

# Supplement to Chapter 6

## REVIEW QUESTIONS

- 6.1** For the chemical reaction  $A_2 + 2B \leftrightarrow 2AB$  derive the equilibrium condition relating the affinities of  $A_2$ ,  $B$ , and  $AB$ .
- 6.2** For the reaction shown above, derive the law of mass action.
- 6.3** For a reaction of the form  $aA + bB \leftrightarrow rR$ , derive Van't Hoff's law,  $\partial \log K / \partial \beta = W$ .
- 6.4** What does Van't Hoff's Law say about the temperature dependence of the equilibrium constant for an exothermic (energy-releasing) reaction?
- 6.5** For an ideal gas, how is the partition function of the gas  $Z$  related to the partition function of a single molecule?
- 6.6** In the formula for the partition function of a diatomic molecule,  $z = z(\text{trans}) \times z(\text{int})$ , what are  $z(\text{trans})$  and  $z(\text{int})$ ?
- 6.7** Derive  $z(\text{int})$  for a diatomic molecule, using the usual approximations.
- 6.8** What is  $z(\text{int})$  for an atom?
- 6.9** For the dissociation reaction  $AB \leftrightarrow A + B$ , derive the equilibrium constant  $K$ .
- 6.10** Derive the Saha equation for the ionization of hydrogen.
- 6.11** Write down the formula for  $dE$  in the energy representation.
- 6.12** Define the Helmholtz free energy  $F(T, V)$ , the enthalpy  $H(S, p)$ , and the Gibbs free energy  $G(T, p)$ .
- 6.13** Write equations for  $dF$ ,  $dH$ , and  $dG$ .
- 6.14** Show that  $(\partial V / \partial T)_p = -(\partial S / \partial p)_T$ .
- 6.15** Define the constant pressure specific heat  $C_p$ , the coefficient of thermal expansion  $\beta_p$ , and the compressibility  $\kappa_T$ .
- 6.16** Show that  $(\partial x / \partial y)_z = -(\partial z / \partial y)_x / (\partial z / \partial x)_y$ .
- 6.17** How can we eliminate  $H$  in an expression of the form  $(\partial H / \partial x)_y$ ?
- 6.18** How do we transform  $(\partial S / \partial p)_V$  into an expression involving derivatives of the form  $[\partial(S \text{ or } V) / \partial(p \text{ or } T)]_{(T \text{ or } p)}$ ?
- 6.19** Show that  $C_p - C_v = TV\beta_p^2 / \kappa_T$ .
- 6.20** Explain the meaning of the terms in the Clausius–Clapeyron equation,  $\partial p / \partial T = (S_G - S_L) / (V_G - V_L)$ .

**6.21** Derive the Clausius–Clapeyron equation.

**6.22** What approximations are necessary in deriving the equation  $\log p(T) = \text{const.} - L/RT$  for the two-phase equilibrium pressure?

**6.23** Using a system composed of a dielectric capacitor and a vacuum capacitor, show that  $E = \partial f / \partial D$ , where  $f(n, T, D)$  is the free energy of the dielectric.

**6.24** What is the corresponding relation for magnetic fields?

**6.25** Assuming that  $E \sim D$ , show that  $f(n, T, D) = f_o(n, T) + D^2/2\epsilon$ .

## EXERCISES

**Exercise 6.1** Both bromine and chlorine are highly soluble in water. In an aqueous solution of both gases the electron transfer reaction



has an equilibrium constant  $K = 4 \times 10^4$ . What is the ratio of the concentration of chlorine ions to that of bromine ions if the concentrations of chlorine and bromine molecules are equal?

**Solution** The mass action formula for the reaction is

$$\frac{n_{\text{Cl}^-}^2 n_{\text{Br}_2}}{n_{\text{Cl}_2} n_{\text{Br}^-}^2} = 4 \times 10^4 \quad (\text{S6.2})$$

If  $n_{\text{Br}_2} = n_{\text{Cl}_2}$ , then  $n_{\text{Cl}^-}/n_{\text{Br}^-} = (4 \times 10^4)^{1/2} = 200$ .

**Exercise 6.2** A vessel contains a mixed gas of ammonia ( $\text{NH}_3$ ), hydrogen ( $\text{H}_2$ ), and nitrogen ( $\text{N}_2$ ) in chemical equilibrium at 600 K and 10 atmospheres. The partial pressures, in atmospheres, of the three constituents are 0.22 ( $\text{NH}_3$ ), 2.32 ( $\text{N}_2$ ), and 7.46 ( $\text{H}_2$ ). At fixed temperature, the pressure is increased to 20 atmospheres. What will be the partial pressures of the three gases at the higher total pressure? Treat all the gases as ideal.

**Solution** The relevant chemical reaction is



According to the law of mass action [Eq. (6.9)],

$$\frac{n_A^2}{n_N n_H^3} = K \quad (\text{S6.4})$$

where  $n_A$ ,  $n_N$ , and  $n_H$  are the densities of ammonia, nitrogen, and hydrogen. For an ideal gas at fixed temperature the density is proportional to the partial pressure. Thus we could write Eq. (S6.4) in terms of the partial pressures.

$$\frac{p_A^2}{p_N p_H^3} = K_p \quad (\text{S6.5})$$

where  $K_p$  is another constant. From the data given, we can calculate  $K_p$ .

$$K_p = \frac{(0.22)^2}{(2.32)(7.46)^3} \text{ atm}^{-2} = 5.03 \times 10^{-5} \text{ atm}^{-2} \quad (\text{S6.6})$$

At a pressure of 20 atmospheres the partial pressures satisfy the two relations

$$p_A + p_N + p_H = 20 \text{ atm} \quad (\text{S6.7})$$

and

$$\frac{p_A^2}{p_N p_H^3} = K_p = 5.03 \times 10^{-5} \text{ atm}^{-2} \quad (\text{S6.8})$$

One more relationship is needed in order to fix the values of the three unknowns. The conservation of the number of nitrogen and hydrogen atoms is expressed by the equations

$$n_A V + 2n_N V = n_A^o V^o + 2n_N^o V^o \quad (\text{S6.9})$$

and

$$3n_A V + 2n_H V = 3n_A^o V^o + 2n_H^o V^o \quad (\text{S6.10})$$

where the superscripted quantities are the values at 10 atmospheres. In order to eliminate the new variables  $V^o$  and  $V$ , we equate the ratios of the corresponding sides of the two equations. Again using the fact that at fixed temperature the densities are proportional to the partial pressures, we obtain the relation

$$\frac{p_A + 2p_N}{3p_A + 2p_H} = \frac{p_A^o + 2p_N^o}{3p_A^o + 2p_H^o} = 0.312 \quad (\text{S6.11})$$

where the final step uses the given data on the original partial pressures. This gives the linear equation

$$p_A + 2p_N = 0.312(3p_A + 2p_H) \quad (\text{S6.12})$$

The two linear equations can be used to solve for  $p_N$  and  $p_H$  as linear functions of  $p_A$ . When these expressions are substituted for  $p_N$  and  $p_H$  in Eq. (S6.8), a fourth-order polynomial equation for  $p_A$  is obtained. There exist rather complicated exact formulas for solving fourth-order polynomial equations, or the equation may be solved numerically. However, modern symbolic mathematics programs, such as *Mathematica*, have made such calculations unnecessary. One need only enter the set of three simultaneous linear and nonlinear equations in order to obtain the four possible solutions. The only solution with positive values for all the pressures is  $p_A = 0.84 \text{ atm}$ ,  $p_N = 4.53 \text{ atm}$ , and  $p_H = 14.62 \text{ atm}$ .

**Exercise 6.3** Using the information in Table 6.1, calculate the internal partition functions for the atoms oxygen, magnesium, sulfur, and calcium in the temperature range  $100 < T < 3000 \text{ K}$ .

**Solution** For oxygen,  $g_0 = 5$ ,  $g_1 = 3$ ,  $\varepsilon_1 = 228 \text{ K}$ ,  $g_2 = 1$ , and  $\varepsilon_2 = 326 \text{ K}$ . Below  $3000 \text{ K}$ , one can ignore the higher excited states. Thus

$$z_{\text{O}}(\text{int}) = 5 + 3e^{-228/T} + e^{-326/T} \quad (\text{S6.13})$$

Similar calculations for Mg, S, and Ca give

$$z_{\text{Mg}}(\text{int}) = 1 \quad (\text{S6.14})$$

$$z_{\text{S}}(\text{int}) = 5 + 3e^{-571/T} + e^{-825/T} \quad (\text{S6.15})$$

and

$$z_{\text{Ca}}(\text{int}) = 1 \tag{S6.16}$$

The most questionable approximation in this calculation is the neglect of the  $^1D_2$  state in sulfur, which, at 3000 K, is equal to 0.7% of the sum of the terms given.

**Exercise 6.4** For molecular oxygen,

$$\log z_{\text{O}_2}(\text{int}) = \varepsilon_B/kT + \log(kTI/\hbar^2) - \log(1 - e^{-\hbar\omega/kT}) \tag{S6.17}$$

By evaluating the three terms separately at a number of temperatures from  $T = 100$  to 10,000 K, determine their relative importance in any calculation of the equilibrium constant for a reaction involving  $\text{O}_2$ .

**Solution** From Table 6.1, we see that

$$\begin{aligned} \varepsilon_B/k &= 60,000 \text{ K,} \\ \hbar^2/kI &= 4.14 \text{ K,} \\ \text{and } \hbar\omega/k &= 2250 \text{ K.} \end{aligned}$$

Therefore,

$$\log z_{\text{O}_2}(\text{int}) = 60,000/T + \log(T/4.14) - \log(1 - e^{-2250/T}) \equiv \phi_B + \phi_R + \phi_V \tag{S6.18}$$

$T$	$\phi_B$	$\phi_R$	$\phi_V$
100	600	3.18	$1.69 \times 10^{-10}$
500	120	4.79	$1.12 \times 10^{-2}$
1000	60	5.49	0.11
3000	20	6.59	0.64
10000	6	7.79	1.60

**Table S6.1** Values of terms in the internal canonical potential of  $\text{O}_2$ .

In terms of its absolute size and its rate of change with  $T$ , the term  $\varepsilon_B/kT$  clearly dominates the other two terms. Thus a reasonably good approximation for  $z_{\text{O}_2}(\text{int})$  is simply

$$z_{\text{O}_2}(\text{int}) = e^{60000/T} \tag{S6.19}$$

**Exercise 6.5** For the ideal gas dissociation reaction



the *degree of dissociation*  $r$  is defined as the fraction of atoms in the dissociated state. Therefore,  $r = n_A/(n_A + 2n_{A_2})$ . Show that

$$r = (1 + 4\beta p/K)^{-1/2} \tag{S6.21}$$

where  $p$  is the pressure,  $\beta = 1/kT$ , and  $K$  is the equilibrium constant.

**Solution** Letting  $x = n_A$  and  $y = n_{A_2}$ , we can write the equilibrium equation and the ideal gas law as

$$x^2 = Ky \quad \text{and} \quad x + y = \beta p \tag{S6.22}$$

Using the second equation to eliminate  $y$  in the first gives the following quadratic equation for  $x$ .

$$x^2 + Kx - K\beta p = 0 \quad (\text{S6.23})$$

The only positive solution of this equation is

$$x = [(K/2)^2 + K\beta p]^{1/2} - K/2 \quad (\text{S6.24})$$

$r$  is defined as  $x/(x + 2y)$ . Using the ideal gas law to eliminate  $y$  in this expression, we see that

$$\begin{aligned} r &= \frac{x}{2\beta p - x} \\ &= \frac{[(K/2)^2 + K\beta p]^{1/2} - K/2}{K/2 + 2\beta p - [(K/2)^2 + K\beta p]^{1/2}} \\ &= \frac{(1 + 4\beta p/K)^{1/2} - 1}{1 + 4\beta p/K - (1 + 4\beta p/K)^{1/2}} \end{aligned} \quad (\text{S6.25})$$

Letting  $\lambda = (1 + 4\beta p/K)^{1/2}$ , we can write this as

$$r = \frac{\lambda - 1}{\lambda^2 - \lambda} = \lambda^{-1} \quad (\text{S6.26})$$

**Exercise 6.6** Using Eq. (S6.13), determine the degree of dissociation of  $\text{O}_2$  between  $T = 1000$  and  $3000$  K for a fixed pressure of  $10^{-6}$  atm (Fig. S6.1).

**Solution** From Eq. (S6.13) we get

$$z_{\text{O}}(\text{int}) = 5 + 3e^{-228/T} + e^{-326/T} \quad (\text{S6.27})$$

Using data given in Table 6.1, one can calculate

$$z_{\text{O}_2}(\text{int}) = \frac{(T/4.14)e^{60000/T}}{(1 - e^{-2250/T})} \quad (\text{S6.28})$$

For  $\text{O}_2$  the reduced mass is half the mass of an oxygen atom.

$$\mu = 8u = 1.33 \times 10^{-26} \text{ kg} \quad (\text{S6.29})$$

Therefore

$$\lambda_{\mu} = \frac{h}{\sqrt{2\pi\mu kT}} = \frac{6.17 \times 10^{-10}}{\sqrt{T}} \quad (\text{S6.30})$$

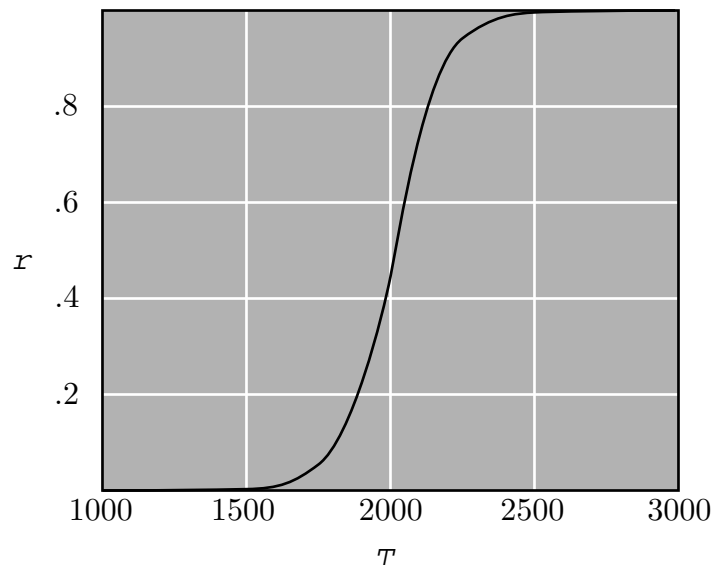
From Eq. (6.29) we see that

$$K = \frac{z_{\text{O}}^2}{z_{\text{O}_2}\lambda_{\mu}^3} \quad (\text{S6.31})$$

Using the formula

$$r = (1 + 4\beta p/K)^{-1/2} \quad (\text{S6.32})$$

with  $p = 0.101 \text{ N/m}^2$  the function  $r(T)$  has been plotted over the range  $1000 < T < 3000$  K. One can see that almost complete molecular dissociation takes place within the temperature interval  $1500 < T < 2500$  K. Notice that the actual dissociation temperature is much less than the naive estimate,  $T \approx 60,000$  K, based



**Fig. S6.1** A graph of the degree of dissociation of  $\text{O}_2$  as a function of  $T$  for a fixed pressure of  $10^{-6}$  atm.

only on the binding energy of the diatomic molecule. The much greater amount of phase space available to two unbound atoms, in comparison to a single molecule, strongly tilts the equilibrium toward dissociation.

**Exercise 6.7** Redo the previous exercise, using the approximation  $z_{\text{O}_2}(\text{int}) = \exp(60000/T)$ , mentioned in Exercise 6.4.

**Solution** With this approximation

$$K = \frac{(5 + 3e^{-228/T} + e^{-326/T})^2}{(6.17 \times 10^{-10}/\sqrt{T})^3 e^{60000/T}} \quad (\text{S6.33})$$

The function

$$r = (1 + 4\beta p/K)^{-1/2} \quad (\text{S6.34})$$

with  $p = 0.101 \text{ N/m}^2$  is plotted below in Fig. S6.2. One can see that this approximation, which ignores the rotational and vibrational degrees of freedom of the molecule, exaggerates the phase-space effect that was mentioned in the last exercise, thus shifting the dissociation temperature to an even lower value.

**Exercise 6.8** At a fixed temperature of 2000 K, plot the degree of dissociation of oxygen as a function of pressure in the range  $0 < p < 1 \text{ N/m}^2 \approx 10^{-5}$  atm.

**Solution** According to Exercise 6.6, the equilibrium constant for oxygen dissociation is

$$K = \frac{z_{\text{O}}}{z_{\text{O}_2} \lambda_{\mu}^3} \quad (\text{S6.35})$$

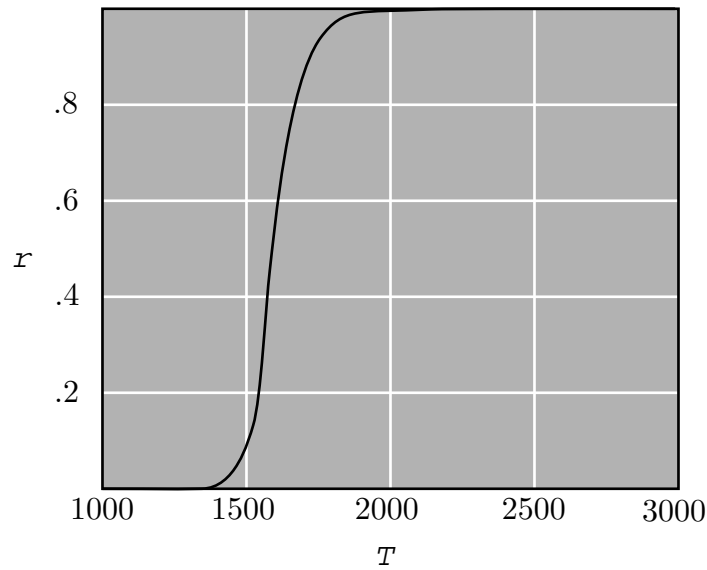
where

$$z_{\text{O}} = 5 + 3e^{-228/T} + e^{-326/T} \quad (\text{S6.36})$$

$$z_{\text{O}_2} = (T/4.14)e^{60000/T}/(1 - e^{-2250/T}) \quad (\text{S6.37})$$

and

$$\lambda_{\mu} = (6.17 \times 10^{-10})/\sqrt{T} \quad (\text{S6.38})$$



**Fig. S6.2** A graph of the degree of dissociation of O<sub>2</sub> as a function of  $T$ , neglecting rotational and vibrational degrees of freedom.

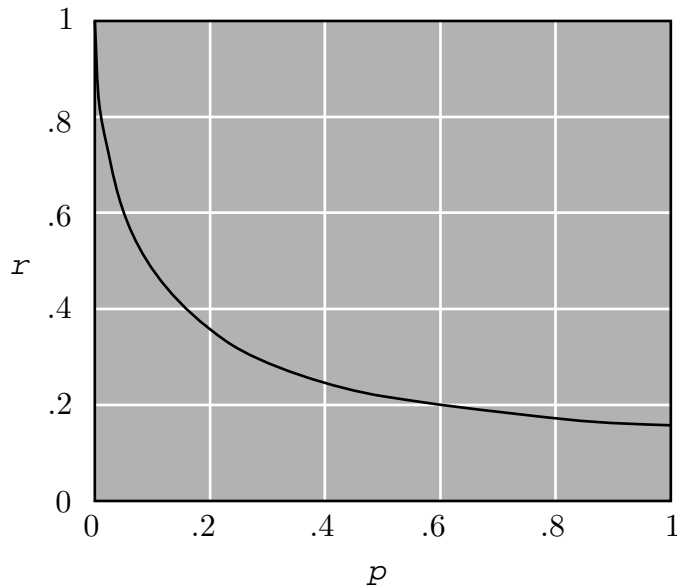
At a temperature of 2000 K,

$$\frac{4\beta}{K} = \frac{4z_{\text{O}_2}\lambda_\mu^3}{kTz_{\text{O}}^2} = 40.0 \text{ m}^2/\text{N} \tag{S6.39}$$

The degree of dissociation as a function of pressure is therefore

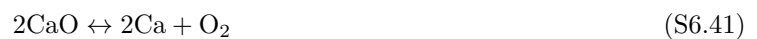
$$r = (1 + 40p)^{-1/2} \tag{S6.40}$$

This is plotted, in the range  $0 < p < 1 \text{ N/m}^2$  in Fig. S6.3.



**Fig. S6.3** The degree of dissociation of O<sub>2</sub> as a function of pressure (in N/m<sup>2</sup>) for  $T = 2000 \text{ K}$ .

**Exercise 6.9** Plot  $\log K$  for the ideal gas reaction



in the temperature range  $1000 < T < 10,000$  K.

**Solution** From Eq. (6.10), we see that

$$\log K = 2f_{\text{Ca}}^o + f_{\text{O}_2}^o - 2f_{\text{CaO}}^o \quad (\text{S6.42})$$

Using Eq. (6.29), we can write this in the form

$$\log K = 2 \log z_{\text{Ca}}(\text{int}) + \log z_{\text{O}_2}(\text{int}) - 2 \log z_{\text{CaO}}(\text{int}) - 3 \log(\lambda_{\text{Ca}}^2 \lambda_{\text{O}_2} / \lambda_{\text{CaO}}^2) \quad (\text{S6.43})$$

But

$$\begin{aligned} \frac{\lambda_{\text{Ca}}^2 \lambda_{\text{O}_2}}{\lambda_{\text{CaO}}^2} &= \frac{h}{\sqrt{2\pi kT}} \frac{m_{\text{Ca}} + m_{\text{O}}}{m_{\text{Ca}} \sqrt{2m_{\text{O}}}} \\ &= 4.32 \times 10^{-10} / \sqrt{T} \end{aligned} \quad (\text{S6.44})$$

From the data in Table 6.2, we can calculate

$$z_{\text{Ca}}(\text{int}) = 1 + e^{-21808/T} + 3e^{-21883/T} + 5e^{-22036/T} \quad (\text{S6.45})$$

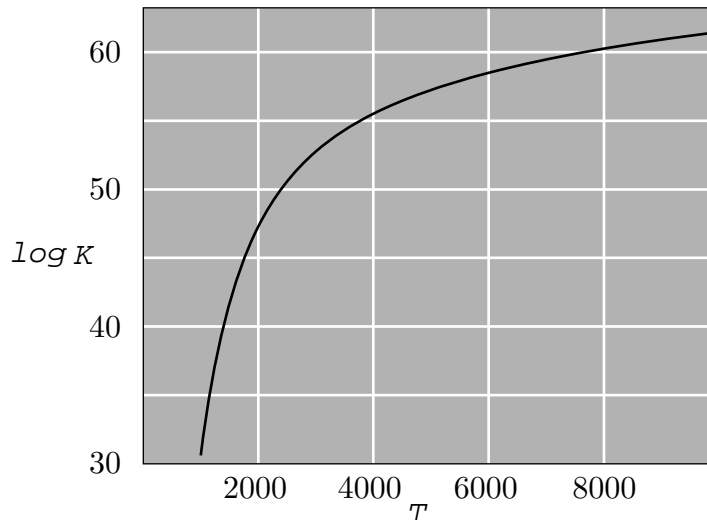
From Table 6.1 and Eqs. (6.35) and (6.37), we get

$$z_{\text{O}_2}(\text{int}) = \frac{(T/4.14)e^{60000/T}}{(1 - e^{-2250/T})} \quad (\text{S6.46})$$

and

$$z_{\text{CaO}}(\text{int}) = \frac{(T/0.5)e^{47000/T}}{(1 - e^{-1056/T})} \quad (\text{S6.47})$$

Using any computer plotting program, it is now easy to plot  $\log K$  from Eq. (S6.43), as shown in Fig. S6.4.



**Fig. S6.4** The logarithm of the equilibrium constant for the ideal gas reaction  $2\text{CaO} \leftrightarrow 2\text{Ca} + \text{O}_2$ .

**Exercise 6.10** An ideal gas is any substance that satisfies the equation  $pV = NRT$ , where  $N$  is the particle number in moles. Show that, for an ideal gas, the molar specific heats,  $C_p$  and  $C_V$ , differ by the gas constant. That is, that

$$C_p - C_V = R \quad (\text{S6.48})$$



**Solution** For one mole, the ideal gas equation is

$$pV = RT \quad (\text{S6.49})$$

This equation allows us to evaluate the derivatives

$$\left(\frac{\partial V}{\partial T}\right)_p = \beta_p V = \frac{R}{p} \quad (\text{S6.50})$$

and

$$\left(\frac{\partial V}{\partial p}\right) = -\kappa_T V = -\frac{RT}{p^2} \quad (\text{S6.51})$$

But, by Eq. (6.87),

$$\begin{aligned} C_p - C_V &= \frac{TV\beta_p^2}{\kappa_T} \\ &= TV \frac{(R/pV)^2}{(RT/p^2V)} = R \end{aligned} \quad (\text{S6.52})$$

**Exercise 6.11** From the entropy function for a monatomic ideal gas, determine the affinity as a function of temperature and density and verify that it satisfies Eq. (5.78) for all densities. [The reason why there is no low-density restriction in applying Eq. (5.78) to an ideal gas is that, for an ideal gas, the basic assumption made in deriving that equation, namely the use of Poisson's formula, is valid at all densities because the particles are not statistically correlated.]

**Solution** For a monatomic ideal gas

$$S^o = N(\log V + \frac{3}{2} \log E - \frac{5}{2} \log N + C) \quad (\text{S6.53})$$

This gives

$$\alpha = \frac{\partial S^o}{\partial N} = \log V + \frac{3}{2} \log E - \frac{5}{2} \log N + C - \frac{5}{2} \quad (\text{S6.54})$$

But  $E = \frac{3}{2}NkT$ . When this is used in Eq. (S6.54), one obtains

$$\alpha = -\log(N/V) + \frac{3}{2} \log T + C' \quad (\text{S6.55})$$

**Exercise 6.12** The affinity of a simple substance can be written as a function of the inverse temperature and the pressure. Starting from Eq. (5.45), which gives  $\partial\alpha/\partial\beta$  along an isobar, derive a formula for the finite change,  $\alpha(\beta_2, p) - \alpha(\beta_1, p)$ , as an integral involving the constant pressure specific heat  $C_p$  and the enthalpy at  $\beta_1$ .

**Solution** Equation (5.45) states that

$$\left(\frac{\partial\alpha}{\partial\beta}\right)_p = -(\varepsilon + pv) \equiv -h \quad (\text{S6.56})$$

where  $h = H/N$  is the enthalpy per particle if everything is being expressed in rational units or the enthalpy per mole in practical units. Taking another derivative and using the fact that  $C_p = (\partial h/\partial T)_p = -\beta^{-2}(\partial h/\partial\beta)_p$  gives

$$\left(\frac{\partial^2\alpha}{\partial\beta^2}\right)_p = \frac{C_p}{\beta^2} \quad (\text{S6.57})$$

Using the formula, familiar from mechanics, that

$$x(t_2) = x(t_1) + v(t_1)(t_2 - t_1) + \int_{t_1}^{t_2} dt' \int_{t_1}^{t'} dt a(t) \quad (\text{S6.58})$$

we can combine Eqs. (S6.56) and (S6.57) to get

$$\alpha(\beta_2, p) = \alpha(\beta_1, p) - h(\beta_1, p)(\beta_2 - \beta_1) + \int_{\beta_1}^{\beta_2} d\beta' \int_{\beta_1}^{\beta'} d\beta \frac{C_p(\beta, p)}{\beta^2} \quad (\text{S6.59})$$

**Exercise 6.13** Show that, according to Debye's theory, the entropy of a crystal is equal to one-third of its specific heat when  $T \ll T_D$ .

**Solution** For a crystal, expansion is such a small effect that there is no necessity to distinguish between  $C_p$  and  $C_V$ . The entropy is given by the integral

$$S = \int_o^T \frac{dQ}{T} = \int_o^T \frac{C dT}{T} \quad (\text{S6.60})$$

But, at low  $T$ , the specific heat is proportional to  $T^3$ . By Eq. (4.33),

$$C = \frac{12\pi^4 NkT^3}{5T_D^3} \equiv C_o T^3 \quad (\text{S6.61})$$

Thus

$$S = C_o \int_o^T T^2 dT = \frac{1}{3} C_o T^3 \quad (\text{S6.62})$$

which shows that  $S = C/3$ .

**Exercise 6.14** In Section 6.11 it was shown how an arbitrary partial derivative involving the variables  $p$ ,  $T$ ,  $S$ ,  $V$ ,  $E$ ,  $F$ ,  $H$ ,  $G$ , and  $\mu$  could be transformed into an expression involving  $p$ ,  $T$ , and the five "handbook functions,"  $S$ ,  $V$ ,  $C_p$ ,  $\beta_p$ , and  $\kappa_T$ . In 1941, P. W. Bridgeman (*Physical Review*, **3**, p. 273) published a table that allows the results of such a calculation to be written down immediately. The table is reproduced as Table S6.2, and its use is illustrated by two examples.

$$\left(\frac{\partial G}{\partial p}\right)_V \rightarrow \frac{(\partial G)_V}{(\partial p)_V} \rightarrow \frac{SV\kappa_T - V^2\beta_p}{-V\beta_p} = V - \frac{S\kappa_T}{\beta_p} \quad (\text{S6.63})$$

and

$$\left(\frac{\partial F}{\partial V}\right)_p \rightarrow \frac{(\partial F)_p}{(\partial V)_p} \rightarrow \frac{-S - pV\beta_p}{V\beta_p} = -\frac{S}{V\beta_p} - p \quad (\text{S6.64})$$

That is, we first replace the partial derivative  $(\partial x/\partial y)_a$  by a fraction made up of the mathematically meaningless symbols  $(\partial x)_a$  and  $(\partial y)_a$ . We look up each symbol in the table (it will always be found either in the first column or the second, never in both), and replace it by the quantity shown in the last column. The resulting fraction gives the value of the partial derivative in the  $p$ - $T$  representation.

Work out each of the following partial derivatives, first using Bridgeman's table, and then using the method of Section 6.11. (a)  $(\partial F/\partial S)_p$ ; (b)  $(\partial E/\partial T)_G$ .

**Solution** (a)

$$\left(\frac{\partial F}{\partial S}\right)_p \rightarrow \frac{(\partial F)_p}{(\partial S)_p} = -\frac{S + pV\beta_p}{C_p/T} \quad (\text{S6.65})$$

**Table S6.2** The Bridgeman transformation table\*

$(\partial T)_p$	$-(\partial p)_T$	$\longrightarrow$	1
$(\partial V)_p$	$-(\partial p)_V$	$\longrightarrow$	$V\beta$
$(\partial S)_p$	$-(\partial p)_S$	$\longrightarrow$	$C/T$
$(\partial E)_p$	$-(\partial p)_E$	$\longrightarrow$	$C - pV\beta$
$(\partial H)_p$	$-(\partial p)_H$	$\longrightarrow$	$C$
$(\partial G)_p$	$-(\partial p)_G$	$\longrightarrow$	$-S$
$(\partial F)_p$	$-(\partial p)_F$	$\longrightarrow$	$-S - pV\beta$
$(\partial V)_T$	$-(\partial T)_V$	$\longrightarrow$	$V\kappa$
$(\partial S)_T$	$-(\partial T)_S$	$\longrightarrow$	$V\beta$
$(\partial E)_T$	$-(\partial T)_E$	$\longrightarrow$	$TV\beta - pV\kappa$
$(\partial H)_T$	$-(\partial T)_H$	$\longrightarrow$	$TV\beta - V$
$(\partial G)_T$	$-(\partial T)_G$	$\longrightarrow$	$-V$
$(\partial F)_T$	$-(\partial T)_F$	$\longrightarrow$	$-pV\kappa$
$(\partial S)_V$	$-(\partial V)_S$	$\longrightarrow$	$V^2\beta^2 - VC\kappa/T$
$(\partial E)_V$	$-(\partial V)_E$	$\longrightarrow$	$TV^2\beta^2 - VC\kappa$
$(\partial H)_V$	$-(\partial V)_H$	$\longrightarrow$	$TV^2\beta^2 - VC\kappa - V^2\beta$
$(\partial G)_V$	$-(\partial V)_G$	$\longrightarrow$	$SV\kappa - V^2\beta$
$(\partial F)_V$	$-(\partial V)_F$	$\longrightarrow$	$SV\kappa$
$(\partial E)_S$	$-(\partial S)_E$	$\longrightarrow$	$pV^2\beta^2 - pVC\kappa/T$
$(\partial H)_S$	$-(\partial S)_H$	$\longrightarrow$	$-VC/T$
$(\partial G)_S$	$-(\partial S)_G$	$\longrightarrow$	$SV\beta - VC/T$
$(\partial F)_S$	$-(\partial S)_F$	$\longrightarrow$	$pV^2\beta^2 + SV\beta - pVC\kappa/T$
$(\partial H)_E$	$-(\partial E)_H$	$\longrightarrow$	$pV^2\beta + pVC\kappa - VC - pTV^2\beta^2$
$(\partial G)_E$	$-(\partial E)_G$	$\longrightarrow$	$pV^2\beta + TSV\beta - VC - pSV\kappa$
$(\partial F)_E$	$-(\partial E)_F$	$\longrightarrow$	$pTV^2\beta^2 - pVC\kappa$
$(\partial G)_H$	$-(\partial H)_G$	$\longrightarrow$	$TSV\beta - VC - VS$
$(\partial F)_H$	$-(\partial H)_F$	$\longrightarrow$	$(TV\beta - V)(S + pV\beta) - pV\kappa$
$(\partial F)_G$	$-(\partial G)_F$	$\longrightarrow$	$pSV\kappa - SV - pV^2\beta$

\*In this table  $C \equiv C_p$ ,  $\beta \equiv \beta_p$ , and  $\kappa \equiv \kappa_T$ .

To verify this by the method of Section 6.11, we first note that  $dF = -S dT - p dV$ , and thus

$$\left(\frac{\partial F}{\partial S}\right)_p = -S\left(\frac{\partial T}{\partial S}\right)_p - p\left(\frac{\partial V}{\partial S}\right)_p \tag{S6.66}$$

The first expression is eliminated using

$$\left(\frac{\partial T}{\partial S}\right) = \frac{1}{(\partial S/\partial T)_p} = \frac{T}{C_p} \tag{S6.67}$$

The second expression requires the third partial derivative identity.

$$\left(\frac{\partial V}{\partial S}\right)_p = \frac{(\partial V/\partial T)_p}{(\partial S/\partial T)_p} = \frac{V\beta_p}{C_p/T} \tag{S6.68}$$

The result agrees with Bridgeman's table. (b) By Bridgeman's table,

$$\begin{aligned} \left(\frac{\partial E}{\partial T}\right)_G &\rightarrow \frac{(\partial E)_G}{(\partial T)_G} = \frac{-pV^2\beta_p - TSV\beta_p + VC_p + pSV\kappa_T}{V} \\ &= C_p + pS\kappa_T - pV\beta_p - TSV\beta_p \end{aligned} \tag{S6.69}$$

By Section 6.11, we first use  $dE = T dS - p dV$ .

$$\left(\frac{\partial E}{\partial T}\right)_G = dT \left(\frac{\partial S}{\partial T}\right)_G - p \left(\frac{\partial V}{\partial T}\right)_G \quad (\text{S6.70})$$

Both terms on the right-hand side require the second partial derivative identity.

$$\left(\frac{\partial S}{\partial T}\right)_G = -\frac{(\partial G/\partial T)_S}{(\partial G/\partial S)_T} \quad (\text{S6.71})$$

and

$$\left(\frac{\partial V}{\partial T}\right)_G = -\frac{(\partial G/\partial T)_V}{(\partial G/\partial V)_T} \quad (\text{S6.72})$$

These are followed by use of the differential relation  $dG = -S dT + V dp$ , giving

$$\left(\frac{\partial G}{\partial T}\right)_S = -S + V \left(\frac{\partial p}{\partial T}\right)_S \quad (\text{S6.73})$$

$$\left(\frac{\partial G}{\partial S}\right)_T = -S \cdot 0 + V \left(\frac{\partial p}{\partial S}\right)_T = 1/\beta_p \quad (\text{S6.74})$$

$$\left(\frac{\partial G}{\partial T}\right)_V = -S + V \left(\frac{\partial p}{\partial T}\right)_V \quad (\text{S6.75})$$

$$\left(\frac{\partial G}{\partial V}\right)_T = -S \cdot 0 + V \left(\frac{\partial p}{\partial V}\right)_T = -1/\kappa_T \quad (\text{S6.76})$$

To transform the remaining expressions, we need the second partial derivative identity.

$$\left(\frac{\partial p}{\partial T}\right)_S = -\frac{(\partial S/\partial T)_p}{(\partial S/\partial p)_T} = \frac{C_p/T}{V\beta_p} \quad (\text{S6.77})$$

$$\left(\frac{\partial p}{\partial T}\right)_V = -\frac{(\partial V/\partial T)_p}{(\partial V/\partial p)_T} = \beta_p/\kappa_T \quad (\text{S6.78})$$

Making all the back substitutions verifies Eq. (S6.68) (and gives one an appreciation for the efficiency of Bridgeman's table).