

Chapter - 7 Equilibrium

Equilibrium

Equilibrium is actually a state, when forces from both the side become equal. According to chemistry: It is a point in a chemical reaction, when rate of forward reaction becomes equal to rate of backward reaction.

Equilibrium Mixture

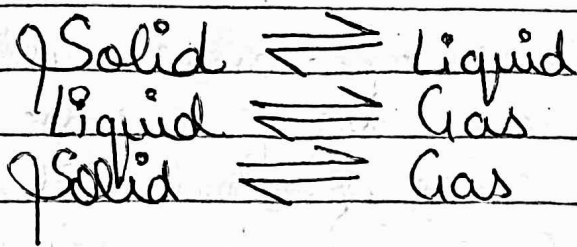
The mixture of reactants and products in the equilibrium state is called an equilibrium mixture.

There are two types of Equilibrium

1. Chemical Equilibrium
2. Ionic Equilibrium

Equilibrium in Physical Processes

It is achieved in all physical processes, when all state variables like pressure, temperature, etc. becomes constant. The most familiar examples are Phase Transformation Processes, e.g.



i) Solid - Liquid Equilibrium

The equilibrium is represented as
$$\text{H}_2\text{O}(\text{s}) \rightleftharpoons \text{H}_2\text{O}(\text{l})$$

Rate of melting of ice = Rate of freezing of water.

The system here is in dynamic equilibrium and following can be inferred:

- i) Both the opposing processes occur simultaneously
- ii) Both the processes occur at the same rate so that the amount of ice and water remains constant.

ii) Liquid - Vapour Equilibrium

When liquid water is allowed to evaporate in a closed vessel, the process of evaporation continues for some time and then seems to stop. This can be seen from the fact that water level falls for some time and then becomes constant.

As evaporation is carried out in a closed vessel thereafter, sometime condensation also starts and during this process a stage is reached when rate of evaporation

Becomes equal to rate of condensation.
Such a stage when rate of evaporation becomes equal to rate of condensation is called state of dynamic equilibrium.

Rate of evaporation = Rate of condensation

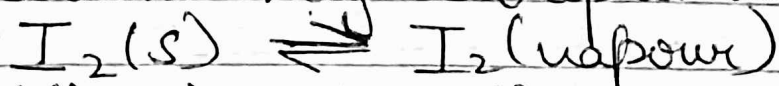


iii) Solid - Vapour equilibrium

This type of equilibrium is attained where solids sublime to vapour phase.

For example, when solid iodine is placed in a closed vessel, violet vapours start appearing in the vessel whose intensity increases with time and ultimately, it becomes constant.

The equilibrium may be represented as



Rate of sublimation of solid I_2 to form vapour = Rate of condensation of I_2 vapour to give solid I_2 .

Equilibrium involving Dissolution of Solids or Gases in liquids.

Solid in liquids

→ What is solution?

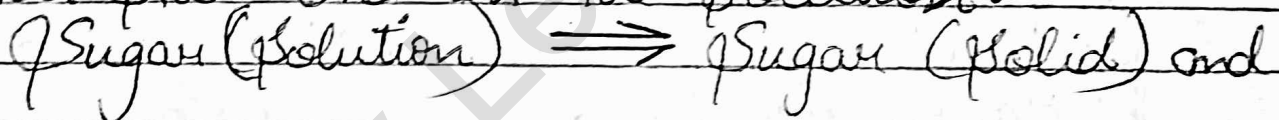
dissolves

When a limited amount of salt or sugar is dissolved in a given amount of water at room temperature.

→ What is Saturated Solution

At a given temperature state is reached when no more solute can be dissolved then the solution is called Saturated Solution.

In a saturated solution, a dynamic equilibrium exists between the solute molecules in the solid state and in the solution:



The rate of dissolution of sugar = rate of crystallisation of sugar.

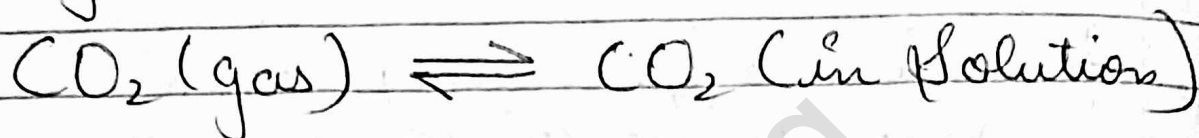
Here dissolution and precipitation takes place with the same speed. On adding a small amount of radioactive sugar to the saturated solution it will be found that the sugar present in the solution as well as in the solid state is radioactive.

Gases in liquids

This type of equilibrium can be seen by the following example:

Let us consider a sealed soda water

Water bottle in carbon dioxide (CO_2) gas is dissolved under high pressure. A state of equilibrium is attained between CO_2 present in the solution and vapours of the gas.



Henry's law

It states that the mass of a gas dissolved in a given mass of a solvent at any temp. is proportional to the pressure of the gas above the solvent.

Mathematically,

$$m \propto P$$
$$m = K_H P \quad (\text{where } K_H = \text{Henry's constant})$$

General Characteristics of Equilibria Involving Physical Processes.

- i) Equilibrium is possible only in a closed system at a given temperature.
- ii) Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
- iii) All measurable properties of the system remain constant.
- iv) When equilibrium is attained for a physical

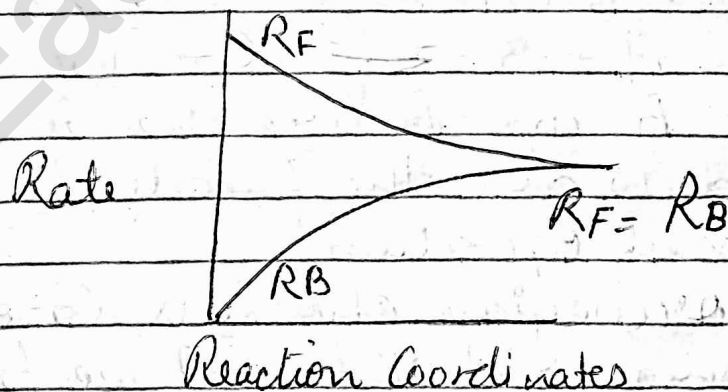
process, it is characterised by constant value of one of its Parameters at a given temperature.

✓) The value of equilibrium constant represents the extent to which the process proceeds before equilibrium is achieved.

Equilibrium in Chemical Processes - Dynamic Equilibrium

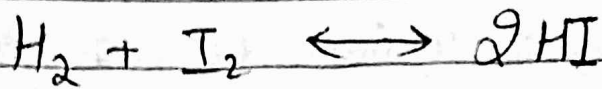
If a reversible reaction is carried out in a closed vessel, a stage is attained where the speed of the forward reaction equals the speed of the backward reaction. It corresponds to chemical equilibrium. At equilibrium,

Rate of forward reaction = Rate of backward reaction.



→ Reversible reaction

The reaction that can be achieved from both sides. We come across lot of examples, one is given below:



Characteristics of Chemical Equilibrium

1. Equilibrium can be attained from either side.
2. Equilibrium is dynamic in nature, i.e., at equilibrium reaction does not stop.
3. At equilibrium, there is no change in the concentration of various species.
4. The equilibrium state remains unaffected by the presence of catalyst. Catalyst helps to attain the equilibrium state rapidly.
5. The observable physical properties of the process become constant.

Laws of Chemical Equilibrium Constant

A general reversible reaction:



where A and B are the reactants, C and D are the products in the balanced equation.

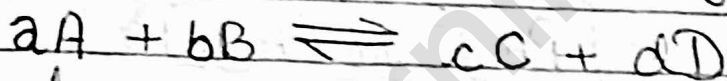
The Norwegian chemists Cato Maximilian Guldberg and Peter Waage proposed in 1864 that the concentrations in an equilibrium mixture are related by the following equilibrium equation.

$$K_c = \frac{[\text{C}][\text{D}]}{[\text{A}][\text{B}]}$$

where K_c is the equilibrium constant and the expression on the right side is called the equilibrium constant expression. The equilibrium equation is also known as the 'law of mass action.'

Equilibrium Constant

The equilibrium constant for a general reaction,

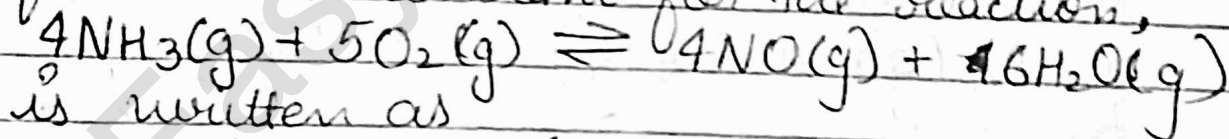


is expressed as,

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

where $[A]$, $[B]$, $[C]$ and $[D]$ are the equilibrium concentrations of the reactants and products.

Equilibrium constant for the reaction,



is written as

$$K_c = \frac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_2]^5}$$

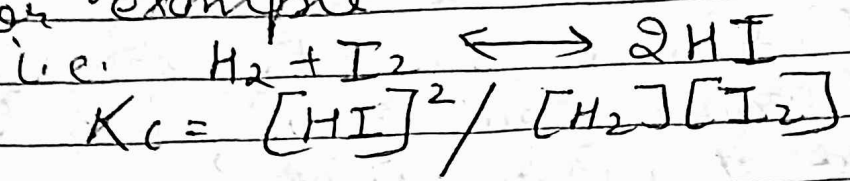
While writing expression for equilibrium constant, symbol for phases (s, l, g) are generally ignored.

At particular instant of time: The equilibrium constant is called as reaction quotient (Q).

$$\text{i.e. } Q = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

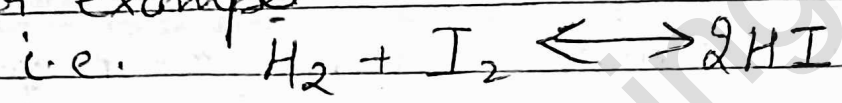
At equilibrium, $Q = K_c$

For example



In cases of gases, we can also express it in terms of their partial pressures:

For example

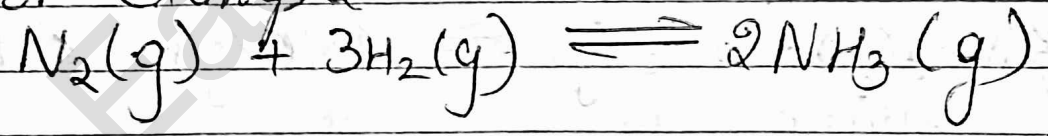


$$K_p = \frac{[P_H]^2}{[P_H][P_I]}$$

Homogeneous Equilibria

In a homogeneous system, all the reactants and products are in the same phase.

For example:

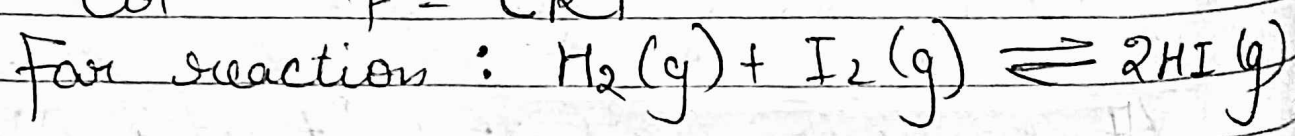


Equilibrium constant in Gaseous Systems

According to gas equation i.e. $PV = nRT$

Or $P = \frac{nRT}{V}$

Or $P = CRT$



We can write either

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

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

further, since

$$P_{HI} = [HI(g)] RT$$

$$P_{I_2} = [I_2(g)] RT$$

$$P_{H_2} = [H_2(g)] RT$$

Therefore,

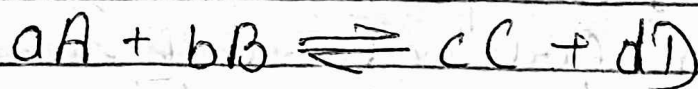
$$\begin{aligned} K_p &= \frac{(P_{HI})^2}{P_{H_2} (P_{I_2})} = \frac{[HI(g)]^2 [RT]^2}{[H_2(g)] RT \cdot [I_2(g)] RT} \\ &= \frac{[HI(g)]^2}{[H_2(g)] [I_2(g)]} = K_c \end{aligned}$$

In this example, $K_p = K_c$ i.e. both the equilibrium constant are equal.

Please ~~at~~ K_p Note

1. If change in gaseous moles = 0 then $K_p = K_c$
2. If change in gaseous moles is greater than 0, then $K_p = K_c RT$ or $K_p > K_c$
3. If change in gaseous moles is less than zero, then $K_p < K_c$.

For a general reaction,



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

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

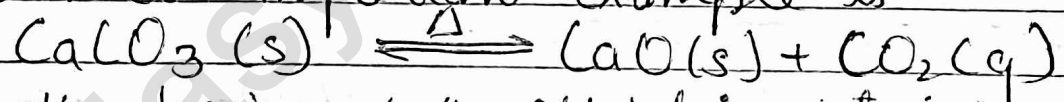
$$= \frac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{\Delta n} = K_c (RT)^{\Delta n}$$

Where $\Delta n = (\text{number of moles of gaseous products}) - (\text{number of moles of gaseous reactants})$

Heterogeneous Equilibria

Equilibrium in a system having more than one phase is called heterogeneous equilibrium.

The most important example is



On the basis of the stoichiometric eqⁿ we can write

$$K_c = \frac{[\text{CaO}(s)] [\text{CO}_2(g)]}{[\text{CaCO}_3(s)]}$$

Since $[\text{CaCO}_3(s)]$ and $[\text{CaO}(s)]$ are both constant, therefore modified equilibrium constant for the thermal decomposition of calcium carbonate will be..

$$K'_c = [\text{CO}_2(g)]$$

or

$$K_p = P_{\text{CO}_2}$$

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Experimentally, it has been found that at 1100 K, the pressure of CO_2 in equilibrium with $\text{CaCO}_3(\text{s})$ and $\text{CaO}(\text{s})$, is $2 \times 10^5 \text{ Pa}$. Therefore, equilibrium constant at 1100 K for the above reaction is:

$$K_p = P_{\text{CO}_2} = \frac{2 \times 10^5 \text{ Pa}}{10^5 \text{ Pa}} = 2.00$$

Applications of Equilibrium Constants

1. Predict the extent of a reaction on the basis of its magnitude.
2. Predict the direction of the reaction, and
3. Calculate equilibrium concentration.

→ Predicting the extent of a Reaction

The magnitude of K_c or K_p is directly proportional to the concentrations of products and inversely proportional to the concentrations of the reactants.

* If value of K is large, the reaction goes in forward reaction.

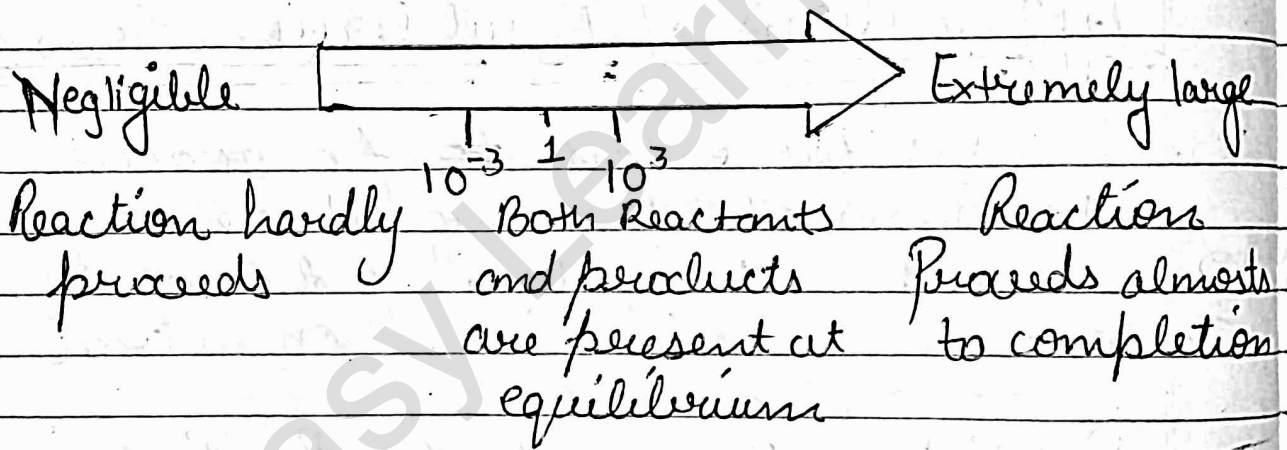
* If value of K is less, the reaction goes in backward reaction.

* If $K > 10^3$, the extent in this case is large and a reaction proceed almost to

completion

- * If value of K is less than 10^{-3} , then the reaction proceeds to smaller extent.
- * If value of K is between 10^{-3} to 10^3 , then there is a appreciable concentration of reactants and products.

These generalisations are illustrated as.



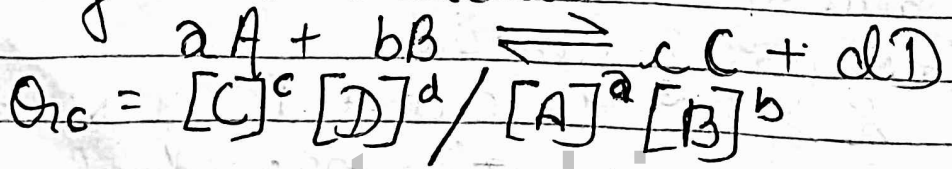
→ Predicting the Direction of the Reaction

It tell us whether the reaction is going towards products or reactants.

For this purpose, we calculate the reaction Quotient = Q_r .

Q_r (Q_c with molar concentrations and Q_p with Partial Pressures)

For general reaction



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- * If $Q_c > K_c$, the reaction will proceed in the direction of reactants
 - * If $Q_c < K_c$, the reaction will proceed in the direction of the products
 - * If $Q_c = K_c$, the reaction mixture is already at equilibrium.

Calculating Equilibrium Concentrations

The equilibrium constant can be calculated by the following steps:

1. Write the balanced chemical equation.
2. Under the balanced chemical 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.
3. Write the equilibrium constant expression or reaction and substitute the concentrations in it.
4. Calculate the equilibrium concentrations from the calculated value of K .
5. Check your results by substituting them into the equilibrium equation.

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Relationship b/w Equilibrium constant K , Reaction Quotient Q and Gibbs energy G .

- * ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
- * ΔG is positive, then the reaction is non-spontaneous.
- * ΔG is 0, reaction has achieved equilibrium.

A mathematical expression of thermodynamic view of equilibrium can be described by the equation.

$$\Delta G = \Delta G^\ominus + RT \ln Q$$

where, G^\ominus is standard Gibbs energy.

At equilibrium, when $\Delta G = 0$ and $Q = K_c$, the eqⁿ becomes,

$$\Delta G = \Delta G^\ominus + RT \ln K = 0$$

$$\Delta G^\ominus = -RT \ln K$$

$$\ln K = \frac{-\Delta G^\ominus}{RT}$$

Taking antilog of both sides, we get,

$$\boxed{K = e^{-\Delta G^\ominus/RT}}$$

- * If $\Delta G^\ominus < 0$, then $-\Delta G^\ominus/RT$ is positive and $e^{-\Delta G^\ominus/RT} > 1$, making $K > 1$, which implies a spontaneous reaction.
- * If $\Delta G^\ominus > 0$, then $-\Delta G^\ominus/RT$ is negative,

and $e^{-\Delta G^\ominus/RT} < 1$, i.e. $K < 1$, which implies a non-spontaneous reaction.

Factors affecting Equilibria

Le Chatelier's Principle

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.

Factors

1. Effect of Concentration Change

- * The concentration of the reactants or products added is relieved by the reaction which consumes the substance which is added.
- * The concentration of reactants or products removed is relieved by the reaction which is in the direction that replenishes the substance which is removed.
- * When the concentration of the reactant or product is changed, there is a change in the composition of the mixture in chemical equilibrium.

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2. Effect of Pressure Change

Change in Pressure happens due to the change in the volume. If there is a change in Pressure it can affect the gaseous reaction as the total number of gaseous reactants and products are now different. According to Le Chatelier's Principle, in heterogeneous chemical equilibrium, the change of pressure in both liquid and solid can be ignored because the volume is independent of Pressure.

3. Effect of Inert Gas Addition

When an Inert Gas like argon is added to a constant volume it ~~does~~ does not take part in the reaction so the equilibrium remains undisturbed. If the gas added is a reactant or product involved in the reaction then the reaction quotient will change.

4. Effect of Temperature Change

The effect of temperature on chemical equilibrium depends upon the sign of ΔH of the reaction and follows Le-Chatelier's Principle.

- * As temperature increases the equilibrium constant of an exothermic reaction decreases.
- * In an endothermic reaction the equilibrium constant increases with increase in Temp.

Along with equilibrium constant, the rate of reaction is also affected by the change in temperature. As per Le Chatelier's Principle, the equilibrium shifts towards the reactant side when the temperature increases in case of exothermic reactions, ~~the~~ for endothermic reactions the equilibrium shifts towards the product side with an increase in temperature.