# *Chapter 3: chemical equilibrium*



## I. Basic concepts

***I.1. Equilibrium :*** It is defined as the state when measurable properties such as position speed, temperature, concentration and pressure do not change with time.

Equilibirum can be of a no. of types. For example: physical equilibrium, thermal equilibrium, mechanical equilibrium, chemical equilibrium etc.

***I.2.1. Thermal Equilibrium :*** It is that type of equilibrium where the thermal energy between two or more substances are equal in nature.

***I.2.2. Physical Equilibrium***

The type of equilibrium which develops between different phases and there is no change in chemical composition. In physical equilibrium, there is the existence of same substance in different physical states.

- Solid-liquid equilibrium :

$$H_2O\ (s) \rightleftharpoons H_2O\ (l)$$

Rate of transfer of ice is equal to the rate of freezing of water

- Liquid-vapour equilibrium

Rate of vaporization = Rate of condensation,

$$H_2O\ (l) \rightleftharpoons H_2O\ (g)$$

Conditions necessary for a Liquid-Vapour Equilibrium

- The system must be a closed system.
- The system must be at a constant temperature.
- The visible properties of the system should not change with time.

- Solid-vapour equilibrium

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Certain solid substances on heating get converted directly into vapour without passing through the liquid phase. This process is called sublimation. The vapour when cooled, gives back the solid, it is called deposition or desublimation.

$$NH_4Cl\ (s) \overset{heat}{\rightleftharpoons} NH_4Cl\ (g)$$

***I.2.3. Chemical equilibrium :*** Chemical reaction is a process in which one or more reactants react to produce one or more products.

$$N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$$

Chemical reaction can be classifed as :

- Irreversible Reactions
- Reversible reactions

**a.** Irreversible Reaction : the reaction is said to go to completion and this is indicated by ( $\longrightarrow$ ) : $A + B \longrightarrow C + D$

The reaction stops when all of limiting reagent has been used up.

Eg : 2Mg(s) + O2(g) → 2MgO(s)

**b.** Reversible reaction : Many chemical reactions do not go to completion but instead attain a state of chemicalequilibrium. Indiccated by : ( $\rightleftharpoons$ ).

A reaction said to be reversible if under certain conditions of temperature and pression the forward reaction and revers reaction occur simultaneously.

$$A + B \underset{rate2}{\overset{rate1}{\rightleftharpoons}} C + D$$

With passing time, there is decrease in the concentration of reactants A and B, the increase in the concentration of products C and D which leads to a decrease in the rate of forward reaction and an increase in the rate of revers (backward) reaction.

When the two reactions occur at the same rate and system will reaches a state of equilibrium.

**rate1 = rate2**

$$\text{Eg : } N_2O_4\ (g) \underset{rate2}{\overset{rate1}{\rightleftharpoons}} 2NO_2\ (g)$$

### *I.4. The Concept of Chemical Equilibrium :*

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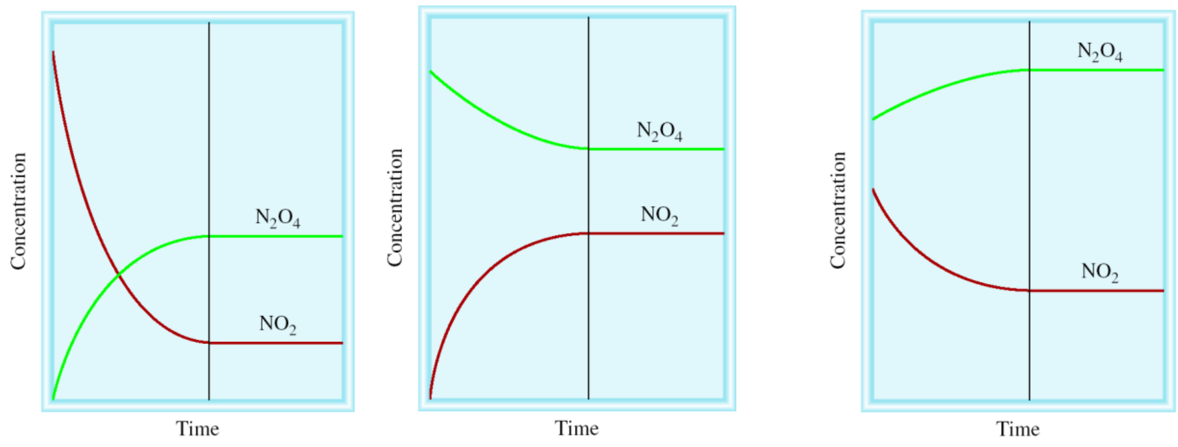
As a system approaches equilibrium, both the forward and reverse reactions are occurring.

- ✓ the rates of the forward and reverse reactions are equal
- ✓ the concentrations of the reactants and products remain constant
- ✓ Equilibrium is a dynamic process . the conversions of reactants to products and products to reactants are still going on, although there is no net change in the number of reactant and product molecules
- ✓ The same state of equilibrium (characterized by its equilibrium constant which is discussed later can be reached whether the reaction is started from the reactants or products side. For example, the same equilibrium

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

is established whether we start the reaction with $N_2O_4$ or $NO_2$




Start with $NO_2$ Start with $N_2O_4$ Start with $NO_2$ & $N_2O_4$

- ✓ When reaction attains equilibrium at certain temperature and pressure, $\Delta G = 0$
- ✓ Chemical equilibrium can be achieved from either direction.

⇒ Equilibrium is a dynamic process . the conversions of reactants to products and products to reactants are still going on, although there is no net change in the number of reactant and product molecules.

### *I.5. Homogeneous and heterogeneous Equilibria:*

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### a. Homogeneous Equilibria:

In a equilibrium system, all the reactants and products are in same phase is known as Homogenous system.

For example,

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

In the above reaction all reactants and products are in gaseous phase.

### b. Heterogeneous Equilibria:

In a equilibrium system having more than one phase is called heterogeneous equilibrium. The familiar example for this type of system is the equilibrium between water vapour and liquid water in a closed container.

$$H_2O(l) \rightleftharpoons H_2\ O(vap)$$

Similarly, there is equilibrium between a solid and its saturated solution is a heterogeneous equilibrium.

$$Ca(OH)_2\ (s) \rightleftharpoons Ca^{2+}\ (aq) + 2OH^-\ (aq)$$

In the above reaction, all reactants and products are homogeneous solution phase.

## II. Equilibrium Constant Expression :

Consider the following reversible reaction :

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

At equilibrium the concentrations of A, B, C and D become constant. Also, it has been found experimentally that irrespective of the starting concentrations of A and B the following ratio of concentration terms always remains constant.

The **equilibrium constant, Kc,** is the ratio of the equilibrium concentrations of products over the equilibrium concentrations of reactants each raised to the power of their stoichiometric coefficients.

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

**EQUILIBRIUM CONSTANT 'K'**

For a General Reaction of the type

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

The equilibrium constant expression is

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

where $K_c$ is Equilibrium constant

- **Law of mass action :** The value of the equilibrium constant expression, Kc, is constant for a given reaction at equilibrium and at a constant temperature.

⇒ The equilibrium concentrations of reactants and products may vary, but the value for Kc remains the same.

## *II.1. Magnitude of Kc*

⇒ If the Kc value is large (Kc >> 1), the equilibrium lies to the right and the reaction mixture contains mostly products.

⇒ If the Kc value is small (Kc <<1), the equilibrium lies to the left and the reaction mixture contains mostly reactants.

⇒ If the Kc value is close to 1 (0.10 < Kc < 10), the mixture contains appreciable amounts of both reactants and products.

## *II. 2. Pressure Equilibrium Constant $K_p$*

In case of gases their partial pressures can also be used in place of molar concentrations (since the two are directly proportional to each other) in the law of equilibrium. The new equilibrium constant, ***Kp*,** is called the pressure equilibrium constant. For the general gas phase reaction :

$$a\,A\,(g) + b\,B\,(g) \rightleftharpoons c\,C\,(g) + d\,D\,(g)$$

*K*p is given by :

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

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## II.3. Relation between $K_p$ and $K_c$ :

For a general gas phase reaction at equilibrium

$$a\,A\,(g) + b\,B\,(g) \rightleftharpoons c\,C\,(g) + d\,D\,(g)$$

The pressure and concentration equilibrium constants Kp and Kc are :

$$K_c = \frac{[A]^a\,[B]^b}{[C]^c\,[D]^d} \text{ and } K_p = \frac{P_A^a\ P_B^b}{P_C^c\ P_D^d}$$

For a gaseous substance i, the ideal gas equation is

$$p_i V = n_i RT$$

where $p_i$ and $n_i$ are its partial pressure and amount in a gaseous mixture and $V$ and $T$ are its volume and temperature and R is the gas constant. The relation may be written as :

$$p_i = \frac{n_i}{V} RT = C_i\,RT$$

Where $c_i$ is the molar concentration or molarity of '$i$' expressed in moles per litre. This relation can be used for replacing the partial pressure terms in the expression for $K_p$.

$$K_p = \frac{[C]^c(RT)^c[D]^d(RT)^d}{[A]^a(RT)^a[B]^b(RT)^b}$$

$$K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b}\,(RT)^{(c+d)-(a+b)}$$

$$K_p = \frac{[C]^c[D]^d}{[A]^a[B]^b}\,(RT)^{\Delta n}$$

For example

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

$\Delta n = 2-(3+1) = -2$

## II.4. Manipulating Equilibrium Expressions :

1. Reversing the direction of a reaction:

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ vs. $2NO_2(g) \rightleftharpoons N2O4(g)$

$K_c = \frac{[NO_2]^2}{[N_2O_2]}$ Vs. $K'_c = \frac{[N_2O_2]}{[NO_2]^2}$

Clearly $K_c = K'_c$

2. Coefficient changes

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$ vs. $2N_2O_4(g) \rightleftharpoons 4NO_2(g)$

$K_c = \frac{[NO_2]^2}{[N_2O_2]}$ Vs. $K'_c = \frac{[NO_2]^4}{[N_2O_2]^2}$

Clearly $K'_c = K_c^2$

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3. Adding chemical reactions together

$N_2O_4(g) \rightleftarrows 2NO_2(g)$ $\quad K_{c1} = \frac{[NO_2]^2}{[N_2O_4]}$

$2NO2(g) \rightleftarrows 2NO(g) + O2(g)$ $\quad K_{c2} = \frac{[NO]^2[O_2]}{[NO_2]^2}$

$N_2O_4(g) \rightleftarrows 2NO(g) + O_2(g)$ $\quad K_c = \frac{[NO]^2\,]O_2]}{[N_2O_4]}$

Clearly $K_c = K_{c1}\ x\ K_{c2}$

*Example :* Given the following data:

(1) $N_2(g) + O_2(g) \rightleftarrows 2NO(g)$ $K_{c1} = 4.3 \times 10^{-25}$

(2) $2NO(g) + O_2(g) \rightleftarrows 2NO_2(g)$ $K_{c2} = 6.4 \times 10^{9}$

Determine the values of the equilibrium constants for the following reactions:

(a) $4NO(g) \rightleftarrows N_2(g) + 2NO_2(g)$

(b) $4NO_2(g) \rightleftarrows 2N_2(g) + 4O_2(g)$

(c) $2NO(g) + 2NO_2(g) \rightleftarrows 3O_2(g) + 2N_2(g)$

Solution:

(a) Try reversing (1) and adding this to (2):

$2NO + 2NO + \cancel{O_2} \rightleftarrows N_2 + \cancel{O_2} + 2NO_2$

This is what we want and thus $Kc = (1/K_{c1})(K_{c2)} = 1.5 \times 10^{34}$

(b) Try reversing both (1) and (2), and add them:

$\cancel{2NO} + 2NO_2 \rightleftarrows N_2 + O_2 + \cancel{2NO} + O_2$

Then we can double this to get what we want, which gives $Kc = [\ (1/K_{c1})\ (1/K_{c2})\ ]2 = (3.6 \times 10^{14})^2 = 1.3 \times 10^{29}$

(c) Try reversing both 2 x (1) and (2), and add them:

$4NO + 2NO_2 \rightleftarrows 2N_2 + 2O_2 + 2NO + O_2$

which gives $Kc = (1/K_{c1})^2\ (1/K_{c2}) = 8.5 \times 10^{38}$

### ***II.5. Predicting the Direction of the Reaction- Reaction Quotient:***

We can predict the direction in which reaction will proceed at any stage with the help of the equilibrium constant. Reaction Quotient Q will calculate for this purpose. The same way as the equilibrium constant $K_c$, Reaction Quotient will define are not necessarily equilibrium values.

$$aA + bB \rightleftarrows cC + dD$$

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

- the reaction proceeds in the direction of reactants when $Q_c > K_c$
- the reaction proceeds in the direction of products when $Q_c < K_c$
- the reaction mixture is already at equilibrium when $Q_c = K_c$

*Example :*

Suppose a gaseous mixture from an industrial plant has the following composition at 1200 K:

0.02 M CO ; 0.02 M $H_2$ ; 0.001 M $CH_4$ ; 0.001 M $H_2O$

Would the following reaction go forward or in reverse?

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

To answer this question we need to calculate the reaction quotient ($Q_c$), and compare its value to that of $K_c$

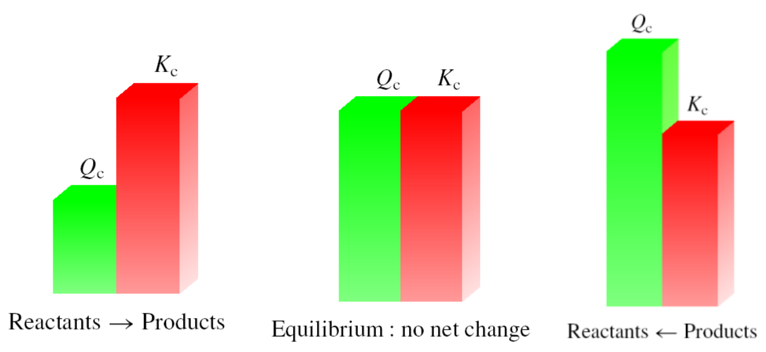
The reaction quotient ($Q_c$) is an expression that has the same form as the equilibrium constant expression but whose concentration values are not necessarily those at equilibrium.

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

$$Q_c = \frac{0.001\ x\ 0.001}{0.02\ x\ 0.02^3}$$

$$Q_c = 6.25$$

Remember that Kc = 3.93 for this reaction at 1200 K. Thus we have that $Q_c > K_c$ For $Q_c$ to become equal to $K_c$ the reaction must shift to the left.




## III. Calculating Equilibrium Concentrations:

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed:

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction:

(a) The initial concentration,

(b) The change in concentration on going to equilibrium, and

(c) The equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to so

lve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x.

Step 5. Check your results by substituting them into the equilibrium equation.

***Example :*** A closed system initially containing 1.000 x $10^{-3}$ M $H_2$ and 2.000 x $10^{-3}$ M $I_2$ At 448°C is allowed to reach equilibrium. Analysis of the equilibrium mixture shows that the concentration of HI is 1.87 x $10^{-3}$ M. Calculate $K_c$ at 448°C for the reaction:

$$H2\ (g) + I2\ (g) \rightleftarrows 2\ HI\ (g)$$

| | $[H_2]$ M | $[I_2]$ M | [HI] M |
|---|---|---|---|
| **initially** | 1.000 $10^{-3}$ | 2.000 $10^{-3}$ | 0 |
| **change** | -x | -x | +2x |
| **At equilibrium** | 6.5 $10^{-5}$ | 1.065 $10^{-3}$ | 1.87 $10^{-3}$ |

2x = 1.87 $10^{-3} \Rightarrow x = \frac{1.87\ 10^{-3}}{2} = 9.35\ 10^{-4}\ M$

At equilibrium : $[H_2] = [H_2]_i - x = 1.000\ x\ 10^{-3} - 9.35\ x\ 10^{-4} = 6.5\ x\ 10^{-5} M$

$$[I_2] = [I_2]_i - x = 2.000\ x\ 10^{-3} - 9.35\ x\ 10^{-4} = 1.065\ x\ 10^{-3} M$$

and, therefore, the equilibrium constant : $K_c = \frac{[HI]^2}{[H_2]\ [I_2]} = \frac{1.87\ x\ 10^{-3}}{(6.5\ x\ 10^{-5})\ (1.065\ x\ 10^{-3})} = 51$

## IV. Le Chatelier's principle:

This principle helps to decide what course of reaction adopts and make a qualitative prediction about the effect of changes in conditions on equilibrium.

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It states that, "a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change." $\Rightarrow$ Systems shift from « Q » towards « K »
This principle is applicable for all physical and chemical equilibrium systems.

Factors that Affect Equilibrium :

- ✓ Concentration
- ✓ Temperature
- ✓ Pressure For gaseous systems only
- ✓ The presence of a catalyst

### *IV.1. Concentration Changes*

**•Add more reactant $\Rightarrow$ Shift to products**

**•Remove reactants $\Rightarrow$ Shift to reactants**

**• Add more product $\Rightarrow$ *Shift to reactants***

**• Remove products $\Rightarrow$ *Shift to products***

***Reaction Quotient*** **: The reaction quotient for an equilibrium system is the same as the equilibrium expression, but the concentrations are NOT at equilibrium!**

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

**$Q = [NO_2]^2 / [N_2O_4]$**

- Changes in concentration are best understood in terms of what would happen to "Q" if the concentrations were changed.

*Example :*

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

- ✓ **If $Q_c = K_c$ at equilibrium**
- ✓ **If $Q_c < K_c$ then there are too many reactants, the reaction will shift in the forward direction (the products)**
- ✓ **If $Q_c > K_c$ then there are too many products, the reaction will shift to the reactants.**

## *IV.2. Temperature Changes*

**Consider heat as a product in exothermic reactions : A + B = AB + Heat**

- **Add heat ⇒ Shift to reactants**
- **Remove heat ⇒ Shift to products**

**Consider heat as a reactant in endothermic reactions : A + B + Heat = AB**

- **Add heat ⇒ Shift to products**
- **Remove heat ⇒ Shift to reactants**

## *IV.3. Pressure Changes*

Only affects equilibrium systems with unequal moles of gaseous reactants and products.

- Increase Pressure : Stress of pressure is reduced by reducing the number of gas molecules in the container . . . . . .

$$\text{Eg : } N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

There are 4 molecules of reactants vs. 2 molecules of products.

⇒ Thus, the reaction shifts to the product ammonia.

- Decrease Pressure : Stress of decreased pressure is reduced by increasing the number of gas molecules in the container.

$$\text{Eg : } PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

There are two product gas molecules vs. one reactant gas molecule.

⇒ Thus, the reaction shifts to the products.

## *IV.4. The Effect of Catalyst :*

A catalyst is a substance that increases the rate of a reaction but is not consumed by it.

A catalyst has no effect on the equilibrium composition of a reaction mixture. A catalyst merely speeds up the reaction to achieve equilibrium.