

CHAPTER 16. Colligative Properties of Solutions

16-1. The number of moles of $\text{KMnO}_4(aq)$ is

$$\text{moles KMnO}_4 = (5.25 \text{ g KMnO}_4) \left(\frac{1 \text{ mol KMnO}_4}{158.04 \text{ g KMnO}_4} \right) = 0.0332 \text{ mol}$$

$$\text{molality} = m = \frac{0.0332 \text{ mol}}{0.250 \text{ kg}} = 0.133 \text{ m}$$

16-2. (a) $\text{CH}_3\text{OH}(l)$ is an organic compound, so $i = 1$ and

$$m_c = im = (1) \left(\frac{1.00 \text{ mol}}{0.500 \text{ kg}} \right) = 2.00 \text{ m}_c$$

(b) $\text{AgNO}_3(s)$ is a strong electrolyte with $i = 2$, so

$$m_c = (2)(2.00 \text{ m}) = 4.00 \text{ m}_c$$

(c) $\text{Ca}(\text{ClO}_4)_2(s)$ is a strong electrolyte with $i = 3$, so

$$m_c = (3)(2.00 \text{ m}) = 6.00 \text{ m}_c$$

16-3. The vapor pressure lowering is

$$\Delta P_1 = 75.0 \text{ Torr} - 63.9 \text{ Torr} = 11.1 \text{ Torr}$$

Using Equation 16.10, we have that

$$x_2 = \frac{\Delta P_1}{P_1^\circ} = \frac{11.1 \text{ Torr}}{75.0 \text{ Torr}} = 0.148$$

The formula mass of benzene, $\text{C}_6\text{H}_6(l)$, is $78.11 \text{ g}\cdot\text{mol}^{-1}$ and that of naphthalene, $\text{C}_{10}\text{H}_8(s)$, is $128.16 \text{ g}\cdot\text{mol}^{-1}$. Now, let z = number of grams of naphthalene in the solution. The mass of benzene is $(41.3 - z)$ grams, and so

$$x_{\text{naph}} = \frac{n_{\text{naph}}}{n_{\text{benz}} + n_{\text{naph}}} = \frac{\frac{z \text{ g}}{128.16 \text{ g}\cdot\text{mol}^{-1}}}{\frac{(41.3 - z) \text{ g}}{78.11 \text{ g}\cdot\text{mol}^{-1}} + \frac{z \text{ g}}{128.17 \text{ g}\cdot\text{mol}^{-1}}} = 0.148$$

Solving for z , we get 9.16 grams.

16-4. The mole fraction of $(\text{NH}_4)_2\text{SO}_4(aq)$ is given by

$$x_{(\text{NH}_4)_2\text{SO}_4} = \frac{n_{(\text{NH}_4)_2\text{SO}_4}}{n_{(\text{NH}_4)_2\text{SO}_4} + n_{\text{H}_2\text{O}}}$$

Because $(\text{NH}_4)_2\text{SO}_4(aq)$ is a strong electrolyte, it dissociates completely into $\text{NH}_4^+(aq)$ and $\text{SO}_4^{2-}(aq)$ ions. Assume a one kilogram solution. The number of moles of ions in one kilogram of a 0.70 m $(\text{NH}_4)_2\text{SO}_4(aq)$ solution is

$$\text{moles of ions} = (3)(0.70 \text{ mol} \cdot \text{kg}^{-1})(1.00 \text{ kg}) = 2.1 \text{ mol}$$

and the number of moles of water is $1000/18.02 \text{ g} \cdot \text{mol}^{-1} = 55.49$ moles. Therefore,

$$x_{(\text{NH}_4)_2\text{SO}_4} = \frac{2.1 \text{ mol}}{2.1 \text{ mol} + 55.49 \text{ mol}} = 0.0365$$

From Table 15.7, we see that $P_{\text{H}_2\text{O}}^\circ = 55.4$ Torr at 40°C . Using Equation 16.10, we have

$$\Delta P_{\text{H}_2\text{O}} = x_{(\text{NH}_4)_2\text{SO}_4} P_{\text{H}_2\text{O}}^\circ = (0.0365)(55.4 \text{ Torr}) = 2.0 \text{ Torr}$$

16-5. Because $\text{NaCl}(aq)$ is a strong electrolyte with $i = 2$, we have

$$m_c = \frac{(2) \left(\frac{3.5 \text{ g NaCl}}{58.44 \text{ g} \cdot \text{mol}^{-1} \text{ NaCl}} \right)}{0.0965 \text{ kg H}_2\text{O}} = 1.24 m_c$$

Now use Equation 16.13 to write

$$\Delta T_b = K_b m_c = (0.513 \text{ K} \cdot m_c^{-1})(1.24 m_c) = 0.64$$

Therefore, the normal boiling point will be 100.64°C .

16-6. We use Equation 16.14 to write

$$\Delta T_f = 5.25 \text{ K} = (1.86 \text{ K} \cdot m_c^{-1}) m_c$$

or $m_c = 2.82 m_c$. For $\text{CaCl}_2(s)$, $i = 3$, and so $m = 0.941 m$.

16-7. We use Equation 16.15 in the form

$$i = \frac{T_f^\circ - T_f}{K_f m} = \frac{5.49 \text{ K} - 2.96 \text{ K}}{(5.07 \text{ K} \cdot m_c^{-1})(1.00 m)} = 0.499$$

where the freezing point of benzene is 5.49°C . Therefore, $i = 0.5$ or $1/2$, a result suggesting the formation of dimers, $(\text{CH}_3\text{COOH})_2$.

16-8. Because $\text{CaCl}_2(s)$ is a strong electrolyte, we use Equation 16.16 with $M_c = 3M$ to write

$$\begin{aligned} \Pi &= RTM_c = (0.083145 \text{ L} \cdot \text{bar} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})(3)(0.10 \text{ mol} \cdot \text{L}^{-1}) \\ &= 7.4 \text{ bar} \end{aligned}$$

The value and units of Π depend upon the value of R used.

16-9. Use Equation 16.16 with $M_c = M$ to write

$$M = \frac{\Pi}{RT} = \frac{19.0 \text{ Torr}}{(62.3637 \text{ L} \cdot \text{Torr} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298 \text{ K})} = 1.02 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

One liter of the solution will contain $(1000 \text{ mL}) \left(\frac{0.550 \text{ g}}{50.0 \text{ mL}} \right) = 11.0 \text{ g}$. Thus we have the correspondence

$$1.02 \times 10^{-3} \text{ mol} \approx 11.0 \text{ g}$$

$$1 \text{ mol} \approx 1.08 \times 10^4 \text{ g}$$

16-10. We use Equation 16.20 in the notation

$$P_{\text{total}} = P_{\text{tol}}^{\circ} + x_{\text{benz}}(P_{\text{benz}}^{\circ} - P_{\text{tol}}^{\circ})$$

Substituting in the values given, we have

$$100.0 \text{ Torr} = 59.2 \text{ Torr} + x_{\text{benz}}(124 \text{ Torr})$$

or $x_{\text{benz}} = 0.329$. Now

$$y_{\text{benz}} = \frac{P_{\text{benz}}}{P_{\text{total}}} = \frac{(0.329)(183 \text{ Torr})}{100.0 \text{ Torr}} = 0.602$$

16-11. We use Equation 16.21 to write

$$M_{\text{gas}} = \frac{P_{\text{gas}}}{k_h} = \frac{1.00 \text{ bar}}{10 \text{ bar} \cdot \text{M}^{-1}} = 0.10 \text{ M}$$

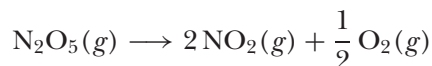
CHAPTER 17. Chemical Kinetics: Rate Laws

17-1. See the text.

17-2. The average rate of production of $O_2(g)$ is

$$\text{rate of reaction} = \frac{\Delta[O_2]}{\Delta t} = \frac{(0.28 - 0.16) \times 10^{-2} \text{ M}}{(20.0 - 10.0) \text{ min}} = 1.2 \times 10^{-4} \text{ M} \cdot \text{min}^{-1}$$

17-3. The equation for the reaction is



According to the chemical equation, one half of a mole of $O_2(g)$ is produced for every mole of $N_2O_5(g)$ consumed. Therefore, at $t = 70.0$ minutes

$$\begin{aligned} [N_2O_5] &= [N_2O_5]_0 - 2 [O_2] = 1.24 \times 10^{-2} \text{ M} - (2)(0.55 \times 10^{-2} \text{ M}) \\ &= 1.4 \times 10^{-3} \text{ M} \end{aligned}$$

$$[NO_2] = 4 [O_2] = (4)(0.55 \times 10^{-2} \text{ M}) = 0.022 \text{ M}$$

17-4. Write

$$(\text{rate of reaction})_0 = k [CH_3N_2CH_3]_0^x$$

where x is the order of the reaction. Dividing the data for run 2 by the data for run 1 gives

$$\frac{3.65 \times 10^{-4}}{2.42 \times 10^{-4}} = \left(\frac{0.913}{0.604} \right)^x$$

$$1.51 = (1.51)^x$$

or $x = 1$. You obtain the same result using the data from the other runs. To evaluate k , we use run 2 (arbitrarily) to obtain

$$k = \frac{(\text{rate of reaction})_0}{[CH_3N_2CH_3]_0} = \frac{3.65 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} \cdot \text{s}^{-1}}{0.913 \text{ mol} \cdot \text{L}^{-1}} = 4.00 \times 10^{-4} \text{ s}^{-1}$$

17-5. Write

$$(\text{rate of reaction})_0 = k [NO]_0^x [Br_2]_0^y$$

Dividing the data for run 2 by the data for run 1 gives

$$2.25 = (1.50)^x$$

or $x = 2$. Dividing the data for run 3 by run 2 gives

$$3.00 = (3.00)^y$$

or $y = 1$. Thus the rate law is

$$\text{rate of reaction} = k [\text{NO}]^2 [\text{Br}_2]$$

We evaluate the rate constant using the data for run 2 (arbitrarily).

$$k = \frac{(\text{rate of reaction})_0}{[\text{NO}]_0^2 [\text{Br}_2]_0} = \frac{2.93 \times 10^{-3} \text{ M} \cdot \text{min}^{-1}}{(1.50 \text{ M})^2 (1.00 \text{ M})} = 1.30 \times 10^{-3} \text{ M}^{-2} \cdot \text{min}^{-1}$$

and so

$$\text{rate of reaction} = (1.30 \times 10^{-3} \text{ M}^{-2} \cdot \text{min}^{-1}) [\text{NO}]^2 [\text{Br}_2]$$

17-6. Use Equation 17.19

$$\begin{aligned} \text{fraction} &= \frac{[\text{A}]}{[\text{A}]_0} = e^{-kt} = e^{-(0.015 \text{ min}^{-1})(60 \text{ min/1 hr})(1.0 \text{ hr})} \\ &= e^{-0.90} = 0.41 \end{aligned}$$

17-7. From Example 17-4, the rate constant of the reaction is $2.20 \times 10^{-5} \text{ s}^{-1}$. Using Equation 17.20, the half-life is

$$t_{1/2} = \frac{0.693}{k} = 3.15 \times 10^4 \text{ s} = 8.75 \text{ hr}$$

The number of half-lives in 35 hours is $35/8.75 = 4.0$. Using Equation 17.21, the fraction remaining after 35 hours (4.0 half-lives) is given by

$$\frac{[\text{A}]}{[\text{A}]_0} = \text{fraction remaining} = \left(\frac{1}{2}\right)^n = \left(\frac{1}{2}\right)^{4.0} = 0.0625$$

17-8. See the text.

17-9. Use Equation 17.23

$$\ln \frac{N}{N_0} = \ln \left(\frac{0.010 N_0}{N_0} \right) = \ln(0.010) = -\frac{0.693 t}{2.41 \times 10^4 \text{ y}}$$

Solving for t gives 1.6×10^5 years.

17-10. We use Equation 17.23 with $t = x t_{1/2}$, where x is the number of half-lives. Realize that 0.010% of its original value means that $N/N_0 = 0.00010$.

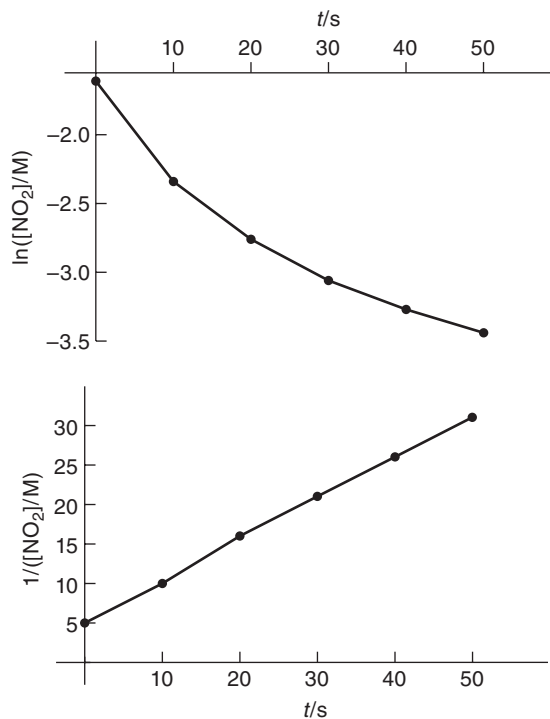
$$\ln \frac{N}{N_0} = \ln(0.00010) = -\left(\frac{0.693}{t_{1/2}}\right) t = -\left(\frac{0.693}{t_{1/2}}\right) x t_{1/2} = -0.693 x$$

Solving for x gives 13 half-lives.

17-11. We use Equation 17.27

$$t = (8.27 \times 10^3 \text{ years}) \ln \left[\frac{15.3 \text{ disintegration} \cdot \text{min}^{-1} \cdot \text{g}^{-1}}{(0.928)(15.3 \text{ disintegration} \cdot \text{min}^{-1} \cdot \text{g}^{-1})} \right] = 618 \text{ years}$$

17-12. Let's see whether the reaction is first-order or second-order. The following two figures show $\ln([\text{NO}_2]/\text{M})$ plotted against t (linear for a first-order reaction) and $1/[\text{NO}_2]/\text{M}^{-1}$ plotted against t (linear for a second-order reaction). You can see from the figures that the reaction is second-order.



We can calculate the value of the rate constant by using the various data sets in Table 17.10 and averaging. For example, using the data for the $t = 10.0$ s run (arbitrarily) we obtain from Equation 17.31

$$\frac{1}{0.096 \text{ M}} = \frac{1}{0.20 \text{ M}} + k (10.0 \text{ s})$$

or $k = 0.54 \text{ M}^{-1} \cdot \text{s}^{-1}$. The other data sets give $0.54 \text{ M}^{-1} \cdot \text{s}^{-1}$, $0.54 \text{ M}^{-1} \cdot \text{s}^{-1}$, $0.53 \text{ M}^{-1} \cdot \text{s}^{-1}$, and $0.53 \text{ M}^{-1} \cdot \text{s}^{-1}$.

17-13. We are given P_{total} in Table 17.13, so we must first determine $P_{\text{N}_2\text{O}_3}$ at various time intervals.

$$P_{\text{total}} = P_{\text{N}_2\text{O}_3} + P_{\text{NO}} + P_{\text{NO}_2}$$

Because we start with only $\text{N}_2\text{O}_3(g)$, $P_{\text{NO}} = P_{\text{NO}_2}$. Thus,

$$P_{\text{NO}} = P_{\text{NO}_2} = P_{\text{N}_2\text{O}_3}^0 - P_{\text{N}_2\text{O}_3}$$

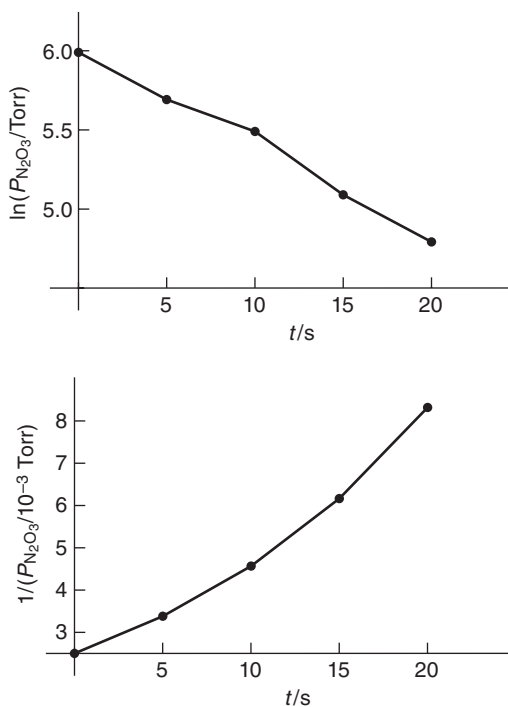
where $P_{\text{N}_2\text{O}_3}^0$ is the initial value of $P_{\text{N}_2\text{O}_3}$. Therefore, we have

$$\begin{aligned} P_{\text{total}} &= P_{\text{N}_2\text{O}_3} + 2 P_{\text{N}_2\text{O}_3}^0 - 2 P_{\text{N}_2\text{O}_3} \\ &= 2 P_{\text{N}_2\text{O}_3}^0 - P_{\text{N}_2\text{O}_3} \end{aligned}$$

or

$$P_{\text{N}_2\text{O}_3} = 2 P_{\text{N}_2\text{O}_3}^0 - P_{\text{total}}$$

where $P_{\text{N}_2\text{O}_3}^0 = 400$ Torr. The following two figures show $\ln(P_{\text{N}_2\text{O}_3}/\text{Torr})$ plotted against t (linear for a first-order reaction) and $(1/P_{\text{N}_2\text{O}_3})/10^{-3} \text{ Torr}^{-1}$ plotted against t (linear for a second-order reaction). You can see from the figures that the reaction is first-order.



We can calculate the value of the rate constant by using the various data sets in Table 17.13 and averaging. For example, using the data for the $t = 5.0$ s run (arbitrarily) we obtain from Equation 17.18,

$$\ln \frac{2 P_{\text{N}_2\text{O}_3}^0 - P_{\text{total}}}{P_{\text{N}_2\text{O}_3}} = \ln \frac{(800 - 504) \text{ Torr}}{400 \text{ Torr}} = -k (5.0 \text{ s})$$

or $k = 0.060 \text{ s}^{-1}$. The other runs give 0.060 s^{-1} , 0.060 s^{-1} , and 0.060 s^{-1} , or 0.060 s^{-1} to two significant figures.

17-14. We use Equation 17.35 with $P_{\text{C}_5\text{H}_6}^0 = 500$ Torr and $k = 7.16 \times 10^{-5} \text{ Torr}^{-1} \cdot \text{s}^{-1}$:

$$t_{1/2} = \frac{1}{k P_{\text{C}_5\text{H}_6}^0} = \frac{1}{(7.16 \times 10^{-5} \text{ Torr}^{-1} \cdot \text{s}^{-1})(500 \text{ Torr})} = 27.9 \text{ s}$$

CHAPTER 18. Chemical Kinetics: Mechanisms

18-1. See the text.

18-2. Using Figure 18.3 as a guide, we see that the value of the activation energy in the reverse direction is $80 \text{ kJ}\cdot\text{mol}^{-1} + 50 \text{ kJ}\cdot\text{mol}^{-1} = 130 \text{ kJ}\cdot\text{mol}^{-1}$.

18-3. The time, t , for an egg to boil is inversely proportional to the value of the rate constant at that temperature. The larger the rate constant, the less time it takes to boil the egg. Using Equation 18.9, we have

$$\ln \frac{k_{100^\circ\text{C}}}{k_{92.2^\circ\text{C}}} = \ln \frac{t_{92.2^\circ\text{C}}}{t_{100^\circ\text{C}}} \approx \frac{(42 \times 10^3 \text{ J}\cdot\text{mol}^{-1})(373.2 \text{ K} - 365.4 \text{ K})}{(8.3145 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(373.2 \text{ K})(365.4 \text{ K})} \\ = 0.29$$

or

$$t_{92} = t_{100}e^{0.29} = (3.0 \text{ min})(1.34) = 4.0 \text{ min}$$

18-4. The slow step controls the overall rate of reaction, and being an elementary step, we see that

$$\text{rate of reaction} = k_1 [\text{Fe}^{2+}] [\text{HNO}_2]$$

18-5. Step (2) controls the overall rate of reaction

$$\text{rate of reaction} = k_2 [\text{NO}] [\text{NO}_3]$$

We can eliminate $[\text{NO}_3]$, an intermediate species, using Step (1)

$$[\text{NO}_3] = \frac{k_1}{k_{-1}} [\text{NO}] [\text{O}_2]$$

Substituting this expression into the rate expression for step 1 yields

$$\text{rate of reaction} = \frac{k_1}{k_{-1}} k_2 [\text{NO}]^2 [\text{O}_2] = k [\text{NO}]^2 [\text{O}_2]$$

which is consistent with the experimentally determined rate law.

18-6. Start with (see Example 18-6) where 2 is the catalyzed reaction and 1 the uncatalyzed reaction

$$\ln k_2 = -\frac{E_{a_2}}{RT} + \ln A_2$$

$$\ln k_1 = -\frac{E_{a_1}}{RT} + \ln A_1$$

Assume that $A_1 = A_2$ and subtract to get

$$\begin{aligned} \ln \frac{k_2}{k_1} &= \frac{E_{a_1} - E_{a_2}}{RT} = \frac{\Delta E}{RT} = \frac{5.00 \times 10^3 \text{ J} \cdot \text{mol}^{-1}}{(8.3145 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})(298.2 \text{ K})} \\ &= 2.02 \end{aligned}$$

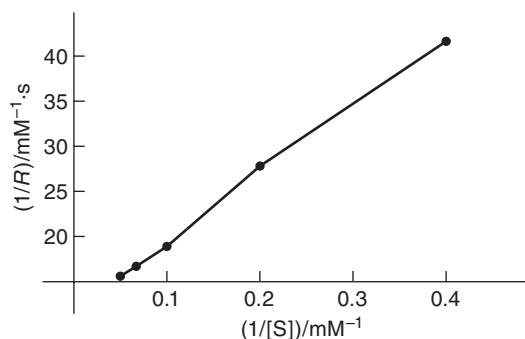
or

$$\frac{k_2}{k_1} = e^{2.02} = 7.5$$

18-7. We must first make a table of $1/R$ and $1/[S]$

$(1/R)/\text{mM}^{-1} \cdot \text{s}$	41.6	27.8	18.9	16.7	15.6
$(1/[S])/mM^{-1}$	0.40	0.20	0.10	0.067	0.050

A plot of $1/R$ against $1/[S]$ is a straight line.



Using the second and third data sets (arbitrarily), we calculate the slope to be

$$\text{slope} = \frac{18.9 \text{ mM}^{-1} \cdot \text{s} - 27.8 \text{ mM}^{-1} \cdot \text{s}}{0.10 \text{ mM}^{-1} - 0.20 \text{ mM}^{-1}} = \frac{-8.9 \text{ mM}^{-1} \cdot \text{s}}{-0.10 \text{ mM}^{-1}} = 89 \text{ s} = \frac{K_M}{R_{\max}}$$

by Equation 18.32. The intercept is about $12 \text{ mM}^{-1} \cdot \text{s}$, so

$$\frac{1}{R_{\max}} = 12 \text{ mM}^{-1} \cdot \text{s}$$

and so $R_{\max} = 0.083 \text{ mM} \cdot \text{s}^{-1}$ and $K_M = 7.4 \text{ mM}$. We used just two data points to determine the slope. A more sophisticated treatment of the linear plot gives $R_{\max} = 0.085 \text{ mM} \cdot \text{s}^{-1}$ and $K_M = 6.4 \text{ mM}$.

CHAPTER 19. Chemical Equilibrium

19-1. From the stoichiometry of the chemical equation, we have

$$\begin{aligned} \left(\frac{\text{change in moles}}{\text{per liter of SO}_2} \right) &= \left(\frac{\text{moles per liter}}{\text{of O}_2 \text{ reacted}} \right) \left(\frac{2 \text{ mol SO}_2}{1 \text{ mol O}_2} \right) \\ &= \left[\frac{(3.500 - 0.075) \text{ mol O}_2}{1 \text{ L}} \right] \left(\frac{2 \text{ mol SO}_2}{1 \text{ mol O}_2} \right) \\ &= 6.850 \text{ mol} \cdot \text{L}^{-1} \end{aligned}$$

Therefore;

$$\begin{aligned} [\text{O}_2]_{\text{eq}} &= 0.075 \text{ M} \\ [\text{SO}_2]_{\text{eq}} &= 8.500 \text{ M} - 6.850 \text{ M} = 1.650 \text{ M} \\ [\text{SO}_3]_{\text{eq}} &= 5.575 \text{ M} + 6.850 \text{ M} = 12.425 \text{ M} \end{aligned}$$

19-2. See the text. Recall that species in a liquid or solid state do not enter the equilibrium-constant expression.

19-3. From the data given, we can construct the following concentration table

Concentration	$2 \text{ SO}_2(g)$	$+ \text{ O}_2(g)$	\rightleftharpoons	$2 \text{ SO}_3(g)$
Initial	3.00 M	6.00 M		1.00 M
Change				+0.40 M
Equilibrium				1.40 M

Because the change in $[\text{SO}_3]$ is +0.40 M, we have that the change in $[\text{SO}_2]$ to reach equilibrium is -0.40 M, and that of $[\text{O}_2]$ is -0.20 M. Thus, the final concentration table is

Concentration	$2 \text{ SO}_2(g)$	$+ \text{ O}_2(g)$	\rightleftharpoons	$2 \text{ SO}_3(g)$
Initial	3.00 M	6.00 M		1.00 M
Change	-0.40 M	-0.20 M		0.40 M
Equilibrium	2.60 M	5.80 M		1.40 M

And so,

$$K_c = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]} = \frac{(1.40 \text{ M})^2}{(2.60 \text{ M})^2(5.80 \text{ M})} = 0.0500 \text{ M}^{-1}$$

19-4. We use Equation 19.18

$$K_p = K_c(RT)^{\Delta v_{\text{gas}}} = K_c(RT)^{-1} = 25 \text{ atm}^{-1}$$

$$K_c = (25 \text{ atm}^{-1})(0.08206 \text{ L}\cdot\text{atm}\cdot\text{mol}^{-1}\cdot\text{K}^{-1})(1020 \text{ K}) = 2.1 \times 10^3 \text{ M}^{-1}$$

19-5. We set up a concentration table

Concentration	2 S(g)	+ C(s)	\rightleftharpoons	CS ₂ (g)
Initial	0.700 M	–		0 M
Change	–2x	–		+x
Equilibrium	0.700 M – 2x	–		x

Now write

$$K_c = \frac{[\text{CS}_2]}{[\text{S}]^2} = \frac{x}{(0.700 \text{ M} - 2x)^2} = 9.40 \text{ M}^{-1}$$

Put this in the standard form of a quadratic equation:

$$37.6 \text{ M}^{-1}x^2 - 27.3x + 4.61 \text{ M} = 0$$

Solving for x gives 0.266 M and 0.467 M. We reject the 0.467 M root because [S] would be negative. Therefore [CS₂] = 0.266 M.

19-6. We set up a pressure table

Pressure	C(s)	+ CO ₂ (g)	\rightleftharpoons	2 CO(g)
Initial	–	0.22 atm		0
Change	–	–x		+2x
Equilibrium	–	0.22 atm – x		2x

Now write

$$K_p = 1.90 \text{ atm} = \frac{(2x)^2}{0.22 \text{ atm} - x} = \frac{4x^2}{0.22 \text{ atm} - x}$$

or

$$4x^2 + 1.90 \text{ atm } x - 0.418 \text{ atm}^2 = 0$$

Solving for x gives 0.164 atm and –0.639 atm. From the stoichiometry of the reaction, x must be a positive number, so we reject the negative value. Therefore,

$$P_{\text{CO}_2} = 0.22 \text{ atm} - 0.164 \text{ atm} = 0.06 \text{ atm}$$

$$P_{\text{CO}} = (2)(0.164 \text{ atm}) = 0.33 \text{ atm}$$

$$P_{\text{total}} = P_{\text{CO}_2} + P_{\text{CO}} = 0.06 \text{ atm} + 0.33 \text{ atm} = 0.39 \text{ atm}$$

19-7. (a) The equilibrium-constant expression tells us that

$$P_{\text{NH}_3} P_{\text{HI}} = 18 \text{ bar}^2$$

$P_{\text{NH}_3} = P_{\text{HI}}$, and so $P_{\text{NH}_3} = 4.24 \text{ bar}$. The total pressure is

$$P_{\text{total}} = P_{\text{NH}_3} + P_{\text{HI}} = 8.5 \text{ bar}$$

(b) In this case,

$$P_{\text{NH}_3} P_{\text{HI}} = (5.0 \text{ bar} + x)(x) = 18 \text{ bar}^2$$

where x is the equilibrium pressure of $\text{HI}(g)$. Solving for x gives 2.4 bar and -7.4 bar. We obviously reject the second root, so that

$$P_{\text{HI}} = 2.4 \text{ bar}$$

$$P_{\text{NH}_3} = 5.0 \text{ bar} + 2.4 \text{ bar} = 7.4 \text{ bar}$$

$$P_{\text{total}} = 7.4 \text{ bar} + 2.4 \text{ bar} = 9.8 \text{ bar}$$

19-8. (a) In this case, the concentration table is

Concentration	$\text{H}_2(g)$	+	$\text{Cl}_2(g)$	\rightleftharpoons	$2 \text{HCl}(g)$
Initial	0.500 M		0.500 M		0.500 M
Change	$-x$		$-x$		$+2x$
Equilibrium	$0.500 \text{ M} - x$		$0.500 \text{ M} - x$		$0.500 \text{ M} + 2x$

Using the equilibrium-constant expression gives

$$\frac{(0.500 \text{ M} + 2x)^2}{(0.500 \text{ M} - x)^2} = 2.5 \times 10^{-4}$$

or

$$\frac{0.500 \text{ M} + 2x}{0.500 \text{ M} - x} = \pm 0.0158$$

giving $x = -0.244 \text{ M}$ or -0.256 M . The concentration of $\text{HCl}(g)$ must be a positive quantity, so we reject the -0.256 M root. Therefore,

$$[\text{H}_2] = [\text{Cl}_2] = 0.744 \text{ M}$$

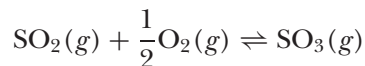
$$[\text{HCl}] = 0.012 \text{ M}$$

As a check,

$$\frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} = \frac{(0.012 \text{ M})^2}{(0.744 \text{ M})^2} = 2.6 \times 10^{-4}$$

(b) See the text.

19-9. The equation



is 1/2 of the reverse of



so

$$K_p = \frac{1}{(0.29 \text{ atm})^{1/2}} = 1.9 \text{ atm}^{-1/2}$$

19-10. (a) Decreasing $[\text{CO}]$ will drive the reaction to the right, and so $[\text{CO}_2]$ decreases.

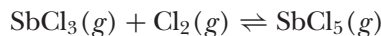
(b) Changing the amount of $\text{C}(s)$, a solid, has no effect on the equilibrium.

19-11. The value of $\Delta H_{\text{rxn}}^\circ$ for the reaction as written is

$$\begin{aligned} \Delta H_{\text{rxn}}^\circ &= \Delta H_f^\circ[\text{SO}_3] - \{\Delta H_f^\circ[\text{SO}_2] + \frac{1}{2}\Delta H_f^\circ[\text{O}_2(g)]\} \\ &= (-395.7 \text{ kJ}\cdot\text{mol}^{-1}) - \{(-296.8 \text{ kJ}\cdot\text{mol}^{-1}) + 0 \text{ kJ}\cdot\text{mol}^{-1}\} \\ &= -98.9 \text{ kJ}\cdot\text{mol}^{-1} < 0 \end{aligned}$$

Because $\Delta H_{\text{rxn}}^{\circ} < 0$, the reaction is exothermic. Therefore, a decrease in temperature will shift the equilibrium to the right, increasing the production of $\text{SO}_3(g)$.

19-12. The equation for the reaction can be written as



Using the data given, the value of K_p is

$$K_p = \frac{P_{\text{SbCl}_5}}{P_{\text{SbCl}_3} P_{\text{Cl}_2}} = \frac{0.228 \text{ bar}}{(0.670 \text{ bar})(0.438 \text{ bar})} = 0.777 \text{ bar}^{-1}$$

We set up the concentration table with the initial pressures halved because we have doubled the volume of the container.

Pressure	$\text{SbCl}_3(g)$	+	$\text{Cl}_2(g)$	\rightleftharpoons	$\text{SbCl}_5(g)$
Initial	0.335 bar		0.219 bar		0.114 bar
Change	+ x		+ x		- x
Equilibrium	0.335 bar + x		0.219 bar + x		0.114 bar - x

Using the equilibrium-constant expression, we have

$$\frac{0.114 \text{ bar} - x}{(0.335 \text{ bar} + x)(0.219 \text{ bar} + x)} = 0.777 \text{ bar}^{-1}$$

or

$$0.777 \text{ bar}^{-1} x^2 + 0.430x + 0.057 \text{ bar} = 0.114 \text{ bar} - x$$

or

$$0.777 \text{ bar}^{-1} x^2 + 1.430x - 0.057 \text{ bar} = 0$$

The two roots are $x = 0.0390 \text{ bar}$ and -1.88 bar . We reject the second root because $[\text{SbCl}_3]$ and $[\text{Cl}_2]$ must be positive quantities. Therefore,

$$P_{\text{SbCl}_3} = 0.335 \text{ bar} + 0.0390 \text{ bar} = 0.374 \text{ bar}$$

$$P_{\text{Cl}_2} = 0.219 \text{ bar} + 0.0390 \text{ bar} = 0.258 \text{ bar}$$

$$P_{\text{SbCl}_5} = 0.114 \text{ bar} - 0.0390 \text{ bar} = 0.075 \text{ bar}$$

Note that the equilibrium position shifts from right to left, in accord with Le Châtelier's principle.

19-13. In this case,

$$Q_P = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(485 \text{ Torr})^2}{150 \text{ Torr}} = 1570 \text{ Torr}$$

and

$$\frac{Q_P}{K_p} = \frac{1570 \text{ Torr}}{1.93 \text{ Torr}} > 1$$

Because $Q_P/K_p > 1$, the reaction will proceed from right to left until $Q_P = K_p$.