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,

water(l) ⇌ ice(s)

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,

Water(l) ⇌Steam(g)

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.

S(rhombic) ⇌ S(monoclinic)

(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

Dissolution if solid in liquid

After the arrival of saturation point the amount of un dissolved 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 gasses in water is always exothermic. As dissolution is spontaneous(takes place on its own) ΔG = -ve, entropy decreases in the process of dissolution ΔS = -ve. Therefore ΔH has 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 reaction in which products do not react back to give the reactant. i.e. reaction can not be retraced at any point

E.g. $AgNO_3 + NaCl \rightarrow AgCl\downarrow + NaNO_3$

$SnCl_2 + 2FECl_3 \rightarrow SnCl_4 + 2FeCl_2$

Free energy change (ΔG) for irreversible reaction ≠ 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

e.g. $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$

$N_2(g) + 3H_2(g) \rightleftharpoons 2HMH_3(g)$

Free energy change ΔG for reversible reaction is zero, ΔG = 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 takes place at the same rate, so that composition of chemical system remains constant

Characteristics of chemical equilibrium

(i)Equilibrium state is attended only when reaction is carried out in closed vessel (system) (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 attended in either direction

(vi) Change in conditions like temperature, pressure or concentration disturb the equilibrium and shift the equilibrium in one direction to attend 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 $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (represents a homogeneous equilibrium in gaseous phase)

$CH_3COOH\ (l) + C_2H_5OH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$ (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 $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

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:

"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 molae 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, where as 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 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 $\propto [C]^c+[D]^d = k_f [C]^c+[D]^d$

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

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

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

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

Relation between K_c and K_p

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

From ideal gas equation PV = nRT

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

Since Volume and temperature for all reactant and product is same

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

Now a/v = concentration = [A] similarly

b/v = [B]. c/V = [C] and d/V = [D]

Thus

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

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

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

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

Here Δn_g is change in number of gaseous molecules

Since, partial pressure are generally noted in atm and concentrations are measured in (moles/litre) , so valur 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

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

Solved numerical

Q) The K_P value for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 460°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

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial pressure	0.5		0.5		0
At equilibrium	(0.5 – x)		(0.5-x)		2x (from stoichiometry of equation)

$$K_P = \frac{P_{HI}^2}{P_{H_2} \times P_{I_2}}$$

$$49 = \frac{(2x)^2}{(0.5-x)^2}$$

X = 0.39 atm

∴ Pressure of H_2 and I_2 at equilibrium = (0.5-x) = 0.11 atm

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

$2H_2O \rightleftharpoons H_3O^+ + OH^-$, $K_2 = 1\times10^{-14}$

Calculate equilibrium constant for reaction

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

Solution

Equilibrium constant for the reaction

$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

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

Equilibrium constant for the reaction

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

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

Taking the ratio of K1 and K_2

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

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

Above ratio is the equilibrium constant of the reaction

$CH_3COOH + OH^- \rightleftharpoons CH_3COO^- + H_2O$

$$\therefore K = \frac{K_1}{K_2} = \frac{1.8\times10^{-5}}{1\times10^{-14}} = 1.8\times10^{9}$$

Q) For the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$; $\Delta H = -46\ kJmol^{-1}$

Calculate the value of K_P. Given $K_C = 0.5\ lit^2mol^{-2}$ at 400^OC

Solution:

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

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

$K_P = 0.5(0.082\times673)^{-2} = 1.641\times10^{-4}$

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

	CH_3COOH	+	C_2H_5OH	$\rightleftharpoons$	$CH_3COOC_2H_5$	+	H_2O
At equilibrium	1-x		3 –x		x		x

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

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

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

X = 0.903 or 4.73 (inadmissible)

∴ 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 initiall concentrations are equilibrium concentrations. So, the system is already at equilibrium

(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

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

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

i) When the equilibrium reaction is reversed

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

$$K'_C = \frac{[N_2][H_2]^3}{[NH_3]^2} = \frac{1}{K_C}$$

ii) When the equation for a reaction is divided by a factor 'n' the value of new equilibrium constant becomes equal to nth root of the previous equilibrium constant k'

$A+B \rightleftharpoons C + D$

$$\frac{1}{n}A + \frac{1}{n}A \leftrightharpoons \frac{1}{n}C + \frac{1}{n}D$$

$$K' = \sqrt[n]{K_c}$$

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

$A+B \rightleftharpoons C + D$

$nA+nB \rightleftharpoons nC + nD$

$K' = K_C^n$

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

Example $A+B \rightleftharpoons C + D$

If above reaction takes placed in two steps

$$A+B \overset{K_1}{\rightleftharpoons} X+Y$$

$$X+Y \overset{K_2}{\rightleftharpoons} C+D$$

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 (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 stoichometry 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 incase 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

$$log\frac{K_2}{K_2} = \frac{\Delta H^0}{2.303R}\left[\frac{T_2 - T_1}{T_2 T_1}\right]$$

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

ΔH^O is the enthalpy of reaction and R is the gas constant

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

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

i.e equilibrium constant does not change with temperature

If $T_2 > T_1$ and ΔH^O is positive (endothermic reaction) then $K_2 > K_1$

But if $T_2 > T_1$ and ΔH^O 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

Units of equilibrium constant

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

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

Similarly partial pressure is measured in terms of atmosphere, hence unit of K_P is (atm) $)^{\Delta n}$, where Δn 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 (ΔG) is related to ΔG^O as follows

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

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

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

If $K > 1$, then ΔG^O is negative. reaction in forward direction is spontaneous

If $K < 1$, then ΔG^O 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.

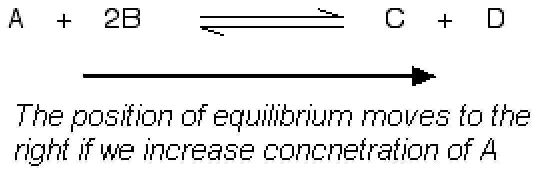
Using Le Chatelier's Principle with a change of concentration

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

$$A + 2B \rightleftharpoons C + D$$

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.

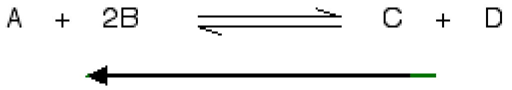


The position of equilibrium moves to the right if we increase concnetration of A

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?

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 concnetration 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:

$$A_{(g)} + 2B_{(g)} \rightleftharpoons C_{(g)} + D_{(g)}$$

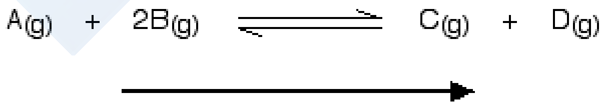
What would happen if we changed the conditions by increasing the pressure?

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.

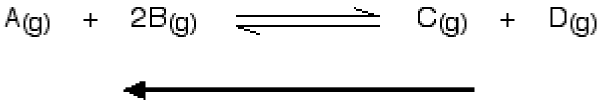
Increasing the pressure on a gas reaction shifts the position of equilibrium towards the side with fewer molecules.



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

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.

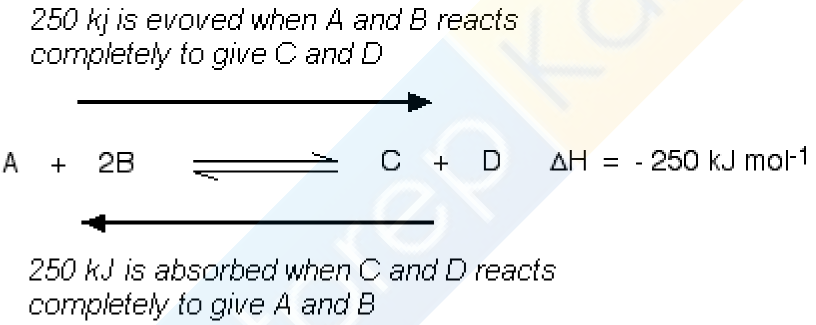
Using Le Chatelier's Principle with a change of temperature

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):

$$A + 2B \rightleftharpoons C + D \qquad \Delta H = -250\ kJ\ mol^{-1}$$

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.

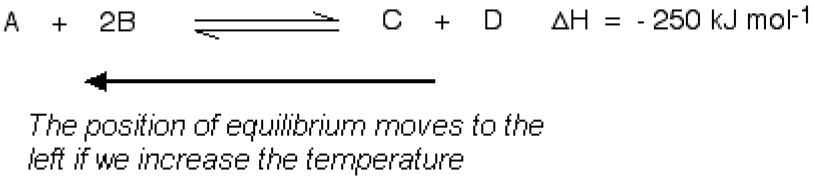


What would happen if you changed the conditions by increasing the temperature?

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.



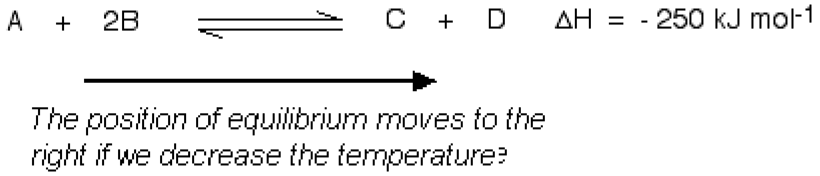
If you were aiming to make as much C and D as possible, increasing the temperature on a reversible reaction where the forward reaction is exothermic isn't a good idea!

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.



$$A + 2B \rightleftharpoons C + D \quad \Delta H = -250\ \text{kJ mol}^{-1}$$

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

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

For example

Let the equilibrium reaction is the dissociation equilibrium of NH_3 into N_2 and H_2

$NH_3(g) \rightleftharpoons (1/2)\ N_2(g) + (3/2)H_2(g)$

Let the initial moles of NH_3 taken be 1 and the moles of NH_3 dissociated at equilibrium be 'x'

Then

	$NH_3(g)$	⇌	$(1/2)\ N_2(g)$	+	$(3/2)H_2(g)$
Moles initially	1		0		0
Moles at equilibrium	1-x		x/2		3x/2

Here, x represents the degree of dissociation (α). If we would have stated with 'a' moles of NH_3 and moles of NH_3 dissociated is taken as 'x', then degree of dissociation of 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 N_2 and H_2 combine to give NH_3 · Degree of dissociation is proportional to temperature

Solved numerical

Q) A sample of HI was found to22% 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 (α) is the fraction of 1mole of HI that has dissociated under the given conditions. If the % dissociation of HI is 22, the degree of dissociation is 0.22

	2HI	⇌	H_2	+	I_2
At equilibrium	(1- α)		α/2		α/2
	1-0.22 =0.78		0.11		0.11

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.11\times0.11}{(0.78)^2} = 0.0199$$

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

	2HI	⇌	H_2	+	I_2
At equilibrium	(1- x)		[(x/2) +1]		x/2

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\left(\frac{x}{2}+1\right)\left(\frac{x}{2}\right)}{(1-x)^2} = 0.0199$$

X=0.037 or -2.4 (not admissible)

Degree of dissociation = 0.037

% of dissociation = 3.7

Note :Introduction of 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

$$CO_2 + C_{graphite} \rightleftharpoons CO$$

Let the decrease in pressure of CO_2 after reaction be p atm

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

Final pressure = (0.5 –p) +2p = 0.8 atm

Therefore p = 0.3atm

Thus after reaction, P_{CO2} = 0.5 -0.3 = 0.2 atm

P_{CO} = 2p = 2×0.3 = 0.6 atm

Equilibrium constant K

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

Q) The equilibrium constant K_P for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at $467^{O}C$ is found to be 636 mm Hg. If the pressure of the gas mixture is 182mm, calculate the percentage dissociation of N_2O_4. At what pressure will it be half dissociated

Solution

Let dissociation of 1 mole of N_2O_4 be α then

NO_2 formed at equilibrium will be= 2α

N_2O_4 at equilibrium will be = (1- α)

Total moles at equilibrium = (1- α)+2 α = 1+ α

If P_T is total pressure at equilibrium then

Pressure of N_2O_4 at equilibrium

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

Pressure of NO_2 at equilibrium

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

Now

$$K_P = \frac{\left(P_{NO_2}\right)^2}{\left(P_{N_2O_4}\right)} = \frac{\left(\frac{2\alpha}{1+\alpha} \times P_T\right)^2}{\frac{1-\alpha}{1+\alpha} \times P_T} = \frac{4\alpha^2 P_T}{1-\alpha^2}$$

Thus

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

α = 0.6829

% dissociation of N_2O_4 = 68.29

When the gas is half dissociated α =0.5 , Let the total pressure be P’

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

P’=477mm

Electrolyte and Non-electrolyte

A compound whose aqueous solution or melt conducts electricity is known as electrolyte, where as 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_2SO_4 etc. They are good conductors of electricity
Whereas those electrolytes which dissociate only partally into ions in aqueous solution are known as weak electrolytes. E.g. CH_3COOH, NH_4OH 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
$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

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 van be applied **to** such systems also.

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

$$AB \leftrightarrow A^+ + B^-$$

Initially t = 0 C 0 0

At equilibrium C(1-α) Cα Cα

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

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

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

For very weak electrolytes,

$\alpha <<< 1, \; (1 - \alpha) = 1$

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

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

Concentration of any ion = $C\alpha = \sqrt{(CK)}$.
From equation (ii) it is a clear that degree of ionization increases on dilution.
If 1mole 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.
$HCl \rightleftharpoons H^+ + Cl^-$
$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
A base is a substance which in aqueous solution gives hydroxyl (OH^-) ions as the only anions
$NaOH \rightleftharpoons Na^+ + OH^-$
$NH_4OH \rightleftharpoons NH_4^+ + OH^-$
Neutralization is nothing but combination of H^+ ions of the acid and OH^- ions of the base to form unionized water

Limitations of Arrhenus concept

(i) It does not explain the acidic character of certain compounds like CO_2, SO_2, $AlCl_3$ etc and basic character of some compounds like Na_2CO_3, NH_3 etc. which does not give H^+ and 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 H^+ and OH^- ions in water

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_2O	⇌	H_3O^+	+	Cl^-
CH_3COOH	+	H_2O	⇌	H_3O^+	+	CH_3COO^-
H_2O	+	NH_3	⇌	NH_4^+	+	NO_3^-
H_2O	+	CO_3^-	⇌	HCO_3^-	+	OH^-

- 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

(i) Electron deficient neutral compounds i.e. molecules in which central atoms has incomplete octatae eg. BF_3, $FeCl_3$, $AlCl_3$ etc

(ii) All simple cation e.g. H^+, Mg^{2+}, Ag^+, Fe+3+ ^{etc}

(iii) Molecules having multiple bond between atoms of different electro-negativities e.g. SO_3, CO_2 etc

(iv) In coordination complexes, metal atoms acts as Lewis acid

(v) Molecules having a central atom with empty d-orbital's, e.g SiF_4, $SnCl_4$

Chemical species which can act as Lewis base

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

$\ddot{N}H_3$, $R\text{-}\underset{..}{\ddot{O}}\text{-}H$, $R-\ddot{N}H_2$

ii) All negatively changed ions e.g. CN^-, OH^-, Cl^- etc

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

Summary of concept to acid and base

Concept	Acid	Base
Arrhenius	H^+ donor	OH^- donor
Bronsted-Lowry	H^+ donor	H^- acceptor
Lewis	e^- pair acceptor	e^- pair donor

Strength of acids and bases

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

$HA + water \quad H^+(aq) + A^-(aq)$

Acid

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

Where K_a is the dissociation constant of acid HA.

Similarly for base $K_b \propto [OH^-]$ 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 H^+ aqueous or 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

$$\frac{Strength\ of\ HA_1}{Stregth\ of\ HA_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

Similarly for equimolar weak base

$$\frac{Strength\ of\ BOH_1}{Stregth\ of\ BOH_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

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 $(COOH)_2$, Sulphuric acid H_2SO_4, phosphoric acid H_3PO_4, carbonic acid (H_2CO_3 are considered as dibasic acid

$$H_2A_{(aq)} \xrightleftharpoons{K_{a1}} H^+ + HA^-$$

$$HA^- \xrightleftharpoons{K_{a2}} H^+ + A^{2-}$$

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

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

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 changed 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 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. What is the order of their acidic strength?

Solution

We know that acidic strength ∝ $\sqrt{R_a}$

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 ($K_a = 4.9\times10^{-10}$) with 0.01M aquesius solution of formic acid which it is 14.5% dissociated

Solution

Applying

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

Degree of dissociation = 14.5% = 0.145

From formula K_a (HCOOH) = $C\alpha^2 = 0.01\times(0.145)^2 = 2.1\times10^{-4}$

Thus

$$\frac{stregth\ of\ formic\ acid}{strength\ of\ HCN} = \sqrt{\frac{2.1\times10^{-4}}{4.9\times10^{-10}}} = 6.5\times10^{2}$$

i.e Formic acid is 6.5×10^{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

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 (CH_3COOH) is a weak base and has a little tendency to accept proton from strong acids alike HCl, HBr, HNO_3, H_2SO_4 ,$HClO_4$

On the basis of equilibrium constant the strength of the above mentioned acids is found in order $HClO_4 > H_2SO_4 > HI > HBr > HCl > HNO_3$

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 H_2O and their relative strength can be compared

Types of solvent

(i)Protophilic solvents : Solvents which have trendency to accept protons are called protophilic solvents e.g. H_2O, C_2H_5OH, liquid NH_3 etc

(ii) Protogenic solvents: Solvents which have tendency to donate protons are called protogenic solvents e.g. HCl, CH_3COOH, H_2O etc

(iii)Amphiprotic solvents: Solvents which can act both as proton acceptor as well as proton donor are called amphiprotic solvents e.g. H_2O, NH_3, C_2H_5OH etc

Aprotic solvents: Solvents which neither donate nor accept protons are call aprotic solvents e.g. CCl_4, Benzene etc

Ionic product of water

Ionic product of water is the product of molar concentration of H_3O^+ ions and OH^- ions in pure water or in any acidic or basic solution. It is a constant at particular temperature

At 298 K

$K_W = [H_3O^+]\,[OH^-] = 1\times10^{-14}$ mol^{2}litre^{-2}

In pure water

$H_2O + H_2O \rightleftharpoons H_3O^- + OH^-$

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

Thus at 298K, $[H_3O^-] = [OH^-] = 1\times10^{-7}$ mole litre^{-1}

With increase in temperature, degree of dissociation increases, so more of H_2O dissociates into H_+ and 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

$$CH_3COOH\ (aq) + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+$$

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

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

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^-

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

Eq(1) × 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 s olution is defiend as negative logarithm of hydrogen ion concentration

pH = -loh$[H^+]$ or pH = - loh $[H_3O^+]$

Similarly, negative logarithm of hydroxyl ion concentration is called pOH

pOH = = -loh $[OH^-]$

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 soides

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

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

$pK_W = pH + pOH = 14$

Thus pH + pOH = 14

And $pK_W = pH + pOH$

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

- 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

BA + H_2O → HA + BOH

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 produing 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

$KCl + H_2 \rightarrow KOH + HCl$

Or $K^+ + Cl^- + H_2O \rightarrow K^+ + OH^- + Cl^- + H^+$

Thus sch 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

Consider the hydrolysis of $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + Na^+ + OH^-$

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 Ka is dissociation constnatof weak acid and KW is ionic product of water

Degree of hydrolysis

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

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

And

$$pH = \frac{1}{2}[pK_W + pK_a + logC]$$

3) Slats of strong acid and weak base

Examples NH_4Cl, $CuSO_4$, $CaCl_2$, $AlCl_3$ etc

$BA + H_2O \rightleftharpoons BOH$ + HA

Salt weak base strong acid

Or $B^- + A^- + H_2O \rightleftharpoons BOH + H^+ + A^-$

$B^+ + H_2O \rightleftharpoons BOH + H^+$

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 canostant of weak base

Degree of hydrolysis

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

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

And

$$pH = \frac{1}{2}[pK_W - pK_a - logC]$$

4) Salts of weak acid and weak base

Examples CH_3COONH_4, $AlPO_4$, $(NH_4)^2CO_3$ etc

$BA + H_2O \rightleftharpoons BOH$ + HA

Salt weak base weak acid

Or $B^{+6} + A^- + H_2O \rightleftharpoons BOH + HA$

These salts involves 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

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

Solved Numerical

Q) Calculate OH^- ion concentration in 5.82M aqueous solution of ammonia, K_a for $NH_4^+ = 5.0\times10^{-10}$M

Solution

$NH_3 + H_2O \rightarrow NH_4OH$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

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 $[OH^-] = C\alpha$

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

But $K_a\times K_b = K_W$

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

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

$$[OH^-] = \sqrt{\frac{10^{-14}}{5\times10^{-10}}\times5.82} = 1.079\times10^{-2}$$

Q) Calculate the pH of 10^{-6}M HCl solution if 1ml of it is diluted to 100ml, $K_W = 1\times10^{-14}$

Solution

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

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

Since concentration of H+ ions is very low, concentration of H+ from water is also taken into account

$[H^+]$ from water = 10-7 M

Total $[H^+] = (10^{-8} + 10^{-7}) = 1.1\times10^{-7}$M

pH = $-\log[H^+] = -\log(1.1\times10^{-7})$

pH = 7 –log1.1 = 6.95

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}×200 = 2	=10^{-2} × 300 = 2

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

Concnetration of [OH^-] left = = 1/500 = 2×10^{-3} M

pOH = -log[OH^-] = -(log2×10^{-3}) = 2.69

pH = 14 –pOH = 14-2.69 v= 11.31

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

Solution:

Since K_1 >> K^2 we can neglect second dissociation and all H^+ ion concentration can be considered from 1st dissociation only

$H_2S \rightleftharpoons H^+ + HS^-$

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

As [H^+] = [HS^-]

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

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

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

Hence pH = -log[H^+] = -log10^{-4} =4.

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

Solution

$NaCN + H_2O \rightleftharpoons NaOH + NHCN$

$Na^+ + CN^- + H_2O \rightleftharpoons Na^+ + OH^{-+\,+\,HCN}$

i.e. $CN^- + H_2O \rightleftharpoons OH^- + HCN$

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

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

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

Taking log on both sides

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

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

$$\log[\mathrm{OH}^-] = \frac{-.3010 - 4.7}{2} = -2.5$$

pOH = 2.5

pH = 14-pOH = 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

$P_xQ_y \rightleftharpoons xP^{y+} + yQ^{x-}$

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

For example $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$

Ionic product = $[MG^{2+}] [OH^-]^{2+}$

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}

$A_xB_y \rightleftharpoons xA^{y+} + yB^x$

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

For example

$Al(OH)_3 \rightleftharpoons Al^{3+} + 3OH^-$, $K_{SP} = [Al^{3+}] [OH^{-+]}3$

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 i

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

	$XY \rightleftharpoons$	$X^+ +$	Y^-
Let solubility be	S	S	S

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

$s = \sqrt{(K_{SP})}$

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

$NaCl \rightleftharpoons Na^+ + Cl^-$, $HCl \rightleftharpoons H^+ + Cl^-$

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

4.Salting out of soap

Soap 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

$RCOONa \rightleftharpoons RCOO^- + Na^+$

$NaCl \rightleftharpoons Na^+ + Cl^-$

Thus ionic prodct $[RCOO^-][[Na^+]$ 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

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$

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

$$\begin{array}{lcl} NH_4OH \rightleftharpoons & NH_4^+ & +OH^- \\ NH_4Cl \rightleftharpoons & NH_4^+ & +Cl^- \\ & \text{common ion} & \end{array}$$

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

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

Where V_1 and V_2 are the diluting solution (1) and (2) respectively. And α_1 and α_2 are their degree of dissociation at respective dilution

Solved Numerical

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

Solution

$Pb(OH)_2 \rightleftharpoons Pb^{2+} + 2OH^-$

S S 2S

$S = 6.7\times10^{-6}M$

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

$K_{SP} = (6.7\times10^{-6})(2\times6.7\times10^{-6})^2 = 1.2\times10^{-15}$

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

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

$1.2\times10^{-15} = [Pb^{2+}][10^{-6}]^2$

$$[Pb^{2+}] = \frac{1.2\times10^{-15}}{10^{-12}} = 1.2\times10^{-3}M$$

i.e. Solubility = 1.2×10^{-3} 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 $Ag_2CO_3 = 8.2\times10^{-12}$)

Solution

$Ag_2CO_3 \rightleftharpoons 2Ag^+ + CO_3^{2-}$

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

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

$$\therefore [Ag^+] = \sqrt{\frac{K_{SP}}{CO_3^{2-}}} = \sqrt{\frac{8.2\times10^{-12}}{1.5}} = 2.34\times10^{-6}M$$

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

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

$\therefore K_{SP}$ for AgCl

$$K_{SP} = (2.34\times10^{-6})\left(\frac{0.0026}{35.5}\right) = 1.71\times10^{-10}$$

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 (CH_3COONH_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 $CH_3COOH + CH_3COONa$. They have pH value less than 7 i.e 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 $NH_4OH + NH_4Cl$. They have pH value more than 7 i.e. pH > 7

pH of buffer solution

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

(i) Acidic buffer :

$$pH = pK_a + log\frac{[salt]}{[acid]}$$

Where K_a is dissociation constant of acid and $pK_a = -lonK_a$, [salt] and [acid] are molar concentration of salt and acid respectively

(ii) Basic buffer

$$pOH = pK_b + log\frac{[salt]}{[base]}$$

Where K_a is dissociation constant of acid and $pK_b = -lonK_b$, [salt] and [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

Q) A buffer solution with pH = 9 is to be prepared by mixing NH_4Cl and NH4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of 1.0 M NH_4OH ($K_b = 1.8\times10^{-8}$)

Solution

Weak base (NH_4OH) + salt of weak base with strong acid (NH_4Cl) = Base buffer

For basic buffer

$$pOH = pK_b + log\frac{[salt]}{[base]}$$

$$pOH = 14 - pH$$

$$pOH = 14 - 9 = 5$$

$$\text{and } pK_b = -\log K_b = -\log(1.8\times10^{-5}) = 4.7447$$

$$[Base] = [NH_4OH] = 1.0M$$

Thus

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

$$Log[salt] = 0.2553$$

On taking antilog

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