

6 Chemical Equilibrium

Problem numbers in italics indicate that the solution is included in the *Student Solutions Manual*.

Conceptual Problems

- Q6.1** It is found that K_p is independent of T for a particular chemical reaction. What does this tell you about the reaction?

This is true if $\Delta H_R = 0$ because $\frac{d \ln K_p}{dT}$ is proportional to ΔH .

- Q6.2** The reaction $A + B \rightleftharpoons C + D$ is at equilibrium for $\xi = 0.1$. What does this tell you about the variation of G_{pure} with ξ ?

It tells you that ΔG_f° for $A + B$ is less than that for $C + D$. If the ΔG_f° of reactants and products were nearly the same, ξ_{eq} would be near 0.5. If the ΔG_f° for the products were much less than those for the reactants, ξ_{eq} would be near 1.

- Q6.3** Under what condition is $K_p = K_x$?

This is the case for a reaction involving gases if $\Delta n = 0$ because, as shown in Equation (6.78),

$$K_x = K_p \left(\frac{P}{P^\circ} \right)^{-\Delta n}$$

- Q6.4** What is the relationship between the K_p for the two reactions $\frac{3}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{N}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$ and $3\text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$?

K_p for the second reaction is the square of K_p for the first reaction, as can be seen the reaction quotient

$$\frac{\left(\frac{P_{\text{NH}_3}}{P^\circ} \right)}{\left(\frac{P_{\text{H}_2}}{P^\circ} \right)^{3/2} \left(\frac{P_{\text{N}_2}}{P^\circ} \right)^{1/2}} \text{ and } \frac{\left(\frac{P_{\text{NH}_3}}{P^\circ} \right)^2}{\left(\frac{P_{\text{H}_2}}{P^\circ} \right)^3 \left(\frac{P_{\text{N}_2}}{P^\circ} \right)}$$

- Q6.5** Under what conditions is $dA \leq 0$ a condition that defines the spontaneity of a process?

This is the case at constant T and V if no nonexpansion work is possible.

- Q6.6** By invoking the pressure dependence of the chemical potential, show that if a valve separating a vessel of pure A from a vessel containing a mixture of A and B is opened, mixing will occur. Both A and B are ideal gases, and the initial pressure in both vessels is 1 bar.

The chemical potential of A in the mixture is less than in the pure gas because $\mu_A(T, P) = \mu_A^\circ(T) + RT \ln \frac{P_A}{P^\circ}$, and $P_A < P^\circ$. Because mass flows from regions of high chemical potential to regions of low chemical potential, pure A will flow into the mixture, and the contents of both vessels will be mixed.

- Q6.7** Under what conditions is $dG \leq 0$ a condition that defines the spontaneity of a process?
This is the case at constant T and P if no nonexpansion work is possible.
- Q6.8** Can equilibrium with respect to the concentration of Ar and H_2 be attained in the system shown in Figure 6.2? If so, what can you say about the partial pressure in each part of the system?
No, because H_2 but not Ar can diffuse through the Pd membrane. Equilibrium can be attained with respect to the partial pressure of H_2 , which will be equal in the two parts of the system.
- Q6.9** Is the equation $(\partial U/\partial V)_T = (\beta T - \kappa P)/\kappa$ valid for liquids, solids, and gases?
Yes. No assumptions have been made in deriving this differential relationship.
- Q6.10** Why is it reasonable to set the chemical potential of a pure liquid or solid substance equal to its standard state chemical potential at that temperature independent of the pressure in considering chemical equilibrium?
The pressure dependence of G for solids and liquids is very small, because the volume of liquids and solids changes very little unless very high pressures are applied. Therefore, it is a good approximation to set the chemical potential of a pure liquid or solid substance equal to its standard state chemical potential at the temperature of interest.
- Q6.11** The reaction $A + B \rightleftharpoons C + D$ is at equilibrium for $\xi = 0.5$. What does this tell you about the variation of G_{pure} with ξ ?
It tells you that ΔG_f° for $A + B$ is equal to that for $C + D$. If the ΔG_f° for the products were much less than those for the reactants, ξ would be near 1. If the ΔG_f° for the reactants were less than those for the products, ξ would be smaller than 0.5.
- Q6.12** Which thermodynamic state function gives a measure of the maximum electric work that can be carried out in a fuel cell?
 ΔG because $dG \leq \delta w_{nonexpansion}$
- Questions 6.13–6.18 refer to the reaction system $CO(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO_2(g)$ at equilibrium for which $\Delta H_R^\circ = -283.0 \text{ kJ mol}^{-1}$.**
- Q6.13** Predict the change in the partial pressure of CO_2 as the temperature is increased at constant total pressure.
It will decrease, following Le Chatelier's principle, because the reaction is exothermic.
- Q6.14** Predict the change in the partial pressure of CO_2 as the pressure is increased at constant temperature.
It will increase, following Le Chatelier's principle, because $\Delta n < 0$.
- Q6.15** Predict the change in the partial pressure of CO_2 as Xe gas is introduced into the reaction vessel at constant pressure and temperature.
It will decrease. Using Le Chatelier's principle, the reaction will shift toward reactants because $\Delta n < 0$ to oppose the decrease in volume.
- Q6.16** Predict the change in the partial pressure of CO_2 as Xe gas is introduced into the reaction vessel at constant volume and temperature.
There will be no change because the equilibrium does not involve Xe.
- Q6.17** Predict the change in the partial pressure of CO_2 as a platinum catalyst is introduced into the reaction vessel at constant volume and temperature.
The catalyst will have no effect because the system is already at equilibrium. A catalyst can increase the rate at which equilibrium is achieved, but cannot change the position of equilibrium.

Q6.18 Predict the change in the partial pressure of CO_2 as O_2 is removed from the reaction vessel at constant pressure and temperature.

It will decrease to reestablish equilibrium as the reactant oxygen is removed.

Q6.19 Calculate the maximum expansion work that is available in carrying out the combustion reactions in Example Problems 6.1 and 6.2. Explain both the magnitude and the sign of the work.

From Example Problem 6.1, the maximum work available is -814 kJ mol^{-1} for methane oxidation and $-5285 \text{ kJ mol}^{-1}$ for octane oxidation. From Example Problem 6.2, the maximum nonexpansion work available is -818 kJ mol^{-1} for methane oxidation and $-5296 \text{ kJ mol}^{-1}$ for octane oxidation. Because $w_{\text{total}} = w_{\text{expansion}} + w_{\text{nonexpansion}}$, the expansion work available is 4 kJ mol^{-1} for methane oxidation and 11 kJ mol^{-1} for octane oxidation. The work is positive because Δn gas is negative. The expansion work is much smaller than the nonexpansion work because the volume change is small.

Q6.20 Is the equation $\Delta G = \Delta H - T\Delta S$ applicable to all processes?

No, only when T is constant. Otherwise, $\Delta G = \Delta H - \Delta(TS)$.

Q6.21 Is the equation $\Delta A = \Delta U - T\Delta S$ applicable to all processes?

No, only when T is constant. Otherwise, $\Delta A = \Delta U - \Delta(TS)$.

Q6.22 Under what conditions is $K_x > K_p$?

$$K_x > K_p \text{ when } (P/P^\circ)^{-\Delta\nu} > 1.$$

Q6.23 Under what conditions is the distribution of products in an ideal gas reactions system at equilibrium unaffected by an increase in the pressure?

The distribution of products in an ideal gas reactions system at equilibrium is unaffected by an increase in the pressure if the number of moles of gaseous products equals the number of moles of gaseous reactants.

Q6.24 If K_p is independent of pressure, why does the degree of dissociation in the reaction $\text{Cl}_2(\text{g}) \rightleftharpoons 2\text{Cl}(\text{g})$ depend on pressure?

The degree of dissociation depends on K_x , which is not independent of pressure.

Questions 6.25–6.28 refer to the reaction system $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2\text{HCl}(\text{g})$ at equilibrium. Assume ideal gas behavior.

Q6.25 How does the total number of moles in the reaction system change as T increases?

It does not change because $\Delta\nu = 0$.

Q6.26 If the reaction is carried out at constant V , how does the total pressure change if T increases?

P changes in accord with the ideal gas law and increases as T increases.

Q6.27 Is the partial pressure of $\text{H}_2(\text{g})$ dependent on T ? If so, how will it change as T decreases?

The reaction is exothermic. Therefore, the equilibrium shifts toward products as the temperature decreases and the partial pressure of $\text{H}_2(\text{g})$ decreases.

Q6.28 If the total pressure is increased at constant T , how will the relative amounts of $\text{H}_2(\text{g})$ and $\text{HCl}(\text{g})$ change?

There will be no change because $\Delta\nu = 0$.

Q6.29 If additional $\text{Cl}_2(\text{g})$ is added to the reaction system at constant total pressure and temperature, how will the partial pressures of $\text{H}_2(\text{g})$ and $\text{HCl}(\text{g})$ change?

The equilibrium constant $K_p = \frac{(P_{\text{HCl}}/P^\circ)^2}{(P_{\text{H}_2}/P^\circ)(P_{\text{Cl}_2}/P^\circ)}$ is unchanged because T is constant. Because the total pressure

is constant, the volume of the system increases, but the partial pressure of all species remains constant.

Q6.30 If additional $\text{Cl}_2(g)$ is added to the reaction system at constant V and T , how will the degree of dissociation of $\text{HCl}(g)$ change?

The equilibrium constant $K_p = \frac{(P_{\text{HCl}}/P^\circ)^2}{(P_{\text{H}_2}/P^\circ)(P_{\text{Cl}_2}/P^\circ)}$ is unchanged because the temperature is constant. As $\text{Cl}_2(g)$ is

added to the reaction system at constant volume, its partial pressure increases and the total pressure increases. Because of the change in partial pressure of $\text{Cl}_2(g)$, the reaction shifts toward products: $P_{\text{HCl}}(g)$ increases and $P_{\text{H}_2}(g)$ decreases. The degree of dissociation is unaffected by the change in total pressure because $\Delta\nu = 0$.

Q6.31 If T is increased at constant total pressure, how will the degree of dissociation of $\text{HCl}(g)$ change?

Because the reaction is exothermic, the degree of dissociation increases as T increases.

Numerical Problems

P6.1 Calculate ΔA_R° and ΔG_R° for the reaction $\text{C}_6\text{H}_6(l) + \frac{15}{2}\text{O}_2(g) \rightarrow 6\text{CO}_2(g) + 3\text{H}_2\text{O}(l)$ at 298 K from the combustion enthalpy of benzene and the entropies of the reactants and products.

All gaseous reactants and products are treated as ideal gases.

$$\Delta G_{\text{combustion}}^\circ = \Delta H_{\text{combustion}}^\circ - T\Delta S_{\text{combustion}}^\circ$$

$$\begin{aligned}\Delta S_{\text{combustion}}^\circ &= 6S^\circ(\text{CO}_2, g) + 3S^\circ(\text{H}_2\text{O}, l) - S^\circ(\text{C}_6\text{H}_6, l) - 15/2S^\circ(\text{O}_2, g) \\ &= 6 \times 213.8 \text{ J mol}^{-1} \text{ K}^{-1} + 3 \times 70.0 \text{ J mol}^{-1} \text{ K}^{-1} - 173.4 \text{ J mol}^{-1} \text{ K}^{-1} - 15/2 \times 205.2 \text{ J mol}^{-1} \text{ K}^{-1} \\ &= -219.6 \text{ J mol}^{-1} \text{ K}^{-1}\end{aligned}$$

$$\Delta G_{\text{combustion}}^\circ = -3268 \times 10^3 \text{ kJ mol}^{-1} - 298.15 \text{ K} \times (-219.6 \text{ J mol}^{-1} \text{ K}^{-1}) = -3203 \times 10^3 \text{ kJ mol}^{-1}$$

$$\begin{aligned}\Delta A_{\text{combustion}}^\circ &= \Delta U_{\text{combustion}}^\circ - T\Delta S_{\text{combustion}}^\circ \\ &= \Delta H_{\text{combustion}}^\circ - \Delta(PV)_{\text{combustion}} - T\Delta S_{\text{combustion}}^\circ \\ &= \Delta G_{\text{combustion}}^\circ + T\Delta S_{\text{combustion}}^\circ - \Delta(PV) - T\Delta S_{\text{combustion}}^\circ \\ &= \Delta G_{\text{combustion}}^\circ - \Delta nRT\end{aligned}$$

where Δn is the change in the number of moles of gas phase species in the reaction

$$\begin{aligned}\Delta A_{\text{combustion}}^\circ &= -3203 \times 10^3 \text{ kJ mol}^{-1} + 1.5 \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \\ &= -3199 \times 10^3 \text{ kJ mol}^{-1}\end{aligned}$$

The change in PV for the liquid can be neglected because liquids are essentially incompressible over the pressure range in this problem.

P6.2 Calculate K_p at 298 and 490. K for the reaction $\text{NO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{NO}_2(g)$ assuming that ΔH_R° is constant over the interval 298–600. K. Do you expect K_p to increase or decrease as the temperature is increased to 600. K?

$$\begin{aligned}\Delta H_R^\circ &= \Delta H_f^\circ(\text{NO}_2, g) - \Delta H_f^\circ(\text{NO}, g) \\ &= 33.2 \times 10^3 \text{ J mol}^{-1} - 91.3 \times 10^3 \text{ J mol}^{-1} = -58.1 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G_R^\circ &= 2\Delta G_f^\circ(\text{NO}_2, g) - \Delta G_f^\circ(\text{NO}, g) \\ &= 51.3 \times 10^3 \text{ J mol}^{-1} - 87.6 \times 10^3 \text{ J mol}^{-1} = -36.3 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

$$\ln K_p(298 \text{ K}) = \frac{\Delta G_R^\circ(298 \text{ K})}{RT} = \frac{-36.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}} = 14.6441$$

$$K_p(298 \text{ K}) = 2.29 \times 10^6$$

Using Equation (6.66),

$$\ln K_p(T_f) = -\frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(525 \text{ K}) = \frac{36.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} + \frac{58.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{490. \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(490. \text{ K}) = 5.46715$$

$$K_p(490. \text{ K}) = 2.37 \times 10^2$$

Because $\Delta H_R^\circ < 0$, K_p decreases as T increases.

P6.3 A sample containing 2.75 moles of N_2 and 6.25 mol of H_2 is placed in a reaction vessel and brought to equilibrium at 52.0 bar and 690. K in the reaction $\frac{1}{2}\text{N}_2(\text{g}) + \frac{3}{2}\text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$.

- Calculate K_p at this temperature.
- Set up an equation relating K_p and the extent of reaction as in Example Problem 6.10.
- Using numerical equation solving software, calculate the number of moles of each species present at equilibrium.

(a) $\Delta H_R^\circ = \Delta H_f^\circ(\text{NH}_3, \text{g}) = -45.9 \times 10^3 \text{ J mol}^{-1}$
 $\Delta G_R^\circ(298.15 \text{ K}) = \Delta G_f^\circ(\text{NH}_3, \text{g}) = -16.5 \times 10^3 \text{ J mol}^{-1}$

$$\ln K_p(T_f) = -\frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(690. \text{ K}) = \frac{16.5 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} + \frac{45.9 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{690. \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$= -3.85931$$

$$K_p(690. \text{ K}) = 2.11 \times 10^{-2}$$

(b)

	$\frac{1}{2}\text{N}_2(\text{g})$	+	$\frac{3}{2}\text{H}_2(\text{g})$	\leftrightarrow	$\text{NH}_3(\text{g})$
Initial number of moles	2.75		6.25		0
Moles present at equilibrium	$2.75 - \xi$		$6.25 - 3\xi$		2ξ
Mole fraction present at equilibrium	$\frac{2.75 - \xi}{9.00 - 2\xi}$		$\frac{6.25 - 3\xi}{9.00 - 2\xi}$		$\frac{2\xi}{9.00 - 2\xi}$
Partial pressure at equilibrium, $P_i = x_i P$	$\frac{2.75 - \xi}{9.00 - 2\xi} P$		$\frac{6.25 - 3\xi}{9.00 - 2\xi} P$		$\left(\frac{2\xi}{9.00 - 2\xi} \right) P$

We next express K_p in terms of n_0 , ξ , and P .

$$K_p(T) = \frac{\left(\frac{P^{\text{eq}}_{\text{NH}_3}}{P^\circ} \right)}{\left(\frac{P^{\text{eq}}_{\text{N}_2}}{P^\circ} \right)^{\frac{1}{2}} \left(\frac{P^{\text{eq}}_{\text{H}_2}}{P^\circ} \right)^{\frac{3}{2}}} = \frac{\left(\frac{2\xi}{9.00 - 2\xi} \right) \frac{P}{P^\circ}}{\left(\left(\frac{2.75 - \xi}{9.00 - 2\xi} \right) \frac{P}{P^\circ} \right)^{\frac{1}{2}} \left(\left(\frac{6.25 - 3\xi}{9.00 - 2\xi} \right) \frac{P}{P^\circ} \right)^{\frac{3}{2}}}$$

The following equation can be solved numerically using a program such as Mathematica.

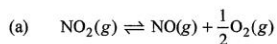
$$K_p(T) = \frac{\left(\frac{2\xi}{9.00 - 2\xi}\right)52.0}{\left(\left(\frac{2.75 - \xi}{9.00 - 2\xi}\right)52.0\right)^{\frac{1}{2}}\left(\left(\frac{6.25 - 3\xi}{9.00 - 2\xi}\right)52.0\right)^{\frac{3}{2}}} = 2.11 \times 10^{-2}$$

The physically meaningful root of the cubic equation is $\xi = 0.7902$. Therefore, there are 1.96 moles of $\text{N}_2(\text{g})$, 3.88 moles of $\text{H}_2(\text{g})$, and 1.58 moles of $\text{NH}_3(\text{g})$ at equilibrium.

P6.4 Consider the equilibrium $\text{NO}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$. One mole of $\text{NO}_2(\text{g})$ is placed in a vessel and allowed to come to equilibrium at a total pressure of 1 bar. An analysis of the contents of the vessel gives the following results:

T	700. K	800. K
$P_{\text{NO}}/P_{\text{NO}_2}$	0.872	2.50

- Calculate K_p at 700. and 800. K.
- Calculate ΔG_R° and ΔH_R° for this reaction at 298.15 K, using only the data in the problem. Assume that ΔH_R° is independent of temperature.
- Calculate ΔG_R° and ΔH_R° using the data tables and compare your answer with that obtained in part (b).



$$K_p = \frac{(P_{\text{NO}}/P^\circ)(P_{\text{O}_2}/P^\circ)^{1/2}}{P_{\text{NO}_2}/P^\circ}$$

At 700. K, $\frac{P_{\text{NO}}}{P_{\text{NO}_2}} = 0.872$ and $P_{\text{O}_2} = \frac{1}{2}P_{\text{NO}}$

$$P_{\text{total}} = P_{\text{NO}} + P_{\text{NO}_2} + P_{\text{O}_2} = 1 \text{ bar}$$

$$1 \text{ bar} = 0.872 P_{\text{NO}_2} + P_{\text{NO}_2} + 0.436 P_{\text{NO}_2}$$

$$P_{\text{NO}_2} = 0.4333 \text{ bar}$$

$$K_p = \frac{(0.872 \times 0.4333) \times \sqrt{0.436 \times 0.4333}}{0.4333} = 0.379$$

At 800. K, $\frac{P_{\text{NO}}}{P_{\text{NO}_2}} = 2.50$ and $P_{\text{O}_2} = \frac{1}{2}P_{\text{NO}}$

$$P_{\text{total}} = P_{\text{NO}} + P_{\text{NO}_2} + P_{\text{O}_2}$$

$$1 \text{ bar} = 2.50 P_{\text{NO}_2} + P_{\text{NO}_2} + 1.25 P_{\text{NO}_2}$$

$$P_{\text{NO}_2} = 0.2105 \text{ bar}$$

$$K_p = \frac{(2.50 \times 0.2105) \times \sqrt{1.25 \times 0.2105}}{0.2105} = 1.28$$

- (b) Assuming that
- ΔH_R°
- is independent of temperature,

$$\ln \frac{K_p(800. \text{ K})}{K_p(700. \text{ K})} = \frac{-\Delta H_R^\circ}{R} \left(\frac{1}{800. \text{ K}} - \frac{1}{700. \text{ K}} \right)$$

$$\Delta H_R^\circ = - \frac{R \times \ln \left(\frac{K_p(800. \text{ K})}{K_p(700. \text{ K})} \right)}{\left(\frac{1}{800. \text{ K}} - \frac{1}{700. \text{ K}} \right)} = 56.7 \times 10^3 \text{ J mol}^{-1}$$

$$\ln K_p(298.15 \text{ K}) = \ln K_p(700. \text{ K}) - \frac{\Delta H_R^\circ}{R} \times \left(\frac{1}{298.15 \text{ K}} - \frac{1}{700. \text{ K}} \right) = -14.1141$$

$$\Delta G_R^\circ(298.15 \text{ K}) = -RT \ln K_p(298.15 \text{ K})$$

$$= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times (-14.1141)$$

$$= 35.0 \times 10^3 \text{ J mol}^{-1}$$

- (c)
- $\Delta H_R^\circ = \Delta H_f^\circ(\text{NO}, g) - \Delta H_f^\circ(\text{NO}_2, g)$
-
- $= 91.3 \times 10^3 \text{ J mol}^{-1} - 33.2 \times 10^3 \text{ J mol}^{-1} = 58.1 \times 10^3 \text{ J mol}^{-1}$

P6.5 The shells of marine organisms contain calcium carbonate CaCO_3 , largely in a crystalline form known as calcite. There is a second crystalline form of calcium carbonate known as aragonite. Physical and thermodynamic properties of calcite and aragonite are given below.

Properties ($T = 298 \text{ K}$, $P = 1 \text{ bar}$)	Calcite	Aragonite
ΔH_f° (kJ mol ⁻¹)	-1206.9	-1207.0
ΔG_f° (kJ mol ⁻¹)	-1128.8	-1127.7
S° (J K ⁻¹ mol ⁻¹)	92.9	88.7
$C_{p,m}$ (J K ⁻¹ mol ⁻¹)	81.9	81.3
Density (g mL ⁻¹)	2.710	2.930

- a. Based on the thermodynamic data given, would you expect an isolated sample of calcite at $T = 298 \text{ K}$ and $P = 1 \text{ bar}$ to convert to aragonite, given sufficient time? Explain.
- b. Suppose the pressure applied to an isolated sample of calcite is increased. Can the pressure be increased to the point that isolated calcite will be converted to aragonite? Explain.
- c. What pressure must be achieved to induce the conversion of calcite to aragonite at $T = 298 \text{ K}$? Assume both calcite and aragonite are incompressible at $T = 298 \text{ K}$.
- d. Can calcite be converted to aragonite at $P = 1.00 \text{ bar}$ if the temperature is increased? Explain.
- (a) $\Delta G_R(298.15 \text{ K}) = \Delta G_f^\circ(\text{calcite}, s) - \Delta G_f^\circ(\text{aragonite}, s)$
 $= 1128.8 \text{ kJ mol}^{-1} - 1127.7 \text{ kJ mol}^{-1}$
 $= 1.1 \text{ kJ mol}^{-1}$

Because $\Delta G_R(298.15 \text{ K}) > 0$, the reaction is not spontaneous.

(b) and (c) $\Delta G(T, P_f) = \Delta G(T, P_i) + \Delta V(P_f - P_i)$

At equilibrium, $\Delta G(T, P_f) = 0$ so that

$$\begin{aligned} P_f &= 1 \text{ bar} - \frac{\Delta G_f(\text{calcite}) - \Delta G_f(\text{aragonite})}{V(\text{calcite}) - V(\text{aragonite})} \\ &= 1 \text{ bar} - \frac{\Delta G_f(\text{calcite}) - \Delta G_f(\text{aragonite})}{M_{\text{CaCO}_3} \times \left[\frac{1}{\rho(\text{calcite})} - \frac{1}{\rho(\text{aragonite})} \right]} \\ P_f &= 1 \text{ bar} - \frac{1.1 \text{ kJ}}{100.9 \times 10^{-3} \text{ kg} \times \left[\frac{1}{2.930 \times 10^3 \text{ kg m}^{-3}} - \frac{1}{2.710 \times 10^3 \text{ kg m}^{-3}} \right]} \\ &= 4.0 \times 10^3 \text{ bar} \end{aligned}$$

(d) Because the reactant and product are essentially equal, K_p will change only slightly with increasing T at constant P . Therefore the conversion will not occur at 1.00 bar.

P6.6 Consider the equilibrium $\text{C}_2\text{H}_6(\text{g}) \rightleftharpoons \text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g})$. At 1000. K and a constant total pressure of 1.00 bar, $\text{C}_2\text{H}_6(\text{g})$ is introduced into a reaction vessel. The total pressure is held constant at 1 bar and at equilibrium the composition of the mixture in mole percent is $\text{H}_2(\text{g})$: 26.0%, $\text{C}_2\text{H}_4(\text{g})$: 26.0%, and $\text{C}_2\text{H}_6(\text{g})$: 48.0%.

- Calculate K_p at 1000. K.
- If $\Delta H_R^\circ = 137.0 \text{ kJ mol}^{-1}$, calculate the value of K_p at 298.15 K.
- Calculate ΔG_R° for this reaction at 298.15 K.

$$(a) \quad K_x(1000. \text{ K}) = \frac{x_{\text{C}_2\text{H}_4} x_{\text{H}_2}}{x_{\text{C}_2\text{H}_6}} = \frac{0.260 \times 0.260}{0.480} = 0.1408$$

$$K_p(1000. \text{ K}) = K_x(1000. \text{ K}) \times \frac{P}{P^\circ} = 1 \times 0.1408 = 0.141$$

$$(b) \quad \ln K_p(298.15 \text{ K}) = \ln K_p(1000. \text{ K}) - \frac{\Delta H_R}{R} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{1000. \text{ K}} \right)$$

$$= -1.96018 - \frac{137.0 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{298.15 \text{ K}} - \frac{1}{1000. \text{ K}} \right) = -40.7502$$

$$K_p(298.15 \text{ K}) = 2.01 \times 10^{-18}$$

$$(c) \quad \Delta G_R(298.15 \text{ K}) = -RT \ln K_p(298.15 \text{ K}) = 1.01 \times 10^5 \text{ J mol}^{-1}$$

P6.7 The pressure dependence of G is quite different for gases and condensed phases. Calculate ΔG_m for the processes $(\text{C}, \text{solid, graphite}, 1 \text{ bar}, 298.15 \text{ K}) \rightarrow (\text{C}, \text{solid, graphite}, 325 \text{ bar}, 298.15 \text{ K})$ and $(\text{He}, \text{g}, 1 \text{ bar}, 298.15 \text{ K}) \rightarrow (\text{He}, \text{g}, 325 \text{ bar}, 298.15 \text{ K})$. By what factor is ΔG_m^\ddagger greater for He than for graphite?

For a solid or liquid, we can assume that the volume is independent of pressure over a limited range in P .

$$\Delta G = \int_{P_i}^{P_f} V dP = V(P_f - P_i)$$

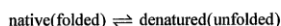
$$\begin{aligned} \Delta G_m(\text{C}, \text{s}, 325 \text{ bar}) &= \Delta G_m(\text{C}, \text{s}, 1 \text{ bar}) + V_m(P_f - P_i) = G_m(\text{C}, \text{s}, 1 \text{ bar}) + \frac{M}{\rho}(P_f - P_i) \\ &= 0 + \frac{12.011 \times 10^{-3} \text{ kg/mol}}{2250 \text{ kg m}^{-3}} \times 324.0 \times 10^5 \text{ Pa} = 173 \text{ J mol}^{-1} \end{aligned}$$

Treating He as an ideal gas,

$$\begin{aligned} G_m(\text{He}, g, 325 \text{ bar}) &= G_m(\text{He}, g, 1 \text{ bar}) + \int_{P_i}^{P_f} V dP \\ &= 0 + RT \ln \frac{P_f}{P_i} = 1 \text{ mole} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \ln \frac{325 \text{ bar}}{1 \text{ bar}} = 14.3 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

This result is a factor of 82.9 greater than that for graphite.

P6.8 Many biological macromolecules undergo a transition called denaturation. Denaturation is a process whereby a structured, biologically active molecule, called the native form, unfolds or becomes unstructured and biologically inactive. The equilibrium is



For a protein at pH = 2 the enthalpy change at 298 K associated with denaturation is $\Delta H^\circ = 418.0 \text{ kJ mol}^{-1}$ and the entropy change at 298 K is $\Delta S^\circ = 1.30 \text{ kJ K}^{-1} \text{ mol}^{-1}$.

- Calculate the Gibbs energy change for the denaturation of the protein at pH = 2 and $T = 310 \text{ K}$. Assume the enthalpy and entropy are temperature-independent between 298.15 K and 310 K.
- Calculate the equilibrium constant for the denaturation of the protein at pH = 2 and $T = 310 \text{ K}$.
- Based on your answer for parts (a) and (b), is the protein structurally stable at pH = 2 and $T = 310 \text{ K}$?

(a) We use the Gibbs–Helmholtz equation to solve this part.

$$\begin{aligned} \Delta G_{den}(298.15 \text{ K}) &= \Delta H_{den} - T\Delta S_{den} = 418.0 \times 10^3 \text{ J mol}^{-1} - 298.15 \text{ K} \times 1.30 \text{ kJ K}^{-1} \text{ mol}^{-1} \\ &= 30.41 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

$$\Delta G_{den}(T_2) = T_2 \times \left[\frac{\Delta G_{den}(T_1)}{T_1} + \Delta H_{den} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

$$\begin{aligned} \Delta G_{den}(310 \text{ K}) &= 310 \text{ K} \times \left[\frac{30.41 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} + 418.0 \times 10^3 \text{ J mol}^{-1} \times \left(\frac{1}{310 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \\ &= 15.0 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

$$(b) \quad K_p(310 \text{ K}) = \exp \left[-\frac{\Delta G_{den}}{RT} \right] = \exp \left[-\frac{15.0 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 310 \text{ K}} \right] = 2.97 \times 10^{-3}$$

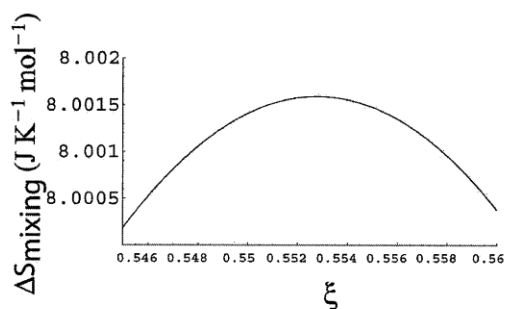
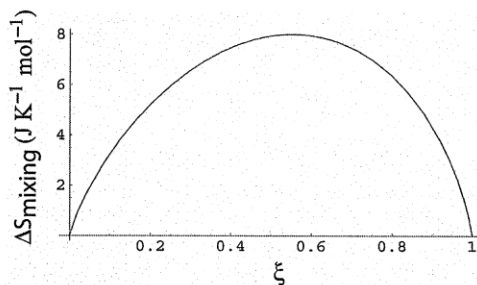
(c) Because $K_p \ll 1$ for the denaturation process, the protein is stable at 310 K.

P6.9 Assume that a sealed vessel at constant pressure of 1 bar initially contains 2.00 mol of $\text{NO}_2(g)$. The system is allowed to equilibrate with respect to the reaction $2\text{NO}_2(g) \rightleftharpoons \text{N}_2\text{O}_4(g)$. The number of moles of $\text{NO}_2(g)$ and $\text{N}_2\text{O}_4(g)$ at equilibrium is $2.00 - 2\xi$ and ξ , respectively, where ξ is the extent of reaction.

- Derive an expression for the entropy of mixing as a function of ξ .
- Graphically determine the value of ξ for which ΔS_{mixing} has its maximum value.
- Write an expression for G_{pure} as a function of ξ . Use Equation (6.104) to obtain values of G_m° for NO_2 and N_2O_4 .
- Plot $G_{mixture} = G_{pure} + \Delta G_{mixing}$ as a function of ξ for $T = 298 \text{ K}$ and graphically determine the value of ξ for which $G_{mixture}$ has its minimum value. Is this value the same as for part (b)?

$$\begin{aligned} (a) \quad \Delta S_{mixing} &= -nR(x_{\text{NO}_2} \ln x_{\text{NO}_2} + x_{\text{N}_2\text{O}_4} \ln x_{\text{N}_2\text{O}_4}) \\ &= -(2.00 - \xi)R \left(\frac{2.00 - 2\xi}{2.00 - \xi} \ln \frac{2.00 - 2\xi}{2.00 - \xi} + \frac{\xi}{2.00 - \xi} \ln \frac{\xi}{2.00 - \xi} \right) \end{aligned}$$

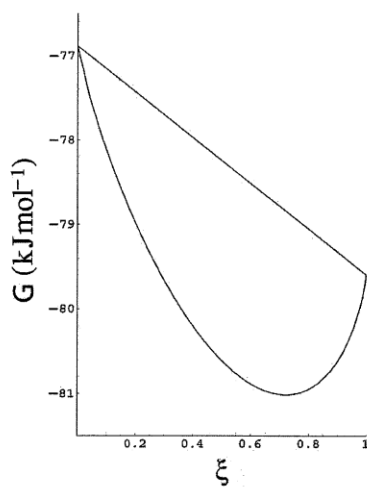
- (b) A plot and a detail plot locating the maximum are shown below.



The value of ξ at the maximum is $\xi = 0.553$.

- (c) $G_{\text{pure}} = (2.00 - 2\xi)\Delta G_f^\circ(\text{NO}_2, g) + \xi\Delta G_f^\circ(\text{N}_2\text{O}_4, g)$.

(d)



We use Equation (6.50) to relate the entropy and Gibbs energy of mixing. The minimum is at $\xi = 0.72$. The minimum in the figure above is shifted to higher values of ξ relative to the ΔS versus ξ curve for mixing because of the contribution of G_{pure} to ΔG_R .

- P6.10** Calculate K_p at 600. K for the reaction $\text{N}_2\text{O}_4(l) \rightleftharpoons 2\text{NO}_2(g)$ assuming that ΔH_R° is constant over the interval 298–725 K.

$$\begin{aligned}\Delta H_R^\circ &= 2\Delta H_f^\circ(\text{NO}_2, g) - \Delta H_f^\circ(\text{N}_2\text{O}_4, l) \\ &= 2 \times 33.2 \times 10^3 \text{ J mol}^{-1} + 19.5 \times 10^3 \text{ J mol}^{-1} = 85.9 \times 10^3 \text{ J mol}^{-1} \\ \Delta G_R^\circ &= 2\Delta G_f^\circ(\text{NO}_2, g) - \Delta G_f^\circ(\text{N}_2\text{O}_4, l) \\ &= 2 \times 51.3 \times 10^3 \text{ J mol}^{-1} - 97.5 \times 10^3 \text{ J mol}^{-1} = 5.1 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

We use the Gibbs–Helmholtz equation to relate the Gibbs reaction energy at two temperatures.

$$\begin{aligned}\ln K_p(T_f) &= -\frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right) \\ \ln K_p(600. \text{ K}) &= -\frac{5.10 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{85.9 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{600. \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\ \ln K_p(600. \text{ K}) &= 15.3762 \\ K_p(600. \text{ K}) &= 4.76 \times 10^6\end{aligned}$$

- P6.11** Consider the equilibrium $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$. At 1150. K, the composition of the reaction mixture is

Substance	$\text{CO}_2(g)$	$\text{H}_2(g)$	$\text{CO}(g)$	$\text{H}_2\text{O}(g)$
Mole %	20.3	20.3	29.7	29.7

- a. Calculate K_p and ΔG_R° at 1150. K.
 b. Given the answer to part (a), use the ΔH_f° of the reaction species to calculate ΔG_R° at 298.15 K. Assume that ΔH_R° is independent of temperature.

- (a) $\text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$

$$K_p = \frac{(P_{\text{CO}_2}/P^\circ) \times (P_{\text{H}_2}/P^\circ)}{(P_{\text{CO}}/P^\circ) \times (P_{\text{H}_2\text{O}}/P^\circ)}$$

For each component, $P_i = x_i P_{\text{total}}$ because $\Delta n = 0$, $K_p = K_x$.

$$K_p = \frac{x_{\text{CO}_2} x_{\text{H}_2}}{x_{\text{CO}} x_{\text{H}_2\text{O}}} = \frac{0.203 \times 0.203}{0.297 \times 0.297} = 0.464$$

$$\begin{aligned}\Delta G_R^\circ &= -RT \ln K_p = -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 1150. \text{ K} \times \ln(0.464) \\ &= 7.28 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

- (b) $\Delta H_R^\circ = \Delta H_f^\circ(\text{CO}_2, g) + \Delta H_f^\circ(\text{H}_2, g) - \Delta H_f^\circ(\text{CO}, g) - \Delta H_f^\circ(\text{H}_2\text{O}, g)$
 $= -393.5 \text{ kJ mol}^{-1} + 110.5 \text{ kJ mol}^{-1} + 241.8 \text{ kJ mol}^{-1}$
 $= -41.2 \text{ kJ mol}^{-1}$

We use the Gibbs–Helmholtz equation and the relationship between ΔG_R° and $\ln K_p$.

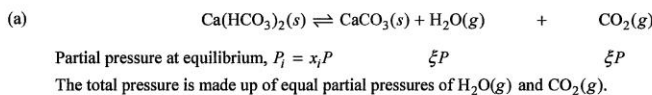
$$\begin{aligned}\ln K_p(298.15 \text{ K}) &= \ln K_p(1150. \text{ K}) - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{1150. \text{ K}} \right) \\ &= \ln K_p(1150. \text{ K}) - \frac{-41.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{298.15 \text{ K}} - \frac{1}{1150 \text{ K}} \right) = 11.54 \\ \Delta G_R^\circ &= -RT \ln K_p(298.15 \text{ K}) = -28.6 \text{ kJ mol}^{-1}\end{aligned}$$

P6.12 For the reaction $\text{C}(\text{graphite}) + \text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{CO}(\text{g}) + \text{H}_2(\text{g})$, $\Delta H_R^\circ = 131.28 \text{ kJ mol}^{-1}$ at 298.15 K. Use the values of $C_{p,m}$ at 298.15 K in the data tables to calculate ΔH_R° at 125.0°C.

$$\begin{aligned}\Delta H(T_2) &= \Delta H(T_1) + \Delta C_{p,m}(T_2 - T_1) \\ \Delta H(398.15 \text{ K}) &= 131.28 \text{ kJ mol}^{-1} \\ &+ 100. \text{ K} \times \left(\begin{array}{l} 29.14 \text{ J K}^{-1} \text{ mol}^{-1} + 28.84 \text{ J K}^{-1} \text{ mol}^{-1} - 8.52 \text{ J K}^{-1} \text{ mol}^{-1} \\ -33.59 \text{ J K}^{-1} \text{ mol}^{-1} \end{array} \right) \\ &= 132.9 \text{ kJ mol}^{-1}\end{aligned}$$

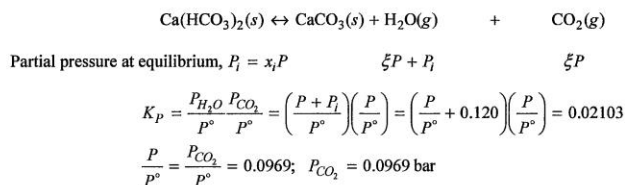
P6.13 $\text{Ca}(\text{HCO}_3)_2(\text{s})$ decomposes at elevated temperatures according to the stoichiometric equation $\text{Ca}(\text{HCO}_3)_2(\text{s}) \rightleftharpoons \text{CaCO}_3(\text{s}) + \text{H}_2\text{O}(\text{g}) + \text{CO}_2(\text{g})$.

- If pure $\text{Ca}(\text{HCO}_3)_2(\text{s})$ is put into a sealed vessel, the air is pumped out, and the vessel and its contents are heated, the total pressure is 0.290 bar. Determine K_p under these conditions.
- If the vessel also contains 0.120 bar $\text{H}_2\text{O}(\text{g})$ at the final temperature, what is the partial pressure of $\text{CO}_2(\text{g})$ at equilibrium?



$$K_p = \frac{P_{\text{H}_2\text{O}} P_{\text{CO}_2}}{P^\circ} = \left(\frac{P_{\text{H}_2\text{O}}}{P^\circ} \right)^2 = \left(\frac{0.290}{2} \right)^2 = 0.0210$$

- (b) If one of the products is originally present



P6.14 Calculate ΔA for the isothermal compression of 2.95 mol of an ideal gas at 325 K from an initial volume of 60.0 L to a final volume of 20.5 L. Does it matter whether the path is reversible or irreversible?

$$dA = -SdT - PdV$$

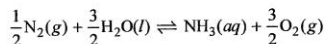
At constant T , we consider the reversible process. Because A is a state function, any path, whether reversible or irreversible, between the same initial and final states will give the same result.

$$\Delta A = - \int_{V_i}^{V_f} PdV = -nRT \ln \frac{V_f}{V_i} = -2.95 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 325 \text{ K} \times \ln \frac{20.5 \text{ L}}{60.0 \text{ L}}$$

$$= 8.56 \times 10^3 \text{ J}$$

P6.15 Nitrogen is a vital element for all living systems, but except for a few types of bacteria, blue-green algae, and some soil fungi, most organisms cannot utilize N_2 from the atmosphere. The formation of "fixed" nitrogen is therefore necessary to sustain life, and the simplest form of fixed nitrogen is ammonia NH_3 .

A possible pathway for ammonia synthesis by a living system is:



where (aq) means the ammonia is dissolved in water and $\Delta G_f^\circ(\text{NH}_3, aq) = -80.3 \text{ kJ mol}^{-1}$.

- Calculate ΔG° for the biological synthesis of ammonia at 298 K.
- Calculate the equilibrium constant for the biological synthesis of ammonia at 298 K.
- Based on your answer to part (b), is the pathway a spontaneous reaction?

$$(a) \quad \Delta G_R(298.15 \text{ K}) = \Delta G_f(\text{NH}_3, aq) - \frac{3}{2}\Delta G_f(\text{H}_2\text{O}, l)$$

$$= -80.3 \times 10^3 \text{ J mol}^{-1} - \frac{3}{2}(-237.1 \times 10^3 \text{ J mol}^{-1}) = 275.4 \times 10^3 \text{ J mol}^{-1}$$

$$(b) \quad K_P = \exp\left[-\frac{\Delta G_R}{RT}\right] = \exp\left[-\frac{275.35 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K}}\right] = 5.42 \times 10^{-49}$$

- Because $K_P \ll 1$, the biological synthesis of ammonia is not spontaneous.

P6.16 Collagen is the most abundant protein in the mammalian body. It is a fibrous protein that serves to strengthen and support tissues. Suppose a collagen fiber can be stretched reversibly with a force constant of $k = 10.0 \text{ N m}^{-1}$ and that the force, F (see Table 2.1), is given by $F = k\ell$. When a collagen fiber is contracted reversibly, it absorbs heat $q_{rev} = 0.050 \text{ J}$. Calculate the change in the Helmholtz energy, ΔA , as the fiber contracts isothermally from $\ell = 0.20$ to 0.10 cm . Calculate also the reversible work performed w_{rev} , ΔS , and ΔU . Assume that the temperature is constant at $T = 310. \text{ K}$.

$$w_{rev} = \int_{0.20 \text{ m}}^{0.10 \text{ m}} k\ell d\ell = \left[\frac{1}{2}k\ell^2 \right]_{0.20 \text{ m}}^{0.10 \text{ m}} = 10.0 \text{ N m}^{-1} \times \frac{(0.10 \text{ m})^2 - (0.20 \text{ m})^2}{2} = -0.015 \text{ J}$$

$$\Delta A = w_{rev} = -0.015 \text{ J}$$

$$\Delta S = \frac{q_{rev}}{T} = \frac{0.050 \text{ J}}{310. \text{ K}} = 1.61 \times 10^{-4} \text{ J K}^{-1}$$

$$\Delta U = \Delta A + T\Delta S = -0.015 \text{ J} + 0.050 \text{ J} = -0.035 \text{ J}$$

P6.17 Calculate $\mu_{\text{O}_2}^{\text{mixture}}(298.15 \text{ K}, 1 \text{ bar})$ for oxygen in air, assuming that the mole fraction of O_2 in air is 0.210. Use the conventional molar Gibbs energy defined in Section 6.17.

We calculate the conventional molar Gibbs energy as described in Example Problem 6.17.

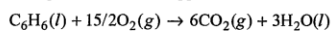
$$\mu_{\text{O}_2}^\circ(T) = -TS^\circ(\text{O}_2, g, 298.15 \text{ K}) = -298.15 \text{ K} \times 205.2 \text{ J K}^{-1} \text{ mol}^{-1} = -61.2 \text{ kJ mol}^{-1}$$

$$\mu_{\text{O}_2}^{\text{mixture}}(T, P) = \mu_{\text{O}_2}^\circ(T) + RT \ln \frac{P}{P^\circ} + RT \ln x_{\text{O}_2}$$

$$= -61.2 \text{ kJ mol}^{-1} + RT \ln \frac{1 \text{ bar}}{1 \text{ bar}} + 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \ln 0.210$$

$$= -65.0 \times 10^3 \text{ J mol}^{-1}$$

P6.18 Calculate the maximum nonexpansion work that can be gained from the combustion of benzene(*l*) and of H₂(*g*) on a per gram and a per mole basis under standard conditions. Is it apparent from this calculation why fuel cells based on H₂ oxidation are under development for mobile applications?

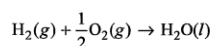


$$w_{\text{nonexpansion}}^{\text{max}} = \Delta G_R^\circ = 3\Delta G_f^\circ(\text{H}_2\text{O}, l) + 6\Delta G_f^\circ(\text{CO}_2, g) - \frac{15}{2}\Delta G_f^\circ(\text{O}_2, g) - \Delta G_f^\circ(\text{C}_6\text{H}_6, l)$$

$$w_{\text{nonexpansion}}^{\text{max}} = 3 \times (-237.1 \text{ kJ mol}^{-1}) + 6 \times (-394.4 \text{ kJ mol}^{-1}) - \frac{15}{2} \times (0) - 124.5 \text{ kJ mol}^{-1}$$

$$= -3202 \text{ kJ mol}^{-1}$$

$$= -3202 \text{ kJ mol}^{-1} \times \frac{1 \text{ mol}}{78.18 \text{ g}} = -40.99 \text{ kJ g}^{-1}$$



$$w_{\text{nonexpansion}}^{\text{max}} = \Delta G_R^\circ = \Delta G_f^\circ(\text{H}_2\text{O}, l) = -237.1 \text{ kJ mol}^{-1}$$

$$w_{\text{nonexpansion}}^{\text{max}} = -237.1 \text{ kJ mol}^{-1} \times \frac{1 \text{ mol}}{2.016 \text{ g}} = -117.6 \text{ kJ g}^{-1}$$

On a per gram basis, nearly three times as much work can be extracted from the oxidation of hydrogen than benzene.

P6.19 You wish to design an effusion source for Br atoms from Br₂(*g*). If the source is to operate at a total pressure of 7.5 Torr, what temperature is required to produce a degree of dissociation of 0.20? What value of the pressure would increase the degree of dissociation to 0.65 at this temperature?

The following results for the degree of dissociation are derived in Example Problems 6.10 and 6.11.

$$K_p(T) = \frac{4\alpha^2 P}{1 - \alpha^2 P^\circ} = \frac{4 \times (0.20)^2}{1 - (0.20)^2} \times \frac{7.5 \text{ Torr}}{760 \text{ Torr}} = 1.644 \times 10^{-3}$$

$$\ln K_p(T_f) = -\frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\Delta H_R^\circ = 2\Delta H_f^\circ(\text{Br}, g) - \Delta H_f^\circ(\text{Br}_2, g)$$

$$= 2 \times 111.9 \times 10^3 \text{ J mol}^{-1} - 30.9 \times 10^3 \text{ J mol}^{-1} = 192.9 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta G_R^\circ = 2\Delta G_f^\circ(\text{Br}, g) - \Delta G_f^\circ(\text{Br}_2, g)$$

$$= 2 \times 82.4 \times 10^3 \text{ J mol}^{-1} - 3.1 \times 10^3 \text{ J mol}^{-1} = 161.7 \times 10^3 \text{ J mol}^{-1}$$

$$\frac{1}{T_f} = \frac{1}{298.15 \text{ K}} - \frac{R}{\Delta H_R^\circ} \left(\ln K_p(T_f) + \frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} \right)$$

$$= \frac{1}{298.15 \text{ K}} - \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{192.9 \times 10^3 \text{ J mol}^{-1}} \times \left(\ln 1.644 \times 10^{-3} + \frac{161.7 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} \right)$$

$$= 8.188 \times 10^{-4} \text{ K}^{-1}$$

$$T_f = 1.2 \times 10^3 \text{ K}$$

$$\alpha = \sqrt{\frac{K_p(T)}{K_p(T) + 4\frac{P}{P^\circ}}}$$

$$\frac{P}{P^\circ} = \frac{K_p}{4} \left(\frac{1}{\alpha^2} - 1 \right) = \frac{1.644 \times 10^{-3}}{4} \times \left(\frac{1}{0.65^2} - 1 \right) = 5.620 \times 10^{-4}$$

$$P = 5.620 \times 10^{-4} P^\circ = 5.620 \times 10^{-4} \times 760. \text{ Torr} = 0.43 \text{ Torr}$$

- P6.20** Calculate ΔG for the isothermal expansion of 2.25 mol of an ideal gas at 325 K from an initial pressure of 12.0 bar to a final pressure of 2.5 bar.

$$dG = -SdT + VdP$$

At constant T , we consider the reversible process. Because G is a state function, any path between the same initial and final states will give the same result.

$$\begin{aligned}\Delta G &= \int_{P_i}^{P_f} VdP = nRT \ln \frac{P_f}{P_i} = 2.25 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 325 \text{ K} \times \ln \frac{2.50 \text{ bar}}{12.0 \text{ bar}} \\ &= -9.54 \times 10^3 \text{ J}\end{aligned}$$

- P6.21** You place 3.00 mol of $\text{NOCl}(g)$ in a reaction vessel. Equilibrium is established with respect to the decomposition reaction $\text{NOCl}(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2}\text{Cl}_2(g)$.

- Derive an expression for K_p in terms of the extent of reaction ξ .
- Simplify your expression for part (a) in the limit that ξ is very small.
- Calculate ξ and the degree of dissociation of NOCl in the limit that ξ is very small at 375 K and a pressure of 2.00 bar.
- Solve the expression derived in part (a) using a numerical equation solver for the conditions stated in the previous part. What is the relative error in ξ made using the approximation of part (b)?

	$\text{NOCl}(g)$	\rightleftharpoons	$\text{NO}(g)$	$+$	$\frac{1}{2}\text{Cl}_2(g)$
(a) Initial number of moles	3.00		0		0
Moles present at equilibrium	$3.00 - \xi$		ξ		$\frac{1}{2}\xi$
Mole fraction present at equilibrium	$\frac{3.00 - \xi}{3.00 + \frac{1}{2}\xi}$		$\frac{\xi}{3.00 + \frac{1}{2}\xi}$		$\frac{\frac{1}{2}\xi}{3.00 + \frac{1}{2}\xi}$
Partial pressure at equilibrium, $P_i = x_i P$	$\left(\frac{3.00 - \xi}{3.00 + \frac{1}{2}\xi}\right)P$		$\left(\frac{\xi}{3.00 + \frac{1}{2}\xi}\right)P$		$\left(\frac{\frac{1}{2}\xi}{3.00 + \frac{1}{2}\xi}\right)P$

We next express K_p in terms of ξ and P .

$$K_p(T) = \frac{\left(\frac{P_{\text{NO}}^{\text{eq}}}{P^\circ}\right)\left(\frac{P_{\text{Cl}_2}^{\text{eq}}}{P^\circ}\right)^{\frac{1}{2}}}{\left(\frac{P_{\text{NOCl}}^{\text{eq}}}{P^\circ}\right)} = \frac{\left(\frac{\xi}{3.00 + \frac{1}{2}\xi}\right)\frac{P}{P^\circ} \left[\left(\frac{\frac{1}{2}\xi}{3.00 + \frac{1}{2}\xi}\right)\frac{P}{P^\circ}\right]^{\frac{1}{2}}}{\left(\frac{3.00 - \xi}{3.00 + \frac{1}{2}\xi}\right)\frac{P}{P^\circ}}$$

- (b) We now derive an expression for K_p that is valid if the extent of reaction is very small.

$$\begin{aligned}K_p(T) &= \frac{\left(\frac{\xi}{3.00 + \frac{1}{2}\xi}\right)\frac{P}{P^\circ} \left[\left(\frac{\frac{1}{2}\xi}{3.00 + \frac{1}{2}\xi}\right)\frac{P}{P^\circ}\right]^{\frac{1}{2}}}{\left(\frac{3.00 - \xi}{3.00 + \frac{1}{2}\xi}\right)\frac{P}{P^\circ}} = \frac{\xi \left(\frac{\xi}{2\left[3.00 + \frac{1}{2}\xi\right]}\right)^{\frac{1}{2}}\frac{P}{P^\circ}}{3.00 - \xi} \\ &= \frac{\xi^{3/2}}{\sqrt{2}(3.00 - \xi)\sqrt{3.00 + \xi/2}} \sqrt{\frac{P}{P^\circ}} \approx \frac{\xi^{3/2}}{3\sqrt{6}} \sqrt{\frac{P}{P^\circ}} \text{ if } \xi \ll 3\end{aligned}$$

$$\begin{aligned}
 \text{(c)} \quad \Delta G_R^\circ &= \Delta G_f^\circ(\text{NO}, g) - \Delta G_f^\circ(\text{NOCl}, g) = 87.6 \times 10^3 \text{ J mol}^{-1} - 66.1 \times 10^3 \text{ J mol}^{-1} \\
 &= 21.5 \times 10^3 \text{ J mol}^{-1} \\
 \Delta H_R^\circ &= \Delta H_f^\circ(\text{NO}, g) - \Delta H_f^\circ(\text{NOCl}, g) = 91.3 \times 10^3 \text{ J mol}^{-1} - 51.7 \times 10^3 \text{ J mol}^{-1} \\
 &= 39.6 \times 10^3 \text{ J mol}^{-1}
 \end{aligned}$$

We next use the Gibbs–Helmholtz equation to calculate the equilibrium constant.

$$\begin{aligned}
 \ln K_p(T_f) &= -\frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right) \\
 \ln K_p(375 \text{ K}) &= -\frac{21.5 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{39.6 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{375 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\
 \ln K_p(375 \text{ K}) &= -5.3996 \\
 K_p(375 \text{ K}) &= 4.52 \times 10^{-3}
 \end{aligned}$$

$$\begin{aligned}
 K_p &= \frac{1}{3\sqrt{6}} \xi^2 \left(\frac{P}{P^\circ} \right)^{\frac{1}{2}} \\
 \xi &= \left[3\sqrt{6} K_p \left(\frac{P}{P^\circ} \right)^{\frac{1}{2}} \right]^{\frac{2}{3}} = \left[\frac{3\sqrt{6} \times 4.52 \times 10^{-3}}{\sqrt{2.00}} \right]^{\frac{2}{3}} = 0.0820
 \end{aligned}$$

The degree of dissociation is $\frac{\xi}{3} = 0.0273$.

(d) Solving the expression of part (a) without approximations gives $\xi = 0.0808$.

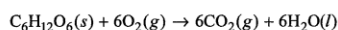
$$\text{The relative error is } \frac{0.0808 - 0.0820}{0.0808} = -1.49\%.$$

P6.22 A sample containing 2.50 moles of He (1 bar, 350. K) is mixed with 1.75 mol of Ne (1 bar, 350. K) and 1.50 mol of Ar (1 bar, 350. K). Calculate ΔG_{mixing} and ΔS_{mixing} .

We assume ideal gas behavior.

$$\begin{aligned}
 \Delta G_{\text{mixing}} &= nRT \sum_i x_i \ln x_i \\
 &= (5.75 \text{ mol}) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times \left(\frac{2.50}{5.75} \ln \frac{2.50}{5.75} + \frac{1.75}{5.75} \ln \frac{1.75}{5.75} + \frac{1.50}{5.75} \ln \frac{1.50}{5.75} \right) \\
 &= -17.9 \times 10^3 \text{ J} \\
 \Delta S_{\text{mixing}} &= -nR \sum_i x_i \ln x_i \\
 &= -(5.75 \text{ mol}) \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \left(\frac{2.50}{5.75} \ln \frac{2.50}{5.75} + \frac{1.75}{5.75} \ln \frac{1.75}{5.75} + \frac{1.50}{5.75} \ln \frac{1.50}{5.75} \right) \\
 &= 51.4 \text{ J K}^{-1}
 \end{aligned}$$

P6.23 A hard-working horse can lift a 350. lb. weight 100. ft. in one minute. Assuming the horse generates energy to accomplish this work by metabolizing glucose:



calculate how much glucose a horse must metabolize to sustain this rate of work for one hour at 298 K.

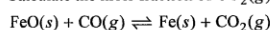
$$\begin{aligned}
 \Delta G_R^\circ &= 6 \times (-237.1 \text{ kJ mol}^{-1}) + 6 \times (-394.4 \text{ kJ mol}^{-1}) - (-910.6 \text{ kJ mol}^{-1}) = 2878.4 \text{ kJ mol}^{-1} \\
 w_{\text{horse}} &= mgh \\
 &= 350. \text{ lb} \times 0.4536 \text{ kg lb}^{-1} \times 100. \text{ ft} \times \text{min}^{-1} \times 0.3048 \text{ m ft}^{-1} \times 9.81 \text{ m s}^{-2} \times 60 \text{ min hr}^{-1} = 2848 \text{ kJ hr}^{-1}
 \end{aligned}$$

$$m_{\text{glucose}} = \frac{w_{\text{reaction}}}{w_{\text{horse}}} M_{\text{glucose}} = \frac{\Delta G_R^\circ}{w_{\text{horse}}} M_{\text{glucose}} = \frac{2848 \text{ kJ}}{2878.4 \text{ kJ mol}^{-1}} \times 180.18 \text{ g mol}^{-1} = 178 \text{ g}$$

P6.24 Consider the reaction $\text{FeO}(s) + \text{CO}(g) \rightleftharpoons \text{Fe}(s) + \text{CO}_2(g)$ for which K_p is found to have the following values:

T	700.°C	1200.°C
K_p	0.688	0.310

- a. Calculate ΔG_R° , ΔS_R° , and ΔH_R° for this reaction at 700.°C. Assume that ΔH_R° is independent of temperature.
- b. Calculate the mole fraction of $\text{CO}_2(g)$ present in the gas phase at 700.°C.



$$K_p = \frac{P_{\text{CO}_2}/P^\circ}{P_{\text{CO}}/P^\circ}$$

$$\ln \frac{K_p(1200.^\circ\text{C})}{K_p(700.^\circ\text{C})} = \frac{\Delta H_R^\circ}{R} \left(\frac{1}{1473.15 \text{ K}} - \frac{1}{973.15 \text{ K}} \right)$$

Assume that ΔH_R° is independent of temperature.

$$\begin{aligned} \Delta H_R^\circ &= \frac{-R \ln \frac{K_p(1473.15 \text{ K})}{K_p(973.15 \text{ K})}}{\left(\frac{1}{1473.15 \text{ K}} - \frac{1}{973.15 \text{ K}} \right)} \\ &= \frac{-8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times \ln \frac{0.310}{0.688}}{\left(\frac{1}{1473.15 \text{ K}} - \frac{1}{973.15 \text{ K}} \right)} = -19.0 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G_R^\circ(700.^\circ\text{C}) &= -RT \ln K_p(700.^\circ\text{C}) \\ &= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 973.15 \text{ K} \times \ln(0.688) = 3.03 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_R^\circ(700.^\circ\text{C}) &= \frac{\Delta H_R^\circ - \Delta G_R^\circ(700.^\circ\text{C})}{T} \\ &= \frac{-19.0 \times 10^3 \text{ J mol}^{-1} - 3.03 \times 10^3 \text{ J mol}^{-1}}{973.15 \text{ K}} = -22.6 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

$$K_p = P_{\text{CO}_2}/P_{\text{CO}} = 0.688$$

$$K_p = K_x \text{ because } \Delta n = 0$$

$$\frac{x_{\text{CO}_2}}{x_{\text{CO}}} = 0.688 \text{ and } x_{\text{CO}_2} + x_{\text{CO}} = 1$$

$$x_{\text{CO}_2} = 0.408 \quad x_{\text{CO}} = 0.592$$

P6.25 Derive an expression for $A(V, T)$ analogous to that for $G(T, P)$ in Equation (6.33).

$$\left(\frac{\partial A}{\partial T} \right)_V = -S \text{ and } \left(\frac{\partial A}{\partial V} \right)_T = -P$$

$$A(T, V_f) = A(T, V_i) - \int_{V_i}^{V_f} P dV$$

Assume constant temperature, ideal gas behavior and choose a reversible path.

$$A(T, V_f) = A(T, V_i) - \int_{V_i}^{V_f} \frac{nRT}{V} dV = A(T, V_i) - nRT \ln \frac{V_f}{V_i}$$

P6.26 Show that

$$\left[\frac{\partial(A/T)}{\partial(1/T)} \right]_V = U$$

Write an expression analogous to Equation (6.36) that would allow you to relate ΔA at two temperatures.

$$\begin{aligned} \left(\frac{\partial A/T}{\partial T} \right)_V &= \frac{1}{T} \left(\frac{\partial A}{\partial T} \right)_V - \frac{A}{T^2} = -\frac{S}{T} - \frac{A}{T^2} = -\frac{A+TS}{T^2} = -\frac{U}{T^2} \\ \left(\frac{\partial A/T}{\partial 1/T} \right)_V &= \left(\frac{\partial A/T}{\partial T} \right)_V \left(\frac{\partial T}{\partial 1/T} \right)_V = \left(\frac{\partial A/T}{\partial T} \right)_V (-T^2) = -T^2 \left(\frac{\partial A/T}{\partial T} \right)_V = U \end{aligned}$$

At constant V and assuming that ΔU is independent of T in the temperature interval between T_1 and T_2 ,

$$\begin{aligned} \int_{T_1}^{T_2} d \left(\frac{\Delta A}{T} \right) &= \int_{T_1}^{T_2} \Delta U d \left(\frac{1}{T} \right) \\ \frac{\Delta A(T_2)}{T_2} &= \frac{\Delta A(T_1)}{T_1} + \Delta U(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \end{aligned}$$

P6.27 A gas mixture with 4.50 mol of Ar, x moles of Ne, and y moles of Xe is prepared at a pressure of 1 bar and a temperature of 298 K. The total number of moles in the mixture is five times that of Ar. Write an expression for ΔG_{mixing} in terms of x . At what value of x does the magnitude of ΔG_{mixing} have its minimum value? Calculate ΔG_{mixing} for this value of x .

If the number of moles of Ne is x , the number of moles of Xe is $y = 18.0 - x$.

$$\begin{aligned} \Delta G_{\text{mixing}} &= nRT \sum_i x_i \ln x_i = nRT \left(\frac{1}{5} \ln \frac{1}{5} + \frac{x}{22.5} \ln \frac{x}{22.5} + \frac{18.0-x}{22.5} \ln \frac{18.0-x}{22.5} \right) \\ \frac{d\Delta G_{\text{mixing}}}{dx} &= nRT \left(\frac{1}{22.5} \ln \frac{x}{22.5} + \frac{x}{22.5} \frac{1}{x} - \frac{1}{22.5} \ln \frac{18.0-x}{22.5} + \frac{18.0-x}{22.5} \frac{1}{18.0-x} (-1) \right) \\ &= nRT \left(\frac{1}{22.5} \ln \frac{x}{22.5} + 1 - \frac{1}{22.5} \ln \frac{18.0-x}{22.5} - 1 \right) = \frac{nRT}{22.5} \ln \frac{x}{18.0-x} = 0 \\ \frac{x}{18.0-x} &= 1; \quad x = 9.00 \\ \Delta G_{\text{mixing}} &= nRT \left(\frac{1}{5} \ln \frac{1}{5} + \frac{2 \times 9.00}{22.5} \ln \frac{9.00}{22.5} \right) \\ &= 22.5 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times (-1.0549) = -58.8 \times 10^3 \text{ J} \end{aligned}$$

P6.28 In Example Problem 6.9, K_p for the reaction $\text{CO}(g) + \text{H}_2\text{O}(l) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g)$ was calculated to be 3.32×10^3 at 298.15 K. At what temperature is $K_p = 5.50 \times 10^3$? What is the highest value that K_p can have by changing the temperature? Assume that ΔH_R° is independent of temperature.

$$\begin{aligned} \ln K_p(T_f) &= \ln K_p(298.15 \text{ K}) - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right) \\ \Delta H_R^\circ &= \Delta H_f^\circ(\text{CO}_2, g) + \Delta H_f^\circ(\text{H}_2, g) - \Delta H_f^\circ(\text{H}_2\text{O}, l) - \Delta H_f^\circ(\text{CO}, g) \\ &= -393.5 \times 10^3 \text{ J mol}^{-1} + 0 + 285.8 \times 10^3 \text{ J mol}^{-1} + 110.5 \times 10^3 \text{ J mol}^{-1} = 2.80 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned}\frac{1}{T_f} &= \frac{1}{298.15 \text{ K}} - \frac{R}{\Delta H_R^\circ} \ln \frac{K_p(T_f)}{K_p(298.15 \text{ K})} \\ &= \frac{1}{298.15 \text{ K}} - \frac{8.314 \text{ J K}^{-1} \text{ mol}^{-1}}{2.80 \times 10^3 \text{ J mol}^{-1}} \times \ln \frac{5.50 \times 10^3}{3.32 \times 10^3} = 1.855 \times 10^{-3} \text{ K}^{-1} \\ T_f &= 539 \text{ K}\end{aligned}$$

Because the reaction is endothermic, K_p increases with temperature. As $T \rightarrow \infty$,

$$\begin{aligned}\frac{1}{298.15 \text{ K}} - \frac{R}{\Delta H_R^\circ} \ln \frac{K_p(T_f \rightarrow \infty)}{K_p(298.15 \text{ K})} &= 0 \\ \ln \frac{K_p(T_f \rightarrow \infty)}{K_p(298.15 \text{ K})} &= \frac{\Delta H_R^\circ}{R \times 298.15 \text{ K}} = \frac{2.80 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} = 1.12957 \\ K_p(T_f \rightarrow \infty) &= 3.094 \times K_p(298.15 \text{ K}) = 3.094 \times 3.32 \times 10^3 = 1.03 \times 10^4\end{aligned}$$

- P6.29** Assuming that ΔH_f° is constant in the interval 275 K–600. K, calculate ΔG° for the process $(\text{H}_2\text{O}, g, 298 \text{ K}) \rightarrow (\text{H}_2\text{O}, g, 600. \text{ K})$. Calculate the relative change in the Gibbs energy.

We use the Gibbs–Helmholtz equation and values from the data tables.

$$\begin{aligned}\Delta G^\circ(T_2) &= T_2 \left[\frac{\Delta G^\circ(T_1)}{T_1} + \Delta H_f^\circ(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right] \\ &= 600. \text{ K} \times \left[\frac{-228.6 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} - 241.8 \times 10^3 \text{ J mol}^{-1} \times \left(\frac{1}{600. \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \\ \Delta G^\circ(600. \text{ K}) &= -215.2 \times 10^3 \text{ J mol}^{-1}\end{aligned}$$

The relative change is $\frac{-215.2 \times 10^3 \text{ J mol}^{-1} + 228.6 \times 10^3 \text{ J mol}^{-1}}{-228.6 \times 10^3 \text{ J mol}^{-1}} = -5.8\%$.

- P6.30** Calculate the degree of dissociation of N_2O_4 in the reaction $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$ at 300. K and a total pressure of 1.50 bar. Do you expect the degree of dissociation to increase or decrease as the temperature is increased to 550. K? Assume that ΔH_R° is independent of temperature.

We set up the following table.

	$\text{N}_2\text{O}_4(g)$	\rightleftharpoons	$2\text{NO}_2(g)$
Initial number of moles	n_0		0
Moles present at equilibrium	$n_0 - \xi$		2ξ
Mole fraction present at equilibrium	$\frac{n_0 - \xi}{n_0 + \xi}$		$\frac{2\xi}{n_0 + \xi}$
Partial pressure at equilibrium, $P_i = x_i P$	$\left(\frac{n_0 - \xi}{n_0 + \xi} \right) P$		$\left(\frac{2\xi}{n_0 + \xi} \right) P$

We next express K_p in terms of n_0 , ξ , and P .

$$K_p(T) = \frac{\left(\frac{P^{eq}}{P^\circ} \right)^2}{\left(\frac{P_{\text{Cl}_2}}{P^\circ} \right)} = \frac{\left[\left(\frac{2\xi}{n_0 + \xi} \right) \frac{P}{P^\circ} \right]^2}{\left(\frac{n_0 - \xi}{n_0 + \xi} \right) \frac{P}{P^\circ}} = \frac{4\xi^2}{(n_0 + \xi)(n_0 - \xi)} \frac{P}{P^\circ} = \frac{4\xi^2}{(n_0)^2 - \xi^2} \frac{P}{P^\circ}$$

We convert this expression for K_p to one in terms of α as in example problem 6.10.

$$K_p(T) = \frac{4\xi^2}{(n_0)^2 - \xi^2} \frac{P}{P^\circ} = \frac{4\alpha^2}{1 - \alpha^2} \frac{P}{P^\circ}$$

$$\left(K_p(T) + 4\frac{P}{P^\circ}\right)\alpha^2 = K_p(T)$$

$$\alpha = \sqrt{\frac{K_p(T)}{K_p(T) + 4\frac{P}{P^\circ}}}$$

$$\Delta G_R^\circ = 2\Delta G_f^\circ(\text{NO}_2, g) - \Delta G_f^\circ(\text{N}_2\text{O}_4, g)$$

$$= 2 \times 51.3 \times 10^3 \text{ J mol}^{-1} - 99.8 \times 10^3 \text{ J mol}^{-1} = 2.8 \times 10^3 \text{ J mol}^{-1}$$

$$\Delta H_R^\circ = 2\Delta H_f^\circ(\text{NO}_2, g) - \Delta H_f^\circ(\text{N}_2\text{O}_4, g)$$

$$= 2 \times 33.2 \times 10^3 \text{ J mol}^{-1} - 11.1 \times 10^3 \text{ J mol}^{-1} = 55.3 \times 10^3 \text{ J mol}^{-1}$$

Using the Gibbs-Helmholtz equation,

$$\ln K_p(T_f) = -\frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(300. \text{ K}) = -\frac{2.8 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{55.3 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{300. \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$

$$\ln K_p(300. \text{ K}) = -0.9920$$

$$K_p(300. \text{ K}) = 0.371$$

$$\alpha = \sqrt{\frac{0.371}{0.371 + 4 \times 1.50}} = 0.241$$

Because $\Delta H_R^\circ > 0$, α increases as T increases.

P6.31 Oxygen reacts with solid glycylglycine $\text{C}_4\text{H}_8\text{N}_2\text{O}_3$ to form urea $\text{CH}_4\text{N}_2\text{O}$, carbon dioxide, and water:



At $T = 298 \text{ K}$ and 1.00 atm, solid glycylglycine has the following thermodynamic properties:

$$\Delta G_f^\circ = -491.5 \text{ kJ mol}^{-1}, \Delta H_f^\circ = -746.0 \text{ kJ mol}^{-1}, S^\circ = 190.0 \text{ J K}^{-1} \text{ mol}^{-1}$$

Calculate ΔG_R° at $T = 298.15 \text{ K}$ and at $T = 310.0 \text{ K}$. State any assumptions that you make.

$$\Delta G_R^\circ(298.15 \text{ K}) = \Delta G_f^\circ(\text{urea}, s) + 3\Delta G_f^\circ(\text{CO}_2, g) + 2\Delta G_f^\circ(\text{H}_2\text{O}, l) - \Delta G_f^\circ(\text{glycylglycine}, s)$$

$$= -197.15 \text{ kJ mol}^{-1} + 3 \times (-394.4 \text{ kJ mol}^{-1}) + 2 \times (-237.1 \text{ kJ mol}^{-1}) - 491.5 \text{ kJ mol}^{-1}$$

$$= -1363 \text{ kJ mol}^{-1}$$

$$\Delta H_R^\circ(298.15 \text{ K}) = \Delta H_f^\circ(\text{urea}, s) + 3\Delta H_f^\circ(\text{CO}_2, g) + 2\Delta H_f^\circ(\text{H}_2\text{O}, l) - \Delta H_f^\circ(\text{glycylglycine}, s)$$

$$= -337.2 \text{ kJ mol}^{-1} + 3 \times (-393.5 \text{ kJ mol}^{-1}) + 2 \times (-285.8 \text{ kJ mol}^{-1}) - 746 \text{ kJ mol}^{-1}$$

$$= -1343 \text{ kJ mol}^{-1}$$

$$\ln K_p(298.15 \text{ K}) = -\frac{\Delta G_R^\circ(298.15 \text{ K})}{RT} = \frac{1363 \text{ kJ mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} = 549.879$$

$$K_p(298.15 \text{ K}) = 6.44 \times 10^{238}$$

$$\Delta G_R(T_2) = T_2 \left[\frac{\Delta G_R(T_1)}{T_1} + \Delta H_R \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

$$\begin{aligned} \Delta G_R(310.0 \text{ K}) &= 310.0 \text{ K} \times \left[\frac{-1363 \text{ kJ mol}^{-1}}{298.15 \text{ K}} - 1343 \text{ kJ mol}^{-1} \times \left(\frac{1}{310.0 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \\ &= -1364. \text{ kJ mol}^{-1} \end{aligned}$$

We have assumed that the enthalpy of reaction is independent of temperature, which is a good approximation over the small temperature range.

- P6.32** Calculate ΔG_R° for the reaction $\text{CO}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{CO}_2$ at 298.15 K. Calculate ΔG_R° at 600. K assuming that ΔH_R° is constant in the temperature interval of interest.

$$\begin{aligned} \Delta G_R^\circ(298.15 \text{ K}) &= \Delta G_f^\circ(\text{CO}_2, g) - \Delta G_f^\circ(\text{CO}, g) - \frac{1}{2}\Delta G_f^\circ(\text{O}_2, g) \\ &= -394.4 \times 10^3 \text{ J mol}^{-1} + 137.2 \times 10^3 \text{ J mol}^{-1} - 0 \\ &= -257.2 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta H_R^\circ(298.15 \text{ K}) &= \Delta H_f^\circ(\text{CO}_2, g) - \Delta H_f^\circ(\text{CO}, g) - \frac{1}{2}\Delta H_f^\circ(\text{O}_2, g) \\ &= -393.5 \times 10^3 \text{ J mol}^{-1} + 110.5 \times 10^3 \text{ J mol}^{-1} - 0 \\ &= -283.0 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

$$\Delta G_R^\circ(T_2) = T_2 \left[\frac{\Delta G_R^\circ(T_1)}{T_1} + \Delta H_R^\circ(T_1) \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \right]$$

Using the Gibbs–Helmholtz equation,

$$\begin{aligned} \Delta G_R^\circ(600. \text{ K}) &= 600. \text{ K} \times \left[\frac{-257.2 \times 10^3 \text{ J mol}^{-1}}{298.15 \text{ K}} - 283.0 \times 10^3 \text{ J mol}^{-1} \times \left(\frac{1}{600. \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \right] \\ &= -231.1 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

- P6.33** A sample containing 2.50 mol of an ideal gas at 325 K is expanded from an initial volume of 10.5 L to a final volume of 60.0 L. Calculate ΔG and ΔA for this process for (a) an isothermal reversible path and (b) an isothermal expansion against a constant external pressure equal to the final pressure. Explain why ΔG and ΔA do or do not differ from one another.

- a. For the isothermal reversible path

$$\begin{aligned} \Delta G &= \int_{P_i}^{P_f} V dP = nRT \ln \frac{P_f}{P_i} = nRT \ln \frac{V_i}{V_f} \\ &= 2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 325 \text{ K} \times \ln \frac{10.5 \text{ L}}{60.0 \text{ L}} = -11.7 \times 10^3 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta A &= - \int_{V_i}^{V_f} P dV = -nRT \ln \frac{V_f}{V_i} \\ &= -2.50 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 325 \text{ K} \times \ln \frac{60.0 \text{ L}}{10.5 \text{ L}} = -11.7 \times 10^3 \text{ J} \end{aligned}$$

- b. Because A and G are state functions, the answers are the same as to part (a) because the systems go between the same initial and final states, $T, V_i \rightarrow T, V_f$.
 $\Delta G - \Delta A = \Delta H - \Delta U = \Delta(PV) = \Delta(nRT)$. Therefore, $\Delta G = \Delta A$ for an ideal gas if T is constant.

P6.34 You have containers of pure O_2 and N_2 at 298 K and 1 atm pressure. Calculate ΔG_{mixing} relative to the unmixed gases of

- a. a mixture of 10. mol of O_2 and 10. mol of N_2
 b. a mixture of 10. mol of O_2 and 20. mol of N_2
 c. Calculate ΔG_{mixing} if 10 mol of pure N_2 is added to the mixture of 10 mol of O_2 and 10 mol of N_2 .
 $\Delta G_{mixing} = nRT(x_1 \ln x_1 + x_2 \ln x_2)$

$$(a) \quad \Delta G_{mixing} = 20 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \left(\frac{1}{2} \ln \frac{1}{2} + \frac{1}{2} \ln \frac{1}{2} \right) = -34.3 \text{ kJ}$$

$$(b) \quad \Delta G_{mixing} = 30 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \left(\frac{1}{3} \ln \frac{1}{3} + \frac{2}{3} \ln \frac{2}{3} \right) = -47.3 \text{ kJ}$$

$$(c) \quad \Delta G_{mixing} = \Delta G_{mixing}(\text{separate gases}) - \Delta G_{mixing}(20 \text{ mol A} + 10 \text{ mol B}) \\ = 30 \text{ mol} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \left(\frac{2}{3} \ln \frac{2}{3} + \frac{1}{3} \ln \frac{1}{3} \right) + 34.3 \text{ kJ} \\ = -47.3 \text{ kJ} + 34.3 \text{ kJ} = -13.0 \text{ kJ}$$

P6.35 In this problem, you calculate the error in assuming that ΔH_R° is independent of T for the reaction $2\text{CuO}(s) \rightleftharpoons 2\text{Cu}(s) + \text{O}_2(g)$.

The following data are given at 25°C:

Compound	CuO(s)	Cu(s)	O ₂ (g)
ΔH_f° (KJ mol ⁻¹)	-157		
ΔG_f° (KJ mol ⁻¹)	-130		
$C_{p,m}^\circ$ (KJ mol ⁻¹)	42.3	24.4	29.4

- a. From Equation (6.65), $\int_{K_p(T_0)}^{K_p(T_f)} d \ln K_p = \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_R^\circ}{T^2} dT$. To a good approximation, we can assume that the

heat capacities are independent of temperature over a limited range in temperature, giving $\Delta H_R^\circ(T) = \Delta H_R^\circ(T_0) + \Delta C_p(T - T_0)$, where $\Delta C_p = \sum_i \nu_i C_{p,m}(i)$. By integrating Equation (6.65), show that

$$\ln K_p(T) = \ln K_p(T_0) - \frac{\Delta H_R^\circ(T_0)}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{T_0 \times \Delta C_p}{R} \left(\frac{1}{T} - \frac{1}{T_0} \right) + \frac{\Delta C_p}{R} \ln \frac{T}{T_0}$$

- b. Using the result from part (a), calculate the equilibrium pressure of oxygen over copper and CuO(s) at 1275 K. How is this value related to K_p for the reaction $2\text{CuO}(s) \rightleftharpoons 2\text{Cu}(s) + \text{O}_2(g)$?
- c. What value would you obtain if you assumed that ΔH_R° were constant at its value for 298.15 K up to 1275 K?

$$\begin{aligned}
 \text{(a)} \quad \int_{T_0}^{T_f} d \ln K_p &= \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_R^\circ}{T^2} dT \\
 \ln K_p(T_f) - \ln K_p(T_0) &= \frac{1}{R} \int_{T_0}^{T_f} \frac{\Delta H_R^\circ + \Delta C_p(T - T_0)}{T^2} dT \\
 &= \frac{\Delta H_R^\circ(T_0)}{R} \times \int_{T_0}^{T_f} \frac{dT}{T^2} + \frac{\Delta C_p}{R} \int_{T_0}^{T_f} \frac{dT}{T} - \frac{\Delta C_p T_0}{R} \int_{T_0}^{T_f} \frac{dT}{T^2} \\
 &= \frac{-\Delta H_R^\circ(T_0)}{R} \left(\frac{1}{T_f} - \frac{1}{T_0} \right) + \frac{\Delta C_p}{R} \ln \frac{T_f}{T_0} + \frac{\Delta C_p T_0}{R} \left(\frac{1}{T_f} - \frac{1}{T_0} \right)
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad 2\text{CuO}(s) &\rightleftharpoons 2\text{Cu}(s) + \text{O}_2(g) \\
 \Delta H_R^\circ(T_0) &= 2 \times 157 \times 10^3 \text{ J mol}^{-1} = 314 \times 10^3 \text{ J mol}^{-1} \\
 \Delta C_p &= 2C_{p,m}(\text{Cu}, s) + C_{p,m}(\text{O}_2, g) - 2C_{p,m}(\text{CuO}, s) \\
 &= (2 \times 24.4 + 29.4 - 2 \times 42.3) \text{ J K}^{-1} \text{ mol}^{-1} \\
 &= -6.4 \text{ J K}^{-1} \text{ mol}^{-1} \\
 \ln K_p(1275 \text{ K}) &= \frac{2 \times 129.7 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K}} \\
 &\quad - \frac{2 \times 157 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left(\frac{1}{1275 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) - \frac{6.4 \text{ J K}^{-1} \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \ln \frac{1275 \text{ K}}{298.15 \text{ K}} \\
 &\quad - \frac{6.4 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \left(\frac{1}{1275 \text{ K}} - \frac{1}{298.15 \text{ K}} \right) \\
 \ln K_p(1275 \text{ K}) &= -8.3659 \\
 K_p(1275 \text{ K}) &= \frac{P_{\text{O}_2}}{P^\circ} = 2.33 \times 10^{-4} \\
 P_{\text{O}_2} &= 2.33 \times 10^{-4} \text{ bar}
 \end{aligned}$$

- (c) This is equivalent to setting $\Delta C_p = 0$. Neglecting the last two terms in the calculation above gives $\ln K_p = -7.8371$ and $P_{\text{O}_2} = 3.95 \times 10^{-4}$ bar.

P6.36 Consider the equilibrium in the reaction $3\text{O}_2(g) \rightleftharpoons 2\text{O}_3(g)$. Assume that ΔH_R° is independent of temperature.

- Without doing a calculation, predict whether the equilibrium position will shift toward reactants or products as the pressure is increased.
 - Without doing a calculation, predict whether the equilibrium position will shift toward reactants or products as the temperature is increased.
 - Calculate K_p at 600. and 700. K. Compare your results with your answer to part (b).
 - Calculate K_x at 600. K and pressures of 1.00 and 2.25 bar. Compare your results with your answer to part (a).
- (a) The number of moles of products is fewer than the number of moles of reactants. Therefore, the equilibrium position will shift toward products as the pressure is increased.
- (b) Using the data tables, $\Delta H_R^\circ > 0$, the equilibrium position will shift toward products as the temperature is increased.

- (c) $\Delta G_R^\circ = 2\Delta G_f^\circ(\text{O}_3, g) = 2 \times 163.2 \times 10^3 \text{ J mol}^{-1}$
 $\Delta H_R^\circ = 2\Delta H_f^\circ(\text{O}_3, g) = 2 \times 142.7 \times 10^3 \text{ J mol}^{-1}$
- $$\ln K_p(T_f) = -\frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{T_f} - \frac{1}{298.15 \text{ K}} \right)$$
- $$\ln K_p(600. \text{ K}) = -\frac{2 \times 163.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{2 \times 142.7 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{600. \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$
- $$\ln K_p(600. \text{ K}) = -73.7529$$
- $$K_p(600. \text{ K}) = 9.32 \times 10^{-33}$$
- $$\ln K_p(700. \text{ K}) = -\frac{2 \times 163.2 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298.15 \text{ K}} - \frac{2 \times 142.7 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \times \left(\frac{1}{700. \text{ K}} - \frac{1}{298.15 \text{ K}} \right)$$
- $$\ln K_p(700. \text{ K}) = -65.5796$$
- $$K_p(700. \text{ K}) = 3.30 \times 10^{-29}$$
- (d) Calculate K_x at 600. K and pressures of 1.00 and 2.25 bar.

$$K_x = K_p \left(\frac{P}{P^\circ} \right)^{-\Delta \nu} = 9.32 \times 10^{-33} \times \left(\frac{1.00 \text{ bar}}{1 \text{ bar}} \right)^{+1} = 9.32 \times 10^{-33} \text{ for } P = 1.00 \text{ bar}$$

$$K_x = K_p \left(\frac{P}{P^\circ} \right)^{-\Delta \nu} = 9.32 \times 10^{-33} \times \left(\frac{2.25 \text{ bar}}{1 \text{ bar}} \right)^{+1} = 2.10 \times 10^{-32} \text{ for } P = 2.25 \text{ bar}$$

P6.37 N_2O_3 dissociates according to the equilibrium $\text{N}_2\text{O}_3(g) \rightleftharpoons \text{NO}_2(g) + \text{NO}(g)$. At 298 K and one bar pressure, the degree of dissociation defined as the ratio of moles of $\text{NO}(g)$ or $\text{NO}_2(g)$ to the initial moles of the reactant assuming that no dissociation occurs is 3.5×10^{-3} . Calculate ΔG_R° for this reaction.

From Example Problem 6.10,

We set up the following table:

	$\text{N}_2\text{O}_3(g)$	\rightleftharpoons	$\text{NO}_2(g)$	+	$\text{NO}(g)$
Initial number of moles	n_0		0		0
Moles present at equilibrium	$n_0 - \delta_{eq}$		δ_{eq}		δ_{eq}
Mole fraction present at equilibrium, x_i	$\frac{n_0 - \delta_{eq}}{n_0 + \delta_{eq}}$		$\frac{\delta_{eq}}{n_0 + \delta_{eq}}$		$\frac{\delta_{eq}}{n_0 + \delta_{eq}}$
Partial pressure at equilibrium, $P_i = x_i P$	$\left(\frac{n_0 - \delta_{eq}}{n_0 + \delta_{eq}} \right) P$		$\frac{\delta_{eq}}{n_0 + \delta_{eq}} P$		$\frac{\delta_{eq}}{n_0 + \delta_{eq}} P$

We next express K_p in terms of n_0 , δ_{eq} , and P :

$$K_p(T) = \frac{\left(\frac{P_{\text{NO}}^{eq}}{P^\circ} \right) \left(\frac{P_{\text{NO}_2}^{eq}}{P^\circ} \right)}{\left(\frac{P_{\text{N}_2\text{O}_3}^{eq}}{P^\circ} \right)} = \frac{\left[\left(\frac{\delta_{eq}}{n_0 + \delta_{eq}} \right) \frac{P}{P^\circ} \right]^2}{\left(\frac{n_0 - \delta_{eq}}{n_0 + \delta_{eq}} \right) \frac{P}{P^\circ}} = \frac{\delta_{eq}^2}{(n_0 + \delta_{eq})(n_0 - \delta_{eq})} \frac{P}{P^\circ} = \frac{\delta_{eq}^2}{(n_0)^2 - \delta_{eq}^2} \frac{P}{P^\circ}$$

This expression is converted into one in terms of δ_{eq} :

Because $\alpha = \delta_{eq}/n_0$

$$K_p(T) = \frac{\delta_{eq}^2}{(n_0)^2 - \delta_{eq}^2} \frac{P}{P^\circ} = \frac{\alpha^2}{1 - \alpha^2} \frac{P}{P^\circ}$$

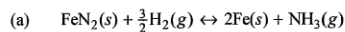
$$\left(K_p(T) + \frac{P}{P^\circ} \right) \alpha^2 = K_p(T)$$

$$\alpha = \sqrt{\frac{K_p(T)}{K_p(T) + \frac{P}{P^\circ}}}$$

$$\begin{aligned} \Delta G_R^\circ &= -RT \ln K_p = -RT \ln \frac{\alpha^2}{1 - \alpha^2} \frac{P}{P^\circ} = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 298 \text{ K} \times \ln \frac{(3.5 \times 10^{-3})^2}{1 - (3.5 \times 10^{-3})^2} \\ &= 28.0 \times 10^3 \text{ J mol}^{-1} \end{aligned}$$

P6.38 If the reaction $\text{Fe}_2\text{N}(s) + \frac{3}{2}\text{H}_2(g) \rightleftharpoons 2\text{Fe}(s) + \text{NH}_3(g)$ comes to equilibrium at a total pressure of 1 bar, analysis of the gas shows that at 700. and 800. K, $P_{\text{NH}_3}/P_{\text{H}_2} = 2.165$ and 1.083, respectively, if only $\text{H}_2(g)$ was initially present in the gas phase and $\text{Fe}_2\text{N}(s)$ was in excess.

- Calculate K_p at 700. and 800. K.
- Calculate ΔS_R° at 700. K and 800. K and ΔH_R° assuming that it is independent of temperature.
- Calculate ΔG_R° for this reaction at 298.15 K.



$$K_p = \frac{P_{\text{NH}_3}/P^\circ}{(P_{\text{H}_2}/P^\circ)^{3/2}}$$

$$P_{\text{total}} = 1 \text{ bar} = P_{\text{NH}_3} + P_{\text{H}_2}$$

At 700. K,

$$1 \text{ bar} = 2.165 P_{\text{H}_2} + P_{\text{H}_2} = 3.165 P_{\text{H}_2}$$

$$P_{\text{H}_2} = 0.316 \text{ bar}, P_{\text{NH}_3} = 0.684 \text{ bar.}$$

$$K_p(700. \text{ K}) = \frac{0.684}{(0.316)^{3/2}} = 3.85$$

At 800. K,

$$1 \text{ bar} = 1.083 P_{\text{H}_2} + P_{\text{H}_2} = 2.083 P_{\text{H}_2}$$

$$P_{\text{H}_2} = 0.480 \text{ bar}, P_{\text{NH}_3} = 0.520 \text{ bar}$$

$$K_p(800. \text{ K}) = \frac{0.520}{(0.480)^{3/2}} = 1.56$$

- (b) Assume that ΔH_R° is independent of temperature.

$$\ln \frac{K_p(800. \text{ K})}{K_p(700. \text{ K})} = \frac{-\Delta H_R^\circ}{R} \left(\frac{1}{800. \text{ K}} - \frac{1}{700. \text{ K}} \right)$$

$$\Delta H_R^\circ = \frac{-R \ln \frac{K_p(800. \text{ K})}{K_p(700. \text{ K})}}{\left(\frac{1}{800. \text{ K}} - \frac{1}{700. \text{ K}} \right)} = -42.0 \text{ kJ mol}^{-1}$$

$$\Delta G_R^\circ(700. \text{ K}) = -RT \ln K_p(700. \text{ K}) = -7.85 \text{ kJ mol}^{-1}$$

$$\Delta G_R^\circ(800. \text{ K}) = -RT \ln K_p(800. \text{ K}) = -2.97 \text{ kJ mol}^{-1}$$

$$\Delta S_R^\circ(700. \text{ K}) = \frac{\Delta H_R^\circ - \Delta G_R^\circ(700. \text{ K})}{700. \text{ K}} = -48.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_R^\circ(800. \text{ K}) = -48.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\begin{aligned} \text{(c) } \ln K_p(298.15 \text{ K}) &= \ln K_p(700. \text{ K}) - \frac{\Delta H_R^\circ}{R} \left(\frac{1}{298.15 \text{ K}} - \frac{1}{700. \text{ K}} \right) \\ &= \ln 3.85 + \frac{42.1 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{ K}^{-1}} \times \left(\frac{1}{298.15 \text{ K}} - \frac{1}{700. \text{ K}} \right) = 11.1 \end{aligned}$$

$$\begin{aligned} \Delta G_R^\circ(298.15 \text{ K}) &= -RT \ln K_p(298.15 \text{ K}) \\ &= -8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298.15 \text{ K} \times 11.1 = -27.4 \text{ kJ mol}^{-1} \end{aligned}$$

P6.39 Assume the internal energy of an elastic fiber under tension (see Problem 6.16) is given by $dU = T dS - P dV - F d\ell$. Obtain an expression for $(\partial G/\partial \ell)_{P,T}$ and calculate the maximum nonexpansion work obtainable when a collagen fiber contracts from $\ell = 20.0$ to 10.0 cm at constant P and T . Assume other properties as described in Problem 6.16.

$$dU = TdS - PdV - \gamma d\ell$$

$$\begin{aligned} dG &= d(U + PV - TS) = TdS - PdV - \gamma d\ell + PdV + VdP - TdS - SdT \\ &= -\gamma d\ell + VdP - SdT \end{aligned}$$

$$\left(\frac{\partial G}{\partial \ell} \right)_{P,T} = -\gamma = k\ell$$

$$\Delta G = w_{\text{rev}} = \int_{0.20 \text{ cm}}^{0.10 \text{ cm}} k\ell d\ell = \left[\frac{1}{2} k\ell^2 \right]_{0.20 \text{ cm}}^{0.10 \text{ cm}} = -10 \text{ N m}^{-1} \times \frac{(0.20 \text{ cm})^2 - (0.10 \text{ cm})^2}{2} = 1.5 \times 10^{-5} \text{ J}$$

P6.40 Under anaerobic conditions, glucose is broken down in muscle tissue to form lactic acid according to the reaction: $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) \rightarrow 2\text{CH}_3\text{CHOHCOOH}(\text{aq})$. Thermodynamic data at $T = 298 \text{ K}$ for glucose and lactic acid are given in the following table.

	$\Delta H_f^\circ (\text{kJ mol}^{-1})$	$C_p (\text{J K}^{-1} \text{ mol}^{-1})$	$S^\circ (\text{J K}^{-1} \text{ mol}^{-1})$
Glucose (s)	-1273.1	219.2	209.2
Lactic Acid (aq)	-673.6	127.6	192.1

Calculate ΔG_R° at $T = 298 \text{ K}$ and $T = 310. \text{ K}$. In your calculation at $310. \text{ K}$, (a) assume that ΔH_R° and ΔS_R° are constant in this temperature interval and (b) calculate ΔH_R° and ΔS_R° at $310. \text{ K}$ using the data in the previous table. Assume all heat capacities are constant in this temperature interval.

$$\begin{aligned} \Delta H_R^\circ(298.15 \text{ K}) &= 2\Delta H_f^\circ(\text{lactic acid}) - \Delta H_f^\circ(\text{glucose}) \\ &= 2 \times (-673.6 \text{ kJ mol}^{-1}) + 1273.1 \text{ kJ mol}^{-1} \\ &= -74.1 \text{ kJ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_R^\circ(298.15 \text{ K}) &= 2S^\circ(\text{lactic acid}) - S^\circ(\text{glucose}) \\ &= 2 \times 192.1 \text{ J K}^{-1} \text{ mol}^{-1} - 209.2 \text{ J K}^{-1} \text{ mol}^{-1} \\ &= 175 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G_R^\circ(298.15 \text{ K}) &= \Delta H_R^\circ(298.15 \text{ K}) - T\Delta S_R^\circ(298.15 \text{ K}) = -126 \text{ kJ mol}^{-1} \\ \Delta H_R^\circ(310. \text{ K}) &= \Delta H_R^\circ(298.15 \text{ K}) + \Delta C_p \Delta T \\ &= -74.1 \text{ kJ mol}^{-1} + (2 \times 127.6 \text{ J K}^{-1} - 219.2 \text{ J K}^{-1} \text{ mol}^{-1}) \times (310. \text{ K} - 298.15 \text{ K}) \\ &= -73.7 \text{ kJ mol}^{-1} \\ \Delta G_R^\circ(310. \text{ K}) &= \Delta H_R^\circ(310. \text{ K}) - 310. \text{ K} \times \Delta S_R^\circ(310. \text{ K}) \\ &= \Delta H_R^\circ(310. \text{ K}) - 310. \text{ K} \times \left[\Delta S_R^\circ(298.15 \text{ K}) + \Delta C_p \ln \frac{310. \text{ K}}{298.15 \text{ K}} \right] \\ &= -73.7 \text{ kJ mol}^{-1} - 310. \text{ K} \times \left[175 \text{ J K}^{-1} \text{ mol}^{-1} + 360 \text{ J K}^{-1} \text{ mol}^{-1} \times \ln \frac{310. \text{ K}}{298.15 \text{ K}} \right] \\ &= -73.7 \text{ kJ mol}^{-1} - 54.7 \text{ kJ mol}^{-1} = -128 \text{ kJ mol}^{-1} \end{aligned}$$

P6.41 Consider the equilibrium $3\text{O}_2(\text{g}) \rightleftharpoons 2\text{O}_3(\text{g})$.

- Using the Data tables, calculate K_p at 298 K.
- Assuming that the extent of reaction at equilibrium ξ_{eq} is much less than 1, show that the degree of reaction defined as half the number of moles of $\text{O}_3(\text{g})$ divided by the initial number moles of $\text{O}_2(\text{g})$ present before dissociation is given by $(1/2)\sqrt{K_p \times P/P^\circ}$.
- Calculate K_x at 298 K and a pressure of 5.00 bar.

$$\begin{aligned} \text{(a)} \quad \ln K_p(298.15) &= -\frac{\Delta G_R^\circ(298.15 \text{ K})}{R \times 298.15 \text{ K}} = \frac{2\Delta G_f^\circ(\text{O}_3(\text{g}))}{R \times 298.15 \text{ K}} \\ &= \frac{2 \times 163200 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 298.15 \text{ K}} = -131.742 \\ K_p(298.15) &= 6.10 \times 10^{-58} \end{aligned}$$

(b) We set up the following table:

	$3\text{O}_2(\text{g})$	\rightleftharpoons	$2\text{O}_3(\text{g})$
Initial number of moles	n_0		0
Moles present at equilibrium	$n_0 - 3\delta_{eq}$		$2\delta_{eq}$
Mole fraction present at equilibrium, x_i	$\frac{n_0 - 3\delta_{eq}}{n_0 - \delta_{eq}}$		$\frac{2\delta_{eq}}{n_0 - \delta_{eq}}$
Partial pressure at equilibrium, $P_i = x_i P$	$\frac{n_0 - 3\delta_{eq}}{n_0 - \delta_{eq}} P$		$\frac{2\delta_{eq}}{n_0 - \delta_{eq}} P$

We next express K_p in terms of n_0 , δ_{eq} , and P :

$$K_p(T) = \frac{\left(\frac{P_{\text{O}_3}^{eq}}{P^\circ}\right)^2}{\left(\frac{P_{\text{O}_2}^{eq}}{P^\circ}\right)^3} = \frac{\left[\frac{2\delta_{eq}}{n_0 - \delta_{eq}} \frac{P}{P^\circ}\right]^2}{\left[\frac{n_0 - 3\delta_{eq}}{n_0 - \delta_{eq}} \frac{P}{P^\circ}\right]^3} = \frac{4\delta_{eq}^2 (n_0 - \delta_{eq}) P^\circ}{(n_0 - 3\delta_{eq})^3 P} \approx \frac{4\delta_{eq}^2 P^\circ}{n_0^2 P}$$

Define $\alpha = \delta_{eq}/n_0$.

$$K_p(T) = 4\alpha^2 \frac{P^\circ}{P}$$

$$\alpha = \frac{1}{2} \sqrt{K_p(T) \frac{P}{P^\circ}}$$

$$\alpha = \frac{1}{2} \sqrt{6.10 \times 10^{-58} \times 5} = 2.76 \times 10^{-29}$$

$$(c) \quad K_x = K_p \left(\frac{P}{P^\circ} \right)^{-\Delta\nu} = 6.10 \times 10^{-58} \times 5^{-1} = 3.05 \times 10^{-57}$$

P6.42 Use the equation $C_{P,m} - C_{V,m} = TV_m\beta^2/\kappa$ and the Data Tables to determine $C_{V,m}$ for $\text{H}_2\text{O}(l)$ at 298 K. Calculate $(C_{P,m} - C_{V,m})/C_{P,m}$.

$$\begin{aligned} C_{P,m} - C_{V,m} &= TV_m\beta^2/\kappa = 298 \text{ K} \times \frac{18.02 \times 10^{-3} \text{ kg mol}^{-1}}{998 \text{ kg m}^{-3}} \times \frac{(2.04 \times 10^{-4} \text{ K}^{-1})^2}{45.9 \times 10^{-6} \text{ bar}^{-1} \times 10^{-5} \text{ bar/Pa}} \\ &= 0.488 \text{ J K}^{-1} \text{ mol}^{-1} \\ (C_{P,m} - C_{V,m})/C_{P,m} &= \frac{0.488 \text{ J K}^{-1} \text{ mol}^{-1}}{75.3 \text{ J K}^{-1} \text{ mol}^{-1}} = 0.648\% \end{aligned}$$

P6.43 As shown in Example Problem 3.5, $(\partial U_m/\partial V)_T = a/V^2_m$ for a van der Waals gas. In this problem, you will compare the change in energy with temperature and volume for N_2 , treating it as a van der Waals gas.

- Calculate ΔU per mole of $\text{N}_2(g)$ at 1 bar pressure and 298 K if the volume is increased by 1.00% at constant T .
- Calculate ΔU per mole of $\text{N}_2(g)$ at 1 bar pressure and 298 K if the temperature is increased by 1.00% at constant V .
- Calculate the ratio of your results in part (a) to the result in part (b). What can you conclude about the relative importance of changes in temperature and volume on ΔU ?

$$(a) \quad V_i = \frac{nRT}{P_i} = \frac{1 \text{ mol} \times 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \times 298 \text{ K}}{10^5 \text{ Pa}} = 0.0248 \text{ m}^3 = 24.8 \text{ L}$$

From Example Problem 3.5,

$$\begin{aligned} \Delta U_T &= \int_{V_i}^{V_f} \left(\frac{\partial U}{\partial V} \right)_T dV = \int_{V_i}^{V_f} \frac{n^2 a}{V^2} dV = n^2 a \left(\frac{1}{V_i} - \frac{1}{V_f} \right) \\ &= 1 \text{ mol} \times 0.137 \text{ m}^3 \text{ mol}^{-1} \times \left(\frac{1}{0.0248 \text{ m}^3} - \frac{1}{1.01 \times 0.0248 \text{ m}^3} \right) = 0.0547 \text{ J} \end{aligned}$$

- $\Delta U_V = C_{V,m}\Delta T = (C_{P,m} - R)\Delta T = (29.12 \text{ J mol}^{-1} \text{ K}^{-1} - 8.314 \text{ J mol}^{-1} \text{ K}^{-1}) \times 2.98 \text{ K} = 62.0 \text{ J}$
- $\Delta U_V/\Delta U_T = 1.13 \times 10^3$. The change in energy with volume can be neglected relative to the change in energy with temperature.