



## PHYSICAL AND CHEMICAL EQUILIBRIUM

Equilibrium is that state of a process in which the concentration of reactants and products becomes constant until the conditions of temperature and pressure are unchanged. It can be a physical equilibrium or chemical equilibrium based on the type of process. It can be physical equilibrium or chemical equilibrium based on the type of process.

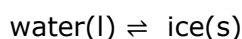
If the opposing process involves only physical change, the equilibrium is called physical equilibrium and if the process involves only chemical change, the equilibrium is called chemical equilibrium.

### Equilibrium in physical processes

When there is a change in the state of occurrence of matter, then a physical transformation is said to have occurred. The equilibrium concepts are also applicable to physical state transformations of matter.

#### (i) Solid-liquid equilibria

Here, the solid and the liquid forms of a substance co exist at characteristic temperature and pressure. At 1 atm and at the melting point of a substance, there is a solid-liquid equilibrium existing. For example, the solid-liquid equilibrium of water at 0°C,

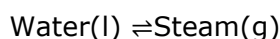


occurs at 1 atm pressure. Here, both the liquid and ice exist together. Also, at melting point of ice or freezing point of water, the rate of melting of ice equals with rate of freezing of water.

With change in pressure the temperature at which this equilibrium onsets changes.

#### (ii) Liquid-vapour equilibrium

Here the vapour and the liquid forms of a substance exist simultaneously at a characteristic temperature called as boiling point and at 1 atm pressure. For example at 100°C which is the boiling point of water, and 1 atm pressure,

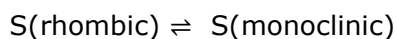


both liquid water and water vapour (steam) exist simultaneously, provided the vapour does not escape.

#### (iii) Solid-solid equilibrium

When a substance existing in a particular crystalline solid transforms to another crystalline form retaining its solid nature at a characteristic temperature called the transition temperature with both the solid forms coexisting, at 1 atm pressure then it is said to be in solid-solid equilibrium.

For example, solid sulphur exhibits equilibrium with rhombic to monoclinic forms at its transition temperature.



#### (iv) Solid-Gas equilibrium

Some solid substances on heating directly change into vapour state. Only those solids sublime which attain the vapour pressure of 1 atm at temperature lesser than their triple point



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### Dissolution of solid in liquid

After the arrival of saturation point the amount of undissolved solid solute and the concentration of solid solute in the solution remains constant. At equilibrium

Rate of dissociation = Rate of precipitation

### (v) Dissolution of gases in liquid

Dissolution of gases in water is always exothermic. As dissolution is spontaneous (takes place on its own)  $\Delta G = -ve$ , entropy decreases in the process of dissolution  $\Delta S = -ve$ . Therefore  $\Delta H$  has to be negative i.e. exothermic. The amount of gas dissolved is given by Henry's law

### Henry's law

The law states that the mass of gas dissolved in a given mass of solvent at a given temperature is directly proportional to the partial pressure of the gas above the solution  
 $m \propto P$  or  $m = kP$

Where  $k$  is constant or proportionality known as Henry's constant

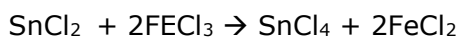
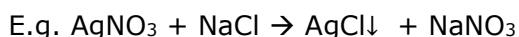
## Chemical equilibrium

Chemical reactions are broadly divided into two categories

(i) irreversible reaction (ii) Reversible reaction

### (i) Irreversible reaction

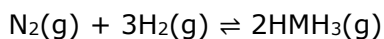
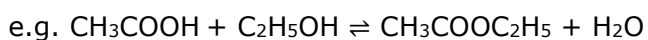
These are the reactions in which products do not react back to give the reactant. i.e. reaction can not be retraced at any point



Free energy change ( $\Delta G$ ) for irreversible reaction  $\neq 0$

### (ii) Reversible reaction

A reaction in which reactants are formed back by the reaction of products with each other at the given conditions of reaction. These reactions if carried out in closed vessel do not go to completion



Free energy change  $\Delta G$  for reversible reaction is zero,  $\Delta G = 0$

## State of equilibrium

Chemical equilibrium is that state of reaction at which the rate of forward reaction is equal to rate of backward reaction.

The concentration of reactant and product becomes constant. At the stage of equilibrium, the reaction seems to be static, but actually it is not so. Only forward and backward reactions take place at the same rate, so that composition of chemical system remains constant

### Characteristics of chemical equilibrium

(i) Equilibrium state is attained only when reaction is carried out in closed vessel (system)



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- (ii) At equilibrium, concentration of all reactants and products becomes constant
- (iii) Equilibrium is dynamic in nature i.e. reaction seems to be static because no change in concentration of reactants or product, but actually reaction takes place in both the directions with same speed
- (iv) Catalyst does not affect the equilibrium, it only fastens the chemical reaction to attain the state of equilibrium
- (v) Chemical equilibrium can be attained in either direction
- (vi) Change in conditions like temperature, pressure or concentration disturb the equilibrium and shift the equilibrium in one direction to attain new equilibrium
- (vii) at the stage of equilibrium free energy change is zero  $\Delta G = 0$

### Homogenous equilibrium

If the reactants and the products in a system are in same phase, the equilibrium is said to be homogeneous

For example  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightleftharpoons 2\text{HI}(\text{g})$  (represents a homogeneous equilibrium in gaseous phase)

$\text{CH}_3\text{COOH}(\text{l}) + \text{C}_2\text{H}_5\text{OH}(\text{l}) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\text{l}) + \text{H}_2\text{O}(\text{l})$  (represents a homogeneous equilibrium in liquid phase)

A phase is homogeneous ( same composition and property throughout) part of a system, separated from other phase ( or homogeneous parts) by bounding surface

- (i) Any number of gases constitute only one phase
- (ii) In liquid system, the number of phases = number of layers in the system. Completely miscible liquids such as ethanol and water constitute a single phase. On the other hand, benzene water has two layers and so two phase
- (ii) Each solid constitutes a separate phase, except in the case of solid solutions. [ A solid solution e.g. lead and silver, forms homogenous mixture]

### Heterogeneous equilibrium

If more than one phase is present in a chemical equilibrium, it is said to be heterogeneous equilibrium

For example  $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$

$3\text{Fe}(\text{s}) + 4\text{H}_2\text{O}(\text{g}) \rightleftharpoons \text{Fe}_3\text{O}_4(\text{s}) + 4\text{H}_2(\text{g})$

Represents a heterogeneous equilibrium involving solid phase and gaseous phase

## Law of chemical equilibrium and equilibrium constant

### Law of Mass action

Two Norwegian Chemists, Guldberg and Waage, studied experimentally a large number of equilibrium reactions. In 1864, they postulated a generalisation called the **Law of Mass action**. It states that:



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"the rate of a chemical reaction is proportional to the active masses of the reactants". By the term 'active mass', it is meant the molar concentration i.e., number of moles per litre.

According to this law, rate of reaction is directly proportional to the product of the molar concentration (active mass) of reactants with each concentration term raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation

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

According to law of active mass action

Rate of forward reaction  $r_f \propto [A]^a [B]^b$

Rate of backward reaction  $r_b \propto [C]^c [D]^d$

Active mass of a substance is simply number of moles dissolved per litre of the solution. Active mass of a gas or liquid is equal to its pressure or molar concentration, whereas active mass of solid is constant and is taken as unity

### Law of Mass Action based on the Molecular Collision theory

We assume that a chemical reaction occurs as the result of the collisions between the reacting molecules. Although some of these collisions are ineffective, the chemical change produced is proportional to the number of collisions actually taking place. Thus at a fixed temperature the rate of a reaction is determined by the number of collisions between the reactant molecules present in unit volume and hence its concentration, which is generally referred to as the active mass.

### Equilibrium constant and equilibrium law

Let us consider a general reaction

$aA + bB \rightleftharpoons cC + dD$

According to law of mass action

Rate of forward reaction  $\propto [A]^a [B]^b = k_f [A]^a [B]^b$

Rate of backward reaction  $\propto [C]^c [D]^d = k_b [C]^c [D]^d$

Here  $k_f$  and  $k_b$  are rate constant for forward reaction and rate constant for backward reaction respectively

At equilibrium

Rate of forward reaction = rate of backward reaction

$k_f [A]^a [B]^b = k_b [C]^c [D]^d$

$$K_{eq} = \frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

Since  $k_f$  and  $k_b$  are constants  $K_{eq}$  is also constant called as equilibrium constant

Above expression is called law of chemical equilibrium

If concentration is measured in moles/lit then  $K_{eq} = K_c$  and if concentration is measured in pressure then  $K_{eq} = K_p$

The distinction between  $K_{eq}$  and  $K_c$  is that the expression of  $K_{eq}$  involves all species (whether they are pure solids, pure liquids, gases, solvents or solutions) while the  $K_c$  expression



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involves only those species whose concentration is a variable ( like pure solids and pure liquids) and solvents

Relation between  $K_c$  and  $K_p$

$$K_p = \frac{P_C^c P_D^d}{P_A^a P_B^b} \text{ --- eq(1)}$$

From ideal gas equation  $PV = nRT$

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

Since Volume and temperature for all reactant and product is same

$$P_A = \frac{aRT}{V}, \quad P_B = \frac{bRT}{V}, \quad P_C = \frac{cRT}{V}, \quad P_D = \frac{dRT}{V}$$

Now  $a/v = \text{concentration} = [A]$  similarly

$b/v = [B]$ ,  $c/v = [C]$  and  $d/v = [D]$

Thus

$$P_A = [A]RT, \quad P_B = [B]RT, \quad P_C = [C]RT, \quad P_D = [D]RT,$$

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

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

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

Here  $\Delta n_g$  is change in number of gaseous molecules

Since, partial pressure are generally noted in atm and concentrations are measured in (moles/litre) , so value of R used in the given expression should be litre-atm per mole per Kelvin =  $R = 0.082$  litre-atm per mole per Kelvin

Case

- (i) If  $\Delta n_g = 0$  then  $K_p = K_c$
- (ii) If  $\Delta n_g < 0$  then  $K_p < K_c$
- (iii) If  $\Delta n_g > 0$  then  $K_p > K_c$

Equilibrium constant in terms of mole fraction ( $K_x$ )

$$K_x = \frac{X_C^c X_D^d}{X_A^a X_B^b}$$

Here  $X_A, X_B, X_C, X_D$  are mole fraction of A, B, C, D respectively,  $K_x$  depends upon pressure temperature and volume of the chemical system

$$K_p = K_x (RT)^{\Delta n_g}$$

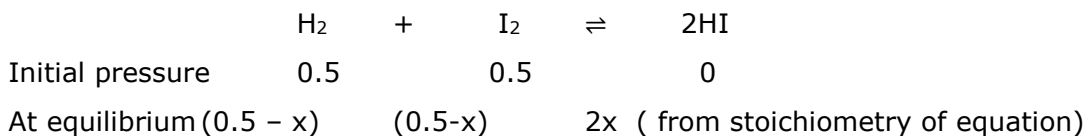


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### Solved numerical

Q) The  $K_P$  value for the reaction  $H_2 + I_2 \rightleftharpoons 2HI$  at  $460^\circ C$  is 49. If the initial pressure of  $H_2$  and  $I_2$  is 0.5atm respectively, determine the partial pressure of each gas at equilibrium

Solution



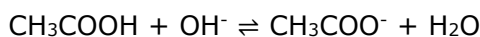
$$K_P = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$$
$$49 = \frac{(2x)^2}{(0.5 - x)^2}$$
$$X = 0.39 \text{ atm}$$

$\therefore$  Pressure of  $H_2$  and  $I_2$  at equilibrium =  $(0.5 - x) = 0.11 \text{ atm}$

Q)  $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$ ;  $K_1 = 1.8 \times 10^{-5}$

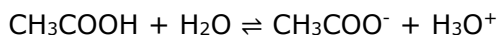
$2H_2O \rightleftharpoons H_3O^+ + OH^-$ ,  $K_2 = 1 \times 10^{-14}$

Calculate equilibrium constant for reaction



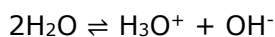
Solution

Equilibrium constant for the reaction



$$K_1 = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$$

Equilibrium constant for the reaction



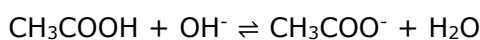
$$K_2 = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Taking the ratio of  $K_1$  and  $K_2$

$$\frac{K_1}{K_2} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]} \times \frac{[H_2O]^2}{[H_3O^+][OH^-]}$$

$$\frac{K_1}{K_2} = \frac{[CH_3COO^-][H_2O]}{[CH_3COOH][OH^-]}$$

Above ratio is the equilibrium constant of the reaction

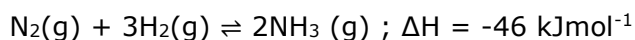


$$\therefore K = \frac{K_1}{K_2} = \frac{1.8 \times 10^{-5}}{1 \times 10^{-14}} = 1.8 \times 10^9$$



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Q) For the reaction



Calculate the value of  $K_p$ . Given  $K_c = 0.5 \text{ lit}^2\text{mol}^{-2}$  at  $400^\circ\text{C}$

Solution:

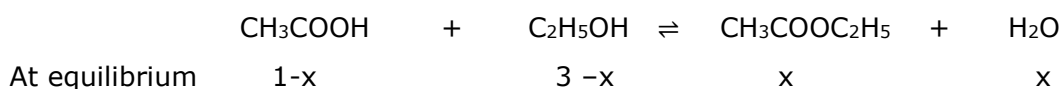
$$K_p = K_c (RT)^{\Delta n}$$

$$\Delta n = 2-4=-2$$

$$K_p = 0.5(0.082 \times 673)^{-2} = 1.641 \times 10^{-4}$$

Q) Determine the amount of ester present under equilibrium when 3 mol of ethyl alcohol react with 1mole of acetic acid, when equilibrium constant of the reaction is 4

Solution



$$K_c = \frac{x \times x}{(1-x)(3-x)}$$

$$4 = \frac{x \times x}{(1-x)(3-x)} = \frac{x^2}{3-4x+x^2}$$

$$3x^2 - 16x + 12 = 0$$

$$X = 0.903 \text{ or } 4.73 \text{ ( inadmissible)}$$

$\therefore$  Amount of ester at equilibrium = 0.903 mole

Predicting the direction of attainment of equilibrium

The reaction quotient is defined as the ratio of concentration of the reaction species at any point of time other than the equilibrium stage.

It is represented by Q. Thus, inserting the starting concentrations of reactant and product in the equilibrium constant expression gives

$$Q = \frac{[C_0]^c [D_0]^d}{[A_0]^a [B_0]^b}$$

Here  $A_0$ ,  $B_0$ ,  $C_0$  and  $D_0$  are the concentration before equilibrium is reached

To determine the direction in which the net reaction will proceed to achieve equilibrium, we compare the values of Q and  $K_c$ . The three possible cases are as follows

(a)  $Q > K_c$ ; for such a system, products must be converted to reactants to reach equilibrium. The system proceeds from right to left to reach equilibrium

(b)  $Q = K_c$ ; The initial concentrations are equilibrium concentrations. So, the system is already at equilibrium

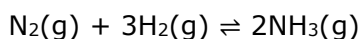


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(c)  $Q < K_c$ ; For such a system., reactants must be converted to products to reach equilibrium. The system proceeds from left to right to attain equilibrium

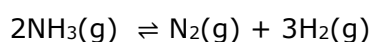
### Mode of writing a chemical equation

The values of  $K_p$  and  $K_c$  also depends on the method of representing a chemical equation for example



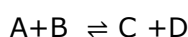
$$K_c = \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3}$$

i) When the equilibrium reaction is reversed



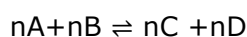
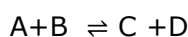
$$K'_c = \frac{[\text{N}_2][\text{H}_2]^3}{[\text{NH}_3]^2} = \frac{1}{K_c}$$

ii) When the equation for a reaction is divided by a factor 'n' the value of new equilibrium constant becomes equal to  $n^{\text{th}}$  root of the previous equilibrium constant  $K'$



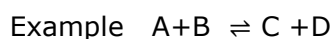
$$\frac{1}{n}\text{A} + \frac{1}{n}\text{B} \rightleftharpoons \frac{1}{n}\text{C} + \frac{1}{n}\text{D}$$
$$K' = \sqrt[n]{K_c}$$

iii) If the equation for reaction is multiplied by a factor 'n' then new equilibrium constant  $K'$  becomes  $K^n$

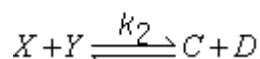
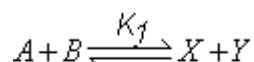


$$K' = K_c^n$$

iv) If the equation is written in number of steps, then its equilibrium constant will be the multiple of the equilibrium constant of each step



If above reaction takes placed in two steps



$$\text{Then } K = K_1 \times K_2$$

### Characteristics of equilibrium constant

(i) The value of equilibrium constant is independent of initial concentration or volume of the reactants

(ii) Its value is not influenced by the presence of catalyst

(iii) Equilibrium constant is not affected by pressure or nature of reactant





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(iv) The value of the equilibrium constant of a particular reaction is always constant depending upon the temperature of the reaction and is independent of the direction from which the equilibrium is attained

(v) Equilibrium constant is not changed by the inert material added to the system

(v) The value of the equilibrium constant depends on the stoichiometry of reactants and products at the equilibrium

### Effect of temperature on equilibrium constant

The value of equilibrium constant for a particular reaction is constant at a given temperature.

In case of endothermic reversible reaction, equilibrium constant, increases with the increase in temperature where as in case of exothermic reaction, equilibrium constant decreases with the increase in temperature. Variation of equilibrium constant with temperature is explained with the help of following equation

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R} \left[ \frac{T_2 - T_1}{T_2 T_1} \right]$$

Where  $K_2$  and  $K_1$  are equilibrium constant at temperature  $T_2$  and  $T_1$  respectively

$\Delta H^\circ$  is the enthalpy of reaction and  $R$  is the gas constant

If  $\Delta H^\circ = 0$ , no heat is absorbed or evolved in the reaction

$$\log \frac{K_2}{K_1} = 0 \text{ or } K_2 = K_1$$

i.e. equilibrium constant does not change with temperature

If  $T_2 > T_1$  and  $\Delta H^\circ$  is positive ( endothermic reaction) then  $K_2 > K_1$

But if  $T_2 > T_1$  and  $\Delta H^\circ$  is negative ( exothermic reaction) then  $K_2 < K_1$

### Significance of equilibrium constant

(1) Magnitude of equilibrium constant gives an idea about the extent of reaction

- Greater value of equilibrium constant ( $>10^3$ ) implies the greater concentration of products in comparison to that of reactants. It means reaction is favourable in forward direction i.e. towards product side

- Smaller value of equilibrium constant ( $<10^{-3}$ ) implies the greater concentration of reactants as compared to that of products. It shows that reaction is favourable in backward direction i.e. towards reactant side
- Intermediate value of equilibrium constant ( $10^{-3}$  to  $10^3$ ) implies the comparable concentration of reactant

(2) Value of equilibrium constant also explains the thermodynamic stability of products.

Greater the value of  $K$ , greater will be the stability of products and instability of reactants.

(3) Equilibrium concentration of reactants and products can be calculated with the help of equilibrium constant



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### Units of equilibrium constant

Concentration of a substance is measured in terms of moles/litre, therefore unit of

$$K_c \text{ is } (\text{mol L}^{-1})^{\Delta n}$$

Similarly partial pressure is measured in terms of atmosphere, hence unit of  $K_p$  is  $(\text{atm})^{\Delta n}$ , where  $\Delta n$  is the difference in number of moles of products and reactant

If  $\Delta n = 0$ , both  $K_c$  and  $K_p$  has no units

If  $\Delta n > 0$ , unit of  $K_c = (\text{mol L}^{-1})^{\Delta n}$ , unit of  $K_p = (\text{atm})^{\Delta n}$

If  $\Delta n < 0$ , unit of  $K_c = (\text{L mol}^{-1})^{\Delta n}$ , unit of  $K_p = (\text{atm}^{-1})^{\Delta n}$

### Equilibrium constant and standard free energy change

We know that free energy change ( $\Delta G$ ) is related to  $\Delta G^\circ$  as follows

$$\Delta G = \Delta G^\circ + 2.303RT \log Q$$

But at equilibrium  $Q = K$  and  $\Delta G = 0$

$$\therefore \Delta G^\circ = -2.303RT \log K$$

If  $K > 1$ , then  $\Delta G^\circ$  is negative. reaction in forward direction is spontaneous

If  $K < 1$ , then  $\Delta G^\circ$  is positive, reaction is spontaneous in backward direction

## Le-Chatelier's principle

A statement of Le Chatelier's Principle

- If a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to counteract the change.

### Using Le Chatelier's Principle with a change of concentration

Suppose we have an equilibrium established between four substances A, B, C and D.



What would happen if concentration of A is increased?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the concentration of A decreases again - by reacting it with B and turning it into C + D. The position of equilibrium moves to the right.



*The position of equilibrium moves to the right if we increase concentration of A*

This is a useful way of converting the maximum possible amount of B into C and D. You might use it if, for example, B was a relatively expensive material whereas A was cheap and plentiful.

What would happen if we changed the conditions by decreasing the concentration of A?



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According to Le Chatelier, the position of equilibrium will move so that the concentration of A increases again. That means that more C and D will react to replace the A that has been removed. The position of equilibrium moves to the left.

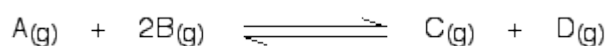


*The position of equilibrium moves to the left if we decrease the concentration of A*

This is essentially what happens if we remove one of the products of the reaction as soon as it is formed. If, for example, you removed C as soon as it was formed, the position of equilibrium would move to the right to replace it. If you kept on removing it, the equilibrium position would keep on moving rightwards - turning this into a one-way reaction.

Using Le Chatelier's Principle with a change of pressure

This only applies to reactions involving gases:



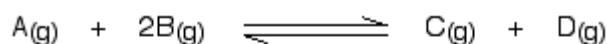
What would happen if we changed the conditions by increasing the pressure?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the pressure is reduced again.

Pressure is caused by gas molecules hitting the sides of their container. The more molecules you have in the container, the higher the pressure will be. The system can reduce the pressure by reacting in such a way as to produce fewer molecules.

In this case, there are 3 molecules on the left-hand side of the equation, but only 2 on the right. By forming more C and D, the system causes the pressure to reduce.

Increasing the pressure on a gas reaction shifts the position of equilibrium towards the side with fewer molecules.



*The position of equilibrium moves to the right if we increase the pressure on the reaction*

What would happen if you changed the conditions by decreasing the pressure?

The equilibrium will move in such a way that the pressure increases again. It can do that by producing more molecules. In this case, the position of equilibrium will move towards the left-hand side of the reaction.



*The position of equilibrium moves to the left if we decrease the pressure on the reaction*



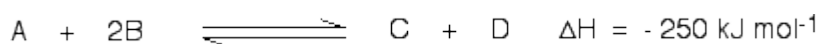
## PHYSICAL AND CHEMICAL EQUILIBRIUM

What happens if there are the same number of molecules on both sides of the equilibrium reaction?

In this case, increasing the pressure has no effect whatsoever on the position of the equilibrium. Because you have the same numbers of molecules on both sides, the equilibrium can't move in any way that will reduce the pressure again.

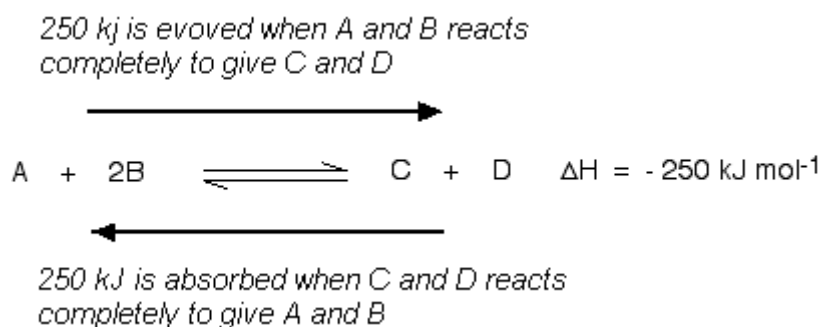
Using Le Chatelier's Principle with a change of temperature

For this, you need to know whether heat is given out or absorbed during the reaction. Assume that our forward reaction is exothermic (heat is evolved):



This shows that 250 kJ is evolved (hence the negative sign) when 1 mole of A reacts completely with 2 moles of B. For reversible reactions, the value is always given as if the reaction was one-way in the forward direction.

The back reaction (the conversion of C and D into A and B) would be endothermic by exactly the same amount.

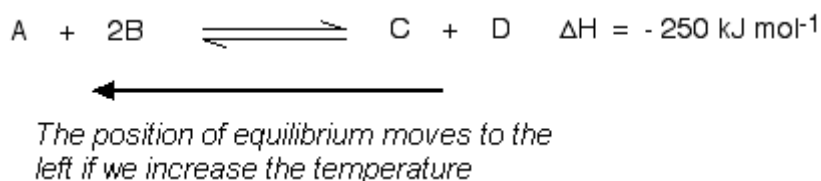


What would happen if you changed the conditions by increasing the temperature?

According to Le Chatelier, the position of equilibrium will move in such a way as to counteract the change. That means that the position of equilibrium will move so that the temperature is reduced again.

Suppose the system is in equilibrium at 300°C, and you increase the temperature to 500°C. How can the reaction counteract the change you have made? How can it cool itself down again?

To cool down, it needs to absorb the extra heat that you have just put in. In the case we are looking at, the *back reaction* absorbs heat. The position of equilibrium therefore moves to the left. The new equilibrium mixture contains more A and B, and less C and D.



If you were aiming to make as much C and D as possible, increasing the temperature on a reversible reaction where the forward reaction is exothermic isn't a good idea!



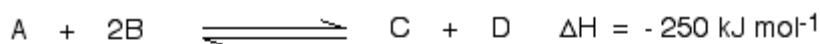
## PHYSICAL AND CHEMICAL EQUILIBRIUM

What would happen if you changed the conditions by decreasing the temperature?

The equilibrium will move in such a way that the temperature increases again.

Suppose the system is in equilibrium at 500°C and you reduce the temperature to 400°C. The reaction will tend to heat itself up again to return to the original temperature. It can do that by favouring the exothermic reaction.

The position of equilibrium will move to the right. More A and B are converted into C and D at the lower temperature.



*The position of equilibrium moves to the right if we decrease the temperature?*

### Le Chatelier's Principle and catalysts

Catalysts have sneaked onto this page under false pretences, because *adding a catalyst makes absolutely no difference to the position of equilibrium*, and Le Chatelier's Principle doesn't apply to them.

This is because a catalyst speeds up the forward and back reaction to the same extent.

Because adding a catalyst doesn't affect the relative rates of the two reactions, it can't affect the position of equilibrium. So why use a catalyst?

For a dynamic equilibrium to be set up, the rates of the forward reaction and the back reaction have to become equal. This doesn't happen instantly. For a very slow reaction, it could take years! A catalyst speeds up the rate at which a reaction reaches dynamic equilibrium.

### Ionic equilibrium

When an ionic compound is dissolved in water or melted, it gets split into its ions. The process is known as ionization or dissociation.

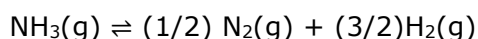
Degree of dissociation

Degree of dissociation of a substance is the fraction of the total number of molecules dissociated into simpler molecules at a particular temperature

$$\text{Degree of dissociation}(\alpha) = \frac{\text{Numer of moles dissociated}}{\text{Total number of moles taken}}$$

For example

Let the equilibrium reaction is the dissociation equilibrium of  $\text{NH}_3$  into  $\text{N}_2$  and  $\text{H}_2$

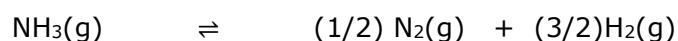


Let the initial moles of  $\text{NH}_3$  taken be 1 and the moles of  $\text{NH}_3$  dissociated at equilibrium be 'x'

Then



## PHYSICAL AND CHEMICAL EQUILIBRIUM



Moles initially	1	0	0
Moles at equilibrium	1-x	x/2	3x/2

Here, x represents the degree of dissociation ( $\alpha$ ). If we would have stated with 'a' moles of  $\text{NH}_3$  and moles of  $\text{NH}_3$  dissociated is taken as 'x', then degree of dissociation of  $\text{NH}_3$  will not be 'x' but would be  $x/a$

The degree of dissociation is defined only for those equilibrium in which dissociation takes place. For example the degree of dissociation cannot be defined for reverse reaction in which  $\text{N}_2$  and  $\text{H}_2$  combine to give  $\text{NH}_3$ . Degree of dissociation is proportional to temperature

### Solved numerical

Q) A sample of HI was found to 22% dissociated when equilibrium was reached. What will be the degree of dissociation if hydrogen is added in the proportion of 1 mole for every mole of HI originally present, the temperature and volume of the system is kept constant

Solution

The degree of dissociation ( $\alpha$ ) is the fraction of 1 mole of HI that has dissociated under the given conditions. If the % dissociation of HI is 22, the degree of dissociation is 0.22

	2HI	$\rightleftharpoons$	H <sub>2</sub>	+	I <sub>2</sub>
At equilibrium (1- $\alpha$ )			$\alpha/2$		$\alpha/2$
	1-0.22 = 0.78		0.11		0.11

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{0.11 \times 0.11}{(0.78)^2} = 0.0199$$

Now adding 1 mole of hydrogen at equilibrium. Let x be the degree of dissociation thus

	2HI	$\rightleftharpoons$	H <sub>2</sub>	+	I <sub>2</sub>
At equilibrium (1- x)			$[(x/2) + 1]$		$x/2$

$$K_c = \frac{[\text{H}_2][\text{I}_2]}{[\text{HI}]^2} = \frac{\left(\frac{x}{2} + 1\right)\left(\frac{x}{2}\right)}{(1-x)^2} = 0.0199$$

X=0.037 or -2.4 (not admissible)

Degree of dissociation = 0.037

% of dissociation = 3.7

Note :Introduction of  $\text{H}_2$  suppresses the dissociation of HI

Q) A vessel at 1000K contains carbon dioxide at a pressure of 0.5 atm. Some of the carbon dioxide is converted to carbon monoxide on addition of graphite. Calculate the value of K, if the total pressure is 0.8atm

Solution



Let the decrease in pressure of  $\text{CO}_2$  after reaction be p atm



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Then, increase in pressure due to CO after reaction =  $2p$  atm

Final pressure =  $(0.5 - p) + 2p = 0.8$  atm

Therefore  $p = 0.3$  atm

Thus after reaction,  $P_{\text{CO}_2} = 0.5 - 0.3 = 0.2$  atm

$P_{\text{CO}} = 2p = 2 \times 0.3 = 0.6$  atm

Equilibrium constant  $K$

$$K = \frac{(0.6)^2}{(0.2)} = 1.8 \text{ atm}$$

Q) The equilibrium constant  $K_p$  for the reaction  $\text{N}_2\text{O}_4(\text{g}) \rightleftharpoons 2\text{NO}_2(\text{g})$  at  $467^\circ\text{C}$  is found to be 636 mm Hg. If the pressure of the gas mixture is 182 mm, calculate the percentage dissociation of  $\text{N}_2\text{O}_4$ . At what pressure will it be half dissociated

Solution

Let dissociation of 1 mole of  $\text{N}_2\text{O}_4$  be  $\alpha$  then

$\text{NO}_2$  formed at equilibrium will be =  $2\alpha$

$\text{N}_2\text{O}_4$  at equilibrium will be =  $(1 - \alpha)$

Total moles at equilibrium =  $(1 - \alpha) + 2\alpha = 1 + \alpha$

If  $P_T$  is total pressure at equilibrium then

Pressure of  $\text{N}_2\text{O}_4$  at equilibrium

$$\left(\frac{1 - \alpha}{1 + \alpha}\right) \times P_T$$

Pressure of  $\text{NO}_2$  at equilibrium

$$\left(\frac{2\alpha}{1 + \alpha}\right) \times P_T$$

Now

$$K_p = \frac{(P_{\text{NO}_2})^2}{(P_{\text{N}_2\text{O}_4})} = \frac{\left(\frac{2\alpha}{1 + \alpha} \times P_T\right)^2}{\frac{1 - \alpha}{1 + \alpha} \times P_T} = \frac{4\alpha^2 P_T}{1 - \alpha^2}$$

Thus

$$636 = \frac{4\alpha^2 \times 182}{1 - \alpha^2}$$

$$\alpha = 0.6829$$

$$\% \text{ dissociation of } \text{N}_2\text{O}_4 = 68.29$$

When the gas is half dissociated  $\alpha = 0.5$ , Let the total pressure be  $P'$

$$636 = \frac{4 \times 0.5^2 \times 182}{1 - 0.5^2} \times P'$$

$$P' = 477 \text{ mm}$$



## PHYSICAL AND CHEMICAL EQUILIBRIUM

### Electrolyte and Non-electrolyte

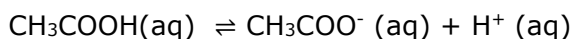
A compound whose aqueous solution or melt conducts electricity is known as electrolyte, whereas non-electrolyte is the compound whose neither aqueous nor melt conducts electricity

### Strong and weak electrolytes

Electrolytes which dissociate almost completely into ions in aqueous solution are known as strong electrolytes. E.g. NaCl, HCl, NaOH, H<sub>2</sub>SO<sub>4</sub> etc. They are good conductors of electricity

Whereas those electrolytes which dissociate only partially into ions in aqueous solution are known as weak electrolytes. E.g. CH<sub>3</sub>COOH, NH<sub>4</sub>OH etc.

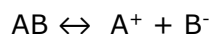
They have conductivity smaller than that of strong electrolytes. Their value of degree of dissociation is much smaller than one i.e.  $\alpha < 1$ . An equilibrium is setup in case of partially ionized weak electrolytes between ions and unionized electrolyte



### Ostwald's Dilution law

The molecules of an electrolyte in solution are constantly splitting up into ions and the ions are constantly reuniting to form unionized molecules. Therefore, a dynamic equilibrium exists between ions and unionized molecules of the electrolyte in solution. It was pointed out by **Ostwald** that like chemical equilibrium, law of mass action can be applied to such systems also.

Consider a binary electrolyte AB which dissociates into A<sup>+</sup> and B<sup>-</sup> ions and the equilibrium state is represented by the equation:



Initially t = 0      C      0      0

At equilibrium    C(1- $\alpha$ )    C $\alpha$     C $\alpha$

So, **dissociation constant** may be given as

$$K_{eq} = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$

$$K_{eq} = \frac{C\alpha^2}{(1-\alpha)} \quad \text{--- --} \text{eq}(i)$$





## PHYSICAL AND CHEMICAL EQUILIBRIUM

For very weak electrolytes,

$$\alpha \ll 1, (1 - \alpha) = 1$$

$$\therefore K_{eq} = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_{eq}}{C}} \quad \text{--- eq(ii)}$$

Concentration of any ion =  $C\alpha = \sqrt{CK}$  .

From equation (ii) it is clear that degree of ionization increases on dilution.

If 1 mole is present in 'V' litres of solution,  $C = 1/V$

$$K_{eq} = \frac{\alpha^2}{V(1 - \alpha)}$$

Is another expression for Ostwald's dilution law

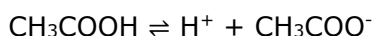
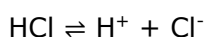
$$\alpha = \sqrt{K_{eq} \times V}$$

Thus, **degree of dissociation** of a weak electrolyte is proportional to the square root of dilution.

Ostwald's dilution law is applicable to weak electrolytes, not strong electrolytes.

The Arrhenius concept

An acid is a substance which in aqueous solution gives hydrogen ion as the only cation ( This definition excludes acid salt.



A base is a substance which in aqueous solution gives hydroxyl ( $\text{OH}^-$ ) ions as the only anions



Neutralization is nothing but combination of  $\text{H}^+$  ions of the acid and  $\text{OH}^-$  ions of the base to form unionized water

### Limitations of Arrhenius concept

- (i) It does not explain the acidic character of certain compounds like  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{AlCl}_3$  etc and basic character of some compounds like  $\text{Na}_2\text{CO}_3$ ,  $\text{NH}_3$  etc. which does not give  $\text{H}^+$  and  $\text{OH}^-$  ions respectively
- (ii) It does not explain the behavior of acids and base in absence of water
- (iii) It does not explain the nature of  $\text{H}^+$  and  $\text{OH}^-$  ions in water



## PHYSICAL AND CHEMICAL EQUILIBRIUM

### Bronsted Lowry Concept of Acid and Base

This concept defines the acids and base in terms of proton donor and proton acceptor. An acid is defined as a substance which can give / donate a proton ( $H^+$ ) where as base is a substance which can accept a proton ( $H^+$ ). This called a protonic theory of acid and base.

In case of acid base reaction, the reverse reaction is also acid base reaction. Every acid forms a conjugate base by loss of proton while every base forms a conjugate acid by the gain of proton ( $H^+$ ). A conjugate pair of acid and base differ by a proton only For example

Donar Acid		Acceptor base		conjugate acid		conjugate base
HCl	+	H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	+	Cl <sup>-</sup>
CH <sub>3</sub> COOH	+	H <sub>2</sub> O	$\rightleftharpoons$	H <sub>3</sub> O <sup>+</sup>	+	CH <sub>3</sub> COO <sup>-</sup>
H <sub>2</sub> O	+	NH <sub>3</sub>	$\rightleftharpoons$	NH <sub>4</sub> <sup>+</sup>	+	NO <sub>3</sub> <sup>-</sup>
H <sub>2</sub> O	+	CO <sub>3</sub> <sup>-</sup>	$\rightleftharpoons$	HCO <sub>3</sub> <sup>-</sup>	+	OH <sup>-</sup>

- A strong acid gives a weak conjugate base and vice versa
- If two acids ( with respect to water ) are mixed together the weak acid will act as base with respect to strong acid
- Acid base reaction always proceed in the direction from the stronger to weaker acid base combination
- For example  
 $H_2SO_4 + NH_3 \rightarrow NH_4^+ + HSO_4^-$  ( both the products are weak)

### Lewis concept of acid and Base

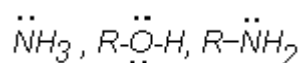
According to this concept, an acid is a substance which can accept a pair of electrons, whereas a base is a substance which can donate a pair of electrons. i.e. acids are electron acceptors and bases are electron donors

### Chemical species which can acts as Lewis acid

- Electron deficient neutral compounds i.e. molecules in which central atoms has incomplete octatae eg. BF<sub>3</sub>, FeCl<sub>3</sub>, AlCl<sub>3</sub> etc
- All simple cation e.g. H<sup>+</sup>, Mg<sup>2+</sup>, Ag<sup>+</sup>, Fe<sup>3+</sup> etc
- Molecules having multiple bond between atoms of different electro-negativities e.g. SO<sub>3</sub>, CO<sub>2</sub> etc
- In coordination complexes, metal atoms acts as Lewis acid
- Molecules having a central atom with empty d-orbital's, e.g SiF<sub>4</sub>, SnCl<sub>4</sub>

### Chemical species which can act as Lewis base

(i) Electron rich neutral compound i.e. molecules with least one lone pair of electrons eg.



ii) All negatively charged ions e.g. CN<sup>-</sup>, OH<sup>-</sup>, Cl<sup>-</sup> etc



## PHYSICAL AND CHEMICAL EQUILIBRIUM

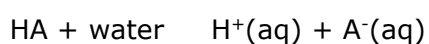
iii) In coordinate compounds, the ligands acts as Lewis base. For CO acts as Lewis base in  $\text{Ni}(\text{CO})_4$

Summary of concept to acid and base

Concept	Acid	Base
Arrhenius	$\text{H}^+$ donor	$\text{OH}^-$ donor
Bronsted-Lowry	$\text{H}^+$ donor	$\text{H}^+$ acceptor
Lewis	$e^-$ pair acceptor	$e^-$ pair donor

Strength of acids and bases

Strength of acid in terms of  $\text{H}^+$  produced i.e. greater the number of  $\text{H}^+$  produced in aqueous solution, stronger is the acid. Whereas strength of base is measured in terms of  $\text{OH}^-$  produced i.e. greater the number of  $\text{OH}^-$  produced in aqueous solution, stronger is the base



Acid

$$k_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \quad \text{or} \quad K_a \propto [\text{H}^+]$$

Where  $K_a$  is the dissociation constant of acid HA.

Similarly for base  $K_b \propto [\text{OH}^-]$  where  $K_b$  is the dissociation constant of a base BOH

It means greater the value of dissociation constant ( $K_a$  or  $K_b$ ), greater is the amount of  $\text{H}^+$  aqueous or  $\text{OH}^-$  produced and stronger is the acid or base respectively.

### Relative strength of acid and bases

Degree of dissociation is considered as measure of strength of an acid, for equimolar acids

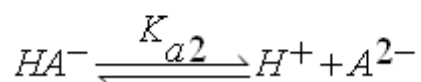
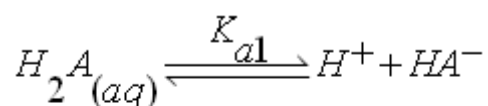
$$\frac{\text{Strength of } \text{HA}_1}{\text{Strength of } \text{HA}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

Similarly for equimolar weak base

$$\frac{\text{Strength of } \text{BOH}_1}{\text{Strength of } \text{BOH}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

### Polybasic acids and polyacidic base

Acids which have more than one ionisable proton per molecule of the acid are known as polybasic or polyprotic acids. For example oxalic acid  $(\text{COOH})_2$ , Sulphuric acid  $\text{H}_2\text{SO}_4$ , phosphoric acid  $\text{H}_3\text{PO}_4$ , carbonic acid  $(\text{H}_2\text{CO}_3)$  are considered as dibasic acid



The ionization constant  $K_{a1}$  and  $K_{a2}$  are given as



## PHYSICAL AND CHEMICAL EQUILIBRIUM

$$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]}, K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]}$$

It is observed that  $K_{a1} > K_{a2} > K_{a3}$

The reason behind the decrease in the dissociation constant of successive stages is that in the first dissociation, a neutral molecule give proton ( $H^+$ ), while in the second stage of dissociation, the proton is coming from the negatively charged molecule and in the third step of dissociation, a doubly negative charged molecule is giving a proton which in turn is more difficult than first two

Similarly, polyacidic bases also ionize in steps For any polyacidic base

$$K_{b1} > K_{b2} > K_{b3}$$

### Solved Numerical

Q) Ionization constant of equimolar solution of HF, HCOOH and HCN at 298K are  $6.8 \times 10^{-4}$ ,  $1.8 \times 10^{-4}$  and  $4.8 \times 10^{-9}$  respectively. What is the order of their acidic strength?

Solution

We know that acidic strength  $\propto \sqrt{K_a}$

Since the ionization constant are in the order

HF > HCOOH > HCN, order of acidic strength is HF > HCOOH > HCN

Q) Compare the strength of HCN ( $K_a = 4.9 \times 10^{-10}$ ) with 0.01M aqueous solution of formic acid which it is 14.5% dissociated

Solution

Applying

$$\frac{\text{strength of formic acid}}{\text{strength of HCN}} = \sqrt{\frac{K_a(\text{formic acid})}{K_a(\text{HCN})}}$$

Degree of dissociation = 14.5% = 0.145

From formula  $K_a(\text{HCOOH}) = C\alpha^2 = 0.01 \times (0.145)^2 = 2.1 \times 10^{-4}$

Thus

$$\frac{\text{strength of formic acid}}{\text{strength of HCN}} = \sqrt{\frac{2.1 \times 10^{-4}}{4.9 \times 10^{-10}}} = 6.5 \times 10^2$$

i.e Formic acid is  $6.5 \times 10^2$  times stronger than HCN

### Effect of solvent on acid strength

Strength of acid depends on the nature of solvent

A leveling solvent is defined as the solvent in which all strong acids dissociate to some extent so that their relative strength cannot be compared

All acids stronger than  $H_3O^+$  appears equally strong in aqueous solution, thus water is known as leveling solvent, this phenomenon is known as leveling effect



## PHYSICAL AND CHEMICAL EQUILIBRIUM

### Differentiating solvents

These are the solvents in which strong acids and strong base ionize to different extent, so their relative strength can be compared

For example: Acetic acid (  $\text{CH}_3\text{COOH}$  ) is a weak base and has a little tendency to accept proton from strong acids alike  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HClO}_4$

On the basis of equilibrium constant the strength of the above mentioned acids is found in order  $\text{HClO}_4 > \text{H}_2\text{SO}_4 > \text{HI} > \text{HBr} > \text{HCl} > \text{HNO}_3$

Liquid ammonia has a such strong tendency to accept proton that even weak acid like acetic acid dissociate to a considerable extent and behave as strong acid

Strong bases also depends on the nature of solvent. Bases ionize to a different extent in a solvent which is weakly acidic in nature like  $\text{H}_2\text{O}$  and their relative strength can be compared

### Types of solvent

(i) Protophilic solvents : Solvents which have tendency to accept protons are called protophilic solvents e.g.  $\text{H}_2\text{O}$ ,  $\text{C}_2\text{H}_5\text{OH}$ , liquid  $\text{NH}_3$  etc

(ii) Protogenic solvents: Solvents which have tendency to donate protons are called protogenic solvents e.g.  $\text{HCl}$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{H}_2\text{O}$  etc

(iii) Amphiprotic solvents: Solvents which can act both as proton acceptor as well as proton donor are called amphiprotic solvents e.g.  $\text{H}_2\text{O}$ ,  $\text{NH}_3$ ,  $\text{C}_2\text{H}_5\text{OH}$  etc

Aprotic solvents: Solvents which neither donate nor accept protons are call aprotic solvents e.g.  $\text{CCl}_4$ , Benzene etc

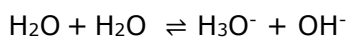
### Ionic product of water

Ionic product of water is the product of molar concentration of  $\text{H}_3\text{O}^+$  ions and  $\text{OH}^-$  ions in pure water or in any acidic or basic solution. It is a constant at particular temperature

At 298 K

$$K_w = [\text{H}_3\text{O}^+] [\text{OH}^-] = 1 \times 10^{-14} \text{ mol}^2 \text{ litre}^{-2}$$

In pure water



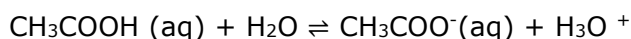
$$[\text{H}_3\text{O}^+] = [\text{OH}^-]$$

Thus at 298K,  $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1 \times 10^{-7} \text{ mole litre}^{-1}$

With increase in temperature, degree of dissociation increases, so more of  $\text{H}_2\text{O}$  dissociates into  $\text{H}^+$  and  $\text{OH}^-$  and hence ionic product increases

### Relation between the ionization constants of acid and their conjugate bases

The equilibrium reaction of acetic acid with water is written as



$$K_{eq} = \frac{[\text{CH}_3\text{COO}^-] + [\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}][\text{H}_2\text{O}]}$$



## PHYSICAL AND CHEMICAL EQUILIBRIUM

$$K_a = K_{eq}[H_2O] = \frac{[CH_3COO^-] + [H_3O^+]}{[CH_3COOH]} \quad \text{--- eq(1)}$$

The conjugate base of acetic acid  $CH_3COO^-$  acts as base in its reaction with water as  
 $CH_3COO^- (aq) + H_2O \rightleftharpoons CH_3COOH(aq) + OH^-$

$$K_b = K_{eq}[H_2O] = \frac{[CH_3COOH] + [OH^-]}{[CH_3COO^-]} \quad \text{--- eq(2)}$$

Eq(1)  $\times$  eq(2)

$$K_a \times K_b = \frac{[CH_3COO^-] + [H_3O^+]}{[CH_3COOH]} \times \frac{[CH_3COOH] + [OH^-]}{[CH_3COO^-]}$$

$$K_a \times K_b = [H_3O^+] \times [OH^-]$$

As we know that  $K_w = [H^+] [OH^-]$  Thus

$$K_w = K_a \times K_b$$

Thus stronger the , weaker the baseacid

### Acidity and pH scale

pH is a convenient method to represent hydrogen ion concentration. pH of solution is defined as negative logarithm of hydrogen ion concentration

$$pH = -\log[H^+] \text{ or } pH = -\log [H_3O^+]$$

Similarly, negative logarithm of hydroxyl ion concentration is called pOH

$$pOH = -\log [OH^-]$$

pH-Scale: A solution is classified as acidic , basic or neutral based on pH value

- (i) If  $pH = pOH = 7$  , then solution is neutral
- (ii) If  $pH < 7$  or  $pOH >$ , then solution is acidic
- (iii) IF  $pH > 7$  or  $[pOH] < 7$ , then solution is basic

pH scale varies from 0 to 14

### Relation between pH and pOH

We know that  $K_w = [H^+] [OH^-] = 10^{-14}$  at 298K

Taking log on both sides

$$\log K_w = \log[H^+] + \log[OH^-] = \log 10^{-14}$$

$$-\log K_w = -\log[H^+] - \log[OH^-] = -\log 10^{-14}$$

$$pK_w = pH + pOH = 14$$

$$\text{Thus } pH + pOH = 14$$

$$\text{And } pK_w = pH + pOH$$

- Higher the concentration of  $H^+$  ions, lower the pH by one unit to tenfold increase of  $H^+$  ion concentration

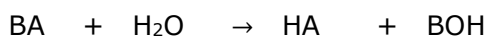


## PHYSICAL AND CHEMICAL EQUILIBRIUM

- pH value decreases on heating since  $H^+$  ion concentration increases
- We know that  $K_w = K_a \times K_b$  thus  $pK_w = pK_a + pK_b$

### Salt Hydrolysis

Salt hydrolysis is a process in which a salt reacts with water to give acid and the base



Salt                      acid              base

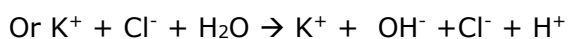
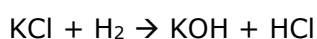
In other words, we can say that hydrolysis is the reverse of neutralization

On the basis of strength of acid and base producing salts, the salts are classified into four categories

#### 1) Salt of strong acid and strong base

Examples NaCl, KCl,  $K_2SO_4$ ,  $Na_2SO_4$ ,  $KNO_3$ ,  $NaNO_3$  etc

Consider the hydrolysis of KCl



Thus such salts only ionize and do not hydrolyse. It is obvious from the reaction that  $[H^+] = [OH^-]$  i.e. solution is neutral

In other words, we can say that salts of strong acid and strong base do not undergo hydrolysis and give a neutral resultant solution

#### 2) Salts of weak acid and strong base

Examples  $CH_3COONa$ ,  $Na_3PO_4$ ,  $K_2CO_3$ ,  $Na_2CO_3$  etc



Such salts undergo anionic hydrolysis since anion reacts with water to give base solution

Hydrolysis constant of such salts

$$K_h = \frac{K_w}{K_a}$$

Where  $K_a$  is dissociation constant of weak acid and  $K_w$  is ionic product of water

Degree of hydrolysis

$$h = \sqrt{\frac{K_h}{C}}$$

$$h = \sqrt{\frac{K_w}{K_a C}}$$

And

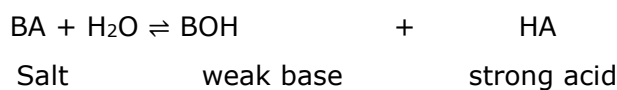
$$pH = \frac{1}{2} [pK_w + pK_a + \log C]$$



## PHYSICAL AND CHEMICAL EQUILIBRIUM

3) Salts of strong acid and weak base

Examples  $\text{NH}_4\text{Cl}$ ,  $\text{CuSO}_4$ ,  $\text{CaCl}_2$ ,  $\text{AlCl}_3$  etc



Or  $\text{B}^- + \text{A}^+ + \text{H}_2\text{O} \rightleftharpoons \text{BOH} + \text{H}^+ + \text{A}^-$

$\text{B}^+ + \text{H}_2\text{O} \rightleftharpoons \text{BOH} + \text{H}^+$

These salts undergo cationic hydrolysis since cation reacts with water to give acidic solution

Hydrolysis constant

$$K_h = \frac{K_w}{K_b}$$

Where  $K_b$  is dissociation constant of weak base

Degree of hydrolysis

$$h = \sqrt{\frac{K_h}{C}}$$

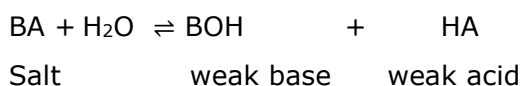
$$h = \sqrt{\frac{K_w}{K_b C}}$$

And

$$pH = \frac{1}{2} [pK_w - pK_a - \log C]$$

4) Salts of weak acid and weak base

Examples  $\text{CH}_3\text{COONH}_4$ ,  $\text{AlPO}_4$ ,  $(\text{NH}_4)_2\text{CO}_3$  etc



Or  $\text{B}^{+6} + \text{A}^- + \text{H}_2\text{O} \rightleftharpoons \text{BOH} + \text{HA}$

These salts involve both cationic and anionic hydrolysis to give almost neutral solution since both acid and base produced are weak

Hydrolysis constant

$$K_h = \frac{K_w}{K_a \times K_b}$$

Degree of hydrolysis  $h = \sqrt{K_h}$  or

$$h = \sqrt{\frac{K_w}{K_a \times K_b}}$$

and

$$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$$





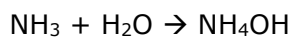
## PHYSICAL AND CHEMICAL EQUILIBRIUM

### Solved Numerical

Q) Calculate  $\text{OH}^-$  ion concentration in 5.82M aqueous solution of ammonia,  
for  $\text{NH}_4^+ = 5.0 \times 10^{-10}\text{M}$

$K_a$

Solution



At equilibrium  $C(1-\alpha)$   $C\alpha$   $C\alpha$

Now

$$K_b = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

Since aqueous solution of ammonia is weak base  $1-\alpha \approx 1$

$$K_b = C\alpha^2$$

$$\alpha = \sqrt{\frac{K_b}{C}}$$

At equilibrium  $[\text{OH}^-] = C\alpha$

$$[\text{OH}^-] = C \sqrt{\frac{K_b}{C}} = \sqrt{K_b C}$$

But  $K_a \times K_b = K_w$

$$\therefore K_b = \frac{K_w}{K_a}$$

$$[\text{OH}^-] = \sqrt{\frac{K_w}{K_a} C}$$

$$[\text{OH}^-] = \sqrt{\frac{10^{-14}}{5 \times 10^{-10}} \times 5.82} = 1.079 \times 10^{-2}$$

Q) Calculate the pH of  $10^{-6}\text{M}$  HCl solution if 1ml of it is diluted to 100ml,  $K_w = 1 \times 10^{-14}$

Solution

Concentration of HCl after dilution =  $10^{-6}/100 = 10^{-8}\text{M}$

Hence  $[\text{H}^+] = 10^{-8}\text{M}$

Since concentration of  $\text{H}^+$  ions is very low, concentration of  $\text{H}^+$  from water is also taken into account

$[\text{H}^+]$  from water =  $10^{-7}\text{M}$

Total  $[\text{H}^+] = (10^{-8} + 10^{-7}) = 1.1 \times 10^{-7}\text{M}$

$\text{pH} = -\log[\text{H}^+] = -\log(1.1 \times 10^{-7})$

$\text{pH} = 7 - \log 1.1 = 6.95$



## PHYSICAL AND CHEMICAL EQUILIBRIUM

Q) What will be the resultant pH when 200ml of an aqueous solution of HCl (pH = 2.) is mixed with 300ml of an aqueous solution of NaOH ( pH = 12.0)?

Solution

HCl	NaOH
pH = $-\log[H^+] = 2$	pH = $-\log[H^+] = 12$
$[H^+] = 10^{-2}M$	$[H^+] = 10^{-12}M$
	$[OH^-] = 10^{-2}M$
Millimoles of $H^+$	Millimoles of $OH^-$
$10^{-2} \times 200 = 2$	$= 10^{-2} \times 300 = 2$

2 millimoles of  $H^+$  will be neutralized with 2 millimoles of  $OH^-$ . Thus, the resulting solution contains 1 millimole of  $OH^-$  in 500ml

Concentration of  $[OH^-]$  left =  $1/500 = 2 \times 10^{-3} M$

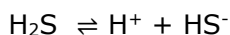
pOH =  $-\log[OH^-] = -(\log 2 \times 10^{-3}) = 2.69$

pH =  $14 - pOH = 14 - 2.69 = 11.31$

Q) Calculate the approximate pH of a 0.1M aqueous  $H_2S$  solution,  $K_1$  and  $K_2$  of  $H_2S$  are  $1.00 \times 10^{-7}$  and  $1.3 \times 10^{-13}$  respectively at  $25^\circ C$

Solution:

Since  $K_1 \gg K_2$  we can neglect second dissociation and all  $H^+$  ion concentration can be considered from 1<sup>st</sup> dissociation only



$$K_1 = \frac{[H^+][HS^-]}{[H_2S]}$$

$$\text{As } [H^+] = [HS^-]$$

$$K_1 = \frac{[H^+]^2}{[H_2S]}$$

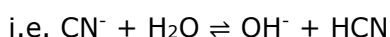
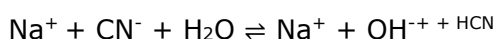
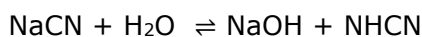
$$[H^+] = \sqrt{K_1 \times [H_2S]}$$

$$[H^+] = \sqrt{10^{-7} \times 0.1} = 10^{-4}$$

$$\text{Hence pH} = -\log[H^+] = -\log 10^{-4} = 4.$$

Q) What is the pH of 0.5M aqueous NaCN solution  $pK_b$  of  $CN^-$  is 4.7

Solution



$$K_b = \frac{[HCN][OH^-]}{[CN^-]}$$

Since at equilibrium  $[OH^-] = [HCN]$

$$K_b = \frac{[OH^-]^2}{[CN^-]}$$



## PHYSICAL AND CHEMICAL EQUILIBRIUM

Taking log on both sides

$$-\log K_b = -2\log[\text{OH}^-] + \log [\text{CN}^{+}]$$

$$2\log[\text{OH}^-] = \log 0.5 - pK_b$$

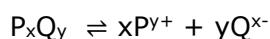
$$\log[\text{OH}^-] = \frac{-0.3010 - 4.7}{2} = -2.5$$

$$p\text{OH} = 2.5$$

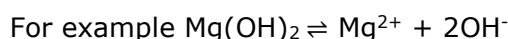
$$p\text{H} = 14 - p\text{OH} = 14 - 2.4 = 11.5$$

### Ionic product

Ionic product of an electrolyte is the product of concentrations of the ions in solution, each raised to the power equal to number of ions produced on dissociation of one mole of the electrolyte, at specific temperature



$$\text{Ionic product} = [P^{y+}]^x [Q^{x-}]^y$$



$$\text{Ionic product} = [\text{Mg}^{2+}] [\text{OH}^-]^2$$

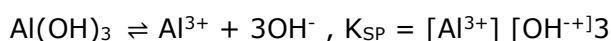
### Solubility product

Solubility product of a sparingly soluble salt at a given temperature is defined as the product of molar concentration of its ions in a saturated solution, with each concentration term raised to the power equal to number of ions present in the chemical equation representing the equilibrium of dissociation of one molecule of the salt. It is represented as  $K_{SP}$



$$\text{Solubility product } K_{SP} = [A^{y+}]^x [B^{x-}]^y$$

For example



### Application of solubility product

#### 1. Predicting precipitate formation

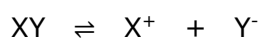
If the ionic product of a sparingly soluble salt exceeds solubility product, then excess of ions combine to form precipitates

If ionic product  $> K_{SP}$  precipitation takes place

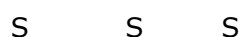
If ionic product  $< K_{SP}$  no precipitation takes place

#### 2. Predicting solubility of sparingly soluble salt

Solubility of a sparingly soluble salt can be calculated from its solubility product at a given temperature



Let solubility be





## PHYSICAL AND CHEMICAL EQUILIBRIUM

$$K_{SP} = [X^+] [Y^-] = (S)(S) = S^2$$

$$S = \sqrt{K_{SP}}$$

### 3. Precipitation of common salt

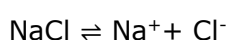
When HCl gas is passed through a saturated solution of impure common salt, the concentration of  $Cl^-$  increases due to ionization of HCl



Thus ionic product  $[Na^+][Cl^-]$  exceeds solubility product and pure NaCl precipitates out

### 4. Salting out of soap

Soaps are sodium salt of long chain fatty acids. When some NaCl is added to soap solution, concentration of  $Na^+$  increases due to ionization of NaCl



Thus ionic product  $[RCOO^-][Na^+]$  exceeds solubility product of soap and soap precipitates out from the solution

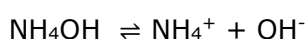
### 5. Qualitative analysis

Various basic radicals are identified and separated by the principle of solubility product and common ion effect

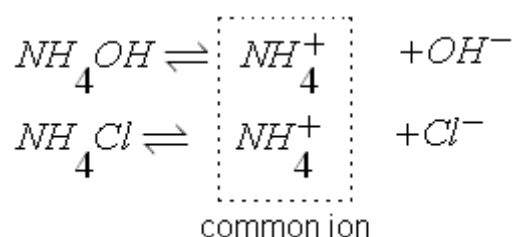
#### Common ion effect

Common ion effect is defined as the suppression of ionization of weak electrolyte by addition of strong electrolytes having an ion common to weak electrolyte.

For example weak base  $NH_4OH$  ionizes to a small extent



When a strong electrolyte like  $NH_4Cl$  or  $NaOH$  is added to this solution, a common ion  $NH_4^+$  and  $OH^-$  respectively is furnished so that the equilibrium is shifted to the right, according to Le-Chatelier's principle



Thus, degree of dissociation of an electrolyte decreases by common ion effect but dissociation constant of the electrolyte remains same

#### Isohydric solutions

The solution of weak electrolytes are said to be isohydric if both have equal concentration of common ion present in them. On mixing such solutions no change in the degree of dissociation of either of the electrolytes occurs. For two isohydric solutions



## PHYSICAL AND CHEMICAL EQUILIBRIUM

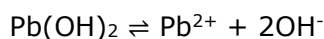
$$\frac{\alpha_1}{V_1} = \frac{\alpha_2}{V_2}$$

Where  $V_1$  and  $V_2$  are the diluting solution (1) and (2) respectively. And  $\alpha_1$  and  $\alpha_2$  are their degree of dissociation at respective dilution

### Solved Numerical

Q) The solubility of  $Pb(OH)_2$  in water is  $6.7 \times 10^{-6} M$ . Calculate the solubility of  $Pb(OH)_2$  in a buffer solution of  $pH = 8$

Solution



$$S = 6.7 \times 10^{-6} M$$

$$K_{SP} = [Pb^{2+}][OH^-]^2$$

$$K_{SP} = (6.7 \times 10^{-6})(2 \times 6.7 \times 10^{-6})^2 = 1.2 \times 10^{-15}$$

In the solution of  $pH = 8$ ,  $[H^+] = 10^{-8} M$

As  $[H^+][OH^-] = K_w$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{10^{-8}} = 10^{-6}$$

$K_{SP}$  of salt remains constant at a particular temperature

$$\text{Again } K_{SP} = [Pb^{2+}][OH^-]^2$$

$$1.2 \times 10^{-15} = [Pb^{2+}][10^{-6}]^2$$

$$[Pb^{2+}] = \frac{1.2 \times 10^{-15}}{10^{-12}} = 1.2 \times 10^{-3} M$$

i.e. Solubility =  $1.2 \times 10^{-3} \text{ mol litre}^{-1}$

Q) A sample of  $AgCl$  was treated with 5.0 ml of 1.5M  $Na_2CO_3$  solution to give  $Ag_2CO_3$ . The remaining solution contains 0.0026g of  $Cl^-$  per litre. Calculate the solubility product of  $AgCl$  ( $K_{SP}$  for  $Ag_2CO_3 = 8.2 \times 10^{-12}$ )

$$K_{SP} \text{ for } Ag_2CO_3 = 8.2 \times 10^{-12}$$

Solution



$$K_{SP} = [Ag^+]^2 [CO_3^{2-}]$$

Given  $[CO_3^{2-}]$  from  $Na_2CO_3 = 1.5M$

$$\therefore [Ag^+] = \sqrt{\frac{K_{SP}}{CO_3^{2-}}} = \sqrt{\frac{8.2 \times 10^{-12}}{1.5}} = 2.34 \times 10^{-6} M$$

Now molar concentration of  $Cl^- = [Cl^-] = 0.0026/35.5$  (atomic mass of  $Cl = 35.5$ )

$$K_{SP} \text{ for } AgCl = [Ag^+][Cl^-]$$

$\therefore K_{SP}$  for  $AgCl$

$$K_{SP} = (2.34 \times 10^{-6}) \left( \frac{0.0026}{35.5} \right) = 1.71 \times 10^{-10}$$



## Buffer Solutions

Buffer solution is defined as a solution which resists the change in its pH value when small amount of acid or base is added to it or when the solution is diluted. Buffer solution has a definite pH value at specific temperature and it does not change on keeping for long time.

### Types of buffers

#### 1. Simple buffer

These are the solutions of salt of weak acid and weak base.

For example Ammonium acetate ( $\text{CH}_3\text{COONH}_4$ )

#### 2. Mixed buffers

These are the mixtures of two solutions. These are further of two types

##### 9i) Acidic buffers

These are the solutions of mixture of weak base and salt of this weakbase with strong acid.

For example  $\text{CH}_3\text{COOH} + \text{CH}_3\text{COONa}$ . They have pH value less than 7 i.e  $\text{pH} < 7$

##### (ii) Basic buffers

These are the solutions of mixture of weak base and salt of this weak base with strong acid. For example  $\text{NH}_4\text{OH} + \text{NH}_4\text{Cl}$ . They have pH value more than 7 i.e.  $\text{pH} > 7$

### pH of buffer solution

pH value of buffer solution is given by Henderson-Hasselbalch equation

(i) Acidic buffer :

$$\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

Where  $K_a$  is dissociation constant of acid and  $\text{p}K_a = -\log K_a$ ,  $[\text{salt}]$  and  $[\text{acid}]$  are molar concentration of salt and acid respectively

(ii) Basic buffer

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

Where  $K_b$  is dissociation constant of acid and  $\text{p}K_b = -\log K_b$ ,  $[\text{salt}]$  and  $[\text{base}]$  are molar concentration of salt and base respectively

Blood as buffer solution

Blood acts as a buffer solution and maintains a pH level of about 7.1. Any change in pH of blood can produce illness or even cause death

### Solved Numerical



## PHYSICAL AND CHEMICAL EQUILIBRIUM

Q) A buffer solution with  $\text{pH} = 9$  is to be prepared by mixing  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ . Calculate the number of moles of  $\text{NH}_4\text{Cl}$  that should be added to one litre of  $1.0 \text{ M NH}_4\text{OH}$  ( $K_b = 1.8 \times 10^{-5}$ )

Solution

Weak base ( $\text{NH}_4\text{OH}$ ) + salt of weak base with strong acid ( $\text{NH}_4\text{Cl}$ ) = Base buffer

For basic buffer

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$\text{pOH} = 14 - \text{pH}$$

$$\text{pOH} = 14 - 9 = 5$$

$$\text{and } \text{p}K_b = -\log K_b = -\log(1.8 \times 10^{-5}) = 4.7447$$

$$[\text{Base}] = [\text{NH}_4\text{OH}] = 1.0 \text{ M}$$

Thus

$$5 = 4.7447 + \log \frac{[\text{salt}]}{1}$$

$$\text{Log}[\text{salt}] = 0.2553$$

On taking antilog

$$[\text{salt}] = 1.8 \text{ mol litre}^{-1}$$