{13.6}$$

This allows us to redefine q, without the ', as a reduced partition function with the ground-state term factored out,

$$q = e^{\varepsilon_0/kT}q'$$
$$= 1 + e^{-(\varepsilon_1-\varepsilon_0)/kT} + e^{-(\varepsilon_2-\varepsilon_0)/kT} + \ldots + e^{-(\varepsilon_t-\varepsilon_0)/kT}. \tag{13.7}$$

In terms of q', the chemical potential μ_A for species A is given by Equation (11.47):

$$\mu_A = -kT \ln\left(\frac{q'_A}{N_A}\right). \tag{13.8}$$

Population *A*   Population *B*

Figure 13.1 Hypothetical energy ladders for the two-state equilibrium $A \rightarrow B$. Two factors contribute to the equilibrium populations of A and B: low energies and high densities of states. A has the lowest energy ground state, but B has the higher density of states.

Similarly for *B*,

$$\mu_B = -kT \ln \left(\frac{q_B'}{N_B} \right). \tag{13.9}$$

At equilibrium, all the energy levels of both species A and B are accessible to any molecule. A given molecule may be species A for a while at one energy level, then it may change to species B, at some other energy level. At equilibrium, the individual molecules of species A and B will be distributed according to the Boltzmann distribution, with the largest number of molecules in the lowest energy state. The number of molecules populating a given state is determined only by the energy, and not by whether the molecule is in the form of A or B.

Figure 13.1 shows a pair of possible energy ladders for A and B, illustrating a case in which the state of lowest energy (and therefore highest population) is the ground state of A. This does not mean that more particles will be A's than B's. The relative numbers of A's and B's is a sum of Boltzmann factors over all the energy levels. If the energy level spacings are closer for B than for A, B may be the species with the greater total population.

Substituting Equations (13.9) and (13.8) into the equilibrium condition $\mu_A = \mu_B$ (Equation (13.5)) gives $q_B'/N_B = q_A'/N_A$. Defining the **equilibrium constant** K as the ratio N_B/N_A gives

$$K = \frac{N_B}{N_A} = \left(\frac{q_B'}{q_A'} \right) = \left(\frac{q_B}{q_A} \right) e^{-(\varepsilon_{0B} - \varepsilon_{0A})/kT}. \tag{13.10}$$

Equation (13.10) gives a way to compute K from the atomic properties of A and B through their partition functions. Equation (13.10) takes no account of the interactions of one molecule with another, and therefore it applies only to isolated particles such as those in the gas phase.

More Complex Equilibria

Let's generalize to the reaction

$$aA + bB \xrightarrow{K} cC, \tag{13.11}$$

where a, b, and c indicate the stoichiometries of species A, B, and C. What is the appropriate way to define an equilibrium constant for this reaction? At constant T and p the condition for equilibrium is

$$dG = \mu_A dN_A + \mu_B dN_B + \mu_C dN_C = 0. \tag{13.12}$$

This equilibrium is subject to two stoichiometric constraints:

$$\frac{N_A}{a} + \frac{N_C}{c} = \text{constant,} \quad \text{and} \quad \frac{N_B}{b} + \frac{N_C}{c} = \text{constant.} \quad (13.13)$$

Here is the logic behind these constraints. Because N_A is the number of particles of type A, and because a is the number of A-type particles required for each stoichiometric conversion to C, N_A/a is the number of stoichiometric conversions that would consume the N_A particles. Similarly, N_C/c is the number of A-type particles that *have already been* stoichiometrically converted to C. The sum $N_A/a + N_C/c$ is the total number of possible stoichiometric conversions of all the A-type particles that were originally put into the reaction vessel. Example 13.1 may make this clearer.

EXAMPLE 13.1 Stoichiometry. Suppose 4 tires T and 6 windows W are needed to construct one car C. Then the 'equilibrium' for the 'reaction' that transforms tires and windows into cars can be written as

$$4T + 6W \rightarrow C.$$
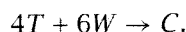
There are two constraints. The first is

$$\frac{T}{4} + C = \text{constant,}$$

so $T + 4C$ is a constant. The number of tires not yet on cars is T. The number of tires already on cars is $4C$. $T + 4C$ is the total number of tires, including those that are on cars and those that are not. ($T/4$ is the number of 'car-units' of tires not yet on cars and C is the number of car-units of tires already on cars.) The other constraint,

$$\frac{W}{6} + C = \text{constant,}$$

describes the conservation of windows, on cars and not yet installed.

Now let's return to chemical equilibria. Taking the differential elements of constraint Equations (13.13), you have

$$dN_A = -\frac{a}{c} dN_C \quad \text{and} \quad dN_B = -\frac{b}{c} dN_C. \quad (13.14)$$

Substituting these constraints into Equation (13.12) leads to

$$\left(\mu_C - \frac{a}{c}\mu_A - \frac{b}{c}\mu_B \right) dN_C = 0, \quad (13.15)$$

so at equilibrium,

$$c\mu_C = a\mu_A + b\mu_B. \quad (13.16)$$

Substituting the definitions of chemical potential from Equations (13.8) and (13.9) into equilibrium Equation (13.16) gives

$$c \left[-kT \ln \left(\frac{q_C'}{N_C} \right) \right] = a \left[-kT \ln \left(\frac{q_A'}{N_A} \right) \right] + b \left[-kT \ln \left(\frac{q_B'}{N_B} \right) \right],$$

$$\Rightarrow \quad \left(\frac{q'_C}{N_C}\right)^c = \left(\frac{q'_A}{N_A}\right)^a \left(\frac{q'_B}{N_B}\right)^b. \tag{13.17}$$

To express the relative numbers of particles of each species present at equilibrium, a natural definition of the equilibrium constant K arises from rearranging Equation (13.17):

$$K = \frac{N_C^c}{N_A^a N_B^b} = \left(\frac{(q'_C)^c}{(q'_A)^a (q'_B)^b}\right)$$

$$= \left(\frac{q_C^c}{q_A^a q_B^b}\right) e^{-(c\varepsilon_{0C} - a\varepsilon_{0A} - b\varepsilon_{0B})/kT}. \tag{13.18}$$

To determine K from experiments, you need some way of detecting the numbers of particles of types A, B, and C at equilibrium, and you need to know the stoichiometric coefficients, a, b, and c. Equation (13.18) allows you to predict chemical equilibria from atomic structures.

Finding Ground-State Energies

To compute equilibrium constants using Equation (13.18), you need to know $\Delta\varepsilon_0 = c\varepsilon_{0C} - a\varepsilon_{0A} - b\varepsilon_{0B}$, the difference in ground state energies. For $A \rightarrow B$, both states A and B must contain the same atoms, so the fully dissociated state of A must be identical to the fully dissociated state of B. Therefore there is a common zero of energy, the fully dissociated state (see Figure 13.2). To define the ground state energies further, we must resolve a matter of the vibrational ground state. Vibrational energies are given by Equation (11.22) as $\varepsilon_v = (v + 1/2)h\nu$. The zero of energy $\varepsilon_v = 0$ is at the bottom of the energy well. However, because there is no energy level there, systems cannot access this state and it cannot be measured experimentally. The lowest energy level accessible to the system is $\varepsilon_0 = (1/2)h\nu$, the zero-point energy. However, we previously used the well-bottom as the zero of energy to derive the vibrational partition function, Equation (11.26)

$$q_{\text{vibration}} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}. \tag{13.19}$$

In order to put chemical equilibria in terms of measurable quantities, we now switch to the zero-point, instead of the well-bottom, as our reference state. This leads to a corresponding change in how we express the vibrational partition function. Figure 13.2 shows the *dissociation energy* $D = -\varepsilon_0 - (1/2)h\nu$ and its relationship to the well-bottom energy. D can be determined from spectroscopic or calorimetric experiments on the dissociation of diatomic molecules, extrapolated to $T = 0$ K. We combine the vibrational part of the partition function Equation (11.26) with the expression for D to get

$$q_{\text{vibration}} e^{-\varepsilon_0/kT} = \left(\frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}\right) e^{(D+h\nu/2)/kT}$$

$$= \left(\frac{1}{1 - e^{-h\nu/kT}}\right) e^{D/kT} = q_{vz} e^{D/kT}, \tag{13.20}$$

Figure 13.2 Definition of dissociation energies. Energy versus the separation r of the atoms in systems A and B. The dissociation energy $D = -\varepsilon_0 - h\nu/2$ has the opposite sign of ε_0 and is smaller in magnitude by $h\nu/2$. The diagram shows the difference in dissociation energies, $\Delta D = D_A - D_B$.
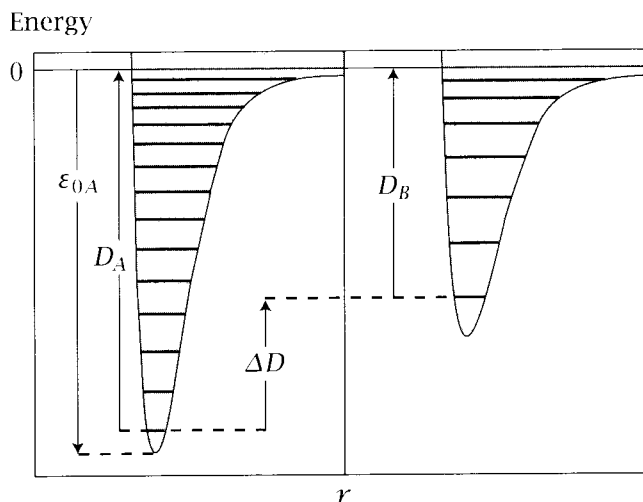
Energy

where q_{vz} is the vibrational partition function defined with its zero of energy at the zero-point instead of at the well-bottom,

$$q_{vz} = \frac{1}{1 - e^{-h\nu/kT}}.$$ (13.21)

To use Equation (13.18), replace products of the vibrational partition function that appear in the full partition function q, and the Boltzmann factor, $q_{\text{vibration}}\exp(-\varepsilon_0/kT)$ with products $q_{vz}\exp(D/kT)$, for each species in the chemical equilibrium. It is these quantities q_{vz} that are implied in the partition functions that follow in this chapter. The next example illustrates how to compute K from partition functions.

EXAMPLE 13.2 Predicting K in a change-of-symmetry reaction. Consider the gas-phase exchange reaction,

$$H_2 + D_2 \xrightarrow{K} 2HD.$$ (13.22)

The equilibrium constant is (see Equation (13.18))

$$K = \left(\frac{q_{HD}^2}{q_{H_2}q_{D_2}}\right)e^{\Delta D/RT}$$ (13.23)

where ΔD is the difference between the molar dissociation energies of all the products and all the reactants. Because these energies are in molar units, divide them by RT rather than kT, to get Boltzmann factors with dimensionless exponents. The dissociation energies are $431.8\,\text{kJ}\,\text{mol}^{-1}$ for H_2, $439.2\,\text{kJ}\,\text{mol}^{-1}$ for D_2, and $435.2\,\text{kJ}\,\text{mol}^{-1}$ for HD. Therefore,

$$\Delta D = 2D_{HD} - D_{H_2} - D_{D_2} = -0.6\,\text{kJ}\,\text{mol}^{-1},$$ (13.24)

so $e^{\Delta D/RT} = 0.79$ at $T = 300\,\text{K}$.

You can write the equilibrium constant as a product of its component translational (t), rotational (r), and vibrational (v) factors, $K = K_t K_r K_v e^{\Delta D/RT}$, where

$$K_t = \frac{\left[(2\pi m_{HD}kTh^{-2})^{3/2}\right]^2}{(2\pi m_{H_2}kTh^{-2})^{3/2}(2\pi m_{D_2}kTh^{-2})^{3/2}}$$

$$= \left(\frac{m_{HD}^2}{m_{H_2}m_{D_2}}\right)^{3/2} = \left(\frac{3^2}{2\times4}\right)^{3/2} = 1.19, \tag{13.25}$$

and

$$K_r = \frac{\left((8\pi^2 I_{HD}kT)/(\sigma_{HD}h^2)\right)^2}{\left((8\pi^2 I_{H_2}kT)/(\sigma_{H_2}h^2)\right)\left((8\pi I_{D_2}kT)/(\sigma_{D_2}h^2)\right)}$$

$$= \left(\frac{\sigma_{H_2}\sigma_{D_2}}{\sigma_{HD}^2}\right)\left(\frac{I_{HD}^2}{I_{H_2}I_{D_2}}\right) = 4\left(\frac{(6.13)^2}{(4.60)(9.19)}\right) = 3.56. \tag{13.26}$$

K_t is the ratio of the appropriate powers of translational partition functions from Equation (11.18), K_r is the ratio of rotational partition functions from Equation (11.30), where $\sigma_{H_2} = \sigma_{D_2} = 2$ and $\sigma_{HD} = 1$. Because the vibrational energies are large for all three species at room temperature, $(h\nu)/kT \gg 1$ and $q_{\text{vibration}} = 1$,

$$K_v = \frac{(1 - e^{-h\nu_{HD}/kT})^{-2}}{(1 - e^{-h\nu_{H_2}/kT})^{-1}(1 - e^{-h\nu_{D_2}/kT})^{-1}} = 1 \tag{13.27}$$

is the ratio of vibrational partition functions q_{vz}, from Equations (13.20) and (13.21). Combining the factors $K = K_t K_r K_v e^{\Delta D/RT}$ gives $K = (1.19)(3.56)(1)(0.79) = 3.35$. As $T \to \infty$, $K \to 4$. The change in rotational symmetry is the main contributor to this equilibrium. The reaction is driven by the gain in entropy due to the rotational asymmetry of the products.

Pressure-Based Equilibrium Constants

Because pressures are easier to measure than particle numbers for gases, it is often more convenient to use equilibrium constants K_p based on pressures rather than equilibrium constants K based on the numbers of molecules. Combining Equation (13.18) with the ideal gas law $N = pV/kT$ gives

$$K = \frac{N_C^c}{N_A^a N_B^b} = \frac{(p_C V/kT)^c}{(p_A V/kT)^a(p_B V/kT)^b} = \frac{q_C^c}{q_A^a q_B^b}e^{\Delta D/kT}. \tag{13.28}$$

Multiply the two terms on the right-hand side of Equation (13.28) by $(V/kT)^{a+b-c}$ to get the pressure-based equilibrium constant K_p:

$$K_p = \frac{p_C^c}{p_A^a p_B^b} = (kT)^{c-a-b}\frac{(q_{0C})^c}{(q_{0A})^a(q_{0B})^b}e^{\Delta D/kT}, \tag{13.29}$$

where $q_0 = q/V = \left[(2\pi mkT)/h^2\right]^{3/2}q_r q_v \ldots$ is the partition function with the volume V factored out.

You can also express chemical potentials in terms of the partial pressures of each gas. Using $\mu = -kT\ln(q'/N)$ from Equation (13.8), factoring out the

volume $q' = q_0'V$, and using the ideal gas law $V = NkT/p$, you have

$$\mu = -kT \ln\left(\frac{q_0'kT}{p}\right) = kT \ln\left(\frac{p}{p_{int}^\circ}\right) = \mu^\circ + kT \ln p, \qquad (13.30)$$

where $p_{int}^\circ = q_0'kT$ and $\mu^\circ = -kT \ln q_0'kT$.

Equation (13.30) will be useful in the following chapters. It divides the chemical potential into a part that depends on pressure ($kT \ln p$) and a part that does not (μ°). μ° is called the *standard-state* chemical potential. Although the rightmost expression ($\mu^\circ + kT \ln p$) would appear to imply that you should take the logarithm of a quantity that is not dimensionless, the preceding expression ($-kT \ln(p/p_{int}^\circ)$) shows that the argument of the logarithm is indeed dimensionless. μ° depends on temperature.

The pressure-based equilibrium constant K_p is computed for a dissociation reaction in Example 13.3.

EXAMPLE 13.3 Dissociation reaction. For the dissociation of iodine, $I_2 \rightarrow 2I$, compute the equilibrium constant at $T = 1000\,\text{K}$. The mass of an iodine atom is $m_I = 0.127\,\text{kg mol}^{-1}/(6.02 \times 10^{23}\,\text{molecules mol}^{-1}) = 2.109 \times 10^{-25}\,\text{kg}$. Table 11.2 and the associated discussion give the ground-state electronic degeneracies as $q_{\text{elec,I}} = 4$, $q_{\text{elec,I}_2} = 1$, $\theta_{\text{rotation}} = 0.0537\,\text{K}$, $\theta_{\text{vibration}} = 308\,\text{K}$, and $\Delta D = -35.6\,\text{kcal mol}^{-1}$. From Equation (13.29), the pressure-based equilibrium constant is

$$K_p = kT\frac{(q_{0I})^2}{q_{0I_2}}e^{\Delta D/RT}. \qquad (13.31)$$

You have

$$kT = RT/\mathcal{N} = \frac{(8.206 \times 10^{-5}\,\text{m}^3\,\text{atm K}^{-1}\,\text{mol}^{-1})(1000\,\text{K})}{6.02 \times 10^{23}\,\text{molecules mol}^{-1}}$$

$$= 1.363 \times 10^{-25}\,\text{m}^3\,\text{atm}, \qquad \text{and}$$

$$e^{\Delta D/RT} = e^{-35,600/(1.987)(1000)} = 1.66 \times 10^{-8}.$$

Factor the partition functions q_0 into translational (q_t), rotational (q_r), vibrational (q_{vz}), and electronic (q_e) components:

$$\frac{q_{0I}^2}{q_{0I_2}} = \left(\frac{q_{tI}^2}{q_{tI_2}}\right)\left(\frac{1}{q_{rI_2}}\right)\left(\frac{1}{q_{vzI_2}}\right)\left(\frac{q_{eI}^2}{q_{eI_2}}\right). \qquad (13.32)$$

For the rotations, $\sigma = 2$, and

$$q_{rI_2} = \frac{T}{2\theta_{\text{rotation}}} = \frac{1000}{2(0.0537)} = 9310.$$

For the vibrations (Equation (13.21)),

$$q_{vzI_2} = \frac{1}{1 - e^{-\theta_{\text{vibration}}/T}} = \frac{1}{1 - e^{-308/1000}}$$

$$= 3.77.$$

For the electronic terms, $q_{eI}^2/q_{eI_2} = 16$. For the translations (which have units of m^{-3} because volume has been factored out), $m_{I_2} = 2m_I$, and

$$\frac{q_{t1}^2}{q_{t1_2}} = \frac{[(2\pi m_1 kT/h^2)^{3/2}]^2}{(2\pi m_{1_2} kT/h^2)^{3/2}} = \left(\frac{\pi m_1 kT}{h^2}\right)^{3/2}$$

$$= \left[\frac{\pi(2.109 \times 10^{-25}\,\text{kg})(1.38 \times 10^{-23}\,\text{JK}^{-1})(1000\,\text{K})}{(6.626 \times 10^{-34}\,\text{Js})^2}\right]^{3/2}$$

$$= 3.01 \times 10^{33}\,\text{m}^{-3}.$$

Combine all these terms using Equations (13.31) and (13.32) to get

$$K_p = \left(1.363 \times 10^{-25}\,\text{m}^3\,\text{atm}\right)\left(1.66 \times 10^{-8}\right)\left(\frac{1}{9310}\right)\left(\frac{1}{3.77}\right) \quad (16)$$

$$\times \left(3.01 \times 10^{33}\,\text{m}^{-3}\right) = 3.1 \times 10^{-3}\,\text{atm}.$$

Figure 13.3 shows that this prediction is quite good. The measured dissociation constant of $I_2 \to 2I$ shown in Figure 13.3 is highly dependent on temperature. This is mainly because of the exponential dependence of the Boltzmann factor $e^{\Delta D/RT}$ on temperature. Increasing the temperature dissociates I_2 into iodine atoms.

K_p (atm)
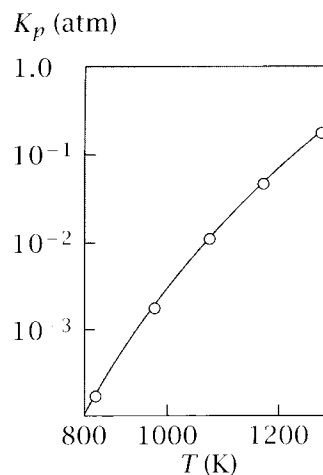
Figure 13.3 Theoretical curve and experimental points for the dissociation of iodine as a function of temperature. Source: ML Perlman and GK Rollefson, *J Chem Phys* **9**, 246 (1941).

Le Chatelier's Principle Describes the Response to Perturbation from Equilibrium

Any perturbation away from a stable equilibrium state must increase the free energy of the system. The system will respond by moving back toward the state of equilibrium. To illustrate, let's return to the general two-state equilibrium,

$$A \xrightarrow{K} B.$$
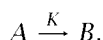
Suppose a fluctuation changes the number of B molecules by an amount dN_B. The resulting change dG in free energy is given by Equations (13.2) and (13.4),

$$dG = (\mu_B - \mu_A)dN_B. \tag{13.33}$$

Define a *reaction coordinate* $\xi = N_B/(N_A + N_B)$, the fractional degree to which the system has proceeded to B (see Figure 13.4). The total number of particles is fixed: $N_A + N_B = N$ so $N_B = N\xi$ and $dN_B = Nd\xi$. Substituting $Nd\xi$ into Equation (13.33) gives

$$dG = (\mu_B - \mu_A)Nd\xi. \tag{13.34}$$

To move toward equilibrium, $dG \leq 0$, implying that the quantities $(\mu_B - \mu_A)$ and $d\xi$ must have opposite signs. If the system fluctuates into a state in which B happens to have the higher chemical potential, $\mu_B > \mu_A$, then the direction toward equilibrium is $d\xi < 0$, meaning that N_B will decrease. The chemical potential μ is sometimes called the **escaping tendency** because the higher the value of μ_B, the greater is the tendency of the system to escape from the state B to enter the state A. *Le Chatelier's principle* is the term that refers to the tendency of a system to return to equilibrium by moving in a direction opposite to that caused by an external perturbation.

Figure 13.4 For the reaction $A \to B$ at equilibrium, the extent of reaction is $\xi = N_B/(N_A + N_B) = \xi_0$. A fluctuation that increases B leads to $\xi = \xi_0 + \Delta\xi$. A stable system returns to equilibrium by reducing the amount of B.
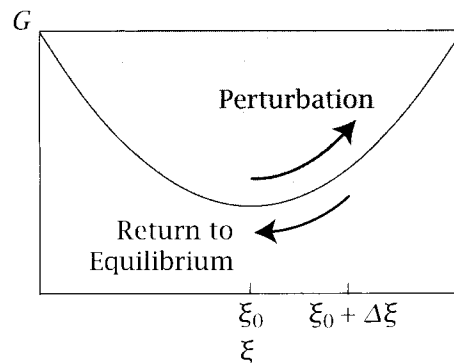
The Temperature Dependence of Equilibrium Is Described by the van 't Hoff Equation

If you measure an equilibrium constant $K(T)$ at different temperatures, you can learn the enthalpy and entropy of the reaction, which are often useful for constructing or testing microscopic models. To illustrate, we return to the two-state equilibrium,

$$A \xrightarrow{K} B.$$
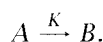
At constant T and p, the condition for equilibrium is $\mu_A = \mu_B$. The pressure-based equilibrium constant is $K_p = p_B/p_A$. Using Equation (13.30) you have, at equilibrium:

$$\mu_A^\circ + kT \ln p_A = \mu_B^\circ + kT \ln p_B$$

$$\Rightarrow \ln K_p = \ln\left(\frac{p_B}{p_A}\right) = \frac{-(\mu_B^\circ - \mu_A^\circ)}{kT} = -\frac{\Delta\mu^\circ}{kT}. \tag{13.35}$$

$\Delta\mu^\circ$ depends only on temperature (see Equation (13.30), not on pressure, and can be expressed in terms of components (see Equation (9.25)).

$$\Delta\mu^\circ = \Delta h^\circ - T\Delta s^\circ.$$

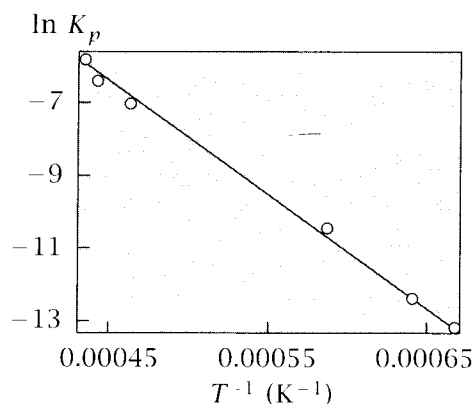The temperature dependence in Equation (13.35) is given by

$$\left(\frac{\partial \ln K_p}{\partial T}\right) = -\frac{\partial}{\partial T}\left(\frac{\Delta\mu^\circ}{kT}\right) = -\frac{\partial}{\partial T}\left(\frac{\Delta h^\circ - T\Delta s^\circ}{kT}\right). \tag{13.36}$$

If $\Delta h^\circ = h_B^\circ - h_A^\circ$ and $\Delta s^\circ = s_B^\circ - s_A^\circ$ are independent of temperature, then Equation (13.36) gives

$$\left(\frac{\partial \ln K_p}{\partial T}\right) = \frac{\Delta h^\circ}{kT^2}. \tag{13.37}$$

An alternative form of Equation (13.37), called the the **van 't Hoff** relation, provides a useful way to plot data to obtain Δh°. Use $d(1/T) = -(1/T^2)dT$:

$$\left(\frac{\partial \ln K_p}{\partial (1/T)}\right) = -\frac{\Delta h^\circ}{k}. \tag{13.38}$$

Figure 13.5 van 't Hoff plot for the dissociation of water in the gas phase, $H_2O \rightarrow H_2 + (1/2)O_2$. Higher temperatures cause more dissociation than lower temperatures. Source: MW Zemansky and RH Dittman, *Heat and Thermodynamics: an Intermediate Textbook*, 6th edition, McGraw-Hill, New York, 1981.

van 't Hoff plots show $\ln K$ versus $1/T$: the slope is $-\Delta h^\circ / k$. Figure 13.5 shows a van 't Hoff plot for the dissociation of water vapor, $H_2O \rightarrow H_2 + (1/2)O_2$. Water is more dissociated at high temperatures than at lower temperatures. For dissociation, $\Delta h^\circ > 0$, which is characteristic of bond-breaking processes. Because this enthalpy change is positive, dissociation must be driven by entropy. Figure 13.5 illustrates a common, but not universal, feature of van 't Hoff plots: they are often linear, implying that Δh° is independent of temperature.

When Δh° is independent of temperature, integration of Equation (13.38) gives

$$\ln \left(\frac{K_p(T_2)}{K_p(T_1)} \right) = \frac{-\Delta h^\circ}{k} \left(\frac{1}{T_2} - \frac{1}{T_1} \right). \tag{13.39}$$

Equation (13.39) can be used to find how K_p depends on temperature if you know Δh°, or to determine Δh° if you measure $K_p(T)$.

EXAMPLE 13.4 Getting Δh° from a van 't Hoff plot. To get the enthalpy of dissociation of water, take two points $(1/T, \ln K)$ from Figure 13.5. At temperatures $T = 1500\,K$ and $2257\,K$, you have $1/T = 6.66 \times 10^{-4}$ and $1/T = 4.43 \times 10^{-4}$, respectively. The corresponding points are $(6.66 \times 10^{-4}, -13.147)$ and $(4.43 \times 10^{-4}, -6.4)$. Use Equation (13.39):

$$\Delta h^\circ = \frac{-R[\ln K_p(T_2) - \ln K_p(T_1)]}{(1/T_2) - (1/T_1)}$$

$$= -(8.314\,J\,K^{-1}\,mol^{-1}) \frac{[-13.1 - (-6.4)]}{(6.64 \times 10^{-4} - 4.43 \times 10^{-4})}$$

$$= 249\,kJ\,mol^{-1}.$$

Other thermodynamic quantities are also readily obtained from Figure 13.5. For example, at $T = 1500\,K$,

$$\Delta\mu^\circ = -RT \ln K_p = -(8.314\,J\,K^{-1}\,mol^{-1})(1500\,K)(-13.147) = 164\,kJ\,mol^{-1}$$

and

$$\Delta s^\circ = \frac{\Delta h^\circ - \Delta\mu^\circ}{T} = \frac{(249 - 164)\,kJ\,mol^{-1}}{1500\,K} = 56.7\,J\,K^{-1}\,mol^{-1}.$$

Equations (13.37) through (13.39) are quite general and apply to any two-state equilibria, not just to those that are in the gas phase or to chemical reactions. Here is a more general derivation showing that Equations (13.37) and (13.38) hold even when $\Delta h°$ is dependent on temperature.

The Gibbs–Helmholtz Equation for Temperature-Dependent Equilibria

Let's generalize beyond chemical equilibria and the gas phase to any dependence of a free energy $G(T)$ on temperature. Rearrange the definition of free energy $G = H - TS$:

$$H = G + TS. \tag{13.40}$$

Substitute Equation (8.27), $S = -(\partial G/\partial T)_p$, into Equation (13.40) to get

$$H = G - T\left(\frac{\partial G}{\partial T}\right)_p. \tag{13.41}$$

Use $d(u/v) = (vu' - uv')/v^2$ with $v = T$ and $u = G$ to express the temperature derivative of G/T as

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = \frac{1}{T}\left(\frac{\partial G}{\partial T}\right)_p - \frac{G}{T^2} = -\frac{1}{T^2}\left(G - T\left(\frac{\partial G}{\partial T}\right)_p\right). \tag{13.42}$$

Substituting Equation (13.41) into the last parentheses of Equation (13.42) leads to the **Gibbs–Helmholtz equation**:

$$\left(\frac{\partial(G/T)}{\partial T}\right)_p = -\frac{H(T)}{T^2}. \tag{13.43}$$

Similarly, for the Helmholtz free energy, you have:

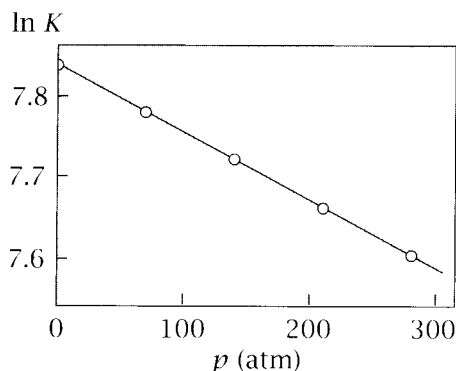$$\left(\frac{\partial(F/T)}{\partial T}\right)_V = -\frac{U(T)}{T^2}. \tag{13.44}$$

Here's an illustration of the Gibbs–Helmholtz equation.

EXAMPLE 13.5 Obtaining $S(T)$ and $H(T)$ from $G(T)$. Suppose the free energy has the temperature dependence $G(T) = aT^3$, where a is a constant. Equation (8.27) then gives $S(T) = -3aT^2$. From Equation (13.41), you get $H(T) = aT^3 - 3aT^3 = -2aT^3$. This is consistent with the result from Equation (13.43): $(d(aT^2)/dT) = 2aT = -H(T)/T^2$. This shows that the Gibbs–Helmholtz equation does *not* mean that the temperature dependence of the Gibbs free energy is solely due to the enthalpy.

Pressure Dependence of the Equilibrium Constant

The dependence on pressure can be derived in much the same way as the dependence on temperature. The pressure dependence $K(p)$ reflects a volume change. The slope of the equilibrium constant with pressure is

$$\frac{\partial \ln K(p)}{\partial p} = \frac{\partial}{\partial p}\left[-\frac{(\mu_B° - \mu_A°)}{kT}\right] = -\frac{1}{kT}\left(\frac{\partial \Delta \mu°}{\partial p}\right). \tag{13.45}$$

Figure 13.6 Applying pressure drives anesthetic molecules into water from lipid bilayer membranes. K is the partition coefficient from water into the bilayer. Source: S Kaneshina, H Kamaya, I Ueda, *J Coll Interf Sci* **93**, 215–224 (1983).

To determine the pressure dependence $\Delta\mu(p)$, use the Gibbs–Duhem equation (9.37). For a single species A the Gibbs–Duhem equation gives $N_A d\mu_A = V dp - S dT$, so

$$d\mu_A = v_A dp - s_A dT, \tag{13.46}$$

where $v_A = V/n_A$ and $s_A = S/n_A$ are the volume and entropy per mole. For species B, $d\mu_B = v_B dp - s_B dT$. Taking the difference gives

$$d(\mu_B^\circ - \mu_A^\circ) = (v_B - v_A)dp - (s_B - s_A)dT,$$

$$\Rightarrow \quad \left(\frac{\partial(\mu_B^\circ - \mu_A^\circ)}{\partial p}\right)_T = v_B - v_A = \Delta v. \tag{13.47}$$

Substituting Equation (13.47) into (13.45) gives

$$\left(\frac{\partial \ln K}{\partial p}\right)_T = -\frac{\Delta v}{kT}. \tag{13.48}$$

Therefore, if B is the state with the smaller volume, $v_B - v_A < 0$, then increasing the pressure will shift the equilibrium from A towards B. Equations (13.37), (13.38), and (13.48) are applicable to complex processes, as illustrated by the following example.

EXAMPLE 13.6 Pressure affects a two-state equilibrium. A common anesthetic drug molecule is halothane (2-bromo-2-chloro-1,1,1-trifluoroethane). Its mode of action is presumed to involve partitioning from water (state A) into lipid bilayer membranes (state B). Figure 13.6 shows how the partitioning equilibrium depends on pressure. Putting values of $(p, \ln K) = (0, 7.84)$ and $(280, 7.6)$ into Equation (13.48) gives $\Delta v = v_{\text{bilayer}} - v_{\text{water}}$:

$$\Delta v = -RT\frac{(\ln K_2 - \ln K_1)}{p_2 - p_1}$$

$$= \frac{(8.205 \times 10^{-5}\,\text{m}^3\,\text{atm}\,\text{K}^{-1}\,\text{mol}^{-1})(300\,\text{K})(7.84 - 7.6)}{280\,\text{atm}} \left(\frac{10^2\,\text{cm}}{\text{m}}\right)^3$$

$$= 21\,\text{cm}^3\,\text{mol}^{-1}.$$

Multiplying by $(10^8 \text{ Å/cm})^3$ and dividing by Avogadro's number gives a volume change of 35 Å^3 per molecule. The anesthetic occupies more volume in the membrane phase than in water. Pressure forces the anesthetic molecules to go into the water, where the volumes they occupy are smaller.

Summary

A remarkable achievement of statistical mechanics is the accurate prediction of gas-phase chemical reaction equilibria from atomic structures. From atomic masses, moments of inertia, bond lengths, and bond strengths, you can calculate partition functions. You can then calculate equilibrium constants and their dependence on temperature and pressure. In Chapter 19, we will apply these ideas to chemical kinetics, which pertains to the *rates* of reactions. Reactions can be affected by the medium they are in. Next we will develop models of liquids and other condensed phases.

Problems

1. Iodine dissociation. Compute the dissociation constant K_p for iodine at $T = 300\,$K.

2. Temperature dependence of a simple equilibrium. In a reaction

$$A \xrightarrow{K} B,$$

the equilibrium constant is $K = 10$ at $T = 300\,$K.
   (a) What is $\Delta\mu°$?
   (b) If $\Delta h° = 10\,$kcal mol^{-1}, what is K at $T = 310\,$K?
   (c) What is $\Delta s°$ at $T = 300\,$K?

3. Dissociation of oxygen, $O_2 \rightarrow 2O$. Compute K_p, the pressure-based equilibrium constant for this dissociation reaction at $T = 3000\,$K. The electronic ground-state degeneracy for O is $g_0(0) = 9$.

4. Temperature dependence of K_p. For the dissociation of oxygen, derive an expression for $d \ln K_p/dT$ near $T = 300\,$K from the expression for K_p that you used in problem 3.

5. Polymerization. Consider a polymerization reaction in the gas phase in which n moles of identical monomers are in equilibrium with one mole of chains of n-mers:

$$n(\bullet) \xrightarrow{K} \underbrace{\bullet\text{-}\bullet\text{-}\bullet\text{-}\bullet\text{-}\bullet}_{n \text{ monomers}}$$

   (a) Do you expect typical polymerization processes to be driven, or opposed, by enthalpy? By entropy? What are the physical origins of these enthalpies and entropies?
   (b) Do you expect polymerizations to be exothermic (giving off heat) or endothermic (taking up heat)? Explain the explosions in some polymerization processes.
   (c) Are polymerization equilibrium constants for long chains more or less sensitive to temperature than for shorter chains?

6. Hydrogen dissociation. A hydrogen atom can dissociate in the gas phase:

$$H \xrightarrow{K} H^+ + e^-.$$
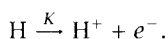
Calculate the equilibrium constant K for temperature $T = 5000\,$K. There is no rotational or vibrational partition function for H, H$^+$, or e$^-$, but there are spin partition functions: $q_s = 1$ for H$^+$, and $q_s = 2$ for e$^-$. $\Delta D = -311\,$kcal mol^{-1}.

7. Free energy along the reaction coordinate. Consider the ideal gas-phase equilibrium $2A \rightarrow B$, at constant temperature and a constant pressure of 1 atm. Assume that there is initially 1 mole of A and no B present, and

that $\mu_A° = 5\,$kcal mol^{-1} and $\mu_B° = 10\,$kcal mol^{-1} at this temperature.
   (a) Show that G, at any time during the reaction, can be written as

$$G = \left(5 + RT\ln\left[\left(\frac{1-2\xi}{1-\xi}\right)^{1-2\xi}\left(\frac{\xi}{1-\xi}\right)^{\xi}\right]\right)\frac{\text{kcal}}{\text{mol}},$$

   where ξ is the extent of reaction.
   (b) What is the value of the extent of reaction ξ at equilibrium?

8. Pressure denaturation of proteins. For a typical protein, folding can be regarded as involving two states, native (N) and denatured (D),

$$N \xrightarrow{K} D.$$
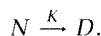
At $T = 300\,$K, $\Delta\mu° = 10\,$kcal mol^{-1}. Applying about 10,000 atm of pressure can denature a protein at $T = 300\,$K. What is the volume change Δv for the unfolding process?

9. Clusters. Sometimes isolated molecules of type A can be in a two-state equilibrium with a cluster of m monomers,

$$mA \xrightarrow{K} A_m,$$
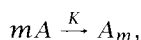
where A_m represents an m-mer cluster.
   (a) At equilibrium, what is the relationship between μ_1, the chemical potential of the monomer, and μ_m, the chemical potential of the molecule in the cluster?
   (b) Express the equilibrium constant K in terms of the partition functions.

Suggested Reading

Elementary and detailed discussions of chemical equilibria:

JH Knox, *Molecular Thermodynamics*, Wiley, New York, 1978.

NO Smith, *Elementary Statistical Thermodynamics: A Problems Approach*, Plenum Press, New York, 1982.

Excellent advanced texts with worked examples:

TL Hill, *Introduction to Statistical Thermodynamics*, Addison-Wesley, New York, 1960.

R Kubo, *Statistical Mechanics, an Advanced Course with Problems and Solutions*, North Holland, Amsterdam, 1965.

DA McQuarrie, *Statistical Mechanics*, Harper and Row, New York, 1976.

CL Tien and JH Lienhard, *Statistical Thermodynamics*, Hemisphere Publishing, New York, 1979.