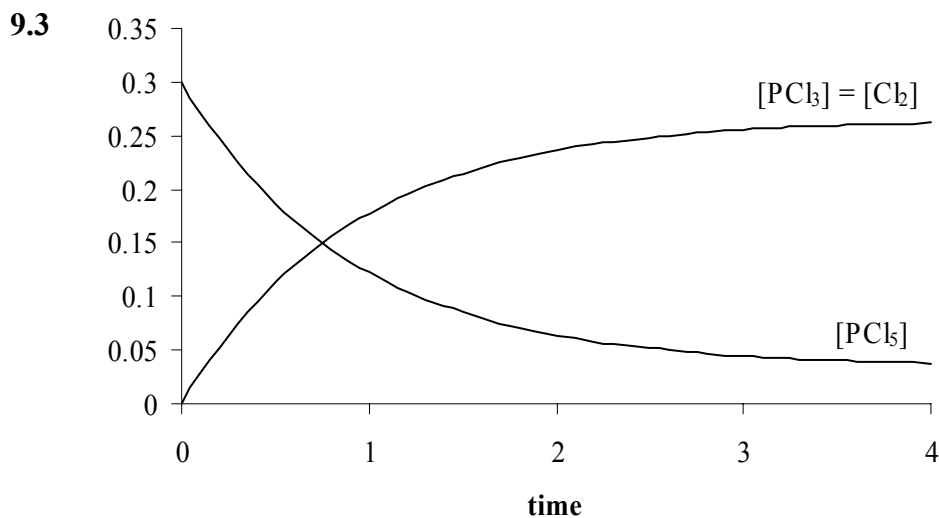


CHAPTER 9

CHEMICAL EQUILIBRIA

- 9.1** (a) False, Equilibrium is dynamic. At equilibrium, the concentrations of reactants and products will not change, but the reaction will continue to proceed in both directions.
- (b) False. Equilibrium reactions are affected by the presence of both products and reactants.
- (c) False. The value of the equilibrium constant is not affected by the amounts of reactants or products added as long as the temperature is constant.
- (d) True.



- 9.5** (a) $K_c = \frac{[\text{COCl}][\text{Cl}]}{[\text{CO}][\text{Cl}_2]}$; (b) $K_c = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]}$; (c) $K_c = \frac{[\text{SO}_2]^2 [\text{H}_2\text{O}]^2}{[\text{H}_2\text{S}]^2 [\text{O}_2]^3}$

- 9.7** (a) Because the volume is the same, the number of moles of O_2 is larger in the second experiment. (b) Because K_C is a constant and the denominator is larger in the second case, the numerator must also be larger; so the concentration of O_2 is larger in the second case. (c) Although $[O_2]^3/[O_3]^2$ is the same, $[O_2]/[O_3]$ will be different, a result seen by solving for K_C in each case. (d) Because K_C is a constant, $[O_2]^3/[O_3]^2$ is the same. (e) Because $[O_2]^3/[O_3]^2$ is the same, its reciprocal must be the same.

9.9
$$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

for condition 1, $K_C = \frac{(0.0137)^2}{(6.47 \times 10^{-3})(0.594 \times 10^{-3})} = 48.8$

for condition 2, $K_C = \frac{(0.0169)^2}{(3.84 \times 10^{-3})(1.52 \times 10^{-3})} = 48.9$

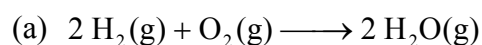
for condition 3, $K_C = \frac{(0.0100)^2}{(1.43 \times 10^{-3})(1.43 \times 10^{-3})} = 48.9$

9.11 (a) $\frac{1}{P_{O_2}^3}$

(b) $P_{H_2O}^7$

(c) $\frac{P_{NO}P_{NO_2}}{P_{N_2O_3}}$

- 9.13** To answer these questions, we will first calculate ΔG° for each reaction and then use that value in the expression $\Delta G^\circ = -RT \ln K$.



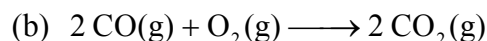
$$\Delta G^\circ_r = 2(\Delta G^\circ_f(\text{H}_2\text{O}, \text{g}) = 2(-228.57 \text{ kJ} \cdot \text{mol}^{-1}) = -457.14 \text{ kJ}$$

$$\Delta G^\circ_r = -RT \ln K \text{ or}$$

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

$$\ln K = -\frac{-457140 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.15 \text{ K})} = +184.42$$

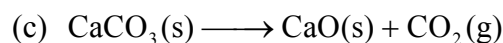
$$K = 1 \times 10^{80}$$



$$\begin{aligned} \Delta G^\circ_r &= 2 \times \Delta G^\circ_f(\text{CO}_2, \text{g}) - [2 \times \Delta G^\circ_f(\text{CO}, \text{g})] \\ &= 2(-394.36 \text{ kJ} \cdot \text{mol}^{-1}) - [2(-137.17 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -514.38 \text{ kJ} \end{aligned}$$

$$\ln K = -\frac{-514380 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298.15 \text{ K})} = +207.5$$

$$K = 1 \times 10^{90}$$



$$\begin{aligned} \Delta G^\circ_r &= \Delta G^\circ_f(\text{CaO}, \text{s}) + \Delta G^\circ_f(\text{CO}_2, \text{g}) - [\Delta G^\circ_f(\text{CaCO}_3, \text{s})] \\ &= (-604.03 \text{ kJ} \cdot \text{mol}^{-1}) + (-394.36 \text{ kJ} \cdot \text{mol}^{-1}) - [-1128.8 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= +130.4 \text{ kJ} \end{aligned}$$

$$\ln K = -\frac{+130400 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = -52.6$$

$$K = 1 \times 10^{-23}$$

9.15 (a) $\Delta G^\circ_r = -RT \ln K$

$$= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1200 \text{ K}) \ln 6.8 = -19 \text{ kJ} \cdot \text{mol}^{-1}$$

(b) $\Delta G^\circ_r = -RT \ln K = -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K}) \ln 1.1 \times 10^{-12}$
 $= +68 \text{ kJ} \cdot \text{mol}^{-1}$

9.17 First we must calculate K for the reaction, which can be done using data from Appendix 2A:

$$\Delta G^\circ_r = 2 \times \Delta G^\circ_f(\text{NO}, \text{g}) = 2 \times 86.55 \text{ kJ} \cdot \text{mol}^{-1} = 173.1 \text{ kJ} \cdot \text{mol}^{-1}$$

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

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

$$\ln K = -\frac{+173\,100 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = -69.9$$

$$K = 4 \times 10^{-31}$$

Because $Q > K$, the reaction will tend to proceed to produce reactants.

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

$$\Delta G_r = \Delta G^\circ_r + RT \ln Q$$

$$\Delta G_r = -RT \ln K + RT \ln Q$$

$$\Delta G_r = -RT \ln K + RT \ln \frac{[\text{I}]^2}{[\text{I}_2]}$$

$$= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1200 \text{ K}) \ln (6.8)$$

$$+ (8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1200 \text{ K}) \ln \frac{(0.98)^2}{(0.13)}$$

$$= 8.3 \times 10^{-1} \text{ kJ} \cdot \text{mol}^{-1}$$

Because ΔG_r is positive, the reaction will be spontaneous to produce I_2 .

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

$$\Delta G_r = \Delta G^\circ_r + RT \ln Q$$

$$\Delta G_r = -RT \ln K + RT \ln Q$$

$$\Delta G_r = -RT \ln K + RT \ln \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(400 \text{ K}) \ln (41)$$

$$+ (8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(400 \text{ K}) \ln \frac{(21)^2}{(4.2)(1.8)^3}$$

$$= -27 \text{ kJ} \cdot \text{mol}^{-1}$$

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

9.23 (a) $K = \frac{P_{\text{NO}}^2 P_{\text{Cl}_2}}{P_{\text{NOCl}}^2} = 1.8 \times 10^{-2}$

$$K = \left(\frac{T}{12.027 \text{ K}} \right)^{\Delta n} K_C$$

$$K_C = \left(\frac{12.027 \text{ K}}{T} \right)^{\Delta n} K = \left(\frac{12.027 \text{ K}}{500 \text{ K}} \right)^{(3-2)} 1.8 \times 10^{-2} = 4.3 \times 10^{-4}$$

$$(b) \quad K = P_{\text{CO}_2} = 167$$

$$K_C = \left(\frac{12.027 \text{ K}}{T} \right)^{\Delta n} K = \left(\frac{12.027 \text{ K}}{1073 \text{ K}} \right)^{(1)} 167 = 1.87$$

9.25 For the reaction written as $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g})$ Eq. 1

$$K = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} P_{\text{H}_2}^3} = 41$$

(a) For the reaction written as $2 \text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g})$ Eq. 2

$$K = \frac{P_{\text{N}_2} P_{\text{H}_2}^3}{P_{\text{NH}_3}^2}$$

$$\text{This is } \frac{1}{K_{\text{Eq. 1}}} = \frac{1}{41} = 0.024$$

(b) For the reaction written as $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g})$ Eq. 3

$$K_{\text{Eq. 3}} = \frac{P_{\text{NH}_3}}{P_{\text{N}_2}^{1/2} P_{\text{H}_2}^{3/2}} = \sqrt{K_{\text{Eq. 1}}} = \sqrt{41} = 6.4$$

Note that Eq. 3 = $\frac{1}{2}$ Eq. 1 and thus $K_{\text{Eq. 3}} = K_{\text{Eq. 1}}^{1/2}$.

(c) For the reaction written as $2 \text{N}_2(\text{g}) + 6 \text{H}_2(\text{g}) \rightarrow 4 \text{NH}_3(\text{g})$ Eq. 4

$$K_{\text{Eq. 4}} = \frac{P_{\text{NH}_3}^4}{P_{\text{N}_2}^2 P_{\text{H}_2}^6} = K_{\text{Eq. 1}}^2 = 41^2 = 1.7 \times 10^3$$

Note that Eq. 4 = 2 Eq. 1 and thus $K_{\text{Eq. 4}} = K_{\text{Eq. 1}}^2$.

9.27 $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2 \text{HI}(\text{g}) \quad K_C = 160$

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$

$$160 = \frac{(2.21 \times 10^{-3})^2}{[\text{H}_2](1.46 \times 10^{-3})}$$

$$[\text{H}_2] = \frac{(2.21 \times 10^{-3})^2}{(160)(1.46 \times 10^{-3})}$$

$$[\text{H}_2] = 2.1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$$

$$\mathbf{9.29} \quad K = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}}$$

$$25 = \frac{P_{\text{PCl}_3} (5.43)}{1.18}$$

$$P_{\text{PCl}_3} = \frac{(25)(1.18)}{5.43} = 5.4$$

$$P_{\text{PCl}_3} = 5.4 \text{ bar}$$

$$\mathbf{9.31} \quad (\text{a}) \quad K = \frac{p_{\text{HI}}^2}{p_{\text{H}_2} \cdot p_{\text{I}_2}} = 160$$

$$Q = \frac{(0.10)^2}{(0.20)(0.10)} = 0.50$$

(b) $Q \neq K$, \therefore the system is not at equilibrium

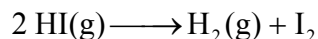
(c) Because $Q < K$, more products will be formed.

$$\mathbf{9.33} \quad (\text{a}) \quad K_C = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2 [\text{O}_2]} = 1.7 \times 10^6$$

$$Q_C = \frac{\left[\frac{1.0 \times 10^{-4}}{0.500} \right]^2}{\left[\frac{1.20 \times 10^{-3}}{0.500} \right]^2 \left[\frac{5.0 \times 10^{-4}}{0.500} \right]} = 6.9$$

(b) Because $Q_C < K_C$, more products will tend to form, which will result in the formation of more SO_3 .

$$9.35 \quad \frac{1.90 \text{ g HI}}{127.91 \text{ g} \cdot \text{mol}^{-1}} = 0.0148 \text{ mol HI}$$



$$0.0172 \text{ mol} - 2x \quad x \quad x$$

$$0.0148 \text{ mol} = 0.0172 \text{ mol} - 2x$$

$$x = 0.0012 \text{ mol}$$

$$K_C = \frac{\left[\frac{0.0012}{2.00} \right] \left[\frac{0.0012}{2.00} \right]}{\left[\frac{0.0148}{2.00} \right]^2} = \frac{\left[\frac{0.0012}{2.00} \right]^2}{\left[\frac{0.0148}{2.00} \right]^2} = 0.0066 \text{ or } 6.6 \times 10^{-3}$$

$$9.37 \quad \frac{25.0 \text{ g NH}_4(\text{NH}_2\text{CO}_2)}{78.07 \text{ g} \cdot \text{mol}^{-1} \text{ NH}_4(\text{NH}_2\text{CO}_2)} = 0.320 \text{ mol NH}_4(\text{NH}_2\text{CO}_2)$$

$$\frac{0.0174 \text{ g CO}_2}{44.01 \text{ g} \cdot \text{mol}^{-1} \text{ CO}_2} = 3.95 \times 10^{-4} \text{ mol CO}_2$$

$$2 \text{ mol NH}_3 \text{ are formed per mol of CO}_2, \text{ so } \text{mol NH}_3 = 2 \times 3.95 \times 10^{-4} \\ = 7.90 \times 10^{-4}$$

$$K_C = [\text{NH}_3]^2 [\text{CO}_2] = \left(\frac{7.90 \times 10^{-4}}{0.250} \right)^2 \left(\frac{3.95 \times 10^{-4}}{0.250} \right) = 1.58 \times 10^{-8}$$

$$9.39 \quad (\text{a}) \text{ The balanced equation is: } \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{ Cl(g)}$$

$$\text{The initial concentration of Cl}_2(\text{g}) \text{ is } \frac{0.0020 \text{ mol Cl}_2}{2.0 \text{ L}} = 0.0010 \text{ mol} \cdot \text{L}^{-1}$$

Concentration (mol · L ⁻¹)	Cl ₂ (g) → 2 Cl(g)	
initial	0.0010	0
change	-x	+2x
equilibrium	0.0010 - x	+2x

$$K_c = \frac{[\text{Cl}]^2}{[\text{Cl}_2]} = \frac{(2x)^2}{(0.0010 - x)} = 1.2 \times 10^{-7}$$

$$4x^2 = (1.2 \times 10^{-7})(0.0010 - x)$$

$$4x^2 + (1.2 \times 10^{-7})x - (1.2 \times 10^{-10}) = 0$$

$$x = \frac{-(1.2 \times 10^{-7}) \pm \sqrt{(1.2 \times 10^{-7})^2 - 4(4)(-1.2 \times 10^{-10})}}{2.4}$$

$$x = \frac{-(1.2 \times 10^{-7}) \pm 4.4 \times 10^{-5}}{8}$$

$$x = -5.5 \times 10^{-6} \text{ or } +5.5 \times 10^{-6}$$

The negative answer is not meaningful, so we choose

$x = +5.5 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$. The concentration of Cl_2 is essentially

unchanged because $0.0010 - 5.5 \times 10^{-6} \cong 0.0010$. The concentration of

Cl atoms is $2 \times (5.5 \times 10^{-6}) = 1.1 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}$. The percentage

decomposition of Cl_2 is given by

$$\frac{5.5 \times 10^{-6}}{0.0010} \times 100 = 0.55\%$$

(b) The balanced equation is: $\text{F}_2(\text{g}) \rightleftharpoons 2 \text{F}(\text{g})$

The problem is worked in an identical fashion to (a) but the equilibrium constant is now 1.2×10^{-4} .

The initial concentration of $\text{F}_2(\text{g})$ is $\frac{0.0020 \text{ mol F}_2}{2.0 \text{ L}} = 0.0010 \text{ mol} \cdot \text{L}^{-1}$

Concentration ($\text{mol} \cdot \text{L}^{-1}$)	$\text{F}_2(\text{g})$	\rightarrow	$2 \text{F}(\text{g})$
initial	0.0010		0
change	$-x$		$+2x$
equilibrium	$0.0010 - x$		$+2x$

$$K_c = \frac{[\text{F}]^2}{[\text{F}_2]} = \frac{(2x)^2}{(0.0010 - x)} = 1.2 \times 10^{-4}$$

$$4x^2 = (1.2 \times 10^{-4})(0.0010 - x)$$

$$4x^2 + (1.2 \times 10^{-4})x - (1.2 \times 10^{-7}) = 0$$

$$x = \frac{-(1.2 \times 10^{-4}) \pm \sqrt{(1.2 \times 10^{-4})^2 - 4(4)(-1.2 \times 10^{-7})}}{2.4}$$

$$x = \frac{-(1.2 \times 10^{-4}) \pm 1.4 \times 10^{-3}}{8}$$

$$x = -1.9 \times 10^{-4} \text{ or } +1.6 \times 10^{-4}$$

The negative answer is not meaningful, so we choose

$x = +1.6 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. The concentration of F_2 is

$0.0010 - 1.6 \times 10^{-4} = 8 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. The concentration of F atoms is

$2 \times (1.6 \times 10^{-4}) = 3.2 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$. The percentage decomposition of F_2

is given by

$$\frac{1.6 \times 10^{-4}}{0.0010} \times 100 = 16\%$$

(c) Cl_2 is more stable. This can be seen even without the aid of the calculation from the larger equilibrium constant for the dissociation for F_2 compared to Cl_2 .

9.41	Concentration (bar)	2 HBr(g)	\rightarrow	$\text{H}_2(\text{g}) + \text{Br}_2(\text{g})$
	initial	1.2×10^{-3}		0 0
	change	$-2x$		$+x$ $+x$
	final	$1.2 \times 10^{-3} - 2x$		$+x$ $+x$

$$K = \frac{p_{\text{H}_2} \cdot p_{\text{Br}_2}}{p_{\text{HBr}}^2}$$

$$7.7 \times 10^{-11} = \frac{(x)(x)}{(1.2 \times 10^{-3} - 2x)^2} = \frac{x^2}{(1.2 \times 10^{-3} - 2x)^2}$$

$$\sqrt{7.7 \times 10^{-11}} = \sqrt{\frac{x^2}{(1.2 \times 10^{-3} - 2x)^2}}$$

$$\frac{x}{(1.2 \times 10^{-3} - 2x)} = 8.8 \times 10^{-6}$$

$$x = (8.8 \times 10^{-6})(1.2 \times 10^{-3} - 2x)$$

$$x + 2(8.8 \times 10^{-6})x = (8.8 \times 10^{-6})(1.2 \times 10^{-3})$$

$$x \cong 1.1 \times 10^{-8}$$

$p_{H_2} = p_{Br_2} = 1.1 \times 10^{-8}$ bar; the pressure of HBr is essentially unaffected by the formation of Br_2 and H_2 .

The percentage decomposition is given by

$$\frac{2(1.1 \times 10^{-8} \text{ bar})}{1.2 \times 10^{-3} \text{ bar}} \times 100 = 1.8 \times 10^{-3}\%$$

9.43 (a) Concentration of PCl_5 initially

$$= \frac{\left(\frac{1.0 \text{ g } PCl_5}{208.22 \text{ g} \cdot \text{mol}^{-1} PCl_5} \right)}{0.250 \text{ L}} = 0.019 \text{ mol} \cdot \text{L}^{-1}$$

Concentration ($\text{mol} \cdot \text{L}^{-1}$)	$PCl_5(\text{g}) \rightarrow$	$PCl_3(\text{g})$	+	Cl_2
initial	0.019	0		0
change	$-x$	$+x$		$+x$
final	$0.019 - x$	$+x$		$+x$

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(x)(x)}{(0.019 - x)} = \frac{x^2}{(0.019 - x)}$$

$$\frac{x^2}{(0.019 - x)} = 1.1 \times 10^{-2}$$

$$x^2 = (1.1 \times 10^{-2})(0.019 - x)$$

$$x^2 + (1.1 \times 10^{-2})x - 2.1 \times 10^{-4} = 0$$

$$x = \frac{-(1.1 \times 10^{-2}) \pm \sqrt{(1.1 \times 10^{-2})^2 - (4)(1)(-2.1 \times 10^{-4})}}{2.1}$$

$$x = \frac{-(1.1 \times 10^{-2}) \pm 0.031}{2.1} = +0.010 \text{ or } -0.021$$

The negative root is not meaningful, so we choose $x = 0.010 \text{ mol} \cdot \text{L}^{-1}$.

$$[\text{PCl}_3] = [\text{Cl}_2] = 0.010 \text{ mol} \cdot \text{L}^{-1}; [\text{PCl}_5] = 0.009 \text{ mol} \cdot \text{L}^{-1}.$$

(b) The percentage decomposition is given by

$$\frac{0.010}{0.019} \times 100 = 53\%$$

9.45 Starting concentration of $\text{NH}_3 = \frac{0.400 \text{ mol}}{2.00 \text{ L}} = 0.200 \text{ mol} \cdot \text{L}^{-1}$

Concentration ($\text{mol} \cdot \text{L}^{-1}$)	$\text{NH}_4\text{HS(s)} \rightarrow$	$\text{NH}_3(\text{g})$	+	$\text{H}_2\text{S(g)}$
initial	—	0.200		0
change	—	+ x		+ x
final	—	$0.200 + x$		+ x

$$K_C = [\text{NH}_3][\text{H}_2\text{S}] = (0.200 + x)(x)$$

$$1.6 \times 10^{-4} = (0.200 + x)(x)$$

$$x^2 + 0.200x - 1.6 \times 10^{-4} = 0$$

$$x = \frac{-(+0.200) \pm \sqrt{(+0.200)^2 - (4)(1)(-1.6 \times 10^{-4})}}{2.1}$$

$$x = \frac{-0.200 \pm 0.2016}{2.1} = +0.0008 \text{ or } -0.2008$$

The negative root is not meaningful, so we choose $x = 8 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$

(note that in order to get this number we have had to ignore our normal significant figure conventions).

$$[\text{NH}_3] = +0.200 \text{ mol} \cdot \text{L}^{-1} + 8 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1} = 0.200 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{H}_2\text{S}] = 8 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

Alternatively, we could have assumed that

$$x \ll 0.2, \text{ the } 0.200x = 1.6 \times 10^{-4}, x = 8.0 \times 10^{-4}.$$

9.47 The initial concentrations of PCl_5 and PCl_3 are calculated as follows:

$$[\text{PCl}_5] = \frac{0.200 \text{ mol}}{4.00 \text{ L}} = 0.0500 \text{ mol} \cdot \text{L}^{-1}; [\text{PCl}_3] = \frac{0.600 \text{ mol}}{4.00 \text{ L}} = 0.150 \text{ mol} \cdot \text{L}^{-1}$$

Concentrations ($\text{mol} \cdot \text{L}^{-1}$)	PCl_5	\rightarrow	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
initial	0.0500		0.150		0
change	$-x$		$+x$		$+x$
final	$0.0500 - x$		$0.150 + x$		$+x$

$$K_c = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = \frac{(0.150 + x)(x)}{(0.0500 - x)} = 33.3$$

$$x^2 + 0.150x = (33.3)(0.0500 - x)$$

$$x^2 + 33.45x - 1.665 = 0$$

$$x = \frac{-33.45 \pm \sqrt{(33.45)^2 - (4)(1)(-1.665)}}{(2)(1)} = \frac{-33.4 \pm 33.6}{2} = 0.0497$$

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

$$[\text{PCl}_5] = 0.0500 \text{ mol} \cdot \text{L}^{-1} - 0.0497 \text{ mol} \cdot \text{L}^{-1} = 3 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{PCl}_3] = 0.150 \text{ mol} \cdot \text{L}^{-1} + 0.0497 \text{ mol} \cdot \text{L}^{-1} = 0.200 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{Cl}_2] = 0.0497 \text{ mol} \cdot \text{L}^{-1}$$

9.49 The initial concentrations of N_2 and O_2 are equal at $0.114 \text{ mol} \cdot \text{L}^{-1}$ because the vessel has a volume of 1.00 L.

Concentrations ($\text{mol} \cdot \text{L}^{-1}$)	$\text{N}_2(\text{g})$	+	$\text{O}_2(\text{g})$	\rightarrow	$2 \text{ NO}(\text{g})$
initial	0.114		0.114		0
change	$-x$		$-x$		$+2x$
final	$0.114 - x$		$0.114 - x$		$+2x$

$$K_c = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(2x)^2}{(0.114 - x)(0.114 - x)} = \frac{(2x)^2}{(0.114 - x)^2}$$

$$1.00 \times 10^{-5} = \frac{(2x)^2}{(0.114 - x)^2}$$

$$\sqrt{1.00 \times 10^{-5}} = \sqrt{\frac{(2x)^2}{(0.114 - x)^2}}$$

$$3.16 \times 10^{-3} = \frac{(2x)}{(0.114 - x)}$$

$$2x = (3.16 \times 10^{-3})(0.114 - x)$$

$$2.00316x = 3.60 \times 10^{-4}$$

$$x = 1.8 \times 10^{-4}$$

$$[\text{NO}] = 2x = 2 \times 1.8 \times 10^{-4} = 3.6 \times 10^{-4}; \text{ the concentrations of } \text{N}_2 \text{ and } \text{O}_2$$

remain essentially unchanged at $0.114 \text{ mol} \cdot \text{L}^{-1}$.

9.51 The initial concentrations of H_2 and I_2 are:

$$[\text{H}_2] = \frac{0.400 \text{ mol}}{3.00 \text{ L}} = 0.133 \text{ mol} \cdot \text{L}^{-1}; [\text{I}_2] = \frac{1.60 \text{ mol}}{3.00 \text{ L}} = 0.533 \text{ mol} \cdot \text{L}^{-1}$$

Concentrations ($\text{mol} \cdot \text{L}^{-1}$)	$\text{H}_2(\text{g})$	+	$\text{I}_2(\text{g})$	\rightarrow	$2 \text{ HI}(\text{g})$
initial	0.133		0.533		0
change	$-x$		$-x$		$+2x$
final	$0.133 - x$		$0.533 - x$		$+2x$

At equilibrium, 60.0% of the H_2 had reacted, so 40.0% of the H_2

remains:

$$(0.400)(0.133 \text{ mol} \cdot \text{L}^{-1}) = 0.133 \text{ mol} \cdot \text{L}^{-1} - x$$

$$x = 0.133 \text{ mol} \cdot \text{L}^{-1} - (0.400)(0.133 \text{ mol} \cdot \text{L}^{-1})$$

$$x = 0.080 \text{ mol} \cdot \text{L}^{-1}$$

$$\text{at equilibrium: } [\text{H}_2] = 0.133 \text{ mol} \cdot \text{L}^{-1} - 0.080 \text{ mol} \cdot \text{L}^{-1} = 0.053 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{I}_2] = 0.533 \text{ mol} \cdot \text{L}^{-1} - 0.080 \text{ mol} \cdot \text{L}^{-1} = 0.453 \text{ mol} \cdot \text{L}^{-1}$$

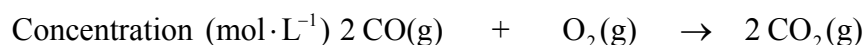
$$[\text{HI}] = 2 \times 0.080 \text{ mol} \cdot \text{L}^{-1} = 0.16 \text{ mol} \cdot \text{L}^{-1}$$

$$K_C = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{0.16^2}{(0.053)(0.453)} = 1.1$$

9.53 Initial concentrations of CO and O₂ are given by

$$[\text{CO}] = \frac{\left(\frac{0.28 \text{ g CO}}{28.01 \text{ g} \cdot \text{mol}^{-1} \text{CO}} \right)}{2.0 \text{ L}} = 5.0 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{O}_2] = \frac{\left(\frac{0.032 \text{ g O}_2}{32.00 \text{ g} \cdot \text{mol}^{-1} \text{O}_2} \right)}{2.0 \text{ L}} = 5.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$



initial	5.0 × 10 ⁻³	5.0 × 10 ⁻⁴	0
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change	-2x	-x	+2x
--------	-----	----	-----

final	5.0 × 10 ⁻³ - 2x	5.0 × 10 ⁻⁴ - x	+2x
-------	-----------------------------	----------------------------	-----

$$K_C = \frac{[\text{CO}_2]^2}{[\text{CO}]^2 [\text{O}_2]}$$

$$= \frac{(2x)^2}{(5.0 \times 10^{-3} - 2x)^2 (5.0 \times 10^{-4} - x)}$$

$$= \frac{4x^2}{(4x^2 - 0.020x + 2.5 \times 10^{-5})(5.0 \times 10^{-4} - x)}$$

$$0.66 = \frac{4x^2}{-4x^3 + 0.022x^2 - 3.5 \times 10^{-5}x + 1.25 \times 10^{-8}}$$

$$4x^2 = (0.66)(-4x^3 + 0.022x^2 - 3.5 \times 10^{-5}x + 1.25 \times 10^{-8})$$

$$6.06x^2 = -4x^3 + 0.022x^2 - 3.5 \times 10^{-5}x + 1.25 \times 10^{-8}$$

$$0 = -4x^3 - 6.04x^2 - 3.5 \times 10^{-5}x + 1.25 \times 10^{-8}$$

$$x = 4.3 \times 10^{-5}$$

$$[\text{CO}_2] = 8.6 \times 10^{-5} \text{ mol} \cdot \text{L}^{-1}; [\text{CO}] = 4.9 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{O}_2] = 4.6 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$$

9.55 Concentrations

(mol · L ⁻¹)	CH ₃ COOH	+	C ₂ H ₅ OH	→	CH ₃ COOC ₂ H ₅	+	H ₂ O
initial	0.32		6.30		0		0
change	-x		-x		+x		+x
final	0.32 - x		6.30 - x		+x		+x

$$K_C = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{(x)(x)}{(0.32 - x)(6.30 - x)} = \frac{x^2}{x^2 - 6.62x + 2.02}$$

$$4.0 = \frac{x^2}{x^2 - 6.62x + 2.02}$$

$$4.0x^2 - 26.48x + 8.08 = x^2$$

$$3.0x^2 - 26.48x + 8.08 = 0$$

$$x = \frac{-(-26.48) \pm \sqrt{(-26.48)^2 - (4)(3.0)(8.08)}}{(2)(3.0)} = \frac{+26.48 \pm 24.58}{6.0}$$

$$x = 8.51 \text{ or } 0.317$$

The root 8.51 is meaningless because it is larger than the concentration of acetic acid and ethanol, so the value 0.317 is chosen. The equilibrium concentration of the product ester is, therefore, 0.317 mol · L⁻¹. The numbers can be confirmed by placing them into the equilibrium expression:

$$K_C = \frac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]} = \frac{(0.317)(0.317)}{(0.320 - 0.317)(6.300 - 0.317)} = 5.6$$

Note: This number does not appear to agree well with the given value of $K_C = 4.0$.

If 0.316 is used, the agreement is better, giving a quotient of 4.1. If 0.315 is used, the quotient is 3.3. The better answer is thus 0.316 mol · L⁻¹. The discrepancy is caused by rounding errors in places that are really beyond the accuracy of the measurement. Given that K_C is only given to two significant figures, the best report of the concentration of ester would be

$0.32 \text{ mol} \cdot \text{L}^{-1}$, even though this value will not satisfy the equilibrium expression as well as $0.316 \text{ mol} \cdot \text{L}^{-1}$.

$$9.57 \quad K_c = \frac{[\text{BrCl}]^2}{[\text{Cl}_2][\text{Br}_2]}$$

$$0.031 = \frac{(0.145)^2}{(0.495)[\text{Br}_2]}$$

$$[\text{Br}_2] = \frac{(0.145)^2}{(0.495)(0.031)} = 1.4 \text{ mol} \cdot \text{L}^{-1}$$

9.59 We can calculate changes according to the reaction stoichiometry:

Amount (mol)	CO(g)	+	$3 \text{ H}_2\text{(g)}$	\rightarrow	$\text{CH}_4\text{(g)}$	+	$\text{H}_2\text{O(g)}$
initial	2.00		3.00		0		0
change	$-x$		$-3x$		$+x$		$+x$
final	$2.00 - x$		$3.00 - 3x$		0.478		$+x$

According to the stoichiometry, $0.478 \text{ mol} = x$; therefore, at equilibrium, there are $2.00 \text{ mol} - 0.478 \text{ mol} = 1.52 \text{ mol CO}$, $3.00 - 3(0.478 \text{ mol}) = 1.57 \text{ mol H}_2$, and $0.478 \text{ mol H}_2\text{O}$. To employ the equilibrium expression, we need either concentrations or pressures; because K_c is given, we will choose to express these as concentrations. This calculation is easy because $V = 10.0 \text{ L}$:

$$[\text{CO}] = 0.152 \text{ mol} \cdot \text{L}^{-1}; [\text{H}_2] = 0.157 \text{ mol} \cdot \text{L}^{-1}; [\text{CH}_4] = 0.0478 \text{ mol} \cdot \text{L}^{-1};$$

$$[\text{H}_2\text{O}] = 0.0478 \text{ mol} \cdot \text{L}^{-1}$$

$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3} = \frac{(0.0478)(0.0478)}{(0.152)(0.157)^3} = 3.88$$

9.61 First, we calculate the initial concentrations of each species:

$$[\text{SO}_2] = [\text{NO}] = \frac{0.100 \text{ mol}}{5.00 \text{ L}} = 0.0200 \text{ mol} \cdot \text{L}^{-1};$$

$$[\text{NO}_2] = \frac{0.200 \text{ mol}}{5.00 \text{ L}} = 0.0400 \text{ mol} \cdot \text{L}^{-1}; [\text{SO}_3] = \frac{0.150 \text{ mol}}{5.00 \text{ L}} = 0.0300 \text{ mol} \cdot \text{L}^{-1}$$

We can use these values to calculate Q in order to see which direction the reactions will go:

$$Q = \frac{(0.0200)(0.0300)}{(0.0200)(0.0400)} = 0.75. \text{ Because } Q < K_c, \text{ the reaction will proceed}$$

to produce more products.

Concentration ($\text{mol} \cdot \text{L}^{-1}$)

	$\text{SO}_2(\text{g})$	+	$\text{NO}_2(\text{g})$	\rightarrow	$\text{NO}(\text{g})$	+	$\text{SO}_3(\text{g})$
initial	0.0200		0.0400		0.0200		0.0300
change	$-x$		$-x$		$+x$		$+x$
final	$0.0200 - x$		$0.0400 - x$		$0.0200 + x$		$0.0300 + x$

$$K_c = \frac{[\text{NO}][\text{SO}_3]}{[\text{SO}_2][\text{NO}_2]}$$

$$85.0 = \frac{(0.0200 + x)(0.0300 + x)}{(0.0200 - x)(0.0400 - x)}$$

$$= \frac{x^2 + 0.0500x + 0.000600}{x^2 - 0.0600x + 0.000800}$$

$$85.0(x^2 - 0.0600x + 0.000800) = x^2 + 0.0500x + 0.000600$$

$$85.0x^2 - 5.10x + 0.0680 = x^2 + 0.0500x + 0.000600$$

$$84.0x^2 - 5.15x + 0.0674 = 0$$

$$x = \frac{-(-5.15) \pm \sqrt{(-5.15)^2 - (4)(84.0)(0.0674)}}{(2)(84.0)} = \frac{+5.15 \pm 1.97}{168}$$

$$x = +0.0424 \text{ or } +0.0189$$

The root 0.0424 is not meaningful because it is larger than the concentration of NO_2 . The root of choice is therefore 0.0189.

At equilibrium:

$$[\text{SO}_2] = 0.0200 \text{ mol} \cdot \text{L}^{-1} - 0.0189 \text{ mol} \cdot \text{L}^{-1} = 0.0011 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{NO}_2] = 0.0400 \text{ mol} \cdot \text{L}^{-1} - 0.0189 \text{ mol} \cdot \text{L}^{-1} = 0.0211 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{NO}] = 0.0200 \text{ mol} \cdot \text{L}^{-1} + 0.0189 \text{ mol} \cdot \text{L}^{-1} = 0.0389 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{SO}_3] = 0.0300 \text{ mol} \cdot \text{L}^{-1} + 0.0189 \text{ mol} \cdot \text{L}^{-1} = 0.0489 \text{ mol} \cdot \text{L}^{-1}$$

To check, we can put these numbers back into the equilibrium constant expression:

$$K_C = \frac{[\text{NO}][\text{SO}_3]}{[\text{SO}_2][\text{NO}_2]}$$

$$\frac{(0.0389)(0.0489)}{(0.0011)(0.0211)} = 82.0$$

Compared to $K_C = 85.0$, this is reasonably good agreement given the nature of the calculation. We can check to see, by trial and error, if a better answer could be obtained. Because the K_C value is low for the concentrations we calculated, we can choose to alter x slightly so that this ratio becomes larger. If we let $x = 0.0190$, the concentrations of NO and SO_3 are increased to 0.0390 and 0.0490, and the concentrations of SO_2 and NO_2 are decreased to 0.0010 and 0.0200 (the stoichiometry of the reaction is maintained by calculating the concentrations in this fashion). Then the quotient becomes 91.0, which is further from the value for K_C than the original answer. So, although the agreement is not the best with the numbers we obtained, it is the best possible, given the limitation on the number of significant figures we are allowed to use in the calculation.

9.63 (a) The initial concentrations are:

$$[\text{PCl}_5] = \frac{1.50 \text{ mol}}{0.500 \text{ L}} = 3.00 \text{ mol} \cdot \text{L}^{-1}; [\text{PCl}_3] = \frac{3.00 \text{ mol}}{0.500 \text{ L}} = 6.00 \text{ mol} \cdot \text{L}^{-1};$$

$$[\text{Cl}_2] = \frac{0.500 \text{ mol}}{0.500 \text{ L}} = 1.00 \text{ mol} \cdot \text{L}^{-1}$$

First calculate Q :

$$Q = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]} = \frac{3.00}{(6.00)(1.00)} = 0.500$$

Because $Q \neq K$, the reaction is not at equilibrium.

(b) Because $Q < K_C$, the reaction will proceed to form products.

(c)

Concentrations ($\text{mol} \cdot \text{L}^{-1}$)	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$	\rightarrow	$\text{PCl}_5(\text{g})$
initial	6.00		1.00		3.00

change	$-x$	$-x$	$+x$
final	$6.00 - x$	$1.00 - x$	$3.00 + x$

$$K_C = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

$$0.56 = \frac{3.00 + x}{(6.00 - x)(1.00 - x)} = \frac{3.00 + x}{x^2 - 7x + 6.00}$$

$$(0.56)(x^2 - 7x + 6.00) = 3.00 + x$$

$$0.56x^2 - 3.92x + 3.36 = 3.00 + x$$

$$0.56x^2 - 4.92x + 0.36 = 0$$

$$x = \frac{-(-4.92) \pm \sqrt{(-4.92)^2 - (4)(0.56)(0.36)}}{(2)(0.56)} = \frac{+4.92 \pm 4.48}{1.12}$$

$$x = 9.2 \text{ or } 0.07$$

Because the root 9.2 is larger than the amount of PCl_3 or Cl_2 available, it is physically meaningless and can be discarded. Thus, $x = 0.071 \text{ mol} \cdot \text{L}^{-1}$, giving

$$[\text{PCl}_5] = 3.00 \text{ mol} \cdot \text{L}^{-1} + 0.07 \text{ mol} \cdot \text{L}^{-1} = 3.07 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{PCl}_3] = 6.00 \text{ mol} \cdot \text{L}^{-1} - 0.07 \text{ mol} \cdot \text{L}^{-1} = 5.93 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{Cl}_2] = 1.00 \text{ mol} \cdot \text{L}^{-1} - 0.07 \text{ mol} \cdot \text{L}^{-1} = 0.93 \text{ mol} \cdot \text{L}^{-1}$$

The number can be checked by substituting them back into the equilibrium constant expression:

$$K_C = \frac{[\text{PCl}_5]}{[\text{PCl}_3][\text{Cl}_2]}$$

$$\frac{(3.07)}{(5.93)(0.93)} \stackrel{?}{=} 0.56$$

$$0.56 \doteq 0.56$$

9.65	Pressures (bar)	2 HCl(g)	\rightarrow	$\text{H}_2\text{(g)}$	+	$\text{Cl}_2\text{(g)}$
	initial	0.22		0		0
	change	$-2x$		$+x$		$+x$
	final	$0.22 - 2x$		$+x$		$+x$

$$K = \frac{P_{\text{H}_2} P_{\text{Cl}_2}}{P_{\text{HCl}}^2}$$

$$3.2 \times 10^{-34} = \frac{(x)(x)}{(0.22 - 2x)^2}$$

Because the equilibrium constant is small, assume that $x \ll 0.22$

$$3.2 \times 10^{-34} = \frac{x^2}{(0.22)^2}$$

$$x^2 = (3.2 \times 10^{-34})(0.22)^2$$

$$x = \sqrt{(3.2 \times 10^{-34})(0.22)^2}$$

$$x = \pm 3.9 \times 10^{-18}$$

The negative root is not physically meaningful and can be discarded. x is small compared to 0.22, so the initial assumption was valid. The pressures at equilibrium are

$$P_{\text{HCl}} = 0.22 \text{ bar}; P_{\text{H}_2} = P_{\text{Cl}_2} = 3.9 \times 10^{-18} \text{ bar}$$

The values can be checked by substituting them into the equilibrium expression:

$$\frac{(3.9 \times 10^{-18})(3.9 \times 10^{-18})}{(0.22)^2} \approx 3.2 \times 10^{-34}$$

$$3.1 \times 10^{-34} \approx 3.2 \times 10^{-34}$$

$$P_{\text{HCl}} = 0.22 \text{ bar}; P_{\text{H}_2} = P_{\text{Cl}_2} = 3.9 \times 10^{-18} \text{ bar}$$

The numbers agree very well for a calculation of this type.

9.67 (a) To determine on which side of the equilibrium position the conditions lie, we will calculate Q :

$$[\text{CO}] = \frac{0.342 \text{ mol}}{3.00 \text{ L}} = 0.114 \text{ mol} \cdot \text{L}^{-1}; [\text{H}_2] = \frac{0.215 \text{ mol}}{3.00 \text{ L}} = 0.0717 \text{ mol} \cdot \text{L}^{-1};$$

$$[\text{CH}_3\text{OH}] = \frac{0.125 \text{ mol}}{3.00 \text{ L}} = 0.0417 \text{ mol} \cdot \text{L}^{-1}$$

$$Q = \frac{[\text{CH}_3\text{OH}]}{[\text{CO}][\text{H}_2]^2} = \frac{0.0417}{(0.114)(0.0717)^2} = 71.1 \times 10^3$$

Because $Q > K_C$, the reaction will proceed to produce more of the reactants, which means that the concentration of methanol will decrease.

(b)

Concentrations (mol · L ⁻¹)	CO(g)	+ 2 H ₂ (g)	→	CH ₃ OH(g)
initial	0.114	0.0717		0.0417
change	+x	+2x		-x
final	0.0114 + x	0.0717 + 2x		0.0417 - x

$$K_C = \frac{0.0417 - x}{(0.0114 + x)(0.0717 + 2x)^2} = 1.1 \times 10^{-2}$$

$$\begin{aligned} 0.0417 - x &= (1.1 \times 10^{-2})(0.114 + x)(0.0717 + 2x)^2 \\ &= (1.2 \times 10^{-3} + 1.1 \times 10^{-2}x)(4x^2 + 0.287x + 5.14 \times 10^{-3}) \\ &= 4.4 \times 10^{-2}x^3 + 8.0 \times 10^{-3}x^2 + 4.0 \times 10^{-4}x + 6.2 \times 10^{-6} \\ 0 &= 4.4 \times 10^{-2}x^3 + 8.0 \times 10^{-3}x^2 + 1.00x - 0.0417 \end{aligned}$$

This equation can be solved approximately, simply by inspection: it is clear that the x term will be very much larger than the x^3 and the x^2 terms, because their coefficients are very small compared to 1.00. This leads to a prediction that $x = 0.0417 \text{ mol} \cdot \text{L}^{-1}$ to within the accuracy of the data.

Essentially all of the CH₃OH will react, so that

$$[\text{CO}] = 0.114 \text{ mol} \cdot \text{L}^{-1} + 0.0417 \text{ mol} \cdot \text{L}^{-1} = 0.156 \text{ mol} \cdot \text{L}^{-1};$$

$$[\text{H}_2] = 0.0717 \text{ mol} \cdot \text{L}^{-1} + 2(0.0417 \text{ mol} \cdot \text{L}^{-1}) = 0.155 \text{ mol} \cdot \text{L}^{-1}.$$

The mathematical situation is odd in that clearly a $[\text{CH}_3\text{OH}] = 0$ will not satisfy the equilibrium constant. Knowing that the methanol concentration is very small compared to the CO and H₂ concentrations, we can now back-calculate to get a concentration value that will satisfy the equilibrium expression:

$$K_C = \frac{y}{(0.156)(0.155)^2} = 1.1 \times 10^{-2}$$

$$y = (1.1 \times 10^{-2})(0.156)(0.155)^2 = 2.6 \times 10^{-4}$$

Alternatively, the cubic equation can be solved with the aid of a graphing calculator like the one supplied on the CD accompanying this book.

- 9.69** Since reactants are strongly favored it is easier to push the reaction as far to the left as possible then start from new initial conditions.

Pressures (bar)	2 HCl(g)	→	H ₂ (g)	+	Cl ₂ (g)
original	2.0		1.0		3.0
new initial	4.0		0		2.0
change	-2 <i>x</i>		+ <i>x</i>		+ <i>x</i>
final	4.0 - 2 <i>x</i>		+ <i>x</i>		2.0 + <i>x</i>

$$K = \frac{P_{\text{H}_2} P_{\text{Cl}_2}}{P_{\text{HCl}}^2}$$

$$3.2 \times 10^{-34} = \frac{(x)(2.0 + x)}{(4.0 - 2x)^2} \approx \frac{(x)(2.0)}{(4.0)^2} = \frac{x}{16}$$

$$x = 2.6 \times 10^{-33} \text{ bar}$$

$$V = \frac{nRT}{p} = \frac{(1 \text{ mole})(8.314 \times 10^{-2} \text{ L bar K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{2.6 \times 10^{-33} \text{ bar}}$$

$$= 9.7 \times 10^{33} \text{ L}$$

- 9.71** (a) According to Le Chatelier's principle, an increase in the partial pressure of CO₂ will result in creation of reactants, which will decrease the H₂ partial pressure.
- (b) According to Le Chatelier's principle, if the CO pressure is reduced, the reaction will shift to form more CO, which will decrease the pressure of CO₂.
- (c) According to Le Chatelier's principle, if the concentration of CO is increased, the reaction will proceed to form more products, which will result in a higher pressure of H₂.
- (d) The equilibrium constant for the reaction is unchanged, because it is unaffected by any change in concentration.

- 9.73** (a) According to Le Chatelier's principle, increasing the concentration of NO will cause the reaction to form reactants in order to reduce the concentration of NO; the amount of water will decrease.
- (b) For the same reason as in (a), the amount of O_2 will increase.
- (c) According to Le Chatelier's principle, removing water will cause the reaction to shift toward products, resulting in the formation of more NO.
- (d) According to Le Chatelier's principle, removing a reactant will cause the reaction to shift in the direction to replace the removed substance; the amount of NH_3 should increase.
- (e) According to Le Chatelier's principle, adding ammonia will shift the reaction to the right, but the equilibrium constant, which is a constant, will not be affected.
- (f) According to Le Chatelier's principle, removing NO will cause the formation of more products; the amount of NH_3 will decrease.
- (g) According to Le Chatelier's principle, adding reactants will promote the formation of products; the amount of oxygen will decrease.
- 9.75** As per Le Chatelier's principle, whether increasing the pressure on a reaction will affect the distribution of species within an equilibrium mixture of gases depends largely upon the difference in the number of moles of gases between the reactant and product sides of the equation. If there is a net increase in the amount of gas, then applying pressure will shift the reaction toward reactants in order to remove the stress applied by increasing the pressure. Similarly, if there is a net decrease in the amount of gas, applying pressure will cause the formation of products. If the number of moles of gas is the same on the product and reactant side, then changing the pressure will have little or no effect on the equilibrium distribution of species present. Using this information, we can apply it to the specific reactions given. The answers are: (a) reactants; (b) reactants; (c) reactants; (d) no change (there is the same number of moles of gas on both sides of the equation); (e) reactants

- 9.77** (a) If the pressure of NO (a product) is increased, the reaction will shift to form more reactants; the pressure of NH_3 should increase.
- (b) If the pressure of NH_3 (a reactant) is decreased, then the reaction will shift to form more reactants; the pressure of O_2 should increase.
- 9.79** 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 examples given, (a) and (b) are endothermic (the values for (b) can be calculated, but we know that it requires energy to break an X—X bond, so those processes will all be endothermic) and raising the temperature should favor the formation of products; (c) and (d) are exothermic and raising the temperature should favor the formation of reactants.
- 9.81** Even though numbers are given, we do not need to do a calculation to answer this qualitative question. Because the equilibrium constant for the formation of ammonia is smaller at the higher temperature, raising the temperature will favor the formation of reactants. Less ammonia will be present at higher temperature, assuming no other changes occur to the system (i.e., the volume does not change, no reactants or products are added or removed from the container, etc.).
- 9.83** To answer this question we must calculate Q :
- $$Q = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(0.500)^2}{(3.00)(2.00)^3} = 0.0104$$
- Because $Q \neq K$, the system is not at equilibrium and because $Q < K$, the reaction will proceed to produce more products.
- 9.85** Because we want the equilibrium constant at two temperatures, we will need to calculate ΔH°_r and ΔS°_r for each reaction:



$$\Delta H^\circ_{\text{r}} = \Delta H^\circ_{\text{f}}(\text{NH}_3, \text{g}) + \Delta H^\circ_{\text{f}}(\text{HCl}, \text{g}) - \Delta H^\circ_{\text{f}}(\text{NH}_4\text{Cl}, \text{s})$$

$$\Delta H^\circ_{\text{r}} = (-46.11 \text{ kJ} \cdot \text{mol}^{-1}) + (-92.31 \text{ kJ} \cdot \text{mol}^{-1}) - (-314.43 \text{ kJ} \cdot \text{mol}^{-1})$$

$$\Delta H^\circ_{\text{r}} = 176.01 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta S^\circ_{\text{r}} = S^\circ(\text{NH}_3, \text{g}) + S^\circ(\text{HCl}, \text{g}) - S^\circ(\text{NH}_4\text{Cl}, \text{s})$$

$$\Delta S^\circ_{\text{r}} = 192.45 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 186.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} - 94.6 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta S^\circ_{\text{r}} = 284.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$$

$$\Delta G^\circ_{\text{r}} = \Delta H^\circ_{\text{r}} - T\Delta S^\circ_{\text{r}}$$

At 298 K:

$$\begin{aligned}\Delta G^\circ_{\text{r}(298 \text{ K})} &= 176.01 \text{ kJ} - (298 \text{ K})(284.8 \text{ J} \cdot \text{K}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= 91.14 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

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

$$\begin{aligned}\ln K &= -\frac{\Delta G^\circ_{\text{r}(298 \text{ K})}}{RT} \\ &= -\frac{91140 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(298 \text{ K})} = -36.8\end{aligned}$$

$$K = 1 \times 10^{-16}$$

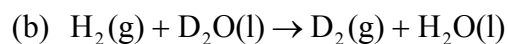
At 423 K:

$$\begin{aligned}\Delta G^\circ_{\text{r}(423 \text{ K})} &= 176.01 \text{ kJ} - (423 \text{ K})(284.8 \text{ J} \cdot \text{K}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= 55.54 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\Delta G^\circ_{\text{r}(423 \text{ K})} = -RT \ln K$$

$$\begin{aligned}\ln K &= -\frac{\Delta G^\circ_{\text{r}(423 \text{ K})}}{RT} \\ &= -\frac{55540 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(423 \text{ K})} = -15.8\end{aligned}$$

$$K = 1 \times 10^{-7}$$



$$\begin{aligned}
\Delta H^\circ_r &= \Delta H^\circ_f(\text{H}_2\text{O}, \text{l}) - [\Delta H^\circ_f(\text{D}_2\text{O}, \text{l})] \\
\Delta H^\circ_r &= (-285.83 \text{ kJ} \cdot \text{mol}^{-1}) - [-294.60 \text{ kJ} \cdot \text{mol}^{-1}] \\
\Delta H^\circ_r &= 8.77 \text{ kJ} \cdot \text{mol}^{-1} \\
\Delta S^\circ_r &= S^\circ(\text{D}_2, \text{g}) + S^\circ(\text{H}_2\text{O}, \text{l}) - [S^\circ(\text{H}_2, \text{g}) + S^\circ(\text{D}_2\text{O}, \text{l})] \\
\Delta S^\circ_r &= 144.96 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 69.91 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\
&\quad - [130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 75.94 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\
\Delta S^\circ_r &= 8.25 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}
\end{aligned}$$

At 298 K:

$$\begin{aligned}
\Delta G^\circ_{r(298 \text{ K})} &= 8.77 \text{ kJ} \cdot \text{mol}^{-1} - (298 \text{ K})(8.25 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= 6.31 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

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

$$\begin{aligned}
\ln K &= -\frac{\Delta G^\circ_{r(298 \text{ K})}}{RT} \\
&= -\frac{6310 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(298 \text{ K})} = -2.55
\end{aligned}$$

$$K = 7.8 \times 10^{-2}$$

At 423 K:

$$\begin{aligned}
\Delta G^\circ_{r(423 \text{ K})} &= 8.77 \text{ kJ} \cdot \text{mol}^{-1} - (423 \text{ K})(8.25 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\
&= 5.28 \text{ kJ} \cdot \text{mol}^{-1}
\end{aligned}$$

$$\ln K = -\frac{5280 \text{ J}}{(8.314 \text{ J} \cdot \text{K}^{-1})(423 \text{ K})} = -1.50$$

$$K = 0.22$$

$$\mathbf{9.87} \quad K = (RT)^{\Delta n} K_c$$

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

$$\ln \left(\frac{(RT_2)^{\Delta n} K_{c2}}{(RT_1)^{\Delta n} K_{c1}} \right) = -\frac{\Delta H_r^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Delta n \ln \left(\frac{T_2}{T_1} \right) + \ln \left(\frac{K_{c2}}{K_{c1}} \right) = - \frac{\Delta H_r^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\ln \left(\frac{K_{c2}}{K_{c1}} \right) = - \frac{\Delta H_r^\circ}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) - \Delta n \ln \left(\frac{T_2}{T_1} \right)$$

9.89 $\Delta G^\circ = -RT \ln K = \Delta H^\circ - T\Delta S^\circ$

$$\Delta G_{298}^\circ = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(298.15 \text{ K}) \ln(9.9197 \times 10^{-15})$$

$$= 7.9933 \times 10^4 \text{ J mol}^{-1}$$

$$\Delta G_{303}^\circ = -(8.3145 \text{ J K}^{-1} \text{ mol}^{-1})(303.15 \text{ K}) \ln(1.4689 \times 10^{-14})$$

$$= 8.0283 \times 10^4 \text{ J mol}^{-1}$$

$$\Delta G_{298}^\circ - \Delta G_{303}^\circ = \Delta H^\circ - (298.15 \text{ K})\Delta S^\circ - [\Delta H^\circ - (303.15 \text{ K})\Delta S^\circ]$$

$$-3.5097 \times 10^2 \text{ J mol}^{-1} = (5.00 \text{ K})\Delta S^\circ$$

$$\Delta S^\circ = -70.194 \text{ J K}^{-1} \text{ mol}^{-1}$$

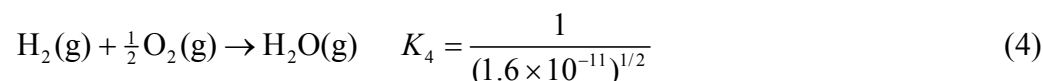
The sign is negative indicating that the product ions create more order in the system probably because of their interaction with solvating water molecules.

- 9.91** (a) According to Le Chatelier's principle, adding a product should cause a shift in the equilibrium toward the reactants side of the equation.
- (b) Because there are equal numbers of moles of gas on both sides of the equation, there will be little or no effect upon compressing the system.
- (c) If the amount of CO_2 is increased, this will cause the reaction to shift toward the formation of products.
- (d) Because the reaction is endothermic, raising the temperature will favor the formation of products.
- (e) If the amount of $\text{C}_6\text{H}_{12}\text{O}_6$ is removed, this will cause the reaction to shift toward the formation of products.
- (f) Because water is a liquid, it is by definition present at unit concentration, so changing the amount of water will not affect the reaction. As long as the glucose solution is dilute, its concentration can be considered unchanged.

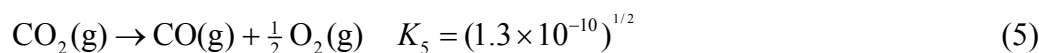
(g) Decreasing the concentration of a reactant will favor the production of more reactants.

- 9.93** (a) In order to solve this problem, we will manipulate the equations with the known K 's so that we can combine them to give the desired overall reaction:

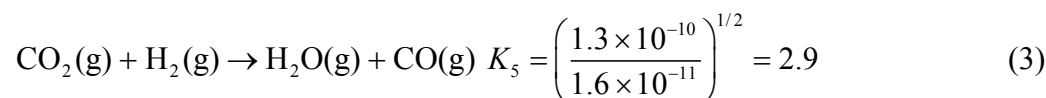
First, reverse equation (1) and multiply it by $\frac{1}{2}$:



Multiply equation (2) by $\frac{1}{2}$ also:



Adding equations (4) and (5) gives the desired reaction. The resultant equilibrium constant will be the product of the K 's for (4) and (5):



- (b) To obtain the K value for a net equation from two (or more) others, the K 's are multiplied, but ΔG°_r 's are added:



$$\begin{aligned} \Delta G^\circ_r &= -RT \ln K \\ &= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1565 \text{ K}) \ln 1.6 \times 10^{-11} \\ &= +3.2 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$



$$\begin{aligned} \Delta G^\circ_r &= -RT \ln K \\ &= -(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1565 \text{ K}) \ln 1.3 \times 10^{-10} \\ &= +3.0 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$

The corresponding values for (4) and (5) are

$$\Delta G^\circ_{r(4)} = -\frac{1}{2}(3.2 \times 10^2 \text{ kJ}) = -1.6 \times 10^2 \text{ kJ}$$

$$\Delta G^\circ_{r(5)} = \frac{1}{2}(3.0 \times 10^2 \text{ kJ}) = 1.5 \times 10^2 \text{ kJ}$$

Summing these two values will give

$$\Delta G^\circ_{r(3)} = -1.6 \times 10^2 \text{ kJ} + 1.5 \times 10^2 \text{ kJ} = -10 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\ln K = -\frac{\Delta G^\circ_r}{RT} = -\frac{-10\,000 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(1565 \text{ K})} = +0.8$$

$$K = 2$$

This value is in reasonable agreement with the one obtained in (a), given the problems in significant figures and due to rounding errors.

9.95	Pressure	$\text{PCl}_5(\text{g})$	\rightarrow	$\text{PCl}_3(\text{g})$	+	$\text{Cl}_2(\text{g})$
	initial	n				
	change	$-n\alpha$		$+n\alpha$		$+n\alpha$
	final	$n(1-\alpha)$		$+n\alpha$		$+n\alpha$

$$K = \frac{(n\alpha)(n\alpha)}{n(1-\alpha)} = \frac{n^2\alpha^2}{n(1-\alpha)} = \frac{n\alpha^2}{(1-\alpha)}$$

$$P = n(1-\alpha) + n\alpha + n\alpha = n(1+\alpha)$$

$$n = \frac{P}{1+\alpha}$$

$$K = \frac{n\alpha^2}{(1-\alpha)} = \left(\frac{P}{1+\alpha}\right)\left(\frac{\alpha^2}{1-\alpha}\right) = \frac{P\alpha^2}{1-\alpha^2}$$

$$(1-\alpha^2)K = P\alpha^2$$

$$K - K\alpha^2 = P\alpha^2$$

$$K = P\alpha^2 + K\alpha^2$$

$$\alpha^2 = \frac{K}{P+K}$$

$$\alpha = \sqrt{\frac{K}{P+K}}$$

(a) For the specific conditions $K = 4.96$ and $P = 0.50$ bar,

$$\alpha = \sqrt{\frac{4.96}{0.50 + 4.96}} = 0.953$$

(b) For the specific conditions $K = 4.96$ and $P = 1.00$ bar,

$$\alpha = \sqrt{\frac{4.96}{1.00 + 4.96}} = 0.912$$

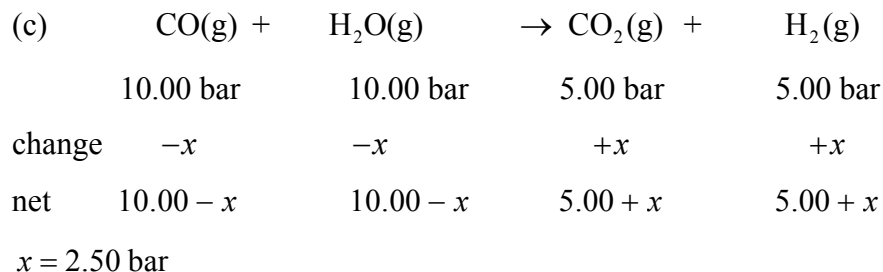
9.97 (a) If $K = 1.00$, then ΔG° must be equal to 0 ($\Delta G^\circ = -RT \ln K$).

(b) This can be calculated by determining the values for ΔH° and ΔS° at 25°C.

$$\begin{aligned}\Delta H^\circ &= -393.51 \text{ kJ} \cdot \text{mol}^{-1} - [(-110.53 \text{ kJ} \cdot \text{mol}^{-1}) + (-241.82 \text{ kJ} \cdot \text{mol}^{-1})] \\ &= -41.16 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 130.68 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 213.74 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \\ &\quad - [197.67 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} + 188.83 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}] \\ &= -42.08 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G &= (-41.16 \text{ kJ} \cdot \text{mol}^{-1})(1000 \text{ J} \cdot \text{kJ}^{-1}) - T(-42.08 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}) = 0 \\ T &= 978 \text{ K (or } 705^\circ\text{C)}\end{aligned}$$

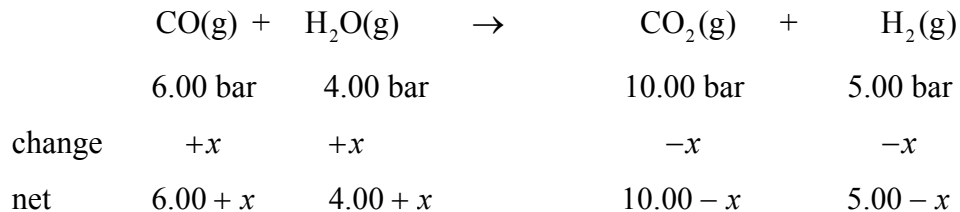


All pressures are equal to 7.50 bar.

(d) First, check Q to determine the direction of the reaction:

$$Q = \frac{(10.00)(5.00)}{(6.00)(4.00)} = 2.08$$

Because Q is greater than 1, the reaction will shift to produce reactants.



$$\frac{(10.00 - x)(5.00 - x)}{(6.00 + x)(4.00 + x)} = 1$$

$$(10.00 - x)(5.00 - x) = (6.00 + x)(4.00 + x)$$

$$x^2 - 15.00x + 50.0 = x^2 + 10.00x + 24.0$$

$$25.00x = 26.0$$

$$x = 1.04 \text{ bar}$$

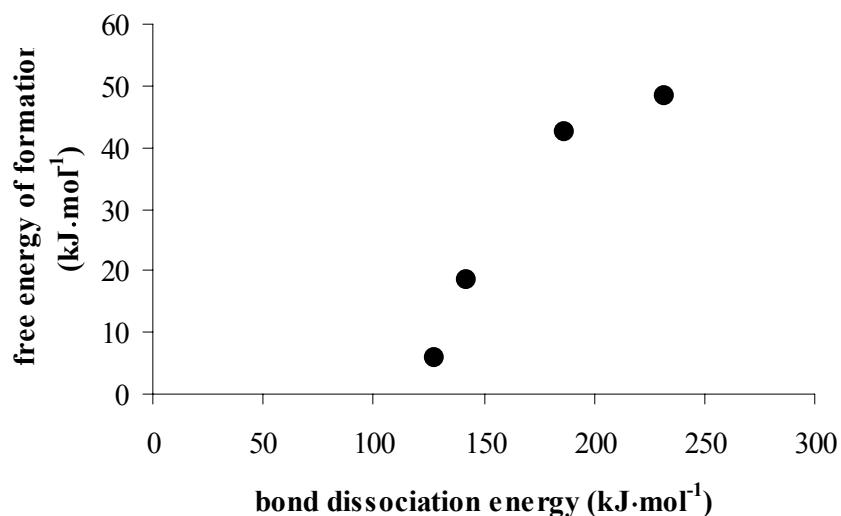
$$P_{\text{CO(g)}} = 7.04 \text{ bar}; P_{\text{H}_2\text{O(g)}} = 5.04 \text{ bar}; P_{\text{CO}_2\text{(g)}} = 8.96 \text{ bar}; P_{\text{H}_2\text{(g)}} = 3.96 \text{ bar}$$

- 9.99** (a) These values are easily calculated from the relationship $\Delta G^\circ = -RT \ln K$. For the atomic species, the free energy of the reaction will be $\frac{1}{2}$ of this value because the equilibrium reactions are for the formation of two moles of halogen atoms.

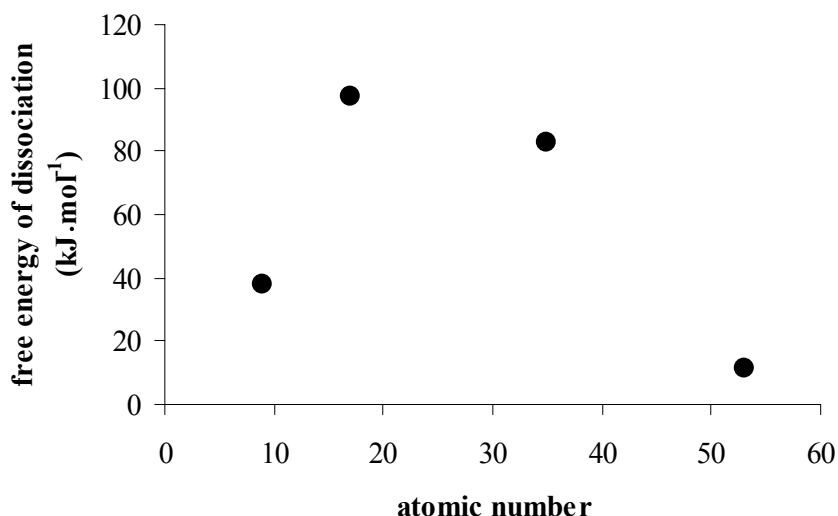
The results are

	Bond Dissociation Energy	ΔG°
Halogen	(kJ · mol ⁻¹)	(kJ · mol ⁻¹)
fluorine	146	19.2
chlorine	230	47.8
bromine	181	42.8
iodine	139	5.6

(b)



There is a correlation between the bond dissociation energy and the free energy of formation of the atomic species, but the relationship is clearly not linear.



For the heavier three halogens, there is a trend to decreasing free energy of formation of the atoms as the element becomes heavier, but fluorine is anomalous. The F—F bond energy is lower than expected, owing to repulsions of the lone pairs of electrons on the adjacent F atoms because the F—F bond distance is so short.

9.101 (a) $K < 1$ but will increase at higher temperature because $\Delta S > 0$.

(b) $K > 1$

(c) $K > 1$

(d) $K > 1$

9.103 (a) Use the relationship $\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$. The value of ΔH° is

first obtained by using the two points given in Table 9.1.

$$\ln \frac{1.7 \times 10^{-3}}{3.4 \times 10^{-5}} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{1200} - \frac{1}{1000} \right)$$

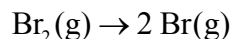
$$\Delta H^\circ = 1.96 \times 10^2 \text{ kJ} \cdot \text{mol}^{-1}$$

We then use this value plus one of the known equilibrium constant points in the equation

$$\ln \frac{K_{298}}{3.4 \times 10^{-5}} = - \left(\frac{196\,000 \text{ J} \cdot \text{mol}^{-1}}{8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}} \right) \left(\frac{1}{298} - \frac{1}{1000} \right)$$

$$K_{298} = 2.6 \times 10^{-29}$$

(b) Using the thermodynamic data in Appendix 2A:

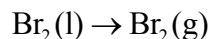


$$\Delta G^\circ = 2(82.40 \text{ kJ} \cdot \text{mol}^{-1}) - 3.11 \text{ kJ} \cdot \text{mol}^{-1} = 161.69 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K = e^{-\Delta G^\circ / RT} = 4.5 \times 10^{-29}$$

For equilibrium constant calculations, this is reasonably good agreement with the value obtained from part (a), especially if one considers that ΔH° will not be perfectly constant over so large a temperature range.

(c) We will use data from Appendix 2A to calculate the vapor pressure of bromine:



$$\Delta G^\circ = 3.11 \text{ kJ} \cdot \text{mol}^{-1}$$

$$K = e^{-\Delta G^\circ / RT} = 0.285$$

The vapor pressure of bromine will, therefore, be 0.285 bar or 0.289 atm.

Remember that because the standard state for the thermodynamic quantities is 1 bar, the values in K will be derived in bar as well.

$$(d) \quad 4.5 \times 10^{-29} = \frac{P_{\text{Br}(\text{g})}^2}{P_{\text{Br}_2(\text{l})}} = \frac{P_{\text{Br}(\text{g})}^2}{0.285 \text{ bar}}$$

$$P_{\text{Br}(\text{g})}^2 = 3.6 \times 10^{-15} \text{ bar or } 3.6 \times 10^{-15} \text{ atm}$$

(e) Use the ideal gas law:

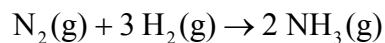
$$PV = nRT$$

$$(0.289 \text{ atm})V = (0.0100 \text{ mol})(0.08206 \text{ L} \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})$$

$$V = 0.846 \text{ L or } 846 \text{ mL}$$

9.105 First, we calculate the equilibrium constant for the conditions given.

$$K = \frac{(23.72)^2}{(3.11)(1.64)^3} = 41.0, \text{ which corresponds to the reaction written as}$$



We then set up the table of anticipated changes upon introduction of the nitrogen:

	$\text{N}_2(\text{g})$	$+ 3 \text{H}_2(\text{g})$	$\rightarrow 2 \text{NH}_3(\text{g})$
initial	4.68 bar	1.64 bar	23.72 bar
change	$-x$	$-3x$	$+2x$
total	$4.68 - x$	$1.64 - 3x$	$23.72 + 2x$

$$41.0 = \frac{(23.72 + 2x)^2}{(4.68 - x)(1.64 - 3x)^3}$$

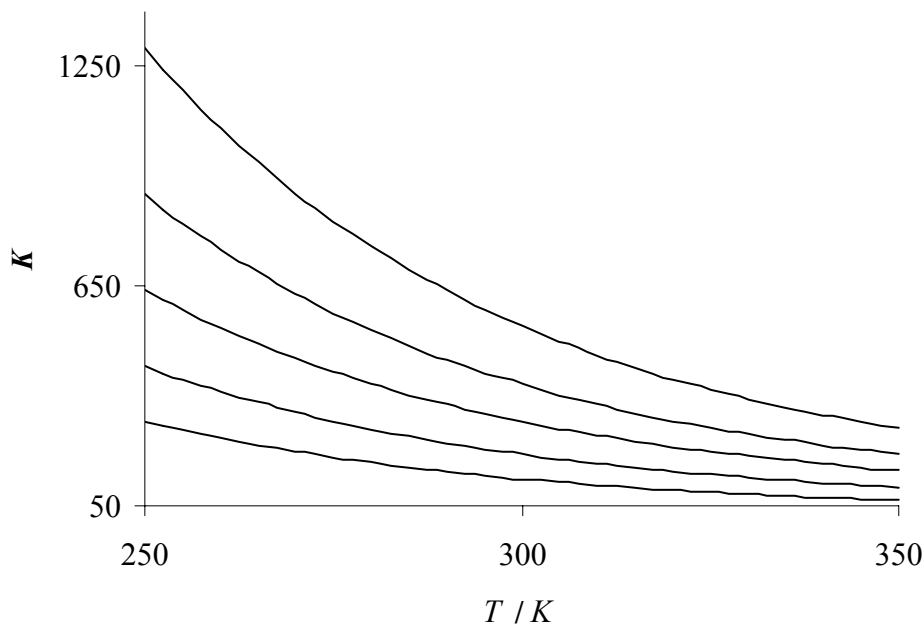
The equation can be solved using a graphing calculator, other computer software, or by trial and error. The solution is $x = 0.176$. The pressures of gases are

$$P_{\text{N}_2} = 4.33 \text{ bar or } 4.39 \text{ atm}$$

$$P_{\text{H}_2} = 1.11 \text{ bar or } 1.12 \text{ atm}$$

$$P_{\text{NH}_3} = 24.07 \text{ bar or } 24.39 \text{ atm}$$

9.107



9.109 (a) $K_C = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2.13)^2}{0.405} = 11.2$

(b) If NO_2 is added, the equilibrium will shift to produce more N_2O_4 .

The amount of NO_2 will be greater than initially present, but less than the $3.13 \text{ mol} \cdot \text{L}^{-1}$ present immediately upon making the addition. K_C will not be affected.

(c)

Concentrations ($\text{mol} \cdot \text{L}^{-1}$)	N_2O_4	\rightarrow	2NO_2
initial	0.405		3.13
change	$+x$		$-2x$
final	$0.405 + x$		$3.13 - 2x$

$$11.2 = \frac{(3.13 - 2x)^2}{0.405 + x}$$

$$(11.2)(0.405 + x) = (3.13 - 2x)^2$$

$$11.2x + 4.536 = 4x^2 - 12.52x + 9.797$$

$$4x^2 - 23.7x + 5.26 = 0$$

$$x = \frac{-(-23.7) \pm \sqrt{(-23.7)^2 - (4)(4)(5.26)}}{(2)(4)} = \frac{23.7 \pm 21.9}{8}$$

$$x = 5.70 \text{ or } 0.23$$

$$\text{At equilibrium } [\text{N}_2\text{O}_4] = 0.405 \text{ mol} \cdot \text{L}^{-1} + 0.23 \text{ mol} \cdot \text{L}^{-1} = 0.64 \text{ mol} \cdot \text{L}^{-1}$$

$$[\text{NO}_2] = 3.13 \text{ mol} \cdot \text{L}^{-1} - 2(0.23 \text{ mol} \cdot \text{L}^{-1}) = 2.67 \text{ mol} \cdot \text{L}^{-1}$$

These concentrations are consistent with the predictions in (b).

9.111 To find the vapor pressure, we first calculate ΔG° for the conversion of the liquid to the gas at 298 K, using the free energies of formation found in the appendix:

$$\begin{aligned}\Delta G^\circ_{\text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{O(g)}} &= \Delta G^\circ_{\text{f}(\text{H}_2\text{O(g)})} - \Delta G^\circ_{\text{f}(\text{H}_2\text{O(l)})} \\ &= (-228.57 \text{ kJ} \cdot \text{mol}^{-1}) - [-237.13 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= 8.56 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ_{\text{D}_2\text{O(l)} \rightarrow \text{D}_2\text{O(g)}} &= \Delta G^\circ_{\text{f}(\text{D}_2\text{O(g)})} - \Delta G^\circ_{\text{f}(\text{D}_2\text{O(l)})} \\ &= (-234.54 \text{ kJ} \cdot \text{mol}^{-1}) - [-243.44 \text{ kJ} \cdot \text{mol}^{-1}] \\ &= 8.90 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

The equilibrium constant for these processes is the vapor pressure of the liquid:

$$K = P_{\text{H}_2\text{O}} \text{ or } K = P_{\text{D}_2\text{O}}$$

Using $\Delta G^\circ = -RT \ln K$, we can calculate the desired values.

For H_2O :

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{8560 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = -3.45$$

$$K = 0.032 \text{ bar}$$

$$0.032 \text{ bar} \times \frac{1 \text{ atm}}{1.01325 \text{ bar}} \times \frac{760 \text{ Torr}}{1 \text{ atm}} = 24 \text{ Torr}$$

For D_2O :

$$\ln K = -\frac{\Delta G^\circ}{RT} = -\frac{8900 \text{ J} \cdot \text{mol}^{-1}}{(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})} = -3.59$$

$$K = 0.028 \text{ bar}$$

$$0.028 \text{ bar} \times \frac{1 \text{ atm}}{1.01325 \text{ bar}} \times \frac{760 \text{ Torr}}{1 \text{ atm}} = 21 \text{ Torr}$$

The answer is that D has a lower zero point energy than H. This makes the $\text{D}_2\text{O} \cdots \text{D}_2\text{O}$ “hydrogen bond” stronger than the $\text{H}_2\text{O} \cdots \text{H}_2\text{O}$ hydrogen bond. Because the hydrogen bond is stronger, the intermolecular forces are stronger, the vapor pressure is lower, and the boiling point is higher.

Potential energy curves for the O—H and O—D bonds as a function of distance:

ΔE = energy required to break O—H or O—D bond.

9.113 First, we derive a general relationship that relates ΔG°_f values to nonstandard state conditions. We do this by returning to the fundamental definition of ΔG and ΔG° .

$$\Delta G^\circ_f = \sum G^\circ_{m(\text{products})} - \sum G^\circ_{m(\text{reactants})}$$

Similarly, for conditions other than standard state, we can write

$$\Delta G_f = \sum G_{m(\text{products})} - \sum G_{m(\text{reactants})}$$

Because $G_m = G^\circ_m + RT \ln Q$,

$$\Delta G_f = \sum (G^\circ_m + RT \ln P_i)_{(\text{products})} - \sum (G^\circ_m + RT \ln P_i)_{(\text{reactants})}$$

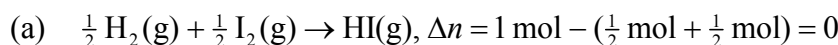
But because all reactants or products in the same system refer to the same standard state,

$$\Delta G_f = \sum G^\circ_{m(\text{products})} - \sum G^\circ_{m(\text{reactants})} + \Delta n(RT \ln Q_{(\text{reactants})})$$

$$\Delta G_f = \Delta G^\circ_f + \Delta n(RT \ln Q_{(\text{reactants})})$$

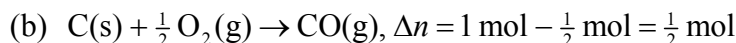
The value ΔG_f , which is the nonstandard value for the conditions of 1 atm,

1 mol · L⁻¹, etc. becomes the new standard value.

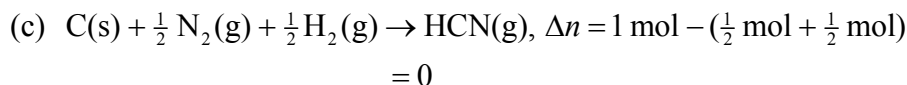


$$1 \text{ atm} = 1.013 \text{ 25 bar}$$

$$\begin{aligned} \Delta G_f &= 1.70 \text{ kJ} \cdot \text{mol} \\ &+ (0)(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})(\ln 1.013 \text{ 25})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= 1.70 \text{ kJ} \cdot \text{mol} \end{aligned}$$

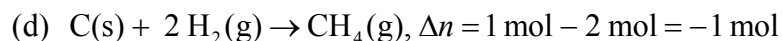


$$\begin{aligned} \Delta G_f &= -137.17 \text{ kJ} \cdot \text{mol} \\ &+ (\frac{1}{2})(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})(\ln 1.013 \text{ 25})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= -137.15 \text{ kJ} \cdot \text{mol}^{-1} \end{aligned}$$



$$1 \text{ Torr} \times \frac{1 \text{ atm}}{760 \text{ Torr}} \times \frac{1.013 \text{ 25 bar}}{1 \text{ atm}} = 1.333 \times 10^{-3} \text{ bar}$$

$$\begin{aligned}\Delta G_f &= 124.7 \text{ kJ} \cdot \text{mol} \\ &+ (0)(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})(\ln 1.333 \times 10^{-3})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= 124.7 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$



$$1 \text{ Pa} = 10^{-5} \text{ bar}$$

$$\begin{aligned}\Delta G_f &= -50.72 \text{ kJ} \cdot \text{mol} \\ &+ (-1)(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1})(298 \text{ K})(\ln 10^{-5})/(1000 \text{ J} \cdot \text{kJ}^{-1}) \\ &= -22.2 \text{ kJ} \cdot \text{mol}^{-1}\end{aligned}$$

- 9.115** (a) (i) Increasing the amount of a reactant will push the equilibrium toward the products. More NO_2 will form. (ii) Removing a product will pull the equilibrium toward products. More NO_2 will form. (iii) Increasing total pressure by adding an inert gas not change the relative partial pressures. There will be no change in the amount of NO_2 . (b) Since there are two moles of gas on both sides of the reaction, the volume cancels out of the equilibrium constant expression and it is possible to use moles directly for each component.

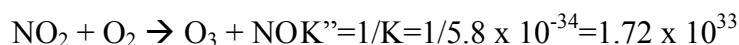
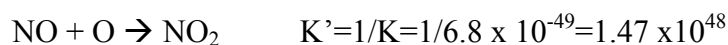
At equilibrium, $\text{SO}_2 = 2.4 \text{ moles} - 1.2 \text{ moles} = 1.2 \text{ moles}$, $\text{SO}_3 = 1.2 \text{ moles}$ and $\text{NO} = 1.2 \text{ moles}$ since the reaction is 1:1:1:1. The original number of moles of NO_2 is set to x .

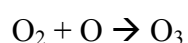
$$K = 3.00 = (1.2)(1.2)/(1.2)(x-1.2) = (1.2)/(x-1.2)$$

$$x = 1.2/3.00 + 1.2$$

$$x = 1.6 \text{ moles of NO}_2$$

- 9.117** (a) Reversing both reactions then adding them together gives the reaction of interest.





$$K = K' * K'' = 2.5 \times 10^{81}$$

(b) Since the initial mixture is equimolar in the two reactants (i.e. each partial pressure is 2.0 bar) and the equilibrium strongly favors products, we can see that essentially all of both reactants will combine to form an equimolar amount of ozone, or a final equilibrium partial pressure of 2.0 bar. Some very small partial pressure, x , of each reactant will be left and must satisfy the equilibrium constant expression:

$$K = 2.5 \times 10^{81} = P_{O_3} / (P_{O_2} \cdot P_{O}) = 2.0 \text{ bar} / (x^2)$$

$$x = 2.8 \times 10^{-41} \text{ bar} = P_{O_2} = P_{O} \text{ and } P_{O_3} = 2.0 \text{ bar at equilibrium}$$