Chemical Equilibrium

Chapter 13

Figure 13.2: The changes in concentrations with time for the reaction:

$$H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$$
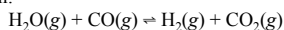
when equimolar quantities of $H_2O(g)$ and $CO(g)$ are mixed.
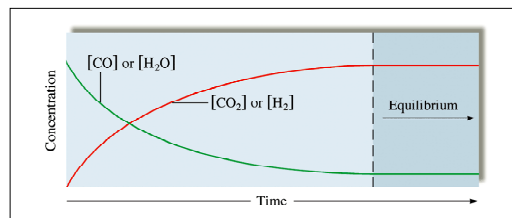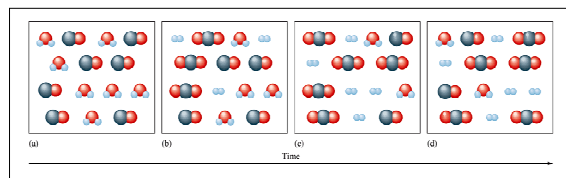

CHEMICAL EQUILIBRIUM

OBJECTIVES:

- **Be able to apply stoichiometry to an equilibrium mixture to determine equilibrium concentrations of reactants and products**

- **Be able to write equilibrium constant expressions from a chemical equation**

- **Be able to obtain the equilibrium constant from the reaction composition at equilibrium**

- **Be able to apply LeChatlier's Principle to decide the effects of changing reaction condition(s) on the equilibrium concentrations of reactants and products**

Figure 13.3: (a) H_2O and CO are mixed in equal numbers and begin to react (b) to form CO_2 and H_2. After time has passed, equilibrium is reached (c) and the numbers of reactant and product molecules then remain constant over time (d).


Chemical Equilibrium

•The state where the concentrations of all reactants and products remain constant with time.

•On the molecular level, there is frantic activity. Equilibrium is not static, but is a highly dynamic situation.

Figure 13.4: The changes with time in the rates of forward and reverse reactions for $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ when equimolar quantities of $H_2O(g)$ and $CO(g)$ are mixed. The rates do not change in the same way with time because the forward reaction has a much larger rate constant than the reverse reaction.
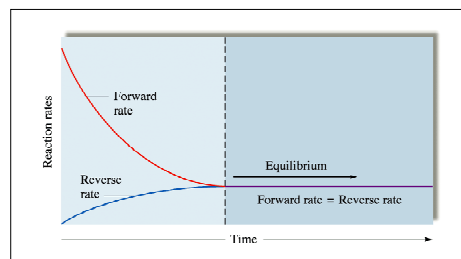
The Law of Mass Action

• For

$jA + kB \leftrightarrow lC + mD$

• The law of mass action is represented by the equilibrium expression:

$$K = \frac{[C]^l [D]^m}{[A]^j [B]^k}$$

TABLE 13.1 Results of Three Experiments for the Reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[NH_3]^2}{[N_2][H_2]^3}$
I	$[N_2]_0 = 1.000\ M$ $[H_2]_0 = 1.000\ M$ $[NH_3]_0 = 0$	$[N_2] = 0.921\ M$ $[H_2] = 0.763\ M$ $[NH_3] = 0.157\ M$	$K = 6.02 \times 10^{-2}$
II	$[N_2]_0 = 0$ $[H_2]_0 = 0$ $[NH_3]_0 = 1.000\ M$	$[N_2] = 0.399\ M$ $[H_2] = 1.197\ M$ $[NH_3] = 0.203\ M$	$K = 6.02 \times 10^{-2}$
III	$[N_2]_0 = 2.00\ M$ $[H_2]_0 = 1.00\ M$ $[NH_3]_0 = 3.00\ M$	$[N_2] = 2.59\ M$ $[H_2] = 2.77\ M$ $[NH_3] = 1.82\ M$	$K = 6.02 \times 10^{-2}$

Equilibrium Expression

• $4NH_3(g) + 7O_2(g) \leftrightarrow 4NO_2(g) + 6H_2O(g)$
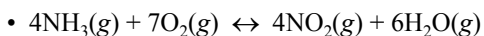
$$K = \frac{[NO_2]^4 [H_2O]^6}{[NH_3]^4 [O_2]^7}$$

Applying Stoichiometry to a Reaction Mixture in Equilibrium

1. Must know the *balanced* equation for the reaction

2. Must know the molar concentrations of reactants and products after reaction has reached equilibrium in order to calculate the equilibrium constant.

3. If we know concentrations of all but one of the components we can calculate the concentration of the missing component, if we know K.

Figure 13.5: A concentration profile for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ when only $N_2(g)$ and $H_2(g)$ are mixed initially.
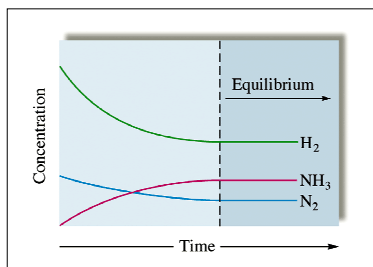
A Problem to Consider

• Applying Stoichiometry to an Equilibrium Mixture.

• Suppose we place 1.000 mol N_2 and 3.000 mol H_2 in a reaction vessel at 450 ºC and 10.0 atmospheres of pressure. The reaction is

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

• What is the composition of the equilibrium mixture if it contains 0.080 mol NH_3?
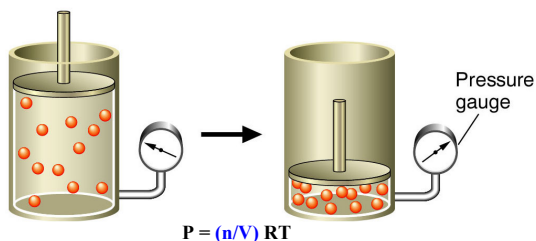
A Problem to Consider

- Using the information given, set up the following table.

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

Starting	1.000	3.000	0
Change	-x	-3x	+2x
Equilibrium	1.000 - x	3.000 - 3x	**2x = 0.080 mol**

- The equilibrium amount of NH_3 was given as 0.080 mol. Therefore, **2x = 0.080 mol NH$_3$** (x = 0.040 mol).

Figure 15.4: The concentration of a gas at a given temperature is proportional to the pressure.

Pressure gauge

$$P = (n/V)\ RT$$

A Problem to Consider

- Using the information given, set up the following table.

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

Starting	1.000	3.000	0
Change	-x	-3x	+2x
Equilibrium	**1.000 - x**	**3.000 - 3x**	**2x = 0.080 mol**

Equilibrium amount of N_2 = **1.000 - 0.040** = 0.960 mol N_2

Equilibrium amount of H_2 = **3.000 - (3 x 0.040)** = 2.880 mol H_2

Equilibrium amount of NH_3 = **2x** = 0.080 mol NH_3

The Equilibrium Constant, K_p

- If we express a gas-phase equilibria in terms of partial pressures, we obtain K_p.
  - Consider the reaction below.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

- The equilibrium-constant expression in terms of partial pressures becomes:

$$K_p = \frac{P_{CH_4}\ P_{H_2O}}{P_{CO}\ P_{H_2}^{3}}$$

The Equilibrium Constant, K_p

- In discussing gas-phase equilibria, it is often more convenient to express concentrations in terms of partial pressures rather than molarities (see Figure 15.4).
  - It can be seen from the ideal gas equation that the partial pressure of a gas is proportional to its molarity.

$$P = \left(\frac{n}{V}\right)RT = MRT$$

The Equilibrium Constant, K_p

- In general, the numerical value of K_p differs from that of K_c.
  - From the relationship n/V=P/RT, we can show that

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

  where Δn is the sum of the moles of gaseous products in a reaction minus the sum of the moles of gaseous reactants.

$$K_P = (M_P/M_R)(RT)^{(moles\ Products\ -\ moles\ Reactants)}$$

K v. K_p

- For $jA + kB \leftrightarrow lC + mD$

- $K_p = K_C(RT)^{\Delta n}$

- Δn = sum of coefficients of gaseous products minus sum of coefficients of gaseous reactants.

A Problem to Consider

- Consider the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

- Since

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

$$K_p = 2.8 \times 10^2 \, (0.08206 \tfrac{L \cdot atm}{mol \cdot K} \times 1273 \, K)^{-1} = 2.7$$

A Problem to Consider

- Consider the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

- K_c for the reaction is 2.8 x 10^2 at 1000 °C. Calculate K_p for the reaction at this temperature.

Equilibrium Constant for the Sum of Reactions

- Similar to the method of combining reactions that we saw using Hess's law in Chapter 6, we can combine equilibrium reactions whose K_c values are known to obtain K_c for the overall reaction.
  - With Hess's law, when we reversed reactions or multiplied them prior to adding them together, we had to manipulate the ΔH's values to reflect what we had done.
  - The rules are a bit different for manipulating K_c.
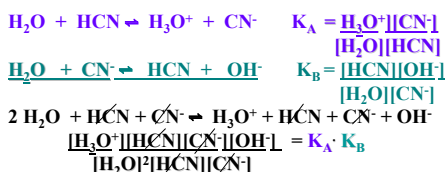
A Problem to Consider

- Consider the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

- We know that

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

From the equation we see that $\Delta n = -1$. We can simply substitute the given reaction temperature and the value of R (0.08206 L·atm/mol·K) to obtain K_p.

Equilibrium Constant for the Sum of Reactions

- If you **reverse** a reaction, **invert** the value of K_c.

2. If you **multiply** each of the coefficients in an equation by the same factor (2, 3, …), **raise K_c to the same power** (2, 3, …).

3. If you **divide** each coefficient in an equation by the same factor (2, 3, …), **take the corresponding root of K_c** (i.e., square root, cube root, …).

4. When you finally combine (that is, add) the individual equations together, take the **product** of the equilibrium constants to obtain the **overall K_c**.

$A + 2B \rightleftharpoons 3C \qquad \dfrac{[C]^3}{[A][B]^2} = K_F$

$3C \rightleftharpoons A + 2B \qquad \dfrac{[A][B]^2}{[C]^3} = K_R = 1/K_F$

$2A + 4B \rightleftharpoons 6C \qquad \dfrac{[C]^6}{[A]^2[B]^4} = K_F^2$

$H_2O + HCN \rightleftharpoons H_3O^+ + CN^- \qquad K_A = \dfrac{[H_3O^+][CN^-]}{[H_2O][HCN]}$

$\underline{H_2O + CN^- \rightleftharpoons HCN + OH^-} \qquad K_B = \dfrac{[HCN][OH^-]}{[H_2O][CN^-]}$

$2H_2O + H\cancel{CN} + \cancel{CN}^- \rightleftharpoons H_3O^+ + H\cancel{CN} + C\cancel{N}^- + OH^-$

$\dfrac{[H_3O^+][H\cancel{CN}][C\cancel{N}^-][OH^-]}{[H_2O]^2[H\cancel{CN}][C\cancel{N}^-]} = K_A \cdot K_B$

$[H_3O^+][OH^-] = K_W$

Equilibrium Constant for the Sum of Reactions

- To combine equations **(1)** and **(2)** to obtain equation **(3)**, we must first reverse equation **(2)**. When we do we must also take the reciprocal of its K_c value.

(1) $\qquad N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_c = 4.1 \times 10^{-31}$

(2) $\qquad N_2O(g) \rightleftharpoons N_2(g) + \tfrac{1}{2}O_2(g) \qquad K_c = \dfrac{1}{2.4 \times 10^{-18}}$

(3) $\qquad N_2O(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons 2NO(g)$
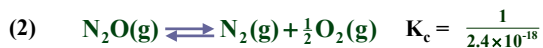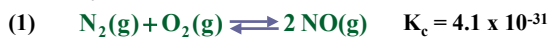
$K_c \text{(overall)} = (4.1 \times 10^{-31}) \times \left(\dfrac{1}{2.4 \times 10^{-18}}\right) = 1.7 \times 10^{-13}$

Equilibrium Constant for the Sum of Reactions

- Similar to the method of combining reactions that we saw using Hess's law in Chapter 6, we can combine equilibrium reactions whose K_c values are known to obtain K_c for the overall reaction.
  - With Hess's law, when we reversed reactions or multiplied them prior to adding them together, we had to manipulate the ΔH's values to reflect what we had done.
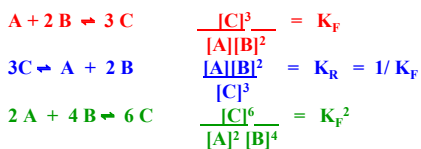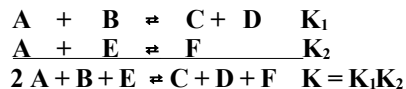 - The rules are a bit different for manipulating K_c.

The Equilibrium Constant for the Sum of Reactions

When two reactions are added together to give an overall reaction, the new equilibrium constant for this reaction is the product of the equilibrium constants for the original reactions.

$A + B \rightleftharpoons C + D \qquad K_1$

$\underline{A + E \rightleftharpoons F \qquad\qquad K_2}$

$2A + B + E \rightleftharpoons C + D + F \qquad K = K_1 K_2$

Equilibrium Constant for the Sum of Reactions

- For example, nitrogen and oxygen can combine to form either $NO(g)$ or $N_2O(g)$ according to the following equilibria.

(1) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) \qquad K_c = 4.1 \times 10^{-31}$

(2) $N_2(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons N_2O(g) \qquad K_c = 2.4 \times 10^{-18}$

  - Using these two equations, we can obtain K_c for the formation of $NO(g)$ from $N_2O(g)$:

(3) $N_2O(g) + \tfrac{1}{2}O_2(g) \rightleftharpoons 2NO(g) \qquad K_c = ?$


Heterogeneous Equilibria

- . . . are equilibria that involve more than one phase.

$\qquad CaCO_3(s) \leftrightarrow CaO(s) + CO_2(g)$

$\qquad K = [CO_2]$

- The position of a heterogeneous equilibrium does not depend on the amounts of pure solids or liquids present.
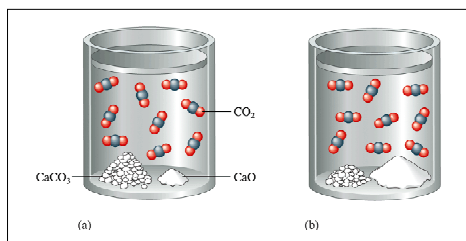
Heterogeneous Equilibria

- A **heterogeneous equilibrium** is an equilibrium that involves reactants and products in more than one phase.
  - The equilibrium of a heterogeneous system is unaffected by the amounts of pure solids or liquids present, as long as some of each is present.
  - The concentrations of pure solids and liquids are always considered to be "1" and therefore, do not appear in the equilibrium expression.

Hydrated copper (II) sulfate on the left. Water applied to anhydrous copper (II) sulfate, on the right, forms the hydrated compound.

$$CuSO_4 \cdot 5H_2O \ (s) \rightleftharpoons CuSO_4 \ (s) + 5 \ H_2O \ (g)$$
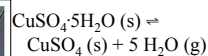
$$K = [H_2O]^5$$

Figure 13.6: The position of the equilibrium $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ does not depend on the amounts of $CaCO_3(s)$ and $CaO(s)$ present.

Reaction Quotient

- . . . helps to determine the direction of the move toward equilibrium.

- The law of mass action is applied with initial concentrations.

Heterogeneous Equilibria

- Consider the reaction below.

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

  - The equilibrium-constant expression contains terms for only those species in the homogeneous gas phase…H_2O, CO, and H_2.

$$K_c = \frac{[CO][H_2]}{[H_2O]}$$

Figure 13.7:
(a) A physical analogy illustrating the difference between thermodynamic and kinetic stabilities.
(b) The reactants H2 and O2 have a strong tendency to form

H2O.
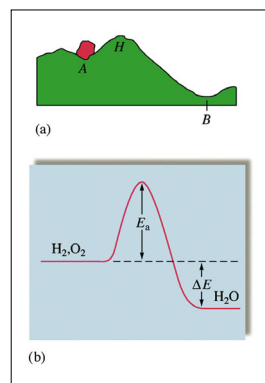
Predicting the Direction of Reaction

- How could we predict the direction in which a reaction at non-equilibrium conditions will shift to reestablish equilibrium?
  - To answer this question, substitute the current concentrations into the reaction quotient expression and compare it to K_c.
  - The **reaction quotient, Q_c**, is an expression that has the same form as the equilibrium-constant expression but whose concentrations are not necessarily at equilibrium.

Reaction Quotient
(continued)

- $H_2(g) + F_2(g) \leftrightarrow 2HF(g)$
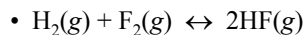
$$Q = \frac{[HF]_0^2}{[H_2]_0 [F_2]_0}$$

Predicting the Direction of Reaction

- For the general reaction

$$aA + bB \rightleftharpoons cC + dD$$

the Q_c expression would be:

$$Q_c = \frac{[C]_i^c [D]_i^d}{[A]_i^a [B]_i^b}$$

A Problem to Consider

- Consider the following equilibrium.

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

- A 50.0 L vessel contains 1.00 mol N_2, 3.00 mol H_2, and 0.500 mol NH_3. In which direction (toward reactants or toward products) will the system shift to reestablish equilibrium at 400 ºC?
- K_c for the reaction at 400 ºC is 0.500.

Predicting the Direction of Reaction

- For the general reaction

$$aA + bB \rightleftharpoons cC + dD$$

- If $Q_c > K_c$, the reaction will shift left…toward reactants.
- If $Q_c < K_c$, the reaction will shift right… toward products.
- If $Q_c = K_c$, then the reaction is at equilibrium.

A Problem to Consider

- First, calculate concentrations from moles of substances.

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

$$\frac{1.00 \text{ mol}}{50.0 \text{ L}} \qquad \frac{3.00 \text{ mol}}{50.0 \text{ L}} \qquad \frac{0.500 \text{ mol}}{50.0 \text{ L}}$$

A Problem to Consider

- First, calculate concentrations from moles of substances.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
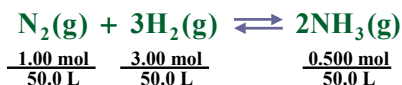
   0.0200 M   **0.0600 M**   **0.0100 M**

- The Q_c expression for the system would be:

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

Calculating Equilibrium Concentrations

- Once you have determined the equilibrium constant for a reaction, you can use it to calculate the concentrations of substances in the equilibrium mixture.

A Problem to Consider

- First, calculate concentrations from moles of substances.

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

   0.0200 M   **0.0600 M**   **0.0100 M**

- Substituting these concentrations into the reaction quotient gives:

$$Q_c = \frac{(0.0100)^2}{(0.0200)(0.0600)^3} = 23.1$$

Solving Equilibrium Problems

- 1. Balance the equation.
- 2. Write the equilibrium expression.
- 3. List the initial concentrations.
- 4. Calculate Q and determine the shift to equilibrium.

A Problem to Consider

- First, calculate concentrations from moles of substances.

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

   0.0200 M   **0.0600 M**   **0.0100 M**

- Because $Q_c = 23.1$ is greater than $K_c = 0.500$, the **reaction will go to the left (toward reactants)** as it approaches equilibrium.

Solving Equilibrium Problems
(continued)

- 5. Define equilibrium concentrations.
- 6. Substitute equilibrium concentrations into equilibrium expression and solve.
- 7. Check calculated concentrations by calculating K.

Calculating Equilibrium Concentrations

- For example, consider the following equilibrium.

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

- Suppose a gaseous mixture contained 0.30 mol CO, 0.10 mol H_2, 0.020 mol H_2O, and an unknown amount of CH_4 per liter.
- What is the concentration of CH_4 in this mixture? The equilibrium constant K_c equals 3.92.

Calculating Equilibrium Concentrations

- First, calculate concentrations from moles of substances.

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$0.30\ M \qquad 0.10\ M \qquad ?? \qquad 0.020\ M$$

- Substituting the known concentrations and the value of K_c gives:

$$3.92 = \frac{[CH_4](0.020M)}{(0.30M)(0.10M)^3}$$

Calculating Equilibrium Concentrations

- First, calculate concentrations from moles of substances.

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$\frac{0.30\ mol}{1.0\ L} \quad \frac{0.10\ mol}{1.0\ L} \qquad ?? \qquad \frac{0.020\ mol}{1.0\ L}$$

Calculating Equilibrium Concentrations

- First, calculate concentrations from moles of substances.

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$0.30\ M \qquad 0.10\ M \qquad ?? \qquad 0.020\ M$$

- You can now solve for $[CH_4]$.

$$[CH_4] = \frac{(3.92)(0.30M)(0.10M)^3}{(0.020M)} = 0.059$$

- The concentration of CH_4 in the mixture is **0.059 mol/L.**

Calculating Equilibrium Concentrations

- First, calculate concentrations from moles of substances.

$$CO(g) + 3\,H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

$$0.30\ M \qquad 0.10\ M \qquad ?? \qquad 0.020\ M$$

- The equilibrium-constant expression is:

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

Calculating Equilibrium Concentrations

- Consider the following equilibrium.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

- Suppose you start with 1.000 mol each of carbon monoxide and water in a 50.0 L container. Calculate the molarity of each substance in the equilibrium mixture at 1000 °C.
- K_c for the reaction is 0.58 at 1000 °C.

Calculating Equilibrium Concentrations

- First, calculate the initial molarities of CO and H_2O.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$\underline{\frac{1.000 \text{ mol}}{50.0 \text{ L}}} \quad \underline{\frac{1.000 \text{ mol}}{50.0 \text{ L}}}$$

Calculating Equilibrium Concentrations

- **Solving for x.**

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Starting	0.0200	0.0200		0	0
Change	-x	-x		+x	+x
Equilibrium	0.0200-x	0.0200-x		x	x

- Substituting the values for equilibrium concentrations, we get:

$$0.58 = \frac{(x)(x)}{(0.0200 - x)(0.0200 - x)}$$

Calculating Equilibrium Concentrations

- First, calculate the initial molarities of CO and H_2O.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

$$\textbf{0.0200 M} \quad \textbf{0.0200 M} \qquad \textbf{0 M} \qquad \textbf{0 M}$$

- The starting concentrations of the products are 0.
- We must now set up a table of concentrations (starting, change, and equilibrium expressions in x).

Calculating Equilibrium Concentrations

- **Solving for x.**

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Starting	0.0200	0.0200		0	0
Change	-x	-x		+x	+x
Equilibrium	0.0200-x	0.0200-x		x	x

- Or:

$$0.58 = \frac{x^2}{(0.0200 - x)^2}$$

Calculating Equilibrium Concentrations

- **Let x be the moles per liter of product formed.**

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Starting	0.0200	0.0200		0	0
Change	-x	-x		+x	+x
Equilibrium	0.0200-x	0.0200-x		x	x

- The equilibrium-constant expression is:

$$K_c = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

Calculating Equilibrium Concentrations

- **Solving for x.**

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Starting	0.0200	0.0200		0	0
Change	-x	-x		+x	+x
Equilibrium	0.0200-x	0.0200-x		x	x

- Taking the square root of both sides we get:

$$0.76 = \frac{x}{(0.0200 - x)}$$

Calculating Equilibrium Concentrations

- **Solving for x.**

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

Starting	0.0200	0.0200		0	0
Change	-x	-x		+x	+x
Equilibrium	0.0200-x	0.0200-x		x	x

- Rearranging to solve for x gives:

$$x = \frac{0.0200 \times 0.76}{1.76} = 0.0086$$

Calculating Equilibrium Concentrations

- In some cases it is necessary to solve a quadratic equation to obtain equilibrium concentrations.
- The next example illustrates how to solve such an equation.

Calculating Equilibrium Concentrations

- **Solving for equilibrium concentrations.**

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$$

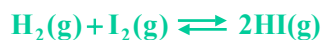|					
Starting	0.0200	0.0200		0	0
Change	-x	-x		+x	+x
Equilibrium	0.0200-x	0.0200-x		x	x

- If you substitute for x in the last line of the table you obtain the following equilibrium concentrations.

  0.0114 M CO   **0.0086 M CO$_2$**
  0.0114 M H$_2$O   **0.0086 M H$_2$**

Calculating Equilibrium Concentrations

- Consider the following equilibrium.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

  - Suppose 1.00 mol H_2 and 2.00 mol I_2 are placed in a 1.00-L vessel. How many moles per liter of each substance are in the gaseous mixture when it comes to equilibrium at 458 °C?
 - K_c at this temperature is 49.7.

Calculating Equilibrium Concentrations

- The preceding example illustrates the three steps in solving for equilibrium concentrations.

  1. Set up a table of concentrations (starting, change, and equilibrium expressions in x).
  2. Substitute the expressions in x for the equilibrium concentrations into the equilibrium-constant equation.
  3. Solve the equilibrium-constant equation for the values of the equilibrium concentrations.

Calculating Equilibrium Concentrations

- The concentrations of substances are as follows.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
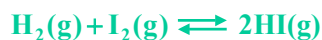
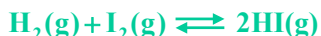|				
Starting	1.00	2.00		0
Change	-x	-x		+2x
Equilibrium	1.00-x	2.00-x		2x

- The equilibrium-constant expression is:

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

Calculating Equilibrium Concentrations

- The concentrations of substances are as follows.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Starting	1.00	2.00	0
Change	-x	-x	+2x
Equilibrium	1.00-x	2.00-x	2x

- Substituting our equilibrium concentration expressions gives:

$$K_c = \frac{(2x)^2}{(1.00 - x)(2.00 - x)}$$

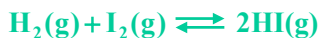## Calculating Equilibrium Concentrations

- **Solving for x.**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Starting	1.00	2.00	0
Change	-x	-x	+2x
Equilibrium	1.00-x	2.00-x	2x

- The two possible solutions to the quadratic equation are:

$$x = 2.33 \qquad \text{and} \qquad x = 0.93$$

Calculating Equilibrium Concentrations

- **Solving for x.**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Starting	1.00	2.00	0
Change	-x	-x	+2x
Equilibrium	1.00-x	2.00-x	2x

- Because the right side of this equation is not a perfect square, you must solve the quadratic equation.

Calculating Equilibrium Concentrations

- **Solving for x.**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Starting	1.00	2.00	0
Change	-x	-x	+2x
Equilibrium	1.00-x	2.00-x	2x

- However, x = 2.33 gives a negative value to 1.00 - x (the equilibrium concentration of H_2), which is not possible.

Only $x = 0.93$ remains.

Calculating Equilibrium Concentrations

- **Solving for x.**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

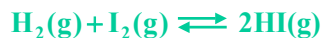| Starting	1.00	2.00	0
Change	-x	-x	+2x
Equilibrium	1.00-x	2.00-x	2x

- The equation rearranges to give:

$$0.920x^2 - 3.00x + 2.00 = 0$$

$$X = \{-b \pm (b^2 - 4ac)^{1/2}\}/2a$$

Calculating Equilibrium Concentrations

- **Solving for equilibrium concentrations.**

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Starting	1.00	2.00	0
Change	-x	-x	+2x
Equilibrium	1.00-x	2.00-x	2x

- If you substitute 0.93 for x in the last line of the table you obtain the following equilibrium concentrations.

0.07 M H_2 1.07 M I_2 1.86 M HI

Procedure for Solving Equilibrium Problems

Procedure for Solving Equilibrium Problems

➡ **1** Write the balanced equation for the reaction.

➡ **2** Write the equilibrium expression using the law of mass action.

➡ **3** List the initial concentrations.

➡ **4** Calculate Q, and determine the direction of the shift to equilibrium.

➡ **5** Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.

➡ **6** Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.

➡ **7** Check your calculated equilibrium concentrations by making sure they give the correct value of K.
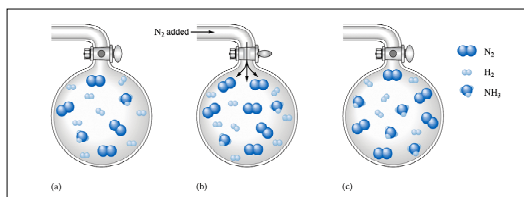

Effects of Changes on the System
(continued)

- 3. Pressure:
- a. Addition of inert gas does not affect the equilibrium position.
- b. Decreasing the volume shifts the equilibrium toward the side with fewer moles.

Le Châtelier's Principle

- . . . if a change is imposed on a system at equilibrium, the position of the equilibrium will shift in a direction that tends to reduce that change.

Figure 13.8: (a) The initial equilibrium mixture of N2, H2, and NH3. (b) Addition of N2.(c) The new equilibrium position for the system containing more N2 (due to addition of N2), less H2, and more NH3 than in (a).

Effects of Changes on the System

- 1. Concentration: The system will shift away from the added component.

- 2. Temperature: K will change depending upon the temperature (treat the energy change as a reactant).

TABLE 13.2 The Percent by Mass of NH_3 at Equilibrium in a Mixture of N_2, H_2, and NH_3 as a Function of Temperature and Total Pressure*

Temperature (°C)	Total Pressure		
	300 atm	400 atm	500 atm
400	48% NH_3	55% NH_3	61% NH_3
500	26% NH_3	32% NH_3	38% NH_3
600	13% NH_3	17% NH_3	21% NH_3

Effects of Pressure Change

- A pressure change caused by changing the volume of the reaction vessel can affect the yield of products in a gaseous reaction **only if the reaction involves a change in the total moles of gas present**

Effects of Pressure Change

- Literally "squeezing" the reaction will cause a **shift in the equilibrium toward the fewer moles of gas**.
- It's a simple step to see that reducing the pressure in the reaction vessel by increasing its volume would have the opposite effect.
- In the event that the **number of moles of gaseous product equals the number of moles of gaseous reactant, vessel volume will have no effect on the position of the equilibrium.**

Effects of Pressure Change

- If the products in a gaseous reaction contain **fewer moles of gas** than the reactants, it is logical that they would require less space.
- So, reducing the volume of the reaction vessel would, therefore, favor the products.
- Conversely, if the reactants require less volume (that is, fewer moles of gaseous reactant), then decreasing the volume of the reaction vessel would shift the equilibrium to the left (toward reactants).

Effect of Temperature Change

- **Temperature** has a significant effect on most reactions (see Figure 15.10).
  - Reaction rates generally increase with an increase in temperature. Consequently, equilibrium is established sooner.
  - In addition, **the numerical value of the equilibrium constant K_c varies with temperature.**

Figure 13.9: (a) A mixture of NH3(g), N2(g), and H2(g) at equilibrium. (b) The volume is suddenly decreased. (c) The new equilibrium position for the system containing more NH3 and less N2 and H2. The reaction N2(g) + 3H2(g) ➜ 2NH3(g) shifts to the right (toward the side with fewer molecules) when the container volume is decreased.
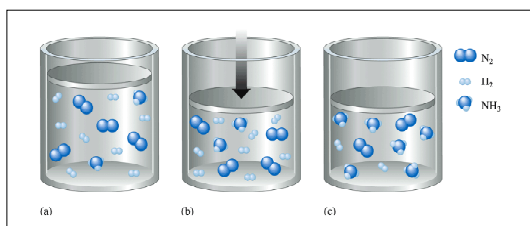

Figure 15.10: The effect of changing the temperature on chemical equilibrium.

Photo courtesy of American Color.

Effect of Temperature Change

- Let's look at "heat" as if it were a **product in exothermic reactions** and a **reactant in endothermic reactions.**
- We see that **increasing the temperature** is analogous to adding **more product (in the case of exothermic reactions)** or adding **more reactant (in the case of endothermic reactions).**
- This ultimately has the same effect as if heat were a physical entity.

Effect of Temperature Change

- For an endothermic reaction, the opposite is true.

$$\text{"heat"} + \text{reactants} \rightleftharpoons \text{products} \quad (\Delta H \text{ is positive})$$

- Increasing temperature would be analogous to adding more reactant, **causing the equilibrium to shift right.**
- This change results in more product at equilibrium, amd a **larger numerical value for K_c.**

Effect of Temperature Change

- For example, consider the following generic exothermic reaction.

$$\text{reactants} \rightleftharpoons \text{products} + \text{"heat"} \quad (\Delta H \text{ is negative})$$

- Increasing temperature would be analogous to adding more product, **causing the equilibrium to shift left.**
- Since "heat" does not appear in the equilibrium-constant expression, this change would result in a **smaller numerical value for K_c.**

Effect of Temperature Change

- In summary:
  - For an **endothermic reaction** (ΔH positive) the amounts of products are increased at equilibrium by an increase in temperature **(K_c is larger at higher temperatures).**
  - For an **exothermic reaction** (ΔH is negative) the amounts of reactants are increased at equilibrium by an increase in temperature **(K_c is smaller at higher temperatures).**

TABLE 13.3
Observed Value of *K* for the Ammonia Synthesis Reaction as a Function of Temperature*

Temperature (K)	*K*
500	90
600	3
700	0.3
800	0.04

Table 15.2 Equilibrium Constant for Methanation at Different Temperatures

Temperature (K)	K_c
298	4.9×10^{27}
800	1.38×10^5
1000	2.54×10^2
1200	3.92

TABLE 13.4 Shifts in the Equilibrium Position for the Reaction 58 kJ + $N_2O_4(g)$ $\rightleftharpoons$ $2NO_2(g)$

Change	Shift
Addition of $N_2O_4(g)$	Right
Addition of $NO_2(g)$	Left
Removal of $N_2O_4(g)$	Left
Removal of $NO_2(g)$	Right
Addition of $He(g)$	None
Decrease container volume	Left
Increase container volume	Right
Increase temperature	Right
Decrease temperature	Left

Effect of a Catalyst

- A **catalyst** is a substance that increases the rate of a reaction but is not consumed by it.
  - It is important to understand that **a catalyst has no effect on the equilibrium composition** of a reaction mixture.
  - A catalyst merely speeds up the attainment of equilibrium.