

25-63. When the pressures in Problem 25-62 are plotted against molality squared, the result is almost a straight line. Curve fit the data to polynomials of the form

$$P = k_H m^2 (1 + c_1 m^{1/2} + c_2 m + c_3 m^{3/2} + \dots)$$

of increasing degree and evaluate k_H .

If the data are fitted to $P = k_H m^2$, k_H turns out to be (in units of $\text{atm} \cdot \text{kg}^2 \cdot \text{mol}^{-2}$) 4.15×10^{-7} . The subsequent fits are (suppressing the units)

k_H	c_1	c_2	c_3	c_4
4.83×10^{-7}	-1.77			
4.92×10^{-7}	-2.24	3.48		
4.93×10^{-7}	-2.33	4.75	-6.21	
4.93×10^{-7}	-2.34	5.07	-9.45	10.3

Thus we see that $k_H = 4.93 \times 10^{-7} \text{ atm} \cdot \text{kg}^2 \cdot \text{mol}^{-2}$.

25-64. When the data in Problem 25-62 are plotted in the form of P/m^2 against $m^{1/2}$, the result is essentially a straight line with a negative slope. Why is this so? Use Debye-Hückel theory to calculate the slope of this line and compare your result with the final value of c_1 in Problem 25-63.

The activity of the HCl(aq) is given by $a_{\text{HCl}} = P/k_H$. Using the fact that $a_{\text{HCl}} = a_{\pm}^2 = m^2 \gamma_{\pm}^2$, we have

$$P = k_H m^2 \gamma_{\pm}^2$$

Note that as $m \rightarrow 0$, $\gamma_{\pm} \rightarrow 1$, and $P \rightarrow k_H m^2$, as expected. The Debye-Hückel expression for γ_{\pm} in this case is

$$\ln \gamma_{\pm} = -1.171 m^{1/2}$$

Substitute this expression for γ_{\pm} into $P = k_H m^2 \gamma_{\pm}^2$ and linearize the exponential according to $e^{-x} = 1 - x + \dots$ to obtain

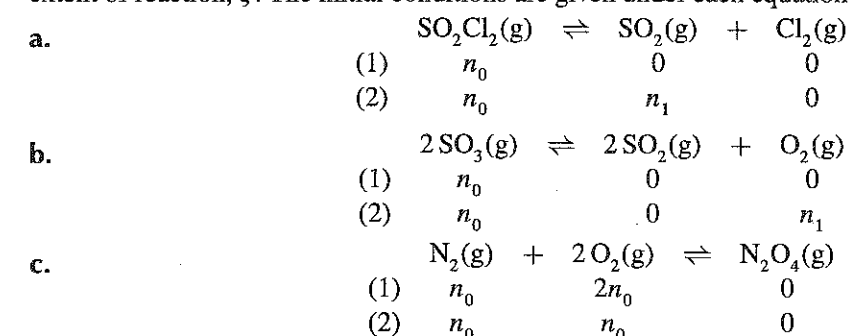
$$P = k_H m^2 (1 - 2.342 m^{1/2} + \dots)$$

Thus, we predict that c_1 in Problem 25-63 is equal to -2.34, in excellent agreement.

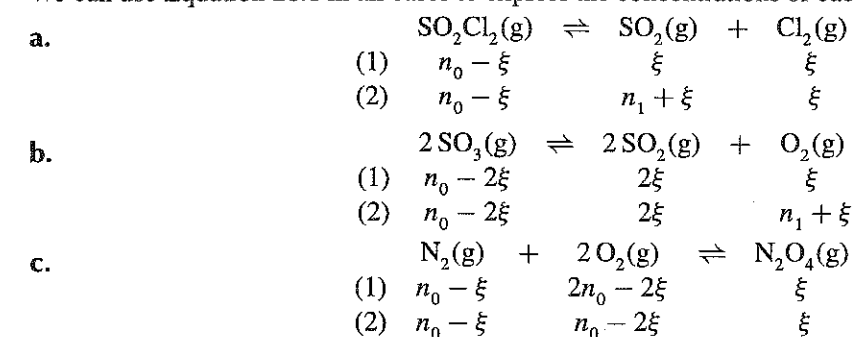
Chemical Equilibrium

PROBLEMS AND SOLUTIONS

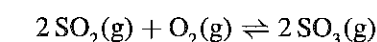
26-1. Express the concentrations of each species in the following chemical equations in terms of the extent of reaction, ξ . The initial conditions are given under each equation.



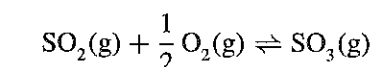
We can use Equation 26.1 in all cases to express the concentrations of each species.



26-2. Write out the equilibrium-constant expression for the reaction that is described by the equation



Compare your result to what you get if the reaction is represented by



Using Equation 26.12, we write K_p for the first chemical equation as

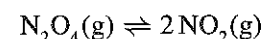
$$K_p(T) = \frac{P_{\text{SO}_3}^2}{P_{\text{O}_2} P_{\text{SO}_2}^2}$$

For the second chemical equation, we again use Equation 26.12 to find

$$K_p'(T) = \frac{P_{\text{SO}_3}}{P_{\text{O}_2}^{1/2} P_{\text{SO}_2}}$$

which is the square root of K_p .

26-3. Consider the dissociation of $\text{N}_2\text{O}_4(\text{g})$ into $\text{NO}_2(\text{g})$ described by



Assuming that we start with n_0 moles of $\text{N}_2\text{O}_4(\text{g})$ and no $\text{NO}_2(\text{g})$, show that the extent of reaction, ξ_{eq} , at equilibrium is given by

$$\frac{\xi_{\text{eq}}}{n_0} = \left(\frac{K_p}{K_p + 4P} \right)^{1/2}$$

Plot ξ_{eq}/n_0 against P given that $K_p = 6.1$ at 100°C . Is your result in accord with Le Châtelier's principle?

At equilibrium, $n_{\text{N}_2\text{O}_4} = n_0 - \xi_{\text{eq}}$ and $n_{\text{NO}_2} = 2\xi_{\text{eq}}$. The partial pressures of the species are then

$$P_{\text{N}_2\text{O}_4} = \frac{n_0 - \xi_{\text{eq}}}{n_0 - \xi_{\text{eq}} + 2\xi_{\text{eq}}} P = \frac{n_0 - \xi_{\text{eq}}}{n_0 + \xi_{\text{eq}}} P$$

and

$$P_{\text{NO}_2} = \frac{2\xi_{\text{eq}}}{n_0 + \xi_{\text{eq}}} P = \frac{2\xi_{\text{eq}}}{n_0 + \xi_{\text{eq}}} P$$

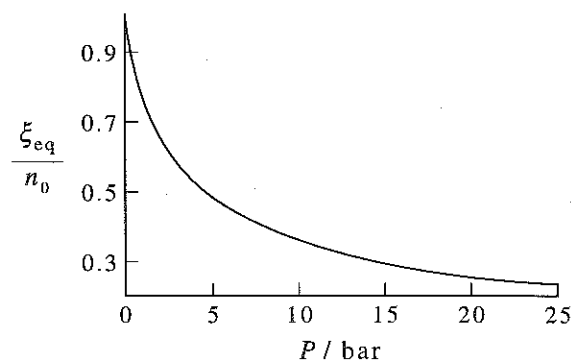
Substituting into the expression for K_p , we find

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{4\xi_{\text{eq}}^2(n_0 + \xi_{\text{eq}})}{(n_0 + \xi_{\text{eq}})^2(n_0 - \xi_{\text{eq}})} P = \frac{4(\xi_{\text{eq}}/n_0)^2}{1 - (\xi_{\text{eq}}/n_0)^2} P$$

Solving this expression for ξ_{eq}/n_0 , we find that

$$\begin{aligned} K_p - K_p(\xi_{\text{eq}}/n_0)^2 &= 4P(\xi_{\text{eq}}/n_0)^2 \\ (4P + K_p)(\xi_{\text{eq}}/n_0)^2 &= K_p \\ \frac{\xi_{\text{eq}}}{n_0} &= \left(\frac{K_p}{K_p + 4P} \right)^{1/2} \end{aligned}$$

A plot of ξ_{eq}/n_0 against P is shown below.



This is in accord with Le Châtelier's principle: as the pressure increases, the reaction occurs to a lesser extent and ξ_{eq} decreases.

26-4. In Problem 26-3 you plotted the extent of reaction at equilibrium against the total pressure for the dissociation of $\text{N}_2\text{O}_4(\text{g})$ to $\text{NO}_2(\text{g})$. You found that ξ_{eq} decreases as P increases, in accord with Le Châtelier's principle. Now let's introduce n_{inert} moles of an inert gas into the system. Assuming that we start with n_0 moles of $\text{N}_2\text{O}_4(\text{g})$ and no $\text{NO}_2(\text{g})$, derive an expression for ξ_{eq}/n_0 in terms of P and the ratio $r = n_{\text{inert}}/n_0$. As in Problem 26-3, let $K_p = 6.1$ and plot ξ_{eq}/n_0 versus P for $r = 0$ (Problem 26-3), $r = 0.50$, $r = 1.0$, and $r = 2.0$. Show that introducing an inert gas into the reaction mixture at constant pressure has the same effect as lowering the pressure. What is the effect of introducing an inert gas into a reaction system at constant volume?

At equilibrium, as before, $n_{\text{N}_2\text{O}_4} = n_0 - \xi_{\text{eq}}$ and $n_{\text{NO}_2} = 2\xi_{\text{eq}}$. However, the total number of moles present has changed to $n_0 + \xi_{\text{eq}} + n_{\text{inert}}$. The partial pressures of the species are then

$$P_{\text{N}_2\text{O}_4} = \frac{n_0 - \xi_{\text{eq}}}{n_0 + \xi_{\text{eq}} + n_{\text{inert}}} P \quad \text{and} \quad P_{\text{NO}_2} = \frac{2\xi_{\text{eq}}}{n_0 + \xi_{\text{eq}} + n_{\text{inert}}} P$$

Substituting into the expression for K_p , we find

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{4\xi_{\text{eq}}^2 P}{(n_0 - \xi_{\text{eq}})(n_0 + n_{\text{inert}} + \xi_{\text{eq}})} = \frac{4(\xi_{\text{eq}}/n_0)^2 P}{(1 - \xi_{\text{eq}}/n_0)(1 + r + \xi_{\text{eq}}/n_0)}$$

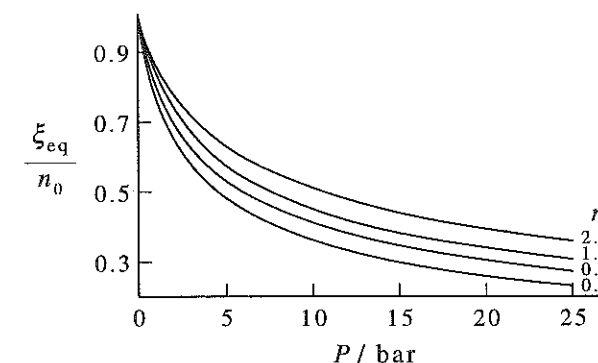
Solving for ξ_{eq}/n_0 gives

$$\frac{\xi_{\text{eq}}}{n_0} = -\frac{K_p r}{2(K_p + 4P)} \pm \frac{1}{2(K_p + 4P)} [K_p^2 r^2 + 4K_p(1+r)(K_p + 4P)]^{1/2}$$

where we have let $r = n_{\text{inert}}/n_0$. When $r = 0$, as in Problem 26-3, this expression becomes

$$\frac{\xi_{\text{eq}}}{n_0} = \pm \frac{[4K_p(K_p + 4P)]^{1/2}}{2(K_p + 4P)} = \pm \left[\frac{K_p}{K_p + 4P} \right]^{1/2}$$

For ξ_{eq} to be positive, we take the positive root. Now we can plot this expression for various values of r :



We see that introducing an inert gas into a constant-pressure reaction system increases the value of ξ_{eq} and so has the same effect as lowering the pressure. Introducing an inert gas into a constant-volume reaction system has no effect on the value of ξ_{eq} .

26-5. Re-do Problem 26-3 with n_0 moles of $\text{N}_2\text{O}_4(\text{g})$ and n_1 moles of $\text{NO}_2(\text{g})$ initially. Let $n_1/n_0 = 0.50$ and 2.0.

Now, at equilibrium, $n_{\text{N}_2\text{O}_4} = n_0 - \xi_{\text{eq}}$ and $n_{\text{NO}_2} = n_1 + 2\xi_{\text{eq}}$. The total number of moles of gas present will be $n_0 + n_1 + \xi_{\text{eq}}$. The partial pressures of the species are then, letting $s = n_1/n_0$,

$$P_{\text{N}_2\text{O}_4} = \frac{n_0 - \xi_{\text{eq}}}{n_0 + n_1 + \xi_{\text{eq}}} P = \frac{1 - \xi_{\text{eq}}/n_0}{1 + s + \xi_{\text{eq}}/n_0} P$$

and

$$P_{\text{NO}_2} = \frac{n_1 + 2\xi_{\text{eq}}}{n_0 + n_1 + \xi_{\text{eq}}} P = \frac{s + 2\xi_{\text{eq}}/n_0}{1 + s + \xi_{\text{eq}}/n_0} P$$

Substituting into the expression for K_p , we find

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(s + 2\xi_{\text{eq}}/n_0)^2}{(1 + s + \xi_{\text{eq}}/n_0)(1 - \xi_{\text{eq}}/n_0)} P$$

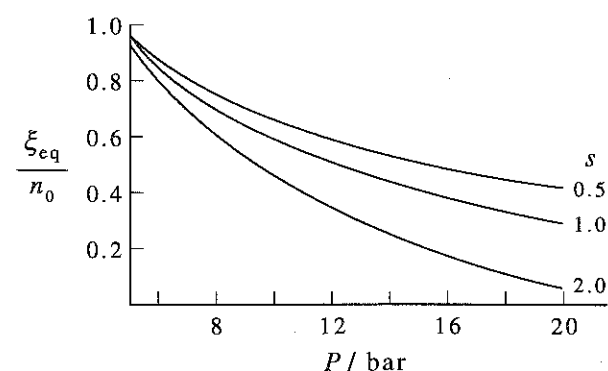
and solving for ξ_{eq}/n_0 gives

$$\frac{\xi_{\text{eq}}}{n_0} = -\frac{s}{2} \pm \frac{1}{2} \left[s^2 - 4 \left(\frac{Ps^2 - K_p s - K_p}{K_p + 4P} \right) \right]^{1/2}$$

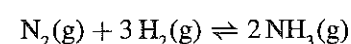
When $s = 0$, as in Problem 26-3, this expression becomes

$$\frac{\xi_{\text{eq}}}{n_0} = \pm \frac{K_p^{1/2}}{2(K_p + 4P)^{1/2}} = \pm \left[\frac{K_p}{(K_p + 4P)} \right]^{1/2}$$

For ξ_{eq} to be positive, we take the positive root. Now we can plot this expression for various values of s :



26-6. Consider the ammonia-synthesis reaction, which can be described by



Suppose initially there are n_0 moles of $\text{N}_2(\text{g})$ and $3n_0$ moles of $\text{H}_2(\text{g})$ and no $\text{NH}_3(\text{g})$. Derive an expression for $K_p(T)$ in terms of the equilibrium value of the extent of reaction, ξ_{eq} , and the pressure, P . Use this expression to discuss how ξ_{eq}/n_0 varies with P and relate your conclusions to Le Châtelier's principle.

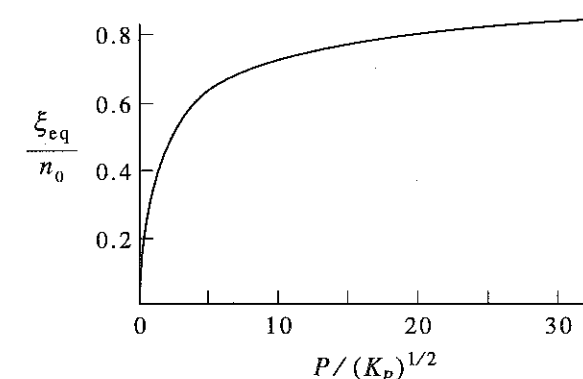
At equilibrium, there will be $n_0 - \xi_{\text{eq}}$ moles of $\text{N}_2(\text{g})$, $3n_0 - 3\xi_{\text{eq}}$ moles of $\text{H}_2(\text{g})$, and $2\xi_{\text{eq}}$ moles of $\text{NH}_3(\text{g})$, yielding a total of $4n_0 - 2\xi_{\text{eq}}$ moles of gas. Then

$$P_{\text{N}_2} = \frac{n_0 - \xi_{\text{eq}}}{4n_0 - 2\xi_{\text{eq}}} P \quad P_{\text{H}_2} = \frac{3n_0 - 3\xi_{\text{eq}}}{4n_0 - 2\xi_{\text{eq}}} P \quad \text{and} \quad P_{\text{NH}_3} = \frac{2\xi_{\text{eq}}}{4n_0 - 2\xi_{\text{eq}}} P$$

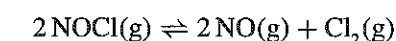
We then express K_p as

$$\begin{aligned} K_p &= \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}} \\ &= \frac{4\xi_{\text{eq}}^2 (4n_0 - 2\xi_{\text{eq}})^2}{(3n_0 - 3\xi_{\text{eq}})^3 (n_0 - \xi_{\text{eq}}) P^2} \\ &= \frac{16(\xi_{\text{eq}}/n_0)^2 (2 - \xi_{\text{eq}}/n_0)^4}{27(2 - \xi_{\text{eq}}/n_0)^2 (1 - \xi_{\text{eq}}/n_0)^4 P^2} \\ &= \frac{16(\xi_{\text{eq}}/n_0)^2 (2 - \xi_{\text{eq}}/n_0)^2}{27(1 - \xi_{\text{eq}}/n_0)^4 P^2} \end{aligned}$$

The following plot of ξ_{eq}/n_0 against P shows that ξ_{eq}/n_0 increases as P increases, as Le Châtelier's principle would dictate.



26-7. Nitrosyl chloride, NOCl , decomposes according to



Assuming that we start with n_0 moles of $\text{NOCl}(\text{g})$ and no $\text{NO}(\text{g})$ or $\text{Cl}_2(\text{g})$, derive an expression for K_p in terms of the equilibrium value of the extent of reaction, ξ_{eq} , and the pressure, P . Given that $K_p = 2.00 \times 10^{-4}$, calculate ξ_{eq}/n_0 when $P = 0.080$ bar. What is the new value of ξ_{eq}/n_0 at equilibrium when $P = 0.160$ bar? Is this result in accord with Le Châtelier's principle?

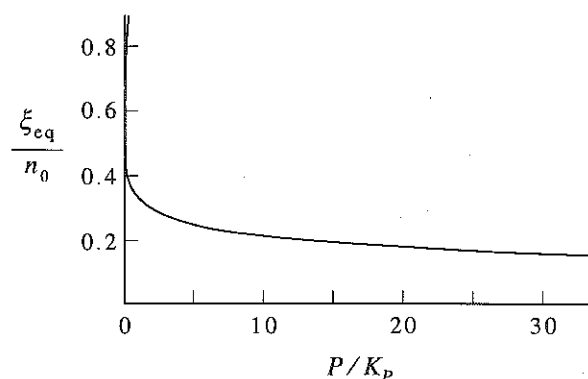
At equilibrium, there will be $n_0 - 2\xi_{\text{eq}}$ moles of $\text{NOCl}(\text{g})$, $2\xi_{\text{eq}}$ moles of $\text{NO}(\text{g})$, and ξ_{eq} moles of $\text{Cl}_2(\text{g})$, making a total of $n_0 + \xi_{\text{eq}}$ moles of gas present. Then

$$P_{\text{NOCl}} = \frac{n_0 - 2\xi_{\text{eq}}}{n_0 + \xi_{\text{eq}}} P \quad P_{\text{NO}} = \frac{2\xi_{\text{eq}}}{n_0 + \xi_{\text{eq}}} P \quad \text{and} \quad P_{\text{Cl}_2} = \frac{\xi_{\text{eq}}}{n_0 + \xi_{\text{eq}}} P$$

We then write K_p as

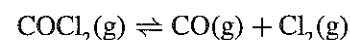
$$K_p = \frac{P_{\text{Cl}_2} P_{\text{NO}}^2}{P_{\text{NOCl}}^2} = \frac{4\xi_{\text{eq}}^3 P}{(n_0 + \xi_{\text{eq}})(n_0 - 2\xi_{\text{eq}})^2} = \frac{4(\xi_{\text{eq}}/n_0)^3 P}{(1 + \xi_{\text{eq}}/n_0)(1 - 2\xi_{\text{eq}}/n_0)^2}$$

A plot of ξ_{eq}/n_0 against P looks like



We see that ξ_{eq}/n_0 decreases as P increases, as Le Châtelier's principle would dictate. Letting $K_p = 2.00 \times 10^{-4}$, we find $\xi_{\text{eq}}/n_0 = 0.0783$ at $P = 0.080$ bar and $\xi_{\text{eq}}/n_0 = 0.0633$ at $P = 0.160$ bar, again in accord with Le Châtelier's principle.

26-8. The value of K_p at 1000°C for the decomposition of carbonyl dichloride (phosgene) according to



is 34.8 if the standard state is taken to be one bar. What would the value of K_p be if for some reason the standard state were taken to be 0.500 bar? What does this result say about the numerical values of equilibrium constants?

Use the definition of K_p to find the value of $K_p(0.500 \text{ bar})$ at the new standard state:

$$\begin{aligned} K_p(1 \text{ bar}) &= \frac{(P_{\text{CO}}/1 \text{ bar})(P_{\text{Cl}_2}/1 \text{ bar})}{(P_{\text{COCl}_2}/1 \text{ bar})} = 34.8 \\ K_p(0.500 \text{ bar}) &= \frac{(P_{\text{CO}}/0.500 \text{ bar})(P_{\text{Cl}_2}/0.500 \text{ bar})}{(P_{\text{COCl}_2}/0.500 \text{ bar})} \\ &= 0.500 K_p(1 \text{ bar}) = 17.4 \end{aligned}$$

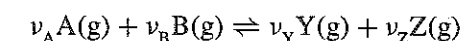
The numerical values of equilibrium constants are dependent on the standard states chosen.

26-9. Most gas-phase equilibrium constants in the recent chemical literature were calculated assuming a standard state pressure of one atmosphere. Show that the corresponding equilibrium constant for a standard state pressure of one bar is given by

$$K_p(\text{bar}) = K_p(\text{atm})(1.01325)^{\Delta\nu}$$

where $\Delta\nu$ is the sum of the stoichiometric coefficients of the products minus that of the reactants.

Consider the reaction described by



(We can extend this case to include as many reactants and products as we desire.) Now write K_p :

$$\begin{aligned} K_p(\text{bar}) &= \frac{(P_Z/1 \text{ bar})^{\nu_Z} (P_Y/1 \text{ bar})^{\nu_Y}}{(P_B/1 \text{ bar})^{\nu_B} (P_A/1 \text{ bar})^{\nu_A}} \\ &= \frac{P_Z^{\nu_Z} P_Y^{\nu_Y}}{(1 \text{ bar})^{\nu_Z + \nu_Y}} \frac{(1 \text{ bar})^{\nu_A + \nu_B}}{P_B^{\nu_B} P_A^{\nu_A}} \\ &= \frac{P_Z^{\nu_Z} P_Y^{\nu_Y}}{P_B^{\nu_B} P_A^{\nu_A}} \left(\frac{1}{1 \text{ bar}} \right)^{\Delta\nu} \left(\frac{1.01325 \text{ bar}}{1 \text{ atm}} \right)^{\Delta\nu} \\ &= \frac{(P_Z/1 \text{ atm})^{\nu_Z} (P_Y/1 \text{ atm})^{\nu_Y}}{(P_B/1 \text{ atm})^{\nu_B} (P_A/1 \text{ atm})^{\nu_A}} (1.01325 \text{ bar})^{\Delta\nu} \\ &= K_p(\text{atm})(1.01325 \text{ bar})^{\Delta\nu} \end{aligned}$$

26-10. Using the data in Table 26.1, calculate $\Delta_r G^\circ(T)$ and $K_p(T)$ at 25°C for

- $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g})$
- $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2 \text{HI}(\text{g})$
- $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$

Use Equations 26.19 and 26.11 to find $\Delta_r G^\circ$ and K_p .

- $\Delta_r G^\circ = 2(51.258 \text{ kJ}\cdot\text{mol}^{-1}) - 97.787 \text{ kJ}\cdot\text{mol}^{-1} = 4.729 \text{ kJ}\cdot\text{mol}^{-1}$
 $K_p = e^{-\Delta_r G^\circ/RT} = 0.148$
- $\Delta_r G^\circ = 2(1.560 \text{ kJ}\cdot\text{mol}^{-1}) - 19.325 \text{ kJ}\cdot\text{mol}^{-1} = -16.205 \text{ kJ}\cdot\text{mol}^{-1}$
 $K_p = e^{-\Delta_r G^\circ/RT} = 690$
- $\Delta_r G^\circ = 2(-16.637 \text{ kJ}\cdot\text{mol}^{-1}) = -33.274 \text{ kJ}\cdot\text{mol}^{-1}$
 $K_p = e^{-\Delta_r G^\circ/RT} = 6.80 \times 10^5$

26-11. Calculate the value of $K_c(T)$ based upon a one $\text{mol}\cdot\text{L}^{-1}$ standard state for each of the equations in Problem 26-10.

Use Equation 26.17, recalling that R must be in units of $\text{L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ because c° is $1 \text{ mol}\cdot\text{L}^{-1}$ and P° is 1 bar:

- $K_c = K_p(RT)^{-\Delta\nu} = (0.148)[(298.15 \text{ K})(0.083145 \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})]^{-1} = 5.97 \times 10^{-3}$
- $K_c = K_p(RT)^{-\Delta\nu} = (690)[(298.15 \text{ K})(0.083145 \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})]^0 = 690$
- $K_c = K_p(RT)^{-\Delta\nu} = (6.80 \times 10^5)[(298.15 \text{ K})(0.083145 \text{ L}\cdot\text{bar}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})]^2 = 4.17 \times 10^8$

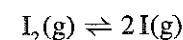
26-12. Derive a relation between K_p and K_c for the following:

- $\text{CO}(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{COCl}_2(\text{g})$
- $\text{CO}(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g}) + \text{H}_2\text{O}(\text{g})$
- $2 \text{BrCl}(\text{g}) \rightleftharpoons \text{Br}_2(\text{g}) + \text{Cl}_2(\text{g})$

Again, use Equation 26.17.

- $K_p = K_c \left(\frac{c^\circ RT}{P^\circ} \right)^{-1}$
- $K_p = K_c \left(\frac{c^\circ RT}{P^\circ} \right)^{-2}$
- $K_p = K_c \left(\frac{c^\circ RT}{P^\circ} \right)^0 = K_c$

26-13. Consider the dissociation reaction of $I_2(g)$ described by



The total pressure and the partial pressure of $I_2(g)$ at 1400°C have been measured to be 36.0 torr and 28.1 torr, respectively. Use these data to calculate K_p (one bar standard state) and K_c (one $\text{mol}\cdot\text{L}^{-1}$ standard state) at 1400°C .

First we express P_{I_2} and P_I in bars:

$$P_{I_2} = 28.1 \text{ torr} \left(\frac{1.01325 \text{ bar}}{760 \text{ torr}} \right) = 0.0375 \text{ bar}$$

$$P_I = P_{\text{tot}} - P_{I_2} = 7.9 \text{ torr} \left(\frac{1.01325 \text{ bar}}{760 \text{ torr}} \right) = 0.0105 \text{ bar}$$

Now use the definitions of K_p and K_c to write

$$K_p = \frac{P_I^2}{P_{I_2}} = 2.94 \times 10^{-3}$$

$$\begin{aligned} K_c &= K_p \left(\frac{P^\circ}{c^\circ RT} \right) \\ &= (2.94 \times 10^{-3}) \left[\frac{1 \text{ bar}}{(1 \text{ mol}\cdot\text{L}^{-1})(1673 \text{ K})(0.083145 \text{ L}\cdot\text{bar}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})} \right] \\ &= 2.11 \times 10^{-5} \end{aligned}$$

26-14. Show that

$$\frac{d \ln K_c}{dT} = \frac{\Delta_r U^\circ}{RT^2}$$

for a reaction involving ideal gases.

We know that

$$K_p = K_c \left(\frac{c^\circ RT}{P^\circ} \right)^{\Delta \nu} \quad (26.17)$$

Now begin with Equation 26.29:

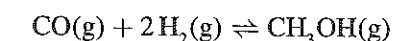
$$\begin{aligned} \frac{\Delta_r H^\circ}{RT^2} &= \frac{d \ln K_p}{dT} = \frac{d}{dT} \left[\ln K_c + \Delta \nu \ln \left(\frac{c^\circ RT}{P^\circ} \right) \right] \\ &= \frac{d \ln K_c}{dT} + \frac{\Delta \nu}{T} \end{aligned}$$

or

$$\frac{d \ln K_c}{dT} = \frac{\Delta_r H^\circ - \Delta \nu RT}{RT^2} = \frac{\Delta_r H^\circ - \Delta(PV)}{RT^2} = \frac{\Delta_r U^\circ}{RT^2}$$

because $U = H + PV$.

26-15. Consider the gas-phase reaction for the synthesis of methanol from $\text{CO}(g)$ and $\text{H}_2(g)$



The value of the equilibrium constant K_p at 500 K is 6.23×10^{-3} . Initially equimolar amounts of $\text{CO}(g)$ and $\text{H}_2(g)$ are introduced into the reaction vessel. Determine the value of ξ_{eq}/n_0 at equilibrium at 500 K and 30 bar.

At equilibrium, the number of moles of $\text{CO}(g)$ will be $n_0 - \xi_{\text{eq}}$, the number of moles of $\text{H}_2(g)$ will be $n_0 - 2\xi_{\text{eq}}$, and the number of moles of $\text{CH}_3\text{OH}(g)$ will be ξ_{eq} . The total moles of gas present will therefore be $2n_0 - 2\xi_{\text{eq}}$. We can now find the partial pressures of each of the components of the mixture:

$$P_{\text{CO}} = \frac{n_0 - \xi_{\text{eq}}}{2(n_0 - \xi_{\text{eq}})} P = \frac{1}{2} P \quad P_{\text{H}_2} = \frac{n_0 - 2\xi_{\text{eq}}}{2(n_0 - \xi_{\text{eq}})} P \quad \text{and} \quad P_{\text{CH}_3\text{OH}} = \frac{\xi_{\text{eq}}}{2(n_0 - \xi_{\text{eq}})} P$$

We then express K_p as

$$K_p = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^2 P_{\text{CO}}} = \frac{4\xi_{\text{eq}}(n_0 - \xi_{\text{eq}})}{P^2(n_0 - 2\xi_{\text{eq}})^2} = \frac{4x(1-x)}{P^2(1-2x)^2}$$

where $x = \xi_{\text{eq}}/n_0$. The value of K_p is 6.23×10^{-3} , so

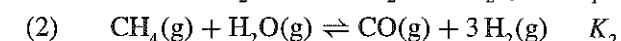
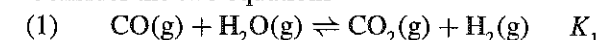
$$\frac{4x(1-x)}{(1-2x)^2} = (30 \text{ bar})^2 (6.23 \times 10^{-3})$$

which we can solve numerically (using the Newton-Raphson method) to find

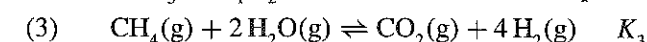
$$x = 0.305 \quad \text{or} \quad x = 0.695$$

Since $x < 0.50$ (otherwise the amount of H_2 present will be a negative quantity), $\xi_{\text{eq}}/n_0 = 0.31$.

26-16. Consider the two equations



Show that $K_3 = K_1 K_2$ for the sum of these two equations



How do you explain the fact that you would add the values of $\Delta_r G^\circ$ but multiply the equilibrium constants when adding Equations 1 and 2 to get Equation 3?

Use Equation 26.12 to express K_1 , K_2 , and K_3 .

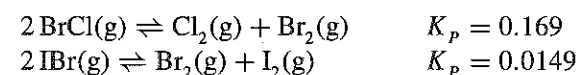
$$K_1 = \frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{H}_2\text{O}} P_{\text{CO}}} \quad K_2 = \frac{P_{\text{H}_2}^3 P_{\text{CO}}}{P_{\text{H}_2\text{O}} P_{\text{CH}_4}}$$

$$K_3 = \frac{P_{\text{H}_2}^4 P_{\text{CO}_2}}{P_{\text{H}_2\text{O}}^2 P_{\text{CH}_4}} = \left(\frac{P_{\text{CO}_2} P_{\text{H}_2}}{P_{\text{H}_2\text{O}} P_{\text{CO}}} \right) \left(\frac{P_{\text{H}_2}^3 P_{\text{CO}}}{P_{\text{H}_2\text{O}} P_{\text{CH}_4}} \right) = K_1 K_2$$

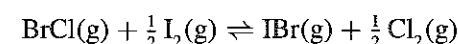
We multiply the equilibrium constants because of their logarithmic relationship with $\Delta_r G^\circ$. Recall that (Equation 26.11) $\Delta_r G^\circ = -RT \ln K_p$. Adding $\Delta_r G_1^\circ$ and $\Delta_r G_2^\circ$ would give

$$-RT \ln K_1 - RT \ln K_2 = -RT \ln K_1 K_2$$

26-17. Given:



Determine K_p for the reaction



We number the equations in order of appearance. Equation 3 can be expressed by

$$\text{Equation 3} = \frac{1}{2} \text{Equation 1} - \frac{1}{2} \text{Equation 2}$$

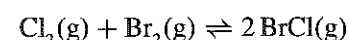
This means that

$$\Delta_r G_3^\circ = \frac{1}{2} \Delta_r G_1^\circ - \frac{1}{2} \Delta_r G_2^\circ$$

or

$$K_3 = \frac{K_1^{1/2}}{K_2^{1/2}} = \frac{(0.169)^{1/2}}{(0.0149)^{1/2}} = 3.37$$

26-18. Consider the reaction described by



at 500 K and a total pressure of one bar. Suppose that we start with one mole each of $\text{Cl}_2\text{(g)}$ and $\text{Br}_2\text{(g)}$ and no BrCl(g) . Show that

$$G(\xi) = (1 - \xi)G_{\text{Cl}_2}^\circ + (1 - \xi)G_{\text{Br}_2}^\circ + 2\xi G_{\text{BrCl}}^\circ + 2(1 - \xi)RT \ln \frac{1 - \xi}{2} + 2\xi RT \ln \xi$$

where ξ is the extent of reaction. Given that $G_{\text{BrCl}}^\circ = -3.694 \text{ kJ} \cdot \text{mol}^{-1}$ at 500 K, plot $G(\xi)$ versus ξ . Differentiate $G(\xi)$ with respect to ξ and show that the minimum value of $G(\xi)$ occurs at $\xi_{\text{eq}} = 0.549$. Also show that

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \Delta_r G^\circ + RT \ln \frac{P_{\text{BrCl}}^2}{P_{\text{Cl}_2} P_{\text{Br}_2}}$$

and that $K_p = 4\xi_{\text{eq}}^2 / (1 - \xi_{\text{eq}})^2 = 5.9$.

As the reaction progresses, the amount of $\text{Cl}_2\text{(g)}$ and $\text{Br}_2\text{(g)}$ can be expressed as $1 - \xi$ and the amount of BrCl(g) will be 2ξ . We can then write the Gibbs energy of the reaction mixture as (Equation 26.20)

$$G(\xi) = (1 - \xi)\bar{G}_{\text{Cl}_2} + (1 - \xi)\bar{G}_{\text{Br}_2} + 2\xi\bar{G}_{\text{BrCl}}$$

Since the reaction is carried out at a total pressure of 1 bar, we can write

$$P_{\text{Cl}_2} = P_{\text{Br}_2} = \frac{1 - \xi}{2} \quad \text{and} \quad P_{\text{BrCl}} = \frac{2\xi}{2} = \xi$$

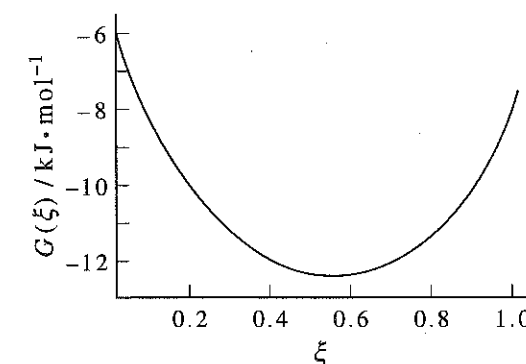
We can use these expressions and Equation 22.59 to write $G(\xi)$ as

$$\begin{aligned} G(\xi) &= (1 - \xi) \left[G_{\text{Cl}_2}^\circ + RT \ln P_{\text{Cl}_2} \right] + (1 - \xi) \left[G_{\text{Br}_2}^\circ + RT \ln P_{\text{Br}_2} \right] \\ &\quad + 2\xi \left[G_{\text{BrCl}}^\circ + RT \ln P_{\text{BrCl}} \right] \\ &= (1 - \xi)G_{\text{Cl}_2}^\circ + (1 - \xi)G_{\text{Br}_2}^\circ + 2\xi G_{\text{BrCl}}^\circ \\ &\quad + 2(1 - \xi)RT \ln \frac{1 - \xi}{2} + 2\xi RT \ln \xi \end{aligned} \quad (1)$$

Substituting the value given in the problem for G_{BrCl}° and zero for $G_{\text{Cl}_2}^\circ$ and $G_{\text{Br}_2}^\circ$ gives

$$\begin{aligned} G(\xi) &= 2\xi(-3694 \text{ J} \cdot \text{mol}^{-1}) + 2(1 - \xi)(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(500 \text{ K}) \ln \frac{1 - \xi}{2} \\ &\quad + 2\xi(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(500 \text{ K}) \ln \xi \\ &= (-7388 \text{ J} \cdot \text{mol}^{-1})\xi + (8314.5 \text{ J} \cdot \text{mol}^{-1}) \left[(1 - \xi) \ln \frac{1 - \xi}{2} + \xi \ln \xi \right] \end{aligned} \quad (2)$$

A plot of $G(\xi)$ against ξ is shown below.



At equilibrium, $0 = (\partial G / \partial \xi)_{T,P}$. We use Equation 2 to express $G(\xi)$ and find that, at equilibrium,

$$0 = -7388 \text{ J} \cdot \text{mol}^{-1} + (8314.5 \text{ J} \cdot \text{mol}^{-1}) \left[-\ln \frac{1 - \xi_{\text{eq}}}{2} - 1 + \ln \xi_{\text{eq}} + 1 \right]$$

$$0 = -7388 \text{ J} \cdot \text{mol}^{-1} + (8314.5 \text{ J} \cdot \text{mol}^{-1}) \ln \frac{2\xi_{\text{eq}}}{1 - \xi_{\text{eq}}}$$

$$\frac{2\xi_{\text{eq}}}{1 - \xi_{\text{eq}}} = 2.432$$

Solving for ξ_{eq} gives $\xi_{\text{eq}} = 0.549$.

Differentiating Equation 1 for $G(\xi)$ explicitly, we find that

$$\begin{aligned}\left(\frac{\partial G}{\partial \xi}\right)_{T,P} &= -G_{\text{Cl}_2}^\circ - G_{\text{Br}_2}^\circ + 2G_{\text{BrCl}}^\circ - 2RT \ln \frac{1-\xi}{2} \\ &\quad + 2(1-\xi)RT \left(\frac{2}{1-\xi}\right) \left(-\frac{1}{2}\right) + 2RT \ln \xi + \frac{2\xi RT}{\xi} \\ &= \Delta_r G^\circ + RT \ln \frac{4}{(1-\xi)^2} - 2RT + RT \ln \xi^2 + 2RT \\ &= \Delta_r G^\circ + RT \ln \left(\frac{2\xi}{1-\xi}\right)^2 = \Delta_r G^\circ + RT \ln \left(\frac{P_{\text{BrCl}}^2}{P_{\text{Cl}_2} P_{\text{Br}_2}}\right)\end{aligned}$$

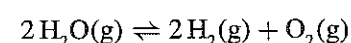
Note that

$$K_P = \frac{P_{\text{BrCl}}^2}{P_{\text{Cl}_2} P_{\text{Br}_2}} = \frac{4\xi_{\text{eq}}^2}{(1-\xi_{\text{eq}})^2}$$

so, at equilibrium,

$$K_P = \frac{4(0.549)^2}{(1-0.549)^2} = 5.9$$

26-19. Consider the reaction described by



at 4000 K and a total pressure of one bar. Suppose that we start with two moles of $\text{H}_2\text{O}(\text{g})$ and no $\text{H}_2(\text{g})$ or $\text{O}_2(\text{g})$. Show that

$$\begin{aligned}G(\xi) &= 2(1-\xi)G_{\text{H}_2\text{O}}^\circ + 2\xi G_{\text{H}_2}^\circ + \xi G_{\text{O}_2}^\circ + 2(1-\xi)RT \ln \frac{2(1-\xi)}{2+\xi} \\ &\quad + 2\xi RT \ln \frac{2\xi}{2+\xi} + \xi RT \ln \frac{\xi}{2+\xi}\end{aligned}$$

where ξ is the extent of reaction. Given that $\Delta_r G^\circ[\text{H}_2\text{O}(\text{g})] = -18.334 \text{ kJ}\cdot\text{mol}^{-1}$ at 4000 K, plot $G(\xi)$ against ξ . Differentiate $G(\xi)$ with respect to ξ and show that the minimum value of $G(\xi)$ occurs at $\xi_{\text{eq}} = 0.553$. Also show that

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta_r G^\circ + RT \ln \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2}$$

and that $K_P = \xi_{\text{eq}}^3 / (2 + \xi_{\text{eq}})(1 - \xi_{\text{eq}})^2 = 0.333$ at one bar.

The amount of H_2O can be expressed by $2 - 2\xi$, the amount of H_2 as 2ξ , and the amount of O_2 as ξ . We can then write the Gibbs energy of the reaction mixture as (Equation 26.20)

$$G(\xi) = (2 - 2\xi)\bar{G}_{\text{H}_2\text{O}} + 2\xi\bar{G}_{\text{H}_2} + \xi\bar{G}_{\text{O}_2}$$

Since the reaction is carried out at a total pressure of one bar, we can write

$$P_{\text{H}_2\text{O}} = \frac{2(1-\xi)}{2+\xi} \quad P_{\text{H}_2} = \frac{2\xi}{2+\xi} \quad \text{and} \quad P_{\text{O}_2} = \frac{\xi}{2+\xi}$$

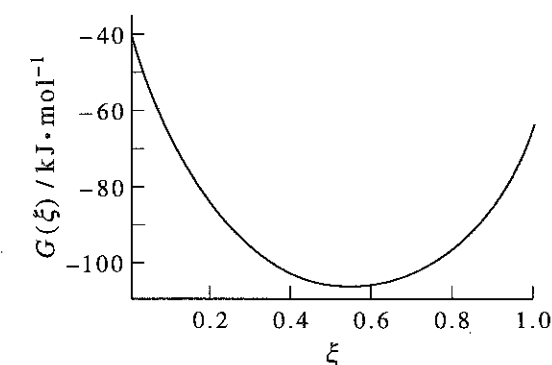
We can use these expressions and Equation 8.59 to write $G(\xi)$ as

$$\begin{aligned}G(\xi) &= 2(1-\xi) \left[G_{\text{H}_2\text{O}}^\circ + RT \ln P_{\text{H}_2\text{O}} \right] + 2\xi \left[G_{\text{H}_2}^\circ + RT \ln P_{\text{H}_2} \right] \\ &\quad + \xi \left[G_{\text{O}_2}^\circ + RT \ln P_{\text{O}_2} \right] \\ &= 2(1-\xi)G_{\text{H}_2\text{O}}^\circ + 2\xi G_{\text{H}_2}^\circ + \xi G_{\text{O}_2}^\circ + 2(1-\xi)RT \ln \frac{2(1-\xi)}{2+\xi} \\ &\quad + 2\xi RT \ln \frac{2\xi}{2+\xi} + \xi RT \ln \frac{\xi}{2+\xi}\end{aligned}$$

Substituting the value given in the problem for $G_{\text{H}_2\text{O}}^\circ$ and zero for $G_{\text{O}_2}^\circ$ and $G_{\text{H}_2}^\circ$ gives

$$\begin{aligned}G(\xi) &= 2(1-\xi)(-18334 \text{ J}\cdot\text{mol}^{-1}) \\ &\quad + 2(1-\xi)(8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(4000 \text{ K}) \ln \frac{2(1-\xi)}{2+\xi} \\ &\quad + 2\xi(8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(4000 \text{ K}) \ln \frac{2\xi}{2+\xi} \\ &\quad + \xi(8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(4000 \text{ K}) \ln \frac{\xi}{2+\xi} \\ &= (-36668 \text{ J}\cdot\text{mol}^{-1})(1-\xi) + (66516 \text{ J}\cdot\text{mol}^{-1})(1-\xi) \ln \frac{2(1-\xi)}{2+\xi} \\ &\quad + (66516 \text{ J}\cdot\text{mol}^{-1})\xi \ln \frac{2\xi}{2+\xi} + (33258 \text{ J}\cdot\text{mol}^{-1})\xi \ln \frac{\xi}{2+\xi}\end{aligned}$$

A plot of $G(\xi)$ against ξ is shown below.



We now differentiate $G(\xi)$ with respect to ξ and find

$$\begin{aligned}\left(\frac{\partial G}{\partial \xi}\right)_{T,P} &= (36668 \text{ J}\cdot\text{mol}^{-1}) \\ &\quad - (66516 \text{ J}\cdot\text{mol}^{-1}) \left\{ \ln \frac{2(1-\xi)}{2+\xi} - \frac{(1-\xi)(2+\xi)}{2(1-\xi)} \left[-\frac{2}{2+\xi} - \frac{2(1-\xi)}{(2+\xi)^2} \right] \right\} \\ &\quad + (66516 \text{ J}\cdot\text{mol}^{-1}) \left\{ \ln \frac{2\xi}{2+\xi} + \frac{\xi(2+\xi)}{2\xi} \left[\frac{2}{2+\xi} - \frac{2\xi}{(2+\xi)^2} \right] \right\} \\ &\quad + (33258 \text{ J}\cdot\text{mol}^{-1}) \left\{ \ln \frac{\xi}{2+\xi} + (2+\xi) \left[\frac{1}{2+\xi} - \frac{\xi}{(2+\xi)^2} \right] \right\} \\ &= (36668 \text{ J}\cdot\text{mol}^{-1}) - (66516 \text{ J}\cdot\text{mol}^{-1}) \left[\ln \frac{2(1-\xi)}{2+\xi} + 1 + \frac{1-\xi}{2+\xi} \right] \\ &\quad + (66516 \text{ J}\cdot\text{mol}^{-1}) \left[\ln \frac{2\xi}{2+\xi} + 1 - \frac{\xi}{2+\xi} \right]\end{aligned}$$

$$\begin{aligned}
 & + (33\,258 \text{ J}\cdot\text{mol}^{-1}) \left[\ln \frac{\xi}{2+\xi} + 1 - \frac{\xi}{2+\xi} \right] \\
 & = 36\,668 \text{ J}\cdot\text{mol}^{-1} + (33\,258 \text{ J}\cdot\text{mol}^{-1}) \left[2 \ln \frac{2+\xi}{2(1-\xi)} - \frac{2(1-\xi)}{2+\xi} + 2 \ln \frac{2\xi}{2+\xi} \right. \\
 & \quad \left. - \frac{2\xi}{2+\xi} + \ln \frac{\xi}{2+\xi} + 1 - \frac{\xi}{2+\xi} \right] \\
 & = 36\,668 \text{ J}\cdot\text{mol}^{-1} + (33\,258 \text{ J}\cdot\text{mol}^{-1}) \ln \frac{\xi^3}{(1-\xi)^2(2+\xi)} \quad (1)
 \end{aligned}$$

At equilibrium, $(\partial G/\partial \xi)_{T,P} = 0$, so

$$\frac{\xi_{\text{eq}}^3}{(1-\xi_{\text{eq}})^2(2+\xi_{\text{eq}})} = \exp \left(\frac{-36\,668 \text{ J}\cdot\text{mol}^{-1}}{33\,258 \text{ J}\cdot\text{mol}^{-1}} \right) = 0.332$$

Solving for ξ_{eq} gives $\xi_{\text{eq}} = 0.553$.

Note that substituting for $\Delta_f G^\circ[\text{H}_2\text{O}(\text{g})]$, R , T , P_{H_2} , P_{O_2} , and $P_{\text{H}_2\text{O}}$ in Equation 1 gives

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = 2\Delta_f G^\circ[\text{H}_2\text{O}(\text{g})] + RT \ln \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2} = \Delta_r G^\circ + RT \ln \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2}$$

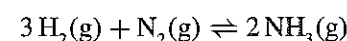
Now

$$K_P = \frac{P_{\text{H}_2}^2 P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2} = \frac{\xi_{\text{eq}}^3}{(1-\xi_{\text{eq}})^2(2+\xi_{\text{eq}})}$$

so

$$K_P = \frac{(0.553)^3}{(1-0.553)^2(2+0.553)} = 0.332$$

26-20. Consider the reaction described by



at 500 K and a total pressure of one bar. Suppose that we start with three moles of $\text{H}_2(\text{g})$, one mole of $\text{N}_2(\text{g})$, and no $\text{NH}_3(\text{g})$. Show that

$$\begin{aligned}
 G(\xi) &= (3-3\xi)G_{\text{H}_2}^\circ + (1-\xi)G_{\text{N}_2}^\circ + 2\xi G_{\text{NH}_3}^\circ \\
 &+ (3-3\xi)RT \ln \frac{3-3\xi}{4-2\xi} + (1-\xi)RT \ln \frac{1-\xi}{4-2\xi} + 2\xi RT \ln \frac{2\xi}{4-2\xi}
 \end{aligned}$$

where ξ is the extent of reaction. Given that $G_{\text{NH}_3}^\circ = 4.800 \text{ kJ}\cdot\text{mol}^{-1}$ at 500 K (see Table 26.4), plot $G(\xi)$ versus ξ . Differentiate $G(\xi)$ with respect to ξ and show that the minimum value of $G(\xi)$ occurs at $\xi_{\text{eq}} = 0.158$. Also show that

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \Delta_r G^\circ + RT \ln \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}}$$

and that $K_P = 16\xi_{\text{eq}}^2(2-\xi_{\text{eq}})^2/27(1-\xi_{\text{eq}})^4 = 0.10$.

The amount of H_2 can be expressed by $3-3\xi$, the amount of N_2 as $1-\xi$, and the amount of NH_3 as 2ξ . We can then write the Gibbs energy of the reaction mixture as

$$G(\xi) = (3-3\xi)\bar{G}_{\text{H}_2} + (1-\xi)\bar{G}_{\text{N}_2} + 2\xi\bar{G}_{\text{NH}_3}$$

Since the reaction is carried out at a total pressure of one bar, we can write

$$P_{\text{H}_2} = \frac{3(1-\xi)}{2(2-\xi)} \quad P_{\text{N}_2} = \frac{1-\xi}{2(2-\xi)} \quad \text{and} \quad P_{\text{NH}_3} = \frac{\xi}{2-\xi}$$

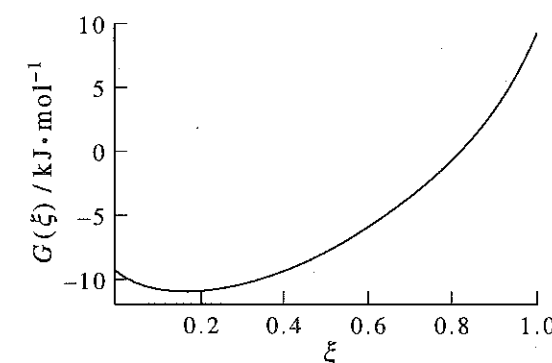
We can use these expressions and Equation 8.59 to write $G(\xi)$ as (Equation 26.20)

$$\begin{aligned}
 G(\xi) &= 3(1-\xi) \left[G_{\text{H}_2}^\circ + RT \ln P_{\text{H}_2} \right] + (1-\xi) \left[G_{\text{N}_2}^\circ + RT \ln P_{\text{N}_2} \right] \\
 &\quad + 2\xi \left[G_{\text{NH}_3}^\circ + RT \ln P_{\text{NH}_3} \right] \\
 &= 3(1-\xi)G_{\text{H}_2}^\circ + (1-\xi)G_{\text{N}_2}^\circ + 2\xi G_{\text{NH}_3}^\circ \\
 &\quad + 3(1-\xi)RT \ln \frac{3(1-\xi)}{2(2-\xi)} + (1-\xi)RT \ln \frac{1-\xi}{2(2-\xi)} \\
 &\quad + 2\xi RT \ln \frac{\xi}{2-\xi}
 \end{aligned}$$

Substituting the appropriate values of G° gives

$$\begin{aligned}
 G(\xi) &= \xi(9600 \text{ J}\cdot\text{mol}^{-1}) + 3(1-\xi)(4157.2 \text{ J}\cdot\text{mol}^{-1}) \ln \frac{3(1-\xi)}{2(2-\xi)} \\
 &\quad + (4157.2 \text{ J}\cdot\text{mol}^{-1}) \left[(1-\xi) \ln \frac{1-\xi}{2(2-\xi)} + 2\xi \ln \frac{\xi}{2-\xi} \right]
 \end{aligned}$$

A plot of $G(\xi)$ against ξ is shown below.



Now we differentiate $G(\xi)$ with respect to ξ :

$$\begin{aligned}
 \left(\frac{\partial G}{\partial \xi} \right)_{T,P} &= 9600 \text{ J}\cdot\text{mol}^{-1} \\
 &\quad + (4157.2 \text{ J}\cdot\text{mol}^{-1}) \left\{ -3 \ln \frac{3(1-\xi)}{2(2-\xi)} + 2(2-\xi) \left[-\frac{3}{2(2-\xi)} + \frac{6(1-\xi)}{4(2-\xi)^2} \right] - \ln \frac{(1-\xi)}{2(2-\xi)} \right. \\
 &\quad \left. + 2(2-\xi) \left[-\frac{1}{2(2-\xi)} + \frac{2(1-\xi)}{4(2-\xi)^2} \right] + 2 \ln \frac{\xi}{2-\xi} + 2(2-\xi) \left[\frac{1}{2-\xi} + \frac{\xi}{(2-\xi)^2} \right] \right\} \\
 &= 9600 \text{ J}\cdot\text{mol}^{-1} + (4157.2 \text{ J}\cdot\text{mol}^{-1}) \left[\ln \frac{16(2-\xi)^2\xi^2}{27(1-\xi)^4} - 3 + \frac{3-3\xi}{2-\xi} - 1 \right. \\
 &\quad \left. + \frac{1-\xi}{2-\xi} + 2 + \frac{2\xi}{2-\xi} \right] \\
 &= 9600 \text{ J}\cdot\text{mol}^{-1} + (4157.2 \text{ J}\cdot\text{mol}^{-1}) \ln \frac{16(2-\xi)^2\xi^2}{27(1-\xi)^4} \quad (1)
 \end{aligned}$$

At equilibrium, $(\partial G/\partial \xi)_{T,P} = 0$, so

$$\frac{16(2 - \xi_{\text{eq}})^2 \xi_{\text{eq}}^2}{27(1 - \xi_{\text{eq}})^4} = \exp\left(\frac{-9600 \text{ J} \cdot \text{mol}^{-1}}{4157.2 \text{ J} \cdot \text{mol}^{-1}}\right) = 0.09934$$

Solving for ξ_{eq} gives $\xi_{\text{eq}} = 0.158$.

Note that substituting for $G_{\text{NH}_3}^\circ$, R , T , P_{NH_3} , P_{N_2} , and P_{H_2} in Equation 1 gives

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 2G_{\text{NH}_3}^\circ + RT \ln \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}} = \Delta_r G^\circ + RT \ln \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}}$$

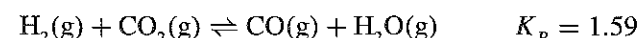
Now

$$K_P = \frac{P_{\text{NH}_3}^2}{P_{\text{H}_2}^3 P_{\text{N}_2}} = \frac{16\xi_{\text{eq}}^2(2 - \xi_{\text{eq}})^2}{27(1 - \xi_{\text{eq}})^4}$$

so

$$K_P = \frac{16(0.158)^2(2 - 0.158)^2}{27(1 - 0.158)^4} = 0.010$$

- 26-21.** Suppose that we have a mixture of the gases $\text{H}_2(\text{g})$, $\text{CO}_2(\text{g})$, $\text{CO}(\text{g})$, and $\text{H}_2\text{O}(\text{g})$ at 1260 K, with $P_{\text{H}_2} = 0.55$ bar, $P_{\text{CO}_2} = 0.20$ bar, $P_{\text{CO}} = 1.25$ bar, and $P_{\text{H}_2\text{O}} = 0.10$ bar. Is the reaction described by the equation



at equilibrium under these conditions? If not, in what direction will the reaction proceed to attain equilibrium?

Use Equation 26.25 to find Q_P and Equation 26.26 to find out which way the reaction will proceed.

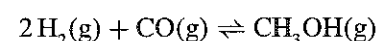
$$Q_P = \frac{P_{\text{H}_2\text{O}} P_{\text{CO}}}{P_{\text{H}_2} P_{\text{CO}_2}} = \frac{(0.10)(1.25)}{(0.55)(0.20)} = 1.14$$

$$\Delta_r G = RT \ln \frac{Q_P}{K_P} = RT \ln \frac{1.14}{1.59}$$

$$\Delta_r G < 0$$

The reaction as written will proceed to the right.

- 26-22.** Given that $K_P = 2.21 \times 10^4$ at 25°C for the equation



predict the direction in which a reaction mixture for which $P_{\text{CH}_3\text{OH}} = 10.0$ bar, $P_{\text{H}_2} = 0.10$ bar, and $P_{\text{CO}} = 0.0050$ bar proceeds to attain equilibrium.

This is done in the same way as the previous problem.

$$Q_P = \frac{P_{\text{CH}_3\text{OH}}}{P_{\text{H}_2}^2 P_{\text{CO}}} = \frac{10}{(0.10)^2(0.0050)} = 2.00 \times 10^5$$

$$\Delta_r G = RT \ln \frac{Q_P}{K_P} = RT \ln \frac{2.00 \times 10^5}{2.21 \times 10^4}$$

$$\Delta_r G > 0$$

Therefore, the reaction as written will proceed to the left.

- 26-23.** The value of K_P for a gas-phase reaction doubles when the temperature is increased from 300 K to 400 K at a fixed pressure. What is the value of $\Delta_r H^\circ$ for this reaction?

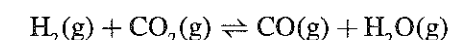
Use Equation 26.31, since we assume that $\Delta_r H^\circ$ remains constant over this temperature range.

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$R \ln 2 = -\Delta_r H^\circ \left(\frac{1}{400 \text{ K}} - \frac{1}{300 \text{ K}} \right)$$

$$\Delta_r H^\circ = 6.91 \text{ kJ} \cdot \text{mol}^{-1}$$

- 26-24.** The value of $\Delta_r H^\circ$ is 34.78 kJ·mol⁻¹ at 1000 K for the reaction described by



Given that the value of K_P is 0.236 at 800 K, estimate the value of K_P at 1200 K, assuming that $\Delta_r H^\circ$ is independent of temperature.

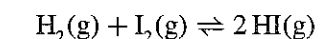
Again, use Equation 26.31:

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{K_P(1200 \text{ K})}{0.236} = -\frac{34\,780 \text{ J} \cdot \text{mol}^{-1}}{8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \left(\frac{1}{1200 \text{ K}} - \frac{1}{800 \text{ K}} \right) = 1.743$$

$$K_P(1200 \text{ K}) = 1.35$$

- 26-25.** The value of $\Delta_r H^\circ$ is -12.93 kJ·mol⁻¹ at 800 K for



Assuming that $\Delta_r H^\circ$ is independent of temperature, calculate K_P at 700 K given that $K_P = 29.1$ at 1000 K.

We do this as we did Problem 26-24, using Equation 26.31.

$$\ln \frac{K_P(T_2)}{K_P(T_1)} = -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$\ln \frac{29.1}{K_P(700 \text{ K})} = -\frac{12\,930 \text{ J} \cdot \text{mol}^{-1}}{8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}} \left(\frac{1}{1000 \text{ K}} - \frac{1}{700 \text{ K}} \right) = 0.666$$

$$K_P(700 \text{ K}) = 14.9$$

26-26. The equilibrium constant for the reaction described by



can be expressed by the empirical formula

$$\ln K = -6.375 + 0.6415 \ln(T/\text{K}) - \frac{11790 \text{ K}}{T}$$

Use this formula to determine $\Delta_r H^\circ$ as a function of temperature. Calculate $\Delta_r H^\circ$ at 25°C and compare your result to the one you obtain from Table 19.2.

Use Equation 26.29:

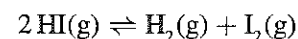
$$\begin{aligned} \frac{d \ln K}{dT} &= \frac{\Delta_r H^\circ}{RT^2} \\ \frac{0.6415}{T} + \frac{11790 \text{ K}}{T^2} &= \frac{\Delta_r H^\circ}{RT^2} \\ 0.6145 RT + (11790 \text{ K}) R &= \Delta_r H^\circ \end{aligned}$$

At 25°C, $\Delta_r H^\circ = 99.6 \text{ kJ} \cdot \text{mol}^{-1}$. The value given in Table 19.2 for $\Delta_r H^\circ[\text{HBr(g)}]$ is $-36.3 \text{ kJ} \cdot \text{mol}^{-1}$ and that given for $\Delta_r H^\circ[\text{Br}_2\text{(g)}]$ is $30.907 \text{ kJ} \cdot \text{mol}^{-1}$. We can write $\Delta_r H^\circ$ (using these values) as

$$\Delta_r H^\circ = \Delta_r H^\circ[\text{Br}_2\text{(g)}] - 2(\Delta_r H^\circ[\text{HBr(g)}]) = 103.5 \text{ kJ} \cdot \text{mol}^{-1}$$

in fairly good agreement with the value of $\Delta_r H^\circ$ found from the equilibrium constant.

26-27. Use the following data for the reaction described by



to obtain $\Delta_r H^\circ$ at 400°C.

T/K	500	600	700	800
$K_p/10^{-2}$	0.78	1.24	1.76	2.31

We wish to express K_p in terms of $1/T$ and use Equation 26.29 to find $\Delta_r H^\circ$.

$1000\text{K}/T$	2	1.67	1.43	1.25
$\ln K_p$	-4.85	-4.39	-4.04	-3.77

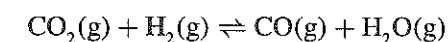
A linear fit gives

$$\begin{aligned} \ln K_p &= -1.9695 - \frac{1445.73 \text{ K}}{T} \\ \frac{d \ln K_p}{dT} &= \frac{1445.73 \text{ K}}{T^2} \\ \Delta_r H^\circ &= R(1445.73 \text{ K}) = 12.02 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

and a fit of the form $a + b/T + c \ln T$ gives

$$\begin{aligned} \ln K_p &= -2.33966 - \frac{1020.3 \text{ K}}{T} + 0.6833 \ln(T/\text{K}) \\ \frac{d \ln K_p}{dT} &= \frac{1020.3 \text{ K}}{T^2} + \frac{0.6833}{T} \\ \Delta_r H^\circ &= R(1020.3 + 0.6833T) = 12.31 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

26-28. Consider the reaction described by



The molar heat capacities of $\text{CO}_2\text{(g)}$, $\text{H}_2\text{(g)}$, CO(g) , and $\text{H}_2\text{O(g)}$ can be expressed by

$$\bar{C}_p[\text{CO}_2\text{(g)}]/R = 3.127 + (5.231 \times 10^{-3} \text{ K}^{-1})T - (1.784 \times 10^{-6} \text{ K}^{-2})T^2$$

$$\bar{C}_p[\text{H}_2\text{(g)}]/R = 3.496 - (1.006 \times 10^{-4} \text{ K}^{-1})T + (2.419 \times 10^{-7} \text{ K}^{-2})T^2$$

$$\bar{C}_p[\text{CO(g)}]/R = 3.191 + (9.239 \times 10^{-4} \text{ K}^{-1})T - (1.41 \times 10^{-7} \text{ K}^{-2})T^2$$

$$\bar{C}_p[\text{H}_2\text{O(g)}]/R = 3.651 + (1.156 \times 10^{-3} \text{ K}^{-1})T + (1.424 \times 10^{-7} \text{ K}^{-2})T^2$$

over the temperature range 300 K to 1500 K. Given that

substance	$\text{CO}_2\text{(g)}$	$\text{H}_2\text{(g)}$	CO(g)	$\text{H}_2\text{O(g)}$
$\Delta_r H^\circ/\text{kJ} \cdot \text{mol}^{-1}$	-393.523	0	-110.516	-241.844

at 300 K and that $K_p = 0.695$ at 1000 K, derive a general expression for the variation of $K_p(T)$ with temperature in the form of Equation 26.34.

We first find the values of $\Delta_r C_p^\circ$ and $\Delta_r H^\circ$:

$$\Delta_r C_p^\circ = C_p^\circ[\text{H}_2\text{O(g)}] + C_p^\circ[\text{CO(g)}] - C_p^\circ[\text{H}_2\text{(g)}] - C_p^\circ[\text{CO}_2\text{(g)}]$$

$$\Delta_r C_p^\circ/R = 0.219 - (3.051 \times 10^{-3} \text{ K}^{-1})T + (1.544 \times 10^{-6} \text{ K}^{-2})T^2$$

$$\begin{aligned} \Delta_r H^\circ(300 \text{ K}) &= \Delta_r H^\circ[\text{H}_2\text{O(g)}] + \Delta_r H^\circ[\text{CO(g)}] - \Delta_r H^\circ[\text{H}_2\text{(g)}] - \Delta_r H^\circ[\text{CO}_2\text{(g)}] \\ &= -241.844 \text{ kJ} \cdot \text{mol}^{-1} - (-110.516 \text{ kJ} \cdot \text{mol}^{-1}) - (-393.523 \text{ kJ} \cdot \text{mol}^{-1}) \\ &= 262.195 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

Now we use Equation 26.32 to find $\Delta_r H^\circ(T)$:

$$\begin{aligned} \Delta_r H^\circ(T) &= \Delta_r H^\circ(300 \text{ K}) + \int_{300}^T \Delta_r C_p^\circ(T) dT \\ &= 262.195 \text{ kJ} \cdot \text{mol}^{-1} + R \int_{300}^T [0.219 - (3.051 \times 10^{-3} \text{ K}^{-1})T \\ &\quad + (1.544 \times 10^{-6} \text{ K}^{-2})T^2] dT \\ &= 262.195 \text{ kJ} \cdot \text{mol}^{-1} + R [0.219(T - 300) - (1.525 \times 10^{-3} \text{ K}^{-1})(T^2 - 300^2) \\ &\quad + (5.145 \times 10^{-7} \text{ K}^{-2})(T^3 - 300^3)] \\ &= 262.195 \text{ kJ} \cdot \text{mol}^{-1} + R [57.681 \text{ K} + 0.219T \\ &\quad - (1.525 \times 10^{-3} \text{ K}^{-1})T^2 + (5.145 \times 10^{-7} \text{ K}^{-2})T^3] \\ &= 262.675 \text{ kJ} \cdot \text{mol}^{-1} + (1.821 \times 10^{-3} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})T \\ &\quad - (1.268 \times 10^{-5} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-2})T^2 + (4.278 \times 10^{-9} \text{ kJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-3})T^3 \end{aligned}$$

This equation is in the form $\alpha + \beta T + \gamma T^2 + \delta T^3$, as was expected (Equation 26.33). Substituting into Equation 26.34, we find that

$$\begin{aligned} \ln K_p(T) &= -\frac{31592}{T} + 0.2190 \ln(T/\text{K}) - (1.525 \times 10^{-3} \text{ K}^{-1})T \\ &\quad + (2.573 \times 10^{-7} \text{ K}^{-2})T^2 + A \end{aligned}$$

At $T = 1000$ K, we know that $K_p = 0.695$, so

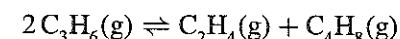
$$\ln 0.695 = -31.592 + 1.513 - 1.526 + 0.2573 + A$$

$$A = 30.984$$

and so

$$\ln K_p(T) = -\frac{31592}{T} + 0.2190 \ln(T/\text{K}) - (1.525 \times 10^{-3} \text{ K}^{-1})T + (2.573 \times 10^{-7} \text{ K}^{-2})T^2 + 30.984$$

26–29. The temperature dependence of the equilibrium constant K_p for the reaction described by



is given by the equation

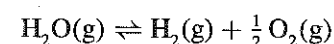
$$\ln K_p(T) = -2.395 - \frac{2505 \text{ K}}{T} + \frac{3.477 \times 10^6 \text{ K}^2}{T^2} \quad 300 \text{ K} < T < 600 \text{ K}$$

Calculate the values of $\Delta_r G^\circ$, $\Delta_r H^\circ$, and $\Delta_r S^\circ$ for this reaction at 525 K.

Use Equation 26.11 to find $\Delta_r G^\circ$, Equation 26.29 to find $\Delta_r H^\circ$, and the relation $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ to find $\Delta_r S^\circ$:

$$\begin{aligned} \Delta_r G^\circ &= -RT \ln K_p = -R(525 \text{ K}) \left[-2.395 - \frac{2505 \text{ K}}{525 \text{ K}} + \frac{3.477 \times 10^6 \text{ K}^2}{(525 \text{ K})^2} \right] \\ &= -23.78 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta_r H^\circ &= RT^2 \frac{d \ln K_p}{dT} = RT^2 \left[\frac{2505 \text{ K}}{T^2} - \frac{6.954 \times 10^6 \text{ K}^2}{T^3} \right] \\ &= -89.30 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta_r S^\circ &= \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = -124.8 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

26–30. At 2000 K and one bar, water vapor is 0.53% dissociated. At 2100 K and one bar, it is 0.88% dissociated. Calculate the value of $\Delta_r H^\circ$ for the dissociation of water at one bar, assuming that the enthalpy of reaction is constant over the range from 2000 K to 2100 K.



At 2000 K and one bar, there will be $0.9947n_0$ moles of $\text{H}_2\text{O}(\text{g})$, $0.0053n_0$ moles of $\text{H}_2(\text{g})$, and $0.00265n_0$ moles of $\text{O}_2(\text{g})$, for a total of $1.00265n_0$ moles. The partial pressures of the various gases are then

$$P_{\text{H}_2\text{O}} = \frac{0.9947}{1.00265} P = 0.9921 P \quad P_{\text{H}_2} = \frac{0.0053}{1.00265} P = 5.286 \times 10^{-3} P$$

and

$$P_{\text{O}_2} = \frac{0.00265}{1.00265} P = 2.643 \times 10^{-3} P$$

and $K_p(2000 \text{ K})$ at one bar is

$$K_p(2000 \text{ K}) = \frac{(2.643 \times 10^{-3})^{1/2} (5.286 \times 10^{-3}) P^{1/2}}{0.9921} = 2.74 \times 10^{-4}$$

Likewise, at 2100 K and one bar, there will be $0.9912n_0$ moles of $\text{H}_2\text{O}(\text{g})$, $0.0088n_0$ moles of $\text{H}_2(\text{g})$, and $0.0044n_0$ moles of $\text{O}_2(\text{g})$, for a total of $1.0044n_0$ moles. The partial pressures of the various gases are then

$$P_{\text{H}_2\text{O}} = \frac{0.9912}{1.0044} P = 0.9868 P \quad P_{\text{H}_2} = \frac{0.0088}{1.0044} P = 8.761 \times 10^{-3} P$$

and

$$P_{\text{O}_2} = \frac{0.0044}{1.0044} P = 4.381 \times 10^{-3} P$$

and $K_p(2000 \text{ K})$ at one bar is

$$K_p(2000 \text{ K}) = \frac{(4.381 \times 10^{-3})^{1/2} (8.761 \times 10^{-3}) P^{1/2}}{0.9868} = 5.88 \times 10^{-4}$$

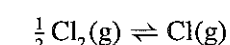
Now we can use Equation 26.31 to find $\Delta_r H^\circ$:

$$\begin{aligned} \ln \frac{K_p(2100 \text{ K})}{K_p(2000 \text{ K})} &= -\frac{\Delta_r H^\circ}{R} \left(\frac{1}{2100 \text{ K}} - \frac{1}{2000 \text{ K}} \right) \\ \Delta_r H^\circ &= 266.5 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

26–31. The following table gives the standard molar Gibbs energy of formation of $\text{Cl}(\text{g})$ at three different temperatures.

T/K	1000	2000	3000
$\Delta_f G^\circ/\text{kJ} \cdot \text{mol}^{-1}$	65.288	5.081	−56.297

Use these data to determine the value of K_p at each temperature for the reaction described by



Assuming that $\Delta_r H^\circ$ is temperature independent, determine the value of $\Delta_r H^\circ$ from these data. Combine your results to determine $\Delta_r S^\circ$ at each temperature. Interpret your results.

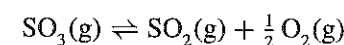
Use Equation 26.11 to find K_p at each temperature, then find $\ln K_p$ for use in determining $\Delta_r H^\circ$.

T/K	$\Delta_f G^\circ/\text{kJ} \cdot \text{mol}^{-1}$	K_p	$\ln K_p$
1000	65.288	3.889×10^{-4}	−7.852
2000	5.081	0.7367	−0.3056
3000	−56.297	9.554	2.257

The best-fit line to a plot of $\ln K_p$ vs. $1/T$ is $\ln K_p = 7.290 - 15148/T$. The slope of this line is $-\Delta_r H^\circ/R$, so $\Delta_r H^\circ = 125.9 \text{ kJ} \cdot \text{mol}^{-1}$. We can use the expression $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$ to find $\Delta_r S^\circ$ at each temperature. These values are tabulated below.

T/K	1000	2000	3000
$\Delta_r S^\circ/\text{J} \cdot \text{mol}^{-1}$	60.61	60.41	60.73

26–32. The following experimental data were determined for the reaction described by



T/K	800	825	900	953	1000
$\ln K_p$	-3.263	-3.007	-1.899	-1.173	-0.591

Calculate $\Delta_r G^\circ$, $\Delta_r H^\circ$, and $\Delta_r S^\circ$ for this reaction at 900 K. State any assumptions that you make.

This is done in the same way as the previous problem. We assume that $\Delta_r H^\circ$ does not vary significantly over the temperature range given. A best-fit line to $\ln K_p$ in $1/T$ is $\ln K_p = 10.216 - (10851 \text{ K})/T$, which gives $\Delta_r H^\circ = 90.2 \text{ kJ}\cdot\text{mol}^{-1}$. Using Equation 26.11 and the relation $\Delta_r G^\circ = \Delta_r H^\circ - T\Delta_r S^\circ$, we find that at 900 K $\Delta_r G^\circ = 14.21 \text{ kJ}\cdot\text{mol}^{-1}$ and $\Delta_r S^\circ = 84.5 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

26–33. Show that

$$\mu = -RT \ln \frac{q(V, T)}{N}$$

if

$$Q(N, V, T) = \frac{[q(V, T)]^N}{N!}$$

Begin with Equation 23.27 and use Stirling's approximation for $N \ln N!$:

$$\begin{aligned} \mu &= -RT \left(\frac{\partial \ln Q}{\partial N} \right)_{T, V} \\ &= -RT \left[\frac{\partial}{\partial N} (N \ln q - N \ln N!) \right]_{T, V} \\ &= -RT \left[\ln q - \frac{\partial}{\partial N} (-N \ln N + N) \right] \\ &= -RT [\ln q - \ln N - 1 + 1] = -RT \ln \frac{q}{N} \end{aligned}$$

26–34. Use Equation 26.40 to calculate $K(T)$ at 750 K for the reaction described by $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$. Use the molecular parameters given in Table 18.2. Compare your value to the one given in Table 26.2 and the experimental value shown in Figure 26.5.

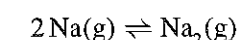
We can use Equation 26.40 to calculate $K(T)$, substituting from Equation 18.39 for the partition functions of H_2 , I_2 , and HI .

$$\begin{aligned} K &= \frac{q_{\text{HI}}^2}{q_{\text{H}_2} q_{\text{I}_2}} \\ &= \left(\frac{m_{\text{HI}}^2}{m_{\text{H}_2} m_{\text{I}_2}} \right)^{3/2} \left[\frac{4\Theta_{\text{rot}}^{\text{H}_2} \Theta_{\text{rot}}^{\text{I}_2}}{(\Theta_{\text{rot}}^{\text{HI}})^2} \right] \frac{(1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T})(1 - e^{-\Theta_{\text{vib}}^{\text{I}_2}/T})}{(1 - e^{-\Theta_{\text{vib}}^{\text{HI}}/T})^2} \exp \frac{2D_0^{\text{HI}} - D_0^{\text{H}_2} - D_0^{\text{I}_2}}{RT} \end{aligned}$$

$$\begin{aligned} &= \left[\frac{(127.9)^2}{(2.016)(253.8)} \right]^{3/2} \left[\frac{4(85.3 \text{ K})(0.0537 \text{ K})}{(9.25 \text{ K})^2} \right] \frac{(1 - e^{-6215/750})(1 - e^{-308/750})}{(1 - e^{-3266/750})^2} \\ &\quad \times \exp \frac{2(8.500 \text{ kJ}\cdot\text{mol}^{-1})}{(8.3145 \times 10^{-3} \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(750 \text{ K})} \\ &= 52.29 \end{aligned}$$

This is in good agreement with the values in the text.

26–35. Use the statistical thermodynamic formulas of Section 26–8 to calculate $K_p(T)$ at 900 K, 1000 K, 1100 K, and 1200 K for the association of $\text{Na}(\text{g})$ to form dimers, $\text{Na}_2(\text{g})$ according to the equation



Use your result at 1000 K to calculate the fraction of sodium atoms that form dimers at a total pressure of one bar. The experimental values of $K_p(T)$ are

T/K	900	1000	1100	1200
K_p	1.32	0.47	0.21	0.10

Plot $\ln K_p$ against $1/T$ to determine the value of $\Delta_r H^\circ$.

We can calculate the partition function of Na using Equation 18.13 (for a monatomic ideal gas) and that of Na_2 using Equation 18.39 (for a diatomic ideal gas):

$$\begin{aligned} \frac{q_{\text{Na}}}{V} &= \left[\frac{2\pi m k_B T}{h^2} \right]^{3/2} q_{\text{elec}} = \left[\frac{2\pi(0.022991 \text{ kg}\cdot\text{mol}^{-1})RT}{N_A^2 h^2} \right]^{3/2} \quad (2) \\ &= 2 [7.543 \times 10^{18} \text{ m}^2\cdot\text{K}^{-1}T]^{3/2} \\ \frac{q_{\text{Na}_2}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} e^{D_0/k_B T} \\ &= [1.508 \times 10^{19} \text{ m}^2\cdot\text{K}^{-1}T]^{3/2} \frac{T}{0.442 \text{ K}} \frac{e^{8707.7 \text{ K}/T}}{1 - e^{-229 \text{ K}/T}} \end{aligned}$$

Using the procedure on page 1070 (where we calculate K_p for H_2O), we have

$$K_p(T) = \frac{(q_{\text{Na}_2}/V)}{(q_{\text{Na}}/V)^2} \left[\frac{(6.022 \times 10^{23} \text{ mol}^{-1})(10^5 \text{ Pa})}{(1 \text{ m}^{-3})(8.3145 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})T} \right]$$

We can substitute into the above expressions to find K_p at 900 K, 1000 K, 1100 K, and 1200 K:

T/K	900	1000	1100	1200
K_p	1.47	0.52	0.22	0.11

Given that $K_p = 0.52$ at 1000 K, let us assume that we begin with n_0 moles of Na and no moles of the dimer. Then at equilibrium we will have $n_0 - 2\xi$ moles of Na and ξ moles of the dimer, so that for a total pressure of 1 bar,

$$P_{\text{Na}} = \frac{n_0 - 2\xi}{n_0 - \xi} P = \frac{1 - 2\xi/n_0}{1 - \xi/n_0} P$$

and

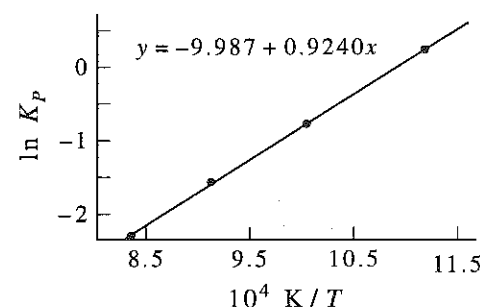
$$P_{\text{Na}_2} = \frac{\xi}{n_0 - \xi} P = \frac{\xi/n_0}{1 - \xi/n_0} P$$

Then

$$K_p = \frac{P_{\text{Na}_2}}{P_{\text{Na}}^2} = \frac{\xi/n_0(1 - \xi/n_0)}{(1 - 2\xi/n_0)^2 P}$$

$$0.52(1 - 2x)^2 = x - x^2$$

where $x = \xi/n_0$. Solving for x gives $x = 0.21$ or $x = 0.78$, but $x < 0.50$, so we find that 21% of the sodium atoms will form dimers at 1000 K.



Plotting the experimental values, we find that $\ln K_p = -9.987 + (9240 \text{ K})/T$. Therefore, $\Delta_r H^\circ = -R(9240 \text{ K}) = -76.8 \text{ kJ} \cdot \text{mol}^{-1}$.

26–36. Using the data in Table 18.2, calculate K_p at 2000 K for the reaction described by the equation



The experimental value is 1.3×10^{-3} .

We can use Equation 18.39 to express the partition functions of O_2 and CO , and Equation 18.57 to express the partition function of CO_2 . At 2000 K,

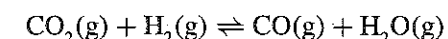
$$\begin{aligned} \frac{q_{\text{CO}}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.02801 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(2000 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \\ &\quad \times \frac{2000 \text{ K}}{2.77 \text{ K}} \frac{1}{1 - e^{-3103/2000}} e^{1072000/(8.3145)(2000)} \\ &= 2.27 \times 10^{64} \text{ m}^{-3} \\ \frac{q_{\text{O}_2}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} 3e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.03200 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(2000 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \\ &\quad \times \frac{2000 \text{ K}}{2(2.07 \text{ K})} \frac{1}{1 - e^{-2256/2000}} 3e^{494100/(8.3145)(2000)} \\ &= 5.23 \times 10^{49} \text{ m}^{-3} \end{aligned}$$

$$\begin{aligned} \frac{q_{\text{CO}_2}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \left[\prod_{j=1}^4 (1 - e^{-\Theta_{\text{vib},j}/T})^{-1} \right] e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.04401 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(2000 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \\ &\quad \times \frac{2000 \text{ K}}{2(0.561 \text{ K})} (1 - e^{-3360/2000})^{-1} (1 - e^{-954/2000})^{-2} (1 - e^{-1890/2000})^{-1} e^{1596 \times 10^3/(8.3145)(2000)} \\ &= 5.88 \times 10^{79} \text{ m}^{-3} \end{aligned}$$

We can now use Equation 26.39 to write (as we did in Section 26–8 for the reaction involving H_2O)

$$\begin{aligned} K_p(T) &= \left[\frac{RT}{N_A(10^5 \text{ Pa})} \right]^{1/2} \frac{(q_{\text{CO}}/V)(q_{\text{O}_2}/V)^{1/2}}{(q_{\text{CO}_2}/V)} \\ &= \left[\frac{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(2000 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(10^5 \text{ Pa})} \right]^{1/2} \frac{(2.27 \times 10^{64} \text{ m}^{-3})(5.23 \times 10^{49} \text{ m}^{-3})^{1/2}}{5.88 \times 10^{79} \text{ m}^{-3}} \\ &= 1.46 \times 10^{-3} \end{aligned}$$

26–37. Using the data in Tables 18.2 and 18.4, calculate the equilibrium constant for the water gas reaction



at 900 K and 1200 K. The experimental values at these two temperatures are 0.43 and 1.37, respectively.

We have expressed the partition functions for CO_2 and CO in Problem 26–36, and those for H_2 and H_2O in Section 26–8. At a temperature T , these partition functions are

$$\begin{aligned} \frac{q_{\text{CO}_2}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \left[\prod_{j=1}^4 (1 - e^{-\Theta_{\text{vib},j}/T})^{-1} \right] e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.04401 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})T}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{T}{2(0.561 \text{ K})} (1 - e^{-3360 \text{ K}/T})^{-1} \\ &\quad \times (1 - e^{-954 \text{ K}/T})^{-2} (1 - e^{-1890 \text{ K}/T})^{-1} e^{1596 \times 10^3 \text{ K}/8.3145T} \\ \frac{q_{\text{H}_2}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} e^{D_0/k_B T} \\ &= \left[\frac{2\pi(2.016 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})T}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{T}{2(85.3 \text{ K})} \frac{1}{1 - e^{-6215/T}} e^{431800 \text{ K}/8.3145T} \\ \frac{q_{\text{CO}}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.02801 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})T}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{T}{2.77 \text{ K}} \frac{1}{1 - e^{-3103 \text{ K}/T}} e^{1072000 \text{ K}/8.3145T} \\ \frac{q_{\text{H}_2\text{O}}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2} \left(\prod_{j=1}^3 \frac{1}{1 - e^{-\Theta_{\text{vib},j}/T}} \right) e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.01801 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})T}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{\pi^{1/2}}{2} \left[\frac{T^3}{(40.1 \text{ K})(20.9 \text{ K})(13.4 \text{ K})} \right]^{1/2} \\ &\quad \times (1 - e^{-5360 \text{ K}/T})^{-1} (1 - e^{-5160 \text{ K}/T})^{-1} (1 - e^{-2290 \text{ K}/T})^{-1} e^{917600 \text{ K}/8.3145T} \end{aligned}$$

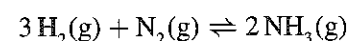
Using Equation 26.39, we can write K_p in terms of the partition functions:

$$K_p = \frac{(q_{\text{H}_2\text{O}}/V)(q_{\text{CO}}/V)}{(q_{\text{CO}_2}/V)(q_{\text{H}_2}/V)}$$

Below are tabulated values for each partition function and K_p at 900 K and 1200 K.

	900 K	1200 K
$q_{\text{CO}_2}/V/\text{m}^{-3}$	1.38×10^{129}	3.22×10^{106}
$q_{\text{H}_2}/V/\text{m}^{-3}$	9.17×10^{56}	1.02×10^{51}
$q_{\text{CO}}/V/\text{m}^{-3}$	4.15×10^{97}	2.49×10^{82}
$q_{\text{H}_2\text{O}}/V/\text{m}^{-3}$	1.72×10^{88}	2.18×10^{75}
K_p	0.56	1.66

26–38. Using the data in Tables 18.2 and 18.4, calculate the equilibrium constant for the reaction



at 700 K. The accepted value is 8.75×10^{-5} (see Table 26.4).

We have expressed the partition function of H_2 in Problem 26–37, and we can use Equation 18.39 to express the partition function of N_2 and Equation 18.60 to express that of NH_3 . At 700 K, these partition functions are

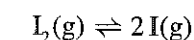
$$\begin{aligned} \frac{q_{\text{H}_2}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} e^{D_0/k_B T} \\ &= \left[\frac{2\pi(2.016 \times 10^{-3} \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(700 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \\ &\quad \times \frac{700 \text{ K}}{2(85.3 \text{ K})} \frac{1}{1 - e^{-6215/700}} e^{431800/(8.3145)(700)} \\ &= 7.15 \times 10^{63} \text{ m}^{-3} \\ \frac{q_{\text{N}_2}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.02802 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(700 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \\ &\quad \times \frac{700 \text{ K}}{2(2.88 \text{ K})} \frac{1}{1 - e^{-3374/700}} e^{941200/(8.3145)(700)} \\ &= 1.08 \times 10^{105} \text{ m}^{-3} \\ \frac{q_{\text{NH}_3}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2} \prod_1^6 (1 - e^{-\Theta_{\text{vib},j}/T})^{-1} e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.03104 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(700 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{\pi^{1/2}}{3} \left[\frac{(700 \text{ K})^3}{(13.6 \text{ K})^2 (8.92 \text{ K})} \right]^{1/2} \\ &\quad \times (1 - e^{-4800/700})^{-1} (1 - e^{-1360/700})^{-1} (1 - e^{-4880/700})^{-2} (1 - e^{-2330/700})^{-2} e^{1158000/(8.3145)(700)} \\ &= 2.13 \times 10^{121} \text{ m}^{-3} \end{aligned}$$

Using Equations 26.39 and 26.17, we can express K_p as

$$\begin{aligned} K_p(T) &= \left(\frac{k_B T}{10^5 \text{ Pa}} \right)^2 \frac{(q_{\text{NH}_3}/V)^2}{(q_{\text{N}_2}/V)(q_{\text{H}_2}/V)^3} \\ &= \left[\frac{k_B(700 \text{ K})}{10^5 \text{ Pa}} \right]^2 \frac{(2.13 \times 10^{121} \text{ m}^{-3})^2}{(1.08 \times 10^{105} \text{ m}^{-3})(7.15 \times 10^{63} \text{ m}^{-3})^3} \\ &= 1.23 \times 10^{-4} = 12.3 \times 10^{-5} \end{aligned}$$

The discrepancy between the calculated value and the experimental value (about 40%) is due to the use of the rigid rotator-harmonic oscillator approximation.

26–39. Calculate the equilibrium constant K_p for the reaction



using the data in Table 18.2 and the fact that the degeneracy of the ground electronic state of an iodine atom is 4 and that the degeneracy of the first excited electronic state is 2 and that its energy is 7580 cm^{-1} . The experimental values of K_p are

T/K	800	900	1000	1100	1200
K_p	3.05×10^{-5}	3.94×10^{-4}	3.08×10^{-3}	1.66×10^{-2}	6.79×10^{-2}

Plot $\ln K_p$ against $1/T$ to determine the value of $\Delta_r H^\circ$. The experimental value is $153.8 \text{ kJ} \cdot \text{mol}^{-1}$.

The degeneracy of the ground electronic state of an iodine atom is 4. The first excited state is $90.677 \text{ kJ} \cdot \text{mol}^{-1}$ above that and its degeneracy is 2, so (using Equations 18.13 and 18.39)

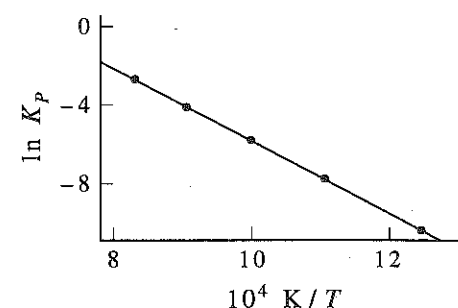
$$\begin{aligned} \frac{q_{\text{I}}}{V} &= \left[\frac{2\pi m k_B T}{h^2} \right]^{3/2} (4 + 2e^{-\epsilon_{\text{ex}}/k_B T}) \\ &= \left[\frac{2\pi(0.1269 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})T}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} (4 + 2e^{-90677 \text{ K}/8.3145T}) \\ \frac{q_{\text{I}_2}}{V} &= \left[\frac{2\pi M k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma \Theta_{\text{rot}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}/T}} e^{D_0/k_B T} \\ &= \left[\frac{2\pi(0.2538 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})T}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{T}{2(0.0537 \text{ K})} \frac{1}{1 - e^{-308 \text{ K}/T}} e^{148800 \text{ K}/8.3145T} \end{aligned}$$

Using Equations 26.39 and 26.17, we can write K_p as

$$K_p = \left(\frac{k_B T}{10^5 \text{ Pa}} \right) \frac{(q_{\text{I}}/V)^2}{(q_{\text{I}_2}/V)}$$

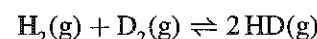
The calculated values of K_p using the partition functions above are

T/K	800	900	1000	1100	1200
K_p	3.14×10^{-5}	4.08×10^{-4}	3.19×10^{-3}	1.72×10^{-2}	7.07×10^{-2}



Plotting the calculated values, we find that $\ln K_p = 12.785 - (18498 \text{ K})/T$. Therefore, $\Delta_r H^\circ = -R(-18498 \text{ K}) = 154.0 \text{ kJ} \cdot \text{mol}^{-1}$.

26-40. Consider the reaction given by



Using the Born-Oppenheimer approximation and the molecular parameters in Table 18.2, show that

$$K(T) = 4.24e^{-77.7 \text{ K}/T}$$

Compare your predictions using this equation to the data in the JANAF tables.

We have an expression for K_p from Equation 26.39:

$$K_p = \frac{(q_{\text{HD}}/V)^2}{(q_{\text{H}_2}/V)(q_{\text{D}_2}/V)}$$

The relevant partition functions are (Equation 18.39)

$$\begin{aligned} \frac{q_{\text{H}_2}}{V} &= \left[\frac{2\pi m_{\text{H}_2} k_B T}{h^2} \right]^{3/2} \frac{T}{2\Theta_{\text{rot}}^{\text{H}_2}} \frac{e^{-\Theta_{\text{vib}}^{\text{H}_2}/2T}}{1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T}} e^{D_e^{\text{H}_2}/RT} \\ \frac{q_{\text{D}_2}}{V} &= \left[\frac{2\pi m_{\text{D}_2} k_B T}{h^2} \right]^{3/2} \frac{T}{2\Theta_{\text{rot}}^{\text{D}_2}} \frac{e^{-\Theta_{\text{vib}}^{\text{D}_2}/2T}}{1 - e^{-\Theta_{\text{vib}}^{\text{D}_2}/T}} e^{D_e^{\text{D}_2}/RT} \\ \frac{q_{\text{HD}}}{V} &= \left[\frac{2\pi m_{\text{HD}} k_B T}{h^2} \right]^{3/2} \frac{T}{\Theta_{\text{rot}}^{\text{HD}}} \frac{e^{-\Theta_{\text{vib}}^{\text{HD}}/2T}}{1 - e^{-\Theta_{\text{vib}}^{\text{HD}}/T}} e^{D_e^{\text{HD}}/RT} \end{aligned}$$

Substituting into K_p gives

$$\begin{aligned} K_p &= \left(\frac{2\pi m_{\text{HD}} k_B T}{h^2} \right)^{3/2} \left(\frac{2\pi m_{\text{H}_2} k_B T}{h^2} \right)^{-3/2} \left(\frac{2\pi m_{\text{D}_2} k_B T}{h^2} \right)^{-3/2} \left(\frac{T}{\Theta_{\text{rot}}^{\text{HD}}} \right)^2 \left(\frac{4\Theta_{\text{rot}}^{\text{H}_2} \Theta_{\text{rot}}^{\text{D}_2}}{T^2} \right) \\ &\quad \times \frac{e^{-2\Theta_{\text{vib}}^{\text{HD}}/2T}}{e^{-\Theta_{\text{vib}}^{\text{H}_2}/2T} e^{-\Theta_{\text{vib}}^{\text{D}_2}/2T}} (1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T}) (1 - e^{-\Theta_{\text{vib}}^{\text{D}_2}/T}) (1 - e^{-\Theta_{\text{vib}}^{\text{HD}}/T})^{-2} e^{(2D_e^{\text{HD}} - D_e^{\text{H}_2} - D_e^{\text{D}_2})/RT} \\ &= \left(\frac{m_{\text{HD}}^2}{m_{\text{H}_2} m_{\text{D}_2}} \right)^{3/2} \left[\frac{4\Theta_{\text{rot}}^{\text{H}_2} \Theta_{\text{rot}}^{\text{D}_2}}{(\Theta_{\text{rot}}^{\text{HD}})^2} \right] \left[\frac{(1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T}) (1 - e^{-\Theta_{\text{vib}}^{\text{D}_2}/T})}{(1 - e^{-\Theta_{\text{vib}}^{\text{HD}}/T})^2} \right] e^{-(2\Theta_{\text{vib}}^{\text{HD}} - \Theta_{\text{vib}}^{\text{H}_2} - \Theta_{\text{vib}}^{\text{D}_2})/2T} \\ &\quad \times e^{(2D_e^{\text{HD}} - D_e^{\text{H}_2} - D_e^{\text{D}_2})/RT} \end{aligned} \quad (1)$$

Under the Born-Oppenheimer approximation, $D_e^{\text{HD}} = D_e^{\text{D}_2} = D_e^{\text{H}_2}$, so the last exponential term becomes 1. Also, k and R_e are the same for HD, H_2 , and D_2 . Then, since $\nu = (k/\mu)^{1/2}/2\pi$ and $I = \mu R_e^2$, we can write Θ_{vib} and Θ_{rot} as

$$\Theta_{\text{vib}} = \frac{h\nu}{k_B} = \frac{hk^{1/2}\pi}{2k_B} \mu^{-1/2} \propto \mu^{-1/2} \quad \text{and} \quad \Theta_{\text{rot}} = \frac{\hbar^2}{2Ik_B} = \frac{\hbar^2}{2R_e^2 k_B} \mu^{-1} \propto \mu^{-1}$$

Recall that $\mu_{\text{AB}} = (m_A m_B)/(m_A + m_B)$. Applying this formula, we find that $\mu_{\text{H}_2} = 0.5 \text{ amu}$, $\mu_{\text{HD}} = 2/3 \text{ amu}$, and $\mu_{\text{D}_2} = 1 \text{ amu}$. We can now write

$$\frac{4\Theta_{\text{rot}}^{\text{H}_2} \Theta_{\text{rot}}^{\text{D}_2}}{(\Theta_{\text{rot}}^{\text{HD}})^2} = \frac{4\mu_{\text{H}_2}^{-1} \mu_{\text{D}_2}^{-1}}{\mu_{\text{HD}}^{-2}} = \frac{4(2/3 \text{ amu})^2}{(0.5 \text{ amu})(1 \text{ amu})} = \frac{32}{9}$$

We can also express $\Theta_{\text{vib}}^{\text{HD}}$ and $\Theta_{\text{vib}}^{\text{D}_2}$ in terms of $\Theta_{\text{vib}}^{\text{H}_2}$:

$$\frac{\Theta_{\text{vib}}^{\text{HD}}}{\Theta_{\text{vib}}^{\text{H}_2}} = \left(\frac{\mu_{\text{H}_2}}{\mu_{\text{HD}}} \right)^{1/2} = \left(\frac{1/2}{2/3} \right)^{1/2} = \frac{\sqrt{3}}{2}$$

$$\Theta_{\text{vib}}^{\text{HD}} = \frac{\sqrt{3}}{2} \Theta_{\text{vib}}^{\text{H}_2}$$

$$\frac{\Theta_{\text{vib}}^{\text{D}_2}}{\Theta_{\text{vib}}^{\text{H}_2}} = \left(\frac{\mu_{\text{H}_2}}{\mu_{\text{D}_2}} \right)^{1/2} = \left(\frac{1/2}{1} \right)^{1/2} = \frac{\sqrt{2}}{2}$$

$$\Theta_{\text{vib}}^{\text{D}_2} = \frac{\sqrt{2}}{2} \Theta_{\text{vib}}^{\text{H}_2}$$

Then

$$2\Theta_{\text{vib}}^{\text{HD}} - \Theta_{\text{vib}}^{\text{H}_2} - \Theta_{\text{vib}}^{\text{D}_2} = (3^{1/2} - 1 - 2^{-1/2}) \Theta_{\text{vib}}^{\text{H}_2} = 155.0 \text{ K}$$

where $\Theta_{\text{vib}}^{\text{H}_2} = 6332 \text{ K}$. Substituting into Equation 1, we find

$$\begin{aligned} K &= \left(\frac{9}{8} \right)^{3/2} \left(\frac{32}{9} \right) \left[\frac{(1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T}) (1 - e^{-\Theta_{\text{vib}}^{\text{D}_2}/T})}{(1 - e^{-\Theta_{\text{vib}}^{\text{HD}}/T})^2} \right] e^{-77.7 \text{ K}/T} \\ &= 4.24e^{-77.7 \text{ K}/T} \end{aligned}$$

where we have neglected factors such as $1 - e^{-\Theta_{\text{vib}}/T}$, since they do not contribute significantly to K for $T < 1000 \text{ K}$. The table below compares calculated values of K with values from the JANAF tables.

T/K	$K_p(\text{calc.})$	$K_p(\text{JANAF})$
200	2.88	2.90
400	3.49	3.48
600	3.73	3.72
800	3.85	3.84
1000	3.92	3.91

26-41. Using the harmonic oscillator-rigid rotator approximation, show that

$$K(T) = \left(\frac{m_{\text{H}_2} m_{\text{Br}_2}}{m_{\text{HBr}}^2} \right)^{3/2} \left(\frac{\sigma_{\text{HBr}}^2}{\sigma_{\text{H}_2} \sigma_{\text{Br}_2}} \right) \left(\frac{(\Theta_{\text{rot}}^{\text{HBr}})^2}{\Theta_{\text{rot}}^{\text{H}_2} \Theta_{\text{rot}}^{\text{Br}_2}} \right) \frac{(1 - e^{-\Theta_{\text{vib}}^{\text{HBr}}/T})^2}{(1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T})(1 - e^{-\Theta_{\text{vib}}^{\text{Br}_2}/T})} e^{(D_0^{\text{H}_2} + D_0^{\text{Br}_2} - 2D_0^{\text{HBr}})/RT}$$

for the reaction described by



Using the values of Θ_{rot} , Θ_{vib} , and D_0 given in Table 18.2, calculate K at 500 K, 1000 K, 1500 K, and 2000 K. Plot $\ln K$ against $1/T$ and determine the value of $\Delta_r H^\circ$.

We have an expression for K_p from Equation 26.39:

$$K_p = \frac{(q_{\text{H}_2}/V)(q_{\text{Br}_2}/V)}{(q_{\text{HBr}}/V)^2}$$

The relevant partition functions are

$$\begin{aligned} \frac{q_{\text{H}_2}}{V} &= \left[\frac{2\pi m_{\text{H}_2} k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma_{\text{H}_2} \Theta_{\text{rot}}^{\text{H}_2}} \frac{1}{1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T}} e^{D_0^{\text{H}_2}/RT} \\ \frac{q_{\text{Br}_2}}{V} &= \left[\frac{2\pi m_{\text{Br}_2} k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma_{\text{Br}_2} \Theta_{\text{rot}}^{\text{Br}_2}} \frac{1}{1 - e^{-\Theta_{\text{vib}}^{\text{Br}_2}/T}} e^{D_0^{\text{Br}_2}/RT} \\ \frac{q_{\text{HBr}}}{V} &= \left[\frac{2\pi m_{\text{HBr}} k_B T}{h^2} \right]^{3/2} \frac{T}{\sigma_{\text{HBr}} \Theta_{\text{rot}}^{\text{HBr}}} \frac{1}{1 - e^{-\Theta_{\text{vib}}^{\text{HBr}}/T}} e^{D_0^{\text{HBr}}/RT} \end{aligned}$$

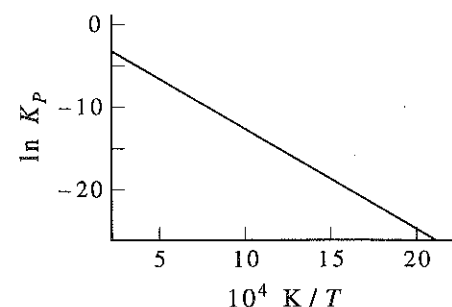
so we write K_p as

$$K(T) = \left(\frac{m_{\text{H}_2} m_{\text{Br}_2}}{m_{\text{HBr}}^2} \right)^{3/2} \left(\frac{\sigma_{\text{HBr}}^2}{\sigma_{\text{H}_2} \sigma_{\text{Br}_2}} \right) \left[\frac{(\Theta_{\text{rot}}^{\text{HBr}})^2}{\Theta_{\text{rot}}^{\text{H}_2} \Theta_{\text{rot}}^{\text{Br}_2}} \right] \frac{(1 - e^{-\Theta_{\text{vib}}^{\text{HBr}}/T})^2}{(1 - e^{-\Theta_{\text{vib}}^{\text{H}_2}/T})(1 - e^{-\Theta_{\text{vib}}^{\text{Br}_2}/T})} e^{(D_0^{\text{H}_2} + D_0^{\text{Br}_2} - 2D_0^{\text{HBr}})/RT}$$

Using the values from Table 18.2, we find that

T/K	500	1000	1500	2000
K_p	8.96×10^{-12}	1.20×10^{-6}	6.63×10^{-5}	4.97×10^{-4}

We can use these values to create a graph of $\ln K_p$ vs. $1/T$ and curve-fit the points linearly to obtain the equation $\ln K_p = -1.70367 - (11876 \text{ K})/T$.

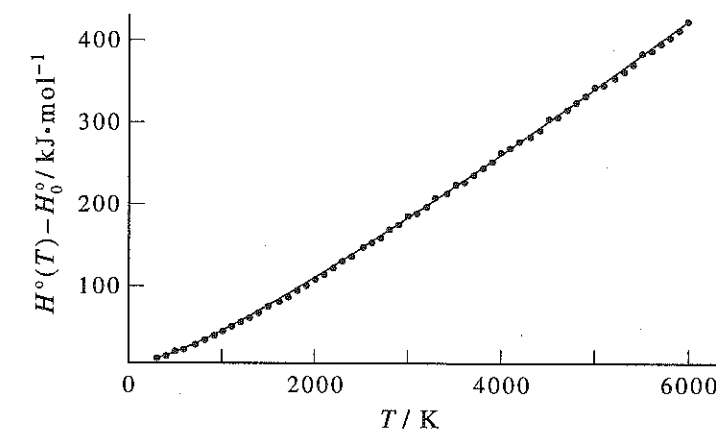


Therefore, $\Delta_r H^\circ = -R(-11876 \text{ K}) = 98.8 \text{ kJ} \cdot \text{mol}^{-1}$ for the reaction (compared to an experimental value of $106.0 \text{ kJ} \cdot \text{mol}^{-1}$).

- 26-42. Use Equation 26.49b to calculate $H^\circ(T) - H^\circ$ for $\text{NH}_3(\text{g})$ from 300 K to 6000 K and compare your values to those given in Table 26.4 by plotting them on the same graph.

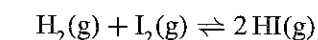
$$H^\circ(T) - H^\circ = 4RT + \sum_j \frac{R\Theta_{\text{vib},j}}{e^{-\Theta_{\text{vib},j}/T} - 1} \quad (26.49b)$$

We use Table 18.4 for the appropriate values of $\Theta_{\text{vib},j}$ to produce the graph below. The data points are from the JANAF tables, and the line is the function represented by Equation 26.49b.



This is a very good fit to the JANAF data.

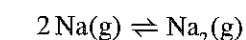
- 26-43. Use the JANAF tables to calculate K_p at 1000 K for the reaction described by



Compare your results to the value given in Table 26.2.

The JANAF tables give $\log K_f = 0.732$ for $\text{HI}(\text{g})$ at 1000 K. The equation given represents the formation of two moles of $\text{HI}(\text{g})$ from its constituent elements, and so $\log K = 2 \log K_f = 1.464$ and $\ln K = 3.37$. The value of $\ln K$ in Table 26.2 is 3.55.

- 26-44. Use the JANAF tables to plot $\ln K_p$ versus $1/T$ from 900 K to 1200 K for the reaction described by



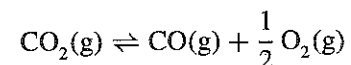
and compare your results to those obtained in Problem 26-35.

We can use Equation 26-11 to find K_p from the values given in the JANAF tables. From the JANAF tables,

T/K	900	1000	1100
$\Delta_f G^\circ[\text{Na}_2(\text{g})]/\text{kJ} \cdot \text{mol}^{-1}$	43.601	34.740	26.068
$\Delta_f G^\circ[\text{Na(g)}]/\text{kJ} \cdot \text{mol}^{-1}$	43.601	34.740	26.068
$\Delta_r G^\circ/\text{kJ} \cdot \text{mol}^{-1}$	-1.819	6.248	14.338
$K_p(\text{JANAF})$	1.28	0.472	0.208

compared to $K_p(900 \text{ K}) = 1.47$, $K_p(1000 \text{ K}) = 0.52$, and $K_p(1100 \text{ K}) = 0.22$ from Problem 26-35.

26-45. In Problem 26-36 we calculated K_p for the decomposition of $\text{CO}_2(\text{g})$ to $\text{CO}(\text{g})$ and $\text{O}_2(\text{g})$ at 2000 K. Use the JANAF tables to calculate K_p and compare your result to the one that you obtained in Problem 26-36.



From the JANAF tables,

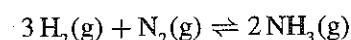
	CO(g)	O ₂ (g)	CO ₂ (g)
$\Delta_f G^\circ / \text{kJ} \cdot \text{mol}^{-1}$	-286.034	0	-396.333

These values give a $\Delta_r G^\circ = 110.299 \text{ kJ} \cdot \text{mol}^{-1}$, and (Equation 26.11)

$$K_p = e^{-\Delta_r G^\circ / RT} = 1.32 \times 10^{-3}$$

compared to $K_p = 1.46 \times 10^{-3}$ from Problem 26-36.

26-46. You calculated K_p at 700 K for the ammonia synthesis reaction in Problem 26-38. Use the data in Table 26.4 to calculate K_p and compare your result to the one that you obtained in Problem 26-38.



From the JANAF tables, we know that at 700 K $\Delta_f G^\circ[\text{NH}_3(\text{g})] = 27.190 \text{ kJ} \cdot \text{mol}^{-1}$. Therefore, for the reaction above, $\Delta_r G^\circ = 2(27.190 \text{ kJ} \cdot \text{mol}^{-1}) = 54.380 \text{ kJ} \cdot \text{mol}^{-1}$, and (Equation 26.11)

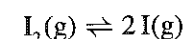
$$K_p = e^{-\Delta_r G^\circ / RT} = 8.75 \times 10^{-5}$$

compared to $K_p = 12.3 \times 10^{-5}$ from Problem 26-38.

26-47. The JANAF tables give the following data for $\text{I}(\text{g})$ at one bar:

T/K	800	900	1000	1100	1200
$\Delta_f G^\circ / \text{kJ} \cdot \text{mol}^{-1}$	34.580	29.039	24.039	18.741	13.428

Calculate K_p for the reaction described by



and compare your results to the values given in Problem 26-39.

The energy of the reaction above will be twice the energy of formation of iodine, or $\Delta_r G^\circ = 2\Delta_f G^\circ[\text{I}(\text{g})]$. Then, using Equation 26.11, we can calculate K_p at each temperature above:

T/K	800	900	1000	1100	1200
$K_p(\text{JANAF})$	3.05×10^{-5}	4.26×10^{-4}	3.08×10^{-3}	1.66×10^{-2}	6.78×10^{-2}
$K_p(\text{calc})$	3.14×10^{-5}	4.08×10^{-4}	3.19×10^{-3}	1.72×10^{-2}	7.07×10^{-2}

where we calculated the values of K_p in Problem 26-39.

26-48. Use Equation 18.60 to calculate the value of $q^0(V, T)/V$ given in the text (page 1076) for $\text{NH}_3(\text{g})$ at 500 K.

We can write Equation 18.60 in terms of D_0 as

$$q(V) = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} V \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2} \left[\prod_{j=1}^6 (1 - e^{-\Theta_{\text{vib,j}}/T})^{-1} \right] e^{D_0/k_B T}$$

We can ignore the last exponential term when we look at q^0 , since q^0 is the energy relative to the ground-state energy. For $\text{NH}_3(\text{g})$, this becomes

$$\begin{aligned} \frac{q}{V} &= \left[\frac{2\pi(0.01709 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(500 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{\pi^{1/2}}{3} \left[\frac{(500 \text{ K})^3}{(13.6 \text{ K})^2 (8.92 \text{ K})} \right]^{1/2} \\ &\quad \times (1 - e^{-48/50})^{-1} (1 - e^{-136/50})^{-1} (1 - e^{-488/50})^{-2} (1 - e^{-233/50})^{-2} \\ &= 2.59 \times 10^{34} \text{ m}^{-3} \end{aligned}$$

26-49. The JANAF tables give the following data for $\text{Ar}(\text{g})$ at 298.15 K and one bar:

$$-\frac{G^\circ - H^\circ(298.15 \text{ K})}{T} = 154.845 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

and

$$H^\circ(0 \text{ K}) - H^\circ(298.15 \text{ K}) = -6.197 \text{ kJ} \cdot \text{mol}^{-1}$$

Use these data to calculate $q^0(V, T)/V$ and compare your result to what you obtain using Equation 18.13.

Use Equation 26.52b to find the exponential term in Equation 26.52a:

$$\begin{aligned} -\frac{(G^\circ - H_0^\circ)}{T} &= -\frac{[G^\circ - H^\circ(298.15 \text{ K})]}{T} + \frac{[H^\circ - H^\circ(298.15 \text{ K})]}{T} \\ &= 154.845 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - \frac{6197 \text{ J} \cdot \text{mol}^{-1}}{298.15 \text{ K}} \\ &= 134.06 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \end{aligned}$$

Now substitute into Equation 26.52a:

$$\begin{aligned} \frac{q^0(V, T)}{V} &= \frac{N_A P^\circ}{RT} e^{-(G^\circ - H_0^\circ)/RT} \\ &= \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(10^5 \text{ Pa})}{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})} e^{134.06/8.3145} \\ &= 2.443 \times 10^{32} \text{ m}^{-3} \end{aligned}$$

Using Equation 18.13 and looking at q^0 as we did in Section 23-5, we find that

$$\begin{aligned} \frac{q^0}{V} &= \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \\ &= \left[\frac{2\pi(0.039948 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \\ &= 2.443 \times 10^{32} \text{ m}^{-3} \end{aligned}$$

26-50. Use the JANAF tables to calculate $q^0(V, T)/V$ for $\text{CO}_2(\text{g})$ at 500 K and one bar and compare your result to what you obtain using Equation 18.57 (with the ground state energy taken to be zero).

Using Equation 26.52b,

$$-\frac{(G^\circ - H_0^\circ)}{T} = 218.290 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + \frac{-9364 \text{ J} \cdot \text{mol}^{-1}}{500 \text{ K}} \\ = 199.562 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Now substitute into Equation 26.52a:

$$\frac{q^0(V, T)}{V} = \frac{N_A P^\circ}{RT} e^{-(G^\circ - H_0^\circ)/RT} \\ = \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(10^5 \text{ Pa})}{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})} e^{199.562/8.3145} \\ = 3.84 \times 10^{35} \text{ m}^{-3}$$

Using Equation 18.57 and looking at q^0 as we did in Section 23-5, we find that

$$\frac{q^0}{V} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \left(\frac{T}{\sigma \Theta_{\text{rot}}} \right) \prod_{j=1}^4 (1 - e^{-\Theta_{\text{vib},j}/T})^{-1} \\ = \left[\frac{2\pi(0.04400 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(500 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \left[\frac{500 \text{ K}}{2(0.561 \text{ K})} \right] \\ \times (1 - e^{336/500})^{-1} (1 - e^{-954/500})^{-2} (1 - e^{-189/500})^{-1} \\ = 3.86 \times 10^{35} \text{ m}^{-3}$$

26-51. Use the JANAF tables to calculate $q^0(V, T)/V$ for $\text{CH}_4(\text{g})$ at 1000 K and one bar and compare your result to what you obtain using Equation 18.60 (with the ground state energy taken to be zero).

Using Equation 26.52b,

$$-\frac{(G^\circ - H_0^\circ)}{T} = 209.370 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + \frac{-10024 \text{ J} \cdot \text{mol}^{-1}}{1000 \text{ K}} \\ = 199.35 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Now substitute into Equation 26.52a:

$$\frac{q^0(V, T)}{V} = \frac{N_A P^\circ}{RT} e^{-(G^\circ - H_0^\circ)/RT} \\ = \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(10^5 \text{ Pa})}{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})} e^{199.35/8.3145} \\ = 1.87 \times 10^{35} \text{ m}^{-3}$$

Using Equation 18.60 and looking at q^0 as we did in Section 23-5, we find that

$$\frac{q^0}{V} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2} \prod_{j=1}^9 (1 - e^{-\Theta_{\text{vib},j}/T})^{-1} \\ = \left[\frac{2\pi(0.01604 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(1000 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})(6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{\pi^{1/2}}{3} \\ \times \left[\frac{(1000 \text{ K})^3}{(7.54 \text{ K})^3} \right]^{1/2} (1 - e^{-417/100})^{-1} (1 - e^{-218/100})^{-2} (1 - e^{-432/100})^{-3} (1 - e^{-187/100})^{-3} \\ = 1.91 \times 10^{35} \text{ m}^{-3}$$

26-52. Use the JANAF tables to calculate $q^0(V, T)/V$ for $\text{H}_2\text{O}(\text{g})$ at 1500 K and one bar and compare your result to what you obtain using Equation 26.45. Why do you think there is some discrepancy?

Using Equation 26.52b,

$$-\frac{(G^\circ - H_0^\circ)}{T} = 218.520 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + \frac{-9904 \text{ J} \cdot \text{mol}^{-1}}{1500 \text{ K}} \\ = 211.9 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$$

Now substitute into Equation 26.52a:

$$\frac{q^0(V, T)}{V} = \frac{N_A P^\circ}{RT} e^{-(G^\circ - H_0^\circ)/RT} \\ = \frac{(6.022 \times 10^{23} \text{ mol}^{-1})(10^5 \text{ Pa})}{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.15 \text{ K})} e^{211.9/8.3145} \\ = 5.66 \times 10^{35} \text{ m}^{-3}$$

Using Equation 18.60 and looking at q^0 as we did in Section 23-5, we find that

$$\frac{q^0}{V} = \left(\frac{2\pi M k_B T}{h^2} \right)^{3/2} \frac{\pi^{1/2}}{\sigma} \left(\frac{T^3}{\Theta_{\text{rot,A}} \Theta_{\text{rot,B}} \Theta_{\text{rot,C}}} \right)^{1/2} \prod_{j=1}^3 (1 - e^{-\Theta_{\text{vib},j}/T})^{-1} \\ = \left[\frac{2\pi(0.018015 \text{ kg} \cdot \text{mol}^{-1})(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(1500 \text{ K})}{(6.022 \times 10^{23} \text{ mol}^{-1})^2 (6.626 \times 10^{-34} \text{ J} \cdot \text{s})^2} \right]^{3/2} \frac{\pi^{1/2}}{3} \\ \times \left[\frac{(1500 \text{ K})^3}{(40.1 \text{ K})(20.9 \text{ K})(13.4 \text{ K})} \right]^{1/2} (1 - e^{-536/150})^{-1} (1 - e^{-516/150})^{-1} (1 - e^{-229/150})^{-1} \\ = 5.51 \times 10^{35} \text{ m}^{-3}$$

The small discrepancy between these two results is probably due to the use of the harmonic-oscillator approximation in obtaining Equation 18.60.

26-53. The JANAF tables give the following data:

	H(g)	Cl(g)	HCl(g)
$\Delta_f H^\circ(0 \text{ K})/\text{kJ} \cdot \text{mol}^{-1}$	216.035	119.621	-92.127

Use these data to calculate D_0 for HCl(g) and compare your value to the one in Table 18.2.

	$\Delta_r H^\circ / \text{kJ} \cdot \text{mol}^{-1}$	
$\frac{1}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{H}(\text{g})$	216.035	(1)
$\frac{1}{2} \text{Cl}_2(\text{g}) \rightleftharpoons \text{Cl}(\text{g})$	119.621	(2)
$\frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g}) \rightleftharpoons \text{HCl}(\text{g})$	-92.127	(3)

We can obtain the reaction $\text{HCl(g)} \rightleftharpoons \text{H(g)} + \text{Cl(g)}$ by subtracting Equation 3 from the sum of Equations 1 and 2, to find

$$D_0 = \Delta_r H^\circ = (216.035 + 119.621 + 92.127) \text{ kJ} \cdot \text{mol}^{-1} = 427.8 \text{ kJ} \cdot \text{mol}^{-1}$$

compared to a value of $427.8 \text{ kJ} \cdot \text{mol}^{-1}$ in Table 18.2.

26-54. The JANAF tables give the following data:

	C(g)	H(g)	CH ₄ (g)
$\Delta_r H^\circ(0 \text{ K}) / \text{kJ} \cdot \text{mol}^{-1}$	711.19	216.035	-66.911

Use these data to calculate D_0 for $\text{CH}_4(\text{g})$ and compare your value to the one in Table 18.4.

	$\Delta_r H^\circ / \text{kJ} \cdot \text{mol}^{-1}$	
$\text{C(s)} \rightleftharpoons \text{C(g)}$	711.19	(1)
$\frac{1}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{H(g)}$	216.035	(2)
$\text{C(s)} + 2\text{H}_2(\text{g}) \rightleftharpoons \text{CH}_4(\text{g})$	-66.911	(3)

We can obtain the reaction $\text{CH}_4(\text{g}) \rightleftharpoons 4\text{H(g)} + \text{C(g)}$ by subtracting Equation 3 from the sum of Equations 1 and four times Equation 2, to find

$$D_0 = \Delta_r H^\circ = [66.911 + 711.19 + 4(216.035)] \text{ kJ} \cdot \text{mol}^{-1} = 1642 \text{ kJ} \cdot \text{mol}^{-1}$$

compared to a value of $1642 \text{ kJ} \cdot \text{mol}^{-1}$ from Table 18.4.

26-55. Use the JANAF tables to calculate D_0 for $\text{CO}_2(\text{g})$ and compare your result to the one given in Table 18.4.

	$\Delta_r H^\circ / \text{kJ} \cdot \text{mol}^{-1}$	
$\text{C(s)} \rightleftharpoons \text{C(g)}$	711.19	(1)
$\frac{1}{2} \text{O}_2(\text{g}) \rightleftharpoons \text{O(g)}$	246.790	(2)
$\text{C(s)} + \text{O}_2(\text{g}) \rightleftharpoons \text{CO}_2(\text{g})$	-393.115	(3)

We can obtain the reaction $\text{CO}_2(\text{g}) \rightleftharpoons 2\text{O(g)} + \text{C(g)}$ by subtracting Equation 3 from the sum of Equations 1 and two times Equation 2, to find

$$D_0 = \Delta_r H^\circ = [393.115 + 711.19 + 2(246.790)] \text{ kJ} \cdot \text{mol}^{-1} = 1598 \text{ kJ} \cdot \text{mol}^{-1}$$

compared to a value of $1596 \text{ kJ} \cdot \text{mol}^{-1}$ in Table 18.4.

26-56. A determination of K_γ (see Example 26-11) requires a knowledge of the fugacity of each gas in the equilibrium mixture. These data are not usually available, but a useful approximation is to take the fugacity coefficient of a gaseous constituent of a mixture to be equal to the value for the pure gas at the *total pressure of the mixture*. Using this approximation, we can use Figure 22.11 to determine γ for each gas and then calculate K_γ . In this problem we shall apply this approximation to the data in Table 26.5. First use Figure 22.11 to estimate that $\gamma_{\text{H}_2} = 1.05$, $\gamma_{\text{N}_2} = 1.05$, and that $\gamma_{\text{NH}_3} = 0.95$ at a total pressure of 100 bar and a temperature of 450°C . In this case $K_\gamma = 0.86$, in fairly good agreement with the value given in Example 26-11. Now calculate K_γ at 600 bar and compare your result with the value given in Example 26-11.

First, we must find the reduced temperatures and reduced pressures of each species at a pressure of 100 bar and a temperature of 450°C (we can use Table 16.5 for critical values):

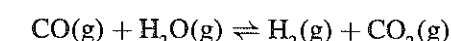
$$\begin{aligned} P_{\text{R}}(\text{N}_2) &= \frac{100 \text{ bar}}{34.0 \text{ bar}} = 2.94 & T_{\text{R}}(\text{N}_2) &= \frac{723 \text{ K}}{126.2 \text{ K}} = 5.73 \\ P_{\text{R}}(\text{H}_2) &= \frac{100 \text{ bar}}{12.838 \text{ bar}} = 7.79 & T_{\text{R}}(\text{H}_2) &= \frac{723 \text{ K}}{32.938 \text{ K}} = 22.0 \\ P_{\text{R}}(\text{NH}_3) &= \frac{100 \text{ bar}}{111.30 \text{ bar}} = 0.898 & T_{\text{R}}(\text{NH}_3) &= \frac{723 \text{ K}}{405.30 \text{ K}} = 1.78 \end{aligned}$$

Using Figure 22.11, it looks as if $\gamma_{\text{H}_2} = 1.05$, $\gamma_{\text{N}_2} = 1.05$, and $\gamma_{\text{NH}_3} = 0.95$. At 600 bar, $P_{\text{R}}(\text{N}_2) = 17.6$, $P_{\text{R}}(\text{H}_2) = 46.7$, and $P_{\text{R}}(\text{NH}_3) = 5.4$, so $\gamma_{\text{H}_2} = 1.3$, $\gamma_{\text{N}_2} = 1.3$, and $\gamma_{\text{NH}_3} = 0.9$. Then

$$K_\gamma = \frac{\gamma_{\text{NH}_3}}{\gamma_{\text{H}_2}^{3/2} \gamma_{\text{N}_2}^{3/2}} = 0.53$$

as compared to the value in Example 26-11 of 0.496. This is within the margin of error created by estimating the values of γ from Figure 22.11.

26-57. Recall from general chemistry that Le Châtelier's principle says that pressure has no effect on a gaseous equilibrium system such as



in which the total number of moles of reactants is equal to the total number of moles of product in the chemical equation. The thermodynamic equilibrium constant in this case is

$$K_f = \frac{f_{\text{CO}_2} f_{\text{H}_2}}{f_{\text{CO}} f_{\text{H}_2\text{O}}} = \frac{\gamma_{\text{CO}_2} \gamma_{\text{H}_2} P_{\text{CO}_2} P_{\text{H}_2}}{\gamma_{\text{CO}} \gamma_{\text{H}_2\text{O}} P_{\text{CO}} P_{\text{H}_2\text{O}}} = K_\gamma K_P$$

If the four gases behaved ideally, then pressure would have no effect on the position of equilibrium. However, because of deviations from ideal behavior, a shift in the equilibrium composition will occur when the pressure is changed. To see this, use the approximation introduced in Problem 26-56 to estimate K_γ at 900 K and 500 bar. Note that K_γ under these conditions is greater than K_γ at one bar, where $K_\gamma \approx 1$ (ideal behavior). Consequently, argue that an increase in pressure causes the equilibrium to shift to the left in this case.

At 900 K and 500 bar,

$$\begin{aligned} P_R(\text{CO}) &= \frac{500 \text{ bar}}{34.935 \text{ bar}} = 14.3 & T_R(\text{CO}) &= \frac{900 \text{ K}}{132.85 \text{ K}} = 6.77 \\ P_R(\text{H}_2\text{O}) &= \frac{500 \text{ bar}}{220.55 \text{ bar}} = 2.27 & T_R(\text{H}_2\text{O}) &= \frac{900 \text{ K}}{647.126 \text{ K}} = 1.39 \\ P_R(\text{H}_2) &= \frac{500 \text{ bar}}{12.838 \text{ bar}} = 38.9 & T_R(\text{H}_2) &= \frac{900 \text{ K}}{32.938 \text{ K}} = 27.3 \\ P_R(\text{CO}_2) &= \frac{500 \text{ bar}}{73.843 \text{ bar}} = 6.77 & T_R(\text{CO}_2) &= \frac{900 \text{ K}}{304.14 \text{ K}} = 2.96 \end{aligned}$$

and so $\gamma_{\text{CO}} \approx 1.3$, $\gamma_{\text{H}_2\text{O}} \approx 0.8$, $\gamma_{\text{H}_2} \approx 1.15$, and $\gamma_{\text{CO}_2} \approx 1.1$. Then

$$K_\gamma = \frac{\gamma_{\text{CO}_2} \gamma_{\text{H}_2}}{\gamma_{\text{H}_2\text{O}} \gamma_{\text{CO}}} = 1.1$$

Since K_f must remain constant, K_p at 500 bar must be smaller than K_p at one bar and so the equilibrium will shift to the left.

- 26-58.** Calculate the activity of $\text{H}_2\text{O}(\text{l})$ as a function of pressure from one bar to 100 bar at 20.0°C . Take the density of $\text{H}_2\text{O}(\text{l})$ to be $0.9982 \text{ g}\cdot\text{mL}^{-1}$ and assume that it is incompressible.

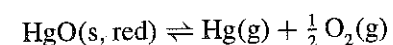
Use Equation 26.69,

$$\begin{aligned} \ln a &= \frac{\bar{V}}{RT} (P - 1) \\ &= \left(\frac{1 \times 10^{-3} \text{ dm}^3}{0.9982 \text{ g}} \right) \left(\frac{18.015 \text{ g}}{1 \text{ mol}} \right) \left[\frac{1}{(0.083145 \text{ dm}^3 \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(293.15 \text{ K})} \right] (P - 1) \\ &= (7.40 \times 10^{-4} \text{ bar}^{-1})(P - 1) \end{aligned}$$

Below are some values of $\ln a$ and a at representative temperatures through the range 1 to 100 bar.

P/bar	$\ln a$	a
1	0	1.00
10	6.67×10^{-3}	1.01
50	3.63×10^{-2}	1.04
100	7.33×10^{-2}	1.08

- 26-59.** Consider the dissociation of $\text{HgO}(\text{s, red})$ to $\text{Hg}(\text{g})$ and $\text{O}_2(\text{g})$ according to



If we start with only $\text{HgO}(\text{s, red})$, then assuming ideal behavior, show that

$$K_p = \frac{2}{3^{3/2}} P^{3/2}$$

where P is the total pressure. Given the following “dissociation pressure” of $\text{HgO}(\text{s, red})$ at various temperatures, plot $\ln K_p$ versus $1/T$.

$t/^\circ\text{C}$	P/atm	$t/^\circ\text{C}$	P/atm
360	0.1185	430	0.6550
370	0.1422	440	0.8450
380	0.1858	450	1.067
390	0.2370	460	1.339
400	0.3040	470	1.674
410	0.3990	480	2.081
420	0.5095		

An excellent curve fit to the plot of $\ln K_p$ against $1/T$ is given by

$$\ln K_p = -172.94 + \frac{4.0222 \times 10^5 \text{ K}}{T} - \frac{2.9839 \times 10^8 \text{ K}^2}{T^2} + \frac{7.0527 \times 10^{10} \text{ K}^3}{T^3}$$

$$630 \text{ K} < T < 750 \text{ K}$$

Use this expression to determine $\Delta_f H^\circ$ as a function of temperature in the interval $630 \text{ K} < T < 750 \text{ K}$. Given that

$$C_p^\circ[\text{O}_2(\text{g})]/R = 4.8919 - \frac{829.931 \text{ K}}{T} - \frac{127962 \text{ K}^2}{T^2}$$

$$C_p^\circ[\text{Hg}(\text{g})]/R = 2.500$$

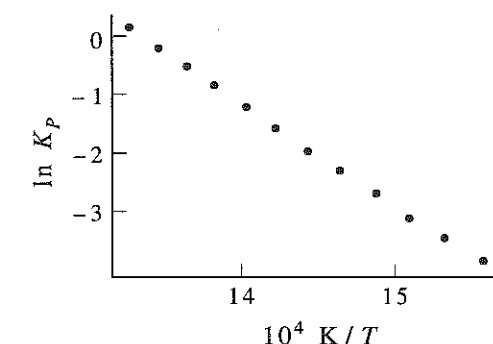
$$C_p^\circ[\text{HgO}(\text{s, red})]/R = 5.2995$$

in the interval $298 \text{ K} < T < 750 \text{ K}$, calculate $\Delta_f H^\circ$, $\Delta_f S^\circ$, and $\Delta_f G^\circ$ at 298 K .

We can write K_p in terms of the partial pressures of mercury and oxygen (assuming an activity of unity for the solid):

$$K_p = P_{\text{O}_2}^{1/2} P_{\text{Hg}} = \left(\frac{1/2 P}{3/2} \right)^{1/2} \left(\frac{P}{3/2} \right) = \frac{2}{3^{3/2}} P^{3/2}$$

Below is a plot of the experimental values of $\ln K_p$ against $1/T$.



We can now use the equation given in the problem for $\ln K_p$ in Equation 26.29 to find $\Delta_f H^\circ$:

$$\begin{aligned} \frac{d \ln K_p}{dT} &= -\frac{4.0222 \times 10^5 \text{ K}}{T^2} + \frac{5.9678 \times 10^8 \text{ K}^2}{T^3} - \frac{2.1158 \times 10^{11} \text{ K}^3}{T^4} \\ \Delta_f H^\circ &= RT^2 \frac{d \ln K_p}{dT} \\ \Delta_f H^\circ &= R \left(-4.022 \times 10^5 \text{ K} + \frac{5.9678 \times 10^8 \text{ K}^2}{T} - \frac{2.1158 \times 10^9 \text{ K}^3}{T^2} \right) \end{aligned}$$

Likewise, we can use Equation 26.11 to find $\Delta_r G^\circ$:

$$\begin{aligned}\Delta_r G^\circ &= -RT \ln K_p \\ &= R \left(172.94T - 4.0222 \times 10^5 \text{ K} + \frac{2.9839 \times 10^8 \text{ K}^2}{T} - \frac{7.0527 \times 10^{10} \text{ K}^3}{T^2} \right)\end{aligned}$$

We can also find an empirical expression for $\Delta_r S^\circ$ using the equation

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T}$$

The expression for $\ln K_p$ used in the above equalities holds for temperatures ranging from 630 K to 750 K. To find the values of $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ at 298 K, we can use the equation

$$\Delta_r H^\circ(298 \text{ K}) = \Delta_r H^\circ(700 \text{ K}) - \int_{298 \text{ K}}^{700 \text{ K}} \Delta C_p^\circ(T) dT \quad (19.57)$$

and the similar equation

$$\Delta_r S^\circ(298 \text{ K}) = \Delta_r S^\circ(700 \text{ K}) - \int_{298 \text{ K}}^{700 \text{ K}} \frac{\Delta C_p^\circ(T)}{T} dT$$

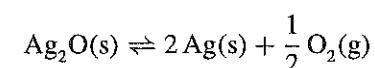
Substituting into the high-temperature expressions for $\Delta_r G^\circ$ and $\Delta_r H^\circ$ at 700 K, we find that $\Delta_r G^\circ(700 \text{ K}) = 9.78 \text{ kJ} \cdot \text{mol}^{-1}$, $\Delta_r H^\circ(700 \text{ K}) = 154.0 \text{ kJ} \cdot \text{mol}^{-1}$, and $\Delta_r S^\circ(700 \text{ K}) = 206.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. Then

$$\begin{aligned}\Delta_r S^\circ(298 \text{ K}) &= 206.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &\quad - R \int_{298 \text{ K}}^{700 \text{ K}} \left[\frac{1}{2} \left(\frac{4.8919}{T} - \frac{829.931 \text{ K}}{T^2} - \frac{127962 \text{ K}^2}{T^3} \right) + \frac{2.500}{T} - \frac{5.2995}{T} \right] dT \\ &= 206.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ &\quad - R \int_{298 \text{ K}}^{700 \text{ K}} \left(-\frac{0.35355}{T} - \frac{414.966 \text{ K}}{T^2} - \frac{63981 \text{ K}^2}{T^3} \right) dT \\ &= 206.1 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + 11.6 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 217.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r H^\circ(298 \text{ K}) &= 154.0 \text{ kJ} \cdot \text{mol}^{-1} \\ &\quad - R \int_{298 \text{ K}}^{700 \text{ K}} \left[\frac{1}{2} \left(\frac{4.8919}{T} - \frac{829.931 \text{ K}}{T^2} - \frac{127962 \text{ K}^2}{T^3} \right) + 2.500 - 5.2995 \right] dT \\ &= 154.0 \text{ kJ} \cdot \text{mol}^{-1} - R \int_{298 \text{ K}}^{700 \text{ K}} \left(-0.35355 - \frac{414.966 \text{ K}}{T} - \frac{63981 \text{ K}^2}{T^2} \right) dT \\ &= 154.0 \text{ kJ} \cdot \text{mol}^{-1} + 5.15 \text{ kJ} \cdot \text{mol}^{-1} = 159.2 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta_r G^\circ(298 \text{ K}) &= \Delta_r H^\circ(298 \text{ K}) - (298 \text{ K}) \Delta_r S^\circ(298 \text{ K}) \\ &= 159.2 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(217.7 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ &= 94.3 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

26-60. Consider the dissociation of $\text{Ag}_2\text{O}(\text{s})$ to $\text{Ag}(\text{s})$ and $\text{O}_2(\text{g})$ according to



Given the following “dissociation pressure” data:

$t/^\circ\text{C}$	173	178	183	188
P/torr	422	509	605	717

Express K_p in terms of P (in torr) and plot $\ln K_p$ versus $1/T$. An excellent curve fit to these data is given by

$$\ln K_p = 0.9692 + \frac{5612.7 \text{ K}}{T} - \frac{2.0953 \times 10^6 \text{ K}^2}{T^2}$$

Use this expression to derive an equation for $\Delta_r H^\circ$ from $445 \text{ K} < T < 460 \text{ K}$. Now use the following heat capacity data:

$$C_p^\circ[\text{O}_2(\text{g})]/R = 3.27 + (5.03 \times 10^{-4} \text{ K}^{-1})T$$

$$C_p^\circ[\text{Ag}(\text{s})]/R = 2.82 + (7.55 \times 10^{-4} \text{ K}^{-1})T$$

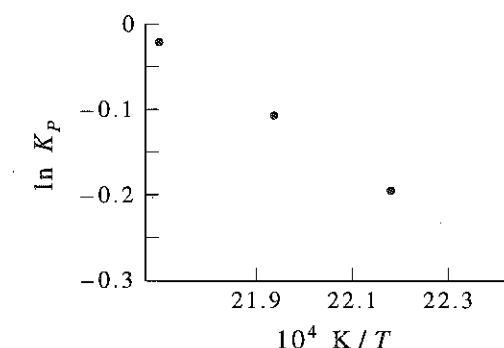
$$C_p^\circ[\text{Ag}_2\text{O}(\text{s})]/R = 6.98 + (4.48 \times 10^{-3} \text{ K}^{-1})T$$

to calculate $\Delta_r H^\circ$, $\Delta_r S^\circ$, and $\Delta_r G^\circ$ at 298 K.

We can write K_p in terms of the partial pressure of oxygen (assuming an activity of unity for the solids):

$$K_p = P_{\text{O}_2}^{1/2} = P^{1/2}$$

Below is a plot of the experimental $\ln K_p$ versus $1/T$ for this reaction.



We can now use the equation given in the problem for $\ln K_p$ in Equation 26.29 to find $\Delta_r H^\circ$ and in Equation 26.11 to find $\Delta_r G^\circ$ (as in the previous problem):

$$\frac{d \ln K_p}{dT} = -\frac{5612.7 \text{ K}}{T^2} + \frac{4.1906 \times 10^6 \text{ K}^2}{T^3}$$

$$\Delta_r H^\circ = RT^2 \frac{d \ln K_p}{dT}$$

$$\Delta_r H^\circ = R \left(-5612.7 \text{ K} + \frac{4.1906 \times 10^6 \text{ K}^2}{T} \right)$$

$$\Delta_r G^\circ = -RT \ln K_p$$

$$= R \left(-0.9692T - 5612.7 \text{ K} + \frac{2.0953 \times 10^6 \text{ K}^2}{T} \right)$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T}$$

The expression for $\ln K_p$ used in the above equalities holds for temperatures ranging from 445 K to 460 K. To find the values of $\Delta_r H^\circ$, $\Delta_r G^\circ$, and $\Delta_r S^\circ$ at 298 K, we can use the equation

$$\Delta_r H^\circ(298 \text{ K}) = \Delta_r H^\circ(450 \text{ K}) - \int_{298 \text{ K}}^{450 \text{ K}} \Delta C_p^\circ(T) dT \quad (19.57)$$

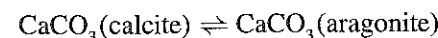
and the similar equation

$$\Delta_r S^\circ(298 \text{ K}) = \Delta_r S^\circ(450 \text{ K}) - \int_{298 \text{ K}}^{450 \text{ K}} \frac{\Delta C_p^\circ(T)}{T} dT$$

Substituting into the high-temperature expressions for $\Delta_r S^\circ$ and $\Delta_r H^\circ$ at 450 K, we find that $\Delta_r S^\circ(450 \text{ K}) = 94.09 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ and $\Delta_r H^\circ(450 \text{ K}) = 30.76 \text{ kJ} \cdot \text{mol}^{-1}$. Then

$$\begin{aligned} \Delta_r S^\circ(298 \text{ K}) &= 94.09 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - R \int_{298 \text{ K}}^{450 \text{ K}} \left[\frac{1}{2} \left(\frac{3.27}{T} + 5.03 \times 10^{-4} \text{ K}^{-1} \right) \right. \\ &\quad \left. + 2 \left(\frac{2.82}{T} + 7.55 \times 10^{-4} \text{ K}^{-1} \right) - \left(\frac{6.98}{T} + 4.48 \times 10^{-3} \text{ K}^{-1} \right) \right] dT \\ &= 94.09 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} - R \int_{298 \text{ K}}^{450 \text{ K}} \left(\frac{0.295}{T} + 1.31 \times 10^{-3} \text{ K}^{-1} \right) dT \\ &= 94.09 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} + 2.42 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} = 96.51 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \\ \Delta_r H^\circ(298 \text{ K}) &= 30.76 \text{ kJ} \cdot \text{mol}^{-1} - R \int_{298 \text{ K}}^{450 \text{ K}} \left\{ \frac{1}{2} [3.27 + (5.03 \times 10^{-4} \text{ K}^{-1})T] \right. \\ &\quad \left. 2 [2.82 + (7.55 \times 10^{-4} \text{ K}^{-1})T] - [6.98 + (4.48 \times 10^{-3} \text{ K}^{-1})T] \right\} dT \\ &= 30.76 \text{ kJ} \cdot \text{mol}^{-1} - R \int_{298 \text{ K}}^{450 \text{ K}} [0.295 + (1.31 \times 10^{-3} \text{ K}^{-1})T] dT \\ &= 30.76 \text{ kJ} \cdot \text{mol}^{-1} + 0.912 \text{ kJ} \cdot \text{mol}^{-1} = 31.67 \text{ kJ} \cdot \text{mol}^{-1} \\ \Delta_r G^\circ(298 \text{ K}) &= \Delta_r H^\circ(298 \text{ K}) - (298 \text{ K}) \Delta_r S^\circ(298 \text{ K}) \\ &= 31.67 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(96.51 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \\ &= 2.910 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

26-61. Calcium carbonate occurs as two crystalline forms, calcite and aragonite. The value of $\Delta_r G^\circ$ for the transition



is $+1.04 \text{ kJ} \cdot \text{mol}^{-1}$ at 25°C . The density of calcite at 25°C is $2.710 \text{ g} \cdot \text{cm}^{-3}$ and that of aragonite is $2.930 \text{ g} \cdot \text{cm}^{-3}$. At what pressure will these two forms of CaCO_3 be at equilibrium at 25°C .

The molar volume of aragonite is

$$\frac{1 \times 10^{-3} \text{ dm}^3}{2.930 \text{ g}} \left(\frac{100.09 \text{ g}}{1 \text{ mol}} \right) = 0.0342 \text{ dm}^3 \cdot \text{mol}^{-1}$$

and the molar volume of calcite is

$$\frac{1 \times 10^{-3} \text{ dm}^3}{2.710 \text{ g}} \left(\frac{100.09 \text{ g}}{1 \text{ mol}} \right) = 0.0369 \text{ dm}^3 \cdot \text{mol}^{-1}$$

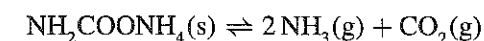
We can use Equation 26.65 for $\Delta_r G^\circ$ and Equation 26.69 to express the logarithmic terms. Note that when the forms are in equilibrium, the pressures will be equal.

$$\begin{aligned} \Delta_r G^\circ &= -RT \ln K_a = -RT \ln \frac{a_{\text{aragonite}}}{a_{\text{calcite}}} \\ 1040 \text{ J} \cdot \text{mol}^{-1} &= -RT \left[\frac{(0.0342 \text{ dm}^3 \cdot \text{mol}^{-1})(P-1)}{RT} - \frac{(0.0369 \text{ dm}^3 \cdot \text{mol}^{-1})(P-1)}{RT} \right] \\ &= (0.0027 \text{ dm}^3 \cdot \text{mol}^{-1})(P-1) \end{aligned}$$

Solving this equation for P gives

$$\begin{aligned} P-1 &= \left(\frac{1040 \text{ J} \cdot \text{mol}^{-1}}{0.0027 \text{ dm}^3 \cdot \text{mol}^{-1}} \right) \left(\frac{0.083145 \text{ dm}^3 \cdot \text{bar}}{8.3145 \text{ J}} \right) \\ P &= 3800 \text{ bar} \end{aligned}$$

26-62. The decomposition of ammonium carbamate, $\text{NH}_2\text{COONH}_4$, takes place according to



Show that if all the $\text{NH}_3(\text{g})$ and $\text{CO}_2(\text{g})$ result from the decomposition of ammonium carbamate, then $K_p = (4/27)P^3$, where P is the total pressure at equilibrium.

We can assume that the activity of the ammonium carbamate is unity, which means it makes no contribution to the equilibrium constant expression. We can write the number of moles of carbon dioxide present at equilibrium as ξ_{eq} and the number of moles of ammonia present at equilibrium as $2\xi_{\text{eq}}$, for a total of $3\xi_{\text{eq}}$ moles. (Since the ammonium carbamate is in solid phase and we have assumed that its activity is unity, it does not contribute to the total number of moles of gas present.) Then

$$P_{\text{NH}_3} = \frac{2\xi}{3\xi} P = \frac{2}{3} P \quad \text{and} \quad P_{\text{CO}_2} = \frac{\xi}{3\xi} P = \frac{1}{3} P$$

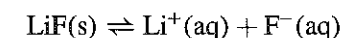
Then

$$K_p = P_{\text{NH}_3}^2 P_{\text{CO}_2} = \frac{4P^2}{9} \left(\frac{P}{3} \right) = \frac{4P^3}{27}$$

at equilibrium.

26-63. Calculate the solubility of $\text{LiF}(\text{aq})$ in water at 25°C . Compare your result to the one you obtain by using concentrations instead of activities. Take $K_{\text{sp}} = 1.7 \times 10^{-3}$.

The equation for the dissolution of $\text{LiF}(\text{s})$ is



and the equilibrium-constant expression is

$$a_{\text{Li}^+} a_{\text{F}^-} = c_{\text{Li}^+} c_{\text{F}^-} \gamma_{\pm}^2 = K_{\text{sp}} = 1.7 \times 10^{-3}$$

or

$$c_{\text{Li}^+} c_{\text{F}^-} = \frac{K_{\text{sp}}}{\gamma_{\pm}^2}$$

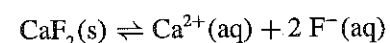
Let the solubility of LiF(s) be s , then $c_{\text{Li}^+} = c_{\text{F}^-} = s$. Therefore, we have

$$s^2 = \frac{K_{\text{sp}}}{\gamma_{\pm}^2} \quad (1)$$

Set $\gamma_{\pm} = 1$ and solve Equation 1 for s to obtain $s = (1.7 \times 10^{-3})^{1/2} \text{ mol} \cdot \text{L}^{-1} = 0.0412 \text{ mol} \cdot \text{L}^{-1}$. Now substitute this result into Equation 26.56 (with $I_c = s$) to calculate $\ln \gamma_{\pm} = -0.198$, or $\gamma_{\pm} = 0.820$. Substitute this value into Equation 1 to obtain $s = 0.0503 \text{ mol} \cdot \text{L}^{-1}$. The next iteration gives $\gamma_{\pm} = 0.807$, and then $s = 0.0511 \text{ mol} \cdot \text{L}^{-1}$. Once more gives $\gamma_{\pm} = 0.806$, so the final result is then $s = 0.0512 \text{ mol} \cdot \text{L}^{-1}$. Thus, $s = 0.051 \text{ mol} \cdot \text{L}^{-1}$ to two significant figures.

- 26-64.** Calculate the solubility of $\text{CaF}_2(\text{aq})$ in a solution that is 0.0150 molar in $\text{MgSO}_4(\text{aq})$. Take $K_{\text{sp}} = 3.9 \times 10^{-11}$ for $\text{CaF}_2(\text{aq})$.

The equation for the dissolution of $\text{CaF}_2(\text{s})$ is



and the equilibrium-constant expression is

$$c_{\text{Ca}^{2+}} c_{\text{F}^{-}}^2 \gamma_{\pm}^3 = K_{\text{sp}} = 3.9 \times 10^{-11}$$

Let the solubility of $\text{CaF}_2(\text{s})$ be s , then $\text{Ca}^{2+}(\text{aq}) = s$ and $\text{F}^{-}(\text{aq}) = 2s$. Therefore, we have

$$s(2s)^2 = 4s^3 = \frac{K_{\text{sp}}}{\gamma_{\pm}^3} \quad (1)$$

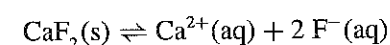
Set $\gamma_{\pm} = 1$ to obtain $s = 2.14 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. This value of s gives

$$\begin{aligned} I_c &= \frac{1}{2} [4s + 2s + (4)(0.0150 \text{ mol} \cdot \text{L}^{-1}) + (4)(0.0150 \text{ mol} \cdot \text{L}^{-1})] \\ &= 0.000641 \text{ mol} \cdot \text{L}^{-1} + 0.0600 \text{ mol} \cdot \text{L}^{-1} = 0.0606 \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$

Substituting this result into Equation 26.56 gives $\gamma_{\pm} = 0.629$. Substitute this value into Equation 1 to obtain $s = 3.40 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. Now $I_c = 0.0610 \text{ mol} \cdot \text{L}^{-1}$, and $\gamma_{\pm} = 0.628$. Now use this result in Equation 1 to get $s = 3.40 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. Another iteration gives $\gamma_{\pm} = 0.628$ and $s = 3.40 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. So, to two significant figures, $s = 3.4 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$.

- 26-65.** Calculate the solubility of $\text{CaF}_2(\text{aq})$ in a solution that is 0.050 molar in $\text{NaF}(\text{aq})$. Compare your result to the one you obtain by using concentrations instead of activities. Take $K_{\text{sp}} = 3.9 \times 10^{-11}$ for $\text{CaF}_2(\text{aq})$.

The equation for the dissolution of $\text{CaF}_2(\text{s})$ is



and the equilibrium-constant expression is (Problem 26-64)

$$4s^3 = \frac{K_{\text{sp}}}{\gamma_{\pm}^3} \quad (1)$$

Set $\gamma_{\pm} = 1$ to obtain $s = 2.14 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. This value of s gives

$$I_c = \frac{1}{2} [4s + 2s + (1)(0.050 \text{ mol} \cdot \text{L}^{-1}) + (1)(0.050 \text{ mol} \cdot \text{L}^{-1})] = 3s + 0.050 \text{ mol} \cdot \text{L}^{-1}$$

Because s is much smaller than $0.050 \text{ mol} \cdot \text{L}^{-1}$, we initially let $I_c = 0.050 \text{ mol} \cdot \text{L}^{-1}$. Substituting this value into Equation 26.56 gives $\gamma_{\pm} = 0.651$. Substitute this result into Equation 1 to obtain $s = 3.28 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. Now $I_c = 0.0510 \text{ mol} \cdot \text{L}^{-1}$, $\gamma_{\pm} = 0.649$, and $s = 3.29 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. Thus, $s = 3.3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$ to two significant figures.