

K is a unitless number because there are an equal number of moles of product gases as moles of reactant gases in the balanced equation. Therefore, we can use units of molecules per liter instead of moles per liter to determine K .

We need to start somewhere, so let's assume 3 molecules of CO react. If 3 molecules of CO react, then 3 molecules of H_2O must react, and 3 molecules each of H_2 and CO_2 are formed. We would have $6 - 3 = 3$ molecules of CO , $8 - 3 = 5$ molecules of H_2O , $0 + 3 = 3$ molecules of H_2 , and $0 + 3 = 3$ molecules of CO_2 present. This will be an equilibrium mixture if $K = 2.0$:

$$K = \frac{\left(\frac{3 \text{ molecules H}_2}{\text{L}} \right) \left(\frac{3 \text{ molecules CO}_2}{\text{L}} \right)}{\left(\frac{5 \text{ molecules H}_2\text{O}}{\text{L}} \right) \left(\frac{3 \text{ molecules CO}}{\text{L}} \right)} = \frac{3}{5}$$

Because this mixture does not give a value of $K = 2.0$, this is not an equilibrium mixture. Let's try 4 molecules of CO reacting to reach equilibrium.

Molecules CO remaining = $6 - 4 = 2$ molecules of CO

Molecules H_2O remaining = $8 - 4 = 4$ molecules of H_2O

Molecules H_2 present = $0 + 4 = 4$ molecules of H_2

Molecules CO_2 present = $0 + 4 = 4$ molecules of CO_2

$$K = \frac{\left(\frac{4 \text{ molecules H}_2}{\text{L}} \right) \left(\frac{4 \text{ molecules CO}_2}{\text{L}} \right)}{\left(\frac{4 \text{ molecules H}_2\text{O}}{\text{L}} \right) \left(\frac{2 \text{ molecules CO}}{\text{L}} \right)} = 2.0$$

Because $K = 2.0$ for this reaction mixture, we are at equilibrium.

16. When equilibrium is reached, there is no net change in the amount of reactants and products present because the rates of the forward and reverse reactions are equal to each other. The first diagram has 4 A_2B molecules, 2 A_2 molecules, and 1 B_2 molecule present. The second diagram has 2 A_2B molecules, 4 A_2 molecules, and 2 B_2 molecules. Therefore, the first diagram cannot represent equilibrium because there was a net change in reactants and products. Is the second diagram the equilibrium mixture? That depends on whether there is a net change between reactants and products when going from the second diagram to the third diagram. The third diagram contains the same numbers and types of molecules as the second diagram, so the second diagram is the first illustration that represents equilibrium.

The reaction container initially contained only A_2B . From the first diagram, 2 A_2 molecules and 1 B_2 molecule are present (along with 4 A_2B molecules). From the balanced reaction, these 2 A_2 molecules and 1 B_2 molecule were formed when 2 A_2B molecules decomposed. Therefore, the initial number of A_2B molecules present equals $4 + 2 = 6$ molecules A_2B .

CHAPTER 13

CHEMICAL EQUILIBRIUM

Questions

- This experiment starts with only H_2 and N_2 , and no NH_3 present. From the initial mixture diagram, there is three times as many H_2 as N_2 molecules. So the green line, at the highest initial concentration is the H_2 plot, the blue line is the N_2 plot, and the red line, which has an initial concentration of zero, is the NH_3 plot.
 - $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightleftharpoons 2\text{NH}_3(\text{g})$; when a reaction starts with only reactants present initially, the reactant concentrations decrease with time while the product concentrations increase with time. This is seen in the various plots. Also notice that the H_2 concentration initially decreases more rapidly as compared to the initial decrease in N_2 concentration. This is due to the stoichiometry in the balanced equation, which dictates that for every 1 molecule of N_2 that reacts, 3 molecules of H_2 must also react. One would expect the NH_3 plot to initially increase faster than the N_2 plot decreases (due to the 2 : 1 mole ratio in the balanced equation), and for the H_2 plot to initially decrease faster than the NH_3 plot increases (due to the 3 : 2 mole ratio). This is seen in the various plots.

c. Equilibrium is reached when the rate of the forward reaction equals the rate of the reverse reaction. At this time, there is no net change in any of the reactant and product concentrations; so the various plots indicate equilibrium has been reached when their concentrations no longer change with time (when the plots reach a plateau).

- No, equilibrium is a dynamic process. Both reactions:



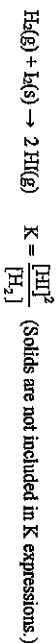
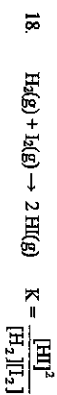
are occurring at equal rates. Thus ^{14}C atoms will be distributed between CO and CO_2 .

- No, it doesn't matter from which direction the equilibrium position is reached (as long as temperature is constant). Both experiments will give the same equilibrium position because both experiments started with stoichiometric amounts of reactants or products.

13. A K value much greater than one ($K \gg 1$) indicates there are relatively large concentrations of product gases/solutes as compared with the concentrations of reactant gases/solutes at equilibrium. A reaction with a very large K value is a good source of products.

14. A K value much less than one ($K \ll 1$) indicates that there are relatively large concentrations of reactant gases/solutes as compared with the concentrations of product gases/solutes at equilibrium. A reaction with a very small K value is a very poor source of products.

17. K and K_p are equilibrium constants, as determined by the law of mass action. For K , concentration units of mol/L are used, and for K_p , partial pressures in units of atm are used (generally). Q is called the reaction quotient. Q has the exact same form as K or K_p , but instead of equilibrium concentrations, initial concentrations are used to calculate the Q value. The use of Q is when it is compared with the K value. When $Q = K$ (or when $Q_p = K_p$), the reaction is at equilibrium. When $Q \neq K$, the reaction is not at equilibrium, and one can deduce the net change that must occur for the system to get to equilibrium.



Some property differences are:

(1) the reactions have different K expressions.

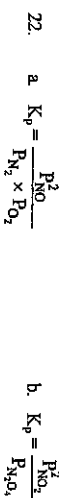
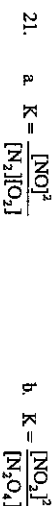
(2) for the first reaction, $K = K_p$ (since $\Delta n = 0$), and for the second reaction, $K \neq K_p$ (since $\Delta n \neq 0$).

(3) a change in the container volume will have no effect on the equilibrium for reaction 1, whereas a volume change will affect the equilibrium for reaction 2 (shifts the reaction left or right depending on whether the volume is decreased or increased).

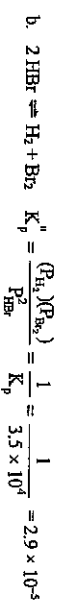
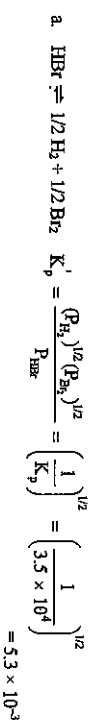
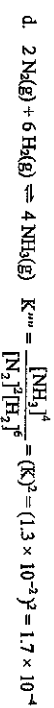
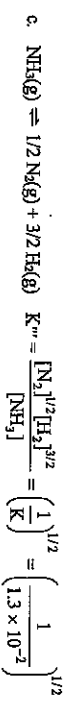
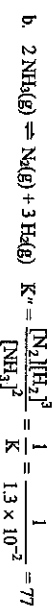
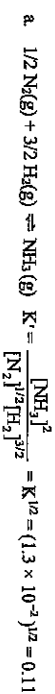
19. We always try to make good assumptions that simplify the math. In some problems we can set up the problem so that the net change x that must occur to reach equilibrium is a small number. This comes in handy when you have expressions like $0.12 - x$ or $0.727 + 2x$, etc. When x is small, we can assume that it makes little difference when subtracted from or added to some relatively big number. When this is the case, $0.12 - x \approx 0.12$ and $0.727 + 2x \approx 0.727$, etc. If the assumption holds by the 5% rule, the assumption is assumed valid. The 5% rule refers to x (or $2x$ or $3x$, etc.) that is assumed small compared to some number. If x (or $2x$ or $3x$, etc.) is less than 5% of the number the assumption was made against, then the assumption will be assumed valid. If the 5% rule fails to work, one can use a math procedure called the method of successive approximations to solve the quadratic or cubic equation. Of course, one could always solve the quadratic or cubic equation exactly. This is generally a last resort (and is usually not necessary).

20. Only statement e is correct. Addition of a catalyst has no effect on the equilibrium position; the reaction just reaches equilibrium more quickly. Statement a is false for reactants that are either solids or liquids (adding more of these has no effect on the equilibrium). Statement b is false always. If temperature remains constant, then the value of K is constant. Statement c is false for exothermic reactions where an increase in temperature decreases the value of K . For statement d, only reactions that have more reactant gases than product gases will shift left with an increase in container volume. If the moles of gas are equal, or if there are more moles of product gases than reactant gases, the reaction will not shift left with an increase in volume.

The Equilibrium Constant



When a reaction is reversed, then $K_{\text{reverse}} = 1/K_{\text{original}}$. When a reaction is multiplied through by a value of n , then $K_{\text{reverse}} = (K_{\text{original}})^n$.



$$c. \quad 1/2 \text{H}_2 + 1/2 \text{Br}_2 \rightleftharpoons \text{HBr} \quad K_p'' = \frac{P_{\text{HBr}}}{(P_{\text{H}_2})^{1/2} (P_{\text{Br}_2})^{1/2}} = (K_p')^{1/2} = 190$$

$$25. \quad 2 \text{NO}(\text{g}) + 2 \text{H}_2(\text{g}) \rightleftharpoons \text{N}_2(\text{g}) + 2 \text{H}_2\text{O}(\text{g}) \quad K = \frac{[\text{N}_2][\text{H}_2\text{O}]^2}{[\text{NO}]^2[\text{H}_2]^2}$$

$$K = \frac{(5.3 \times 10^{-3})(2.9 \times 10^{-3})^2}{(8.1 \times 10^{-3})^2(4.1 \times 10^{-5})^2} = 4.0 \times 10^6$$

$$26. \quad K = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]} = \frac{(4.7 \times 10^{-4} \text{ M})^2}{(0.041 \text{ M})(0.0078 \text{ M})} = 6.9 \times 10^{-4}$$

$$27. \quad [\text{NO}] = \frac{4.5 \times 10^{-3} \text{ mol}}{3.0 \text{ L}} = 1.5 \times 10^{-3} \text{ M}; \quad [\text{Cl}_2] = \frac{2.4 \text{ mol}}{3.0 \text{ L}} = 0.80 \text{ M}$$

$$[\text{NOCl}] = \frac{1.0 \text{ mol}}{3.0 \text{ L}} = 0.33 \text{ M}; \quad K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(1.5 \times 10^{-3})^2(0.80)}{(0.33)^2} = 1.7 \times 10^{-5}$$

$$28. \quad [\text{NO}] = \frac{2.00 \times 10^{-2} \text{ mol}}{2.00 \text{ L}}; \quad [\text{N}_2] = \frac{2.80 \times 10^{-4} \text{ mol}}{2.00 \text{ L}}; \quad [\text{O}_2] = \frac{2.50 \times 10^{-5} \text{ mol}}{2.00 \text{ L}}$$

$$K = \frac{[\text{N}_2][\text{O}_2]^2}{[\text{NO}]^2} = \frac{\left(\frac{2.00 \times 10^{-2}}{2.00}\right)^2 \left(\frac{2.50 \times 10^{-5}}{2.00}\right)^2}{\left(\frac{2.80 \times 10^{-4}}{2.00}\right)^2 \left(\frac{2.00 \times 10^{-2}}{2.00}\right)^2} = \frac{(1.00 \times 10^{-2})^2 (1.25 \times 10^{-5})^2}{(1.40 \times 10^{-4})^2 (1.25 \times 10^{-2})^2}$$

$$= 4.08 \times 10^8$$

If the given concentrations represent equilibrium concentrations, then they should give a value of $K = 4.08 \times 10^8$.

$$\frac{(0.200)^2}{(2.00 \times 10^{-4})^2(0.00245)} = 4.08 \times 10^8$$

Because the given concentrations when plugged into the equilibrium constant expression give a value equal to K (4.08×10^8), this set of concentrations is a system at equilibrium.

$$29. \quad K_p = \frac{P_{\text{NO}}^2 \times P_{\text{O}_2}}{P_{\text{N}_2}^2} = \frac{(6.5 \times 10^{-5})^2(4.5 \times 10^{-5})}{(0.55)^2} = 6.3 \times 10^{-13}$$

$$30. \quad K_p = \frac{P_{\text{NH}_3}^2}{P_{\text{N}_2} \times P_{\text{H}_2}^3} = \frac{(3.1 \times 10^{-2})^2}{(0.85)(3.1 \times 10^{-3})^3} = 3.8 \times 10^4$$

$$\frac{(0.0167)^2}{(0.525)(0.00761)^3} = 1.21 \times 10^3$$

When the given partial pressures in atmospheres are plugged into the K_p expression, the value does not equal the K_p value of 3.8×10^4 . Therefore, one can conclude that the given set of partial pressures does not represent a system at equilibrium.

$$31. \quad K_p = K(\text{RT})^{\Delta n}, \text{ where } \Delta n = \text{sum of gaseous product coefficients} - \text{sum of gaseous reactant coefficients. For this reaction, } \Delta n = 3 - 1 = 2.$$

$$K = \frac{[\text{CO}][\text{H}_2]^2}{[\text{CH}_3\text{OH}]} = \frac{(0.24)(1.1)^2}{(0.15)} = 1.9$$

$$K_p = K(\text{RT})^2 = 1.9(0.08206 \text{ L atm/K}\cdot\text{mol} \times 600. \text{ K})^2 = 4.6 \times 10^3$$

$$32. \quad K_p = K(\text{RT})^{\Delta n}, \quad K = \frac{K_p}{(\text{RT})^{\Delta n}}; \quad \Delta n = 2 - 3 = -1$$

$$K = \frac{0.25}{(0.08206 \text{ L atm/K mol} \times 1100 \text{ K})^{-1}} = 23$$

33. Solids and liquids do not appear in equilibrium expressions. Only gases and dissolved solutes appear in equilibrium expressions.

$$a. \quad K = \frac{[\text{H}_2\text{O}]}{[\text{NH}_3]^2[\text{CO}_2]}; \quad K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{NH}_3}^2 \times P_{\text{CO}_2}}$$

$$b. \quad K = [\text{N}_2][\text{Br}_2]; \quad K_p = P_{\text{N}_2} \times P_{\text{Br}_2}$$

$$c. \quad K = [\text{O}_2]^2; \quad K_p = P_{\text{O}_2}^2$$

$$d. \quad K = \frac{[\text{H}_2\text{O}]}{[\text{H}_2]}; \quad K_p = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$$

$$34. \quad a. \quad K_p = \frac{1}{(P_{\text{O}_2})^{3/2}}$$

$$b. \quad K_p = \frac{1}{P_{\text{CO}_2}}$$

$$c. \quad K_p = \frac{P_{\text{CO}} \times P_{\text{H}_2}}{P_{\text{H}_2\text{O}}}$$

$$d. \quad K_p = \frac{P_{\text{O}_2}^2}{P_{\text{H}_2\text{O}}}$$

35. $K_p = K(\text{RT})^{\Delta n}$, where Δn equals the difference in the sum of the coefficients between gaseous products and gaseous reactants ($\Delta n = \text{mol gaseous products} - \text{mol gaseous reactants}$). When $\Delta n = 0$, then $K_p = K$. In Exercise 33, only reaction d has $\Delta n = 0$, so only reaction d has $K_p = K$.

36. $K_p = K$ when $\Delta n = 0$. In Exercise 34, none of the reactions have $K_p = K$ because none of the reactions have $\Delta n = 0$. The values of Δn for the various reactions are -1.5 , -1 , 1 , and 1 , respectively.

37. Because solids do not appear in the equilibrium constant expression,
- $K = 1/[\text{O}_2]^3$
- .

$$[\text{O}_2] = \frac{1.0 \times 10^{-3} \text{ mol}}{2.0 \text{ L}}; K = \frac{1}{[\text{O}_2]^3} = \frac{1}{\left(\frac{1.0 \times 10^{-3}}{2.0}\right)^3} = \frac{1}{(5.0 \times 10^{-4})^3} = 8.0 \times 10^9$$

- 38.
- $K_p = \frac{P_{\text{H}_2}^4}{P_{\text{H}_2\text{O}}^4}$
- ;
- $P_{\text{total}} = P_{\text{H}_2\text{O}} + P_{\text{H}_2}$
- ;
- $36.3 \text{ torr} = 15.0 \text{ torr} + P_{\text{H}_2}$
- ;
- $P_{\text{H}_2} = 21.3 \text{ torr}$

$$\text{Because } 1 \text{ atm} = 760 \text{ torr, } K_p = \frac{\left(\frac{21.3 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)^4}{\left(\frac{15.0 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}}\right)^4} = 4.07$$

Note: Solids and pure liquids are not included in K expressions.

Equilibrium Calculations

- 39.
- $\text{H}_2\text{O}(\text{g}) + \text{Cl}_2\text{O}(\text{g}) \rightarrow 2 \text{HOCl}(\text{g})$
- $K = \frac{[\text{HOCl}]^2}{[\text{H}_2\text{O}][\text{Cl}_2\text{O}]} = 0.0900$

Use the reaction quotient Q to determine which way the reaction shifts to reach equilibrium. For the reaction quotient, initial concentrations given in a problem are used to calculate the value for Q . If $Q < K$, then the reaction shifts right to reach equilibrium. If $Q > K$, then the reaction shifts left to reach equilibrium. If $Q = K$, then the reaction does not shift in either direction because the reaction is already at equilibrium.

$$\text{a. } Q = \frac{[\text{HOCl}]_0^2}{[\text{H}_2\text{O}]_0[\text{Cl}_2\text{O}]_0} = \frac{\left(\frac{1.0 \text{ mol}}{1.0 \text{ L}}\right)^2}{\left(\frac{0.10 \text{ mol}}{1.0 \text{ L}}\right)\left(\frac{0.10 \text{ mol}}{1.0 \text{ L}}\right)} = 1.0 \times 10^2$$

$Q > K$, so the reaction shifts left to produce more reactants to reach equilibrium.

$$\text{b. } Q = \frac{\left(\frac{0.084 \text{ mol}}{2.0 \text{ L}}\right)^2}{\left(\frac{0.98 \text{ mol}}{2.0 \text{ L}}\right)\left(\frac{0.080 \text{ mol}}{2.0 \text{ L}}\right)} = 0.090 = K; \text{ at equilibrium}$$

$$\text{c. } Q = \frac{\left(\frac{0.25 \text{ mol}}{3.0 \text{ L}}\right)^2}{\left(\frac{0.56 \text{ mol}}{3.0 \text{ L}}\right)\left(\frac{0.0010 \text{ mol}}{3.0 \text{ L}}\right)} = 110$$

$Q > K$, so the reaction shifts to the left to reach equilibrium.

40. As in Exercise 39, determine
- Q
- for each reaction, compare this value to
- K_p
- (
- $= 0.0900$
-), and then determine which direction the reaction shifts to reach equilibrium. Note that for this reaction,
- $K = K_p$
- because
- $\Delta n = 0$
- .

$$\text{a. } Q = \frac{P_{\text{HOCl}}^2}{P_{\text{H}_2\text{O}} \times P_{\text{Cl}_2\text{O}}} = \frac{(1.00 \text{ atm})^2}{(1.00 \text{ atm})(1.00 \text{ atm})} = 1.00$$

$Q > K_p$, so the reaction shifts left to reach equilibrium.

$$\text{b. } Q = \frac{(21.0 \text{ torr})^2}{(200. \text{ torr})(49.8 \text{ torr})} = 4.43 \times 10^{-2} < K_p$$

The reaction shifts right to reach equilibrium. Note: Because Q and K_p are unitless, we can use any pressure units when determining Q without changing the numerical value.

$$\text{c. } Q = \frac{(20.0 \text{ torr})^2}{(296 \text{ torr})(15.0 \text{ torr})} = 0.0901 \approx K_p; \text{ at equilibrium}$$

- 41.
- $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
- $K_p = P_{\text{CO}_2} = 1.04$

a. $Q = P_{\text{CO}_2}$; we only need the partial pressure of CO_2 to determine Q because solids do not appear in equilibrium expressions (or Q expressions). At this temperature, all CO_2 will be in the gas phase. $Q = 2.55$, so $Q > K_p$; the reaction will shift to the left to reach equilibrium; the mass of CaO will decrease.

b. $Q = 1.04 = K_p$, so the reaction is at equilibrium; mass of CaO will not change.

c. $Q = 1.04 = K_p$, so the reaction is at equilibrium; mass of CaO will not change.

d. $Q = 0.211 < K_p$; the reaction will shift to the right to reach equilibrium; mass of CaO will increase.

- 42.
- $\text{CH}_3\text{CO}_2\text{H} + \text{C}_2\text{H}_5\text{OH} \rightleftharpoons \text{CH}_3\text{CO}_2\text{C}_2\text{H}_5 + \text{H}_2\text{O}$
- $K = \frac{[\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{CO}_2\text{H}][\text{C}_2\text{H}_5\text{OH}]} = 2.2$

a. $Q = \frac{(0.22)(0.10)}{(0.010)(0.010)} = 220 > K$; reaction will shift left to reach equilibrium, so the concentration of water will decrease.

- b. $Q = \frac{(0.22)(0.0020)}{(0.0020)(0.10)} = 2.2 = K$; reaction is at equilibrium, so the concentration of water will remain the same.
- c. $Q = \frac{(0.88)(0.12)}{(0.044)(6.0)} = 0.40 < K$; because $Q < K$, the concentration of water will increase because the reaction shifts right to reach equilibrium.
- d. $Q = \frac{(4.4)(4.4)}{(0.88)(0.0)} = 2.2 = K$; at equilibrium, so the water concentration is unchanged.
- e. $K = 2.2 = \frac{(2.0)[H_2O]}{(0.10)(5.0)}$, $[H_2O] = 0.55 M$

f. Water is a product of the reaction, but it is not the solvent. Thus the concentration of water must be included in the equilibrium expression because it is a solute in the reaction. When water is the solvent, then it is not included in the equilibrium expression.

$$43. K = \frac{[H_2]^{1/2}[O_2]}{[H_2O]^2}, 2.4 \times 10^{-3} = \frac{(1.9 \times 10^{-2})^{1/2}[O_2]}{(0.11)^2}, [O_2] = 0.080 M$$

$$\text{Moles of } O_2 = 2.0 L \times \frac{0.080 \text{ mol } O_2}{L} = 0.16 \text{ mol } O_2$$

$$44. K_p = \frac{P_{H_2O}^2}{P_{NO}^2 \times P_{B_2}}, 109 = \frac{(0.0768)^2}{P_{NO}^2 \times 0.0159}, P_{NO} = 0.0583 \text{ atm}$$

$$45. SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g) \quad K = \frac{[SO_3][NO]}{[SO_2][NO_2]}$$

To determine K , we must calculate the equilibrium concentrations. The initial concentrations are:

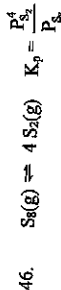
$$[SO_2]_0 = [NO]_0 = 0; \quad [SO_2]_0 = [NO_2]_0 = \frac{2.00 \text{ mol}}{1.00 L} = 2.00 M$$

Next, we determine the change required to reach equilibrium. At equilibrium, $[NO] = 1.30 \text{ mol}/1.00 L = 1.30 M$. Because there was zero NO present initially, $1.30 M$ of SO_2 and $1.30 M$ NO_2 must have reacted to produce $1.30 M$ NO as well as $1.30 M$ SO_3 , all required by the balanced reaction. The equilibrium concentration for each substance is the sum of the initial concentration plus the change in concentration necessary to reach equilibrium. The equilibrium concentrations are:

$$[SO_2] = [NO] = 0 + 1.30 M = 1.30 M; \quad [SO_2] = [NO_2] = 2.00 M - 1.30 M = 0.70 M$$

We now use these equilibrium concentrations to calculate K :

$$K = \frac{[SO_3][NO]}{[SO_2][NO_2]} = \frac{(1.30)(1.30)}{(0.70)(0.70)} = 3.4$$



$$\text{Initially: } P_{S_8} = 1.00 \text{ atm and } P_{S_2} = 0 \text{ atm}$$

Change: Because 0.25 atm of S_8 remain at equilibrium, $1.00 \text{ atm} - 0.25 \text{ atm} = 0.75 \text{ atm}$ of S_8 must have reacted in order to reach equilibrium. Because there is a $4 : 1$ mole ratio between S_2 and S_8 (from the balanced reaction), $4(0.75 \text{ atm}) = 3.0 \text{ atm}$ of S_2 must have been produced when the reaction went to equilibrium (moles and pressure are directly related at constant T and V).

$$\text{Equilibrium: } P_{S_8} = 0.25 \text{ atm, } P_{S_2} = 0 + 3.0 \text{ atm} = 3.0 \text{ atm; solving for } K_p:$$

$$K_p = \frac{(3.0)^4}{0.25} = 3.2 \times 10^2$$

47.

When solving equilibrium problems, a common method to summarize all the information in the problem is to set up a table. We commonly call this table an ICE table because it summarizes initial concentrations, changes that must occur to reach equilibrium, and equilibrium concentrations (the sum of the initial and change columns). For the change column, we will generally use the variable x , which will be defined as the amount of reactant (or product) that must react to reach equilibrium. In this problem, the reaction must shift right to reach equilibrium because there are no products present initially. Therefore, x is defined as the amount of reactant SO_3 that reacts to reach equilibrium, and we use the coefficients in the balanced equation to relate the net change in SO_3 to the net change in SO_2 and O_2 . The general ICE table for this problem is:

	$2 SO_3(g)$	\rightleftharpoons	$2 SO_2(g)$	$+$	$O_2(g)$		$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2}$
Initial	12.0 mol/3.0 L		0		0		
	Let x mol/L of SO_3 react to reach equilibrium.						
Change	$-x$		$+x$		$+x/2$		
Equil.	$4.0 - x$		x		$x/2$		

From the problem, we are told that the equilibrium SO_2 concentration is $3.0 \text{ mol}/3.0 L = 1.0 M$ ($[SO_2]_e = 1.0 M$). From the ICE table setup, $[SO_2]_e = x$, so $x = 1.0$. Solving for the other equilibrium concentrations: $[SO_3]_e = 4.0 - x = 4.0 - 1.0 = 3.0 M$; $[O_2]_e = x/2 = 1.0/2 = 0.50 M$.

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(1.0)^2(0.50)}{(3.0)^2} = 0.056$$

Alternate method: Fractions in the change column can be avoided (if you want) by defining x differently. If we were to let $2x$ mol/L of SO_3 react to reach equilibrium, then the ICE table setup is:



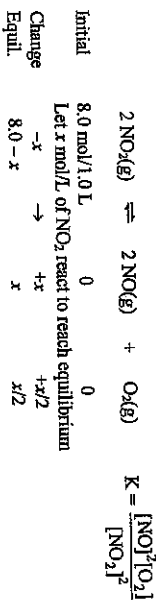
Initial $4.0 M$ 0 0
Let $2x$ mol/L of SO_2 react to reach equilibrium.

Change $-2x$ \rightarrow $+2x$ $+x$
Equil. $4.0 - 2x$ $2x$ x

Solving: $2x = [\text{SO}_2]_e = 1.0 M$, $x = 0.50 M$; $[\text{SO}_3]_e = 4.0 - 2(0.50) = 3.0 M$, $[\text{O}_2]_e = x = 0.50 M$

These are exactly the same equilibrium concentrations as solved for previously, thus K will be the same (as it must be). The moral of the story is to define x in a manner that is most comfortable for you. Your final answer is independent of how you define x initially.

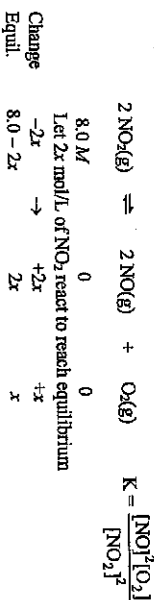
48. When solving equilibrium problems, a common method to summarize all the information in the problem is to set up a table. We commonly call this table the ICE table because it summarizes initial concentrations, changes that must occur to reach equilibrium, and equilibrium concentrations (the sum of the initial and change columns). For the change column, we will generally use the variable x , which will be defined as the amount of reactant (or product) that must react to reach equilibrium. In this problem, the reaction must shift right since there are no products present initially. The general ICE table for this problem is:



Note that we must use the coefficients in the balanced equation to determine the amount of products produced when x mol/L of NO_2 reacts to reach equilibrium. In the problem, we are told that $[\text{NO}]_e = 2.0 M$. From the set-up, $[\text{NO}]_e = x = 2.0 M$. Solving for the other concentrations: $[\text{NO}]_e = 8.0 - x = 8.0 - 2.0 = 6.0 M$; $[\text{O}_2]_e = x/2 = 2.0/2 = 1.0 M$. Calculating K :

$$K = \frac{[\text{NO}]^2[\text{O}_2]}{[\text{NO}_2]^2} = \frac{(2.0 M)^2(1.0 M)}{(6.0 M)^2} = 0.11 \text{ mol/L}$$

Alternate method: Fractions in the change column can be avoided (if you want) by defining x differently. If we were to let $2x$ mol/L of NO_2 react to reach equilibrium, then the ICE table set-up is:



Solving: $2x = [\text{NO}]_e = 2.0 M$, $x = 1.0 M$; $[\text{NO}_2]_e = 8.0 - 2(1.0) = 6.0 M$, $[\text{O}_2]_e = x = 1.0 M$

These are exactly the same equilibrium concentrations as solved for previously, thus K will be the same (as it must be). The moral of the story is to define x in a manner that is most comfortable for you. Your final answer is independent of how you define x initially.

49. $3 \text{H}_2(\text{g}) + \text{N}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$

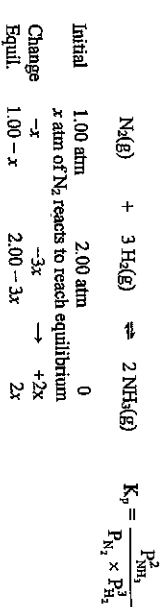
Initial	$[\text{H}_2]_0$	$[\text{N}_2]_0$	0
	x mol/L of N_2 reacts to reach equilibrium		
Change	$-3x$	$-x$	$+2x$
Equil.	$[\text{H}_2]_0 - 3x$	$[\text{N}_2]_0 - x$	$2x$

From the problem:

$$[\text{NH}_3]_e = 4.0 M = 2x, \quad x = 2.0 M, \quad [\text{H}_2]_e = 5.0 M = [\text{H}_2]_0 - 3x, \quad [\text{N}_2]_e = 8.0 M = [\text{N}_2]_0 - x$$

$$5.0 M = [\text{H}_2]_0 - 3(2.0 M), \quad [\text{H}_2]_0 = 11.0 M, \quad 8.0 M = [\text{N}_2]_0 - 2.0 M, \quad [\text{N}_2]_0 = 10.0 M$$

50. $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$ with only reactants present initially, the net change that must occur to reach equilibrium is a conversion of reactants into products. At constant volume and temperature, $n \propto P$. Thus, if x atm of N_2 reacts to reach equilibrium, then $3x$ atm of H_2 must also react to form $2x$ atm of NH_3 (from the balanced equation). Let's summarize the problem in a table that lists what is present initially, what change in terms of x that occurs to reach equilibrium, and what is present at equilibrium (initial + change). This table is typically called an ICE table for initial, change, and equilibrium.



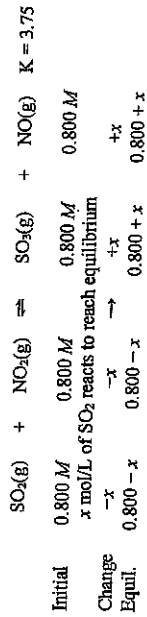
From the setup: $P_{\text{total}} = 2.00 \text{ atm} = P_{\text{N}_2} + P_{\text{H}_2} + P_{\text{NH}_3}$

$$2.00 \text{ atm} = (1.00 - x) + (2.00 - 3x) + 2x = 3.00 - 2x, \quad x = 0.500$$

$$P_{\text{H}_2} = 2.00 - 3x = 2.00 - 3(0.500) = 0.50 \text{ atm}$$

$$K_p = \frac{(2x)^2}{(1.00 - x)(2.00 - 3x)^3} = \frac{[2(0.500)]^2}{(1.00 - 0.500)[2.00 - 3(0.500)]^3} = \frac{(1.00)^2}{(0.50)(0.50)^3} = 16$$

51. $Q = 1.00$, which is less than K . The reaction shifts to the right to reach equilibrium. Summarizing the equilibrium problem in a table:



Plug the equilibrium concentrations into the equilibrium constant expression:

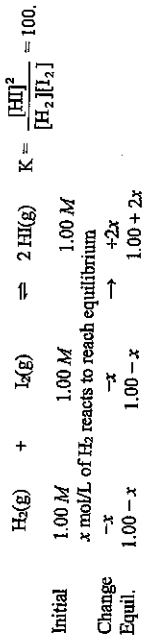
$$K = \frac{[\text{SO}_3][\text{NO}]}{[\text{SO}_2][\text{NO}_2]} = 3.75 = \frac{(0.800 + x)^2}{(0.800 - x)^2}; \text{ take the square root of both sides and solve for } x.$$

$$\frac{0.800 + x}{0.800 - x} = 1.94, \quad 0.800 + x = 1.55 - (1.94)x, \quad (2.94)x = 0.75, \quad x = 0.26 \text{ M}$$

The equilibrium concentrations are:

$$[\text{SO}_2] = [\text{NO}] = 0.800 + x = 0.800 + 0.26 = 1.06 \text{ M}; \quad [\text{SO}_3] = [\text{NO}_2] = 0.800 - x = 0.54 \text{ M}$$

52. $Q = 1.00$, which is less than K . Reaction shifts right to reach equilibrium.

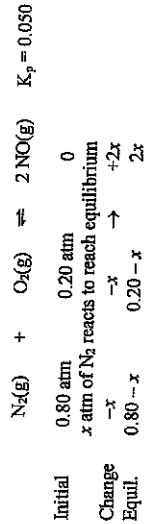


$$K = 100 = \frac{(1.00 + 2x)^2}{(1.00 - x)^2}; \text{ taking the square root of both sides:}$$

$$10.0 = \frac{1.00 + 2x}{1.00 - x}, \quad 10.0 - (10.0)x = 1.00 + 2x, \quad (12.0)x = 9.0, \quad x = 0.75 \text{ M}$$

$$[\text{H}_2] = [\text{I}_2] = 1.00 - 0.75 = 0.25 \text{ M}, \quad [\text{HI}] = 1.00 + 2(0.75) = 2.50 \text{ M}$$

53. Because only reactants are present initially, the reaction must proceed to the right to reach equilibrium. Summarizing the problem in a table:



$$K_p = 0.050 = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} \times P_{\text{O}_2}} = \frac{(2x)^2}{(0.80 - x)(0.20 - x)}, \quad 0.050(0.16 - (1.00)x + x^2) = 4x^2$$

$$4x^2 = 8.0 \times 10^{-3} - (0.050)x + (0.050)x^2, \quad (3.95)x^2 + (0.050)x - 8.0 \times 10^{-3} = 0$$

Solving using the quadratic formula (see Appendix 1 of the text):

$$x = \frac{-b \pm (b^2 - 4ac)^{1/2}}{2a} = \frac{-0.050 \pm [(0.050)^2 - 4(3.95)(-8.0 \times 10^{-3})]^{1/2}}{2(3.95)}$$

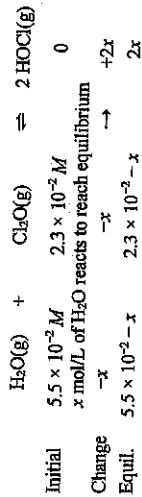
$x = 3.9 \times 10^{-2}$ atm or $x = -5.2 \times 10^{-2}$ atm; only $x = 3.9 \times 10^{-2}$ atm makes sense (x cannot be negative), so the equilibrium NO concentration is:

$$P_{\text{NO}} = 2x = 2(3.9 \times 10^{-2} \text{ atm}) = 7.8 \times 10^{-2} \text{ atm}$$



a. The initial concentrations of H_2O and Cl_2O are:

$$\frac{1.0 \text{ g H}_2\text{O}}{1.0 \text{ L}} \times \frac{1 \text{ mol}}{18.02 \text{ g}} = 5.5 \times 10^{-2} \text{ mol/L}, \quad \frac{2.0 \text{ g Cl}_2\text{O}}{1.0 \text{ L}} \times \frac{1 \text{ mol}}{86.90 \text{ g}} = 2.3 \times 10^{-2} \text{ mol/L}$$



$$K = 0.090 = \frac{(2x)^2}{(5.5 \times 10^{-2} - x)(2.3 \times 10^{-2} - x)}$$

$$1.14 \times 10^{-4} - (7.02 \times 10^{-3})x - 1.14 \times 10^{-4} = 0 \quad (\text{We carried extra significant figures.})$$

$$(3.91)x^2 + (7.02 \times 10^{-3})x - 1.14 \times 10^{-4} = 0 \quad (\text{We carried extra significant figures.})$$

Solving using the quadratic formula:

$$\frac{-7.02 \times 10^{-3} \pm (4.93 \times 10^{-5} + 1.78 \times 10^{-3})^{1/2}}{7.82} = 4.6 \times 10^{-3} \text{ or } -6.4 \times 10^{-3}$$

A negative answer makes no physical sense; we can't have less than nothing. Thus $x = 4.6 \times 10^{-3} \text{ M}$.

$$[\text{HOCl}] = 2x = 9.2 \times 10^{-3} \text{ M}; \quad [\text{Cl}_2\text{O}] = 2.3 \times 10^{-2} - x = 0.023 - 0.0046 = 1.8 \times 10^{-2} \text{ M}$$

$$[\text{H}_2\text{O}] = 5.5 \times 10^{-2} - x = 0.055 - 0.0046 = 5.0 \times 10^{-2} \text{ M}$$



Initial	0	0	1.0 mol/2.0 L = 0.50 M
Change	$-2x$	$+x$	$-2x$
Equil.	x	x	$0.50 - 2x$

$$K = 0.090 = \frac{[\text{HOCl}]^2}{[\text{H}_2\text{O}][\text{Cl}_2\text{O}]} = \frac{(0.50 - 2x)^2}{x^2}$$

The expression is a perfect square, so we can take the square root of each side:

$$0.30 = \frac{0.50 - 2x}{x}, \quad (0.30)x = 0.50 - 2x, \quad (2.30)x = 0.50$$

$x = 0.217$ (We carried extra significant figures.)

$$x = [\text{H}_2\text{O}] = [\text{Cl}_2\text{O}] = 0.217 = 0.22 \text{ M}, \quad [\text{HOCl}] = 0.50 - 2x = 0.50 - 0.434 = 0.07 \text{ M}$$



Initial	0.50 atm	0.50 atm	0
Change	$-2x$	$-x$	$+2x$
Equil.	$0.50 - 2x$	$0.50 - x$	$2x$

$$K_p = 0.25 = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}} = \frac{(2x)^2}{(0.50 - 2x)^2(0.50 - x)}$$

This will give a cubic equation. Graphing calculators can be used to solve this expression. If you don't have a graphing calculator, an alternative method for solving a cubic equation is to use the method of successive approximations (see Appendix 1 of the text). The first step is to guess a value for x . Because the value of K is small ($K < 1$), not much of the forward reaction will occur to reach equilibrium. This tells us that x is small. Let's guess that $x = 0.050$ atm. Now we take this estimated value for x and substitute it into the equation everywhere that x appears except for one. For equilibrium problems, we will substitute the estimated value for x into the denominator and then solve for the numerator value of x . We continue this process until the estimated value of x and the calculated value of x converge on the same number. This is the same answer we would get if we were to solve the cubic equation exactly. Applying the method of successive approximations and carrying extra significant figures:

$$\frac{4x^2}{[0.50 - 2(0.050)]^2 [0.50 - (0.050)]} = \frac{4x^2}{(0.40)^2 (0.45)} = 0.25, \quad x = 0.067$$

$$\frac{4x^2}{[0.50 - 2(0.067)]^2 [0.50 - (0.067)]} = \frac{4x^2}{(0.366)^2 (0.433)} = 0.25, \quad x = 0.060$$

$$\frac{4x^2}{(0.38)^2 (0.44)} = 0.25, \quad x = 0.063; \quad \frac{4x^2}{(0.374)^2 (0.437)} = 0.25, \quad x = 0.062$$

The next trial gives the same value for $x = 0.062$ atm. We are done except for determining the equilibrium concentrations. They are:

$$P_{\text{SO}_2} = 0.50 - 2x = 0.50 - 2(0.062) = 0.376 = 0.38 \text{ atm}$$

$$P_{\text{O}_2} = 0.50 - x = 0.438 = 0.44 \text{ atm}; \quad P_{\text{SO}_3} = 2x = 0.124 = 0.12 \text{ atm}$$

56. a. The reaction must proceed to products to reach equilibrium because no product is present initially. Summarizing the problem in a table where x atm of N_2O_4 reacts to reach equilibrium:

$\text{N}_2\text{O}_4(\text{g})$	\rightleftharpoons	$2 \text{NO}_2(\text{g})$	$K_p = 0.25$
Initial		4.5 atm	0
Change		$-x$	$+2x$
Equil.		$4.5 - x$	$2x$

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(2x)^2}{4.5 - x} = 0.25, \quad 4x^2 = 1.125 - (0.25)x, \quad 4x^2 + (0.25)x - 1.125 = 0$$

We carried extra significant figures in this expression (as will be typical when we solve an expression using the quadratic formula). Solving using the quadratic formula (Appendix 1 of text):

$$x = \frac{-0.25 \pm [(0.25)^2 - 4(4)(-1.125)]^{1/2}}{2(4)} = \frac{-0.25 \pm 4.25}{8}, \quad x = 0.50 \text{ (Other value is negative.)}$$

$$P_{\text{O}_2} = 2x = 1.0 \text{ atm}; \quad P_{\text{N}_2\text{O}_4} = 4.5 - x = 4.0 \text{ atm}$$

- b. The reaction must shift to reactants (shifts left) to reach equilibrium.

$\text{N}_2\text{O}_4(\text{g})$	\rightleftharpoons	$2 \text{NO}_2(\text{g})$
Initial		9.0 atm
Change		$-2x$
Equil.		$9.0 - 2x$

$$K_p = \frac{(9.0 - 2x)^2}{x} = 0.25, \quad 4x^2 - (36.25)x + 81 = 0 \text{ (carrying extra significant figures)}$$

$$\text{Solving: } x = \frac{-(-36.25) \pm [(-36.25)^2 - 4(4)(81)]^{1/2}}{2(4)}, \quad x = 4.0 \text{ atm}$$

The other value, 5.1, is impossible. $P_{\text{N}_2\text{O}_4} = x = 4.0$ atm; $P_{\text{NO}_2} = 9.0 - 2x = 1.0$ atm

c. No, we get the same equilibrium position starting with either pure N_2O_4 or pure NO_2 in stoichiometric amounts.

57. a. The reaction must proceed to products to reach equilibrium because only reactants are present initially. Summarizing the problem in a table:



Initial	$\frac{2.0 \text{ mol}}{2.0 \text{ L}} = 1.0 \text{ M}$	0	0	
Change	$-2x$	$+2x$	$+x$	
Equil.	$1.0 - 2x$	$2x$	x	

$$K = 1.6 \times 10^{-5} = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2x)^2(x)}{(1.0 - 2x)^2}$$

If we assume that $1.0 - 2x \approx 1.0$ (from the small size of K , we know that the product concentrations will be small), then:

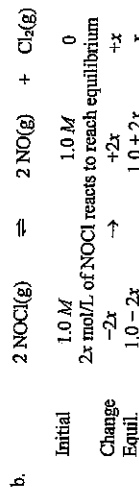
$$1.6 \times 10^{-5} = \frac{4x^3}{1.0^2}, \quad x = 1.6 \times 10^{-2}; \quad \text{now we must check the assumption.}$$

$$1.0 - 2x = 1.0 - 2(0.016) = 0.97 = 1.0 \text{ (to proper significant figures)}$$

Our error is about 3%; that is, $2x$ is 3.2% of 1.0 M . Generally, if the error we introduce by making simplifying assumptions is less than 5%, we go no further; the assumption is said to be valid. We call this the 5% rule. Solving for the equilibrium concentrations:

$$[\text{NO}] = 2x = 0.032 \text{ M}; \quad [\text{Cl}_2] = x = 0.016 \text{ M}; \quad [\text{NOCl}] = 1.0 - 2x = 0.97 \text{ M} \approx 1.0 \text{ M}$$

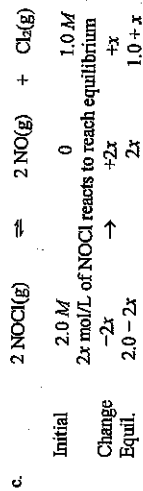
Note: If we were to solve this cubic equation exactly (a longer process), we get $x = 0.016$. This is the exact same answer we determined by making a simplifying assumption. We saved time and energy. Whenever K is a very small value ($K \ll 1$), always make the assumption that x is small. If the assumption introduces an error of less than 5%, then the answer you calculated making the assumption will be considered the correct answer.



$$1.6 \times 10^{-5} = \frac{(1.0 + 2x)^2(x)}{(1.0 - 2x)^2} = \frac{(1.0)^2(x)}{(1.0)^2} \quad (\text{assuming } 2x \ll 1.0)$$

$x = 1.6 \times 10^{-5}$; assumptions are great ($2x$ is $3.2 \times 10^{-3}\%$ of 1.0).

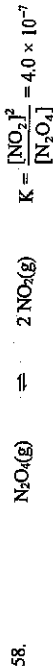
$$[\text{Cl}_2] = 1.6 \times 10^{-5} \text{ M and } [\text{NOCl}] = [\text{NO}] = 1.0 \text{ M}$$



$$1.6 \times 10^{-5} = \frac{(2x)^2(1.0 + x)}{(2.0 - 2x)^2} = \frac{4x^2}{4.0} \quad (\text{assuming } x \ll 1.0)$$

Solving: $x = 4.0 \times 10^{-3}$; assumptions good (x is 0.4% of 1.0 and $2x$ is 0.4% of 2.0).

$$[\text{Cl}_2] = 1.0 + x = 1.0 \text{ M}; \quad [\text{NO}] = 2(4.0 \times 10^{-3}) = 8.0 \times 10^{-3} \text{ M}; \quad [\text{NOCl}] = 2.0 \text{ M}$$



Initial	1.0 mol/10.0 L	0	
Change	$-x$	$+2x$	
Equil.	$0.10 - x$	$2x$	

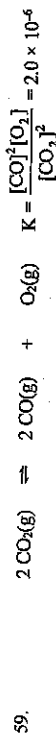
$$K = \frac{[\text{NO}_2]^2}{[\text{N}_2\text{O}_4]} = \frac{(2x)^2}{0.10 - x} = 4.0 \times 10^{-7}; \quad \text{because } K \text{ has a small value, assume that } x \text{ is small compared to } 0.10, \text{ so that } 0.10 - x \approx 0.10. \text{ Solving:}$$

$$4.0 \times 10^{-7} \approx \frac{4x^2}{0.10}, \quad 4x^2 = 4.0 \times 10^{-8}, \quad x = 1.0 \times 10^{-4} \text{ M}$$

Checking the assumption by the 5% rule: $\frac{x}{0.10} \times 100 = \frac{1.0 \times 10^{-4}}{0.10} \times 100 = 0.10\%$

Because this number is less than 5%, we will say that the assumption is valid.

$$[\text{N}_2\text{O}_4] = 0.10 - 1.0 \times 10^{-4} = 0.10 \text{ M}; \quad [\text{NO}_2] = 2x = 2(1.0 \times 10^{-4}) = 2.0 \times 10^{-4} \text{ M}$$



Initial	2.0 mol/5.0 L	0	0	
Change	$-2x$	$+2x$	$+x$	
Equil.	$0.40 - 2x$	$2x$	x	

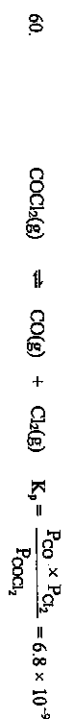
$$K = 2.0 \times 10^{-6} = \frac{[\text{CO}]^2[\text{O}_2]}{[\text{CO}_2]^2} = \frac{(2x)^2(x)}{(0.40 - 2x)^2}; \quad \text{assuming } 2x \ll 0.40:$$

$$2.0 \times 10^{-6} \approx \frac{4x^3}{(0.40)^2}, \quad 2.0 \times 10^{-6} = \frac{4x^3}{0.16}, \quad x = 4.3 \times 10^{-3} \text{ M}$$

Checking assumption: $\frac{2(4.3 \times 10^{-3})}{0.40} \times 100 = 2.2\%$, assumption is valid by the 5% rule.

$$[\text{CO}_2] = 0.40 - 2x = 0.40 - 2(4.3 \times 10^{-3}) = 0.39 \text{ M}$$

$$[\text{CO}] = 2x = 2(4.3 \times 10^{-3}) = 8.6 \times 10^{-3} \text{ M}, [\text{O}_2] = x = 4.3 \times 10^{-3} \text{ M}$$



Initial	1.0 atm	0	0
	x atm of COCl_2 reacts to reach equilibrium	$-x$	$+x$
Change	$-x$	$+x$	$+x$
Equil.	$1.0 - x$	x	x

$$6.8 \times 10^{-9} = \frac{P_{\text{CO}} \times P_{\text{Cl}_2}}{P_{\text{COCl}_2}} = \frac{x^2}{1.0 - x} \approx \frac{x^2}{1.0} \quad (\text{Assuming } 1.0 - x \approx 1.0)$$

$x = 8.2 \times 10^{-5}$ atm; assumption is good (x is $8.2 \times 10^{-3}\%$ of 1.0).

$$P_{\text{COCl}_2} = 1.0 - x = 1.0 - 8.2 \times 10^{-5} = 1.0 \text{ atm}, P_{\text{CO}} = P_{\text{Cl}_2} = x = 8.2 \times 10^{-5} \text{ atm}$$

61. This is a typical equilibrium problem except that the reaction contains a solid. Whenever solids and liquids are present, we basically ignore them in the equilibrium problem.



Initial	0	0	0
	Some $\text{NH}_4\text{OCONH}_2$ decomposes to produce $2x$ atm of NH_3 and x atm of CO_2 .	$+2x$	$+x$
Change	\rightarrow	$+2x$	$+x$
Equil.		$2x$	x

$$K_p = 2.9 \times 10^{-3} = P_{\text{NH}_3}^2 \times P_{\text{CO}_2} = (2x)^2(x) = 4x^3$$

$$x = \left(\frac{2.9 \times 10^{-3}}{4} \right)^{1/3} = 9.0 \times 10^{-2} \text{ atm}, P_{\text{NH}_3} = 2x = 0.18 \text{ atm}, P_{\text{CO}_2} = x = 9.0 \times 10^{-2} \text{ atm}$$

$$P_{\text{total}} = P_{\text{NH}_3} + P_{\text{CO}_2} = 0.18 \text{ atm} + 0.090 \text{ atm} = 0.27 \text{ atm}$$



For this system to reach equilibrium, some of the $\text{NH}_4\text{Cl}(\text{s})$ decomposes to form equal moles of $\text{NH}_3(\text{g})$ and $\text{HCl}(\text{g})$ at equilibrium. Because moles of HCl produced = moles of NH_3 produced, the partial pressures of each gas must be equal to each other.

$$\text{At equilibrium: } P_{\text{total}} = P_{\text{NH}_3} + P_{\text{HCl}} \text{ and } P_{\text{NH}_3} = P_{\text{HCl}}$$

$$P_{\text{total}} = 4.4 \text{ atm} = 2P_{\text{NH}_3}, 2.2 \text{ atm} = P_{\text{NH}_3} = P_{\text{HCl}}, K_p = (2.2)(2.2) = 4.8$$

Le Chatelier's Principle

63. a. No effect; adding more of a pure solid or pure liquid has no effect on the equilibrium position.
 b. Shifts left; $\text{HF}(\text{g})$ will be removed by reaction with the glass. As $\text{HF}(\text{g})$ is removed, the reaction will shift left to produce more $\text{HF}(\text{g})$.
 c. Shifts right; as $\text{H}_2\text{O}(\text{g})$ is removed, the reaction will shift right to produce more $\text{H}_2\text{O}(\text{g})$.
64. When the volume of a reaction container is increased, the reaction itself will want to increase its own volume by shifting to the side of the reaction that contains the most molecules of gas. When the molecules of gas are equal on both sides of the reaction, then the reaction will remain at equilibrium no matter what happens to the volume of the container.
- a. Reaction shifts left (to reactants) because the reactants contain 4 molecules of gas compared with 2 molecules of gas on the product side.
 b. Reaction shifts right (to products) because there are more product molecules of gas (2) than reactant molecules (1).
 c. No change because there are equal reactant and product molecules of gas.
 d. Reaction shifts right.
- e. Reaction shifts right to produce more $\text{CO}_2(\text{g})$. One can ignore the solids and only concentrate on the gases because gases occupy a relatively huge volume compared with solids. We make the same assumption when liquids are present (only worry about the gas molecules).
65. a. Right b. Right c. No effect; $\text{He}(\text{g})$ is neither a reactant nor a product.
 d. Left, because the reaction is exothermic, heat is a product.
 $\text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{CO}_2(\text{g}) + \text{heat}$
 Increasing T will add heat. The equilibrium shifts to the left to use up the added heat.
- e. No effect; because the moles of gaseous reactants equals the moles of gaseous products (2 mol versus 2 mol), a change in volume will have no effect on the equilibrium.
66. a. The moles of SO_2 will increase because the reaction will shift left to use up the added $\text{O}_2(\text{g})$.
 b. Increase, because there are fewer reactant gas molecules than product gas molecules, the reaction shifts left with a decrease in volume.
 c. No effect; the partial pressures of sulfur trioxide, sulfur dioxide, and oxygen are unchanged, so the reaction is still at equilibrium.

- d. Increase; heat + 2 SO₃ ⇌ 2 SO₂ + O₂; decreasing T will remove heat, shifting this endothermic reaction to the left to add heat.
- e. Decrease
67. a. Left b. Right c. Left
- d. No effect; the reactant and product concentrations/partial pressures are unchanged.
- e. No effect; because there are equal numbers of product and reactant gas molecules, a change in volume has no effect on this equilibrium position.
- f. Right; a decrease in temperature will shift the equilibrium to the right because heat is a product in this reaction (as is true in all exothermic reactions).
68. a. Shift to left
- b. Shift to right; because the reaction is endothermic (heat is a reactant), an increase in temperature will shift the equilibrium to the right.
- c. No effect; the reactant and product concentrations/partial pressures are unchanged.
- d. Shift to right

e. Shift to right; because there are more gaseous product molecules than gaseous reactant molecules, the equilibrium will shift right with an increase in volume.

69. An endothermic reaction, where heat is a reactant, will shift right to products with an increase in temperature. The amount of NH₃(g) will increase as the reaction shifts right, so the smell of ammonia will increase.

70. As temperature increases, the value of K decreases. This is consistent with an exothermic reaction. In an exothermic reaction, heat is a product, and an increase in temperature shifts the equilibrium to the reactant side (as well as lowering the value of K).

Additional Exercises

71.
$$\begin{array}{l} \text{O}_2(\text{g}) + \text{NO}(\text{g}) \rightleftharpoons \text{NO}_2(\text{g}) \\ \text{NO}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons \text{NO}(\text{g}) + \text{O}_3(\text{g}) \end{array} \quad \begin{array}{l} K = 1/(6.8 \times 10^{-48}) = 1.5 \times 10^{48} \\ K = 1/(5.8 \times 10^{-34}) = 1.7 \times 10^{33} \\ K = (1.5 \times 10^{48})(1.7 \times 10^{33}) = 2.6 \times 10^{81} \end{array}$$
72. a.
$$\begin{array}{l} \text{Na}_2\text{O}(\text{s}) \rightleftharpoons \text{Na}_2\text{O}(\text{g}) \\ 2 \text{Na}(\text{l}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{O}_2(\text{s}) \\ \text{Na}_2\text{O}(\text{s}) + 1/2 \text{O}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{O}_2(\text{s}) \end{array} \quad \begin{array}{l} K_1 \\ K_2 \\ K = (K_1)(1/K_2) \end{array}$$

$$K = (K_1)(1/K_2) = \frac{2 \times 10^{-25}}{5 \times 10^{-29}} = 4 \times 10^3$$

- b.
$$\begin{array}{l} \text{NaO}(\text{g}) \rightleftharpoons \text{Na}(\text{l}) + 1/2 \text{O}_2(\text{g}) \\ \text{Na}_2\text{O}(\text{s}) \rightleftharpoons 2 \text{Na}(\text{l}) + 1/2 \text{O}_2(\text{g}) \\ 2 \text{Na}(\text{l}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{O}_2(\text{s}) \end{array} \quad \begin{array}{l} K_2 \\ K_1 \\ 1/K_3 \end{array}$$
- $$\text{NaO}(\text{g}) + \text{Na}_2\text{O}(\text{s}) \rightleftharpoons \text{Na}_2\text{O}_2(\text{s}) + \text{Na}(\text{l}) \quad K = K_2(K_1)(1/K_3) = 8 \times 10^{-2}$$
- c.
$$\begin{array}{l} 2 \text{NaO}(\text{g}) \rightleftharpoons 2 \text{Na}(\text{l}) + \text{O}_2(\text{g}) \\ 2 \text{Na}(\text{l}) + \text{O}_2(\text{g}) \rightleftharpoons \text{Na}_2\text{O}_2(\text{s}) \\ 2 \text{NaO}(\text{g}) \rightleftharpoons \text{Na}_2\text{O}_2(\text{s}) \end{array} \quad \begin{array}{l} (K_2)^2 \\ 1/K_3 \\ K = (K_2)^2(1/K_3) = 8 \times 10^{18} \end{array}$$
73.
$$5.63 \text{ g C}_3\text{H}_6\text{O}_3 \times \frac{1 \text{ mol C}_3\text{H}_6\text{O}_3}{114.10 \text{ g}} = 0.0493 \text{ mol C}_3\text{H}_6\text{O}_3 \text{ initially}$$

$$\text{Total moles of gas at equilibrium} = n_{\text{total}} = \frac{P_{\text{total}}V}{RT} = \frac{1.63 \text{ atm} \times 2.50 \text{ L}}{0.08206 \text{ L atm} / \text{K mol} \times 473 \text{ K}} = 0.105 \text{ mol}$$



Initial	0.0493 mol	0	0	0	0
Change	-x	+x	+3x		
Equil.	0.0493 - x	x	3x		

$$0.105 \text{ mol total} = 0.0493 - x + x + 3x = 0.0493 + 3x, \quad x = 0.0186 \text{ mol}$$

$$K = \frac{[\text{C}_3\text{H}_6][\text{CO}]^3}{[\text{C}_3\text{H}_6\text{O}_3]} = \frac{\left[\frac{0.0186 \text{ mol C}_3\text{H}_6}{2.50 \text{ L}} \right] \left[\frac{3(0.0186 \text{ mol CO})}{2.50 \text{ L}} \right]^3}{\left[\frac{(0.0493 - 0.0186) \text{ mol C}_3\text{H}_6\text{O}_3}{2.50 \text{ L}} \right]} = 6.74 \times 10^{-6}$$

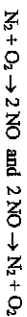
74. a.
$$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g}) \quad K_p = 1 \times 10^{-31} = \frac{P_{\text{NO}}^2}{P_{\text{N}_2} \times P_{\text{O}_2}} = \frac{P_{\text{NO}}^2}{(0.8)(0.2)}$$

$$\text{Solving: } P_{\text{NO}} = 1 \times 10^{-16} \text{ atm}$$

$$\text{In } 1.0 \text{ cm}^3 \text{ of air: } n_{\text{NO}} = \frac{PV}{RT} = \frac{(1 \times 10^{-16} \text{ atm})(1.0 \times 10^{-3} \text{ L})}{\left(\frac{0.08206 \text{ L atm}}{\text{K mol}} \right) (298 \text{ K})} = 4 \times 10^{-21} \text{ mol NO}$$

$$\frac{4 \times 10^{-21} \text{ mol NO}}{\text{cm}^3} \times \frac{6.02 \times 10^{23} \text{ molecules}}{\text{mol NO}} = \frac{2 \times 10^3 \text{ molecules NO}}{\text{cm}^3}$$

- b. There is more NO in the atmosphere than we would expect from the value of K . The answer must lie in the rates of the reaction. At 25°C, the rates of both reactions:



are so slow that they are essentially zero. Very strong bonds must be broken, the activation energy is very high. Therefore, the reaction essentially doesn't occur at low temperatures. Nitric oxide, however, can be produced in high-energy or high-temperature environments because the production of NO is endothermic. In nature, some NO is produced by lightning, and the primary manmade source is automobiles. At these high temperatures, K will increase, and the rates of the reaction will also increase, resulting in a higher production of NO. Once the NO gets into a more normal temperature environment, it doesn't go back to N_2 and O_2 because of the slow rate.



Initial	392.0 torr	0
Equil.	$392.0 - 2x$	$3x$

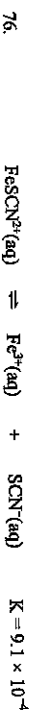
Using Dalton's law of partial pressure:

$$P_{\text{total}} = 488.0 \text{ torr} = P_{\text{AsH}_3} + P_{\text{H}_2} = 392.0 - 2x + 3x, \quad x = 96.0 \text{ torr}$$

$$P_{\text{H}_2} = 3x = 3(96.0) = 288 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.379 \text{ atm}$$

b. $P_{\text{AsH}_3} = 392.0 - 2(96.0) = 200.0 \text{ torr} \times \frac{1 \text{ atm}}{760 \text{ torr}} = 0.2632 \text{ atm}$

$$K_p = \frac{(P_{\text{H}_2})^3}{(P_{\text{AsH}_3})^2} = \frac{(0.379)^3}{(0.2632)^2} = 0.786$$



Initial	2.0 M	0	0
Change	x mol/L of FeSCN^{2+} reacts to reach equilibrium	$-x$	$+x$
Equil.	$2.0 - x$	x	x

$$9.1 \times 10^{-4} = \frac{[\text{Fe}^{3+}][\text{SCN}^{-}]}{[\text{FeSCN}^{2+}]} = \frac{x^2}{2.0 - x} = \frac{x^2}{2.0} \quad (\text{assuming } 2.0 - x \approx 2.0)$$

$x = 4.3 \times 10^{-2} \text{ M}$; assumption good by the 5% rule (x is 2.2% of 2.0).

$$[\text{FeSCN}^{2+}] = 2.0 - x = 2.0 - 4.3 \times 10^{-2} = 2.0 \text{ M}; \quad [\text{Fe}^{3+}] = [\text{SCN}^{-}] = x = 4.3 \times 10^{-2} \text{ M}$$

77. There is a little trick we can use to solve this problem without having to solve a quadratic equation. Because K is very large ($K \gg 1$), the reaction will have mostly products at equilibrium. So we will let the reaction go to completion (with Fe^{3+} limiting), and then solve an equilibrium problem to determine the molarity of reactants present at equilibrium (see the following set-up).



Before	0.020 M	0.10 M	0
Change	Let 0.020 mol/L Fe^{3+} react completely (K is large; products dominate).	Fe^{3+} react completely (K is large; products dominate).	0
After	-0.020	-0.020	+0.020
Change	0	0.08	0.020
Equil.	x mol/L FeSCN^{2+} reacts to reach equilibrium	$+x$	$-x$
Equil.	x	$0.08 + x$	$0.020 - x$

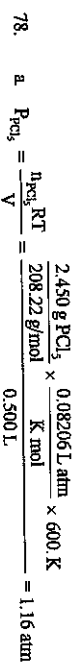
$$K = 1.1 \times 10^3 = \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^{-}]} = \frac{0.020 - x}{(x)(0.08 + x)} \approx \frac{0.020}{(0.08)x}$$

$x = 2 \times 10^{-4} \text{ M}$; x is 1% of 0.020. Assumptions are good by the 5% rule.

$$x = [\text{Fe}^{3+}] = 2 \times 10^{-4} \text{ M}; \quad [\text{SCN}^{-}] = 0.08 + 2 \times 10^{-4} = 0.08 \text{ M}$$

$$[\text{FeSCN}^{2+}] = 0.020 - 2 \times 10^{-4} = 0.020 \text{ M}$$

Note: At equilibrium, we do indeed have mostly products present. Our assumption to first let the reaction go to completion is good.



Initial	1.16 atm	0	0
Change	x atm of PCl_5 reacts to reach equilibrium	$-x$	$+x$
Equil.	$1.16 - x$	x	x

$$K_p = \frac{x^2}{1.16 - x} = 11.5, \quad x^2 + (11.5)x - 13.3 = 0$$

Using the quadratic formula: $x = 1.06 \text{ atm}$

$$P_{\text{PCl}_5} = 1.16 - 1.06 = 0.10 \text{ atm}$$

c. $P_{\text{PCl}_5} = P_{\text{Cl}_2} = 1.06 \text{ atm}$; $P_{\text{PCl}_3} = 0.10 \text{ atm}$

$$P_{\text{total}} = P_{\text{PCl}_5} + P_{\text{PCl}_3} + P_{\text{Cl}_2} = 0.10 + 1.06 + 1.06 = 2.22 \text{ atm}$$

d. Percent dissociation = $\frac{x}{1.16} \times 100 = \frac{1.06}{1.16} \times 100 = 91.4\%$



Initial	P_0	0	0	P_0 = initial pressure of SO_2Cl_2
Change	$-x$	$+x$	$+x$	
Equil.	$P_0 - x$	x	x	

$$P_{\text{total}} = 0.900 \text{ atm} = P_0 - x + x + x = P_0 + x$$

$$\frac{x}{P_0} \times 100 = 12.5, P_0 = (8.00)x$$

Solving: $0.900 = P_0 + x = (9.00)x$, $x = 0.100 \text{ atm}$

$$x = 0.100 \text{ atm} = P_{\text{Cl}_2} = P_{\text{SO}_2}; P_0 - x = 0.800 - 0.100 = 0.700 \text{ atm} = P_{\text{SO}_2\text{Cl}_2}$$

$$K_p = \frac{P_{\text{Cl}_2} \times P_{\text{SO}_2}}{P_{\text{SO}_2\text{Cl}_2}} = \frac{(0.100)^2}{0.700} = 1.43 \times 10^{-2}$$

80. $K = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(0.400 M)^2}{(0.0500 M)(0.0100 M)} = 320$; $0.200 \text{ mol F}_2/5.00 \text{ L} = 0.0400 M \text{ F}_2$ added

After F_2 has been added, the concentrations of species present are $[\text{HF}] = 0.400 M$, $[\text{H}_2] = [\text{F}_2] = 0.0500 M$. $Q = (0.400)^2/(0.0500)^2 = 64.0$; because $Q < K$, the reaction will shift right to reestablish equilibrium.

	$\text{H}_2(\text{g})$	+	$\text{F}_2(\text{g})$	\rightleftharpoons	$2 \text{ HF}(\text{g})$
Initial	$0.0500 M$		$0.0500 M$		$0.400 M$
	$x \text{ mol/L of F}_2$ reacts to reach equilibrium		$-x$		$+2x$
Change	$-x$		$-x$		$+2x$
Equil.	$0.0500 - x$		$0.0500 - x$		$0.400 + 2x$

$$K = 320 = \frac{(0.400 + 2x)^2}{(0.0500 - x)^2}; \text{ taking the square root of each side:}$$

$$17.9 = \frac{0.400 + 2x}{0.0500 - x}, 0.895 - (17.9)x = 0.400 + 2x, (19.9)x = 0.495, x = 0.0249 \text{ mol/L}$$

$$[\text{HF}] = 0.400 + 2(0.0249) = 0.450 M; [\text{H}_2] = [\text{F}_2] = 0.0500 - 0.0249 = 0.0251 M$$

81. $\text{CoCl}_2(\text{s}) + 6 \text{ H}_2\text{O}(\text{g}) \rightleftharpoons \text{CoCl}_2 \cdot 6\text{H}_2\text{O}(\text{s})$; if rain is imminent, there would be a lot of water vapor in the air. Because water vapor is a reactant gas, the reaction would shift to the right and would take on the color of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, pink

82. a. Doubling the volume will decrease all concentrations by a factor of one-half.

$$Q = \frac{\frac{1}{2}[\text{FeSCN}^{2+}]_{\text{eq}}}{\left(\frac{1}{2}[\text{Fe}^{3+}]_{\text{eq}}\right)\left(\frac{1}{2}[\text{SCN}^-]_{\text{eq}}\right)} = 2K, Q > K$$

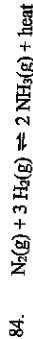
The reaction will shift to the left to reestablish equilibrium.

b. Adding Ag^+ will remove SCN^- through the formation of $\text{AgSCN}(\text{s})$. The reaction will shift to the left to produce more SCN^- .

c. Removing Fe^{3+} as $\text{Fe}(\text{OH})_3(\text{s})$ will shift the reaction to the left to produce more Fe^{3+} .

d. Reaction will shift to the right as Fe^{3+} is added.

83. $\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$; sodium hydroxide (NaOH) will react with the H^+ on the product side of the reaction. This effectively removes H^+ from the equilibrium, which will shift the reaction to the right to produce more H^+ and CrO_4^{2-} . Because more CrO_4^{2-} is produced, the solution turns yellow.



a. This reaction is exothermic, so an increase in temperature will decrease the value of K (see Table 13.3 of text.) This has the effect of lowering the amount of $\text{NH}_3(\text{g})$ produced at equilibrium. The temperature increase, therefore, must be for kinetics reasons. As temperature increases, the reaction reaches equilibrium much faster. At low temperatures, this reaction is very slow, too slow to be of any use.

b. As $\text{NH}_3(\text{g})$ is removed, the reaction shifts right to produce more $\text{NH}_3(\text{g})$.

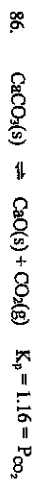
c. A catalyst has no effect on the equilibrium position. The purpose of a catalyst is to speed up a reaction so it reaches equilibrium more quickly.

d. When the pressure of reactants and products is high, the reaction shifts to the side that has fewer gas molecules. Since the product side contains two molecules of gas as compared to four molecules of gas on the reactant side, then the reaction shifts right to products at high pressures of reactants and products.

85. $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \quad K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]} = 4.5 \times 10^{-3}$

At equilibrium, $[PCl_5] = 2[PCl_3]$.

$$\text{Substituting: } 4.5 \times 10^{-3} = \frac{[PCl_5][Cl_2]}{2[PCl_3]}, \quad [Cl_2] = 2(4.5 \times 10^{-3}) = 9.0 \times 10^{-3} M$$



Some of the 20.0 g of $CaCO_3$ will react to reach equilibrium. The amount that reacts is the quantity of $CaCO_3$ required to produce a CO_2 pressure of 1.16 atm (from the K_p expression).

$$n_{CO_2} = \frac{P_{CO_2} V}{RT} = \frac{1.16 \text{ atm} \times 10.0 L}{0.08206 L \cdot \text{atm} \times 1073 K} = 0.132 \text{ mol } CO_2$$

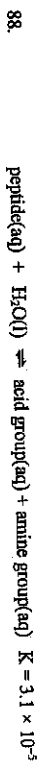
$$\text{Mass } CaCO_3 \text{ reacted} = 0.132 \text{ mol } CO_2 \times \frac{1 \text{ mol } CaCO_3}{\text{mol } CO_2} \times \frac{100.09 \text{ g}}{\text{mol } CaCO_3} = 13.2 \text{ g } CaCO_3$$

$$\text{Mass percent of } CaCO_3 \text{ reacted} = \frac{13.2 \text{ g}}{20.0 \text{ g}} \times 100 = 66.0\%$$



From the problem, $[\alpha\text{-D-glucose}] = 2[\beta\text{-D-glucose}]$, so:

$$K = \frac{[\beta\text{-D-glucose}]}{2[\beta\text{-D-glucose}]} = \frac{1}{2} = 0.50$$



Initial	$\frac{1.0 \text{ mol}}{1.0 L} = 1.0 M$	0	0
Change	$-x$	$+x$	$+x$
Equil.	$1.0 - x$	x	x

x mol/L peptide reacts to reach equilibrium.

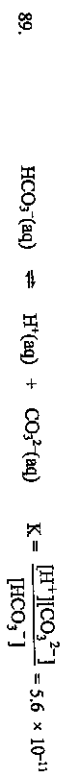
Note: Because water is not included in the K expression, the amount of water present initially and the amount of water that reacts are not needed to solve this problem.

$$K = 3.1 \times 10^{-5} = \frac{x(x)}{1.0 - x}, \quad 3.1 \times 10^{-5} \approx \frac{x^2}{1.0} \quad (\text{assuming } 1.0 - x \approx 1.0)$$

$$x = \sqrt{3.1 \times 10^{-5}} = 5.6 \times 10^{-3} M, \quad \text{assumption good (0.56\% error)}$$

$$[\text{peptide}] = 1.0 - x = 1.0 - 5.6 \times 10^{-3} = 1.0 M$$

$$[\text{acid group}] = [\text{amine group}] = x = 5.6 \times 10^{-3} M$$



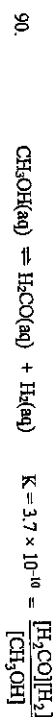
Initial	0.16 mol/1.0 L	0	0
Change	$-x$	$+x$	$+x$
Equil.	$0.16 - x$	x	x

x mol/L HCO_3^- reacts to reach equilibrium.

$$5.6 \times 10^{-11} = \frac{x(x)}{0.16 - x} \approx \frac{x^2}{0.16} \quad (\text{assuming } x \ll 0.16)$$

$$x = \sqrt{5.6 \times 10^{-11} (0.16)} = 3.0 \times 10^{-6} M, \quad \text{assumption good (8} \times 10^{-3}\% \text{ error)}$$

$$[CO_3^{2-}] = x = 3.0 \times 10^{-6} M$$



Initial	1.24 M	0	0
Change	$-x$	$+x$	$+x$
Equil.	$1.24 - x$	x	x

x mol/L CH_3OH reacts to reach equilibrium.

$$3.7 \times 10^{-10} = \frac{x(x)}{1.24 - x} \approx \frac{x^2}{1.24} \quad (\text{assuming } x \ll 1.24)$$

$$x = 2.1 \times 10^{-5} M, \quad \text{assumption good (1.7} \times 10^{-3}\% \text{ error)}$$

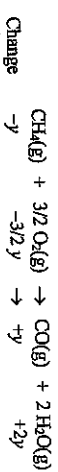
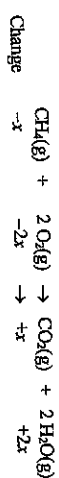
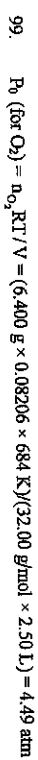
$$[H_2CO] = [H_2] = x = 2.1 \times 10^{-5} M, \quad [CH_3OH] = 1.24 - 2.1 \times 10^{-5} = 1.24 M$$

As formaldehyde is removed from the equilibrium by forming some other substance, the equilibrium shifts right to produce more formaldehyde. Hence the concentration of methanol (a reactant) decreases as formaldehyde (a product) reacts to form formic acid.

Chem Work Problems

The answers to the problems 91-98 (or a variation to these problem) are found in OWL. These problems are also assignable in OWL.

Challenge Problems



Amount of O₂ reacted = 4.49 atm - 0.326 atm = 4.16 atm O₂

$$2x + 3/2 y = 4.16 \text{ atm O}_2 \text{ and } 2x + 2y = 4.45 \text{ atm H}_2\text{O}$$

Solving using simultaneous equations:

$$\begin{array}{r} 2x + 2y = 4.45 \\ -2x - (3/2)y = -4.16 \\ \hline \end{array}$$

$$(0.50)y = 0.29, y = 0.58 \text{ atm} = P_{\text{CO}}$$

$$2x + 2(0.58) = 4.45, x = \frac{4.45 - 1.16}{2} = 1.65 \text{ atm} = P_{\text{CO}_2}$$

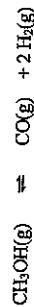
100. $4.72 \text{ g CH}_3\text{OH} \times \frac{1 \text{ mol}}{32.04 \text{ g}} = 0.147 \text{ mol CH}_3\text{OH}$ initially

$$\text{Graham's law of effusion: } \frac{\text{Rate}_1}{\text{Rate}_2} = \sqrt{\frac{M_2}{M_1}}$$

$$\frac{\text{Rate}_{\text{H}_2}}{\text{Rate}_{\text{CH}_3\text{OH}}} = \sqrt{\frac{M_{\text{CH}_3\text{OH}}}{M_{\text{H}_2}}} = \sqrt{\frac{32.04}{2.016}} = 3.987$$

The effused mixture has 33.0 times as much H₂ as CH₃OH. When the effusion rate ratio is multiplied by the equilibrium mole ratio of H₂ to CH₃OH, the effused mixture will have 33.0 times as much H₂ as CH₃OH. Let n_{H_2} and $n_{\text{CH}_3\text{OH}}$ equal the equilibrium moles of H₂ and CH₃OH, respectively.

$$33.0 = 3.987 \times \frac{n_{\text{H}_2}}{n_{\text{CH}_3\text{OH}}}, \frac{n_{\text{H}_2}}{n_{\text{CH}_3\text{OH}}} = 8.28$$



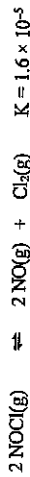
Initial	0.147 mol	0	0	0
Change	-x	→	+x	+2x
Equil.	0.147 - x		x	2x

$$\text{From the ICE table, } 8.28 = \frac{n_{\text{H}_2}}{n_{\text{CH}_3\text{OH}}} = \frac{2x}{0.147 - x}$$

Solving: $x = 0.118 \text{ mol}$

$$K = \frac{[\text{CO}][\text{H}_2]^2}{[\text{CH}_3\text{OH}]} = \frac{\left(\frac{0.118 \text{ mol}}{1.00 \text{ L}}\right)^2 \left(\frac{2(0.118 \text{ mol})}{1.00 \text{ L}}\right)}{\left(\frac{0.147 - 0.118}{1.00 \text{ L}}\right) \text{ mol}} = 0.23$$

101. There is a little trick we can use to solve this problem in order to avoid solving a cubic equation. Because K for this reaction is very small ($K \ll 1$), the reaction will contain mostly reactants at equilibrium (the equilibrium position lies far to the left). We will let the products react to completion by the reverse reaction, and then we will solve the forward equilibrium problem to determine the equilibrium concentrations. Summarizing these steps in a table:



Before	0	2.0 M	1.0 M	
Change	+2.0	←	-2.0	-1.0
After	2.0	0	0	0
Change	-2x	→	+2x	+x
Equil.	2.0 - 2x		2x	x

$$K = 1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(2.0 - 2x)^2} \approx \frac{4x^3}{2.0^2} \quad (\text{assuming } 2.0 - 2x \approx 2.0)$$

$$x^3 = 1.6 \times 10^{-5}, x = 2.5 \times 10^{-2} \text{ M, assumption good by the 5\% rule } (2x \text{ is } 2.5\% \text{ of } 2.0).$$

$$[\text{NOCl}] = 2.0 - 0.050 = 1.95 \text{ M} = 2.0 \text{ M}; [\text{NO}] = 0.050 \text{ M}; [\text{Cl}_2] = 0.025 \text{ M}$$

Note: If we do not break this problem into two parts (a stoichiometric part and an equilibrium part), then we are faced with solving a cubic equation. The setup would be:

2 NOCl	⇌	2 NO	+	Cl ₂
Initial		0		2.0 M
Change		+2y		← -2y
Equil.		2y		2.0 - 2y
		$1.6 \times 10^{-5} = \frac{(2.0 - 2y)^2(1.0 - y)}{(2y)^2}$		

If we say that y is small to simplify the problem, then:

$$1.6 \times 10^{-5} = \frac{2.0^2}{4y^2}; \text{ we get } y = 250. \text{ This is impossible!}$$

To solve this equation, we cannot make any simplifying assumptions; we have to solve the cubic equation exactly.

102. a

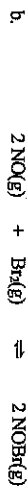
	2 NO(g)	+	Br ₂ (g)	⇌	2 NOBr(g)
Initial	98.4 torr		41.3 torr		0
Change	-2x		-x		+2x
Equil.	98.4 - 2x		41.3 - x		2x

$$P_{\text{total}} = P_{\text{NO}} + P_{\text{Br}_2} + P_{\text{NOBr}} = (98.4 - 2x) + (41.3 - x) + 2x = 139.7 - x$$

$$P_{\text{total}} = 110.5 = 139.7 - x, \quad x = 29.2 \text{ torr}, \quad P_{\text{NO}} = 98.4 - 2(29.2) = 40.0 \text{ torr} = 0.0526 \text{ atm}$$

$$P_{\text{Br}_2} = 41.3 - 29.2 = 12.1 \text{ torr} = 0.0159 \text{ atm}, \quad P_{\text{NOBr}} = 2(29.2) = 58.4 \text{ torr} = 0.0768 \text{ atm}$$

$$K_p = \frac{P_{\text{NOBr}}^2}{P_{\text{NO}} \times P_{\text{Br}_2}} = \frac{(0.0768 \text{ atm})^2}{(0.0526 \text{ atm})(0.0159 \text{ atm})} = 134$$



Initial	0.30 atm	0.30 atm	0
	2x atm of NO reacts to reach equilibrium		
Change	-2x	-x	+2x
Equil.	0.30 - 2x	0.30 - x	2x

This would yield a cubic equation, which can be difficult to solve unless you have a graphing calculator. Because K_p is pretty large, let's approach equilibrium in two steps: Assume the reaction goes to completion, and then solve the back-equilibrium problem.

2 NO + Br ₂	⇌	2 NOBr	
Before	0.30 atm	0.30 atm	0
	Let 0.30 atm NO react completely.		
Change	-0.30	-0.15	+0.30
After	0	0.15	0.30
	2y atm of NOBr reacts to reach equilibrium		
Change	+2y	+y	-2y
Equil.	2y	0.15 + y	0.30 - 2y

$$K_p = 134 = \frac{(0.30 - 2y)^2}{(2y)^2(0.15 + y)}, \quad \frac{(0.30 - 2y)^2}{(0.15 + y)} = 134 \times 4y^2 = 536y^2$$

If $y \ll 0.15$: $\frac{(0.30)^2}{0.15} \approx 536y^2$, then $y = 0.034$; assumptions are poor (y is 23% of 0.15).

Use 0.034 as an approximation for y , and solve by successive approximations (see Appendix 1 in the text):

$$\frac{(0.30 - 0.068)^2}{0.15 + 0.034} = 536y^2, \quad y = 0.023; \quad \frac{(0.30 - 0.046)^2}{0.15 + 0.023} = 536y^2, \quad y = 0.026$$

$$\frac{(0.30 - 0.052)^2}{0.15 + 0.026} = 536y^2, \quad y = 0.026 \text{ atm} \quad (\text{We have converged on the correct answer.})$$

So: $P_{\text{NO}} = 2y = 0.052 \text{ atm}$; $P_{\text{Br}_2} = 0.15 + y = 0.18 \text{ atm}$; $P_{\text{NOBr}} = 0.30 - 2y = 0.25 \text{ atm}$

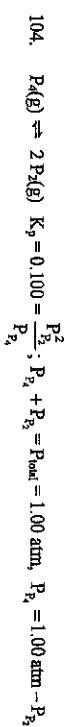


Initial	0	0	P_0	P_0 = initial pressure of NH_3
	2x atm of NH_3 reacts to reach equilibrium			
Change	+x	+3x	-2x	
Equil.	x	3x	$P_0 - 2x$	

From problem, $P_0 - 2x = \frac{P_0}{2.00}$, so $P_0 = (4.00)x$

$$K_p = \frac{[(4.00)x - 2x]^2}{(x)(3x)^3} = \frac{[(2.00)x]^2}{(x)(3x)^3} = \frac{(4.00)x^2}{27x^4} = \frac{4.00}{27x^2} = 5.3 \times 10^5, \quad x = 5.3 \times 10^{-4} \text{ atm}$$

$$P_0 = (4.00)x = 4.00(5.3 \times 10^{-4} \text{ atm}) = 2.1 \times 10^{-3} \text{ atm}$$



$$\text{Let } y = P_{\text{P}_2} \text{ at equilibrium, then } K_p = \frac{y^2}{1.00 - y} = 0.100$$

$$\text{Solving: } y = 0.270 \text{ atm} = P_{\text{P}_2}; \quad P_{\text{P}_4} = 1.00 - 0.270 = 0.73 \text{ atm}$$

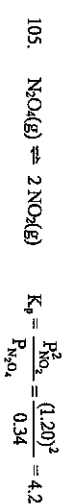
To solve for the fraction dissociated, we need the initial pressure of P_4 (mol \propto pressure)

$\text{P}_4(\text{g})$	⇌	$2 \text{ P}_2(\text{g})$	
Initial	P_0	0	P_0 = initial pressure of P_4 in atm.
	x atm of P_4 reacts to reach equilibrium		
Change	-x	+2x	
Equil.	$P_0 - x$	2x	

$$P_{\text{total}} = P_0 - x + 2x = 1.00 \text{ atm} = P_0 + x$$

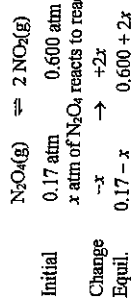
$$\text{Solving: } 0.270 \text{ atm} = P_2 = 2x, \quad x = 0.135 \text{ atm}, \quad P_0 = 1.00 - 0.135 = 0.87 \text{ atm}$$

Fraction dissociated = $\frac{x}{P_0} = \frac{0.135}{0.87} = 0.16$, or 16% of P_4 is dissociated to reach equilibrium.



Doubling the volume decreases each partial pressure by a factor of 2 ($P = nRT/V$). $P_{\text{NO}_2} = 0.600 \text{ atm}$ and $P_{\text{N}_2\text{O}_4} = 0.17 \text{ atm}$ are the new partial pressures.

$$Q = \frac{(0.600)^2}{0.17} = 2.1, \text{ so } Q < K; \text{ equilibrium will shift to the right.}$$



$$K_p = 4.2 = \frac{(0.600 + 2x)^2}{(0.17 - x)}, \quad 4x^2 + (6.6)x - 0.354 = 0 \quad (\text{carrying extra significant figures})$$

Solving using the quadratic formula: $x = 0.052$

$$P_{\text{NO}_2} = 0.600 + 2(0.052) = 0.704 \text{ atm}; \quad P_{\text{N}_2\text{O}_4} = 0.17 - 0.052 = 0.12 \text{ atm}$$



Initial 0
 Let some $\text{NaHCO}_3(\text{s})$ decompose to form x atm each of $\text{CO}_2(\text{g})$ and $\text{H}_2\text{O}(\text{g})$ at equilibrium.

Change $+x$
 Equil. x

$$K_p = 0.25 = P_{\text{CO}_2} \times P_{\text{H}_2\text{O}}, \quad 0.25 = x^2, \quad x = P_{\text{CO}_2} = P_{\text{H}_2\text{O}} = 0.50 \text{ atm}$$

b. $n_{\text{CO}_2} = \frac{P_{\text{CO}_2} V}{RT} = \frac{(0.50 \text{ atm})(1.00 \text{ L})}{(0.08206 \text{ L atm/K} \cdot \text{mol})(398 \text{ K})} = 1.5 \times 10^{-2} \text{ mol CO}_2$

Mass of Na_2CO_3 produced:

$$1.5 \times 10^{-2} \text{ mol CO}_2 \times \frac{1 \text{ mol Na}_2\text{CO}_3}{\text{mol CO}_2} \times \frac{105.99 \text{ g Na}_2\text{CO}_3}{\text{mol Na}_2\text{CO}_3} = 1.6 \text{ g Na}_2\text{CO}_3$$

Mass of NaHCO_3 reacted:

$$1.5 \times 10^{-2} \text{ mol CO}_2 \times \frac{2 \text{ mol NaHCO}_3}{1 \text{ mol CO}_2} \times \frac{84.01 \text{ g NaHCO}_3}{\text{mol}} = 2.5 \text{ g NaHCO}_3$$

Mass of NaHCO_3 remaining = $10.0 - 2.5 = 7.5 \text{ g}$

c. $10.0 \text{ g NaHCO}_3 \times \frac{1 \text{ mol NaHCO}_3}{84.01 \text{ g NaHCO}_3} \times \frac{1 \text{ mol CO}_2}{2 \text{ mol NaHCO}_3} = 5.95 \times 10^{-2} \text{ mol CO}_2$

When all of the NaHCO_3 has just been consumed, we will have $5.95 \times 10^{-2} \text{ mol CO}_2$ gas at a pressure of 0.50 atm (from a).

$$V = \frac{nRT}{P} = \frac{(5.95 \times 10^{-2} \text{ mol})(0.08206 \text{ L atm/K} \cdot \text{mol})(398 \text{ K})}{(0.50 \text{ atm})} = 3.9 \text{ L}$$

107. a. $\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$; because the temperature is constant, the value of K will be the same for both container volumes. Since we now the volume in the final mixture, let's calculate K using this mixture. In this final mixture, 2 N_2 molecules, 2 H_2 molecules, and 6 NH_3 molecules are present in a 1.0 L container. Using units of molecules/L for concentrations:

$$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{6 \text{ NH}_3 \text{ molecules}}{1.00 \text{ L}}\right)^2}{\left(\frac{2 \text{ N}_2 \text{ molecules}}{1.00 \text{ L}}\right)\left(\frac{2 \text{ H}_2 \text{ molecules}}{1.00 \text{ L}}\right)^3} = 2.25 \frac{\text{L}^2}{\text{molecules}^2}$$

For the K value in typical mol/L units for the concentrations:

$$K = 2.25 \frac{\text{L}^2}{\text{molecules}^2} \times \left(\frac{6.022 \times 10^{23} \text{ molecules}}{\text{mol}}\right)^2 = 8.16 \times 10^{47} \frac{\text{L}^2}{\text{mol}^2} = 8.16 \times 10^{47}$$

- b. Because temperature is constant, the initial mixture at the larger volume must also have $K = 2.25 \text{ L}^2/\text{molecules}^2$. In the initial mixture, there are 2 N_2 molecules, 4 H_2 molecules, and 8 H_2 molecules in some unknown volume, V .

$$K = 2.25 = \frac{\left(\frac{2 \text{ NH}_3 \text{ molecules}}{V}\right)^2}{\left(\frac{4 \text{ N}_2 \text{ molecules}}{V}\right)\left(\frac{8 \text{ H}_2 \text{ molecules}}{V}\right)^3} = \frac{4V^2}{4(512)} = \frac{V^2}{512}$$

$$V = \sqrt{2.25(512)} = 33.9 \text{ L}; \text{ the volume of the initial container would be } 33.9 \text{ L.}$$

108. a. If the volume is increased, equilibrium will shift to the right, so the mole percent of N_2O_5 decomposed will be greater than 0.50% .

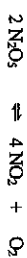


Initial	1.000 atm	0	0
Change	-0.0050	$+0.010$	$+0.0025$
Equil.	0.995	0.010	0.0025

$$K_p = \frac{(0.010)^4(0.0025)}{(0.995)^2} = 2.5 \times 10^{-11}$$

The new volume is 10.0 times the old volume. Therefore, the initial partial pressure of N_2O_5 will decrease by a factor of 10.0 .

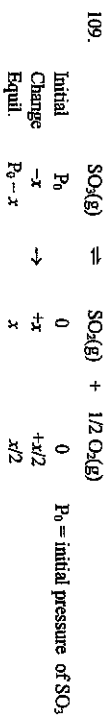
$$P_{\text{N}_2\text{O}_5} = 1.00 \text{ atm} \times \frac{1.00}{10.0} = 0.100 \text{ atm}$$



Initial	0.100 atm	0	0
Change	-2x	+4x	+x
Equil.	0.100 - 2x	4x	x

$$2.5 \times 10^{-11} = \frac{(4x)^4(x)}{(0.100 - 2x)^2} \approx \frac{(4x)^4(x)}{(0.100)^2}, \quad 2x = 2.0 \times 10^{-3} \text{ atm} = P_{\text{N}_2\text{O}_5} \text{ decomposed}$$

$$\frac{2.0 \times 10^{-3}}{0.100} \times 100 = 2.0\% \text{ N}_2\text{O}_5 \text{ decomposed (moles and } P \text{ are directly related)}$$



Average molar mass of the mixture is:

$$\text{average molar mass} = \frac{RT}{P} = \frac{(1.60 \text{ g/L})(0.08206 \text{ L atm/K} \cdot \text{mol})(873 \text{ K})}{1.80 \text{ atm}} = 63.7 \text{ g/mol}$$

The average molar mass is determined by:

$$\text{average molar mass} = \frac{n_{\text{SO}_2}(80.07 \text{ g/mol}) + n_{\text{SO}_3}(64.07 \text{ g/mol}) + n_{\text{O}_2}(32.00 \text{ g/mol})}{n_{\text{total}}}$$

Because $\chi_A = \text{mol fraction of component A} = n_A/n_{\text{total}} = P_A/P_{\text{total}}$:

$$63.7 \text{ g/mol} = \frac{P_{\text{SO}_2}(80.07) + P_{\text{SO}_3}(64.07) + P_{\text{O}_2}(32.00)}{P_{\text{total}}}$$

$$P_{\text{total}} = P_0 - x + x + x/2 = P_0 + x/2 = 1.80 \text{ atm}, \quad P_0 = 1.80 - x/2$$

$$63.7 = \frac{(P_0 - x)(80.07) + x(64.07) + \frac{x}{2}(32.00)}{1.80}$$

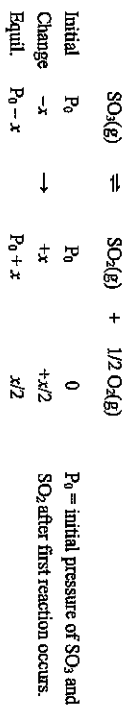
$$63.7 = \frac{(1.80 - 3/2x)(80.07) + x(64.07) + \frac{x}{2}(32.00)}{1.80}$$

$$115 = 144 - (120/1)x + (64.07)x + (16.00)x, \quad (40.07)x = 29, \quad x = 0.73 \text{ atm}$$

$$P_{\text{SO}_2} = P_0 - x = 1.80 - (3/2)x = 0.71 \text{ atm}, \quad P_{\text{SO}_3} = 0.73 \text{ atm}, \quad P_{\text{O}_2} = x/2 = 0.37 \text{ atm}$$

$$K_p = \frac{P_{\text{SO}_2} \times P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} = \frac{(0.73)(0.37)^{1/2}}{(0.71)} = 0.63$$

110. The first reaction produces equal amounts of SO_2 and SO_3 . Using the second reaction, calculate the SO_2 , SO_3 and O_2 partial pressures at equilibrium.



$$P_{\text{total}} = P_0 - x + P_0 + x + x/2 = 2P_0 + x/2 = 0.836 \text{ atm}$$

$$P_{\text{O}_2} = x/2 = 0.0275 \text{ atm}, \quad x = 0.0550 \text{ atm}$$

$$2P_0 + x/2 = 0.836 \text{ atm}, \quad 2P_0 = 0.836 - 0.0275 = 0.809 \text{ atm}, \quad P_0 = 0.405 \text{ atm}$$

$$P_{\text{SO}_2} = P_0 - x = 0.405 - 0.0550 = 0.350 \text{ atm}, \quad P_{\text{SO}_3} = P_0 + x = 0.405 + 0.0550 = 0.460 \text{ atm}$$

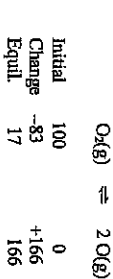
For the reaction $2 \text{FeSO}_4(\text{s}) \rightleftharpoons \text{Fe}_2\text{O}_3(\text{s}) + \text{SO}_2(\text{g}) + \text{SO}_3(\text{g})$:

$$K_p = P_{\text{SO}_2} \times P_{\text{SO}_3} = (0.460)(0.350) = 0.161$$

For the reaction $\text{SO}_2(\text{g}) \rightleftharpoons \text{SO}_3(\text{g}) + 1/2 \text{O}_2(\text{g})$:

$$K_p = \frac{P_{\text{SO}_2} \times P_{\text{O}_2}^{1/2}}{P_{\text{SO}_3}} = \frac{(0.460)(0.0275)^{1/2}}{0.350} = 0.218$$

111. When exactly 100 O_2 molecules are initially present at 5000 K and 1.000 atm:

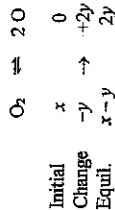


$$\text{Mole fraction } \text{O} = \chi_{\text{O}} = \frac{166}{183} = 0.9071 \text{ and } \chi_{\text{O}_2} = 0.0929, \quad P_{\text{O}_2} = \chi_{\text{O}_2} P_{\text{total}} \text{ and } P_{\text{O}} = \chi_{\text{O}} P_{\text{total}}$$

Because initially $P_{\text{total}} = 1.000 \text{ atm}$, $P_{\text{O}_2} = 0.0929 \text{ atm}$ and $P_{\text{O}} = 0.9071 \text{ atm}$.

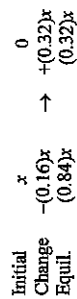
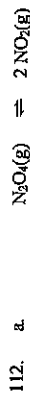
$$K_p = \frac{P_{\text{O}}^2}{P_{\text{O}_2}} = \frac{(0.9071)^2}{0.0929} = 8.86 \text{ atm}$$

At 95.0% O_2 dissociated, let x = initial partial pressure of O_2 and y = amount (atm) of O_2 that dissociates to reach equilibrium.

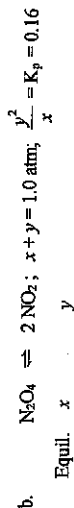


$$\frac{(2y)^2}{x-y} = 8.86; \frac{y}{x} \times 100 = 95.0; \text{ we have two equations and two unknowns.}$$

Solving: $x = 0.123$ atm and $y = 0.117$ atm; $P_{\text{total}} = (x-y) + 2y = 0.240$ atm

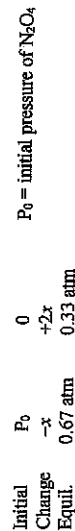
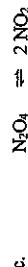


$$(0.84)x + (0.32)x = 1.5 \text{ atm; } K_p = \frac{(0.42)^2}{1.1} = 0.16$$



We have 2 equations and 2 unknowns. Solving:

$$x = 0.67 \text{ atm } (= P_{N_2O_4}) \text{ and } y = 0.33 \text{ atm } (= P_{NO_2})$$



$$2x = 0.33; x = 0.165 \text{ (using extra sig. figs.)}$$

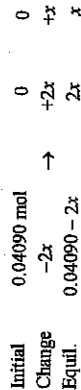
$$P_0 - x = 0.67; P_0 = 0.67 + 0.165 = 0.84 \text{ atm; } \frac{0.165}{0.84} \times 100 = 20.0\% \text{ dissociated}$$

113. a. Because the density (mass/volume) decreased while the mass remained constant (mass is conserved in a chemical reaction), the volume must have increased as reactants were converted to products. The volume increased because the number of moles of gas increased ($V \propto n$ at constant T and P).

$$\frac{\text{Density (initial)}}{\text{Density (equil.)}} = \frac{4.495 \text{ g/L}}{4.086 \text{ g/L}} = 1.100 = \frac{V_{\text{equil.}}}{V_{\text{initial}}} = \frac{n_{\text{equil.}}}{n_{\text{initial}}}$$

Assuming an initial volume of 1.000 L:

$$4.495 \text{ g NOBr} \times \frac{1 \text{ mol NOBr}}{109.91 \text{ g}} = 0.04090 \text{ mol NOBr initially}$$



$$\frac{n_{\text{equil.}}}{n_{\text{initial}}} = \frac{0.04090 - 2x + 2x + x}{0.04090} = 1.100; \text{ solving: } x = 0.00409 \text{ mol}$$

If the initial volume is 1.000 L, then the equilibrium volume will be 1.110 (1.000 L) = 1.110 L. Solving for the equilibrium concentrations:

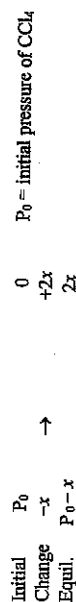
$$[NOBr] = \frac{0.03272 \text{ mol}}{1.100 \text{ L}} = 0.02975 \text{ M; } [NO] = \frac{0.00818 \text{ mol}}{1.100 \text{ L}} = 0.00744 \text{ M}$$

$$[Br_2] = \frac{0.00409 \text{ mol}}{1.100 \text{ L}} = 0.00372 \text{ M}$$

$$K = \frac{(0.00744)^2(0.00372)}{(0.02975)^2} = 2.33 \times 10^{-4}$$

b. The argon gas will increase the volume of the container. This is because the container is a constant-pressure system, and if the number of moles increases at constant T and P , the volume must increase. An increase in volume will dilute the concentrations of all gaseous reactants and gaseous products. Because there are more moles of product gases versus reactant gases (3 mol versus 2 mol), the dilution will decrease the numerator of K more than the denominator will decrease. This causes $Q < K$ and the reaction shifts right to get back to equilibrium.

Because temperature was unchanged, the value of K will not change. K is a constant as long as temperature is constant.



$$P_{\text{total}} = P_0 - x + 2x = P_0 + x = 1.20 \text{ atm}$$

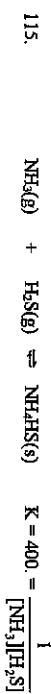
$$K_p = \frac{(2x)^2}{P_0 - x} = 0.76; 4x^2 = (0.76)P_0 - (0.76)x; P_0 = \frac{4x^2 + (0.76)x}{0.76}$$

Substituting into $P_0 + x = 1.20$:

$$\frac{4x^2}{0.76} + x + x = 1.20 \text{ atm}, (5.3)x^2 + 2x - 1.20 = 0, \text{ solving using the quadratic formula:}$$

$$x = \frac{-2 \pm (4 + 25.4)^{1/2}}{2(5.3)} = 0.32 \text{ atm}, P_0 + 0.32 = 1.20, P_0 = 0.88 \text{ atm}$$

Integrative Problems



Initial	$\frac{2.00 \text{ mol}}{5.00 \text{ L}}$	$\frac{2.00 \text{ mol}}{5.00 \text{ L}}$
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x mol/L of NH_3 reacts to reach equilibrium

Change	$-x$	$-x$
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Equil.	$0.400 - x$	$0.400 - x$
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$$K = 400 = \frac{1}{(0.400 - x)(0.400 - x)}, \quad 0.400 - x = \left(\frac{1}{400}\right)^{1/2} = 0.0500, \quad x = 0.350 \text{ M}$$

Moles $\text{NH}_4\text{HS}(\text{s})$ produced = $5.00 \text{ L} \times \frac{0.350 \text{ mol NH}_3}{\text{L}} \times \frac{1 \text{ mol NH}_4\text{HS}}{\text{mol NH}_3} = 1.75 \text{ mol}$

Total moles $\text{NH}_4\text{HS}(\text{s}) = 2.00 \text{ mol}$ initially + 1.75 mol produced = 3.75 mol total

$$3.75 \text{ mol NH}_4\text{HS} \times \frac{51.12 \text{ g NH}_4\text{HS}}{\text{mol NH}_4\text{HS}} = 192 \text{ g NH}_4\text{HS}$$

$$[\text{H}_2\text{S}]_e = 0.400 \text{ M} - x = 0.400 \text{ M} - 0.350 \text{ M} = 0.050 \text{ M/HS}$$

$$P_{\text{H}_2\text{S}} = \frac{n_{\text{H}_2\text{S}}RT}{V} = \frac{n_{\text{H}_2\text{S}}}{V} \times RT = \frac{0.050 \text{ mol}}{\text{L}} \times \frac{0.08206 \text{ L atm}}{\text{K mol}} \times 308.2 \text{ K} = 1.3 \text{ atm}$$

116. See the hint for Exercise 71.



$$\text{C}(\text{g}) + \text{D}(\text{g}) \rightleftharpoons 2 \text{ B}(\text{g}) \quad K = K_1 \times K_2 = 0.579$$

$$K_p = K(\text{RT})^{\Delta n}, \quad \Delta n = 2 - (1 + 1) = 0, \text{ because } \Delta n = 0, K_p = K = 0.579.$$



Initial	1.50 atm	1.50 atm
Equil.	$1.50 - x$	$1.50 - x$

$$0.579 = K = \frac{(2x)^2}{(1.50 - x)(1.50 - x)} = \frac{(2x)^2}{(1.50 - x)^2}$$

$$\frac{2x}{1.50 - x} = (0.579)^{1/2} = 0.761, \quad x = 0.413 \text{ atm}$$

$$P_{\text{B}} \text{ (at equilibrium)} = 2x = 2(0.413) = 0.826 \text{ atm}$$

$$P_{\text{total}} = P_{\text{C}} + P_{\text{D}} + P_{\text{B}} = 2(1.50 - 0.413) + 0.826 = 3.00 \text{ atm}$$

$$P_{\text{B}} = \chi_{\text{B}} P_{\text{total}}, \quad \chi_{\text{B}} = \frac{P_{\text{B}}}{P_{\text{total}}} = \frac{0.826 \text{ atm}}{3.00 \text{ atm}} = 0.275$$

117. Initial moles $\text{VCl}_4 = 6.6834 \text{ g VCl}_4 \times 1 \text{ mol VCl}_4 / 192.74 \text{ g VCl}_4 = 3.4676 \times 10^{-2} \text{ mol VCl}_4$

$$\text{Total molality of solute particles} = i m = \frac{\Delta T}{K_f} = \frac{5.97^\circ\text{C}}{29.8^\circ\text{C kg/mol}} = 0.200 \text{ mol/kg}$$

Because we have 0.1000 kg CCl_4 , the total moles of solute particles present is:

$$0.200 \text{ mol/kg}(0.1000 \text{ kg}) = 0.0200 \text{ mol}$$



$$K = \frac{[\text{V}_2\text{Cl}_8]}{[\text{VCl}_4]^2}$$

Initial	$3.4676 \times 10^{-2} \text{ mol}$	0
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$2x$ mol VCl_4 reacts to reach equilibrium

Equil.	$3.4676 \times 10^{-2} - 2x$	x
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Total moles solute particles = $0.0200 \text{ mol} = \text{mol VCl}_4 + \text{mol V}_2\text{Cl}_8 = 3.4676 \times 10^{-2} - 2x + x$

$$0.0200 = 3.4676 \times 10^{-2} - x, \quad x = 0.0147 \text{ mol}$$

At equilibrium, we have $0.0147 \text{ mol V}_2\text{Cl}_8$ and $0.0200 - 0.0147 = 0.0053 \text{ mol VCl}_4$. To determine the equilibrium constant, we need the total volume of solution in order to calculate equilibrium concentrations. The total mass of solution is $100.0 \text{ g} + 6.6834 \text{ g} = 106.7 \text{ g}$.

$$\text{Total volume} = 106.7 \text{ g} \times 1 \text{ cm}^3 / 1.696 \text{ g} = 62.91 \text{ cm}^3 = 0.06291 \text{ L}$$

The equilibrium concentrations are:

$$[V_2Cl_6] = \frac{0.0147 \text{ mol}}{0.0629 \text{ L}} = 0.234 \text{ mol/L}; [VCl_4] = \frac{0.0053 \text{ mol}}{0.0629 \text{ L}} = 0.084 \text{ mol/L}$$

$$K = \frac{[V_2Cl_6]}{[VCl_4]^2} = \frac{0.234}{(0.084)^2} = 33$$

118. Assuming 100.00 g naphthalene:

$$93.71 \text{ g C} \times \frac{1 \text{ mol C}}{12.01 \text{ g}} = 7.803 \text{ mol C}$$

$$6.29 \text{ g H} \times \frac{1 \text{ mol H}}{1.008 \text{ g}} = 6.24 \text{ mol H}; \frac{7.803}{6.24} = 1.25$$

Empirical formula = $(C_{1.25}H)_x = C_5H_4$; molar mass = $\frac{32.8 \text{ g}}{0.256 \text{ mol}} = 128 \text{ g/mol}$

Because the empirical mass (64.08 g/mol) is one-half of 128, the molecular formula is $C_{10}H_8$.



Initial

0

Equil.

Let some $C_{10}H_8(s)$ sublime to form $x \text{ mol/L}$ of $C_{10}H_8(g)$ at equilibrium.

$$K = 4.29 \times 10^{-6} = [C_{10}H_8] = x$$

Mol $C_{10}H_8$ sublimed = $5.00 \text{ L} \times 4.29 \times 10^{-6} \text{ mol/L} = 2.15 \times 10^{-5} \text{ mol}$ $C_{10}H_8$ sublimed

Mol $C_{10}H_8$ initially = $3.00 \text{ g} \times \frac{1 \text{ mol } C_{10}H_8}{128.16 \text{ g}} = 2.34 \times 10^{-2} \text{ mol}$ $C_{10}H_8$ initially

Percent $C_{10}H_8$ sublimed = $\frac{2.15 \times 10^{-5} \text{ mol}}{2.34 \times 10^{-2} \text{ mol}} \times 100 = 0.0919\%$

Marathon Problem

119. $\frac{2.00 \text{ g}}{165 \text{ g/mol}} = 0.0121 \text{ mol XY}$ (initially)

$(0.350)(0.0121 \text{ mol}) = 4.24 \times 10^{-3} \text{ mol XY}$ dissociated

	XY	\rightleftharpoons	X	+	Y
Initial	0.0121 mol		0		0
Change	-0.00424	→	+0.00424		+0.00424
Equil.	0.0079 mol		0.00424 mol		0.00424 mol

Total moles of gas = $0.0079 + 0.00424 + 0.00424 = 0.0164 \text{ mol}$

For an ideal gas at constant P and T, $V \propto n$. So: $\frac{V_{\text{final}}}{V_{\text{initial}}} = \frac{n_{\text{final}}}{n_{\text{initial}}} = \frac{0.0164 \text{ mol}}{0.0121 \text{ mol}} = 1.36$

$$V_{\text{initial}} = \frac{nRT}{P} = \frac{(0.0121 \text{ mol})(0.08206 \text{ L atm/K mol})(298 \text{ K})}{0.967 \text{ atm}} = 0.306 \text{ L}$$

$$V_{\text{final}} = 0.306 \text{ L}(1.36) = 0.416 \text{ L}$$

Because mass is conserved in a chemical reaction:

$$\text{density (final)} = \frac{\text{mass}}{\text{volume}} = \frac{2.00 \text{ g}}{0.416 \text{ L}} = 4.81 \text{ g/L}$$

$$K = \frac{[X][Y]}{[XY]} = \frac{\left(\frac{0.00424 \text{ mol}}{0.416 \text{ L}}\right)^2}{\left(\frac{0.0079 \text{ mol}}{0.416 \text{ L}}\right)} = 5.5 \times 10^{-3}$$

