

Chapter 5 -Chemical equilibrium

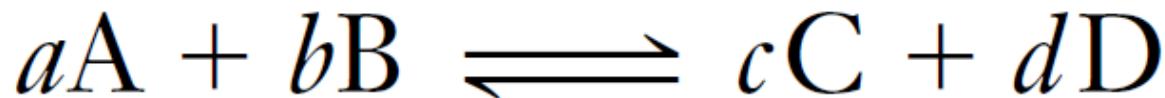


Chapter 6 – Chemical Equilibrium

- 6.1 The Equilibrium Condition*
- 6.2 The Equilibrium Constant (K)*
- 6.3 Equilibrium Expressions Involving Pressures*
- 6.4 The concept of activity*
- 6.5 Heterogeneous equilibria*
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Basic concepts

- Most chemical reactions do not go to completion
- **Reactions that** do not go to completion *and that can occur in either direction are called **reversible reactions**.*



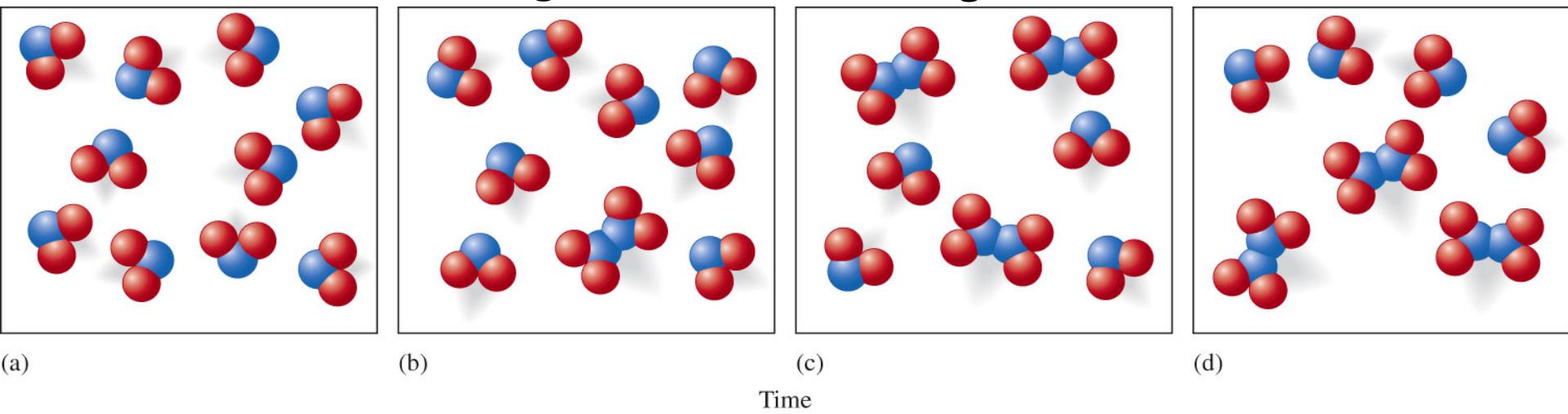
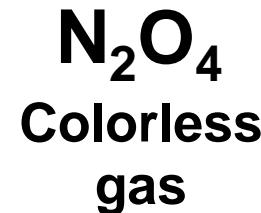
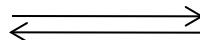
Basic concepts

- The chemical equilibrium is the state in which concentrations of all reactants and products remain constant with time.
- On the molecular level there is frenetic activity. Equilibrium is **not static**; it is a highly **dynamic** situation.
- In a system at equilibrium, the equilibrium is said to lie toward the right if more C and D are present than A and B, and to lie toward the left if more A and B are present.



Basic concepts

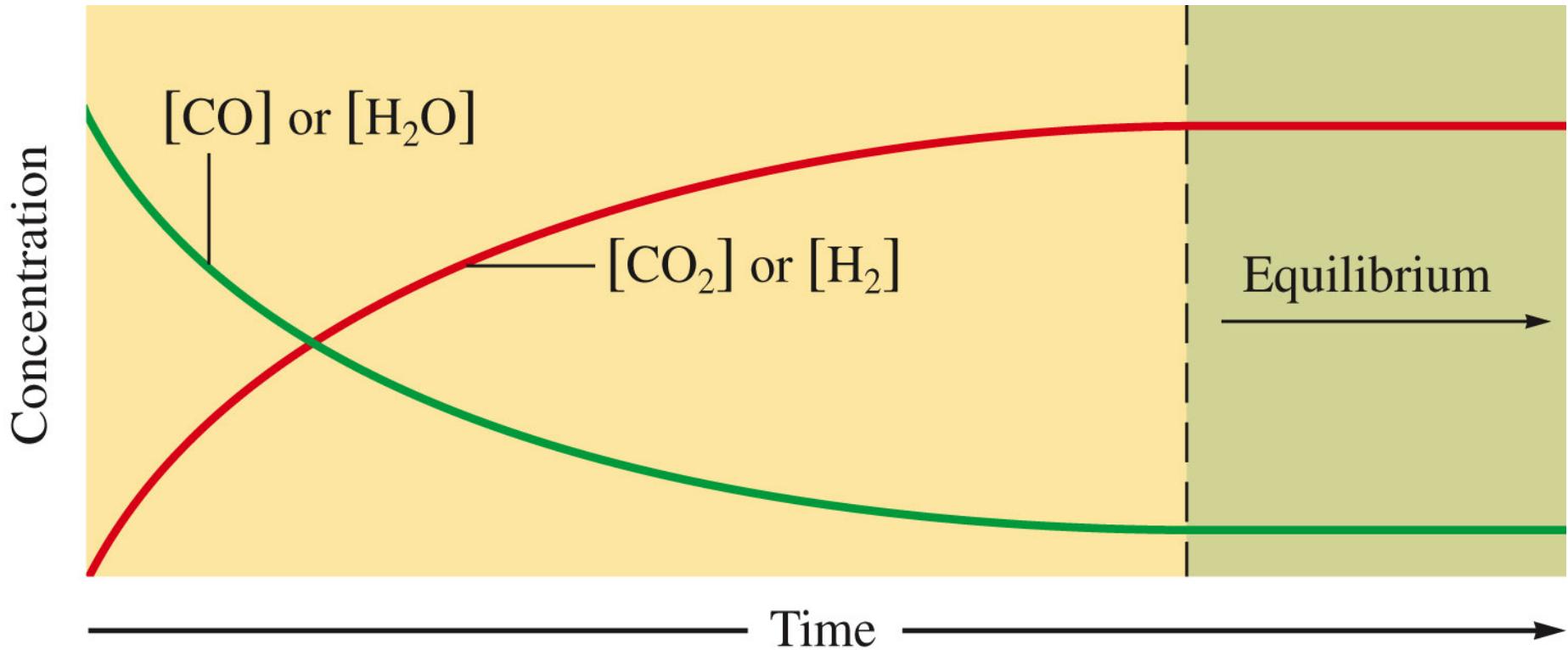
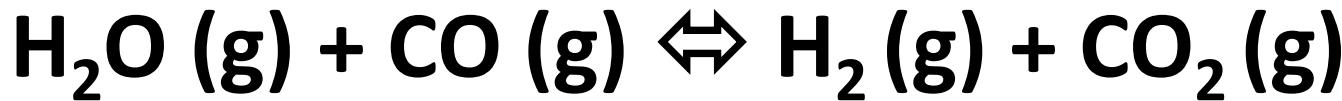
Dimerization of nitrogen dioxide



- The reaction has stopped short of completion
- The system has reached **Chemical Equilibrium** (*state in which the concentration of all reactants and products remain constant with time*)

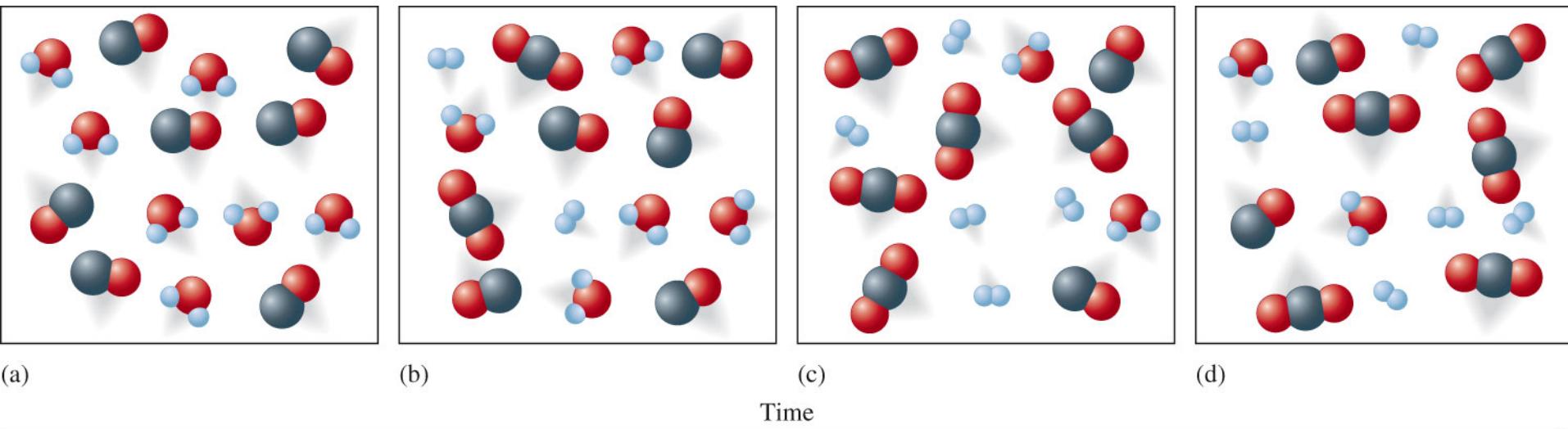
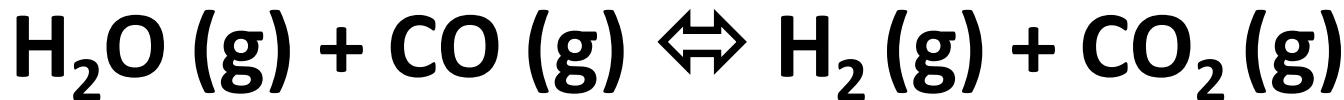
The Equilibrium condition

Changes in concentration for the reaction



The Equilibrium condition

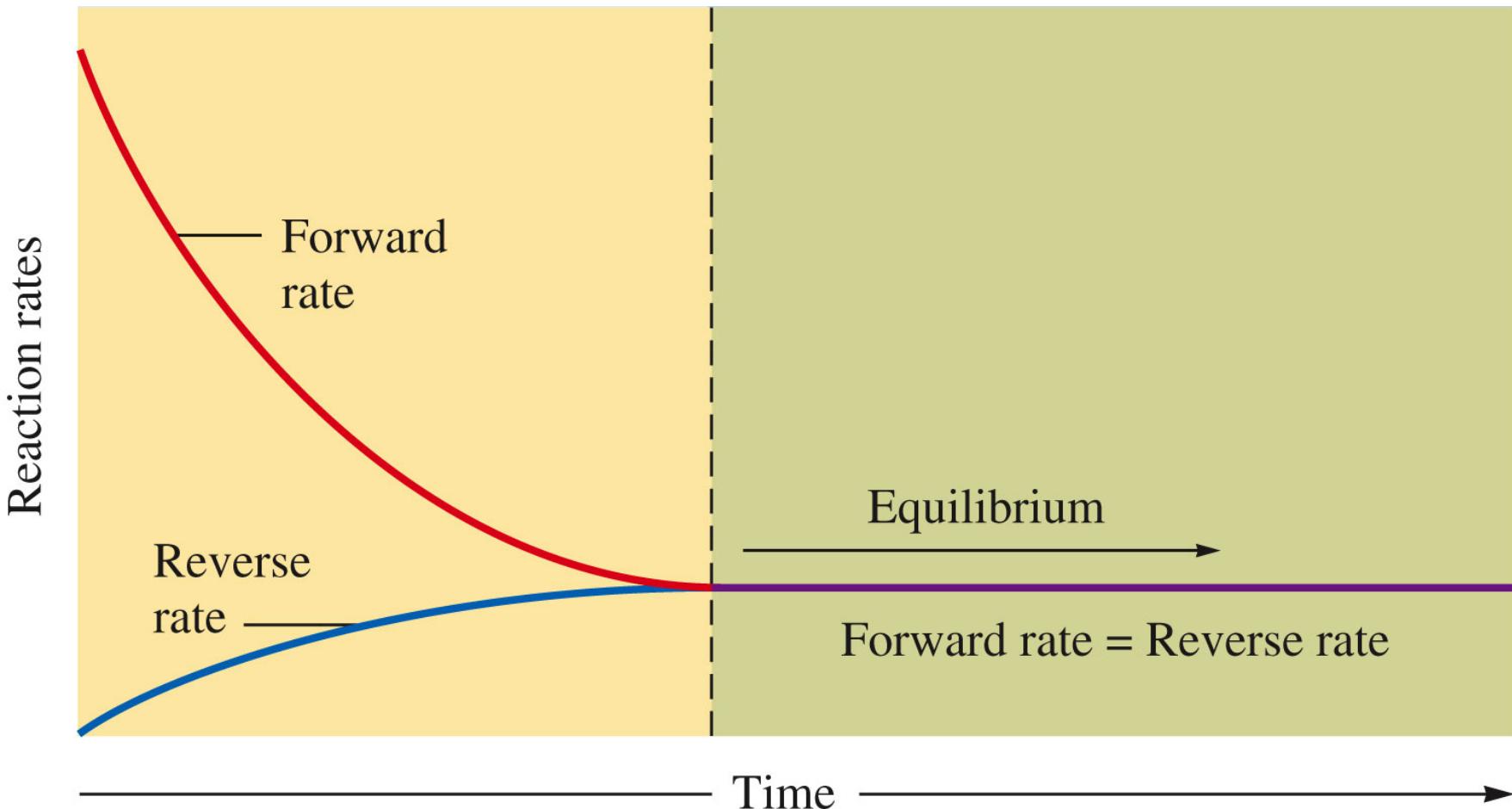
Changes in concentration for the reaction



- Although the equilibrium position lies far to the right, the concentrations of reactants never reach zero
- The reactants will always be present in small but constant concentrations

The Equilibrium condition

Changes with Time in Reaction Rates of Forward and Reverse Reactions for

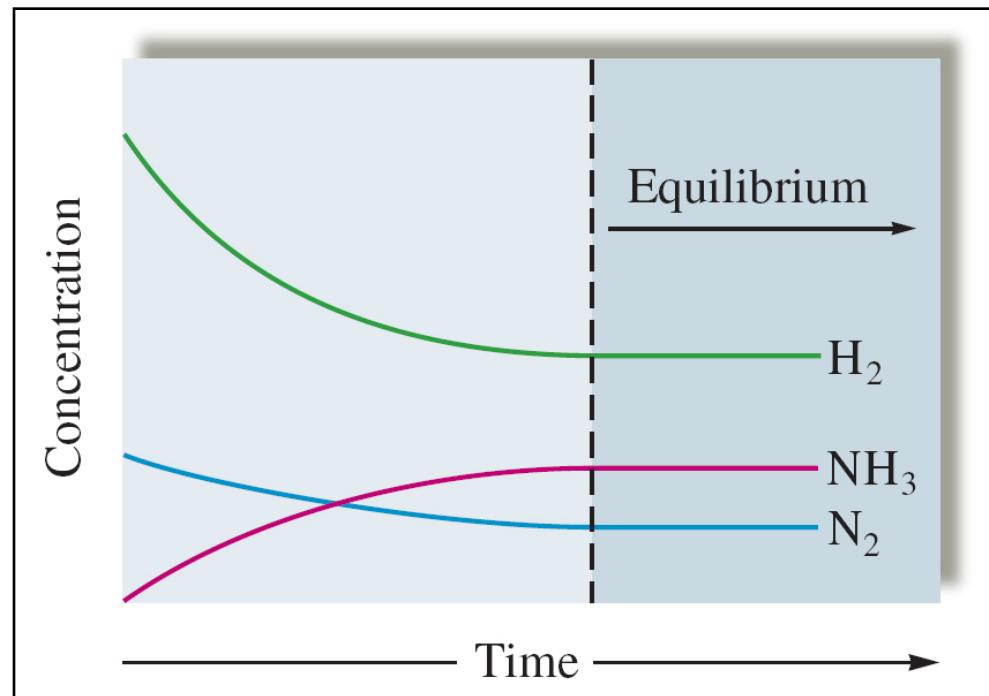
$$\text{H}_2\text{O (g)} + \text{CO (g)} \rightleftharpoons \text{H}_2\text{ (g)} + \text{CO}_2\text{ (g)}$$


The Equilibrium condition

Characteristics of Chemical Equilibrium



- When we mix N_2 , H_2 , and NH_3 in a closed container at 25° C , we do not see a change in the concentrations over time regardless of the original amounts of gas.
- Two possibilities exist
 - The system is at chemical equilibrium \times
 - The forward and reverse reactions are so slow that the system moves towards equilibrium at a rate that cannot be detected ✓



The Equilibrium constant (K)

Law of mass action (based on experimental observations):



at equilibrium, the constant K is given by

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

**K = constant , doesn't change
but concentration can change**

The Equilibrium constant (K)

Table 6.1

Results of Three Experiments for the Reaction $\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)$

Experiment	Initial Concentrations	Equilibrium Concentrations	$K = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$
I	$[\text{N}_2]_0 = 1.000 \text{ M}$ $[\text{H}_2]_0 = 1.000 \text{ M}$ $[\text{NH}_3]_0 = 0$	$[\text{N}_2] = 0.921 \text{ M}$ $[\text{H}_2] = 0.763 \text{ M}$ $[\text{NH}_3] = 0.157 \text{ M}$	$K = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2$
II	$[\text{N}_2]_0 = 0$ $[\text{H}_2]_0 = 0$ $[\text{NH}_3]_0 = 1.000 \text{ M}$	$[\text{N}_2] = 0.399 \text{ M}$ $[\text{H}_2] = 1.197 \text{ M}$ $[\text{NH}_3] = 0.203 \text{ M}$	$K = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2$
III	$[\text{N}_2]_0 = 2.00 \text{ M}$ $[\text{H}_2]_0 = 1.00 \text{ M}$ $[\text{NH}_3]_0 = 3.00 \text{ M}$	$[\text{N}_2] = 2.59 \text{ M}$ $[\text{H}_2] = 2.77 \text{ M}$ $[\text{NH}_3] = 1.82 \text{ M}$	$K = 6.02 \times 10^{-2} \text{ L}^2/\text{mol}^2$

For a reaction at a given temperature, there are many equilibrium positions but only one value of K.

The Equilibrium constant (K)

Example 6.1

The following equilibrium concentrations were observed for the Haber process at 127°C:

$$[\text{NH}_3] = 3.1 \times 10^{-2} \text{ mol/L}$$

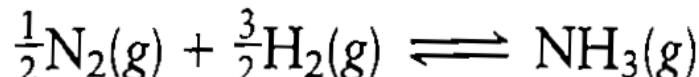
$$[\text{N}_2] = 8.5 \times 10^{-1} \text{ mol/L}$$

$$[\text{H}_2] = 3.1 \times 10^{-3} \text{ mol/L}$$

- Calculate the value of K at 127°C for this reaction.
- Calculate the value of the equilibrium constant at 127°C for the reaction



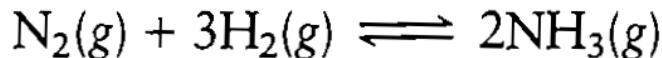
- Calculate the value of the equilibrium constant at 127°C for the reaction given by the equation



The Equilibrium constant (K)

Example 6.1 - Solution

- a. The balanced equation for the Haber process is



Thus, using the law of mass action to construct the expression for K , we have

$$\begin{aligned} K &= \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{(3.1 \times 10^{-2} \text{ mol/L})^2}{(8.5 \times 10^{-1} \text{ mol/L})(3.1 \times 10^{-3} \text{ mol/L})^3} \\ &= 3.8 \times 10^4 \text{ L}^2/\text{mol}^2 \end{aligned}$$

- b. This reaction is written in the reverse order of the equation given in part a. This leads to the equilibrium expression

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

which is the reciprocal of the expression used in part a. So

$$K' = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K} = \frac{1}{3.8 \times 10^4 \text{ L}^2/\text{mol}^2} = 2.6 \times 10^{-5} \text{ mol}^2/\text{L}^2$$

The Equilibrium constant (K)

Example 6.1 - Solution

c. We use the law of mass action: $K'' = \frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}}$

If we compare this expression with the one obtained in part a, we see that since

$$\frac{[\text{NH}_3]}{[\text{N}_2]^{1/2}[\text{H}_2]^{3/2}} = \left(\frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \right)^{1/2}$$

then

$$K'' = K^{1/2}$$

Thus

$$K'' = K^{1/2} = (3.8 \times 10^4 \text{ L}^2/\text{mol}^2)^{1/2} = 1.9 \times 10^2 \text{ L/mol}$$

Some Important conclusions

We can draw some important conclusions from the results of Example 6.1. For a reaction of the form



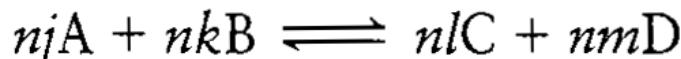
the equilibrium expression is

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

If this reaction is reversed, the new equilibrium expression is

$$K' = \frac{[A]^j[B]^k}{[C]^l[D]^m} = \frac{1}{K}$$

If the original reaction is multiplied by some factor n to give



the equilibrium expression becomes

$$K'' = \frac{[C]^{nl}[D]^{nm}}{[A]^{nj}[B]^{nk}} = K^n$$

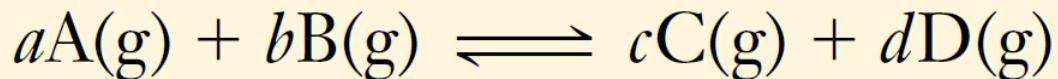
Characteristics of the equilibrium expression

- The equilibrium expression for a reaction written in reverse is the reciprocal of that for the original reaction.
- When the balanced equation for a reaction is multiplied by a factor n , the equilibrium expression for the new reaction is the original expression raised to the n th power. Thus $K_{\text{new}} = (K_{\text{original}})^n$.
- The apparent units for K are determined by the powers of the various concentration terms. The (apparent) units for K therefore depend on the reaction being considered.

Equilibrium expressions involving pressures

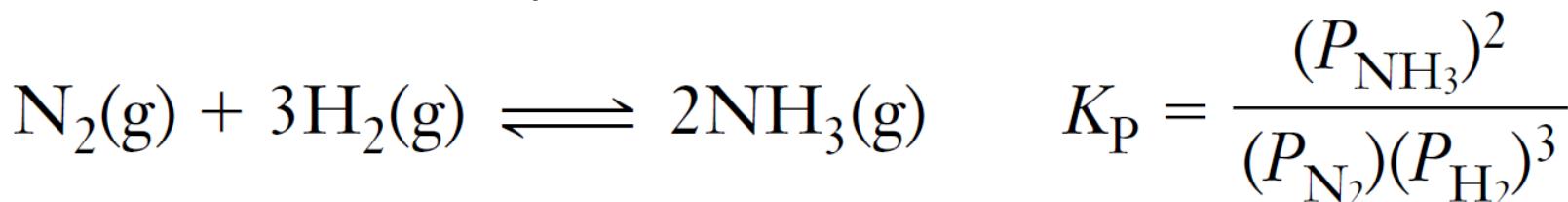
- Relation between K_{eq} (K or K_c and K_p)

$$PV = nRT \quad \text{or} \quad P = \left(\frac{n}{V} \right) RT = CRT$$

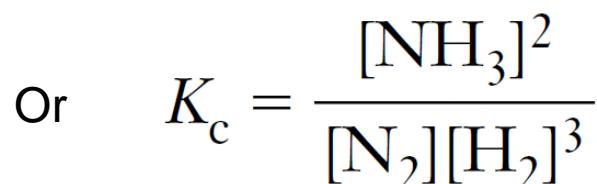
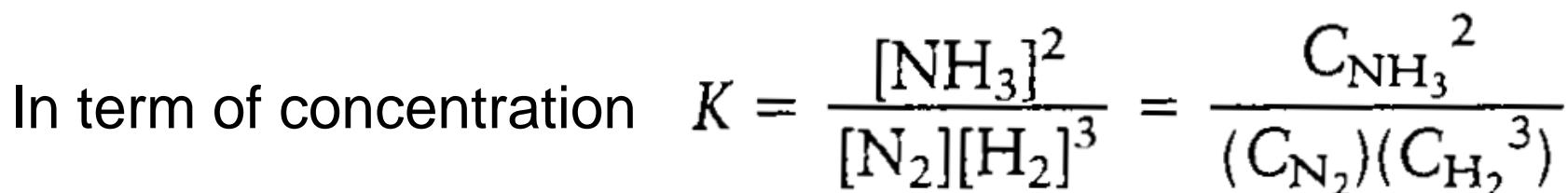


$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

- If we consider the synthesis of Ammonia



equilibrium partial pressures of the gases.



Equilibrium expressions involving pressures

Relationship between K_P and K_c

- If the ideal gas equation is rearranged, the molar concentration of a gas is

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

- Substituting P/RT for n/V in the K_c expression for the formation of NH_3

$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} = \frac{\left(\frac{P_{\text{NH}_3}}{RT}\right)^2}{\left(\frac{P_{\text{N}_2}}{RT}\right)\left(\frac{P_{\text{H}_2}}{RT}\right)^3} = \frac{(P_{\text{NH}_3})^2}{(P_{\text{N}_2})(P_{\text{H}_2})^3} \times \frac{\left(\frac{1}{RT}\right)^2}{\left(\frac{1}{RT}\right)^4}$$
$$= K_P (RT)^2 \quad \text{and} \quad K_P = K_c (RT)^{-2}$$

In general the relationship between K_c and K_P is

$$K_P = K_c(RT)^{\Delta n} \quad \text{or} \quad K_c = K_P(RT)^{-\Delta n} \quad \Delta n = (n_{\text{gas prod}}) - (n_{\text{gas react}})$$

For reactions in which equal numbers of moles of gases appear on both sides of the equation, $\Delta n = 0$ and $K_P = K_c$.

Equilibrium expressions involving pressures

Relationship between K_p and K_c

$$K_p = K_c (RT)^{\Delta n_{\text{gas}}}$$



$$K_p = K_c (RT)^{\Delta n} = (0.286)[(0.0821)(773)]^{-2} = 7.10 \times 10^{-5}$$

we considered that for the ammonia reaction at 500 °C (or 773 K), $K_c = 0.286$.

Note: Be Careful About the Value of R

We use 0.08206 $\frac{\text{L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}$

The concept of activity

$$\text{Activity (ith component)} = a_i = \frac{P_i}{P_{\text{Reference}}}$$

P_i = partial pressure of the ith gaseous component

$P_{\text{reference}}$ = 1 atm (exactly)

$$a_{\text{pure solid}} = 1$$

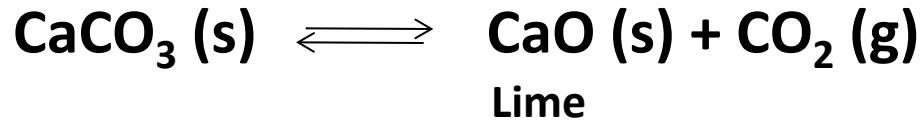
$$a_{\text{pure liquid}} = 1$$

Heterogeneous equilibria

Substances that are involved in reaction at \rightleftharpoons are found in more than 1 phase

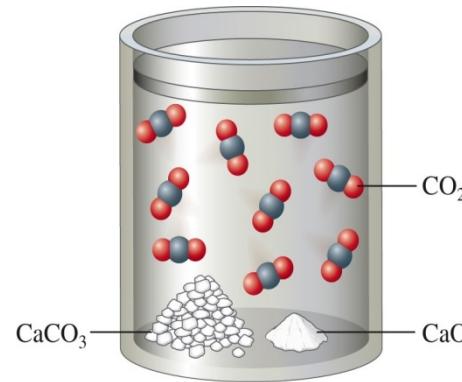
Experiments → Heterogeneous \rightleftharpoons does not depend on the amount of solids or liquids

Solids (not dissolved) and liquid (solvent) do not figure in K_c expression
Only dissolved solutes (aq) and gases are taken

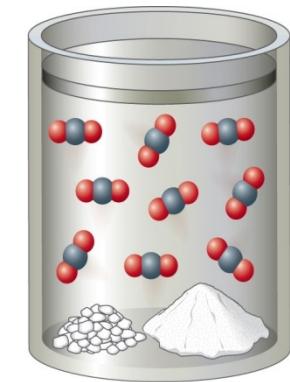


Lime

The position of equilibrium does not depend on the amounts of **CaCO₃(s)** and **CaO (s)** present so they are not inserted in K expression



(a)



(b)

$$K = \frac{[\text{CO}_2](1)}{1} = [\text{CO}_2]$$

$$K_p = \frac{P_{\text{CO}_2}(1)}{1} = P_{\text{CO}_2}$$

The activity of a pure solid or liquid is always 1

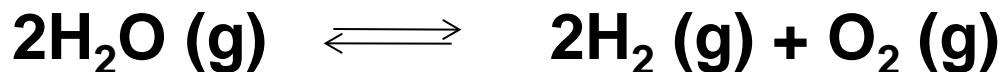
Heterogeneous equilibria

If pure solids or pure liquids are involved in a chemical reaction, their concentrations are not included in the equilibrium expression



$$K = [\text{H}_2]^2[\text{O}_2]$$

$$K_p = P_{\text{H}_2}^2 P_{\text{O}_2}$$



$$K = \frac{[\text{H}_2]^2[\text{O}_2]}{[\text{H}_2\text{O}]^2}$$

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

Applications of the equilibrium constant

- By knowing k , we can predict several important features:
 - If the system is at \rightleftharpoons or not (for a set of given [])
 - The tendency of a Rx to occur (not speed): forward or reverse
 - The extent to which the forward or reverse reaction will take place (How the \rightleftharpoons will proceed if it is not at \rightleftharpoons)
- If $K \gg 1 \rightarrow$ at \rightleftharpoons $[P] \gg [R] \rightarrow$
 - Rx° goes essentially to completion
 - The \rightleftharpoons lies to the right
 - Product formation is largely favored
- If $k \ll 1 \rightarrow$ at \rightleftharpoons $[R] \gg [P] \rightarrow$
 - at equilibrium mostly reactant are present
 - The \rightleftharpoons lies to the left
 - Product formation is largely not favored

Applications of the equilibrium constant

Reaction Quotient

The reaction quotient is obtained by applying the law of mass action but using **initial concentrations** instead of equilibrium concentrations.



$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0 [\text{H}_2]_0^3}$$

In order to determine in which direction a system will shift to reach \rightleftharpoons

1. **If $Q = K$** : the system is already at \rightleftharpoons (no shift)
2. **If $Q > K$** ; to $\downarrow Q$ we must $\downarrow [\text{P}]$ and $\uparrow [\text{R}]$ so reactions will proceed \leftarrow (**from right to left**) consuming products and forming reactants
3. **If $Q < K$** ; to $\uparrow Q$, we must $\downarrow [\text{R}]$ and $\uparrow [\text{P}]$ so reactions will proceed \rightarrow (**from left to right**) consuming reactant and forming products.

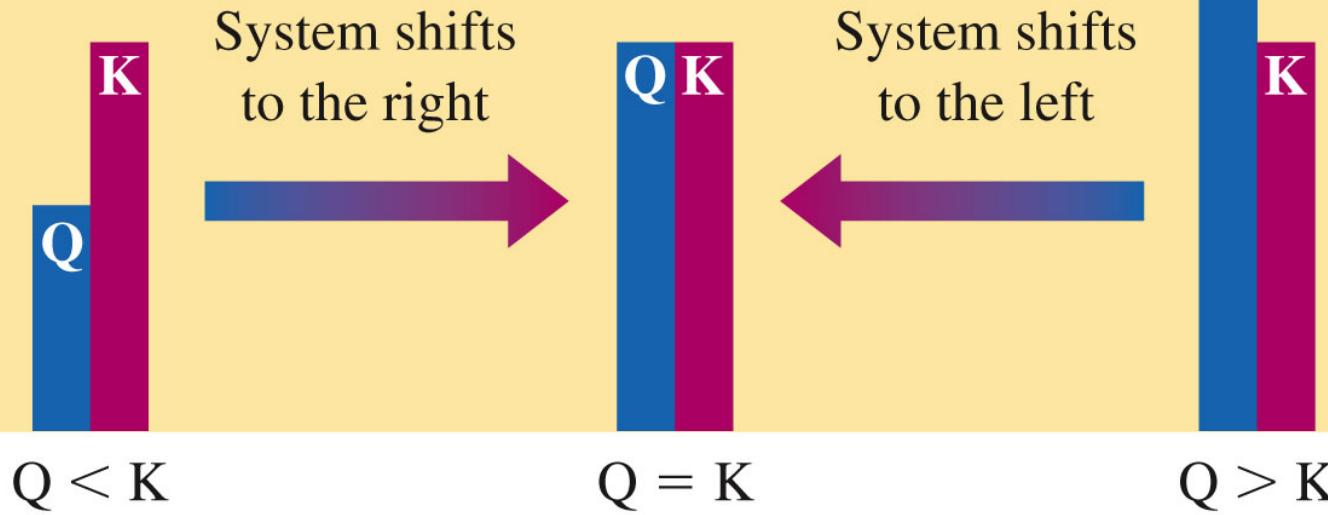
Applications of the equilibrium constant

Reaction Quotient

$$\frac{[\text{products}]_0}{[\text{reactants}]_0} = \text{too small}$$

System is
at equilibrium

$$\frac{[\text{products}]_0}{[\text{reactants}]_0} = \text{too large}$$



Applications of the equilibrium constant

Example 6.2

For the synthesis of ammonia at 500°C, the equilibrium constant is $6.0 \times 10^{-2} \text{ L}^2/\text{mol}^2$. Predict the direction in which the system will shift to reach equilibrium in each of the following cases.

- a. $[\text{NH}_3]_0 = 1.0 \times 10^{-3} \text{ M}$; $[\text{N}_2]_0 = 1.0 \times 10^{-5} \text{ M}$; $[\text{H}_2]_0 = 2.0 \times 10^{-3} \text{ M}$
- b. $[\text{NH}_3]_0 = 2.00 \times 10^{-4} \text{ M}$; $[\text{N}_2]_0 = 1.50 \times 10^{-5} \text{ M}$; $[\text{H}_2]_0 = 3.54 \times 10^{-1} \text{ M}$
- c. $[\text{NH}_3]_0 = 1.0 \times 10^{-4} \text{ M}$; $[\text{N}_2]_0 = 5.0 \text{ M}$; $[\text{H}_2]_0 = 1.0 \times 10^{-2} \text{ M}$

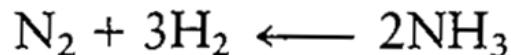
Applications of the equilibrium constant

Example 6.2 - Solution

a. First we calculate the value of Q :

$$\begin{aligned} Q &= \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} \\ &= \frac{(1.0 \times 10^{-3} \text{ mol/L})^2}{(1.0 \times 10^{-5} \text{ mol/L})(2.0 \times 10^{-3} \text{ mol/L})^3} \\ &= 1.3 \times 10^7 \text{ L}^2/\text{mol}^2 \end{aligned}$$

Since $K = 6.0 \times 10^{-2} \text{ L}^2/\text{mol}^2$, Q is much greater than K . For the system to attain equilibrium, the concentrations of the products must be decreased and the concentrations of the reactants increased. The system will shift to the left:



Applications of the equilibrium constant

Example 6.2 - Solution

b. We calculate the value of Q :

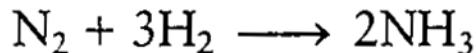
$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(2.00 \times 10^{-4} \text{ mol/L})^2}{(1.50 \times 10^{-5} \text{ mol/L})(3.54 \times 10^{-1} \text{ mol/L})^3}$$
$$= 6.01 \times 10^{-2} \text{ L}^2/\text{mol}^2$$

In this case $Q = K$, so the system is at equilibrium. No shift will occur.

c. The value of Q is

$$Q = \frac{[\text{NH}_3]_0^2}{[\text{N}_2]_0[\text{H}_2]_0^3} = \frac{(1.0 \times 10^{-4} \text{ mol/L})^2}{(5.0 \text{ mol/L})(1.0 \times 10^{-2} \text{ mol/L})^3}$$
$$= 2.0 \times 10^{-3} \text{ L}^2/\text{mol}^2$$

Here Q is less than K , so the system will shift to the right, attaining equilibrium by increasing the concentration of the product and decreasing the concentrations of the reactants:



Applications of the equilibrium constant

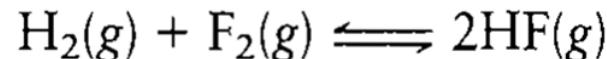
Example 6.3

Assume that the reaction for the formation of gaseous hydrogen fluoride from hydrogen and fluorine has an equilibrium constant of 1.15×10^2 at a certain temperature. In a particular experiment at this temperature 3.000 mol of each component was added to a 1.500-L flask. Calculate the equilibrium concentrations of all species.

Applications of the equilibrium constant

Example 6.3 - Solution

The balanced equation for the reaction is



The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}$$

We first calculate the initial concentrations:

$$[\text{HF}]_0 = [\text{H}_2]_0 = [\text{F}_2]_0 = \frac{3.000 \text{ mol}}{1.500 \text{ L}} = 2.000 \text{ M}$$

From the value of Q ,

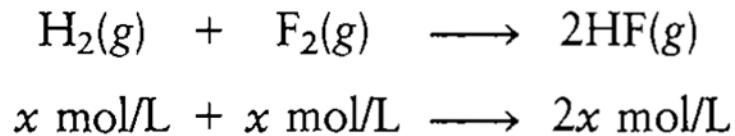
$$Q = \frac{[\text{HF}]_0^2}{[\text{H}_2]_0[\text{F}_2]_0} = \frac{(2.000)^2}{(2.000)(2.000)} = 1.000$$

which is much less than K , we know that the system must shift to the right to each equilibrium.

Applications of the equilibrium constant

Example 6.3 - Solution

What change in the concentrations is necessary? Since the answer to this question is presently unknown, we will define the change needed in terms of x . Let x equal the number of moles per liter of H_2 consumed to reach equilibrium. The stoichiometry of the reaction shows that x mol/L of F_2 will also be consumed and that $2x$ mol/L of HF will be formed:



Now the equilibrium concentrations can be expressed in terms of x :

Applications of the equilibrium constant

Example 6.3 - Solution

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[H_2]_0 = 2.000$	$-x$	$[H_2] = 2.000 - x$
$[F_2]_0 = 2.000$	$-x$	$[F_2] = 2.000 - x$
$[HF]_0 = 2.000$	$+2x$	$[HF] = 2.000 + 2x$

These concentrations can be represented in a shorthand table as follows:

	$H_2(g)$	+	$F_2(g)$	\rightleftharpoons	$2HF(g)$
Initial:	2.000		2.000		2.000
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$2.000 - x$		$2.000 - x$		$2.000 + 2x$

To solve for x , we substitute the equilibrium concentrations into the equilibrium expression:

$$K = 1.15 \times 10^2 = \frac{[HF]^2}{[H_2][F_2]} = \frac{(2.000 + 2x)^2}{(2.000 - x)^2}$$

Applications of the equilibrium constant

Example 6.3 - Solution

The right side of this equation is a perfect square, so taking the square root of both sides gives

$$\sqrt{1.15 \times 10^2} = \frac{2.000 + 2x}{2.000 - x}$$

which yields $x = 1.528$. The equilibrium concentrations can now be calculated:

$$[\text{H}_2] = [\text{F}_2] = 2.000 \text{ M} - x = 0.472 \text{ M}$$

$$[\text{HF}] = 2.000 \text{ M} + 2x = 5.056 \text{ M}$$

Check: Checking these values by substituting them into the equilibrium expression gives

$$\frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(5.056)^2}{(0.472)^2} = 1.15 \times 10^2$$

which agrees with the given value of K .

Solving equilibrium problems

- Write the balanced equation for the reaction.
- Write the equilibrium expression using the law of mass action.
- List the initial concentrations.
- Calculate Q and determine the direction of the shift to equilibrium.
- Define the change needed to reach equilibrium, and define the equilibrium concentrations by applying the change to the initial concentrations.
- Substitute the equilibrium concentrations into the equilibrium expression, and solve for the unknown.
- Check your calculated equilibrium concentrations by making sure that they give the correct value of K .

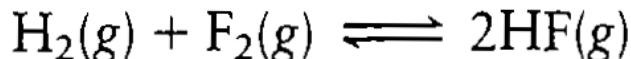
Solving equilibrium problems

Suppose that for the synthesis of hydrogen fluoride from hydrogen and fluorine, 3 moles of H_2 and 6 moles of F_2 are mixed in a 3 L flask. The equilibrium constant is $1.15 \cdot 10^2$. Calculate the equilibrium concentration of each component.

Solving equilibrium problems

Solution

- We begin as usual by writing the balanced equation for the reaction:



- The equilibrium expression is

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]}.$$

- The initial concentrations are

$$[\text{H}_2]_0 = \frac{3.000 \text{ mol}}{3.000 \text{ L}} = 1.000 \text{ M}$$

$$[\text{F}_2]_0 = \frac{6.000 \text{ mol}}{3.000 \text{ L}} = 2.000 \text{ M}$$

$$[\text{HF}]_0 = 0$$

- There is no need to calculate Q ; since no HF is initially present, we know that the system must shift to the right to reach equilibrium.
- If we let x represent the number of moles per liter of H_2 consumed to reach equilibrium, we can represent the concentrations as follows:

Solving equilibrium problems

Solution

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[H_2]_0 = 1.000$	$-x$	$[H_2] = 1.000 - x$
$[F_2]_0 = 2.000$	$-x$	$[F_2] = 2.000 - x$
$[HF]_0 = 0$	$+2x$	$[HF] = 0 + 2x$

Or in shorthand form:

	$H_2(g)$	+	$F_2(g)$	\rightleftharpoons	$2HF(g)$
Initial:	1.000		2.000		0
Change:	$-x$		$-x$		$+2x$
Equilibrium:	$1.000 - x$		$2.000 - x$		$2x$

Solving equilibrium problems

Solution

- Substituting the equilibrium concentrations into the equilibrium expression gives

$$K = 1.15 \times 10^2 = \frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(2x)^2}{(1.000 - x)(2.000 - x)}$$

To solve for x , we perform the indicated multiplication,

$$(1.000 - x)(2.000 - x)(1.15 \times 10^2) = (2x)^2$$

to give

$$(1.15 \times 10^2)x^2 - 3.000(1.15 \times 10^2)x + 2.000(1.15 \times 10^2) = 4x^2$$

and collect terms,

$$(1.11 \times 10^2)x^2 - (3.45 \times 10^2)x + 2.30 \times 10^2 = 0$$

This expression is a quadratic equation of the general form

$$ax^2 + bx + c = 0$$

where the roots can be obtained from the quadratic formula:

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

Solving equilibrium problems

Solution

In this example $a = 1.11 \times 10^2$, $b = -3.45 \times 10^2$, and $c = 2.30 \times 10^2$. Substituting these values into the quadratic formula gives two values for x :

$$x = 2.14 \text{ mol/L} \quad \text{and} \quad x = 0.968 \text{ mol/L}$$

Both of these results cannot be valid (since a *given* set of initial concentrations leads to only *one* equilibrium position). How can we choose between them? Since the expression for the equilibrium concentration of H_2 is

$$[\text{H}_2] = 1.000 \text{ M} - x$$

the value of x cannot be 2.14 mol/L (because subtracting 2.14 M from 1.000 M gives a negative concentration for H_2 , which is physically impossible). Thus the correct value for x is 0.968 mol/L, and the equilibrium concentrations are as follows:

$$[\text{H}_2] = 1.000 \text{ M} - 0.968 \text{ M} = 3.2 \times 10^{-2} \text{ M}$$

$$[\text{F}_2] = 2.000 \text{ M} - 0.968 \text{ M} = 1.032 \text{ M}$$

$$[\text{HF}] = 2(0.968 \text{ M}) = 1.936 \text{ M}$$

Solving equilibrium problems

Solution

- We can check these concentrations by substituting them into the equilibrium expression

$$\frac{[\text{HF}]^2}{[\text{H}_2][\text{F}_2]} = \frac{(1.936)^2}{(3.2 \times 10^{-2})(1.032)} = 1.13 \times 10^2$$

This value is in close agreement with the given value for K (1.15×10^2), so the calculated equilibrium concentrations are correct.

Solving equilibrium problems

Treating systems that have small K

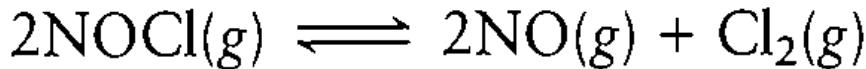
Consider gaseous NOCl , which decomposes to form the gases NO and Cl_2 . At 35° C the equilibrium constant is $1.6 \times 10^{-5} \text{ mol/L}$. In an experiment in which 1 mole of NOCl is placed in a 2 L flask, what are the equilibrium concentrations?

Solving equilibrium problems

Treating systems that have small K

Solution

The balanced equation is



and

$$K = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = 1.6 \times 10^{-5} \text{ mol/L}$$

The initial concentrations are

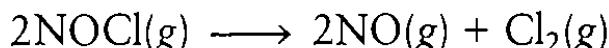
$$[\text{NOCl}]_0 = \frac{1.0 \text{ mol}}{2.0 \text{ L}} = 0.50 \text{ M}, \quad [\text{NO}]_0 = 0, \quad [\text{Cl}_2]_0 = 0$$

Solving equilibrium problems

Treating systems that have small K

Solution

Since there are no products initially, the system will move to the right to reach equilibrium. We will define x as the change in concentration of Cl_2 needed to reach equilibrium. The changes in the concentrations of NOCl and NO can then be obtained from the balanced equation:



The concentrations can be summarized as follows:

Initial Concentration (mol/L)	Change (mol/L)	Equilibrium Concentration (mol/L)
$[\text{NOCl}]_0 = 0.50$	$-2x$	$[\text{NOCl}] = 0.50 - 2x$
$[\text{NO}]_0 = 0$	$+2x$	$[\text{NO}] = 0 + 2x = 2x$
$[\text{Cl}_2]_0 = 0$	$+x$	$[\text{Cl}_2] = 0 + x = x$

Or in shorthand form:

	$2\text{NOCl}(g)$	\rightleftharpoons	$2\text{NO}(g)$	+	$\text{Cl}_2(g)$
Initial:	0.50		0		0
Change:	$-2x$		$+2x$		$+x$
Equilibrium:	$0.50 - 2x$		$2x$		x

Solving equilibrium problems

Treating systems that have small K

Solution

The equilibrium concentrations must satisfy the equilibrium expression:

$$K = 1.6 \times 10^{-5} = \frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2x)^2(x)}{(0.50 - 2x)^2}$$

Multiplying and collecting terms results in an equation that requires complicated methods to solve directly. However, we can avoid this situation by recognizing that since K is so small (1.6×10^{-5} mol/L), the system will not proceed far to the right to reach equilibrium. That is, x represents a relatively small number. Consequently, the term $(0.50 - 2x)$ can be approximated by 0.50. That is, when x is small,

$$0.50 - 2x \approx 0.50$$

Making this approximation allows us to simplify the equilibrium expression:

$$1.6 \times 10^{-5} = \frac{(2x)^2(x)}{(0.50 - 2x)^2} \approx \frac{(2x)^2(x)}{(0.50)^2} = \frac{4x^3}{(0.50)^2}$$

Solving for x^3 gives

$$x^3 = \frac{(1.6 \times 10^{-5})(0.50)^2}{4} = 1.0 \times 10^{-6}$$

Solving equilibrium problems

Treating systems that have small K

Solution

and $x = 1.0 \times 10^{-2}$ (mol/L).

Next, we must check the validity of the approximation. If $x = 1.0 \times 10^{-2}$, then

$$0.50 - 2x = 0.50 - 2(1.0 \times 10^{-2}) = 0.48$$

The difference between 0.50 and 0.48 is 0.02, or 4% of the initial concentration of NOCl, a relatively small discrepancy that will have little effect on the outcome. That is, since $2x$ is very small compared with 0.50, the value of x obtained in the approximate solution should be very close to the exact value. We use this approximate value of x to calculate the equilibrium concentrations:

$$[\text{NOCl}] = 0.50 - 2x = 0.48 \text{ M} \approx 0.50 \text{ M}$$

$$[\text{NO}] = 2x = 2(1.0 \times 10^{-2} \text{ M}) = 2.0 \times 10^{-2} \text{ M}$$

$$[\text{Cl}_2] = x = 1.0 \times 10^{-2} \text{ M}$$

Check:
$$\frac{[\text{NO}]^2[\text{Cl}_2]}{[\text{NOCl}]^2} = \frac{(2.0 \times 10^{-2})^2(1.0 \times 10^{-2})}{(0.50)^2} = 1.6 \times 10^{-5}$$

Since the given value of K is 1.6×10^{-5} , these calculated concentrations are correct.

This problem turned out to be relatively easy to solve because the *small value of K and the resulting small shift to the right to reach equilibrium allowed simplification.*

Le Chatelier principle

Le Chatelier Principle states that:

“If a change in conditions (a stress) is imposed on a system at equilibrium, the equilibrium position will shift in a direction that tends to reduce that change in conditions.”



Henri Louis Le Chatelier

Le Chatelier principle

The effect of a change in concentration

If [reactant] is ↓ equilibrium shift ← to ↑

If [product] is ↓ equilibrium shift → to ↑

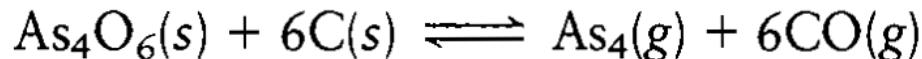
If [reactant] is ↑ equilibrium shift → to ↓

If [product] is ↑ equilibrium shift ← to ↓

Le Chatelier principle

Example 6.4

Arsenic can be extracted from its ores by first reacting the ore with oxygen (a process called *roasting*) to form solid As_4O_6 , which is then reduced with carbon:



Predict the direction of the shift of the equilibrium position for this reaction in response to each of the following changes in conditions.

- a. addition of CO
- b. addition or removal of C or As_4O_6
- c. removal of As_4

Le Chatelier principle

Example 6.4 - Solution

- a. Le Châtelier's principle predicts that the shift will be away from the substance whose concentration is increased. The equilibrium position will shift to the left when CO is added.
 - b. Since the amount of a pure solid has no effect on the equilibrium position, changing the amount of C or As₄O₆ will have no effect.
 - c. If gaseous As₄ is removed, the equilibrium position will shift to the right to form more products. In industrial processes the desired product is often continuously removed from the reaction system to increase the yield.
-

Le Chatelier principle

The effect of a change in pressure

There are 3 ways to change P of a gas:

1-Add or remove a gas reactant or product at constant V.
The effect will be the same as with [].

2-Add an inert gas, which doesn't react with anything , it will ↑ the total pressure of the system but has no effect on the [] or partial pressure of R or P **so there will be no shift in ⇌**

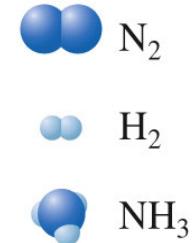
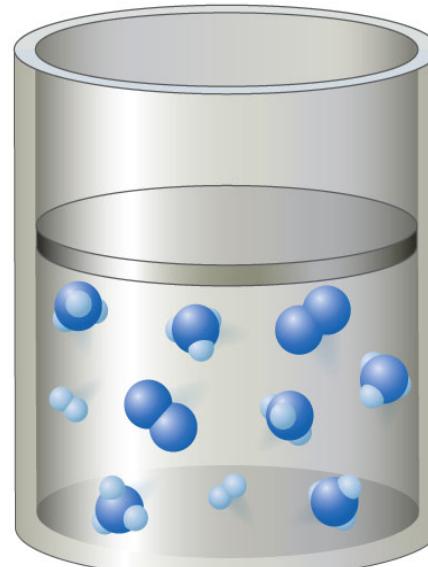
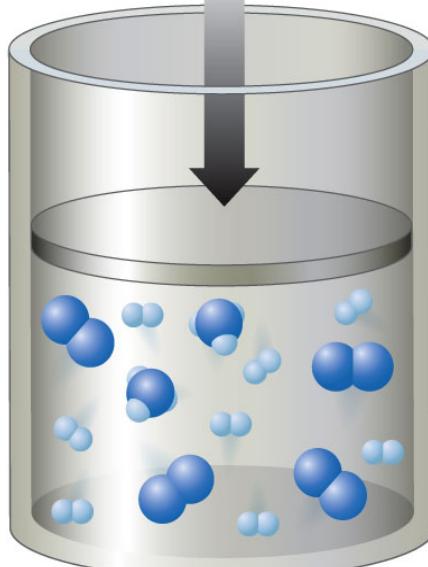
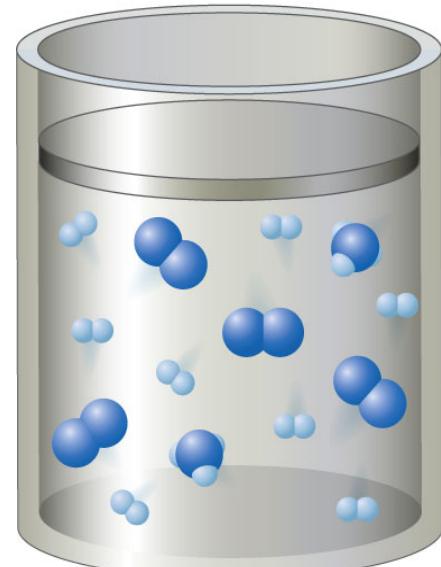
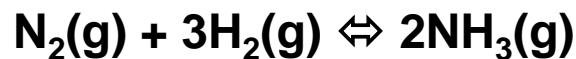
Le Chatelier principle

The effect of a change in pressure

3-Change the volume of the container.

If $V \downarrow$, $P \uparrow$, the system will shift toward the smallest # of gas molecules (**$V = K \cdot n$, V and n are directly related**).

If $V \uparrow$, $P \downarrow$, the \rightleftharpoons will shift toward the biggest # of gas molecules.



$$V = \left(\frac{RT}{P} \right)^{\frac{1}{n}}$$

At cte T and P

V

(a)

(b)

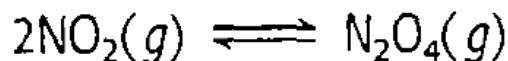
(c)

Le Chatelier principle

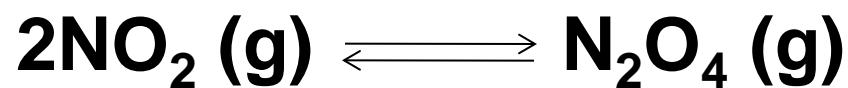
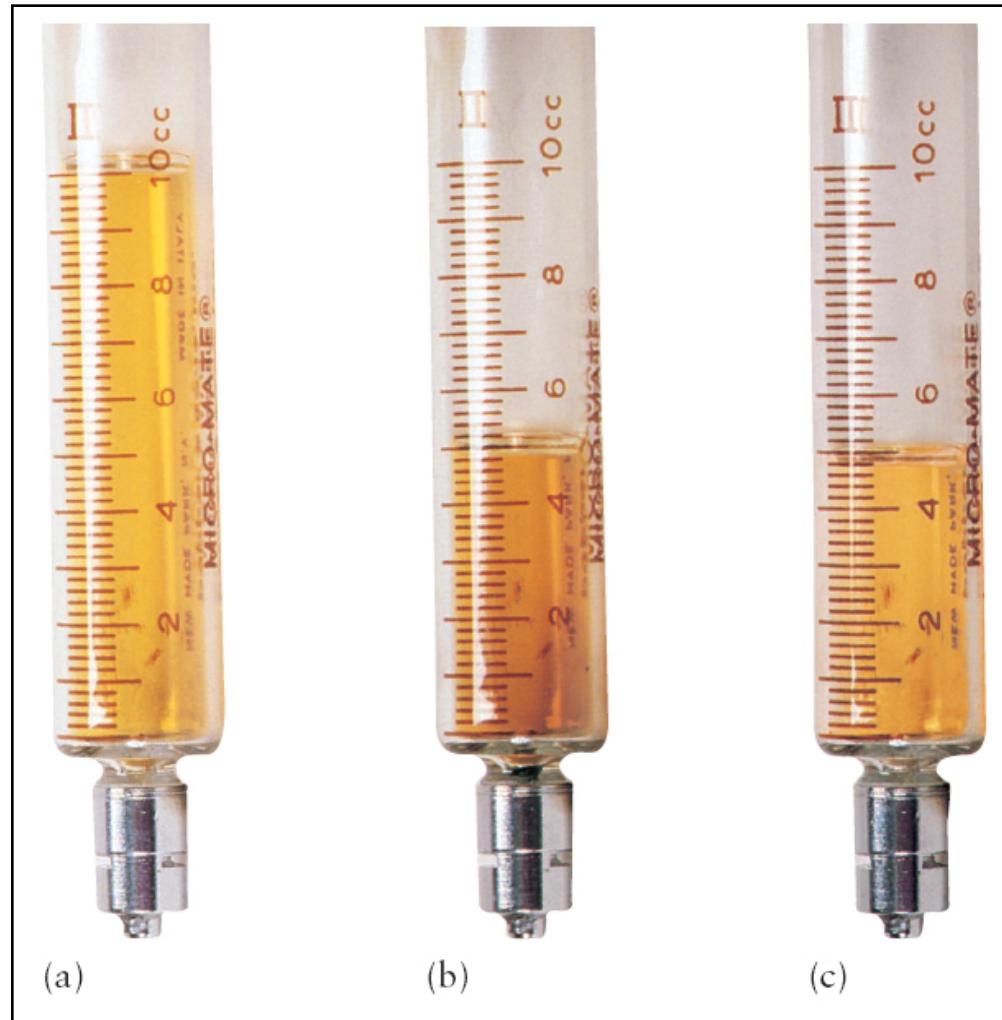
The effect of a change in pressure

Figure 6.10

(a) Brown $\text{NO}_2(g)$ and colorless $\text{N}_2\text{O}_4(g)$ at equilibrium in a syringe. (b) The volume is suddenly decreased, giving a greater concentration of both N_2O_4 and NO_2 (indicated by the darker brown color). (c) A few seconds after the sudden volume decrease, the color becomes much lighter brown as the equilibrium shifts from brown $\text{NO}_2(g)$ to colorless $\text{N}_2\text{O}_4(g)$. This is predicted by Le Châtelier's principle, since in the equilibrium



the product side has the smaller number of molecules.



Brown gas

Colorless gas

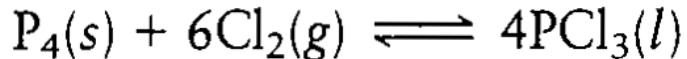
Le Chatelier principle

The effect of a change in pressure

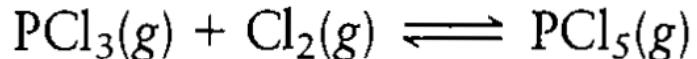
Example 6.5

Predict the shift in equilibrium position that will occur for each of the following processes when the volume is reduced.

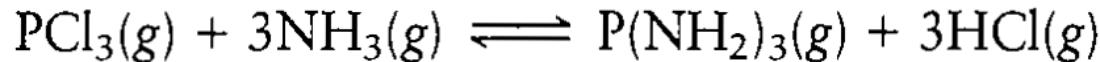
- a. the preparation of liquid phosphorus trichloride:



- b. the preparation of gaseous phosphorus pentachloride:



- c. the reaction of phosphorus trichloride with ammonia:



Le Chatelier principle

The effect of a change in pressure

Example 6.5 -Solution

- a. Since P_4 and PCl_3 are a pure solid and a pure liquid, respectively, we need to consider only the effect of the decrease in volume on Cl_2 . The position of the equilibrium will shift to the right, since the reactant side contains six gaseous molecules and the product side has none.
 - b. Decreasing the volume will shift the given reaction to the right, since the product side contains only one gaseous molecule and the reactant side has two.
 - c. Both sides of the balanced reaction equation have four gaseous molecules. A change in volume will have no effect on the equilibrium position. There is no shift in this case.
-

Le Chatelier principle

The effect of a change in temperature



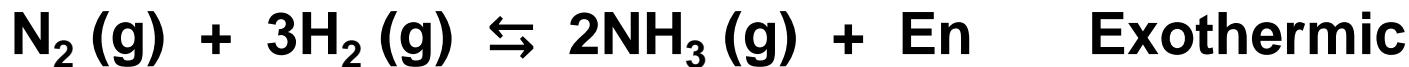
Endothermic energy is treated as reactant



Exothermic energy is treated as product

K only change with T

For an exothermic reaction where En is a product , an \uparrow in T° will shift the reaction in direction to consume En (to the left) and the opposite will be true.



An \uparrow in T° will make $[NH_3] \downarrow$ and $[N_2], [H_2] \uparrow$ so $K \downarrow$

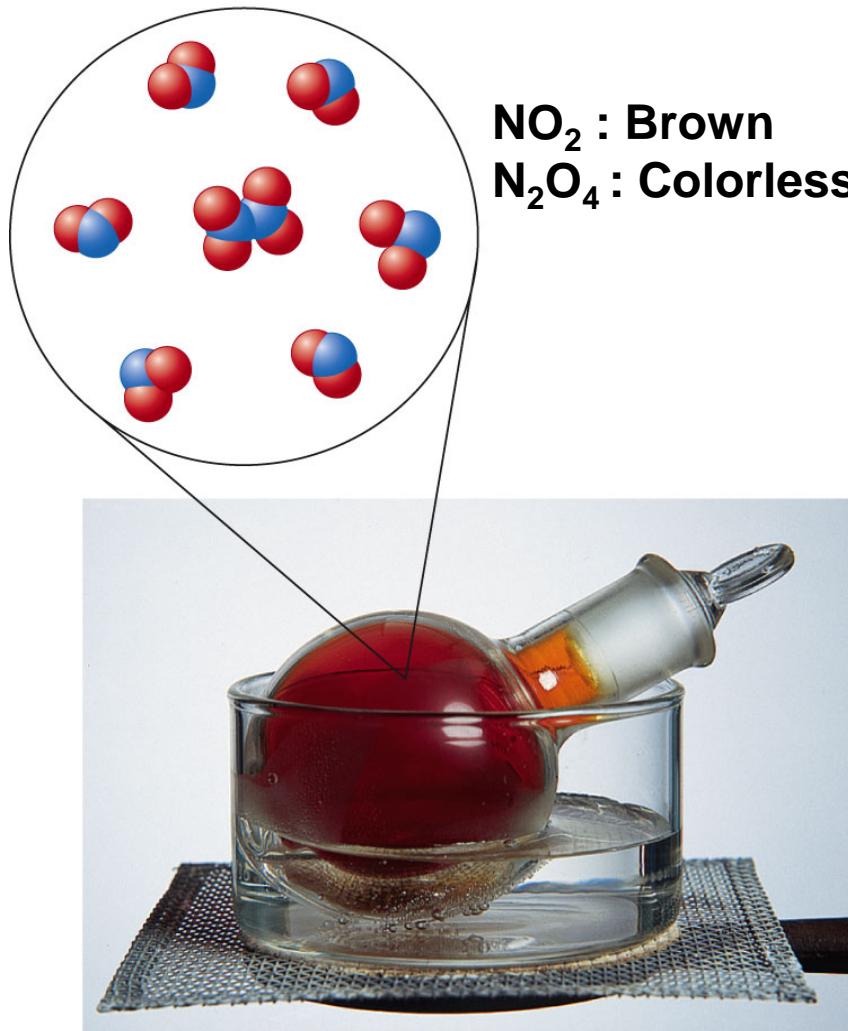


If $T \uparrow$, heat is added (it's a reactant) so \rightleftharpoons shift \rightarrow , $[CO_2] \uparrow$; $K \uparrow$

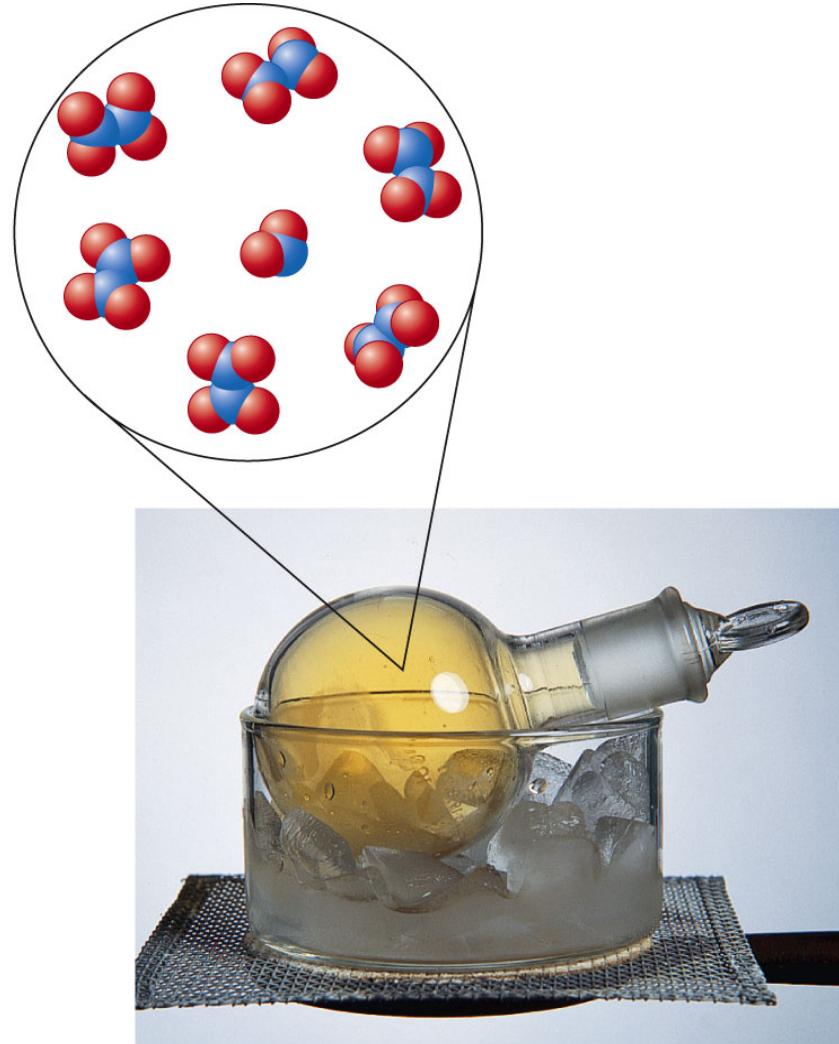
Shifting the $\text{N}_2\text{O}_4 \rightarrow 2\text{NO}_2$ Equilibrium by Changing the Temperature

Endothermic reaction

- (a) At 100 °C the flask is definitely reddish brown due to a large amount in NO_2 present
(b) At 0 °C the equilibrium is shifted toward colorless N_2O_4



(a)



(b)

Le Chatelier principle

The effect of a change in temperature

Table 6.3

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

*For this exothermic reaction, the value of K decreases as the temperature increases, as predicted by Le Châtelier's principle.

Table 6.4**Endothermic reaction**

Shifts in the Equilibrium Position for the Reaction
 $\text{N}_2\text{O}_4(g) \rightleftharpoons 2\text{NO}_2(g)$

Change	Shift
Addition of $\text{N}_2\text{O}_4(g)$	Right
Addition of $\text{NO}_2(g)$	Left
Removal of $\text{N}_2\text{O}_4(g)$	Left
Removal of $\text{NO}_2(g)$	Right
Addition of $\text{He}(g)$	None
Decrease in container volume	Left
Increase in container volume	Right
Increase in temperature	Right
Decrease in temperature	Left

Le Chatelier principle

Explain how the following changes in reaction conditions will affect the position of the equilibrium below, and explain your reasoning.

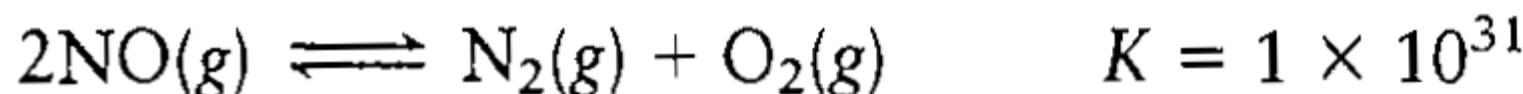
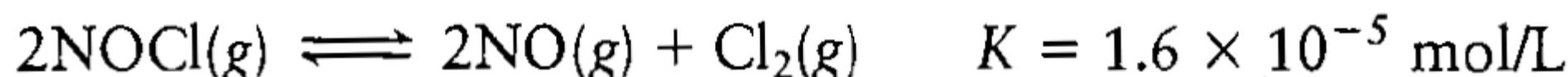


- 1) The pressure of A in the reaction chamber is increased.
The reaction is pushed toward products.
- 2) The temperature of the reaction is increased by 20° C.
Because heat can be thought of as being a product, the reaction will be pushed toward reactants.
- 3) A catalyst is added to the system.
No change. A catalyst doesn't change the equilibrium position, it only changes how quickly equilibrium is reached.
- 4) As the reaction progresses, more of compound B is steadily added to the reaction chamber.
The reaction is pushed toward products.
- 5) An inhibitor is added to the reaction chamber.
No change, though the reaction will move more slowly.
- 6) Argon gas is added to the reaction chamber, doubling the pressure.
No change. If the partial pressure of gaseous compounds is changed, the equilibrium will shift position. However, adding argon gas doesn't change the partial pressures of A, so the equilibrium position is unaffected.

HOMEWORK

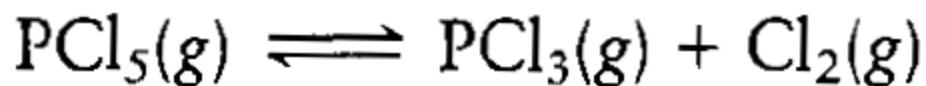
Chap.6: 15, 27, 37, 46, 49, 61, 64, 70, 77

1. Consider the following reactions at some temperature:



For each reaction some quantities of the reactants were placed in separate containers and allowed to come to equilibrium. Describe the relative amounts of reactants and products that are present at equilibrium. At equilibrium, which is faster, the forward or reverse reaction in each case?

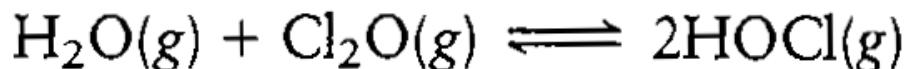
A sample of gaseous PCl_5 was introduced into an evacuated flask so that the pressure of pure PCl_5 would be 0.50 atm at 523 K. However, PCl_5 decomposes to gaseous PCl_3 and Cl_2 , and the actual pressure in the flask was found to be 0.84 atm. Calculate K_p for the decomposition reaction



at 523 K. Also calculate K at this temperature.

37

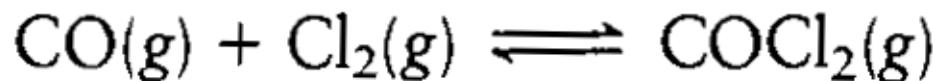
At 25°C, $K = 0.090$ for the reaction



For which of the following sets of conditions is the system at equilibrium? For those that are not at equilibrium, in which direction will the system shift?

- a) A 1.0 L flask contains 1.0 mole of HOCl, 0.10 mole of Cl₂O and 0.1 mole of H₂O
- b) A 2.0 L flask contains 0.084 mole of HOCl, 0.080 mole of Cl₂O and 0.98 mole of H₂O
- c) A 3.0 L flask contains 0.25 mole of HOCl, 0.0010 mole of Cl₂O and 0.56 mole of H₂O

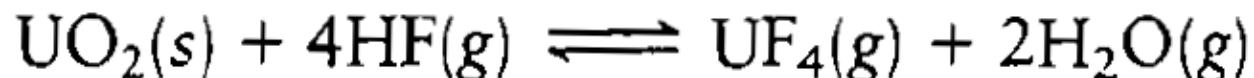
Lexan is a plastic used to make compact discs, eyeglass lenses, and bullet-proof glass. One of the compounds used to make Lexan is phosgene (COCl_2), a poisonous gas. Phosgene is produced by the reaction



for which $K = 4.5 \times 10^9 \text{ L/mol}$ at 100°C .

- Calculate K_p at 100°C .
- Equal moles of CO and Cl_2 are reacted at 100°C . If the total pressure at equilibrium is 5.0 atm, calculate the equilibrium partial pressures of all the gases.

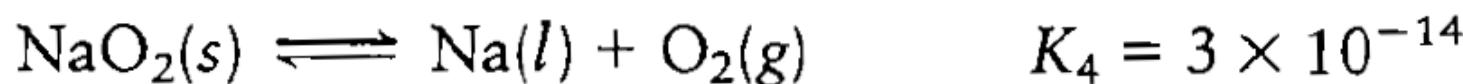
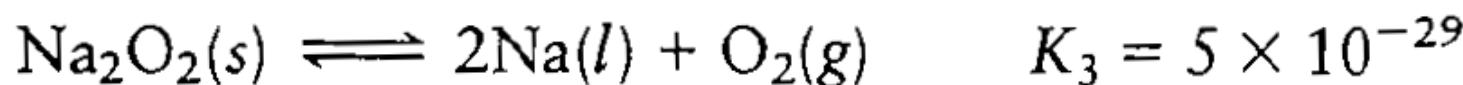
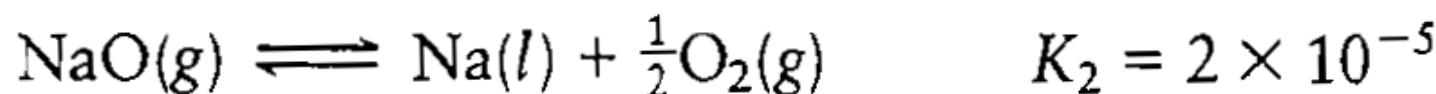
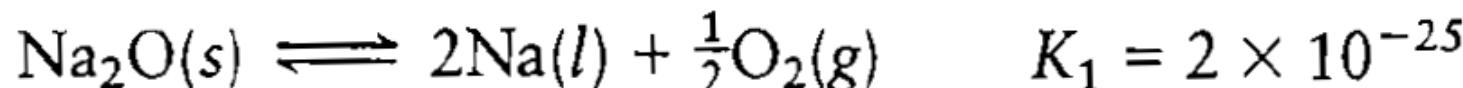
Suppose the reaction system



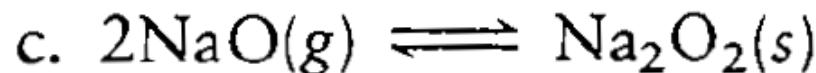
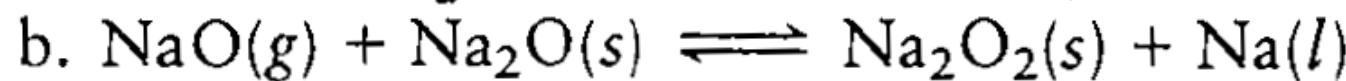
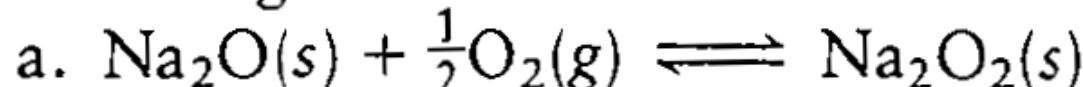
has already reached equilibrium. Predict the effect that each of the following changes will have on the equilibrium position. Tell whether the equilibrium will shift to the right, will shift to the left, or will not be affected.

- a. More $\text{UO}_2(s)$ is added to the system.
- b. The reaction is performed in a glass reaction vessel; $\text{HF}(g)$ attacks and reacts with glass.
- c. Water vapor is removed.

Given the following equilibrium constants at 427°C,



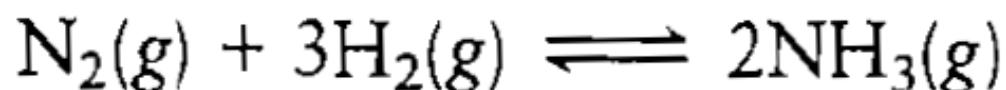
determine the values for the equilibrium constants for the following reactions.



(Hint: When reaction equations are added, the equilibrium expressions are multiplied.)

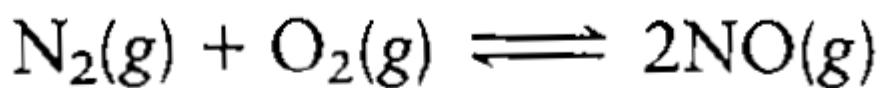
70

At 25°C, $K_p = 5.3 \times 10^5 \text{ atm}^{-2}$ for the reaction



When a certain partial pressure of $\text{NH}_3(g)$ is put into an otherwise empty rigid vessel at 25°C, equilibrium is reached when 50.0% of the original ammonia has decomposed. What was the original partial pressure of ammonia before any decomposition occurred?

At 25°C, $K_p \approx 1 \times 10^{-31}$ for the reaction



- a. Calculate the concentration of NO (in molecules/cm³) that can exist in equilibrium in air at 25°C. In air $P_{\text{N}_2} = 0.8$ atm and $P_{\text{O}_2} = 0.2$ atm.
- b. Typical concentrations of NO in relatively pristine environments range from 10^8 to 10^{10} molecules/cm³. Why is there a discrepancy between these values and your answer to part a?

The partial pressures of an equilibrium mixture of $\text{N}_2\text{O}_4(g)$ and $\text{NO}_2(g)$ are $P_{\text{N}_2\text{O}_4} = 0.34$ atm and $P_{\text{NO}_2} = 1.20$ atm at a certain temperature. The volume of the container is doubled. Find the partial pressures of the two gases when a new equilibrium is established.