

CHAPTER 14

CHEMICAL EQUILIBRIUM

14.13 $K_c = \frac{[B]}{[A]}$

- (1) With $K_c = 10$, products are favored at equilibrium. Because the coefficients for both A and B are one, we expect the concentration of B to be 10 times that of A at equilibrium. Choice (a) is the best choice with 10 B molecules and 1 A molecule.
- (2) With $K_c = 0.10$, reactants are favored at equilibrium. Because the coefficients for both A and B are one, we expect the concentration of A to be 10 times that of B at equilibrium. Choice (d) is the best choice with 10 A molecules and 1 B molecule.

You can calculate K_c in each case without knowing the volume of the container because the mole ratio between A and B is the same. Volume will cancel from the K_c expression. Only moles of each component are needed to calculate K_c .

- 14.14 Note that we are comparing similar reactions at equilibrium – two reactants producing one product, all with coefficients of one in the balanced equation.
- (a) The reaction, $A + C \rightleftharpoons AC$ has the largest equilibrium constant. Of the three diagrams, there is the most product present at equilibrium.
- (b) The reaction, $A + D \rightleftharpoons AD$ has the smallest equilibrium constant. Of the three diagrams, there is the least amount of product present at equilibrium.

- 14.15 When the equation for a reversible reaction is written in the opposite direction, the equilibrium constant becomes the reciprocal of the original equilibrium constant.

$$K' = \frac{1}{K} = \frac{1}{4.17 \times 10^{-34}} = 2.40 \times 10^{33}$$

- 14.16 The problem states that the system is at equilibrium, so we simply substitute the equilibrium concentrations into the equilibrium constant expression to calculate K_c .

Step 1: Calculate the concentrations of the components in units of mol/L. The molarities can be calculated by simply dividing the number of moles by the volume of the flask.

$$[H_2] = \frac{2.50 \text{ mol}}{12.0 \text{ L}} = 0.208 \text{ M}$$

$$[S_2] = \frac{1.35 \times 10^{-5} \text{ mol}}{12.0 \text{ L}} = 1.13 \times 10^{-6} \text{ M}$$

$$[H_2S] = \frac{8.70 \text{ mol}}{12.0 \text{ L}} = 0.725 \text{ M}$$

Step 2: Once the molarities are known, K_c can be found by substituting the molarities into the equilibrium constant expression.

$$K_c = \frac{[\text{H}_2\text{S}]^2}{[\text{H}_2]^2[\text{S}_2]} = \frac{(0.725)^2}{(0.208)^2(1.13 \times 10^{-6})} = \mathbf{1.08 \times 10^7}$$

If you forget to convert moles to moles/liter, will you get a different answer? Under what circumstances will the two answers be the same?

14.17 Using Equation (14.5) of the text: $K_P = K_c(0.0821 T)^{\Delta n}$

where, $\Delta n = 2 - 3 = -1$

and $T = (1273 + 273) \text{ K} = 1546 \text{ K}$

$$K_P = (2.24 \times 10^{22})(0.0821 \times 1546)^{-1} = \mathbf{1.76 \times 10^{20}}$$

14.18 Strategy: The relationship between K_c and K_P is given by Equation (14.5) of the text. What is the change in the number of moles of gases from reactant to product? Recall that

$$\Delta n = \text{moles of gaseous products} - \text{moles of gaseous reactants}$$

What unit of temperature should we use?

Solution: The relationship between K_c and K_P is given by Equation (14.5) of the text.

$$K_P = K_c(0.0821 T)^{\Delta n}$$

Rearrange the equation relating K_P and K_c , solving for K_c .

$$K_c = \frac{K_P}{(0.0821 T)^{\Delta n}}$$

Because $T = 623 \text{ K}$ and $\Delta n = 3 - 2 = 1$, we have:

$$K_c = \frac{K_P}{(0.0821 T)^{\Delta n}} = \frac{1.8 \times 10^{-5}}{(0.0821)(623 \text{ K})} = \mathbf{3.5 \times 10^{-7}}$$

14.19 We can write the equilibrium constant expression from the balanced equation and substitute in the pressures.

$$K_P = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} P_{\text{O}_2}} = \frac{(0.050)^2}{(0.15)(0.33)} = \mathbf{0.051}$$

Do we need to know the temperature?

14.20 The equilibrium constant expressions are:

(a)
$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

$$(b) \quad K_c = \frac{[\text{NH}_3]}{[\text{N}_2]^{\frac{1}{2}}[\text{H}_2]^{\frac{3}{2}}}$$

Substituting the given equilibrium concentration gives:

$$(a) \quad K_c = \frac{(0.25)^2}{(0.11)(1.91)^3} = \mathbf{0.082}$$

$$(b) \quad K_c = \frac{(0.25)}{(0.11)^{\frac{1}{2}}(1.91)^{\frac{3}{2}}} = \mathbf{0.29}$$

Is there a relationship between the K_c values from parts (a) and (b)?

14.21 The equilibrium constant expression for the two forms of the equation are:

$$K_c = \frac{[\text{I}]}{[\text{I}_2]} \quad \text{and} \quad K'_c = \frac{[\text{I}_2]}{[\text{I}]^2}$$

The relationship between the two equilibrium constants is

$$K'_c = \frac{1}{K_c} = \frac{1}{3.8 \times 10^{-5}} = 2.6 \times 10^4$$

K_P can be found as shown below.

$$K_P = K'_c(0.0821 T)^{\Delta n} = (2.6 \times 10^4)(0.0821 \times 1000)^{-1} = \mathbf{3.2 \times 10^2}$$

14.22 Because pure solids do not enter into an equilibrium constant expression, we can calculate K_P directly from the pressure that is due solely to $\text{CO}_2(\text{g})$.

$$K_P = P_{\text{CO}_2} = \mathbf{0.105}$$

Now, we can convert K_P to K_c using the following equation.

$$K_P = K_c(0.0821 T)^{\Delta n}$$

$$K_c = \frac{K_P}{(0.0821 T)^{\Delta n}}$$

$$K_c = \frac{0.105}{(0.0821 \times 623)^{(1-0)}} = \mathbf{2.05 \times 10^{-3}}$$

14.23 We substitute the given pressures into the reaction quotient expression.

$$Q_P = \frac{P_{\text{PCl}_3} P_{\text{Cl}_2}}{P_{\text{PCl}_5}} = \frac{(0.223)(0.111)}{(0.177)} = 0.140$$

The calculated value of Q_P is less than K_P for this system. The system will change in a way to increase Q_P until it is equal to K_P . To achieve this, the pressures of PCl_3 and Cl_2 must **increase**, and the pressure of PCl_5 must **decrease**.

Could you actually determine the final pressure of each gas?

14.24 Strategy: Because they are constant quantities, the concentrations of solids and liquids do not appear in the equilibrium constant expressions for heterogeneous systems. The total pressure at equilibrium that is given is due to both NH_3 and CO_2 . Note that for every 1 atm of CO_2 produced, 2 atm of NH_3 will be produced due to the stoichiometry of the balanced equation. Using this ratio, we can calculate the partial pressures of NH_3 and CO_2 at equilibrium.

Solution: The equilibrium constant expression for the reaction is

$$K_P = P_{\text{NH}_3}^2 P_{\text{CO}_2}$$

The total pressure in the flask (0.363 atm) is a sum of the partial pressures of NH_3 and CO_2 .

$$P_T = P_{\text{NH}_3} + P_{\text{CO}_2} = 0.363 \text{ atm}$$

Let the partial pressure of $\text{CO}_2 = x$. From the stoichiometry of the balanced equation, you should find that $P_{\text{NH}_3} = 2P_{\text{CO}_2}$. Therefore, the partial pressure of $\text{NH}_3 = 2x$. Substituting into the equation for total pressure gives:

$$P_T = P_{\text{NH}_3} + P_{\text{CO}_2} = 2x + x = 3x$$

$$3x = 0.363 \text{ atm}$$

$$x = P_{\text{CO}_2} = 0.121 \text{ atm}$$

$$P_{\text{NH}_3} = 2x = 0.242 \text{ atm}$$

Substitute the equilibrium pressures into the equilibrium constant expression to solve for K_P .

$$K_P = P_{\text{NH}_3}^2 P_{\text{CO}_2} = (0.242)^2(0.121) = 7.09 \times 10^{-3}$$

14.25 Of the original 1.05 moles of Br_2 , 1.20% has dissociated. The amount of Br_2 dissociated in molar concentration is:

$$[\text{Br}_2] = 0.0120 \times \frac{1.05 \text{ mol}}{0.980 \text{ L}} = 0.0129 \text{ M}$$

Setting up a table:

	$\text{Br}_2(\text{g})$	\rightleftharpoons	$2\text{Br}(\text{g})$
Initial (M):	$\frac{1.05 \text{ mol}}{0.980 \text{ L}} = 1.07 \text{ M}$		0
Change (M):	-0.0129		+2(0.0129)
Equilibrium (M):	1.06		0.0258

$$K_c = \frac{[\text{Br}]^2}{[\text{Br}_2]} = \frac{(0.0258)^2}{1.06} = 6.3 \times 10^{-4}$$

- 14.26** If the CO pressure at equilibrium is 0.497 atm, the balanced equation requires the chlorine pressure to have the same value. The initial pressure of phosgene gas can be found from the ideal gas equation.

$$P = \frac{nRT}{V} = \frac{(3.00 \times 10^{-2} \text{ mol})(0.0821 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(800 \text{ K})}{(1.50 \text{ L})} = 1.31 \text{ atm}$$

Since there is a 1:1 mole ratio between phosgene and CO, the partial pressure of CO formed (0.497 atm) equals the partial pressure of phosgene reacted. The phosgene pressure at equilibrium is:

	CO(g)	+	Cl ₂ (g)	⇌	COCl ₂ (g)
Initial (atm):	0		0		1.31
Change (atm):	+0.497		+0.497		-0.497
Equilibrium (atm):	0.497		0.497		0.81

The value of K_P is then found by substitution.

$$K_P = \frac{P_{\text{COCl}_2}}{P_{\text{CO}}P_{\text{Cl}_2}} = \frac{0.81}{(0.497)^2} = 3.3$$

- 14.27** Let x be the initial pressure of NOBr. Using the balanced equation, we can write expressions for the partial pressures at equilibrium.

$$P_{\text{NOBr}} = (1 - 0.34)x = 0.66x$$

$$P_{\text{NO}} = 0.34x$$

$$P_{\text{Br}_2} = 0.17x$$

The sum of these is the total pressure.

$$0.66x + 0.34x + 0.17x = 1.17x = 0.25 \text{ atm}$$

$$x = 0.21 \text{ atm}$$

The equilibrium pressures are then

$$P_{\text{NOBr}} = 0.66(0.21) = 0.14 \text{ atm}$$

$$P_{\text{NO}} = 0.34(0.21) = 0.071 \text{ atm}$$

$$P_{\text{Br}_2} = 0.17(0.21) = 0.036 \text{ atm}$$

We find K_P by substitution.

$$K_P = \frac{(P_{\text{NO}})^2 P_{\text{Br}_2}}{(P_{\text{NOBr}})^2} = \frac{(0.071)^2 (0.036)}{(0.14)^2} = 9.3 \times 10^{-3}$$

The relationship between K_P and K_c is given by

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

We find K_c (for this system $\Delta n = +1$)

$$K_c = \frac{K_P}{(RT)^{\Delta n}} = \frac{K_P}{RT} = \frac{9.3 \times 10^{-3}}{(0.0821 \times 298)^1} = 3.8 \times 10^{-4}$$

14.28 In this problem, you are asked to calculate K_c .

Step 1: Calculate the initial concentration of NOCl. We carry an extra significant figure throughout this calculation to minimize rounding errors.

$$[\text{NOCl}]_0 = \frac{2.50 \text{ mol}}{1.50 \text{ L}} = 1.667 \text{ M}$$

Step 2: Let's represent the change in concentration of NOCl as $-2x$. Setting up a table:

	$2\text{NOCl}(\text{g})$	\rightleftharpoons	$2\text{NO}(\text{g})$	$+$	$\text{Cl}_2(\text{g})$
Initial (M):	1.667		0		0
Change (M):	$-2x$		$+2x$		$+x$
Equilibrium (M):	$1.667 - 2x$		$2x$		x

If 28.0 percent of the NOCl has dissociated at equilibrium, the amount reacted is:

$$(0.280)(1.667 \text{ M}) = 0.4668 \text{ M}$$

In the table above, we have represented the amount of NOCl that reacts as $2x$. Therefore,

$$2x = 0.4668 \text{ M}$$

$$x = 0.2334 \text{ M}$$

The equilibrium concentrations of NOCl, NO, and Cl_2 are:

$$[\text{NOCl}] = (1.67 - 2x)\text{M} = (1.667 - 0.4668)\text{M} = 1.200 \text{ M}$$

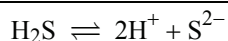
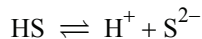
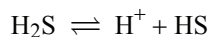
$$[\text{NO}] = 2x = 0.4668 \text{ M}$$

$$[\text{Cl}_2] = x = 0.2334 \text{ M}$$

Step 3: The equilibrium constant K_c can be calculated by substituting the above concentrations into the equilibrium constant expression.

$$K_c = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(0.4668)^2(0.2334)}{(1.200)^2} = \mathbf{0.0353}$$

14.29 The target equation is the sum of the first two.



Since this is the case, the equilibrium constant for the combined reaction is the product of the constants for the component reactions (Section 14.2 of the text). The equilibrium constant is therefore:

$$K_c = K_c'K_c'' = \mathbf{9.5 \times 10^{-27}}$$

What happens in the special case when the two component reactions are the same? Can you generalize this relationship to adding more than two reactions? What happens if one takes the difference between two reactions?

$$14.30 \quad K = K'K''$$

$$K = (6.5 \times 10^{-2})(6.1 \times 10^{-5})$$

$$K = 4.0 \times 10^{-6}$$

14.31 Given:

$$K'_P = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = 1.3 \times 10^{14}$$

$$K''_P = \frac{P_{\text{COCl}_2}}{P_{\text{CO}}P_{\text{Cl}_2}} = 6.0 \times 10^{-3}$$

For the overall reaction:

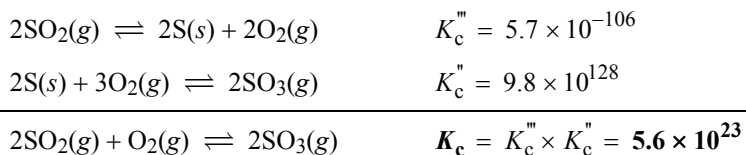
$$K_P = \frac{P_{\text{COCl}_2}^2}{P_{\text{CO}_2}P_{\text{Cl}_2}^2} = K'_P(K''_P)^2 = (1.3 \times 10^{14})(6.0 \times 10^{-3})^2 = 4.7 \times 10^9$$

14.32 To obtain 2SO_2 as a reactant in the final equation, we must reverse the first equation and multiply by two.

For the equilibrium, $2\text{SO}_2(\text{g}) \rightleftharpoons 2\text{S}(\text{s}) + 2\text{O}_2(\text{g})$

$$K_c''' = \left(\frac{1}{K_c'} \right)^2 = \left(\frac{1}{4.2 \times 10^{52}} \right)^2 = 5.7 \times 10^{-106}$$

Now we can add the above equation to the second equation to obtain the final equation. Since we add the two equations, the equilibrium constant is the product of the equilibrium constants for the two reactions.



14.35 (a) Assuming the self-ionization of water occurs by a single elementary step mechanism, the equilibrium constant is just the ratio of the forward and reverse rate constants.

$$K = \frac{k_f}{k_r} = \frac{k_1}{k_{-1}} = \frac{2.4 \times 10^{-5}}{1.3 \times 10^{11}} = 1.8 \times 10^{-16}$$

(b) The product can be written as:

$$[\text{H}^+][\text{OH}^-] = K[\text{H}_2\text{O}]$$

What is $[\text{H}_2\text{O}]$? It is the concentration of pure water. One liter of water has a mass of 1000 g (density = 1.00 g/mL). The number of moles of H_2O is:

$$1000 \text{ g} \times \frac{1 \text{ mol}}{18.0 \text{ g}} = 55.5 \text{ mol}$$

The concentration of water is 55.5 mol/1.00 L or 55.5 M. The product is:

$$[\text{H}^+][\text{OH}^-] = (1.8 \times 10^{-16})(55.5) = 1.0 \times 10^{-14}$$

We assume the concentration of hydrogen ion and hydroxide ion are equal.

$$[\text{H}^+] = [\text{OH}^-] = (1.0 \times 10^{-14})^{1/2} = 1.0 \times 10^{-7} \text{ M}$$

- 14.36** At equilibrium, the value of K_c is equal to the ratio of the forward rate constant to the rate constant for the reverse reaction.

$$K_c = \frac{k_f}{k_r} = \frac{k_f}{5.1 \times 10^{-2}} = 12.6$$

$$k_f = (12.6)(5.1 \times 10^{-2}) = 0.64$$

The forward reaction is third order, so the units of k_f must be:

$$\text{rate} = k_f[\text{A}]^2[\text{B}]$$

$$k_f = \frac{\text{rate}}{(\text{concentration})^3} = \frac{\text{M/s}}{\text{M}^3} = 1/\text{M}^2 \cdot \text{s}$$

$$k_f = 0.64 / \text{M}^2 \cdot \text{s}$$

- 14.39** Given:

$$K_p = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}} = 5.60 \times 10^4$$

Initially, the total pressure is $(0.350 + 0.762)$ atm or 1.112 atm. As the reaction progresses from left to right toward equilibrium there will be a decrease in the number of moles of molecules present. (Note that 2 moles of SO_2 react with 1 mole of O_2 to produce 2 moles of SO_3 , or, at constant pressure, three atmospheres of reactants forms two atmospheres of products.) Since pressure is directly proportional to the number of molecules present, at equilibrium the total pressure will be less than 1.112 atm.

- 14.40 Strategy:** We are given the initial concentrations of the gases, so we can calculate the reaction quotient (Q_c). How does a comparison of Q_c with K_c enable us to determine if the system is at equilibrium or, if not, in which direction the net reaction will proceed to reach equilibrium?

Solution: Recall that for a system to be at equilibrium, $Q_c = K_c$. Substitute the given concentrations into the equation for the reaction quotient to calculate Q_c .

$$Q_c = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{[0.48]^2}{[0.60][0.76]^3} = 0.87$$

Comparing Q_c to K_c , we find that $Q_c < K_c$ ($0.87 < 1.2$). The ratio of initial concentrations of products to reactants is too small. To reach equilibrium, reactants must be converted to products. The system proceeds from left to right (consuming reactants, forming products) to reach equilibrium.

Therefore, **$[\text{NH}_3]$ will increase** and **$[\text{N}_2]$ and $[\text{H}_2]$ will decrease** at equilibrium.

- 14.41** The balanced equation shows that one mole of carbon monoxide will combine with one mole of water to form hydrogen and carbon dioxide. Let x be the depletion in the concentration of either CO or H_2O at equilibrium (why can x serve to represent either quantity?). The equilibrium concentration of hydrogen must then also be equal to x . The changes are summarized as shown in the table.

	H_2	$+$	CO_2	\rightleftharpoons	H_2O	$+$	CO
Initial (M):	0		0		0.0300		0.0300
Change (M):	$+x$		$+x$		$-x$		$-x$
Equilibrium (M):	x		x		$(0.0300 - x)$		$(0.0300 - x)$

The equilibrium constant is:

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = 0.534$$

Substituting,

$$\frac{(0.0300 - x)^2}{x^2} = 0.534$$

Taking the square root of both sides, we obtain:

$$\frac{(0.0300 - x)}{x} = \sqrt{0.534}$$

$$x = 0.0173 \text{ M}$$

The number of moles of H_2 formed is:

$$0.0173 \text{ mol/L} \times 10.0 \text{ L} = \mathbf{0.173 \text{ mol H}_2}$$

14.42 Strategy: The equilibrium constant K_P is given, and we start with pure NO_2 . The partial pressure of O_2 at equilibrium is 0.25 atm. From the stoichiometry of the reaction, we can determine the partial pressure of NO at equilibrium. Knowing K_P and the partial pressures of both O_2 and NO , we can solve for the partial pressure of NO_2 .

Solution: Since the reaction started with only pure NO_2 , the equilibrium concentration of NO must be twice the equilibrium concentration of O_2 , due to the 2:1 mole ratio of the balanced equation. Therefore, the equilibrium partial pressure of **NO** is $(2 \times 0.25 \text{ atm}) = \mathbf{0.50 \text{ atm}}$.

We can find the equilibrium NO_2 pressure by rearranging the equilibrium constant expression, then substituting in the known values.

$$K_P = \frac{P_{\text{NO}}^2 P_{\text{O}_2}}{P_{\text{NO}_2}^2}$$

$$P_{\text{NO}_2} = \sqrt{\frac{P_{\text{NO}}^2 P_{\text{O}_2}}{K_P}} = \sqrt{\frac{(0.50)^2 (0.25)}{158}} = \mathbf{0.020 \text{ atm}}$$

14.43 Notice that the balanced equation requires that for every two moles of HBr consumed, one mole of H_2 and one mole of Br_2 must be formed. Let $2x$ be the depletion in the concentration of HBr at equilibrium. The equilibrium concentrations of H_2 and Br_2 must therefore each be x . The changes are shown in the table.

	H_2	$+$	Br_2	\rightleftharpoons	2HBr
Initial (M):	0		0		0.267
Change (M):	$+x$		$+x$		$-2x$
Equilibrium (M):	x		x		$(0.267 - 2x)$

The equilibrium constant relationship is given by:

$$K_c = \frac{[\text{HBr}]^2}{[\text{H}_2][\text{Br}_2]}$$

Substitution of the equilibrium concentration expressions gives

$$K_c = \frac{(0.267 - 2x)^2}{x^2} = 2.18 \times 10^6$$

Taking the square root of both sides we obtain:

$$\frac{0.267 - 2x}{x} = 1.48 \times 10^3$$

$$x = 1.80 \times 10^{-4}$$

The equilibrium concentrations are:

$$[\text{H}_2] = [\text{Br}_2] = 1.80 \times 10^{-4} \text{ M}$$

$$[\text{HBr}] = 0.267 - 2(1.80 \times 10^{-4}) = 0.267 \text{ M}$$

If the depletion in the concentration of HBr at equilibrium were defined as x , rather than $2x$, what would be the appropriate expressions for the equilibrium concentrations of H_2 and Br_2 ? Should the final answers be different in this case?

14.44 Strategy: We are given the initial amount of I_2 (in moles) in a vessel of known volume (in liters), so we can calculate its molar concentration. Because initially no I atoms are present, the system could not be at equilibrium. Therefore, some I_2 will dissociate to form I atoms until equilibrium is established.

Solution: We follow the procedure outlined in Section 14.4 of the text to calculate the equilibrium concentrations.

Step 1: The initial concentration of I_2 is $0.0456 \text{ mol}/2.30 \text{ L} = 0.0198 \text{ M}$. The stoichiometry of the problem shows 1 mole of I_2 dissociating to 2 moles of I atoms. Let x be the amount (in mol/L) of I_2 dissociated. It follows that the equilibrium concentration of I atoms must be $2x$. We summarize the changes in concentrations as follows:

	$\text{I}_2(\text{g})$	\rightleftharpoons	$2\text{I}(\text{g})$
Initial (M):	0.0198		0.000
Change (M):	$-x$		$+2x$
Equilibrium (M):	$(0.0198 - x)$		$2x$

Step 2: Write the equilibrium constant expression in terms of the equilibrium concentrations. Knowing the value of the equilibrium constant, solve for x .

$$K_c = \frac{[\text{I}]^2}{[\text{I}_2]} = \frac{(2x)^2}{(0.0198 - x)} = 3.80 \times 10^{-5}$$

$$4x^2 + (3.80 \times 10^{-5})x - (7.52 \times 10^{-7}) = 0$$

The above equation is a quadratic equation of the form $ax^2 + bx + c = 0$. The solution for a quadratic equation is

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Here, we have $a = 4$, $b = 3.80 \times 10^{-5}$, and $c = -7.52 \times 10^{-7}$. Substituting into the above equation,

$$x = \frac{(-3.80 \times 10^{-5}) \pm \sqrt{(3.80 \times 10^{-5})^2 - 4(4)(-7.52 \times 10^{-7})}}{2(4)}$$

$$x = \frac{(-3.80 \times 10^{-5}) \pm (3.47 \times 10^{-3})}{8}$$

$$x = 4.29 \times 10^{-4} M \quad \text{or} \quad x = -4.39 \times 10^{-4} M$$

The second solution is physically impossible because you cannot have a negative concentration. The first solution is the correct answer.

Step 3: Having solved for x , calculate the equilibrium concentrations of all species.

$$[\text{I}] = 2x = (2)(4.29 \times 10^{-4} M) = \mathbf{8.58 \times 10^{-4} M}$$

$$[\text{I}_2] = (0.0198 - x) = [0.0198 - (4.29 \times 10^{-4})] M = \mathbf{0.0194 M}$$

Tip: We could have simplified this problem by assuming that x was small compared to 0.0198. We could then assume that $0.0198 - x \approx 0.0198$. By making this assumption, we could have avoided solving a quadratic equation.

14.45 Since equilibrium pressures are desired, we calculate K_P .

$$K_P = K_c(0.0821 T)^{\Delta n} = (4.63 \times 10^{-3})(0.0821 \times 800)^1 = 0.304$$

	$\text{COCl}_2(\text{g})$	\rightleftharpoons	$\text{CO}(\text{g})$	$+$	$\text{Cl}_2(\text{g})$
Initial (atm):	0.760		0.000		0.000
Change (atm):	$-x$		$+x$		$+x$
Equilibrium (atm):	$(0.760 - x)$		x		x

$$\frac{x^2}{(0.760 - x)} = 0.304$$

$$x^2 + 0.304x - 0.231 = 0$$

$$x = 0.352 \text{ atm}$$

At equilibrium:

$$P_{\text{COCl}_2} = (0.760 - 0.352) \text{ atm} = \mathbf{0.408 \text{ atm}}$$

$$P_{\text{CO}} = \mathbf{0.352 \text{ atm}}$$

$$P_{\text{Cl}_2} = \mathbf{0.352 \text{ atm}}$$

- 14.46 (a) The equilibrium constant, K_c , can be found by simple substitution.

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{CO}_2][\text{H}_2]} = \frac{(0.040)(0.050)}{(0.086)(0.045)} = \mathbf{0.52}$$

- (b) The magnitude of the reaction quotient Q_c for the system after the concentration of CO_2 becomes 0.50 mol/L, but before equilibrium is reestablished, is:

$$Q_c = \frac{(0.040)(0.050)}{(0.50)(0.045)} = 0.089$$

The value of Q_c is smaller than K_c ; therefore, the system will shift to the right, increasing the concentrations of CO and H_2O and decreasing the concentrations of CO_2 and H_2 . Let x be the depletion in the concentration of CO_2 at equilibrium. The stoichiometry of the balanced equation then requires that the decrease in the concentration of H_2 must also be x , and that the concentration increases of CO and H_2O be equal to x as well. The changes in the original concentrations are shown in the table.

	CO_2	+	H_2	\rightleftharpoons	CO	+	H_2O
Initial (M):	0.50		0.045		0.050		0.040
Change (M):	$-x$		$-x$		$+x$		$+x$
Equilibrium (M):	$(0.50 - x)$		$(0.045 - x)$		$(0.050 + x)$		$(0.040 + x)$

The equilibrium constant expression is:

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{CO}_2][\text{H}_2]} = \frac{(0.040 + x)(0.050 + x)}{(0.50 - x)(0.045 - x)} = 0.52$$

$$0.52(x^2 - 0.545x + 0.0225) = x^2 + 0.090x + 0.0020$$

$$0.48x^2 + 0.373x - (9.7 \times 10^{-3}) = 0$$

The positive root of the equation is $x = 0.025$.

The equilibrium concentrations are:

$$[\text{CO}_2] = (0.50 - 0.025) M = \mathbf{0.48 M}$$

$$[\text{H}_2] = (0.045 - 0.025) M = \mathbf{0.020 M}$$

$$[\text{CO}] = (0.050 + 0.025) M = \mathbf{0.075 M}$$

$$[\text{H}_2\text{O}] = (0.040 + 0.025) M = \mathbf{0.065 M}$$

- 14.47 The equilibrium constant expression for the system is:

$$K_P = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}}$$

The total pressure can be expressed as:

$$P_{\text{total}} = P_{\text{CO}_2} + P_{\text{CO}}$$

If we let the partial pressure of CO be x , then the partial pressure of CO_2 is:

$$P_{\text{CO}_2} = P_{\text{total}} - x = (4.50 - x)\text{atm}$$

Substitution gives the equation:

$$K_P = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} = \frac{x^2}{(4.50 - x)} = 1.52$$

This can be rearranged to the quadratic:

$$x^2 + 1.52x - 6.84 = 0$$

The solutions are $x = 1.96$ and $x = -3.48$; only the positive result has physical significance (why?). The equilibrium pressures are

$$P_{\text{CO}} = x = \mathbf{1.96 \text{ atm}}$$

$$P_{\text{CO}_2} = (4.50 - 1.96) = \mathbf{2.54 \text{ atm}}$$

14.48 The initial concentrations are $[\text{H}_2] = 0.80 \text{ mol}/5.0 \text{ L} = 0.16 \text{ M}$ and $[\text{CO}_2] = 0.80 \text{ mol}/5.0 \text{ L} = 0.16 \text{ M}$.

	$\text{H}_2(\text{g})$	+	$\text{CO}_2(\text{g})$	\rightleftharpoons	$\text{H}_2\text{O}(\text{g})$	+	$\text{CO}(\text{g})$
Initial (M):	0.16		0.16		0.00		0.00
Change (M):	-x		-x		+x		+x
Equilibrium (M):	$0.16 - x$		$0.16 - x$		x		x

$$K_c = \frac{[\text{H}_2\text{O}][\text{CO}]}{[\text{H}_2][\text{CO}_2]} = 4.2 = \frac{x^2}{(0.16 - x)^2}$$

Taking the square root of both sides, we obtain:

$$\frac{x}{0.16 - x} = 2.0$$

$$x = 0.11 \text{ M}$$

The equilibrium concentrations are:

$$[\text{H}_2] = [\text{CO}_2] = (0.16 - 0.11) \text{ M} = \mathbf{0.05 \text{ M}}$$

$$[\text{H}_2\text{O}] = [\text{CO}] = \mathbf{0.11 \text{ M}}$$

- 14.53** (a) Addition of more $\text{Cl}_2(\text{g})$ (a reactant) would shift the position of equilibrium to the **right**.
 (b) Removal of $\text{SO}_2\text{Cl}_2(\text{g})$ (a product) would shift the position of equilibrium to the **right**.
 (c) Removal of $\text{SO}_2(\text{g})$ (a reactant) would shift the position of equilibrium to the **left**.
- 14.54** (a) Removal of $\text{CO}_2(\text{g})$ from the system would shift the position of equilibrium to the **right**.
 (b) Addition of more solid Na_2CO_3 would have **no effect**. $[\text{Na}_2\text{CO}_3]$ does not appear in the equilibrium constant expression.
 (c) Removal of some of the solid NaHCO_3 would have **no effect**. Same reason as (b).

- 14.55** (a) This reaction is endothermic. (Why?) According to Section 14.5, an increase in temperature favors an endothermic reaction, so the equilibrium constant should become **larger**.
- (b) This reaction is exothermic. Such reactions are favored by decreases in temperature. The magnitude of K_c should **decrease**.
- (c) In this system heat is neither absorbed nor released. A change in temperature should have **no effect** on the magnitude of the equilibrium constant.

14.56 Strategy: A change in pressure can affect only the volume of a gas, but not that of a solid or liquid because solids and liquids are much less compressible. The stress applied is an increase in pressure. According to Le Châtelier's principle, the system will adjust to partially offset this stress. In other words, the system will adjust to decrease the pressure. This can be achieved by shifting to the side of the equation that has fewer moles of gas. Recall that pressure is directly proportional to moles of gas: $PV = nRT$ so $P \propto n$.

Solution:

- (a) Changes in pressure ordinarily do not affect the concentrations of reacting species in condensed phases because liquids and solids are virtually incompressible. Pressure change should have **no effect** on this system.
- (b) Same situation as (a).
- (c) Only the product is in the gas phase. An increase in pressure should favor the reaction that decreases the total number of moles of gas. The equilibrium should shift to the **left**, that is, the amount of B should decrease and that of A should increase.
- (d) In this equation there are equal moles of gaseous reactants and products. A shift in either direction will have no effect on the total number of moles of gas present. There will be **no change** when the pressure is increased.
- (e) A shift in the direction of the reverse reaction (**left**) will have the result of decreasing the total number of moles of gas present.
- 14.57** (a) A pressure increase will favor the reaction (forward or reverse?) that decreases the total number of moles of gas. The equilibrium should shift to the **right**, i.e., more I_2 will be produced at the expense of I.
- (b) If the concentration of I_2 is suddenly altered, the system is no longer at equilibrium. Evaluating the magnitude of the reaction quotient Q_c allows us to predict the direction of the resulting equilibrium shift. The reaction quotient for this system is:

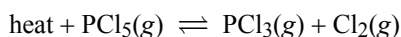
$$Q_c = \frac{[I_2]_0}{[I]_0^2}$$

Increasing the concentration of I_2 will increase Q_c . The equilibrium will be reestablished in such a way that Q_c is again equal to the equilibrium constant. More I will form. The system shifts to the **left** to establish equilibrium.

- (c) The forward reaction is exothermic. A decrease in temperature will shift the system to the **right** to reestablish equilibrium.
- 14.58 Strategy:** (a) What does the sign of ΔH° indicate about the heat change (endothermic or exothermic) for the forward reaction? (b) The stress is the addition of Cl_2 gas. How will the system adjust to partially offset the stress? (c) The stress is the removal of PCl_3 gas. How will the system adjust to partially offset the stress? (d) The stress is an increase in pressure. The system will adjust to decrease the pressure. Remember, pressure is directly proportional to moles of gas. (e) What is the function of a catalyst? How does it affect a reacting system not at equilibrium? at equilibrium?

Solution:

- (a) The stress applied is the heat added to the system. Note that the reaction is endothermic ($\Delta H^\circ > 0$). Endothermic reactions absorb heat from the surroundings; therefore, we can think of heat as a reactant.



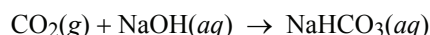
The system will adjust to remove some of the added heat by undergoing a decomposition reaction (from **left to right**)

- (b) The stress is the addition of Cl_2 gas. The system will shift in the direction to remove some of the added Cl_2 . The system shifts from **right to left** until equilibrium is reestablished.
- (c) The stress is the removal of PCl_3 gas. The system will shift to replace some of the PCl_3 that was removed. The system shifts from **left to right** until equilibrium is reestablished.
- (d) The stress applied is an increase in pressure. The system will adjust to remove the stress by decreasing the pressure. Recall that pressure is directly proportional to the number of moles of gas. In the balanced equation we see 1 mole of gas on the reactants side and 2 moles of gas on the products side. The pressure can be decreased by shifting to the side with the fewer moles of gas. The system will shift from **right to left** to reestablish equilibrium.
- (e) The function of a catalyst is to increase the rate of a reaction. If a catalyst is added to the reacting system not at equilibrium, the system will reach equilibrium faster than if left undisturbed. If a system is already at equilibrium, as in this case, the addition of a catalyst will not affect either the concentrations of reactant and product, or the equilibrium constant.
- 14.59** (a) Increasing the temperature favors the endothermic reaction so that the concentrations of SO_2 and O_2 will increase while that of SO_3 will decrease.
- (b) Increasing the pressure favors the reaction that decreases the number of moles of gas. The concentration of SO_3 will increase.
- (c) Increasing the concentration of SO_2 will lead to an increase in the concentration of SO_3 and a decrease in the concentration of O_2 .
- (d) A catalyst has no effect on the position of equilibrium.
- (e) Adding an inert gas at constant volume has no effect on the position of equilibrium.
- 14.60** There will be no change in the pressures. A catalyst has no effect on the position of the equilibrium.
- 14.61** (a) If helium gas is added to the system without changing the pressure or the temperature, the volume of the container must necessarily be increased. This will decrease the partial pressures of all the reactants and products. A pressure decrease will favor the reaction that increases the number of moles of gas. The position of equilibrium will shift to the **left**.
- (b) If the volume remains unchanged, the partial pressures of all the reactants and products will remain the same. The reaction quotient Q_c will still equal the equilibrium constant, and there will be **no change** in the position of equilibrium.
- 14.62** For this system, $K_P = [\text{CO}_2]$.
This means that to remain at equilibrium, the pressure of carbon dioxide must stay at a fixed value as long as the temperature remains the same.

- (a) If the volume is increased, the pressure of CO_2 will drop (Boyle's law, pressure and volume are inversely proportional). Some CaCO_3 will break down to form more CO_2 and CaO . (**Shift right**)
- (b) Assuming that the amount of added solid CaO is not so large that the volume of the system is altered significantly, there should be **no change** at all. If a huge amount of CaO were added, this would have the effect of reducing the volume of the container. What would happen then?
- (c) Assuming that the amount of CaCO_3 removed doesn't alter the container volume significantly, there should be **no change**. Removing a huge amount of CaCO_3 will have the effect of increasing the container volume. The result in that case will be the same as in part (a).

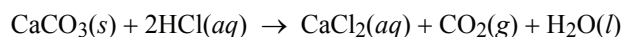
- (d) The pressure of CO_2 will be greater and will exceed the value of K_P . Some CO_2 will combine with CaO to form more CaCO_3 . (**Shift left**)

- (e) Carbon dioxide combines with aqueous NaOH according to the equation



This will have the effect of reducing the CO_2 pressure and causing more CaCO_3 to break down to CO_2 and CaO . (**Shift right**)

- (f) Carbon dioxide does not react with hydrochloric acid, but CaCO_3 does.



The CO_2 produced by the action of the acid will combine with CaO as discussed in (d) above. (**Shift left**)

- (g) This is a decomposition reaction. Decomposition reactions are endothermic. Increasing the temperature will favor this reaction and produce more CO_2 and CaO . (**Shift right**)

- 14.63** (i) The temperature of the system is not given.
 (ii) It is not stated whether the equilibrium constant is K_P or K_C (would they be different for this reaction?).
 (iii) A balanced equation is not given.
 (iv) The phases of the reactants and products are not given.

- 14.64** (a) Since the total pressure is 1.00 atm, the sum of the partial pressures of NO and Cl_2 is

$$1.00 \text{ atm} - \text{partial pressure of NOCl} = 1.00 \text{ atm} - 0.64 \text{ atm} = 0.36 \text{ atm}$$

The stoichiometry of the reaction requires that the partial pressure of NO be twice that of Cl_2 . Hence, the partial pressure of NO is **0.24 atm** and the partial pressure of Cl_2 is **0.12 atm**.

- (b) The equilibrium constant K_P is found by substituting the partial pressures calculated in part (a) into the equilibrium constant expression.

$$K_P = \frac{P_{\text{NO}}^2 P_{\text{Cl}_2}}{P_{\text{NOCl}}^2} = \frac{(0.24)^2 (0.12)}{(0.64)^2} = \mathbf{0.017}$$

- 14.65** (a) $K_P = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} P_{\text{O}_2}} = \frac{P_{\text{NO}}^2}{(3.0)(0.012)} = 2.9 \times 10^{-11}$

$$P_{\text{NO}} = 1.0 \times 10^{-6} \text{ atm}$$

$$(b) \quad 4.0 \times 10^{-31} = \frac{P_{\text{NO}}^2}{(0.78)(0.21)}$$

$$P_{\text{NO}} = 2.6 \times 10^{-16} \text{ atm}$$

- (c) Since K_P increases with temperature, it is endothermic.
 (d) Lightening. The electrical energy promotes the endothermic reaction.

14.66 The equilibrium expression for this system is given by:

$$K_P = P_{\text{CO}_2} P_{\text{H}_2\text{O}}$$

- (a) In a closed vessel the decomposition will stop when the product of the partial pressures of CO_2 and H_2O equals K_P . Adding more sodium bicarbonate will have **no effect**.
 (b) In an open vessel, $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ will escape from the vessel, and the partial pressures of CO_2 and H_2O will never become large enough for their product to equal K_P . Therefore, equilibrium will never be established. Adding more sodium bicarbonate will result in the production of **more CO_2 and H_2O** .

14.67 The relevant relationships are:

$$K_c = \frac{[\text{B}]^2}{[\text{A}]} \quad \text{and} \quad K_P = \frac{P_{\text{B}}^2}{P_{\text{A}}}$$

$$K_P = K_c(0.0821 T)^{\Delta n} = K_c(0.0821 T) \quad \Delta n = +1$$

We set up a table for the calculated values of K_c and K_P .

T ($^{\circ}\text{C}$)	K_c	K_P
200	$\frac{(0.843)^2}{(0.0125)} = 56.9$	$56.9(0.0821 \times 473) = 2.21 \times 10^3$
300	$\frac{(0.764)^2}{(0.171)} = 3.41$	$3.41(0.0821 \times 573) = 1.60 \times 10^2$
400	$\frac{(0.724)^2}{(0.250)} = 2.10$	$2.10(0.0821 \times 673) = 116$

Since K_c (and K_P) decrease with temperature, the reaction is exothermic.

14.68 (a) The equation that relates K_P and K_c is:

$$K_P = K_c(0.0821 T)^{\Delta n}$$

For this reaction, $\Delta n = 3 - 2 = 1$

$$K_c = \frac{K_P}{(0.0821 T)} = \frac{2 \times 10^{-42}}{(0.0821 \times 298)} = 8 \times 10^{-44}$$

- (b) Because of a very large activation energy, the reaction of hydrogen with oxygen is infinitely slow without a catalyst or an initiator. The action of a single spark on a mixture of these gases results in the explosive formation of water.

14.69 Using data from Appendix 3 we calculate the enthalpy change for the reaction.

$$\Delta H^\circ = 2\Delta H_f^\circ(\text{NOCl}) - 2\Delta H_f^\circ(\text{NO}) - \Delta H_f^\circ(\text{Cl}_2) = 2(51.7 \text{ kJ/mol}) - 2(90.4 \text{ kJ/mol}) - (0) = -77.4 \text{ kJ/mol}$$

The enthalpy change is negative, so the reaction is exothermic. The formation of NOCl will be favored by low temperature.

A pressure increase favors the reaction forming fewer moles of gas. The formation of NOCl will be favored by high pressure.

14.70 (a) Calculate the value of K_P by substituting the equilibrium partial pressures into the equilibrium constant expression.

$$K_P = \frac{P_B}{P_A^2} = \frac{(0.60)}{(0.60)^2} = 1.7$$

(b) The total pressure is the sum of the partial pressures for the two gaseous components, A and B. We can write:

$$P_A + P_B = 1.5 \text{ atm}$$

and

$$P_B = 1.5 - P_A$$

Substituting into the expression for K_P gives:

$$K_P = \frac{(1.5 - P_A)}{P_A^2} = 1.7$$

$$1.7P_A^2 + P_A - 1.5 = 0$$

Solving the quadratic equation, we obtain:

$$P_A = 0.69 \text{ atm}$$

and by difference,

$$P_B = 0.81 \text{ atm}$$

Check that substituting these equilibrium concentrations into the equilibrium constant expression gives the equilibrium constant calculated in part (a).

$$K_P = \frac{P_B}{P_A^2} = \frac{0.81}{(0.69)^2} = 1.7$$

14.71 (a) The balanced equation shows that equal amounts of ammonia and hydrogen sulfide are formed in this decomposition. The partial pressures of these gases must just be half the total pressure, i.e., 0.355 atm. The value of K_P is

$$K_P = P_{\text{NH}_3} P_{\text{H}_2\text{S}} = (0.355)^2 = 0.126$$

(b) We find the number of moles of ammonia (or hydrogen sulfide) and ammonium hydrogen sulfide.

$$n_{\text{NH}_3} = \frac{PV}{RT} = \frac{(0.355 \text{ atm})(4.000 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(297 \text{ K})} = 0.0582 \text{ mol}$$

$$n_{\text{NH}_4\text{HS}} = 6.1589 \text{ g} \times \frac{1 \text{ mol}}{51.12 \text{ g}} = 0.1205 \text{ mol (before decomposition)}$$

From the balanced equation the percent decomposed is

$$\frac{0.0582 \text{ mol}}{0.1205 \text{ mol}} \times 100\% = \mathbf{48.3\%}$$

(c) If the temperature does not change, K_P has the same value. The total pressure will still be 0.709 atm at equilibrium. In other words the amounts of ammonia and hydrogen sulfide will be twice as great, and the amount of solid ammonium hydrogen sulfide will be:

$$[0.1205 - 2(0.0582)]\text{mol} = \mathbf{0.0041 \text{ mol NH}_4\text{HS}}$$

14.72 Total number of moles of gas is:

$$0.020 + 0.040 + 0.96 = 1.02 \text{ mol of gas}$$

You can calculate the partial pressure of each gaseous component from the mole fraction and the total pressure.

$$P_{\text{NO}} = X_{\text{NO}} P_T = \frac{0.040}{1.02} \times 0.20 = 0.0078 \text{ atm}$$

$$P_{\text{O}_2} = X_{\text{O}_2} P_T = \frac{0.020}{1.02} \times 0.20 = 0.0039 \text{ atm}$$

$$P_{\text{NO}_2} = X_{\text{NO}_2} P_T = \frac{0.96}{1.02} \times 0.20 = 0.19 \text{ atm}$$

Calculate K_P by substituting the partial pressures into the equilibrium constant expression.

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{NO}}^2 P_{\text{O}_2}} = \frac{(0.19)^2}{(0.0078)^2 (0.0039)} = \mathbf{1.5 \times 10^5}$$

14.73 Since the reactant is a solid, we can write:

$$K_P = (P_{\text{NH}_3})^2 P_{\text{CO}_2}$$

The total pressure is the sum of the ammonia and carbon dioxide pressures.

$$P_{\text{total}} = P_{\text{NH}_3} + P_{\text{CO}_2}$$

From the stoichiometry,

$$P_{\text{NH}_3} = 2P_{\text{CO}_2}$$

Therefore:

$$P_{\text{total}} = 2P_{\text{CO}_2} + P_{\text{CO}_2} = 3P_{\text{CO}_2} = 0.318 \text{ atm}$$

$$P_{\text{CO}_2} = 0.106 \text{ atm}$$

$$P_{\text{NH}_3} = 0.212 \text{ atm}$$

Substituting into the equilibrium expression:

$$K_P = (0.212)^2(0.106) = 4.76 \times 10^{-3}$$

- 14.74** Set up a table that contains the initial concentrations, the change in concentrations, and the equilibrium concentration. Assume that the vessel has a volume of 1 L.

	H ₂	+	Cl ₂	⇌	2HCl
Initial (M):	0.47		0		3.59
Change (M):	+x		+x		-2x
Equilibrium (M):	(0.47 + x)		x		(3.59 - 2x)

Substitute the equilibrium concentrations into the equilibrium constant expression, then solve for x . Since $\Delta n = 0$, $K_c = K_P$.

$$K_c = \frac{[\text{HCl}]^2}{[\text{H}_2][\text{Cl}_2]} = \frac{(3.59 - 2x)^2}{(0.47 + x)x} = 193$$

Solving the quadratic equation,

$$x = 0.10$$

Having solved for x , calculate the equilibrium concentrations of all species.

$$[\text{H}_2] = 0.57 \text{ M} \quad [\text{Cl}_2] = 0.10 \text{ M} \quad [\text{HCl}] = 3.39 \text{ M}$$

Since we assumed that the vessel had a volume of 1 L, the above molarities also correspond to the number of moles of each component.

From the mole fraction of each component and the total pressure, we can calculate the partial pressure of each component.

$$\text{Total number of moles} = 0.57 + 0.10 + 3.39 = 4.06 \text{ mol}$$

$$P_{\text{H}_2} = \frac{0.57}{4.06} \times 2.00 = 0.28 \text{ atm}$$

$$P_{\text{Cl}_2} = \frac{0.10}{4.06} \times 2.00 = 0.049 \text{ atm}$$

$$P_{\text{HCl}} = \frac{3.39}{4.06} \times 2.00 = 1.67 \text{ atm}$$

- 14.75** Set up a table that contains the initial concentrations, the change in concentrations, and the equilibrium concentrations. The initial concentration of I₂(g) is 0.054 mol/0.48 L = 0.1125 M. The amount of I₂ that dissociates is (0.0252)(0.1125 M) = 0.002835 M. We carry extra significant figures throughout this calculation to minimize rounding errors.

	I_2	\rightleftharpoons	$2I$
Initial (M):	0.1125		0
Change (M):	-0.002835		+(2)(0.002835)
Equilibrium (M):	0.1097		0.005670

Substitute the equilibrium concentrations into the equilibrium constant expression to solve for K_c .

$$K_c = \frac{[I]^2}{[I_2]} = \frac{(0.005670)^2}{0.1097} = 2.93 \times 10^{-4} = \mathbf{2.9 \times 10^{-4}}$$

$$K_P = K_c(0.0821 T)^{\Delta n}$$

$$K_P = (2.93 \times 10^{-4})(0.0821 \times 860)^1 = \mathbf{0.021}$$

- 14.76** This is a difficult problem. Express the equilibrium number of moles in terms of the initial moles and the change in number of moles (x). Next, calculate the mole fraction of each component. Using the mole fraction, you should come up with a relationship between partial pressure and total pressure for each component. Substitute the partial pressures into the equilibrium constant expression to solve for the total pressure, P_T .

The reaction is:

	N_2	+	$3 H_2$	\rightleftharpoons	$2 NH_3$
Initial (mol):	1		3		0
Change (mol):	- x		- $3x$		$2x$
Equilibrium (mol):	$(1 - x)$		$(3 - 3x)$		$2x$

$$\text{Mole fraction of } NH_3 = \frac{\text{mol of } NH_3}{\text{total number of moles}}$$

$$X_{NH_3} = \frac{2x}{(1 - x) + (3 - 3x) + 2x} = \frac{2x}{4 - 2x}$$

$$0.21 = \frac{2x}{4 - 2x}$$

$$x = 0.35 \text{ mol}$$

Substituting x into the following mole fraction equations, the mole fractions of N_2 and H_2 can be calculated.

$$X_{N_2} = \frac{1 - x}{4 - 2x} = \frac{1 - 0.35}{4 - 2(0.35)} = 0.20$$

$$X_{H_2} = \frac{3 - 3x}{4 - 2x} = \frac{3 - 3(0.35)}{4 - 2(0.35)} = 0.59$$

The partial pressures of each component are equal to the mole fraction multiplied by the total pressure.

$$P_{NH_3} = 0.21P_T \quad P_{N_2} = 0.20P_T \quad P_{H_2} = 0.59P_T$$

Substitute the partial pressures above (in terms of P_T) into the equilibrium constant expression, and solve for P_T .

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

$$4.31 \times 10^{-4} = \frac{(0.21)^2 P_T^2}{(0.59 P_T)^3 (0.20 P_T)}$$

$$4.31 \times 10^{-4} = \frac{1.07}{P_T^2}$$

$$P_T = 5.0 \times 10^1 \text{ atm}$$

14.77 For the balanced equation: $K_c = \frac{[\text{H}_2]^2 [\text{S}_2]}{[\text{H}_2\text{S}]^2}$

$$[\text{S}_2] = \frac{[\text{H}_2\text{S}]^2}{[\text{H}_2]^2} K_c = \left(\frac{4.84 \times 10^{-3}}{1.50 \times 10^{-3}} \right)^2 (2.25 \times 10^{-4}) = 2.34 \times 10^{-3} M$$

14.78 We carry an additional significant figure throughout this calculation to minimize rounding errors. The initial molarity of SO_2Cl_2 is:

$$[\text{SO}_2\text{Cl}_2] = \frac{6.75 \text{ g SO}_2\text{Cl}_2 \times \frac{1 \text{ mol SO}_2\text{Cl}_2}{135.0 \text{ g SO}_2\text{Cl}_2}}{2.00 \text{ L}} = 0.02500 M$$

The concentration of SO_2 at equilibrium is:

$$[\text{SO}_2] = \frac{0.0345 \text{ mol}}{2.00 \text{ L}} = 0.01725 M$$

Since there is a 1:1 mole ratio between SO_2 and SO_2Cl_2 , the concentration of SO_2 at equilibrium (0.01725 M) equals the concentration of SO_2Cl_2 reacted. The concentrations of SO_2Cl_2 and Cl_2 at equilibrium are:

	$\text{SO}_2\text{Cl}_2(\text{g})$	\rightleftharpoons	$\text{SO}_2(\text{g})$	+	$\text{Cl}_2(\text{g})$
Initial (M):	0.02500		0		0
Change (M):	-0.01725		+0.01725		+0.01725
Equilibrium (M):	0.00775		0.01725		0.01725

Substitute the equilibrium concentrations into the equilibrium constant expression to calculate K_c .

$$K_c = \frac{[\text{SO}_2][\text{Cl}_2]}{[\text{SO}_2\text{Cl}_2]} = \frac{(0.01725)(0.01725)}{(0.00775)} = 3.84 \times 10^{-2}$$

- 14.79** For a 100% yield, 2.00 moles of SO_3 would be formed (why?). An 80% yield means $2.00 \text{ moles} \times (0.80) = 1.60 \text{ moles}$ SO_3 is formed.

The amount of SO_2 remaining at equilibrium = $(2.00 - 1.60)\text{mol} = 0.40 \text{ mol}$

The amount of O_2 reacted = $\frac{1}{2} \times (\text{amount of } \text{SO}_2 \text{ reacted}) = (\frac{1}{2} \times 1.60)\text{mol} = 0.80 \text{ mol}$

The amount of O_2 remaining at equilibrium = $(2.00 - 0.80)\text{mol} = 1.20 \text{ mol}$

Total moles at equilibrium = moles SO_2 + moles O_2 + moles $\text{SO}_3 = (0.40 + 1.20 + 1.60) \text{ mol} = 3.20 \text{ moles}$

$$P_{\text{SO}_2} = \frac{0.40}{3.20} P_{\text{total}} = 0.125 P_{\text{total}}$$

$$P_{\text{O}_2} = \frac{1.20}{3.20} P_{\text{total}} = 0.375 P_{\text{total}}$$

$$P_{\text{SO}_3} = \frac{1.60}{3.20} P_{\text{total}} = 0.500 P_{\text{total}}$$

$$K_P = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 P_{\text{O}_2}}$$

$$0.13 = \frac{(0.500 P_{\text{total}})^2}{(0.125 P_{\text{total}})^2 (0.375 P_{\text{total}})}$$

$$P_{\text{total}} = \mathbf{328 \text{ atm}}$$

- 14.80** $\text{I}_2(\text{g}) \rightleftharpoons 2\text{I}(\text{g})$

Assuming 1 mole of I_2 is present originally and α moles reacts, at equilibrium: $[\text{I}_2] = 1 - \alpha$, $[\text{I}] = 2\alpha$. The total number of moles present in the system = $(1 - \alpha) + 2\alpha = 1 + \alpha$. From Problem 14.109(a) in the text, we know that K_P is equal to:

$$K_P = \frac{4\alpha^2}{1 - \alpha^2} P \quad (1)$$

If there were no dissociation, then the pressure would be:

$$P = \frac{nRT}{V} = \frac{\left(1.00 \text{ g} \times \frac{1 \text{ mol}}{253.8 \text{ g}}\right) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (1473 \text{ K})}{0.500 \text{ L}} = 0.953 \text{ atm}$$

$$\frac{\text{observed pressure}}{\text{calculated pressure}} = \frac{1.51 \text{ atm}}{0.953 \text{ atm}} = \frac{1 + \alpha}{1}$$

$$\alpha = 0.584$$

Substituting in equation (1) above:

$$K_P = \frac{4\alpha^2}{1 - \alpha^2} P = \frac{(4)(0.584)^2}{1 - (0.584)^2} \times 1.51 = \mathbf{3.13}$$

- 14.81** Panting decreases the concentration of CO_2 because CO_2 is exhaled during respiration. This decreases the concentration of carbonate ions, shifting the equilibrium to the left. Less CaCO_3 is produced. Two possible solutions would be either to cool the chickens' environment or to feed them carbonated water.
- 14.82** According to the ideal gas law, pressure is directly proportional to the concentration of a gas in mol/L if the reaction is at constant volume and temperature. Therefore, pressure may be used as a concentration unit. The reaction is:

	N_2	+	3H_2	\rightleftharpoons	2NH_3
Initial (atm):	0.862		0.373		0
Change (atm):	$-x$		$-3x$		$+2x$
Equilibrium (atm):	$(0.862 - x)$		$(0.373 - 3x)$		$2x$

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

$$4.31 \times 10^{-4} = \frac{(2x)^2}{(0.373 - 3x)^3 (0.862 - x)}$$

At this point, we need to make two assumptions that $3x$ is very small compared to 0.373 and that x is very small compared to 0.862. Hence,

$$0.373 - 3x \approx 0.373$$

and

$$0.862 - x \approx 0.862$$

$$4.31 \times 10^{-4} \approx \frac{(2x)^2}{(0.373)^3 (0.862)}$$

Solving for x ,

$$x = 2.20 \times 10^{-3} \text{ atm}$$

The equilibrium pressures are:

$$P_{\text{N}_2} = [0.862 - (2.20 \times 10^{-3})] \text{ atm} = \mathbf{0.860 \text{ atm}}$$

$$P_{\text{H}_2} = [0.373 - (3)(2.20 \times 10^{-3})] \text{ atm} = \mathbf{0.366 \text{ atm}}$$

$$P_{\text{NH}_3} = (2)(2.20 \times 10^{-3} \text{ atm}) = \mathbf{4.40 \times 10^{-3} \text{ atm}}$$

Was the assumption valid that we made above? Typically, the assumption is considered valid if x is less than 5 percent of the number that we said it was very small compared to. Is this the case?

- 14.83 (a)** The sum of the mole fractions must equal one.

$$X_{\text{CO}} + X_{\text{CO}_2} = 1 \quad \text{and} \quad X_{\text{CO}_2} = 1 - X_{\text{CO}}$$

According to the hint, the average molar mass is the sum of the products of the mole fraction of each gas and its molar mass.

$$(X_{\text{CO}} \times 28.01 \text{ g}) + [(1 - X_{\text{CO}}) \times 44.01 \text{ g}] = 35 \text{ g}$$

Solving,

$$X_{\text{CO}} = \mathbf{0.56} \quad \text{and} \quad X_{\text{CO}_2} = \mathbf{0.44}$$

(b) Solving for the pressures $P_{\text{total}} = P_{\text{CO}} + P_{\text{CO}_2} = 11 \text{ atm}$

$$P_{\text{CO}} = X_{\text{CO}}P_{\text{total}} = (0.56)(11 \text{ atm}) = 6.2 \text{ atm}$$

$$P_{\text{CO}_2} = X_{\text{CO}_2}P_{\text{total}} = (0.44)(11 \text{ atm}) = 4.8 \text{ atm}$$

$$K_P = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}} = \frac{(6.2)^2}{4.8} = \mathbf{8.0}$$

14.84 (a) The equation is:

	fructose	\rightleftharpoons	glucose
Initial (M):	0.244		0
Change (M):	-0.131		+0.131
Equilibrium (M):	0.113		0.131

Calculating the equilibrium constant,

$$K_c = \frac{[\text{glucose}]}{[\text{fructose}]} = \frac{0.131}{0.113} = \mathbf{1.16}$$

(b) **Percent converted** = $\frac{\text{amount of fructose converted}}{\text{original amount of fructose}} \times 100\%$

$$= \frac{0.131}{0.244} \times 100\% = \mathbf{53.7\%}$$

14.85 If you started with radioactive iodine in the solid phase, then you should find radioactive iodine in the vapor phase at equilibrium. Conversely, if you started with radioactive iodine in the vapor phase, you should find radioactive iodine in the solid phase. Both of these observations indicate a dynamic equilibrium between solid and vapor phase.

14.86 (a) There is only one gas phase component, O_2 . The equilibrium constant is simply

$$K_P = P_{\text{O}_2} = \mathbf{0.49 \text{ atm}}$$

(b) From the ideal gas equation, we can calculate the moles of O_2 produced by the decomposition of CuO .

$$n_{\text{O}_2} = \frac{PV}{RT} = \frac{(0.49 \text{ atm})(2.0 \text{ L})}{(0.0821 \text{ L} \cdot \text{atm}/\text{K} \cdot \text{mol})(1297 \text{ K})} = 9.2 \times 10^{-3} \text{ mol O}_2$$

From the balanced equation,

$$(9.2 \times 10^{-3} \text{ mol O}_2) \times \frac{4 \text{ mol CuO}}{1 \text{ mol O}_2} = 3.7 \times 10^{-2} \text{ mol CuO decomposed}$$

$$\text{Fraction of CuO decomposed} = \frac{\text{amount of CuO lost}}{\text{original amount of CuO}}$$

$$= \frac{3.7 \times 10^{-2} \text{ mol}}{0.16 \text{ mol}} = \mathbf{0.23}$$

- (c) If a 1.0 mol sample were used, the pressure of oxygen would still be the same (0.49 atm) and it would be due to the same quantity of O_2 . Remember, a pure solid does not affect the equilibrium position. The moles of CuO lost would still be 3.7×10^{-2} mol. Thus the fraction decomposed would be:

$$\frac{0.037}{1.0} = \mathbf{0.037}$$

- (d) If the number of moles of CuO were less than 3.7×10^{-2} mol, the equilibrium could not be established because the pressure of O_2 would be less than 0.49 atm. Therefore, the smallest number of moles of CuO needed to establish equilibrium must be slightly greater than 3.7×10^{-2} mol.

- 14.87** If there were 0.88 mole of CO_2 initially and at equilibrium there were 0.11 moles, then $(0.88 - 0.11)$ moles = 0.77 moles reacted.

	NO	+	CO ₂	⇌	NO ₂	+	CO
Initial (mol):	3.9		0.88		0		0
Change (mol):	-0.77		-0.77		+0.77		+0.77
Equilibrium (mol):	(3.9 - 0.77)		0.11		0.77		0.77

Solving for the equilibrium constant:
$$K_c = \frac{(0.77)(0.77)}{(3.9 - 0.77)(0.11)} = \mathbf{1.7}$$

In the balanced equation there are equal number of moles of products and reactants; therefore, the volume of the container will not affect the calculation of K_c . We can solve for the equilibrium constant in terms of moles.

- 14.88** We first must find the initial concentrations of all the species in the system.

$$[H_2]_0 = \frac{0.714 \text{ mol}}{2.40 \text{ L}} = 0.298 \text{ M}$$

$$[I_2]_0 = \frac{0.984 \text{ mol}}{2.40 \text{ L}} = 0.410 \text{ M}$$

$$[HI]_0 = \frac{0.886 \text{ mol}}{2.40 \text{ L}} = 0.369 \text{ M}$$

Calculate the reaction quotient by substituting the initial concentrations into the appropriate equation.

$$Q_c = \frac{[HI]_0^2}{[H_2]_0[I_2]_0} = \frac{(0.369)^2}{(0.298)(0.410)} = 1.11$$

We find that Q_c is less than K_c . The equilibrium will shift to the right, decreasing the concentrations of H_2 and I_2 and increasing the concentration of HI.

We set up the usual table. Let x be the decrease in concentration of H_2 and I_2 .

	H ₂	+	I ₂	⇌	2 HI
Initial (M):	0.298		0.410		0.369
Change (M):	-x		-x		+2x
Equilibrium (M):	(0.298 - x)		(0.410 - x)		(0.369 + 2x)

The equilibrium constant expression is:

$$K_c = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} = \frac{(0.369 + 2x)^2}{(0.298 - x)(0.410 - x)} = 54.3$$

This becomes the quadratic equation

$$50.3x^2 - 39.9x + 6.48 = 0$$

The smaller root is $x = 0.228 M$. (The larger root is physically impossible.)

Having solved for x , calculate the equilibrium concentrations.

$$\begin{aligned} [\text{H}_2] &= (0.298 - 0.228) M = \mathbf{0.070 M} \\ [\text{I}_2] &= (0.410 - 0.228) M = \mathbf{0.182 M} \\ [\text{HI}] &= [0.369 + 2(0.228)] M = \mathbf{0.825 M} \end{aligned}$$

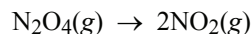
- 14.89** Since we started with pure A, then any A that is lost forms equal amounts of B and C. Since the total pressure is P , the pressure of B + C = $P - 0.14 P = 0.86 P$. The pressure of B = C = $0.43 P$.

$$K_P = \frac{P_B P_C}{P_A} = \frac{(0.43 P)(0.43 P)}{0.14 P} = \mathbf{1.3 P}$$

- 14.90** The gas cannot be (a) because the color became lighter with heating. Heating (a) to 150°C would produce some HBr, which is colorless and would lighten rather than darken the gas.

The gas cannot be (b) because Br_2 doesn't dissociate into Br atoms at 150°C , so the color shouldn't change.

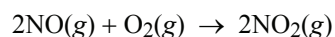
The gas must be (c). From 25°C to 150°C , heating causes N_2O_4 to dissociate into NO_2 , thus darkening the color (NO_2 is a brown gas).



Above 150°C , the NO_2 breaks up into colorless NO and O_2 .



An increase in pressure shifts the equilibrium back to the left, forming NO_2 , thus darkening the gas again.



- 14.91** Since the catalyst is exposed to the reacting system, it would catalyze the $2A \rightarrow B$ reaction. This shift would result in a decrease in the number of gas molecules, so the gas pressure decreases. The piston would be pushed down by the atmospheric pressure. When the cover is over the box, the catalyst is no longer able to favor the forward reaction. To reestablish equilibrium, the $B \rightarrow 2A$ step would dominate. This would increase the gas pressure so the piston rises and so on.

Conclusion: Such a catalyst would result in a perpetual motion machine (the piston would move up and down forever) which can be used to do work without input of energy or net consumption of chemicals. Such a machine cannot exist.

14.92 Given the following: $K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = 1.2$

(a) Temperature must have units of Kelvin.

$$K_P = K_c(0.0821 T)^{\Delta n}$$

$$K_P = (1.2)(0.0821 \times 648)^{(2-4)} = 4.2 \times 10^{-4}$$

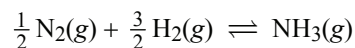
(b) Recalling that,

$$K_{\text{forward}} = \frac{1}{K_{\text{reverse}}}$$

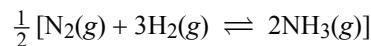
Therefore,

$$K_c' = \frac{1}{1.2} = 0.83$$

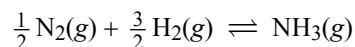
(c) Since the equation



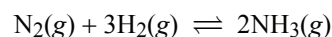
is equivalent to



then, K_c' for the reaction:



equals $(K_c)^{\frac{1}{2}}$ for the reaction:



Thus,

$$K_c' = (K_c)^{\frac{1}{2}} = \sqrt{1.2} = 1.1$$

(d) For K_P in part (b):

$$K_P = (0.83)(0.0821 \times 648)^{+2} = 2.3 \times 10^3$$

and for K_P in part (c):

$$K_P = (1.1)(0.0821 \times 648)^{-1} = 0.021$$

- 14.93** (a) Color deepens (b) increases (c) decreases
 (d) increases (e) unchanged

14.94 The vapor pressure of water is equivalent to saying the partial pressure of $\text{H}_2\text{O}(\text{g})$.

$$K_P = P_{\text{H}_2\text{O}} = 0.0231$$

$$K_c = \frac{K_P}{(0.0821 T)^{\Delta n}} = \frac{0.0231}{(0.0821 \times 293)^1} = 9.60 \times 10^{-4}$$

14.95 Potassium is more volatile than sodium. Therefore, its removal shifts the equilibrium from left to right.

14.96 We can calculate the average molar mass of the gaseous mixture from the density.

$$\mathcal{M} = \frac{dRT}{P}$$

Let $\overline{\mathcal{M}}$ be the average molar mass of NO_2 and N_2O_4 . The above equation becomes:

$$\overline{\mathcal{M}} = \frac{dRT}{P} = \frac{(2.3 \text{ g/L})(0.0821 \text{ L} \cdot \text{atm/K} \cdot \text{mol})(347 \text{ K})}{1.3 \text{ atm}}$$

$$\overline{\mathcal{M}} = 50.4 \text{ g/mol}$$

The average molar mass is equal to the sum of the molar masses of each component times the respective mole fractions. Setting this up, we can calculate the mole fraction of each component.

$$\overline{\mathcal{M}} = X_{\text{NO}_2} \mathcal{M}_{\text{NO}_2} + X_{\text{N}_2\text{O}_4} \mathcal{M}_{\text{N}_2\text{O}_4} = 50.4 \text{ g/mol}$$

$$X_{\text{NO}_2} (46.01 \text{ g/mol}) + (1 - X_{\text{NO}_2}) (92.01 \text{ g/mol}) = 50.4 \text{ g/mol}$$

$$X_{\text{NO}_2} = 0.905$$

We can now calculate the partial pressure of NO_2 from the mole fraction and the total pressure.

$$P_{\text{NO}_2} = X_{\text{NO}_2} P_T$$

$$P_{\text{NO}_2} = (0.905)(1.3 \text{ atm}) = 1.18 \text{ atm} = \mathbf{1.2 \text{ atm}}$$

We can calculate the partial pressure of N_2O_4 by difference.

$$P_{\text{N}_2\text{O}_4} = P_T - P_{\text{NO}_2}$$

$$P_{\text{N}_2\text{O}_4} = (1.3 - 1.18) \text{ atm} = \mathbf{0.12 \text{ atm}}$$

Finally, we can calculate K_P for the dissociation of N_2O_4 .

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(1.2)^2}{0.12} = \mathbf{12}$$

14.97 (a) Since both reactions are endothermic (ΔH° is positive), according to Le Châtelier's principle the products would be favored at high temperatures. Indeed, the steam-reforming process is carried out at very high temperatures (between 800°C and 1000°C). It is interesting to note that in a plant that uses natural gas (methane) for both hydrogen generation and heating, about one-third of the gas is burned to maintain the high temperatures.

In each reaction there are more moles of products than reactants; therefore, we expect products to be favored at low pressures. In reality, the reactions are carried out at high pressures. The reason is that when the hydrogen gas produced is used captively (usually in the synthesis of ammonia), high pressure leads to higher yields of ammonia.

- (b) (i) The relation between K_c and K_p is given by Equation (14.5) of the text:

$$K_p = K_c(0.0821 T)^{\Delta n}$$

Since $\Delta n = 4 - 2 = 2$, we write:

$$K_p = (18)(0.0821 \times 1073)^2 = \mathbf{1.4 \times 10^5}$$

- (ii) Let x be the amount of CH_4 and H_2O (in atm) reacted. We write:

	CH_4	+	H_2O	\rightleftharpoons	CO	+	3H_2
Initial (atm):	15		15		0		0
Change (atm):	$-x$		$-x$		$+x$		$+3x$
Equilibrium (atm):	$15 - x$		$15 - x$		x		$3x$

The equilibrium constant is given by:

$$K_p = \frac{P_{\text{CO}}P_{\text{H}_2}^3}{P_{\text{CH}_4}P_{\text{H}_2\text{O}}}$$

$$1.4 \times 10^5 = \frac{(x)(3x)^3}{(15-x)(15-x)} = \frac{27x^4}{(15-x)^2}$$

Taking the square root of both sides, we obtain:

$$3.7 \times 10^2 = \frac{5.2x^2}{15-x}$$

which can be expressed as

$$5.2x^2 + (3.7 \times 10^2 x) - (5.6 \times 10^3) = 0$$

Solving the quadratic equation, we obtain

$$x = 13 \text{ atm}$$

(The other solution for x is negative and is physically impossible.)

At equilibrium, the pressures are:

$$P_{\text{CH}_4} = (15 - 13) = \mathbf{2 \text{ atm}}$$

$$P_{\text{H}_2\text{O}} = (15 - 13) = \mathbf{2 \text{ atm}}$$

$$P_{\text{CO}} = \mathbf{13 \text{ atm}}$$

$$P_{\text{H}_2} = 3(13 \text{ atm}) = \mathbf{39 \text{ atm}}$$

- 14.98** (a) shifts to right (b) shifts to right (c) no change (d) no change
 (e) no change (f) shifts to left

$$14.99 \quad K_P = P_{\text{NH}_3} P_{\text{HCl}}$$

$$P_{\text{NH}_3} = P_{\text{HCl}} = \frac{2.2}{2} = 1.1 \text{ atm}$$

$$K_P = (1.1)(1.1) = \mathbf{1.2}$$

14.100 The equilibrium is: $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$

$$K_P = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{0.15^2}{0.20} = 0.113$$

Volume is doubled so pressure is halved. Let's calculate Q_P and compare it to K_P .

$$Q_P = \frac{\left(\frac{0.15}{2}\right)^2}{\left(\frac{0.20}{2}\right)} = 0.0563 < K_P$$

Equilibrium will shift to the right. Some N_2O_4 will react, and some NO_2 will be formed. Let x = amount of N_2O_4 reacted.

	$\text{N}_2\text{O}_4(\text{g})$	\rightleftharpoons	$2\text{NO}_2(\text{g})$
Initial (atm):	0.10		0.075
Change (atm):	$-x$		$+2x$
Equilibrium (atm):	$0.10 - x$		$0.075 + 2x$

Substitute into the K_P expression to solve for x .

$$K_P = 0.113 = \frac{(0.075 + 2x)^2}{0.10 - x}$$

$$4x^2 + 0.413x - 5.68 \times 10^{-3} = 0$$

$$x = 0.0123$$

At equilibrium:

$$P_{\text{NO}_2} = 0.075 + 2(0.0123) = 0.0996 \approx \mathbf{0.100 \text{ atm}}$$

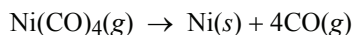
$$P_{\text{N}_2\text{O}_4} = 0.10 - 0.0123 = \mathbf{0.09 \text{ atm}}$$

Check:

$$K_P = \frac{(0.100)^2}{0.09} = 0.111 \quad \text{close enough to } 0.113$$

14.101 (a) React Ni with CO above 50°C . Pump away the $\text{Ni}(\text{CO})_4$ vapor (shift equilibrium to right), leaving the solid impurities behind.

(b) Consider the reverse reaction:



$$\Delta H^\circ = 4\Delta H_f^\circ(\text{CO}) - \Delta H_f^\circ[\text{Ni}(\text{CO})_4]$$

$$\Delta H^\circ = (4)(-110.5 \text{ kJ/mol}) - (1)(-602.9 \text{ kJ/mol}) = 160.9 \text{ kJ/mol}$$

The decomposition is endothermic, which is favored at high temperatures. Heat $\text{Ni}(\text{CO})_4$ above 200°C to convert it back to Ni.

14.102 (a) Molar mass of $\text{PCl}_5 = 208.2 \text{ g/mol}$

$$P = \frac{nRT}{V} = \frac{\left(2.50 \text{ g} \times \frac{1 \text{ mol}}{208.2 \text{ g}}\right) \left(0.0821 \frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right) (523 \text{ K})}{0.500 \text{ L}} = \mathbf{1.03 \text{ atm}}$$

(b)

	PCl_5	\rightleftharpoons	PCl_3	+	Cl_2
Initial (atm)	1.03		0		0
Change (atm)	$-x$		$+x$		$+x$
Equilibrium (atm)	$1.03 - x$		x		x

$$K_P = 1.05 = \frac{x^2}{1.03 - x}$$

$$x^2 + 1.05x - 1.08 = 0$$

$$x = 0.639$$

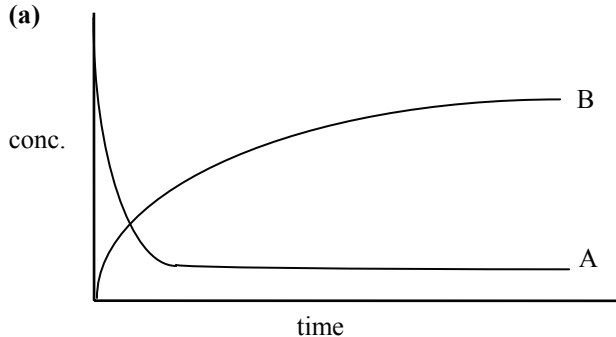
At equilibrium:

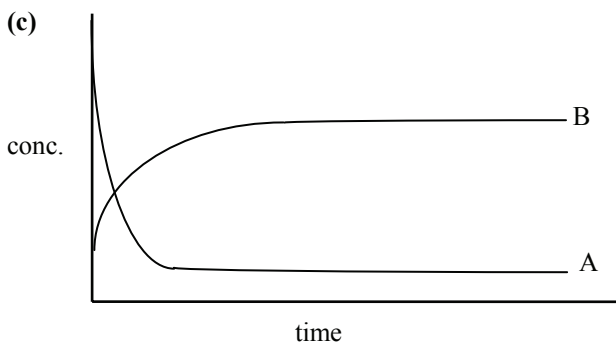
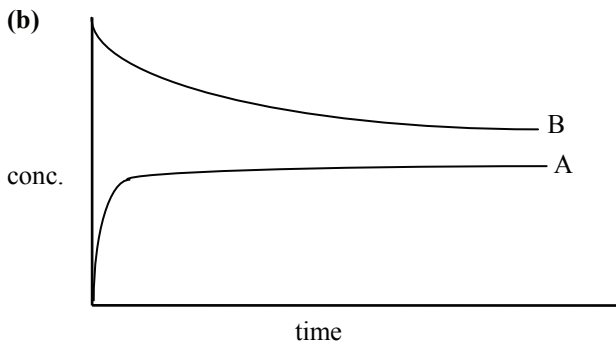
$$P_{\text{PCl}_5} = 1.03 - 0.639 = \mathbf{0.39 \text{ atm}}$$

(c) $P_T = (1.03 - x) + x + x = 1.03 + 0.639 = \mathbf{1.67 \text{ atm}}$

(d) $\frac{0.639 \text{ atm}}{1.03 \text{ atm}} = \mathbf{0.620}$

14.103 (a)





- 14.104 (a) $K_P = P_{\text{Hg}} = 0.0020 \text{ mmHg} = 2.6 \times 10^{-6} \text{ atm} = 2.6 \times 10^{-6}$ (equil. constants are expressed without units)

$$K_c = \frac{K_P}{(0.0821T)^{\Delta n}} = \frac{2.6 \times 10^{-6}}{(0.0821 \times 299)^1} = 1.1 \times 10^{-7}$$

- (b) Volume of lab = (6.1 m)(5.3 m)(3.1 m) = 100 m³

$$[\text{Hg}] = K_c$$

$$\text{Total mass of Hg vapor} = \frac{1.1 \times 10^{-7} \text{ mol}}{1 \text{ L}} \times \frac{200.6 \text{ g}}{1 \text{ mol}} \times \frac{1 \text{ L}}{1000 \text{ cm}^3} \times \left(\frac{1 \text{ cm}}{0.01 \text{ m}}\right)^3 \times 100 \text{ m}^3 = 2.2 \text{ g}$$

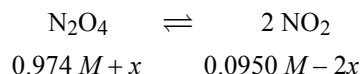
The concentration of mercury vapor in the room is:

$$\frac{2.2 \text{ g}}{100 \text{ m}^3} = 0.022 \text{ g/m}^3 = 22 \text{ mg/m}^3$$

Yes! This concentration exceeds the safety limit of 0.05 mg/m³. Better clean up the spill!

- 14.105 Initially, at equilibrium: $[\text{NO}_2] = 0.0475 \text{ M}$ and $[\text{N}_2\text{O}_4] = 0.487 \text{ M}$. At the instant the volume is halved, the concentrations double.

$[\text{NO}_2] = 2(0.0475 \text{ M}) = 0.0950 \text{ M}$ and $[\text{N}_2\text{O}_4] = 2(0.487 \text{ M}) = 0.974 \text{ M}$. The system is no longer at equilibrium. The system will shift to the left to offset the increase in pressure when the volume is halved. When a new equilibrium position is established, we write:



$$K_c = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(0.0950 - 2x)^2}{(0.974 + x)}$$

$$4x^2 - 0.3846x + 4.52 \times 10^{-3} = 0$$

Solving $x = 0.0824 M$ (impossible) and $x = 0.0137 M$

At the new equilibrium,

$$[\text{N}_2\text{O}_4] = 0.974 + 0.0137 = \mathbf{0.988 M}$$

$$[\text{NO}_2] = 0.0950 - (2 \times 0.0137) = \mathbf{0.0676 M}$$

As we can see, the new equilibrium concentration of NO_2 is *greater* than the initial equilibrium concentration ($0.0475 M$). Therefore, the gases should look *darker*!

- 14.106** There is a temporary dynamic equilibrium between the melting ice cubes and the freezing of water between the ice cubes.
- 14.107** (a) A catalyst speeds up the rates of the forward and reverse reactions to the same extent.
 (b) A catalyst would not change the energies of the reactant and product.
 (c) The first reaction is exothermic. Raising the temperature would favor the reverse reaction, increasing the amount of reactant and decreasing the amount of product at equilibrium. The equilibrium constant, K , would decrease. The second reaction is endothermic. Raising the temperature would favor the forward reaction, increasing the amount of product and decreasing the amount of reactant at equilibrium. The equilibrium constant, K , would increase.
 (d) A catalyst lowers the activation energy for the forward and reverse reactions to the same extent. Adding a catalyst to a reaction mixture will simply cause the mixture to reach equilibrium sooner. The same equilibrium mixture could be obtained without the catalyst, but we might have to wait longer for equilibrium to be reached. If the same equilibrium position is reached, with or without a catalyst, then the equilibrium constant is the same.
- 14.108** First, let's calculate the initial concentration of ammonia.

$$[\text{NH}_3] = \frac{14.6 \text{ g} \times \frac{1 \text{ mol NH}_3}{17.03 \text{ g NH}_3}}{4.00 \text{ L}} = 0.214 M$$

Let's set up a table to represent the equilibrium concentrations. We represent the amount of NH_3 that reacts as $2x$.

	$2\text{NH}_3(\text{g})$	\rightleftharpoons	$\text{N}_2(\text{g})$	$+$	$3\text{H}_2(\text{g})$
Initial (M):	0.214		0		0
Change (M):	$-2x$		$+x$		$+3x$
Equilibrium (M):	$0.214 - 2x$		x		$3x$

Substitute into the equilibrium constant expression to solve for x .

$$K_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2}$$

$$0.83 = \frac{(x)(3x)^3}{(0.214 - 2x)^2} = \frac{27x^4}{(0.214 - 2x)^2}$$

Taking the square root of both sides of the equation gives:

$$0.91 = \frac{5.20x^2}{0.214 - 2x}$$

Rearranging,

$$5.20x^2 + 1.82x - 0.195 = 0$$

Solving the quadratic equation gives the solutions:

$$x = 0.086 \text{ M and } x = -0.44 \text{ M}$$

The positive root is the correct answer. The equilibrium concentrations are:

$$[\text{NH}_3] = 0.214 - 2(0.086) = \mathbf{0.042 \text{ M}}$$

$$[\text{N}_2] = \mathbf{0.086 \text{ M}}$$

$$[\text{H}_2] = 3(0.086) = \mathbf{0.26 \text{ M}}$$

14.109 (a) From the balanced equation

	N_2O_4	\rightleftharpoons	2NO_2
Initial (mol):	1		0
Change (mol):	$-\alpha$		$+2\alpha$
Equilibrium (mol):	$(1 - \alpha)$		2α

The total moles in the system = (moles N_2O_4 + moles NO_2) = $[(1 - \alpha) + 2\alpha] = 1 + \alpha$. If the total pressure in the system is P , then:

$$P_{\text{N}_2\text{O}_4} = \frac{1 - \alpha}{1 + \alpha} P \quad \text{and} \quad P_{\text{NO}_2} = \frac{2\alpha}{1 + \alpha} P$$

$$K_P = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{\left(\frac{2\alpha}{1 + \alpha}\right)^2 P^2}{\left(\frac{1 - \alpha}{1 + \alpha}\right) P}$$

$$K_P = \frac{\left(\frac{4\alpha^2}{1 + \alpha}\right) P}{1 - \alpha} = \frac{4\alpha^2}{1 - \alpha^2} P$$

(b) Rearranging the K_P expression:

$$4\alpha^2 P = K_P - \alpha^2 K_P$$

$$\alpha^2(4P + K_P) = K_P$$

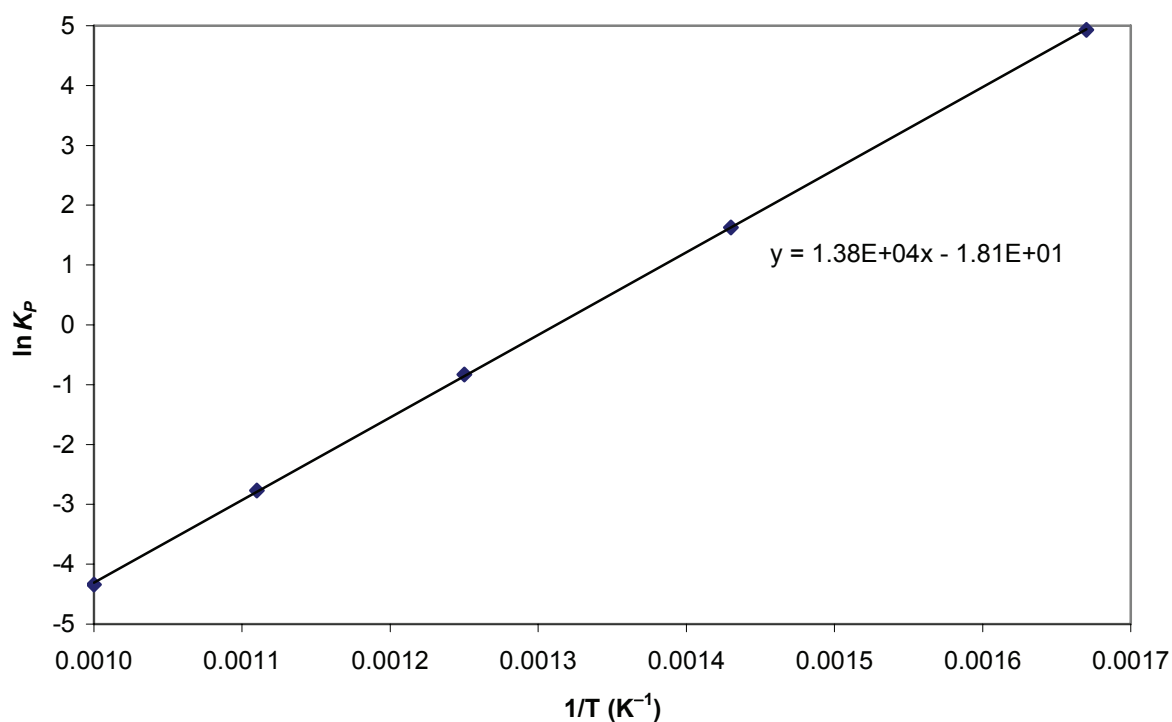
$$\alpha^2 = \frac{K_P}{4P + K_P}$$

$$\alpha = \sqrt{\frac{K_P}{4P + K_P}}$$

K_P is a constant (at constant temperature). Thus, as P increases, α must decrease, indicating that the system shifts to the **left**. This is also what one would predict based on Le Châtelier's principle.

14.110 To determine ΔH° , we need to plot $\ln K_P$ versus $1/T$ (y vs. x).

$\ln K_P$	$1/T$
4.93	0.00167
1.63	0.00143
-0.83	0.00125
-2.77	0.00111
-4.34	0.00100



The slope of the plot equals $-\Delta H^\circ/R$.

$$1.38 \times 10^4 \text{ K} = -\frac{\Delta H^\circ}{8.314 \text{ J/mol} \cdot \text{K}}$$

$$\Delta H^\circ = -1.15 \times 10^5 \text{ J/mol} = -115 \text{ kJ/mol}$$

14.111 (a) We start by writing the van't Hoff equation at two different temperatures.

$$\ln K_1 = \frac{-\Delta H^\circ}{RT_1} + C$$

$$\ln K_2 = \frac{-\Delta H^\circ}{RT_2} + C$$

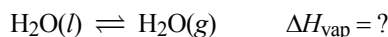
$$\ln K_1 - \ln K_2 = \frac{-\Delta H^\circ}{RT_1} - \frac{-\Delta H^\circ}{RT_2}$$

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

Assuming an endothermic reaction, $\Delta H^\circ > 0$ and $T_2 > T_1$. Then, $\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) < 0$, meaning that

$\ln \frac{K_1}{K_2} < 0$ or $K_1 < K_2$. A larger K_2 indicates that there are more products at equilibrium as the temperature is raised. This agrees with LeChatelier's principle that an increase in temperature favors the forward endothermic reaction. The opposite of the above discussion holds for an exothermic reaction.

(b) Treating



as a heterogeneous equilibrium, $K_P = P_{\text{H}_2\text{O}}$.

We substitute into the equation derived in part (a) to solve for ΔH_{vap} .

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

$$\ln \frac{31.82 \text{ mmHg}}{92.51 \text{ mmHg}} = \frac{\Delta H^\circ}{8.314 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{323 \text{ K}} - \frac{1}{303 \text{ K}} \right)$$

$$-1.067 = \Delta H^\circ (-2.458 \times 10^{-5})$$

$$\Delta H^\circ = 4.34 \times 10^4 \text{ J/mol} = 43.4 \text{ kJ/mol}$$

14.112 Initially, the pressure of SO_2Cl_2 is 9.00 atm. The pressure is held constant, so after the reaction reaches equilibrium, $P_{\text{SO}_2\text{Cl}_2} + P_{\text{SO}_2} + P_{\text{Cl}_2} = 9.00 \text{ atm}$. The amount (pressure) of SO_2Cl_2 reacted must equal the pressure of SO_2 and Cl_2 produced for the pressure to remain constant. If we let $P_{\text{SO}_2} + P_{\text{Cl}_2} = x$, then the pressure of SO_2Cl_2 reacted must be $2x$. We set up a table showing the initial pressures, the change in pressures, and the equilibrium pressures.

	$\text{SO}_2\text{Cl}_2(g)$	\rightleftharpoons	$\text{SO}_2(g)$	$+$	$\text{Cl}_2(g)$
Initial (atm):	9.00		0		0
Change (atm):	$-2x$		$+x$		$+x$
Equilibrium (atm):	$9.00 - 2x$		x		x

Again, note that the change in pressure for SO_2Cl_2 ($-2x$) does not match the stoichiometry of the reaction, because we are expressing changes in pressure. The total pressure is kept at 9.00 atm throughout.

$$K_P = \frac{P_{\text{SO}_2} P_{\text{Cl}_2}}{P_{\text{SO}_2\text{Cl}_2}}$$

$$2.05 = \frac{(x)(x)}{9.00 - 2x}$$

$$x^2 + 4.10x - 18.45 = 0$$

Solving the quadratic equation, $x = 2.71$ atm. At equilibrium,

$$P_{\text{SO}_2} = P_{\text{Cl}_2} = x = \mathbf{2.71 \text{ atm}}$$

$$P_{\text{SO}_2\text{Cl}_2} = 9.00 - 2(2.71) = \mathbf{3.58 \text{ atm}}$$

14.113 Using Equation (13.11) of the text, we can calculate k_{-1} .

$$k = Ae^{-E_a/RT}$$

Then, we can calculate k_1 using the expression

$$K_c = \frac{k_1}{k_{-1}} \quad (\text{see Section 14.3 of the text})$$

$$k_{-1} = (1.0 \times 10^{12} \text{ s}^{-1}) e^{-\left(\frac{41 \times 10^3 \text{ J/mol}}{(8.314 \text{ J/mol}\cdot\text{K})(298 \text{ K})}\right)}$$

$$k_{-1} = 6.5 \times 10^4 \text{ s}^{-1}$$

$$K_c = \frac{k_1}{k_{-1}}$$

$$9.83 \times 10^3 = \frac{k_1}{6.5 \times 10^4 \text{ s}^{-1}}$$

$$k_1 = \mathbf{6.4 \times 10^8 \text{ s}^{-1}}$$

14.114 We start with a table.

	A ₂	+	B ₂	⇌	2AB
Initial (mol):	1		3		0
Change (mol):	$-\frac{x}{2}$		$-\frac{x}{2}$		+x
Equilibrium (mol):	$1 - \frac{x}{2}$		$3 - \frac{x}{2}$		x

After the addition of 2 moles of A,

	A_2	+	B_2	\rightleftharpoons	$2AB$
Initial (mol):	$3 - \frac{x}{2}$		$3 - \frac{x}{2}$		x
Change (mol):	$-\frac{x}{2}$		$-\frac{x}{2}$		$+x$
Equilibrium (mol):	$3 - x$		$3 - x$		$2x$

We write two different equilibrium constants expressions for the two tables.

$$K = \frac{[AB]^2}{[A_2][B_2]}$$

$$K = \frac{x^2}{\left(1 - \frac{x}{2}\right)\left(3 - \frac{x}{2}\right)} \quad \text{and} \quad K = \frac{(2x)^2}{(3-x)(3-x)}$$

We equate the equilibrium constant expressions and solve for x .

$$\frac{x^2}{\left(1 - \frac{x}{2}\right)\left(3 - \frac{x}{2}\right)} = \frac{(2x)^2}{(3-x)(3-x)}$$

$$\frac{1}{\frac{1}{4}(x^2 - 8x + 12)} = \frac{4}{x^2 - 6x + 9}$$

$$-6x + 9 = -8x + 12$$

$$x = 1.5$$

We substitute x back into one of the equilibrium constant expressions to solve for K .

$$K = \frac{(2x)^2}{(3-x)(3-x)} = \frac{(3)^2}{(1.5)(1.5)} = 4.0$$

Substitute x into the other equilibrium constant expression to see if you obtain the same value for K . Note that we used moles rather than molarity for the concentrations, because the volume, V , cancels in the equilibrium constant expressions.

14.115 (a) First, we calculate the moles of I_2 .

$$\text{mol } I_2 = 0.032 \text{ g } I_2 \times \frac{1 \text{ mol } I_2}{253.8 \text{ g } I_2} = 1.26 \times 10^{-4} \text{ mol}$$

Let x be the number of moles of I_2 that dissolves in CCl_4 , so $(1.26 \times 10^{-4} - x)$ mol remains dissolved in water. We set up expressions for the concentrations of I_2 in CCl_4 and H_2O .

$$[I_2(aq)] = \frac{(1.26 \times 10^{-4} - x) \text{ mol}}{0.200 \text{ L}} \quad \text{and} \quad [I_2(CCl_4)] = \frac{x \text{ mol}}{0.030 \text{ L}}$$

Next, we substitute these concentrations into the equilibrium constant expression and solve for x .

$$K = \frac{[\text{I}_2(\text{CCl}_4)]}{[\text{I}_2(\text{aq})]}$$

$$83 = \frac{\frac{x}{0.030}}{\frac{(1.26 \times 10^{-4} - x)}{0.200}}$$

$$83(1.26 \times 10^{-4} - x) = 6.67x$$

$$x = 1.166 \times 10^{-4}$$

The fraction of I_2 remaining in the aqueous phase is:

$$\text{fraction } (f) = \frac{(1.26 \times 10^{-4}) - (1.166 \times 10^{-4})}{1.26 \times 10^{-4}} = \mathbf{0.075}$$

- (b) The first extraction leaves only 7.5% I_2 in the water. The next extraction with 0.030 L of CCl_4 will leave only $(0.075)(0.075) = 5.6 \times 10^{-3}$. This is the fraction remaining after the second extraction which is only 0.56%.
- (c) For a single extraction using 0.060 L of CCl_4 , we let y be the number of moles of I_2 in CCl_4 .

$$83 = \frac{\frac{y}{0.060}}{\frac{(1.26 \times 10^{-4} - y)}{0.200}}$$

$$83(1.26 \times 10^{-4} - y) = 3.33y$$

$$y = 1.211 \times 10^{-4}$$

The fraction of I_2 remaining in the aqueous phase is:

$$\text{fraction } (f) = \frac{(1.26 \times 10^{-4}) - (1.211 \times 10^{-4})}{1.26 \times 10^{-4}} = \mathbf{0.039}$$

The fraction of I_2 remaining dissolved in water is 0.039 or 3.9%. The extraction with 0.060 L of CCl_4 is not as effective as two separate extractions of 0.030 L each.