# CHAPTER 9

CHEMICAL EQUILIBRIA

9.2   (a) True

(b) False. Changing the rate of a reaction will not affect the value of the equilibrium constant; it merely changes how fast one gets to equilibrium.

(c) True

(d) False. The *standard* reaction free energy ΔG_r° is not 0 at equilibrium. The reaction free energy ΔG_r, which is dependent upon the concentrations of the products and reactants, is 0 at equilibrium.

9.4 Cl_2 decreases from 2.15 to 2.13 bar, PCl_3 decreases from 1.28 to 1.26 bar, and PCl_5 increases from 0.02 to 0.04 bar. The shapes for the curves can only be determined accurately if the rate law for the reaction is known (see Chapter 13).
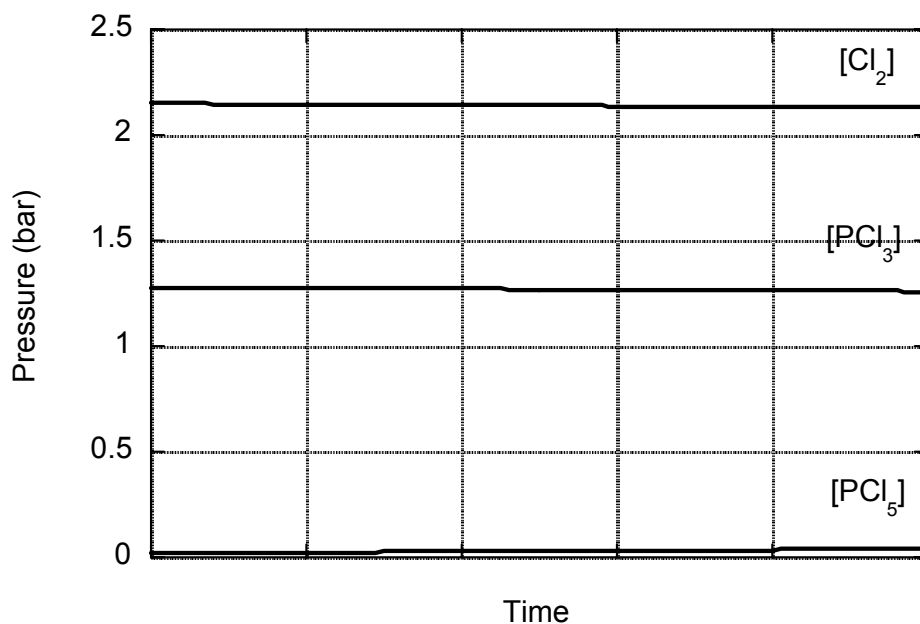
9.6 (a) $K = \dfrac{P_{NO_2}^{\ 2}}{P_{NO}^{\ 2}\,P_{O_2}}$; (b) $K = \dfrac{P_{SbCl_3}\,P_{Cl_2}}{P_{SbCl_5}}$; (c) $K = \dfrac{P_{N_2H_4}}{P_{N_2}\,P_{H_2}^{\ 2}}$

9.8 All values should be the same because the same amounts of the substances are present at equilibrium. It doesn't matter whether we begin with reactants or with products; the equilibrium composition will be the same if the same amounts of materials are used. If different amounts had been used, only (e) would be the same in the two containers. A more detailed analysis follows:

$H_2(g) + Br_2(g) \rightarrow 2\ HBr(g)$
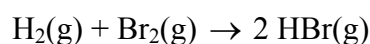
The equilibrium constant expression for this system is

$$K_C = \frac{[HBr]^2}{[H_2][Br_2]}$$

In terms of the change in concentration, x, of H_2 and Br_2 that has come about at equilibrium, we may write

$$K_C = \frac{[2\,x]^2}{[0.05 - x][0.05 - x]} = \frac{[2\,x]^2}{[0.05 - x]^2} \qquad (1)$$

in the first container, and in terms of the change in concentration, y, of HBr that has come about at equilibrium in the second container, we may write

$$K_C = \frac{[0.10 - y]^2}{\left[\dfrac{y}{2}\right]\left[\dfrac{y}{2}\right]} = \frac{[0.10 - y]^2}{\left(\dfrac{y}{2}\right)^2} \qquad (2)$$

Because K_C is a constant, and because the relative amounts of starting materials are in the ratio of their stoichiometric factors, we must have

$$\frac{[2\,x]^2}{[0.05 - x]^2} = \frac{[0.10 - y]^2}{\left(\dfrac{y}{2}\right)^2}$$

$$\frac{[2\,x]}{[0.05 - x]} = \frac{[0.10 - y]}{\left(\dfrac{y}{2}\right)}$$

Cross multiplying:

$$xy = (0.05 - x)(0.10 - y)$$
$$xy = 0.005 - 0.05\ y - 0.10\ x + xy$$
$$y = 0.10 - 2\ x$$

This may also be seen by solving quadratic equations for Eqs. 1 and 2 for x and y to obtain any value of K_C.

(a) $[Br_2] = 0.05 - x$ in the first container, $[Br_2] = y/2$ in the second container. Because $y/2 = 0.05 - x$ satisfies the conditions of Eq. 3, the concentrations and hence the amounts of Br_2 are the same in the two cases.

(b) $[H_2] = 0.05 - x = y/2$, as above; hence the concentrations of H_2 are the same in both systems.

(c) Because all concentrations are the same in both cases, this ratio will also be the same.

(d) For the same reason as in part (c), this ratio is the same in both cases.

(e) This ratio is the equilibrium constant, so it must be the same for both systems.

(f) Because all the concentrations and amounts are the same in both cases, and because the volumes and temperatures are the same, the total pressure must be the same:

$$P = \frac{(n_{H_2} + n_{Br_2} + n_{HBr})\ RT}{V}$$

9.10 $K = P_{NH_3}\ P_{H_2S}$
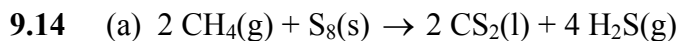
For condition 1, $K = 0.307 \times 0.307 = 0.0942$
For condition 2, $K = 0.364 \times 0.258 = 0.0939$
For condition 3, $K = 0.539 \times 0.174 = 0.0938$

9.12   (a) $\dfrac{[Cl^-]^2[ClO_3^-]}{[ClO^-]^3}$

(b) $[CO_2]$

(c) $\dfrac{[\text{H}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$

9.14 (a) $2\,\text{CH}_4(\text{g}) + \text{S}_8(\text{s}) \rightarrow 2\,\text{CS}_2(\text{l}) + 4\,\text{H}_2\text{S}(\text{g})$

$$\begin{aligned}
\Delta G^\circ_{\text{r}} &= 2 \times \Delta G^\circ_{\text{f}}(\text{CS}_2,\,\text{l}) + 4 \times \Delta G^\circ_{\text{f}}(\text{H}_2\text{S},\,\text{g}) \\
&\quad - [2 \times \Delta G^\circ_{\text{f}}(\text{CH}_4,\,\text{g})] \\
&= 2(65.27\ \text{kJ}\cdot\text{mol}^{-1}) + 4\,(-33.56\ \text{kJ}\cdot\text{mol}^{-1}) \\
&\quad - [2\,(-50.72\ \text{kJ}\cdot\text{mol}^{-1})] \\
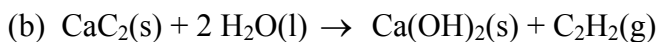&= +97.74\ \text{kJ}\cdot\text{mol}^{-1}
\end{aligned}$$

$\Delta G^\circ = -RT \ln K$

or

$$\ln K = -\dfrac{\Delta G^\circ}{RT}$$

$$\ln K = -\dfrac{+97\,740\ \text{J}\cdot\text{mol}^{-1}}{(8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})} = -39.4$$

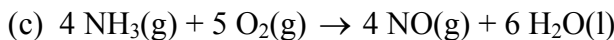$K = 8 \times 10^{-18}$

(b) $\text{CaC}_2(\text{s}) + 2\,\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca(OH)}_2(\text{s}) + \text{C}_2\text{H}_2(\text{g})$

$$\begin{aligned}
\Delta G^\circ_{\text{r}} &= \Delta G^\circ_{\text{f}}(\text{Ca(OH)}_2,\,\text{s}) + \Delta G^\circ_{\text{f}}(\text{C}_2\text{H}_2,\,\text{g}) \\
&\quad - [\Delta G^\circ_{\text{f}}(\text{CaC}_2,\,\text{s}) + 2 \times \Delta G^\circ_{\text{f}}(\text{H}_2\text{O},\,\text{l})] \\
&= (-898.49\ \text{kJ}\cdot\text{mol}^{-1}) + (+209.20\ \text{kJ}\cdot\text{mol}^{-1}) \\
&\quad - [(-64.9\ \text{kJ}\cdot\text{mol}^{-1}) + 2(-237.13\ \text{kJ}\cdot\text{mol}^{-1})] \\
&= -150.1\ \text{kJ}\cdot\text{mol}^{-1}
\end{aligned}$$

$$\ln K = -\dfrac{-150\,100\ \text{J}\cdot\text{mol}^{-1}}{(8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})} = +60.6$$
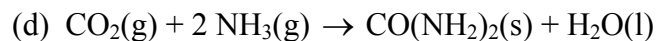
$K = 2 \times 10^{26}$

(c) $4\,\text{NH}_3(\text{g}) + 5\,\text{O}_2(\text{g}) \rightarrow 4\,\text{NO}(\text{g}) + 6\,\text{H}_2\text{O}(\text{l})$

$$\begin{aligned}
\Delta G^\circ_{\text{r}} &= 4\Delta G^\circ_{\text{f}}(\text{NO},\,\text{g}) + 6\Delta G^\circ_{\text{f}}(\text{H}_2\text{O},\,\text{l}) - [4\Delta G^\circ_{\text{f}}(\text{NH}_3,\,\text{g})] \\
&= 4(86.55\ \text{kJ}\cdot\text{mol}^{-1}) + 6(-237.13\ \text{kJ}\cdot\text{mol}^{-1}) - [4(-16.45\ \text{kJ}\cdot\text{mol}^{-1})] \\
&= -1010.8\ \text{kJ}\cdot\text{mol}^{-1}
\end{aligned}$$

$$\ln K = -\dfrac{-1010.8 \times 10^3\ \text{J}\cdot\text{mol}^{-1}}{(8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})(298\ \text{K})} = +408$$

$K \cong 10^{177}$

(d) $CO_2(g) + 2\,NH_3(g) \rightarrow CO(NH_2)_2(s) + H_2O(l)$

$$\Delta G^\circ_r = \Delta G^\circ_f(CO(NH_2)_2, s) + \Delta G^\circ_f(H_2O, l)$$
$$\qquad - [\Delta G^\circ_f(CO_2, g) + 2 \times \Delta G^\circ_f(NH_3, g)]$$
$$= (-197.33\ kJ \cdot mol^{-1}) + (-237.13\ kJ \cdot mol^{-1})$$
$$\qquad - [(-394.36\ kJ \cdot mol^{-1}) + 2(-16.45\ kJ \cdot mol^{-1})]$$
$$= -7.20\ kJ \cdot mol^{-1}$$

$$\ln K = -\frac{-7.20 \times 10^3\ J}{(8.314\ J \cdot K^{-1} \cdot mol^{-1})(298\ K)} = +2.91$$

$$K = 18$$

9.16 (a) $\Delta G^\circ_r = -RT \ln K$
$$= -(8.314\ J \cdot K^{-1} \cdot mol^{-1})(700\ K)\ln 54$$
$$= -23.2\ kJ \cdot mol^{-1}$$

(b) $\Delta G^\circ_r = -RT \ln K$
$$= -(8.314\ J \cdot K^{-1} \cdot mol^{-1})(298\ K)\ln 0.30$$
$$= +2.98\ kJ \cdot mol^{-1}$$

9.18 $\Delta G^\circ_r = \Delta G^\circ_f(CO_2, g)$
$$= -394.36\ kJ \cdot mol^{-1}$$

$$\Delta G^\circ = -RT \ln K$$

$$\ln K = -\frac{\Delta G^\circ}{RT}$$

$$\ln K = -\frac{-394.36 \times 10^3\ J \cdot mol^{-1}}{(8.314\ J \cdot K^{-1} \cdot mol^{-1})(298\ K)} = +159.17$$

$$K = 1.3 \times 10^{69}$$

In practice, no K will be so precise. A better estimate would be 1×10^{69}.

Because $Q < K$, the reaction will tend to proceed to produce products.

9.20 The free energy at a specific set of conditions is given by

$$\Delta G_\mathrm{r} = \Delta G^\circ_\mathrm{r} + RT \ln Q$$

$$\Delta G_\mathrm{r} = -RT \ln K + RT \ln Q$$

$$\Delta G_\mathrm{r} = -RT \ln K + RT \ln \frac{p_{\mathrm{Cl}_5}}{p_{\mathrm{Cl}_3} \cdot p_{\mathrm{Cl}_2}}$$

$$= -(8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}})(503\ \mathrm{K}) \ln 49$$

$$+ (8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}})(503\ \mathrm{K}) \ln \frac{(1.33)}{(0.22)(0.41)}$$

$$= -5.0\ \mathrm{kJ \cdot mol^{-1}}$$

Because ΔG_r is negative, the reaction will be spontaneous to form products.

9.22 The free energy at a specific set of conditions is given by

$$\Delta G_\mathrm{r} = \Delta G^\circ_\mathrm{r} + RT \ln Q$$

$$\Delta G_\mathrm{r} = -RT \ln K + RT \ln Q$$

$$\Delta G_\mathrm{r} = -RT \ln K + RT \ln \frac{[\mathrm{HI}]^2}{[\mathrm{H}_2][\mathrm{I}_2]}$$

$$= -(8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}})(700\ \mathrm{K}) \ln 54$$

$$+ (8.314\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}})(700\ \mathrm{K}) \ln \frac{(2.17)^2}{(0.16)(0.25)}$$

$$= 4.5\ \mathrm{kJ \cdot mol^{-1}}$$

Because ΔG_r is positive, the reaction will proceed to form reactants.

9.24 (a) $K = \dfrac{P_{\mathrm{SO}_3}{}^2}{P_{\mathrm{SO}_2}{}^2\, P_{\mathrm{O}_2}} = 3.4$

$$K = \left(\frac{T}{12.027\ \mathrm{K}}\right)^{\Delta n} K_\mathrm{C}$$

$$K_C = \left(\frac{12.027\ \mathrm{K}}{T}\right)^{\Delta n} K = \left(\frac{12.027\ \mathrm{K}}{1000\ \mathrm{K}}\right)^{(2-3)} 3.4 = 2.8 \times 10^2$$

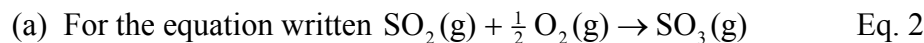(b) $K = P_{\mathrm{NH}_3} P_{\mathrm{H}_2\mathrm{S}} = 9.4 \times 10^{-2}$
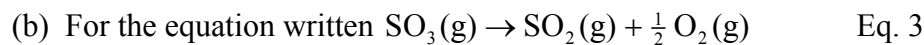
$$K_C = \left(\frac{12.02 \text{ K}}{T}\right)^{\Delta n} \quad K = \left(\frac{12.027 \text{ K}}{297 \text{ K}}\right)^{(2-0)} \quad 9.4 \times 10^{-2} = 1.5 \times 10^{-4}$$

9.26 For the equation written $2 \text{ SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{ SO}_3(\text{g})$ \hfill Eq. 1

$$K = \frac{P_{\text{SO}_3}{}^2}{P_{\text{SO}_2}{}^2 P_{\text{O}_2}} = 2.5 \times 10^{10}$$

(a) For the equation written $\text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{SO}_3(\text{g})$ \hfill Eq. 2
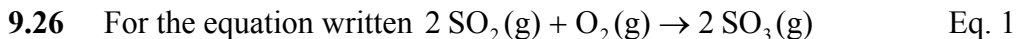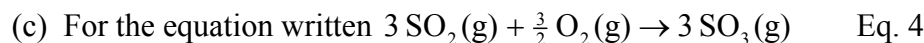
$$K_{\text{Eq. 2}} = \frac{P_{\text{SO}_3}}{P_{\text{SO}_2} P_{\text{O}_2}{}^{1/2}} = \sqrt{K_{\text{Eq. 1}}} = \sqrt{2.5 \times 10^{10}} = 1.6 \times 10^5$$

(b) For the equation written $\text{SO}_3(\text{g}) \rightarrow \text{SO}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g})$ \hfill Eq. 3
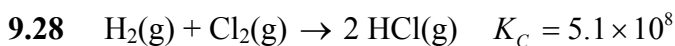
This equation is the reverse of Eq. 2, so $K_{\text{Eq. 3}} = \dfrac{1}{K_{\text{Eq. 2}}} = \dfrac{1}{\sqrt{K_{\text{Eq. 1}}}}$

$$K_{\text{Eq. 2}} = \frac{P_{\text{SO}_2} P_{\text{O}_2}{}^{1/2}}{P_{\text{SO}_3}} = \frac{1}{\sqrt{K_{\text{Eq. 1}}}} = \frac{1}{\sqrt{2.5 \times 10^{10}}} = 6.3 \times 10^{-6}$$

(c) For the equation written $3 \text{ SO}_2(\text{g}) + \frac{3}{2}\text{O}_2(\text{g}) \rightarrow 3 \text{ SO}_3(\text{g})$ \hfill Eq. 4

This equation is $\frac{3}{2} \times$ Eq. 1, so $K_{\text{Eq. 4}} = K_{\text{Eq. 1}}{}^{3/2}$

$$K_{\text{Eq. 2}} = \frac{P_{\text{SO}_3}{}^3}{P_{\text{SO}_2}{}^3 P_{\text{O}_2}{}^{3/2}} = K_{\text{Eq. 1}}{}^{3/2} = (2.5 \times 10^{10})^{3/2} = 4.0 \times 10^{15}$$

9.28 $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2 \text{ HCl}(\text{g}) \quad K_C = 5.1 \times 10^8$

$$K_C = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]}$$

$$5.1 \times 10^8 = \frac{(1.45 \times 10^{-3})^2}{[\text{H}_2](2.45 \times 10^{-3})}$$

$$[\text{H}_2] = \frac{(1.45 \times 10^{-3})^2}{(5.1 \times 10^8)(2.45 \times 10^{-3})}$$

$$[\text{H}_2] = 1.7 \times 10^{-12} \text{ mol} \cdot \text{L}^{-1}$$

9.30 $K = \dfrac{P_{SbCl_3} P_{Cl_2}}{P_{SbCl_5}}$

$3.5 \times 10^{-4} = \dfrac{(5.02 \times 10^{-3}) P_{Cl_2}}{0.072}$

$P_{Cl_2} = \dfrac{(3.5 \times 10^{-4})(0.072)}{5.02 \times 10^{-3}} = 5.0 \times 10^{-3}$ bar

9.32 (a) $K_C = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = 0.278$

$Q_C = \dfrac{[0.122]^2}{[0.417][0.524]^3} = 0.248$

(b) $Q_C \ne K_C$; therefore the system is not at equilibrium.

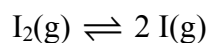(c) Because $Q_C < K_C$, more products will be formed.

9.34 (a) $K_C = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = 62$

$Q_C = \dfrac{[1.12 \times 10^{-4}]^2}{[2.23 \times 10^{-3}][1.24 \times 10^{-3}]^3} = 2.95 \times 10^3$

(b) Because $Q_C > K_C$, ammonia will decompose to form reactants.

9.36 $\dfrac{1.00 \text{ g } I_2}{253.8 \text{ g} \cdot \text{mol}^{-1}} = 0.003\ 94 \text{ mol } I_2;\ \dfrac{0.830 \text{ g } I_2}{253.8 \text{ g} \cdot \text{mol}^{-1}} = 0.003\ 27 \text{ mol } I_2$

$I_2(g) \rightleftharpoons 2\ I(g)$

$0.003\ 94 \text{ mol} - x \qquad 2\,x$

$0.003\ 94 \text{ mol} - x = 0.003\ 27 \text{ mol}$

$x = 0.000\ 67 \text{ mol};\ 2\,x = 0.0013 \text{ mol}$

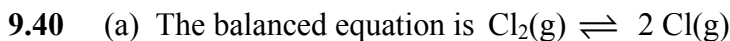$K_C = \dfrac{\left[\dfrac{0.0013}{1.00}\right]^2}{\left[\dfrac{0.003\ 27}{1.00}\right]} = 5.2 \times 10^{-4}$

9.38

Pressure (Torr)	CO(g) +	H₂O(g) ⇌	CO₂(g) +	H₂(g)
initial	200	200	0	0
final	200 − 88	200 − 88	88	88

Note: Because pressure is directly proportional to the number of moles of a substance, the pressure changes can be used directly in calculating the reaction stoichiometry. Technically, to achieve the correct standard state condition, the Torr must be converted to bar $(750.1\ \text{Torr} \cdot \text{bar}^{-1})$; however, in this case those conversion factors will cancel because there are equal numbers of moles of gas on both sides of the equation.

$$K = \frac{P_{CO_2} P_{H_2}}{P_{CO} P_{H_2O}} = \frac{\left(\dfrac{88}{750.1}\right)\left(\dfrac{88}{750.1}\right)}{\left(\dfrac{112}{750.1}\right)\left(\dfrac{112}{750.1}\right)} = 0.62$$

9.40 (a) The balanced equation is $Cl_2(g) \rightleftharpoons 2\ Cl(g)$

The initial concentration of $Cl_2(g)$ is $\dfrac{0.0050\ \text{mol Cl}_2}{2.0\ \text{L}} = 0.0025\ \text{mol} \cdot \text{L}^{-1}$

Concentration $(\text{mol} \cdot \text{L}^{-1})$	Cl₂(g) ⇌	2 Cl(g)
initial	0.0025	0
change	−x	+2 x
equilibrium	0.0025 − x	+2 x

$$K_C = \frac{[Cl]^2}{[Cl_2]} = \frac{(2\,x)^2}{(0.0025 - x)} = 1.7 \times 10^{-3}$$

$$4\,x^2 = (1.7 \times 10^{-3})(0.0025 - x)$$

$$4\,x^2 + (1.7 \times 10^{-3})x - (4.25 \times 10^{-6}) = 0$$

$$x = \frac{-(1.7 \times 10^{-3}) \pm \sqrt{(1.7 \times 10^{-3})^2 - 4(4)(-4.3 \times 10^{-6})}}{2 \times 4}$$

$$x = \frac{-(1.7 \times 10^{-3}) \pm 8.47 \times 10^{-3}}{8}$$

$$x = -1.3 \times 10^{-3} \text{ or } + 8.5 \times 10^{-4}$$

The negative answer is not meaningful, so we choose $x =$

$8.5 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. The concentration of Cl_2 is $0.0025 - 8.5 \times 10^{-4}$

$= 0.0017$. The concentration of Cl atoms is $2 \times (8.5 \times 10^{-4})$

$= 1.7 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. The percentage decomposition of Cl_2 is given by

$$\frac{8.5 \times 10^{-4}}{0.0025} \times 100 = 34\%$$

(b) The balanced equation is $Br_2(g) \rightleftharpoons 2 \, Br(g)$

The initial concentration of $Br_2(g)$ is $\dfrac{5.0 \text{ mol } Br_2}{2.0 \text{ L}} = 2.5 \text{ mol} \cdot \text{L}^{-1}$

Concentration $(\text{mol} \cdot \text{L}^{-1})$	$Br_2(g)$	$\rightleftharpoons$	$2 \, Br(g)$
initial	2.5		0
change	$-x$		$+2x$
equilibrium	$2.5 - x$		$+2x$

$$K_C = \frac{[Br]^2}{[Br_2]} = \frac{(2x)^2}{(2.5 - x)} = 1.7 \times 10^{-3}$$

$$4x^2 = (1.7 \times 10^{-3})(2.5 - x)$$

$$4x^2 + (1.7 \times 10^{-3})x - (4.25 \times 10^{-3}) = 0$$

$$x = \frac{-(1.7 \times 10^{-3}) \pm \sqrt{(1.7 \times 10^{-3})^2 - 4(4)(-4.25 \times 10^{-3})}}{2 \times 4}$$

$$x = \frac{-(1.7 \times 10^{-3}) \pm 2.608 \times 10^{-1}}{8}$$

$$x = -3.3 \times 10^{-2} \text{ or } + 3.2 \times 10^{-2}$$

The negative answer is not meaningful, so we choose $x =$

$3.2 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$. The concentration of Br_2 is $2.5 - 3.2 \times 10^{-2} \approx 2.5$.

The concentration of Br atoms is $2 \times (3.2 \times 10^{-2}) = 6.4 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$.

he percentage decomposition of Br_2 is given by

$$\frac{3.2 \times 10^{-2}}{2.5} \times 100 = 1.3\%$$

(c) At this temperature, Cl_2 and Br_2 are equally stable since their

equilibrium constants are the same. If we had used the same initial

amounts of Cl_2 and Br_2 in parts (a) and (b), then the percent decomposition would have been the same as well.

9.42

Pressure (bar)	2 BrCl(g)	$\rightleftharpoons$	$Br_2(g)$	+	$Cl_2(g)$
initial	1.4×10^{-3}		0		0
change	$-2x$		$+x$		$+x$
final	$1.4 \times 10^{-3} - 2x$		$+x$		$+x$

$$K = \frac{p_{Br_2} \cdot p_{Cl_2}}{p_{BrCl}^2}$$

$$32 = \frac{(x)(x)}{(1.4 \times 10^{-3} - 2x)^2} = \frac{x^2}{(1.4 \times 10^{-3} - 2x)^2}$$

$$\sqrt{32} = \sqrt{\frac{x^2}{(1.4 \times 10^{-3} - 2x)^2}}$$

$$\frac{x}{(1.4 \times 10^{-3} - 2x)} = \sqrt{32}$$

$$x = (\sqrt{32})(1.4 \times 10^{-3} - 2x)$$

$$x + 2\sqrt{32}\, x = (\sqrt{32})(1.4 \times 10^{-3})$$

$$(1 + 2\sqrt{32})\, x = (\sqrt{32})(1.4 \times 10^{-3})$$

$$x = \frac{(\sqrt{32})(1.4 \times 10^{-3})}{(1 + 2\sqrt{32})}$$

$$x = 6.4 \times 10^{-4}$$

$$p_{Br_2} = p_{Cl_2} = 6.4 \times 10^{-4}\ \text{bar} = 0.64\ \text{mbar}$$

$$p_{BrCl} = 1.4 \times 10^{-3}\,\text{bar} - 2\,(6.4 \times 10^{-4}\,\text{bar}) = 1.2 \times 10^{-4}\ \text{bar} = 0.12\ \text{mbar}$$

The percentage decomposition is given by

$$\frac{2\,(6.4 \times 10^{-4}\,\text{bar})}{1.4 \times 10^{-3}\,\text{bar}} \times 100 = 91\%$$

9.44 (a) concentration of PCl_5 initially =

$$\frac{\left(\dfrac{2.0 \text{ g } PCl_5}{208.22 \text{ g} \cdot \text{mol}^{-1} PCl_5}\right)}{0.300 \text{ L}} = 0.032 \text{ mol} \cdot \text{L}^{-1}$$

Concentration $(\text{mol} \cdot \text{L}^{-1})$	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
initial	0.032		0		0
change	$-x$		$+x$		$+x$
final	$0.032 - x$		$+x$		$+x$

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x)(x)}{(0.032 - x)} = \frac{x^2}{(0.032 - x)}$$

$$\frac{x^2}{(0.032 - x)} = 0.61$$

$$x^2 = (0.61)(0.032 - x)$$

$$x^2 + (0.61)x - 0.020 = 0$$

$$x = \frac{-(0.61) \pm \sqrt{(0.61)^2 - (4)(1)(-0.020)}}{2 \cdot 1}$$

$$x = \frac{-(0.61) \pm 0.67}{2 \cdot 1} = +0.03 \text{ or } -0.64$$

The negative root is not meaningful, so we choose $x = 0.03 \text{ mol} \cdot \text{L}^{-1}$.

$[PCl_3] = [Cl_2] = 0.03 \text{ mol} \cdot \text{L}^{-1}$;

$[PCl_5] = 0.032 - 0.03 \text{ mol} \cdot \text{L}^{-1} = 0.002 \text{ mol} \cdot \text{L}^{-1}$. The solution of this problem again points up the problems with following the significant figure conventions for calculations of this type, because we would use only one significant figure as imposed by the subtraction in the quadratic equation solution. The fact that the equilibrium constant is given to two significant figures, however, suggests that the concentrations could be determined to that level of accuracy. Plugging the answers back into the equilibrium expression gives a value of 0.45, which seems somewhat off from the starting value of 0.61. The closest agreement to the equilibrium expression comes from using $[PCl_3] = [Cl_2] = 0.0305 \text{ mol} \cdot \text{L}^{-1}$ and

$[PCl_5] = 0.0015 \text{ mol} \cdot L^{-1}$; this gives an equilibrium constant of 0.62. Rounding these off to two significant figures gives

$[PCl_3] = [Cl_2] = 0.030 \text{ mol} \cdot L^{-1}$ and $[PCl_5] = 0.0015$, which in the equilibrium expression produces a value of 0.60. The percentage decomposition is given by

$$\frac{0.030}{0.032} \times 100\% = 94\%$$

9.46 Starting concentration of $NH_3 = \dfrac{0.200 \text{ mol}}{2.00 \text{ L}} = 0.100 \text{ mol} \cdot L^{-1}$

Concentration $(\text{mol} \cdot L^{-1})$	$NH_4HS(s)$	$\rightleftharpoons$	$NH_3(g)$	$+$	$H_2S(g)$
initial	—		0.100		0
change	—		$+x$		$+x$
final	—		$0.100 + x$		$+x$

$K_C = [NH_3][H_2S] = (0.100 + x)(x)$

$1.6 \times 10^{-4} = (0.100 + x)(x)$

$x^2 + 0.100\, x - 1.6 \times 10^{-4} = 0$

$x = \dfrac{-(+0.100) \pm \sqrt{(+0.100)^2 - (4)(1)(-1.6 \times 10^{-4})}}{2 \cdot 1}$

$x = \dfrac{-0.100 \pm 0.1031}{2 \cdot 1} = +0.002 \text{ or } -0.102$

The negative root is not meaningful, so we choose $x = 2 \times 10^{-3} \text{ mol} \cdot L^{-1}$.

$[NH_3] = +0.100 \text{ mol} \cdot L^{-1} + 2 \times 10^{-3} \text{ mol} \cdot L^{-1}$

$\quad = 0.102 \text{ mol} \cdot L^{-1}$

$[H_2S] = 2 \times 10^{-3} \text{ mol} \cdot L^{-1}$

Alternatively, we could have assumed that $x \ll 0.100$, in which case

$0.100\, x = 1.6 \times 10^{-4}$ or $x = 1.6 \times 10^{-3}$.

9.48 The initial concentrations of PCl_3 and Cl_2 are calculated as follows:

$$[PCl_3] = \frac{0.200 \text{ mol}}{8.00 \text{ L}} = 0.0250 \text{ mol} \cdot L^{-1}; [Cl_2] = \frac{0.600 \text{ mol}}{8.00 \text{ L}}$$

$$= 0.0750 \text{ mol} \cdot L^{-1}$$

Concentrations $(\text{mol} \cdot L^{-1})$ PCl$_5$	$\rightleftharpoons$	PCl$_3$(g)	+	Cl$_2$(g)
initial	0	0.0250		0.0750
change	$+x$	$-x$		$-x$
final	$+x$	$0.0250 - x$		$0.0750 - x$

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(0.0250 - x)(0.0750 - x)}{(+x)} = 33.3$$

$$x^2 - 0.100\,x + 0.001\,875 = 33.3\,x$$

$$x^2 - 33.40\,x + 0.001\,875 = 0$$

$$x = \frac{+33.40 \pm \sqrt{(-33.40)^2 - (4)(1)(0.001\,875)}}{(2)(1)} = \frac{+33.40 \pm 33.399\,89}{2}$$

$$= +5.5 \times 10^{-5} \text{ or } +33.4$$

The root +33.4 has no physical meaning because it is greater than the starting concentrations of PCl$_3$ and Cl$_2$, so it can be discarded.

$$[PCl_5] = 5.5 \times 10^{-5} \text{ mol} \cdot L^{-1}; [PCl_3] = 0.0250 \text{ mol} \cdot L^{-1}$$

$$- 5.5 \times 10^{-5} \text{ mol} \cdot L^{-1} = 0.0249 \text{ mol} \cdot L^{-1};$$

$[Cl_2] = 0.0750 \text{ mol} \cdot L^{-1} - 5.5 \times 10^{-5} \text{ mol} \cdot L^{-1} = 0.0749 \text{ mol} \cdot L^{-1}$. Note that the normal conventions concerning significant figures were ignored in order to obtain a meaningful answer.

9.50 The initial concentrations of N$_2$ and O$_2$ are

$$[N_2] = \frac{0.0140 \text{ mol}}{10.0 \text{ L}} = 0.001\,40 \text{ mol} \cdot L^{-1}; [O_2] = \frac{0.240 \text{ mol}}{10.0 \text{ L}}$$

$$= 0.0214 \text{ mol} \cdot L^{-1}$$

Concentrations $(\text{mol} \cdot L^{-1})$	N$_2$(g)	+	O$_2$(g)	$\rightleftharpoons$	2 NO(g)
initial	0.001 40		0.0214		0
change	$-x$		$-x$		$+2x$
final	$0.001\,40 - x$		$0.0214 - x$		$+2x$

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2\,x)^2}{(0.001\,40 - x)(0.0214 - x)}$$

$$1.00 \times 10^{-5} = \frac{(2\,x)^2}{(0.001\,40 - x)(0.0214 - x)}$$

$$1.00 \times 10^{-5} = \frac{4\,x^2}{x^2 - 0.0228\,x + 3.0 \times 10^{-5}}$$

$$4\,x^2 = (1.00 \times 10^{-5})(x^2 - 0.0228x + 3.0 \times 10^{-5})$$

$$4\,x^2 = 1.00 \times 10^{-5}\,x^2 - 2.28 \times 10^{-7}\,x + 3.0 \times 10^{-10}$$

$$4\,x^2 + 2.28 \times 10^{-7}\,x - 3.0 \times 10^{-10} = 0$$

$$x = \frac{-2.28 \times 10^{-7} \pm \sqrt{(2.28 \times 10^{-7})^2 - (4)(4)(-3.0 \times 10^{-10})}}{(2)(4)}$$

$$x = \frac{-2.28 \times 10^{-7} \pm 6.93 \times 10^{-5}}{8} = 8.6 \times 10^{-6} \text{ or } -8.7 \times 10^{-6}$$

The negative root can be discarded because it has no physical meaning.

$[NO] = 2\,x = 2(8.6 \times 10^{-6}) = 1.7 \times 10^{-5}\,\text{mol}\cdot\text{L}^{-1}$; the concentrations of N_2

and O_2 remain essentially unchanged at $0.001\,39\,\text{mol}\cdot\text{L}^{-1}$ and

$0.0214\,\text{mol}\cdot\text{L}^{-1}$, respectively.

9.52   The initial concentrations of N_2 and H_2 are

$$[N_2] = [H_2] = \frac{0.20\,\text{mol}}{25.0\,\text{L}} = 0.0080\,\text{mol}\cdot\text{L}^{-1}.$$

At equilibrium, 5.0 % of the N_2 had reacted, so 95.0 % of the N_2 remains:

$$[N_2] = (0.950)(0.0080\,\text{mol}\cdot\text{L}^{-1}) = 0.0076\,\text{mol}\cdot\text{L}^{-1}$$

If 5.0 % reacted, then

$$0.050 \times 0.200\,\text{mol}\ N_2 \times \frac{2\,\text{mol}\ NH_3}{\text{mol}\ N_2} = 0.020\,\text{mol}\ NH_3 \text{ formed.}$$

The concentration of NH_3 formed $= \dfrac{0.020\,\text{mol}}{25.0\,\text{L}} = 8.0 \times 10^{-4}\,\text{mol}\cdot\text{L}^{-1}.$

The amount of

$$H_2 \text{ reacted} = 0.050 \times 0.200\,\text{mol}\ N_2 \times \frac{3\,\text{mol}\ H_2}{\text{mol}\ N_2} = 0.030\,\text{mol}\ H_2 \text{ used.}$$

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Concentration of H_2 present at equilibrium

$$= \frac{0.200 \text{ mol} - 0.030 \text{ mol}}{25.0 \text{ L}} = 0.0068 \text{ mol} \cdot L^{-1}.$$

$$K_C = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(8.0 \times 10^{-4})^2}{(0.0076)(0.0068)^3} = 2.7 \times 10^2$$

9.54 Note: The volume of the system is not used because we are given pressures and K.

Pressures (bar)	$N_2(g)$	$+$	$3 H_2(g)$	$\rightleftharpoons$	$2 NH_3(g)$
initial	0.025		0.015		0
change	$-x$		$-3x$		$+2x$
final	$0.025 - x$		$0.015 - 3x$		$+2x$

$$K = \frac{P_{NH_3}^2}{P_{N_2} P_{H_2}^3} = \frac{(2x)^2}{(0.025 - x)(0.015 - 3x)^3} = 0.036$$

Solving this explicitly will lead to a high-order equation, so first check to see if the assumption that $3x \ll 0.015$ can be used to simplify the math:

$$\frac{(2x)^2}{(0.025)(0.015)^3} = 0.036$$

$$4x^2 = 3.04 \times 10^{-9}$$

$$x = 2.8 \times 10^{-5}$$

Comparing x to 0.015, we see that the approximation was justified.

At equilibrium, $P_{NH_3} = 2 \times 2.8 \times 10^{-5}$ bar $= 5.6 \times 10^{-5}$ bar ; the pressures of N_2 and H_2 remain essentially unchanged.

9.56 Concentrations

$(mol \cdot L^{-1})$	CH_3COOH	$+$	C_2H_5OH	$\rightleftharpoons$	$CH_3COOC_2H_5$	$+$	H_2O
initial	0.024		0.059		0		0.015
change	$-x$		$-x$		$+x$		$+x$
final	$0.024 - x$		$0.059 - x$		$+x$		$0.015 + x$

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{(x)(0.015 + x)}{(0.024 - x)(0.059 - x)}$$

$$= \frac{x^2 + 0.015\,x}{x^2 - 0.083\,x + 0.0014}$$

$$4.0 = \frac{x^2 + 0.015\,x}{x^2 - 0.083\,x + 0.001\,42}$$

$$4.0\,x^2 - 0.332\,x + 0.005\,68 = x^2 + 0.015\,x$$

$$3.0\,x^2 - 0.347\,x + 0.005\,68 = 0$$

$$x = \frac{-(-0.347) \pm \sqrt{(-0.347)^2 - (4)(3.0)(0.005\,68)}}{(2)(3.0)} = \frac{+0.347 \pm 0.228}{6.0}$$

$$x = 0.0958 \text{ or } 0.0198$$

The root 0.0958 is meaningless because it is larger than the initial concentration of acetic acid and ethanol, so the value 0.0198 is chosen. The equilibrium concentration of the product ester is, therefore, $0.0198 \text{ mol} \cdot L^{-1}$. The numbers can be confirmed by placing them into the equilibrium expression:

$$K_C = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{(0.0198)(0.015 + 0.0198)}{(0.024 - 0.0198)(0.059 - 0.0198)} = 4.1$$

This is reasonably good agreement, given the nature of the calculation. Given that the K_C value is reported to only two significant figures, the best report of the concentration of ester will be $0.020 \text{ mol} \cdot L^{-1}$.

9.58 $$K = \frac{P_{PCl_5}}{P_{PCl_3} P_{Cl_2}}$$

$$3.5 \times 10^4 = \frac{1.3 \times 10^2}{(9.56)P_{Cl_2}}$$

$$P_{Cl_2} = \frac{1.3 \times 10^2}{(9.56)(3.5 \times 10^4)} = 3.9 \times 10^{-4} \text{ bar}$$

9.60 We use the reaction stoichiometry to calculate the amounts of substances present at equilibrium:

Amounts (mol)	CO(g)	+	H₂O(g)	⇌	CO₂(g)	+	H₂(g)
initial	1.000		1.000		0		0
change	−x		−x		+x		+x
final	1.000 − x		1.000 − x		0.665		+x

(a) Because $x = 0.665$ mol, there will be $(1.000 - 0.665)$ mol $= 0.335$ mol CO; 0.335 mol H_2O; 0.665 mol H_2. The concentrations are easy to calculate because $V = 10.00$ L:

$$[CO] = [H_2O] = 0.0335 \text{ mol} \cdot L^{-1}; [CO_2] = [H_2] = 0.0665 \text{ mol} \cdot L^{-1}$$

(b) $K_C = \dfrac{[CO_2][H_2]}{[CO][H_2O]} = \dfrac{(0.0665)^2}{(0.0335)^2} = 3.94$

9.62 The initial concentration of $H_2S = \dfrac{0.100 \text{ mol}}{10.0 \text{ L}} = 0.0100 \text{ mol} \cdot L^{-1}$

The final concentration of $H_2 = \dfrac{0.0285 \text{ mol}}{10.0 \text{ L}} = 0.002\,85 \text{ mol} \cdot L^{-1}$

Concentrations (mol·L⁻¹)	2 H₂S(g)	⇌	2 H₂(g)	+	S₂(g)
initial	0.0100		0		0
change	−2 x		+2 x		+x
final	0.0100 − 2 x		0.002 85		+x

Thus, $2\,x = 0.002\,85 \text{ mol} \cdot L^{-1}$ or $x = 0.001\,42 \text{ mol} \cdot L^{-1}$

At equilibrium:

$[H_2S] = 0.0100 \text{ mol} \cdot L^{-1} - 0.002\,85 \text{ mol} \cdot L^{-1} = 0.0072 \text{ mol} \cdot L^{-1}$

$[H_2] = 0.002\,85 \text{ mol} \cdot L^{-1}$

$[S_2] = 0.001\,42 \text{ mol} \cdot L^{-1}$

$K_C = \dfrac{(0.002\,85)^2(0.001\,42)}{(0.0072)^2} = 2.22 \times 10^{-4}$

9.64 The initial concentration of $PCl_5 = \dfrac{0.865 \text{ mol}}{0.500 \text{ L}} = 1.73 \text{ mol} \cdot L^{-1}$

Concentrations (mol·L^{-1})	PCl$_5$(g)	$\rightleftharpoons$	PCl$_3$(g)	+	Cl$_2$(g)
initial	1.73		0		0
change	$-x$		$+x$		$+x$
final	$1.73 - x$		$+x$		$+x$

$K_C = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

$1.80 = \dfrac{(x)(x)}{(1.73 - x)} = \dfrac{x^2}{(1.73 - x)}$

$(1.80)(1.73 - x) = x^2$

$x^2 + 1.80\,x - 3.114 = 0$

$x = \dfrac{-1.80 \pm \sqrt{(1.80)^2 - (4)(1 - 3.114)}}{(2)(1)} = \dfrac{-1.80 \pm 3.96}{2}$

$x = +1.08 \text{ or } -2.88$

The negative root is not physically meaningful and can be discarded. The concentrations of PCl$_3$ and Cl$_2$ are, therefore, $1.08 \text{ mol} \cdot L^{-1}$ at equilibrium, and the concentration of PCl$_5$ is $1.73 \text{ mol} \cdot L^{-1} - 1.08 \text{ mol} \cdot L^{-1}$

$= 0.65 \text{ mol} \cdot L^{-1}$. These numbers can be checked by substituting back into the equilibrium expression:

$K_C = \dfrac{[PCl_3][Cl_2]}{[PCl_5]}$

$\dfrac{(1.08)^2}{(0.65)} = 1.79$

which compares well to K_C (1.80).

9.66 We use the ideal gas relationship to find the initial concentration of $HCl(g)$ at 25°C:

$$n = \frac{PV}{RT}$$

$$n = \frac{\left(1.00 \text{ bar} \times \dfrac{1 \text{ atm}}{1.013\,25 \text{ bar}}\right)(4.00 \text{ L})}{(0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(273 \text{ K})} = 0.176 \text{ mol}$$

$$[\text{HCl}] = \frac{0.176 \text{ mol}}{12.00 \text{ L}} = 0.0147 \text{ mol} \cdot \text{L}^{-1}$$

Concentrations (mol·L^{-1})	2 HCl(g) +	I$_2$(s) ⇌	2 HI(g) +	Cl$_2$(g)
initial	0.0147	—	0	0
change	$-2\,x$	—	$+2\,x$	$+x$
final	$0.147 - 2\,x$	—	$+2\,x$	$+x$

$$K_C = \frac{[\text{HI}]^2[\text{Cl}_2]}{[\text{HCl}]^2}$$

$$1.6 \times 10^{-34} = \frac{(2\,x)^2(x)}{(0.0147 - 2\,x)^2}$$

Because the equilibrium constant is very small, we will assume that $x \ll$ 0.0147:

$$1.6 \times 10^{-34} = \frac{4\,x^3}{(0.0147)^2}$$

$$x^3 = \frac{(1.6 \times 10^{-34})(0.0147)^2}{4}$$

$$x = \sqrt[3]{\frac{(1.6 \times 10^{-34})(0.0147)^2}{4}} = 2.1 \times 10^{-13}$$

At equilibrium:

$$[\text{HI}] = 2 \times 2.1 \times 10^{-13} = 4.2 \times 10^{-13}$$

$$[\text{Cl}_2] = 2.1 \times 10^{-13}$$

$$[\text{HCl}] = 0.0147 \text{ mol} \cdot \text{L}^{-1}$$

9.68 initial $[NH_3] = \dfrac{\left(\dfrac{25.6\ \text{g}}{17.03\ \text{g}\cdot\text{mol}^{-1}}\right)}{5.00\ \text{L}} = 0.301\ \text{mol}\cdot\text{L}^{-1}$

Concentrations $(\text{mol}\cdot\text{L}^{-1})$	$2\ NH_3(g) \rightleftharpoons$	$N_2(g)$	$+$	$3\ H_2(g)$
initial	0.301	0		0
change	$-2x$	$+x$		$+3x$
final	$0.301 - 2x$	$+x$		$+3x$

$$K_C = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$\frac{(x)(3x)^3}{(0.301 - 2x)^2} = 0.395$$

$$\frac{27\,x^4}{(0.301 - 2x)^2} = 0.395$$

$$\sqrt{\frac{27\,x^4}{(0.301 - 2x)^2}} = \sqrt{0.395}$$

$$\frac{3\sqrt{3}\,x^2}{(0.301 - 2x)} = 0.628$$

$$3\sqrt{3}\,x^2 = (0.628)(0.301 - 2x) = 0.189 - 1.26x$$

$$5.20\,x^2 + 1.26x - 0.189 = 0$$

$$x = \frac{-1.26 \pm \sqrt{(1.26)^2 - (4)(5.20)(-0.189)}}{(2)(5.20)} = \frac{-1.26 \pm 2.34}{10.4}$$

$$x = +0.105 \text{ or } -0.396$$

The negative root is discarded because it is not physically meaningful.

Thus, at equilibrium we should have

$[N_2] = 0.105\ \text{mol}\cdot\text{L}^{-1}; [H_2] = 0.315\ \text{mol}\cdot\text{L}^{-1}; [NH_3] = 0.091\ \text{mol}\cdot\text{L}^{-1}.$

9.70 $2\ HCl(g) \rightarrow H_2(g) + Cl_2(g)$
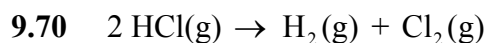
$$K = \frac{P_{H_2}\,P_{Cl_2}}{P_{HCl}^{\ 2}} = 3.2 \times 10^{-34} \qquad \text{(Eq. 1)}$$

At equilibrium, $P_{Total} = P_{H_2} + P_{Cl_2} + P_{HCl} = 3.0\ \text{bar}$. (Eq. 2)

And, since the atomic ratio Cl:H is 1:3,

$$\frac{\text{moles Cl}}{\text{moles H}} = \frac{1}{3} = \frac{n_{HCl} + 2n_{Cl_2}}{n_{HCl} + 2n_{H_2}}$$

$$n_{HCl} + 2n_{H_2} = 3(n_{HCl} + 2n_{Cl_2})$$

$$n_{H_2} = n_{HCl} + 3n_{Cl_2}$$

$P_{gas} \propto n_{gas}$ at T, V constant so

$$P_{H_2} = P_{HCl} + 3P_{Cl_2} \qquad \text{(Eq. 3)}$$

We now have three equations in three unknowns, so we can rearrange and substitute to find each partial pressure.

Substituting equation 3 into equation 2 gives

$$P_{Total} = 4P_{Cl_2} + 2P_{HCl} = 3.0 \text{ bar}$$

$$P_{HCl} = \frac{3.0 \text{ bar}}{2} - 2P_{Cl_2}$$

Substitution back into equation 3 gives

$$P_{H_2} = \frac{3.0 \text{ bar}}{2} + P_{Cl_2}$$

Using these two expressions for partial pressures in equation 1 gives

$$K = \frac{\left(\frac{3.0}{2} + P_{Cl_2}\right) \cdot P_{Cl_2}}{\left(\frac{3.0}{2} - 2P_{Cl_2}\right)^2} = 3.2 \times 10^{-34}$$

Since the equilibrium constant is so small, we would expect the partial pressure of chlorine to be very low at equilibrium, so we can neglect it to simplify this expression.

$$K \approx \frac{\left(\frac{3.0}{2}\right) \cdot P_{Cl_2}}{\left(\frac{3.0}{2}\right)^2} = 3.2 \times 10^{-34}$$

$$P_{Cl_2} = (1.5)(3.2 \times 10^{-34}) = 4.8 \times 10^{-34} \text{ bar}$$

$$P_{HCl} = P_{H_2} = 1.5 \text{ bar}$$

9.72 (a) According to Le Chatelier's principle, an increase in the partial pressure CO_2 will shift the equilibrium to the left, increasing the partial pressure of CH_4.

(b) According to Le Chatelier's principle, a decrease in the partial pressure of CH_4 will shift the equilibrium to the left, decreasing the partial pressure of CO_2.

(c) The equilibrium constant for the reaction is unchanged, because it is unaffected by any change in concentration.

(d) According to Le Chatelier's principle, a decrease in the concentration of H_2O will shift the equilibrium to the right, increasing the concentration of CO_2.

9.74 The questions can all be answered qualitatively using Le Chatelier's principle:

(a) Adding a reactant will promote the formation of products; the amount of HI should increase.

(b) I_2 is solid and already present in excess in the original equilibrium. Adding more solid will not affect the equilibrium so the amount of Cl_2 will not change.

(c) Removing a product will shift the reaction toward the formation of more products; the amount of Cl_2 should increase.

(d) Removing a product will shift the reaction toward the formation of more products; the amount of HCl should decrease.

(e) The equilibrium constant will be unaffected by changes in the concentrations of any of the species present.

(f) Removing the reactant HCl will cause the reaction to shift toward the production of more reactants; the amount of I_2 should increase.

(g) As in (e), the equilibrium constant will be unaffected by the changes to the system.

9.76 Increasing the total pressure on the system by decreasing its volume will shift the equilibrium toward the side of the reaction with fewer numbers of moles of gaseous components. If the total number of moles of gas is the same on the product and reactant sides of the balanced chemical equation, then changing the pressure will have little or no effect on the equilibrium distribution of species present. (a) decrease in the amount of NO_2; (b) increase in the amount and concentration of NO; (c) decrease in the amount of HI; (d) decrease in the amount of SO_2; (e) increase in the amount and concentration of NO_2. (Note that it is not possible to predict whether or not the concentration will increase, decrease, or remain the same in cases where the amount of the substance is decreasing. More specific information about the extent of the changes in the amount and the volume is needed in those cases.)

9.78 (a) The partial pressure of SO_3 will decrease when the partial pressure of SO_2 is decreased. According to Le Chatelier's principle, a decrease in the partial pressure of a reactant will shift the equilibrium to the left, decreasing the partial pressure of the products, in this case SO_3.
(b) When the partial pressure of SO_2 increases, the partial pressure of O_2 will decrease. According to Le Chaltelier's principle, an increase in the partial pressure of a reactant shifts the equilibrium toward products, decreasing the partial pressure of the other reactant, O_2.

9.80 If a reaction is exothermic, raising the temperature will tend to shift the reaction toward reactants, whereas if the reaction is endothermic, a shift toward products will be observed. For the specific reactions given, raising the temperature should favor products in (a) and reactants in (b) and (c).

9.82 Even though numbers are given, we do not need to do a calculation to answer this qualitative question. Because the equilibrium constant is larger at lower temperatures (4.0×10^{24} at 298 K vs. 2.5×10^{10} at 500 K, see

Table 9.2, page 334), more products will be present at the lower temperature. Thus we expect more SO_3 to be present at 25°C than at 500 K, assuming that no other changes occur to the system (the volume is fixed and no reactants or products are added or removed from the vessel).

9.84 To answer this question, we must calculate Q:

$$Q = \frac{[ClF]^2}{[Cl_2][F_2]} = \frac{(0.92)^2}{(0.18)(0.31)} = 15$$

Because $Q \neq K$, the system is not at equilibrium, and because $Q < K$, the reaction will proceed to produce more products so ClF will tend to form.

9.86 (a) $HgO(s) \rightleftharpoons Hg(l) + \frac{1}{2}O_2(g)$

$\Delta H°_r = -[\Delta H°_f(HgO, s)]$

$\Delta H°_r = -[-90.83 \text{ kJ} \cdot \text{mol}^{-1}]$

$\Delta H°_r = +90.83 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta S°_r = S°(Hg, l) + \frac{1}{2} \times S°(O_2, g) - [S°(HgO, s)]$

$\Delta S°_r = 76.02 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + \frac{1}{2} \times 205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
$\quad - [70.29 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}]$

$\Delta S°_r = 108.30 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

At 298 K:

$\Delta G°_{r(298 \text{ K})} = 90.83 \text{ kJ} - (298 \text{ K})(108.30 \text{ J} \cdot \text{K}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$

$\quad = 58.56 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta G°_{r(298 \text{ K})} = -RT \ln K$

$\ln K = -\dfrac{\Delta G°_{r(298 \text{ K})}}{RT}$

$\quad = -\dfrac{58\,560 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(298 \text{ K})} = -23.6$

$K = 6 \times 10^{-11}$

At 373 K:

$\Delta G°_{r(373 \text{ K})} = 90.83 \text{ kJ} - (373 \text{ K})(108.3 \text{ J} \cdot \text{K}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$

$\quad = 50.4 \text{ kJ} \cdot \text{mol}^{-1}$

$$\ln K = -\frac{50\,400 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(373 \text{ K})} = -16.3$$

$$K = 8 \times 10^{-8}$$

(b) propene (C_3H_6, g) $\rightarrow$ cyclopropane (C_3H_6, g)

$$\Delta H^\circ_{\text{r}} = \Delta H^\circ_{\text{f}}(\text{cyclopropane, g}) - [\Delta H^\circ_{\text{f}}(\text{propene, g})]$$

$$\Delta H^\circ_{\text{r}} = 53.30 \text{ kJ} \cdot \text{mol}^{-1} - [(20.42 \text{ kJ} \cdot \text{mol}^{-1})]$$

$$\Delta H^\circ_{\text{r}} = +32.88 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S^\circ_{\text{r}} = S^\circ(\text{cyclopropane, g}) - [S^\circ(\text{propene, g})]$$

$$\Delta S^\circ_{\text{r}} = 237.4 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - [266.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}]$$

$$\Delta S^\circ_{\text{r}} = -29.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

At 298 K:

$$\Delta G^\circ_{\text{r(298 K)}} = 32.88 \text{ kJ} \cdot \text{mol}^{-1}$$
$$- (298 \text{ K})(-29.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$
$$= 41.58 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G^\circ_{\text{r(298 K)}} = -RT \ln K$$

$$\ln K = -\frac{\Delta G^\circ_{\text{r(298 K)}}}{RT}$$

$$= -\frac{41\,580 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(298 \text{ K})} = -16.8$$

$$K = 5 \times 10^{-8}$$

At 373 K:

$$\Delta G^\circ_{\text{r(373 K)}} = 32.88 \text{ kJ} \cdot \text{mol}^{-1}$$
$$- (373 \text{ K})(-29.2 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$
$$= 43.8 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln K = -\frac{43\,800 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(373 \text{ K})} = -14.1$$

$$K = 7 \times 10^{-7}$$

9.88 We can think of the vaporization of a liquid as an equilibrium reaction, e.g., for substance A, $A(l) \rightleftharpoons A(g)$. This reaction has an equilibrium constant expression $K = P_A$. Since P_A is the pressure of the gas above a

liquid, it is the equilibrium vapor pressure of that liquid. Therefore, the vapor pressure varies with temperature in the same way that this equilibrium constant varies with temperature.

The van't Hoff equation, $\ln \dfrac{K_2}{K_1} = \dfrac{\Delta H_r^\circ}{R}\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)$, (see 16, page 354), gives the temperature dependence of K. To make this equation fit the special case of vapor pressure all we need to do is substitute P for K and ΔH_{vap}° for ΔH_r°.

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}^\circ}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

This relationship is known as the Clausius-Clapeyron equation (see equation 4, page 285). Since $\Delta H_{vap}^\circ > 0$, vapor pressure increases with temperature.

9.90   Recall $\Delta G_r^\circ = -RT \ln K = \Delta H_r^\circ - T\Delta S_r^\circ$ and $K = 10^{-pK}$

and $\ln \dfrac{K_2}{K_1} = \dfrac{\Delta H_r^\circ}{R}\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)$, the van't Hoff equation (see equation 16, page 354).

Rearranging and plugging in values,

$$\Delta H_r^\circ = \left(\ln \frac{K_2}{K_1}\right)\frac{R}{\left(\dfrac{1}{T_1}-\dfrac{1}{T_2}\right)} = \left(\ln \frac{10^{-13.8330}}{10^{-15.136}}\right)\frac{8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}}{\dfrac{1}{293\ \text{K}}-\dfrac{1}{303\ \text{K}}}$$

$$= (3.000)(7.381\times10^4\ \text{J}\cdot\text{mol}^{-1})$$
$$= 221.4\ \text{kJ}\cdot\text{mol}^{-1}$$

$$\Delta S_r^\circ = R\ln K + \frac{\Delta H_r^\circ}{T}$$

$$= (8.314\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1})\ln(10^{-15.136}) + \frac{221.4\times10^3\ \text{J}\cdot\text{mol}^{-1}}{293\ \text{K}}$$

$$= 465.9\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$$

The sign on ΔS_r° is positive because of the randomization that occurs as deuterons dissociate and redistribute throughout the liquid.

From the results above, the "autoprotolysis" constant of heavy water at 25°C is

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r^\circ}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln K_2 = \left(\frac{221.4 \times 10^3 \ \mathrm{J \cdot mol^{-1}}}{8.314 \ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}}\right)\left(\frac{1}{293 \ \mathrm{K}} - \frac{1}{298 \ \mathrm{K}}\right) + \ln 10^{-15.136}$$

$$= -33.327$$

$K_{\mathrm{D, 298\,K}} = 3.359 \times 10^{-15}$ or $pK_{\mathrm{D, 298\,K}} = 14.474$

Since $pK_{\mathrm{H, 298\,K}} = 14.00$ for regular water $< pK_{\mathrm{D, 298\,K}} = 14.474$,

substitution of D for H causes reactants, i.e., the associated molecules, to be favored more in heavy water than in regular water even though we expect D and H to be chemically equivalent. We can suggest that this observation is another example of the kinetic isotope effect where the zero-point energy of the O-D bond is lower than that of the O-H bond (see the solutions to Exercises 17.55 and 17.85 for further discussion). If bond dissociation is the rate-limiting step in the mechanism, and if only the vibrational energy of the ground state of the water molecules is changed appreciably, then the activation barrier for dissociation is bigger in heavy water since the zero-point energy is lower due to the heavier mass of D. This increase in the activation energy for bond dissociation causes the rate of dissociation to decrease while the rate of association is not changed appreciably. The position of equilibrium then favors the associated D_2O molecules more than it does in the H_2O molecules.

9.92 (a) $\Delta H^\circ_r = -[2\Delta H^\circ_f(O_3, g)]$

$= -[2(142.7 \ \mathrm{kJ \cdot mol^{-1}})]$

$= -285.4 \ \mathrm{kJ \cdot mol^{-1}}$

$$\Delta S^\circ_r = 3S^\circ(O_2, g) - [2S^\circ(O_3, g)]$$
$$= 3(205.14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) - [2(238.93 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})]$$
$$= 137.56 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

At 298 K:

$$\Delta G^\circ_{r(298 \text{ K})} = -285.4 \text{ kJ} \cdot \text{mol}^{-1}$$
$$- (298 \text{ K})(137.56 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1})$$
$$= -326.4 \text{ kJ} \cdot \text{mol}^{-1}$$

or directly from ΔG°_f values

$$\Delta G^\circ_r = -2\Delta G^\circ_f(O_3, g)$$
$$= -2(163.2 \text{ kJ} \cdot \text{mol}^{-1})$$
$$= -326.4 \text{ kJ} \cdot \text{mol}^{-1}$$

(b) $\Delta G^\circ_{r(298 \text{ K})} = -RT \ln K$

$$\ln K = -\frac{\Delta G^\circ_{r(298 \text{ K})}}{RT}$$

$$= -\frac{-326\,390 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(298 \text{ K})} = +132$$

$$K = 10^{57}$$

The equilibrium constant for the decomposition of ozone to oxygen is extremely large, making this process extremely favorable. Note: The presence of ozone in the upper atmosphere is largely due to kinetic factors that inhibit the decomposition; however, in the presence of a suitable catalyst, this process should occur extremely readily.

9.94 $[N_2O_4] = \dfrac{\left(\dfrac{2.50 \text{ g}}{92.02 \text{ g} \cdot \text{mol}^{-1}}\right)}{2.00 \text{ L}} = 0.0136 \text{ mol} \cdot \text{L}^{-1}; [NO_2] = \dfrac{\left(\dfrac{0.330 \text{ g}}{46.01 \text{ g} \cdot \text{mol}^{-1}}\right)}{2.00 \text{ L}}$

$$= 0.003\,59 \text{ mol} \cdot \text{L}^{-1}$$

Concentration (mol $\cdot$ L^{-1})	N$_2$O$_4$(g)	$\rightleftharpoons$	2 NO$_2$(g)
initial	0.0136		0.003 59
change	$-x$		$+2x$
final	$0.0136 - x$		$0.003\,59 + 2x$

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$$K_{\Psi} = \frac{[NO_2]^2}{[N_2O_4]}$$

$$4.66 \times 10^{-3} = \frac{(0.003\,59 + 2\,x)^2}{0.0136 - x}$$

$$(4.66 \times 10^{-3})(0.0136 - x) = (0.003\,59 + 2\,x)^2$$

$$6.34 \times 10^{-5} - 4.66 \times 10^{-3}\,x = 4\,x^2 + 1.44 \times 10^{-2}\,x + 1.29 \times 10^{-5}$$

$$4\,x^2 + 1.91 \times 10^{-2}\,x - 5.05 \times 10^{-5} = 0$$

Solving by using the quadratic equation gives $x = 1.89 \times 10^{-3}$.

$$[N_2O_4] = 0.0136 \text{ mol} \cdot L^{-1} - 1.89 \times 10^{-3} \text{ mol} \cdot L^{-1} = 0.012 \text{ mol} \cdot L^{-1}$$

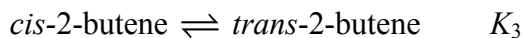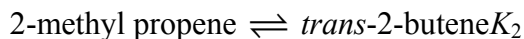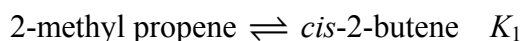$$[NO_2] = 0.003\,59 \text{ mol} \cdot L^{-1} + 2\,(1.89 \times 10^{-3} \text{ mol} \cdot L^{-1}) = 0.0074 \text{ mol} \cdot L^{-1}$$

These numbers can be checked by substituting them into the equilibrium expression:

$$\frac{(0.0074)^2}{0.012} \stackrel{?}{=} 4.66 \times 10^{-3}$$

$$4.6 \times 10^{-3} \stackrel{\vee}{=} 4.66 \times 10^{-3}$$

9.96 We can write an equilibrium expression for the interconversion of each pair of isomers:

2-methyl propene $\rightleftharpoons$ cis-2-butene K_1

2-methyl propene $\rightleftharpoons$ trans-2-butene K_2

cis-2-butene $\rightleftharpoons$ trans-2-butene K_3

We need to calculate only two of these values in order to determine the ratios.

The K's can be obtained from the ΔG°_r's for each interconversion:

$$\Delta G^{\circ}_1 = 65.86 \text{ kJ} \cdot \text{mol}^{-1} - 58.07 \text{ kJ} \cdot \text{mol}^{-1} = 7.79 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G^{\circ}_2 = 62.97 \text{ kJ} \cdot \text{mol}^{-1} - 58.07 \text{ kJ} \cdot \text{mol}^{-1} = 4.90 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G^{\circ}_3 = 62.97 \text{ kJ} \cdot \text{mol}^{-1} - 65.86 \text{ kJ} \cdot \text{mol}^{-1} = -2.89 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G°_r = -RT \ln K; \ln K = \frac{\Delta G°_r}{-RT}$$

$$\ln K_1 = \frac{\Delta G°_1}{-RT} = -\frac{7790 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = -3.14; K_1 = 0.043$$

$$\ln K_2 = \frac{\Delta G°_2}{-RT} = -\frac{4900 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = -1.98; K_2 = 0.14$$

$$\ln K_3 = \frac{\Delta G°_3}{-RT} = -\frac{-2890 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = +1.17; K_3 = 3.2$$

Each K gives a ratio of two of the isomers:

$$K_1 = \frac{[\textit{cis}\text{-2-butene}]}{[\text{2-methylpropene}]}; K_2 = \frac{[\textit{trans}\text{-2-butene}]}{[\text{2-methylpropene}]}; K_3 = \frac{[\textit{trans}\text{-2-butene}]}{[\textit{cis}\text{-2-butene}]}$$

We will choose to use the first two K's to calculate the final answer:

$$\frac{[\textit{cis}\text{-2-butene}]}{[\text{2-methylpropene}]} = 0.043 \qquad \frac{[\textit{trans}\text{-2-butene}]}{[\text{2-methylpropene}]} = 0.14$$

If we let the number of moles of 2-methylpropene = 1, then there will be 0.14 mol *trans*-2-butene and 0.043 mol *cis*-2-butene. The total number of moles will be 1 mol + 0.14 mol + 0.043 mol = 1.18 mol. The percentage of each will be

$$\% \text{ 2-methylpropene} = \frac{1 \text{ mol}}{1.18 \text{ mol}} \times 100\% = 85\%$$

$$\% \textit{ cis}\text{-2-butene} = \frac{0.043 \text{ mol}}{1.18 \text{ mol}} \times 100\% = 4\%$$

$$\% \textit{ trans}\text{-2-butene} = \frac{0.14 \text{ mol}}{1.18 \text{ mol}} \times 100\% = 12\%$$

(The sum of these should be 100% but varies by 1%, due to limitations in the use of significant figures/rounding conventions.)

The relative amounts are what we would expect, based upon the free energies of formation (the more negative or less positive value corresponding to the thermodynamically more stable compound), which indicate that the most stable compound is the 2-methylpropene followed by *trans*-2-butene with *cis*-2-butene being the least stable isomer. We can use K_3 as a check of these numbers:

$$K_3 = 3.2 \stackrel{?}{=} \frac{[\textit{trans}\text{-2-butene}]}{[\textit{cis}\text{-2-butene}]} = \frac{\dfrac{0.14}{V}}{\dfrac{0.043}{V}}$$

$$3.2 \cong 3.3$$

9.98

	A	$\rightleftharpoons$ 2 B	+	3 C
initial	10.00 atm	0 atm		0 atm
change	$-x$	$+2x$		$+3x$
final	$10.00 - x$	$+2x$		$+3x$

The equilibrium expression is $K = \dfrac{P_B{}^2 \times P_C{}^3}{P_A}$

We can also write $P_{total} = 10.00 - x + 2x + 3x = 10.00 + 4x = 15.76$

$x = 1.44$ atm

$P_A = 8.56$ atm; $P_B = 2.88$ atm; $P_C = 4.32$ atm

$$K = \frac{(2.88)^2 (4.32)^3}{8.56} = 78.1$$

$\Delta G° = -RT \ln K = -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})\ln(78.1)$

$= -10.8 \text{ kJ} \cdot \text{mol}^{-1}$

9.100 (a) First we calculate the initial pressure of the gas at 127°C using the ideal gas relationship:

$$PV = nRT$$

$$PV = \frac{m}{M} RT$$

$$P = \frac{mRT}{MV}$$

$$= \frac{(10.00 \text{ g})(0.082\,06 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}{(17.03 \text{ g} \cdot \text{mol}^{-1})(4.00 \text{ L})}$$
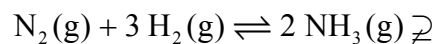
$$= 3.59 \text{ atm}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{3.59 \text{ atm}}{298 \text{ K}} = \frac{P_2}{400 \text{ K}}$$

$P_2 = 4.82$ atm or 4.88 bar (1 atm = 1.01325 bar)

From Table 9.1 we find that the equilibrium constant is 41 for the equation

$N_2(g) + 3\,H_2(g) \rightleftharpoons 2\,NH_3(g)\rightleftharpoons$

Although this exercise technically begins with pure ammonia and allows it to dissociate into $N_2(g)$ and $H_2(g)$, we can use the same expression.

pressure (bar)	$N_2(g)$ +	$3\,H_2(g) \rightleftharpoons$	$2\,NH_3(g)$
initial	0	0	4.88
change	$+x$	$+3x$	$-2x$
final	$+x$	$+3x$	$4.88 - 2x$

$$\frac{(4.88 - 2\,x)^2}{(x)(3\,x)^3} = 41$$

$$\frac{(4.88 - 2\,x)^2}{27\,x^4} = 41$$

$$\frac{4.88 - 2\,x}{3\sqrt{3}\,x^2} = \sqrt{41}$$

$$4.88 - 2\,x = 3\sqrt{123}\,x^2$$

$$33.3\,x^2 + 2\,x - 4.88 = 0$$

$$x = 0.354$$

$P_{NH_3} = 4.17$ bar or 4.11 atm; $P_{N_2} = 0.354$ bar or 0.349 atm; $P_{H_2} = 1.06$ bar or 1.05 atm

$P_{total} = 4.11$ atm + 0.349 atm + 1.05 atm = 5.51 atm

(b) The equilibrium constant can be calculated from $\Delta G°$ at 400 K, which can be obtained from $\Delta H°$ and $\Delta S°$. The values are

$\Delta H° = 2(-46.11 \text{ kJ} \cdot \text{mol}^{-1}) = -92.22 \text{ kJ} \cdot \text{mol}^{-1}$

$\Delta S° = 2(192.45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) - [(191.61 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
$\qquad + 3(130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})]$
$\qquad = -198.75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$

$\Delta G° = (-92.22 \text{ kJ} \cdot \text{mol}^{-1})(1000 \text{ J} \cdot \text{K}^{-1})$
$\qquad - (400 \text{ K})(-198.75 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})$
$\qquad = -12.72 \text{ kJ} \cdot \text{mol}^{-1} = -12720 \text{ J} \cdot \text{mol}^{-1}$

$K = e^{-\Delta G°/RT} = e^{+12720 \text{ J·mol}^{-1}/(8.314 \text{ J·K}^{-1}·\text{mol}^{-1})(400\text{K})} = 46$

This is reasonably good agreement considering the logarithmic nature of these calculations. For comparison, the $\Delta G°$ value calculated from $K = 41$ at 400 K is 12.34 kJ · mol^{-1}.

9.102 (a)

pressure (bar)	2 AsH₃(g) ⇌ 2 As(s) + 3 H₂(g)	
	2 AsH$_3$(g)	3 H$_2$(g)
initial	0.52	
change	$-2x$	$+3x$
final	$0.52 - 2x$	$+3x$

At equilibrium, total pressure = 0.64 bar.

$0.64 = 0.52 - 2x + 3x = 0.52 + x$

$x = 0.12$ bar

$P_{\text{AsH}_3} = 0.52 \text{ bar} - 2(0.12 \text{ bar}) = 0.28 \text{ bar}$

$P_{H_2} = 3(0.12 \text{ bar}) = 0.36 \text{ bar}$

(b) Find the number of moles of AsH$_3$ that decomposed and relate it to the mass of As.

$n = \dfrac{PV}{RT} = \dfrac{(0.24 \text{ bar})(1.00 \text{ L})}{(0.0831 \text{ L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})}$

$= 9.69 \times 10^{-3} \text{ mol AsH}_3 \text{ decomposed}$

mass As $= (9.69 \times 10^{-3} \text{ mol AsH}_3) \left(\dfrac{2 \text{ mol As}}{2 \text{ mol AsH}_3} \right) \left(\dfrac{74.9 \text{ g As}}{1 \text{ mol As}} \right)$

$= 0.73 \text{ g As}$

(c) $K = \dfrac{P_{H_2}^3}{P_{AsH_3}^2} = \dfrac{(0.36)^3}{(0.28)^2} = 0.60$

9.104 The free energy change for the reaction is calculated from the equation

$\Delta G = \Delta G^\circ + RT \ln Q = -RT \ln K + RT \ln Q$

In order to determine the range of Cl_2 pressures that we need to examine, we will first calculate the equilibrium pressures of the gases present.
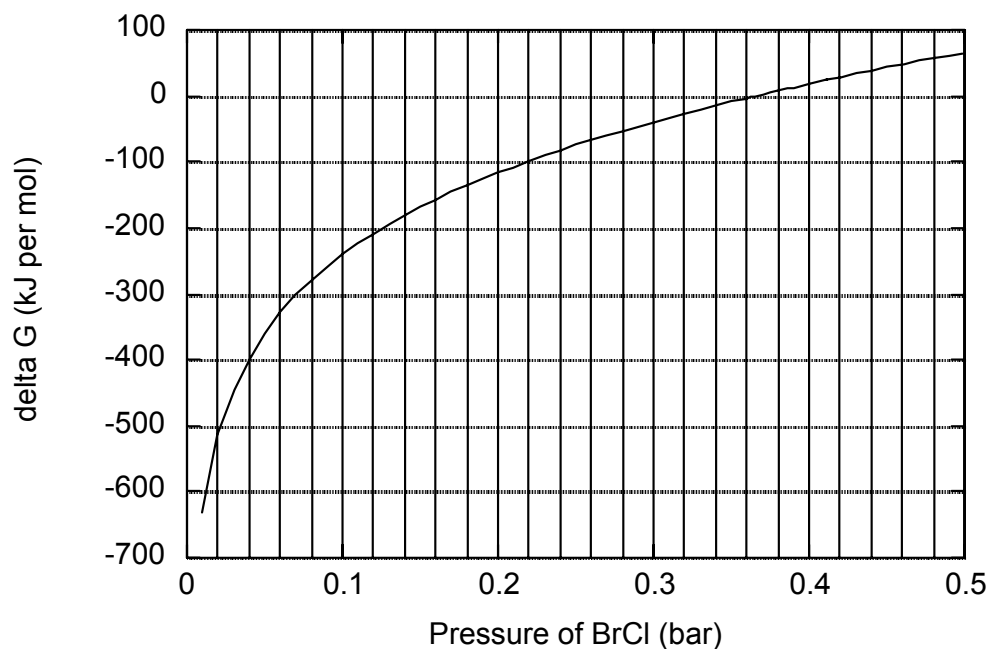
	$Br_2(g)$	$+$	$Cl_2(g)$	$\rightleftharpoons$	$2 \; BrCl(g)$
initial	1.00 bar		1.00 bar		0
change	$-x$		$-x$		$2\,x$
final	$1.00 - x$		$1.00 - x$		$2\,x$

$0.2 = \dfrac{P_{BrCl}^2}{P_{Br_2} \; P_{Cl_2}} = \dfrac{(2\,x)^2}{(1.00 - x)^2}$

$\sqrt{0.2} = \dfrac{2\,x}{1.00 - x}$

$x = 0.183 \approx 0.2$

In other words, equilibrium will be reached when $P_{BrCl} = 2x = 0.36 \; \text{bar}$, at the point on the graph where $\Delta G = 0$.
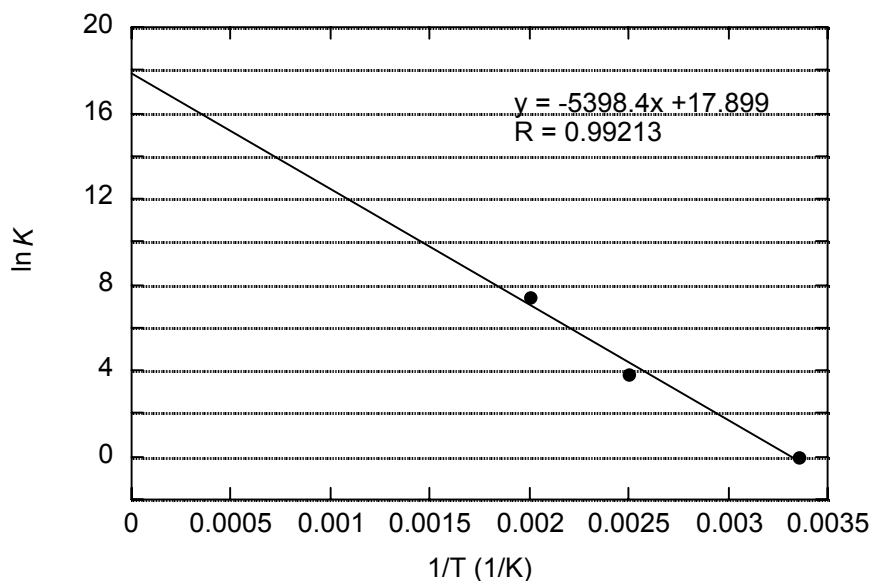
Notice that the free energy change for the reaction is most negative the farther the system is from equilibrium and that the value approaches 0 as equilibrium is attained.

9.106 The graph is generated for ln K vs. $1/T$ according to the relationship

$$\ln K = -\frac{\Delta H°}{R} \cdot \frac{1}{T} + \frac{\Delta S°}{R}$$

where $-\dfrac{\Delta H°}{R}$ is the slope and $\dfrac{\Delta S°}{R}$ is the intercept.

$y = -5398.4x + 17.899$
$R = 0.99213$

$$-\frac{\Delta H°}{R} = -5398 \text{ K}$$

$$\Delta H° = 44.9 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\frac{\Delta S°}{R} = 17.9$$

$$\Delta S° = 149 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

Because the reaction involves breaking only the N—N bond, the enthalpy of reaction should be an approximation of the N—N bond strength. Notice that this value is considerably less than the average 163 kJ · mol^{-1} value for N—N bonds given in Table 2.2. Therefore it is a very weak N—N bond.

9.108 (a) Since we are only using two temperatures, it really is not necessary to make graphs in order to determine $\Delta H°$ and $\Delta S°$. We can easily substitute into the van't Hoff equation, $\ln\dfrac{K_2}{K_1} = \dfrac{\Delta H_r°}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$, for each halogen to get $\Delta H°$, then use it to find $\Delta S°$ from $\Delta G° = \Delta H° - T\Delta S = -RT \ln K$. A spread sheet will work well.

(b) & (c) Results from our spread sheet based on the relationships given above and data from Table 9.2 are given below. The $\Delta S°$ values are for the reactions $X_2(g) \rightleftharpoons 2\,X(g)$, so we can calculate the standard molar entropies for the atomic species using data from Appendix 2A and the relationship $\Delta S° = 2S°_m\,(X, g) - S°_m\,(X_2, g)$.

Halogen	$\Delta H°$ $kJ \cdot mol^{-1}$	$\Delta S°$ $J \cdot K^{-1} \cdot mol^{-1}$	$S°(X_2, g)$ $J \cdot K^{-1} \cdot mol^{-1}$	$S°(X, g)$ $J \cdot K^{-1} \cdot mol^{-1}$
Fluorine	164	126	202.78	164
Chlorine	256	160	223.07	192
Bromine	195	110	245.46	178
Iodine	163	152	260.69	206

9.110 The general form of this type of equation is

$$\ln K = -\dfrac{\Delta H°_r}{R}\left(\dfrac{1}{T}\right) + \dfrac{\Delta S°_r}{R}$$

which is easily derived from the relationships

$\Delta G°_r = -RT \ln K$ and $\Delta G°_r = \Delta H°_r - T\Delta S°_r$. By inspection, we can see that for the original expression to be valid,

$-\dfrac{\Delta H°_r}{R} = -21\,700$, which gives $\Delta H°_r$

$\qquad = +(21\,700\ K)(8.314\ J \cdot K^{-1} \cdot mol^{-1})/(1000\ J \cdot kJ^{-1}) = 180\ kJ \cdot mol^{-1}$

9.112 (a) $K = \dfrac{1}{P_{PH_3} \cdot P_{BCl_3}}$

(b) $K = K_c(RT)^{\Delta n}$

$K_c = \dfrac{K}{(RT)^{\Delta n}} = \dfrac{19.2}{[(0.08314 \text{ L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(333 \text{ K})]^{-2}}$

$= 1.48 \times 10^4$

(c) The initial pressure of PH_3 is:

$P_{PH_3} = \dfrac{nRT}{V} = \dfrac{(0.0128 \text{ mol})(0.08314 \text{ L} \cdot \text{bar} \cdot \text{K}^{-1}\text{mol}^{-1})(333 \text{ K})}{0.500 \text{ L}}$

$= 0.7088 \text{ bar}$

pressure (bar)	$PH_3(g)$	$+$	$BCl_3(g)$	$\rightleftharpoons$	$PH_3BCl_3(s)$
initial	0.7088		0		
change	$+x$		$+x$		
equilibrium	$0.7088 + x$		x		

$K = 19.2 = \dfrac{1}{P_{PH_3} \cdot P_{BCl_3}} = \dfrac{1}{(0.7088 + x)x}$

$x^2 + 0.7088x - 0.05208 = 0$

$x = \dfrac{-0.7088 \pm \sqrt{(0.7088)^2 + 4(0.05208)}}{2}$

$= 0.06712$ (negative root isn't physically possible)

So $P_{PH_3} = 0.7088 + 0.06712 = 0.7759 \text{ bar}$

and $c_{PH_3} = \dfrac{P_{PH_3}}{RT} = \dfrac{0.7759 \text{ bar}}{(0.08314 \text{ L} \cdot \text{bar} \cdot \text{K}^{-1}\text{mol}^{-1})(333 \text{ K})} = 0.0280 \text{ mol} \cdot \text{L}^{-1}$

(d) K increases as T increases, so the equilibrium position is shifting toward products with the addition of heat. The reaction is endothermic.
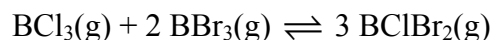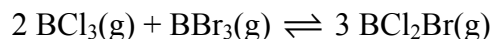
(e) $K = K_c(RT)^{\Delta n}$

$K_c = \dfrac{K}{(RT)^{\Delta n}} = \dfrac{26.2}{[(0.08314 \text{ L} \cdot \text{bar} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(343 \text{ K})]^{-2}}$

$= 2.13 \times 10^4$

(f) PH_3 has a lone pair of electrons to donate in order to form an adduct with BCl_3, which can be an electron acceptor. Therefore PH_3 is a Lewis base while BCl_3 is a Lewis acid.

9.114 (a) The values of the standard free energies of formation are

Compound	$\Delta G°_f \, (kJ \cdot mol^{-1})$
$BCl_3(g)$	−387.969
$BBr_3(g)$	−236.914
$BCl_2Br(g)$	−338.417
$BClBr_2(g)$	−287.556

(b) A number of equilibrium reactions are possible including

$2\,BCl_2Br(g) \rightleftharpoons BCl_3(g) + BClBr_2(g)$

$2\,BClBr_2(g) \rightleftharpoons BBr_3(g) + BCl_2Br(g)$

$2\,BCl_3(g) + BBr_3(g) \rightleftharpoons 3\,BCl_2Br(g)$

$BCl_3(g) + 2\,BBr_3(g) \rightleftharpoons 3\,BClBr_2(g)$

(c) BCl_3 because it is the most stable as determined by its $\Delta G°_f$ value.

(d) No. Although the equilibrium reaction given in the exercise would require that these two partial pressures be equal, there are other equilibria occurring as in (b) that will cause the values to be unequal.

(e) We will solve this problem graphically rather than by writing a computer program to solve a system of simultaneous equations. Standard free energies of formation are only used to get equilibrium constants for two essential reactions from $K = e^{\frac{-\Delta G_r^\circ}{RT}}$ and

$\Delta G_r^\circ = \sum n_{prods} \Delta G_f^\circ - \sum m_{reacts} \Delta G_f^\circ$.

In order to solve this part of the problem, first we need to figure out the independent reactions between the four species. If we consider BCl_3 and BBr_3 as pure species in terms of the halogens atoms, then the mixed species $BClBr_2$ and BCl_2Br can be made from the pure species by these two reactions:

(1) $BCl_3 + 2\,BBr_3 \rightleftharpoons 3\,BClBr_2$ $K_1 = \exp\left(\dfrac{871}{8.314 \times 298.15}\right) = 1.421$

(2) $2\,BCl_3 + BBr_3 \rightleftharpoons 3\,BCl_2Br$ $K_2 = \exp\left(\dfrac{2399}{8.314 \times 298.15}\right) = 2.632$

All other reactions between the species can be derived from these two essential reactions, so there are only two independent reactions for the system.

Let $P_{BCl_3} = x$, and $P_{BBr_3} = y$ then $K_1 = \dfrac{P_{BClBr_2}^{\,3}}{xy^2}$ and $K_2 = \dfrac{P_{BCl_2Br}^{\,3}}{x^2 y}$

so $P_{BClBr_2} = K_1^{1/3} x^{1/3} y^{2/3}$, and $P_{BCl_2Br} = K_2^{1/3} x^{2/3} y^{1/3}$

Atom balances are determined by the initial composition of the system. Balancing B atoms we get

$$P_{BCl_3}^{o} + P_{BBr_3}^{o} = P_{BCl_3} + P_{BCl_2Br} + P_{BClBr_2} + P_{BBr_3}$$

where $P_{BCl_3}^{o} = P_{BBr_3}^{o} = 1\,bar$ are the initial pressures. Balancing Cl atoms and Br atoms gives us

$$3P_{BCl_3}^{o} = 3P_{BCl_3} + 2P_{BCl_2Br} + P_{BClBr_2}$$

$$3P_{BBr_3}^{o} = P_{BCl_2Br} + 2P_{BClBr_2} + 3P_{BBr_3}$$

(Notice that the B balance is not an independent condition because it is implied by the Cl and Br balances.) In terms of x and y, the Cl balance and Br balance can be written as

Cl balance: $3x + 2K_2^{1/3} x^{2/3} y^{1/3} + K_1^{1/3} x^{1/3} y^{2/3} = 3$

Br balance: $K_2^{1/3} x^{2/3} y^{1/3} + 2K_1^{1/3} x^{1/3} y^{2/3} + 3y = 3$

Subtracting the second equation from the first equation, dividing the resulting equation by y, and also using this new definition

$$\left(\frac{x}{y}\right)^{1/3} \equiv z$$

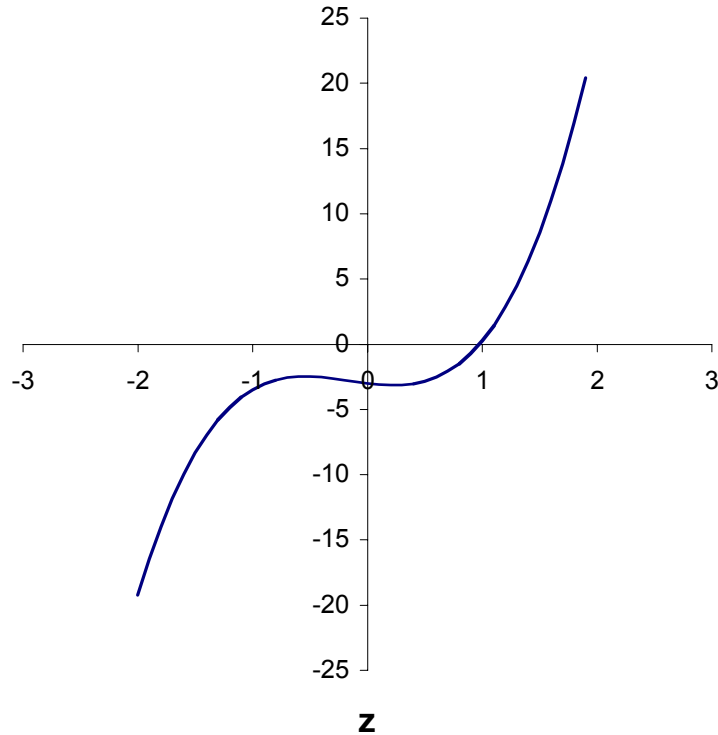we arrive at following equation in terms of z:

$$3z^3 + K_2^{1/3} z^2 - K_1^{1/3} z - 3 = 0$$

$$3z^3 + 1.381z^2 - 1.124z - 3 = 0$$

This cubic equation can be solved graphically by noting where

$f(z) = 3z^3 + 1.381z^2 - 1.124z - 3$ crosses 0. The only real root is

$z = 0.975$.

Substituting $x = z^3 y$ back into the Cl balance equation gives

$$y = \frac{3}{3z^3 + 2K_2^{1/3}z^2 + K_1^{1/3}z}$$

$$= \frac{3}{3(0.975)^3 + 2(1.381)(0.975)^2 + (1.124)(0.975)}$$

$$= 0.461$$

Then $x = z^3 y = (0.975)^3 (0.461) = 0.428$

And finally:

$$P_{BClBr_2} = \left((1.421)(0.428)(0.461)^2\right)^{1/3} = 0.506$$

$$P_{BCl_2Br} = \left((2.632)(0.428)^2(0.461)\right)^{1/3} = 0.606$$

The results can be summarized as:

$$P_{BCl_3} = 0.428 \text{ bar}$$

$$P_{BBr_3} = 0.461 \text{ bar}$$

$$P_{BCl_2Br} = 0.606 \text{ bar}$$

$$P_{BClBr_2} = 0.506 \text{ bar}$$

Note that in part (c) we predicted that BCl_3 is the most abundant species in the equilibrated mixture. However, this calculation reveals that it is the least abundant species at equilibrium given the stated initial conditions. The result is simply non-intuitive. What we need to recognize is that the formation reactions and their corresponding values of free energy of reaction describe equilibria between the elements $B(s)$, $Cl_2(g)$, and $Br_2(l)$ and the boron trihalides under standard conditions. In our mixture the compounds are certainly not in equilibrium with their elements in their standard states, so the prediction in part (c) fails.

Also note that in this system, $B(s)$ and $Br_2(l)$ cannot exist at same time, because the equilibrium constant of $B(s) + 1.5\ Br_2(l) \rightleftharpoons BBr_3(g)$ is very large, while the actual pressure of $BBr_3(g)$ is way below this equilibrium constant. $B(s)$ may exist from a microscopic amount of decomposition of $BCl_3(g)$, so $Br_2(l)$ can not exist. This condition further prevents BCl_2Br and $BClBr_2$ from decomposing into their elements, so only $BCl_3(g)$ may decompose to a small extent. Clearly, this small amount of $Cl_2(g)$ is far below standard conditions.

9.116 (a) Find Q to see if the reaction is at equilibrium.

cyclohexane (C) $\rightleftharpoons$ methylcyclohexane (M)
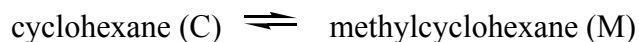
$$Q = \frac{[M]}{[C]} = \frac{0.100}{0.0200} = 5.00 > K = 0.140$$

The reaction will proceed to the left to form more reactant.

(b)

	[C]	[M]
initial	0.0200	0.100
change	$+x$	$-x$
equil	$0.0200 + x$	$0.100 - x$

$$K = \frac{[M]}{[C]} = \frac{0.100 - x}{0.0200 + x} = 0.140$$

$$0.100 - x = (0.140)(0.0200 + x)$$

$$1.140x = 9.72 \times 10^{-2}$$

$$x = 8.53 \times 10^{-2}$$

$$[M] = 0.100 - 0.0853 = 0.0147 = 0.015 \text{ M}$$

$$[C] = 0.0200 + 0.0853 = 0.1053 \text{ M}$$

(c) At equilibrium, [C] = 0.100 M. The total concentration of all species is 0.120 M. Therefore, [M] = 0.020 at equilibrium.

$$K_{50°C} = \frac{[M]}{[C]} = \frac{0.100}{0.020} = 5.0$$

(d) As the temperature increased, K also increased resulting in the reaction forming more products: $C + heat \rightleftharpoons M$. Therefore, the reaction is endothermic.

9.118 Refer to Graham's Law of Effusion, equation 19, page 144, which states that the ratio of the rates of effusion of two gases, both at the same temperature, is equal to the square-root of the inverse ratio of their molar masses.

$$\frac{\text{Rate of effusion of } H_2}{\text{Rate of effusion of HI}} = \sqrt{\frac{M_{HI}}{M_{H_2}}}$$

$$= \sqrt{\frac{127.9 \text{ g} \cdot \text{mol}^{-1}}{2.016 \text{ g} \cdot \text{mol}^{-1}}}$$

$$= 7.97$$

This treatment suggests that H_2 effuses ~8 times faster than HI. However, it is also important to note that the partial pressure of each gas affects the collision frequency of the molecules with the pinhole. Therefore, an expression that takes this dependence into account is

$$\frac{\text{Rate of effusion of } H_2}{\text{Rate of effusion of HI}} = \frac{P_{H_2}}{P_{HI}} \sqrt{\frac{M_{HI}}{M_{H_2}}}$$

The partial pressure of hydrogen is 0.7 atm, or 0.69 bar. The partial pressure of HI can be found from

$$K = \frac{P_{HI}^2}{P_{H_2}}$$

$$P_{HI} = \sqrt{K \cdot P_{H_2}} = (0.345 \times 0.69)^{1/2} = 0.49 \text{ bar}$$

$$\frac{\text{Rate of effusion of } H_2}{\text{Rate of effusion of HI}} = \frac{P_{H_2}}{P_{HI}} \sqrt{\frac{M_{HI}}{M_{H_2}}} = \left(\frac{0.69 \text{ bar}}{0.49 \text{ bar}}\right) \sqrt{\frac{127.9 \text{ g} \cdot \text{mol}^{-1}}{2.016 \text{ g} \cdot \text{mol}^{-1}}}$$

$$= 11$$

$$= 10 \text{ (to 1 sig fig)}$$

So hydrogen effuses ten times as fast as hydrogen iodide under these conditions.