15 Chemical Equilibrium

Visualizing Concepts

15.2 Yes. The first box is pure reactant A. As the reaction proceeds, some A changes to B. In the fourth and fifth boxes, the relative amounts (concentrations) of A and B are constant. Although the reaction is ongoing the rates of A → B and B → A are equal, and the relative amounts of A and B are constant.

15.3 *Analyze.* Given box diagram and reaction type, determine whether $K > 1$ for the equilibrium mixture depicted in the box.

Plan. Assign species in the box to reactants and products. Write an equilibrium expression in terms of concentrations. Find the relationship between numbers of molecules and concentration. Calculate K.

Solve. Let red = A, blue = X, red and blue pairs = AX. (The colors of A and X are arbitrary.) There are 3A, 2B, and 8AX in the box.

M = mol/L. Since moles is a counting unit for particles, mol ratios and particle ratios are equivalent. We can use numbers of particles in place of moles in the molarity formula. V = 1 L, so in this case, [A] = number of A particles.

$$K = \frac{[AX]}{[A][X]}; \quad [AX] = 8/V = 8; [A] = 3/V = 3; [X] = 2/V = 2$$

$$K = \frac{8}{[3][2]} = \frac{8}{6} = 1.33$$

15.5 *Analyze.* Given box diagrams, reaction type, and value of K_c, determine whether each reaction mixture is at equilibrium.

Plan. Analyze the contents of each box, express them as concentrations (see Solution 5.3). Write the equilibrium expression, calculate Q for each mixture, and compare it to K_c. If Q = K, the mixture is at equilibrium. If Q < K, the reaction shifts right (more product). If Q > K, the reaction shifts left (more reactant).

Solve. $K_c = \frac{[AB]^2}{[A_2][B_2]}$.

For this reaction, $\Delta n = 0$, so the volume terms cancel in the equilibrium expression. In this case, the number of each kind of particle can be used as a representation of moles (see Solution 5.3) and molarity.

(a) Mixture 1: $1A_2$, $1B_2$, 6AB; $Q = \frac{6^2}{(1)(1)} = 36$

$Q > K_c$, the mixture is not at equilibrium.

Mixture 2: $3A_2, 2B_2, 3AB$; $Q = \frac{3^2}{(3)(2)} = 1.5$

$Q = K_c$, the mixture is at equilibrium.

Mixture 3: $3A_2, 3B_2, 2AB$; $Q = \frac{2^2}{(3)(3)} = 0.44$

$Q < K_c$, the mixture is not at equilibrium.

(b) Mixture 1 proceeds toward reactants.

Mixture 3 proceeds toward products.

15.6 For the reaction $A_2(g) + B(g) \rightleftharpoons A(g) + AB(g)$, $\Delta n = 0$ and $K_p = K_c$. We can evaluate the equilibrium expression in terms of concentration. Also since $\Delta n = 0$, the volume terms in the expression cancel and we can use number of particles as a measure of moles and molarity. The mixture contains 2A, 4AB and $2A_2$.

$$K_c = \frac{[A][AB]}{[A_2][B]} = \frac{(2)(4)}{(2)(B)} = 2;\ B = 2$$

2 B atoms should be added to the diagram.

15.8 If temperature increases, K of an endothermic reaction increases and K of an exothermic reaction decreases. Calculate the value of K for the two temperatures and compare. For this reaction, $\Delta n = 0$ and $K_p = K_c$. We can ignore volume and use number of particles as a measure of moles and molarity. $K_c = [A][AB]/[A_2][B]$

(1) 300 K, 3A, 5AB, $1A_2$, 1B; $K_c = (3)(5)/(1)(1) = 15$

(2) 500 K, 1A, 3AB, $3A_2$, 3B; $K_c = (1)(3)/(3)(3) = 0.33$

K_c decreases as T increases, so the reaction is exothermic.

Equilibrium; the Equilibrium Constant

15.10 (a) $K_c = \frac{[C][D]}{[A][B]}$; if K_c is large, the numerator of the K_c expression is much greater than the denominator and products will predominate at equilibrium.

(b) $K_c = k_f/k_r$; if K_c is large, k_f is larger than k_r and the forward reaction has the greater rate constant.

15.12 (a) Yes. The algebraic form of the law of mass action depends only on the coefficients of a chemical equation, not on the reaction mechanism.

(b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The *Haber process* is the primary industrial method of nitrogen fixation, that is, of converting $N_2(g)$ into usable forms. The major use of $NH_3(g)$ from the Haber process is for fertilizer.

(c) $K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$

15.14 (a) $K_c = \frac{[NO]^2}{[N_2][O_2]}$ (b) $K_c = \frac{1}{[Cl_2]^2}$

(c) $K_c = \dfrac{[C_2H_6]^2[O_2]}{[C_2H_4]^2[H_2O]^2}$ (d) $K_c = \dfrac{[H_2O]}{[H_2]}$

(e) $K_c = \dfrac{[Cl_2]^2}{[HCl]^4[O_2]}$

homogeneous: (a), (c); heterogeneous: (b), (d), (e)

15.16 (a) equilibrium lies to right, favoring products ($K_c >> 1$)

(b) equilibrium lies to left, favoring reactants ($K_c << 1$)

15.18 $SO_2(g) + Cl_2(g) \rightleftharpoons SO_2Cl_2(g)$, $K_p = 34.5$. $\Delta n = 1 - 2 = -1$

$K_p = K_c(RT)^{\Delta n}$; $34.5 = K_c(RT)^{-1} = K_c/RT$;

$K_c = 34.5\ RT = 34.5(0.08206)(303) = 857.81 = 858$

15.20 (a) $K_p(\text{forward}) = \dfrac{P^2_{NO_2}}{P^2_{NO} \times P_{O_2}} = 1.48 \times 10^4$

$K_p(\text{reverse}) = \dfrac{P^2_{NO} \times P_{O_2}}{P^2_{NO_2}} = \dfrac{1}{1.48 \times 10^4} = 6.76 \times 10^{-5}$

(b) $K_p > 1$ when NO_2 is the product, and $K_p < 1$ when NO_2 is the reactant, so the equilibrium favors NO_2 at this temperature.

15.22 $K_p = \dfrac{P^4_{HCl} \times P_{O_2}}{P^2_{Cl_2} \times P^2_{H_2O}} = 0.0752$

(a) $K_p = \dfrac{P^2_{Cl_2} \times P^2_{H_2O}}{P^4_{HCl} \times P_{O_2}} = \dfrac{1}{0.0752} = 13.298 = 13.3$

(b) $K_p = \dfrac{P^2_{HCl} \times P^{1/2}_{O_2}}{P_{Cl_2} \times P_{H_2O}} = (0.0752)^{1/2} = 0.2742 = 0.274$

(c) $K_p = K_c(RT)^{\Delta n}$; $\Delta n = 2.5 - 2 = 0.5$; $T = 480°C + 273 = 753\ K$

$K_p = K_c(RT)^{1/2}$, $K_c = K_p/(RT)^{1/2} = 0.2742/[0.08206 \times 753]^{1/2} = 0.03488 = 0.0349$

15.24

$$2NO(g) + Br_2(g) \rightleftharpoons 2NOBr(g) \qquad K_1 = 2.0$$

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_2 = \frac{1}{2.1 \times 10^{30}}$$

$$2NO(g) + Br_2(g) + N_2(g) + O_2(g) \rightleftharpoons 2NOBr(g) + 2NO(g)$$

$$N_2(g) + O_2(g) + Br_2(g) \rightleftharpoons 2NOBr(g)$$

$$K_c = K_1 \times K_2 = 2.0 \times \frac{1}{2.1 \times 10^{30}} = 9.524 \times 10^{-31} = 9.5 \times 10^{-31}$$

15.26 (a) $K_p = 1/\,P_{SO_2}$

(b) Na_2O is a pure solid. The molar concentration, the ratio of moles of a substance to volume occupied by the substance, is a constant for pure solids and liquids.

Calculating Equilibrium Constants

15.28 $$[CH_3OH] = \frac{0.0406\ \text{mol}}{2.00\ \text{L}} = 0.0203\ \text{M}$$

$$[CO] = \frac{0.170\ \text{mol CO}}{2.00\ \text{L}} = 0.0850\ M$$

$$[H_2] = \frac{0.302\ \text{mol}\ H_2}{2.00\ \text{L}} = 0.151\ M$$

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.0203}{(0.0850)(0.151)^2} = 10.4743 = 10.5$$

15.30 (a) $$K_p = \frac{P_{PCl_5}}{P_{PCl_3} \times P_{Cl_2}} = \frac{1.30\ \text{atm}}{0.124\ \text{atm} \times 0.157\ \text{atm}} = 66.8$$

(b) Since $K_p > 1$, products (the numerator of the K_p expression) are favored over reactants (the denominator of the K_p expression).

15.32 (a) Calculate the concentrations of $H_2(g)$ and $Br_2(g)$ and the equilibrium concentration of $H_2(g)$. M = mol/L.

$$[H_2]_{init} = 1.374\ g\ H_2 \times \frac{1\ \text{mol}\ H_2}{2.0159\ g\ H_2} \times \frac{1}{2.00\ \text{L}} = 0.34079 = 0.341\ M$$

$$[Br_2] = 70.31\ g\ Br_2 \times \frac{1\ \text{mol}\ Br_2}{159.81\ g\ Br_2} \times \frac{1}{2.00\ \text{L}} = 0.21998 = 0.220\ M$$

$$[H_2]_{equil} = 0.566\ g\ H_2 \times \frac{1\ \text{mol}\ H_2}{2.0159\ g\ H_2} \times \frac{1}{2.00\ \text{L}} = 0.14038 = 0.140\ M$$

	$H_2(g)$	+	$Br_2(g)$	$\rightleftharpoons$	$2HBr(g)$
initial	0.34079 M		0.21998 M		0
change	-0.20041 M		-0.20041 M		+2(0.20041) M
equil.	0.14038 M		0.01957 M		0.40082 M

The change in H_2 is (0.34079 - 0.14038 = 0.20041 = 0.200). The changes in $[Br_2]$ and [HBr] are set by stoichiometry, resulting in the equilibrium concentrations shown in the table.

(b) $$K_c = \frac{[HBr]^2}{[H_2][Br_2]} = \frac{(0.40082)^2}{(0.14038)(0.01957)} = \frac{(0.401)^2}{(0.140)(0.020)} = 58.48 = 58$$

The equilibrium concentration of Br_2 has 3 decimal places and 2 sig figs, so the value of K_c has 2 sig figs.

15.34 (a)

	$N_2O_4(g)$	$\rightleftharpoons$	$2NO_2(g)$
initial	1.500 atm		1.000 atm
change	+0.244 atm		−0.488 atm
equil	1.744 atm		0.512 atm

The change in P_{NO_2} is (1.000 − 0.512) = −0.488 atm, so the change in $P_{N_2O_4}$ is +(0.488/2) = +0.244 atm.

(b) $K_p = \dfrac{P^2_{NO_2}}{P_{N_2O_4}} = \dfrac{(0.512)^2}{(1.744)} = 0.1503 = 0.150$

Applications of Equilibrium Constants

15.36 (a) If the value of Q_c equals the value of K_c, the system is at equilibrium.

(b) In the direction of less products (more reactants), to the left.

(c) $Q_c = 0$ if the concentration of any product is zero.

15.38 Calculate the reaction quotient in each case, compare with

$$K_p = \frac{P^2_{NH_3}}{P_{N_2} \times P^3_{H_2}} = 4.51 \times 10^{-5}$$

(a) $Q = \dfrac{(105)^2}{(35)\,(495)^3} = 2.6 \times 10^{-6}$

Since $Q < K_p$, the reaction will shift to the right to attain equilibrium.

(b) $Q = \dfrac{(35)^2}{(0)\,(595)^3} = \infty$

Since $Q > K_p$, reaction must shift to the left to attain equilibrium. There must be **some** N_2 present to attain equilibrium. In this example, the only source of N_2 is the decomposition of NH_3.

(c) $Q = \dfrac{(26)^2}{(42)^3(202)} = 4.52 \times 10^{-5}$; $Q = K_p$ Reaction is at equilibrium.

15.40 $K_p = \dfrac{P^2_{SO_3}}{P^2_{SO_2} \times P_{O_2}}$; $P_{SO_3} = \left(K_p \times P^2_{SO_2} \times P_{O_2}\right)^{1/2} = [(0.345)(0.165)^2(0.755)]^{1/2} = 0.0842$ atm

15.42 (a) $K_c = \dfrac{[I]^2}{[I_2]} = 3.1 \times 10^{-5}$

$$[I] = \frac{2.67 \times 10^{-2}\text{ g I}}{10.0\text{ L}} \times \frac{1\text{ mol I}}{126.9\text{ g I}} = 2.1040 \times 10^{-5} = 2.10 \times 10^{-5}\,M$$

$$[I_2] = \frac{[I]^2}{K_c} = \frac{(2.104 \times 10^{-5})^2}{3.1 \times 10^{-5}} = 1.428 \times 10^{-5} = 1.43 \times 10^{-5}\,M$$

$$\frac{1.428\times10^{-5}\text{ mol I}_2}{\text{L}}\times 10.0\text{ L}\times\frac{253.8\text{ g I}_2}{\text{mol I}_2} = M = 0.0362\text{ g I}_2$$

Check. $K_c = \dfrac{(2.104\times10^{-5})^2}{1.428\times10^{-5}} = 3.1\times10^{-5}$

(b) $PV = nRT;\ P = \dfrac{gRT}{MM\ V}$

$$P_{SO_3} = \frac{1.57\text{ g SO}_3}{80.06\text{ g/mol}}\times\frac{0.08206\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\times\frac{700\text{ K}}{2.00\text{ L}} = 0.5632 = 0.563\text{ atm}$$

$$P_{O_2} = \frac{0.125\text{ g O}_2}{32.00\text{ g/mol}}\times\frac{0.08206\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}}\times\frac{700\text{ K}}{2.00\text{ L}} = 0.1122 = 0.112\text{ atm}$$

$$K_p = 3.0\times10^4 = \frac{P_{SO_3}^2}{P_{SO_2}^2\times P_{O_2}};\ P_{SO_2} = \left[P_{SO_3}^2/(K_p)(P_{O_2})\right]^{1/2}$$

$$P_{SO_2} = [(0.5632)^2/(3.0\times10^4)(0.1122)]^{1/2} = 9.708\times10^{-3} = 9.7\times10^{-3}\text{ atm}$$

$$\text{g SO}_2 = \frac{MM\,PV}{RT} = \frac{64.06\text{ g SO}_2}{\text{mol SO}_2}\times\frac{\text{K}\bullet\text{mol}}{0.08206\text{ L}\bullet\text{atm}}\times\frac{9.708\times10^{-3}\text{ atm}\times2.00\text{ L}}{700\text{ K}}$$

$$= 0.02165 = 0.022\text{ g SO}_2$$

Check. $K_p = [(9.708\times10^{-3})^2/(0.563)^2(0.1122)] = 3.0\times10^4$

15.44 $[Br_2] = [Cl_2] = 0.30\text{ mol}/1.0\text{ L} = 0.30\ M$

$K_c = \dfrac{[BrCl]^2}{[Br_2][Cl_2]} = 7.0$

	$Br_2(g)$	+	$Cl_2(g)$	$\rightleftharpoons$	$2BrCl(g)$
initial	0.30 *M*		0.30 *M*		0
change	–x		–x		+2x
equil.	(0.30 – x)		(0.30 – x)		+2x

$7.0 = \dfrac{(2x)^2}{(0.30-x)^2}$ (We can solve this exactly by taking the square root of both sides.)

$(7.0)^{1/2} = \dfrac{2x}{0.30-x}$, $2.646(0.30-x) = 2x$, $0.7937 = 4.646x$, $x = 0.1709 = 0.17\ M$

$[BrCl] = 2x = 0.3417 = 0.34\ M$; $[Br_2] = [Cl_2] = 0.30 - x = 0.1291 = 0.13\ M$

Check. $K_c = (0.3417)^2/(0.1291)^2 = 7.0$

15.46 $K_c = [NH_3][H_2S] = 1.2\times10^{-4}$. Because of the stoichiometry, equilibrium concentrations of H_2S and NH_3 will be equal; call this quantity y. Then, $y^2 = 1.2\times10^{-4}$, $y = 0.010954 = 0.011\ M$.

15.48 (a) *Analyze/Plan.* If only $PH_3BCl_3(s)$ is present initially, the equation requires that the equilibrium concentrations of $PH_3(g)$ and $BCl_3(g)$ are equal. Write the K_c expression and solve for $x = [PH_3] = [BCl_3]$. *Solve.*

$K_c = [PH_3][BCl_3]$; $1.87\times10^{-3} = x^2$; $x = 0.043243 = 0.0432\ M$ PH_3 and BCl_3

(b) Since the mole ratios are 1:1:1, mol $PH_3BCl_3(s)$ required = mol PH_3 or BCl_3 produced.

$$\frac{0.043243 \text{ mol } PH_3}{L} \times 0.500 \text{ L} = 0.02162 = 0.0216 \text{ mol } PH_3 = 0.0216 \text{ mol } PH_3BCl_3$$

$$0.02162 \text{ mol } PH_3BCl_3 \times \frac{151.2 \text{ g } PH_3BCl_3}{1 \text{ mol } PH_3BCl_3} = 3.269 = 3.27 \text{ g } PH_3BCl_3$$

In fact, some $PH_3BCl_3(s)$ must remain for the system to be in equilibrium, so a bit more than 3.27 g PH_3BCl_3 is needed.

15.50 $CaCrO_4(s) \rightleftharpoons Ca^{2+}(aq) + CrO_4^{2-}(aq)$ $K_c = [Ca^{2+}][CrO_4^{2-}] = 7.1 \times 10^{-4}$

At equilibrium, $[Ca^{2+}] = [CrO_4^{2-}] = x$

$K_c = 7.1 \times 10^{-4} = x^2$, $x = 0.0266 = 0.027$ *M* Ca^{2+} and CrO_4^{2-}

LeChâtelier's Principle

15.52 (a) increase (b) increase (c) decrease

(d) no effect (e) no effect (f) no effect

15.54 (a) The reaction must be endothermic (+ΔH) if heating increases the fraction of products.

(b) There must be more moles of gas in the products if increasing the volume of the vessel increases the fraction of products.

15.56 (a) $\Delta H^\circ = \Delta H^\circ_f\ CH_3OH(g) - \Delta H^\circ_f\ CO(g) - 2\Delta H^\circ_f\ H_2(g)$

$= -201.2 \text{ kJ} - (-110.5 \text{ kJ}) - 0 \text{ kJ}$

$= -90.7 \text{ kJ}$

(b) The reaction is exothermic; an increase in temperature would decrease the value of K and decrease the yield. A low temperature is needed to maximize yield.

(c) Increasing total pressure would increase the partial pressure of each gas, shifting the equilibrium toward products. The extent of conversion to CH_3OH increases as the total pressure increases.

Additional Exercises

15.58 $CH_4(g) + H_2O(g) \rightarrow CO(g) + 3H_2(g)$

$$K_p = \frac{P_{CO} \times P^3_{H_2}}{P_{CH_4} \times P_{H_2O}};\ P = \frac{g\,RT}{MM\,V};\ T = 1000 \text{ K}$$

$$P_{CO} = \frac{8.62 \text{ g}}{28.01 \text{ g/mol}} \times \frac{0.08206 \text{ L} \bullet \text{atm}}{\text{mol} \bullet \text{K}} \bullet \frac{1000 \text{ K}}{5.00 \text{ L}} = 5.0507 = 5.05 \text{ atm}$$

$$P_{H_2} = \frac{2.60 \text{ g}}{2.016 \text{ g/mol}} \times \frac{0.08206 \text{ L} \bullet \text{atm}}{\text{mol} \bullet \text{K}} \bullet \frac{1000 \text{ K}}{5.00 \text{ L}} = 21.1663 = 21.2 \text{ atm}$$

$$P_{CH_4} = \frac{43.0\text{ g}}{16.04\text{ g/mol}} \times \frac{0.08206\text{ L}\bullet\text{atm}}{\text{mol}\bullet\text{K}} \bullet \frac{1000\text{ K}}{5.00\text{ L}} = 43.9973 = 44.0\text{ atm}$$

$$P_{H_2O} = \frac{48.4\text{ g}}{18.02\text{ g/mol}} \times \frac{0.08206\text{ L}\bullet\text{atm}}{\text{mol}\bullet\text{K}} \bullet \frac{1000\text{ K}}{5.00\text{ L}} = 44.0811 = 44.1\text{ atm}$$

$$K_p = \frac{(5.0507)\,(21.1663)^3}{(43.9973)\,(44.0811)} = 24.6949 = 24.7$$

$$K_p = K_c(RT)^{\Delta n},\ K_c = K_p/(RT)^{\Delta n};\ \Delta n = 4 - 2 = 2$$

$$K_c = (24.6949)/[(0.08206)(1000)]^2 = 3.6673 \times 10^{-3} = 3.67 \times 10^{-3}$$

15.60 (a) $H_2(g) + S(s) \rightleftharpoons H_2S(g) \qquad K_c = [H_2S]/[H_2]$

(b) Calculate the molarities of H_2S and H_2.

$$[H_2S] = \frac{0.46\text{ g}}{34.1\text{ g/mol}} \times \frac{1}{1.0\text{ L}} = 0.01349 = 0.013\ M$$

$$[H_2] = \frac{0.40\text{ g}}{2.02\text{ g/mol}} \times \frac{1}{1.0\text{ L}} = 0.1980 = 0.20\ M$$

$$K_c = 0.01349/0.1980 = 0.06812 = 0.068$$

(c) Since S is a pure solid, its concentration doesn't change during the reaction, so [S] does not appear in the equilibrium expression.

15.61 (a) $K_p = \dfrac{P_{Br_2} \times P_{NO}^2}{P_{NOBr}^2}$; $P = \dfrac{gRT}{PV}$; $T = 100°C + 273 = 373$

$$P_{Br_2} = \frac{4.19\text{ g}}{159.8\text{ g/mol}} \times \frac{0.08206\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}} \times \frac{373}{5.0\text{ L}} = 0.16051 = 0.161\text{ atm}$$

$$P_{NO} = \frac{3.08\text{ g}}{30.01\text{ g/mol}} \times \frac{0.08206\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}} \times \frac{373}{5.0\text{ L}} = 0.62828 = 0.628\text{ atm}$$

$$P_{NOBr} = \frac{3.22\text{ g NOBr}}{109.9\text{ g/mol}} \times \frac{0.08206\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}} \times \frac{373}{5.0\text{ L}} = 0.17936 = 0.179\text{ atm}$$

$$K_p = \frac{(0.16051)\,(0.62828)^2}{(0.17936)^2} = 1.9695 = 1.97 \qquad K_p = K_c(RT)^{\Delta n},\ \Delta n = 3 - 2 = 1$$

$$K_c = K_p/RT = 1.9695/(0.08206)(373) = 0.064345 = 0.0643$$

(b) $P_t = P_{Br_2} + P_{NO} + P_{NOBr} = 0.16051 + 0.62828 + 0.17936 = 0.96815 = 0.968\text{ atm}$

15.63 (a) $K_p = \dfrac{P_{NH_3}^2}{P_{N_2} \times P_{H_2}^3} = 4.34 \times 10^{-3}$; $T = 300°C + 273 = 573\text{ K}$

$$P_{NH_3} = \frac{gRT}{MM \times V} = \frac{1.05\text{ g}}{17.03\text{ g/mol}} \times \frac{0.08206\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}} \times \frac{573\text{ K}}{1.00\text{ L}} = 2.899 = 2.90\text{ atm}$$

	$N_2(g)$ +	$3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
initial	0 atm	0 atm		?
change	x	3x		-2x
equil.	x atm	3x atm		2.899 atm

(Remember, only the change line reflects the stoichiometry of the reaction.)

$$K_p = \frac{(2.899)^2}{(x)\,(3x)^3} = 4.34 \times 10^{-3};\ 27\,x^4 = \frac{(2.899)^2}{4.34 \times 10^{-3}};\ x^4 = 71.725$$

$x = 2.910 = 2.91\text{ atm} = P_{N_2};\ P_{H_2} = 3x = 8.730 = 8.73\text{ atm}$

$$g_{N_2} = \frac{MM \times PV}{RT} = \frac{28.02\text{ g }N_2}{\text{mol }N_2} \times \frac{K \bullet \text{mol}}{0.08206\text{ L} \bullet \text{atm}} \times \frac{2.910\text{ atm} \times 1.00\text{ L}}{573\text{ K}} = 1.73\text{ g }N_2$$

$$g_{H_2} = \frac{2.016\text{ g }H_2}{\text{mol }H_2} \times \frac{K \bullet \text{mol}}{0.08206\text{ L} \bullet \text{atm}} \times \frac{8.730\text{ atm} \times 1.00\text{ L}}{573\text{ K}} = 0.374\text{ g }H_2$$

(b) The initial $P_{NH_3} = 2.899\text{atm} + 2(2.910\text{ atm}) = 8.719 = 8.72\text{ atm}$

$$g_{NH_3} = \frac{17.03\text{ g }NH_3}{\text{mol }NH_3} \times \frac{K \bullet \text{mol}}{0.08206\text{ L} \bullet \text{atm}} \times \frac{8.719\text{ atm} \times 1.00\text{ L}}{573\text{ K}} = 3.16\text{ g }NH_3$$

(c) $P_t = P_{N_2} + P_{H_2} + P_{NH_3} = 2.910\text{ atm} + 8.730\text{ atm} + 2.899\text{ atm} = 14.54\text{ atm}$

15.64

	2IBr	$\rightleftharpoons$	I_2 +	Br_2
initial	0.025 atm		0	0
change	-2x		x	x
equil.	(0.025 - 2x) atm		x	x

$$K_p = 8.5 \times 10^{-3} = \frac{P_{I_2} \times P_{Br_2}}{P_{IBr}^2} = \frac{x^2}{(0.025 - 2x)^2};\quad \text{Taking the square root of both sides}$$

$$\frac{x}{0.025 - 2x} = (8.5 \times 10^{-3})^{1/2} = 0.0922;\ x = 0.0922(0.025 - 2x)$$

$x + 0.184x = 0.002305;\ 1.184x = 0.002305;\ x = 0.001947 = 1.9 \times 10^{-3}$

P_{IBr} at equilibrium = $0.025 - 2(1.947 \times 10^{-3}) = 0.02111 = 0.021$ atm

15.66 $K_p = P_{NH_3} \times P_{H_2S};\quad P_t = 0.614\text{ atm}$

If the equilibrium amounts of NH_3 and H_2S are due solely to the decomposition of $NH_4HS(s)$, the equilibrium pressures of the two gases are equal, and each is 1/2 of the total pressure.

$P_{NH_3} = P_{H_2S} = 0.614\text{ atm}/2 = 0.307\text{ atm}$

$K_p = (0.307)^2 = 0.0943$

15.67 Initial $P_{SO_3} = \dfrac{gRT}{MM\ V} = \dfrac{0.831\text{ g}}{80.07\text{ g/mol}} \times \dfrac{0.08206\text{ L}\bullet\text{atm}}{\text{K}\bullet\text{mol}} \times \dfrac{1100\text{ K}}{1.00\text{ L}} = 0.9368 = 0.937\text{ atm}$

	$2SO_3$	$\rightleftharpoons$	$2SO_2$	+	O_2
initial	0.9368 atm		0		0
change	–2x		+2x		+x
equil.	0.9368–2x		2x		x
[equil.]	0.2104 atm		0.7264 atm		0.3632 atm

$P_t = (0.9368\text{–}2x) + 2x + x;\ 0.9368 + x = 1.300\text{ atm};\ x = 1.300 - 0.9368 = 0.3632 = 0.363\text{ atm}$

$$K_p = \frac{P^2_{SO_2} \times P_{O_2}}{P^2_{SO_3}} = \frac{(0.7264)^2\ (0.3632)}{(0.2104)^2} = 4.3292 = 4.33$$

$K_p = K_p = K_c(RT)^{\Delta n};\ \Delta n = 3 - 2 = 1;\ K_p = K_c(RT)$

$K_c = K_p/RT = 4.3292/[(0.08206)(1100)] = 0.04796 = 0.0480$

15.69 $K_c = [CO_2] = 0.0108;\ [CO_2] = \dfrac{\text{g } CO_2}{44.01\text{ g/mol}} \times \dfrac{1}{10.0\text{ L}}$

In each case, calculate $[CO_2]$ and determine the position of the equilibrium.

(a) $[CO_2] = \dfrac{4.25\text{ g}}{44.01\text{ g/mol}} \times \dfrac{1}{10.0\text{ L}} = 9.657 \times 10^{-3} = 9.66 \times 10^{-3}\ M$

Q = $9.66 \times 10^{-3} > K_c$. The reaction proceeds to the right to achieve equilibrium and the amount of $CaCO_3(s)$ decreases.

(b) $[CO_2] = \dfrac{5.66\text{ g } CO_2}{44.01\text{ g/mol}} \times \dfrac{1}{10.0\text{ L}} = 0.0129\ M$

Q = $0.0129 > K_c$. The reaction proceeds to the left to achieve equilibrium and the amount of $CaCO_3(s)$ increases.

(c) 6.48 g CO_2 means $[CO_2] > 0.0129\ M$; $Q > 0.0129 > K_c$, the amount of $CaCO_3$ increases.

15.70 (a) $K_p = \dfrac{P_{Ni(CO)_4}}{P^4_{CO}}$

(b) Increasing the temperature to 200°C favors the reverse process (decomposition of $Ni(CO)_4(g)$ and thus the value of K_p is smaller at the higher temperature. This is the behavior expected from an exothermic reaction (heat is a product).

(c) At the temperature of the exhaust pipe, the $Ni(CO)_4$ product is a gas and is carried into the atmosphere with other exhaust gases. Thus, equilibrium is never established (we do not have a closed system) and the reaction proceeds to the right as $Ni(CO)_4$ product is removed.

15.72 (a)

	$CCl_4(g)$ $\rightleftharpoons$	$C(s) + 2Cl_2(g)$
initial	2.00 atm	0 atm
change	-x atm	+2x atm
equil.	(2.00-x) atm	2x atm

$$K_p = 0.76 = \frac{P^2_{Cl_2}}{P_{CCl_4}} = \frac{(2x)^2}{(2.00 - x)}$$

$1.52 - 0.76x = 4x^2; \quad 4x^2 + 0.76x - 1.52 = 0$

Using the quadratic formula, $a = 4$, $b = 0.76$, $c = -1.52$

$$x = \frac{-0.76 \pm \sqrt{(0.76)^2 - 4(4)(-1.52)}}{2(4)} = \frac{-0.76 + 4.99}{8} = 0.5287 = 0.53 \text{ atm}$$

$$\text{Fraction } CCl_4 \text{ reacted} = \frac{x \text{ atm}}{2.00 \text{ atm}} = \frac{0.53}{2.00} = 0.264 = 26\%$$

(b) $P_{Cl_2} = 2x = 2(0.5287) = 1.06 \text{ atm}$

$P_{CCl_4} = 2.00 - x = 2.00 - 0.5287 = 1.47 \text{ atm}$

15.73 (a) $$Q = \frac{P_{PCl_5}}{P_{PCl_3} \times P_{Cl_2}} = \frac{(0.20)}{(0.50)(0.50)} = 0.80$$

0.80 (Q) > 0.0870 (K), the reaction proceeds to the left.

(b)

	$PCl_3(g)$ +	$Cl_2(g)$ $\rightleftharpoons$	$PCl_5(g)$
initial	0.50 atm	0.50 atm	0.20 atm
change	+x atm	+x atm	-x atm
equil.	(0.50 + x) atm	(0.50 + x) atm	(0.20 - x) atm

(Since the reaction proceeds to the left, P_{PCl_5} must decrease and P_{PCl_3} and P_{Cl_2} must increase.)

$$K_p = 0.0870 = \frac{(0.20 - x)}{(0.50 + x)(0.50 + x)}; \quad 0.0870 = \frac{(0.20 - x)}{(0.250 + 1.00\,x + x^2)}$$

$0.0870(0.250 + 1.00x + x^2) = 0.20 - x; -0.17825 + 1.0870x + 0.0870\,x^2 = 0$

$$x = \frac{-1.0870 \pm \sqrt{(1.0870)^2 - 4(0.0870)(-0.17825)}}{2(0.0870)} = \frac{-1.0870 + 1.1152}{0.174} = 0.162$$

$P_{PCl_3} = (0.50 + 0.162) \text{ atm} = 0.662 \qquad P_{Cl_2} = (0.50 + 0.162) \text{ atm} = 0.662 \text{ atm}$

$P_{PCl_5} = (0.20 - 0.162) \text{ atm} = 0.038 \text{ atm}$

To two decimal places, the pressures are 0.66, 0.66 and 0.04 atm, respectively. When substituting into the K_p expression, pressures to three decimal places yield a result much closer to 0.0870.

(c) Increasing the volume of the container favors the process where more moles of gas are produced, so the reverse reaction is favored and the equilibrium shifts to the left; the mole fraction of Cl_2 increases.

(d) For an exothermic reaction, increasing the temperature decreases the value of K; more reactants and fewer products are present at equilibrium and the mole fraction of Cl_2 increases.

15.75 (a) Since the volume of the vessel = 1.00 L, mol = *M*. The reaction will proceed to the left to establish equilibrium.

	A(g) +	2B(g) ⇌	2C(g)
initial	0 *M*	0 *M*	1.00 *M*
change	+x *M*	+2x *M*	-2x *M*
equil.	x *M*	2x *M*	(1.00 - 2x) *M*

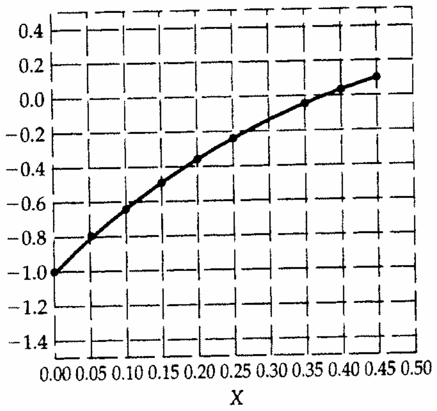
At equilibrium, [C] = (1.00 - 2x) *M*, [B] = 2x *M*.

(b) x must be less than 0.50 *M* (so that [C], 1.00 -2x, is not less than zero).

(c) $K_c = \frac{[C]^2}{[A][B]^2}; \frac{(1.00-2x)^2}{(x)(2x)^2} = 0.25$

$1.00 - 4x + 4x^2 = 0.25(4x)^3; x^3 - 4x^2 + 4x - 1 = 0$

(d)



X	Y
0.0	−1.000
0.05	−0.810
0.10	−0.639
0.15	−0.487
0.20	−0.352
0.25	−0.234
0.35	−0.047
0.40	+0.024
0.45	+0.081
~0.383	0.00

(e) From the plot, x ≈ 0.383 *M*

[A] = x = 0.383 *M*; [B] = 2x = 0.766 *M*

[C] = 1.00 - 2x = 0.234 *M*

Using the K_c expression as a check:

$K_c = 0.25; \quad \frac{(0.234)^2}{(0.383)(0.766)^2} = 0.24;$ the estimated values are reasonable.

15.76 $K_p = \dfrac{P_{O_2} \times P_{CO}^2}{P_{CO_2}^2} \approx 1 \times 10^{-13}$; $P_{O_2} = (0.03)\,(1\text{ atm}) = 0.03\text{ atm}$

$P_{CO} = (0.002)\,(1\text{ atm}) = 0.002\text{ atm}$; $P_{CO_2} = (0.12)\,(1\text{ atm}) = 0.12\text{ atm}$

$$Q = \frac{(0.03)(0.002)^2}{(0.12)^2} = 8.3 \times 10^{-6} = 8 \times 10^{-6}$$

Since $Q > K_p$, the system will shift to the left to attain equilibrium. Thus a catalyst that promoted the attainment of equilibrium would result in a lower CO content in the exhaust.

Integrative Exercises

15.79 (a) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

(b) $K_c = [Ag^+][Cl^-]$

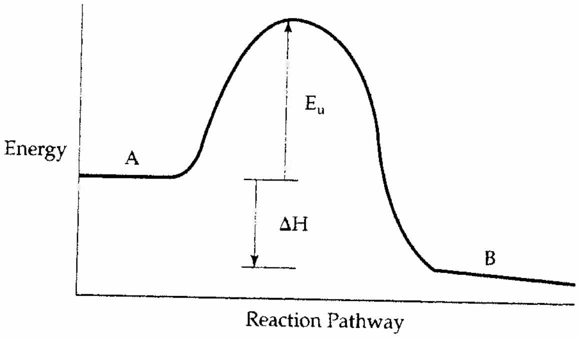
(c) Using thermodynamic data from Appendix C, calculate ΔH for the reaction in part (a).

$$\Delta H^\circ = \Delta H_f^\circ\ Ag^+(aq) + \Delta H_f^\circ\ Cl^-(aq) - \Delta H_f^\circ\ AgCl(s)$$

$$\Delta H^\circ = 105.90\text{ kJ} - 167.2\text{ kJ} - (-127.0\text{ kJ}) = 65.7\text{ kJ}$$

The reaction is endothermic (heat is a reactant), so the solubility of AgCl(s) in $H_2O(l)$ will increase with increasing temperature.

15.81 Consider the energy profile for an exothermic reaction.



The activation energy in the forward direction, E_{af}, equals E_u, and the activation energy in the reverse reaction, E_{ar}, equals $E_u - \Delta H$. (The same is true for an endothermic reaction because the sign of ΔH is the positive and $E_{ar} < E_{af}$). For the reaction in question,

$$K = \frac{k_f}{k_r} = \frac{A_f e^{-E_{af}/RT}}{A_r e^{-E_{ar}/RT}}$$

Since the ln form of the Arrhenius equation is easier to manipulate, we will consider ln K.