7A

CHEMICAL EQUILIBRIUM

IRREVERSIBLE REACTION

Reactions which proceed in such a way that reactants are completely converted (i. e. 100%) in to products are called irreversible reaction.

Characteristics of Irreversible Reaction :

(i) Reactions moves in one direction i.e. in forward direction only i.e. from left to right.

(ii) Products do not react together to produce reactants again i.e. no backward reaction.

(iii) Always carried out in open vessel.

(iv) In such reactions arrow (→) is placed between reactant and product which shows direction of chemical change. [Reactant → Products]

Examples of Irreversible Reaction :

(i) Thermal decomposition reaction :

$$2\,KClO_3(s) \xrightarrow[Heat]{MnO_2} 2KCl(s) + 3O_2(g)$$

(decomposition of potassium chlorate)

(ii) Precipitation reaction :

$$AgNO_3(aq) + NaCl(aq) \rightarrow \underset{\text{white ppt.}}{AgCl(s)} + NaNO_3\,(aq)$$

(iii) Neutralisation reaction : Reaction between strong acid and a strong base to give salt and water is called neutralisation reactions.

$$\underset{\text{Strong Acid}}{H_2SO_4} + \underset{\text{Strong Base}}{2NaOH} \rightarrow \underset{\text{Salt}}{Na_2SO_4} + \underset{\text{Water}}{2H_2O}$$

(iv) Redox and combustion reactions :

$$SnCl_2 + 2FeCl_3 \rightarrow SnCl_4 + 2FeCl_2$$

$$2Mg + O_2 \longrightarrow 2MgO$$

REVERSIBLE REACTION

The chemical reactions which take place in both directions i.e. in the forward direction as well as in backward direction under similar conditions are called reversible reactions.

Forward direction ⇒ Left to right ($\rightharpoonup$)
Backward direction ⇒ Right to left ($\leftharpoondown$)

Reactions which proceed in both the directions and does not reach to completion are called reversible reactions.

Characteristics of Reversible Reaction :

(i) In these reactions arrow (→) is replaced by two half arrows ($\rightleftharpoons$) pointing the reaction in both the directions.

Reactants $\rightleftharpoons$ Products

(ii) Always carried out in closed vessel.

(iii) The reaction never reaches to completion.

(iv) Characterised by the establishment of equilibrium.

(v) Reactions occurs in both the directions.

Examples of Reversible Reactions :

(i) Reaction between gases in closed vessel :

$$2\,SO_2\,(g) + O_2\,(g) \rightleftharpoons 2\,SO_3\,(g) + x\text{ k.cal}$$

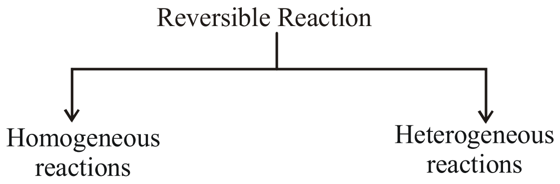
$$N_2\,(g) + 3\,H_2\,(g) \rightleftharpoons 2NH_3(g) + x\text{ k.cal}$$

(ii) Thermal decomposition reactions :

$$CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g) + x\text{ k.cal}$$

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

TYPES OF REVERSIBLE REACTIONS



(A) Homogeneous Reactions : The reversible reaction in which only one phase is present i.e. all the reactants and the products are in same physical state.

Example : $H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$

$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5\,(\ell) + H_2O\,(\ell)$

Homogeneous reactions are of three types.

(i) First Type : When there is no change in number of molecules ($\Delta n = 0$)

Example : $H_2(g) + I_2\,(g) \rightleftharpoons 2HI\,(g)$
$2\,NO(g) \rightleftharpoons N_2(g) + O_2(g)$

(ii) Second Type : When there is increase in number of molecules. ($\Delta n > 0$)

Example : $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$
$2NH_3\,(g) \rightleftharpoons N_2(g) + 3H_2(g)$

(iii) Third Type : When there is decrease in number of molecules. ($\Delta n < 0$)

Example : $N_2\,(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
$2SO_2\,(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

(B) Heterogeneous Reactions : The reversible reaction in which more than one phases is present.

Example : $MgCO_3\,(s) \rightleftharpoons MgO(s) + CO_2(g)$
$3Fe\,(s) + 4\,H_2O\,(\ell) \rightleftharpoons Fe_3O_4\,(s) + 4\,H_2(g)$

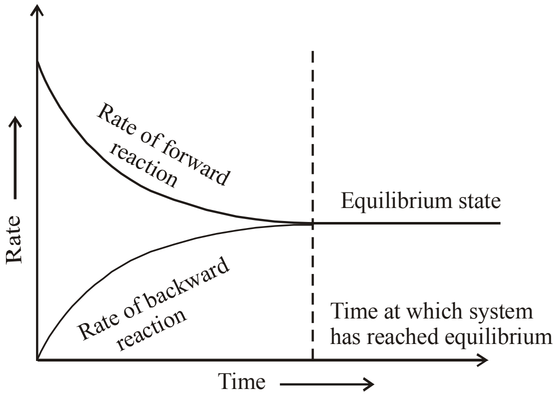
EQUILIBRIUM

Equilibrium is the state at which the concentration of reactants and products do not change with time i.e., concentrations of reactants and products become constant.

At equilibrium state:

(i) Rate of forward reaction (R_f)=Rate of backward reaction (R_b)

(ii) The stage of the reversible reaction at which the concentrations of the reactants and products do not change with the time.



Characteristics of Equilibrium State :

- Equilibrium state can only be achieved if a reversible reaction is carried out in closed vessel.
- Free energy change is zero $\Delta G^\circ = 0$.
- Equilibrium is dynamic in nature.
- Chemical Equilibrium can be attained from either of the side i.e. from side of reactants or products.

$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

or $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

Types of equilibrium :

Equilibrium in a system implies the existence of the following types of equilibrium simultaneously.

1. **Thermal equilibrium:** There is no flow of heat from one part to another i.e. T = constant.
2. **Mechanical equilibrium:** There is no flow of matter from one part to another i.e. P = constant.
3. **Physical equilibrium:** It is a state of equilibrium between the same chemical species in different phases (solid, liquid and gaseous)
4. **Chemical equilibrium:** There is no change in composition of any part of the system with time.

Physical equilibrium :

Thevarious equilibrium which can exist in any physical system are,

Solid $\rightleftharpoons$ Liquid
Liquid $\rightleftharpoons$ Vapour
Solid $\rightleftharpoons$ Gas (vapour)
Solid $\rightleftharpoons$ Saturated solution of solid in a liquid
Gas (vapour) $\rightleftharpoons$ Saturated solution of gas in a liquid

(i) **Solid-liquid equilibrium :**

$H_2O(s) \rightleftharpoons H_2O(\text{liquid})$

Rate of transfer of molecules from ice to water
= Rate of transfer of molecules from water to ice

Rate of melting of ice= Rate of freezing of water

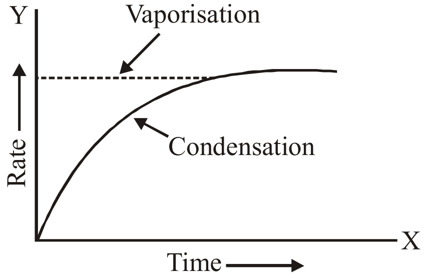
(ii) **Liquid-vapour equilibrium :** When vapour of a liquid exists in equilibrium with the liquid, then

Rate of vaporisation = Rate of condensation,

$H_2O(\text{liquid}) \rightleftharpoons H_2O(\text{vapour})$

Conditions necessary for a liquid-vapour equilibrium

(a) The system must be a closed system i.e., the amount of matter in the system must remain constant.
(b) The system must be at a constant temperature.



(c) The visible properties of the system should not change with time.

(iii) Solid-vapour equilibrium: Certain solid substances on heating get converted directly into vapour without passing through the liquid phase. This process is called sublimation. The vapour when cooled, gives back the solid, it is called disposition.

Solid $\rightleftharpoons$ Vapour

The substances which undergo sublimation are camphor, iodine, ammonium chloride etc.

For example, Ammonium chloride when heated sublimes.

$$NH_4Cl\,(\text{solid}) \underset{\text{Cool}}{\overset{\text{Heat}}{\rightleftharpoons}} NH_4Cl\,(\text{vapour})$$

(iv) Equilibrium between a solid and its solution: When a saturated solution is in contact with the the solid solute, there exists a dynamic equilibrium between the solid and the solution phase.

Solid substance $\rightleftharpoons$ Solution of the substance

Example: Sugar and sugar solution. In a saturated solution, a dynamic equilibrium is established between dissolved sugar and solid sugar.

Sugar (solid) $\rightleftharpoons$ Sugar (aqueous)

At the equilibrium state, the number of sugar molecules going into the solution from the solid sugar is equal to the number of molecules precipitating out from the solution, i.e., at equilibrium,

Rate of dissolution of solid sugar
= Rate of precipitation of sugar from the solution.

(v) Equilibrium between a gas and its solution in a liquid: Gases dissolve in liquids. The solubility of a gas in any liquid depends upon the,

(a) Nature of the gas and liquid.
(b) Temperature of the liquid.
(c) Pressure of the gas over the surface of the solution.

LAW OF CHEMICAL EQUILIBRIUM

Law of Mass Action : At a given temperature, the rate of reaction at a particular instant is proportional to the product of the active masses of the reactants at that instant raised to power which are numerically equal to their respective molecules in stoichiometric equation describing the reaction.

For the reaction : $nA + mB \rightleftharpoons zC + wD$

According to law of mass action

$R_f \propto [A]^n [B]^m$; $R_b \propto [C]^z [D]^w$

$R_f = K_1 [A]^n [B]^m$; $R_b = K_2 [C]^z [D]^w$

At equilibrium : $R_f = R_b$

$K_1 [A]^n [B]^m = K_2 [C]^z [D]^w$

$$\frac{K_1}{K_2} = \frac{[C]^z [D]^w}{[A]^n [B]^m} = \frac{[\text{Product}]}{[\text{Reactant}]}$$

Finally K_c (equilibrium constant) $= \dfrac{K_1}{K_2} = \dfrac{R_f}{R_b} = \dfrac{K_f}{K_b}$

Example 1 :

The equilibrium constant of a reaction is 20.0. At equilibrium, the rate constant of forward reaction is 10.0. Find the rate constant for backward reaction.

Sol. $K_c = 20 \quad K_f = 10, K_b = ?$

$$K_c = \frac{K_f}{K_b} \;;\; 20 = \frac{10}{K_b} \quad \therefore\; K_b = \frac{10}{20} = 0.5$$

EXPRESSION OF K_c

Let 'a' moles of PCl_5 be taken in a closed vessel of volume 'v' litre. Suppose 'x' mole is dissociated at equilibrium.

	$PCl_5(g)$	$\rightleftharpoons$ $PCl_3(g)$	$+ \; Cl_2(g)$
Initial concentration	a	0	0
At equilibrium	$a-x$	x	x
Active mass	$\dfrac{a-x}{v}$	$\dfrac{x}{v}$	$\dfrac{x}{v}$

According to law of mass action

$$K_c = \frac{[\text{Product}]}{[\text{Reactant}]} \;;\; K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

$$K_c = \frac{\frac{x}{v} \times \frac{x}{v}}{\frac{a-x}{v}} = \frac{x^2}{(a-x)v}$$

when a = 1, x becomes degree of dissociation (fraction of one mole dissociated into the products)

$$K_c = \frac{x^2}{(1-x)v}.$$

according to ostwald dilution law $v \propto 1/C$

Hence : $K_c = \dfrac{\alpha^2 C}{(1-\alpha)}$

EQUILIBRIUM CONSTANT IN TERMS OF PRESSURE

It is denoted by K_P

$$\text{Partial pressure} = \frac{\text{no. of moles}}{\text{Total moles}} \times \text{Total pressure}$$

Example: $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

	PCl_5	PCl_3	Cl_2
Initial moles no. of	1	0	0
Moles of equilibrium	$1-x$	x	x

Total moles $1 - x + x + x = 1 + x$

$$P_{PCl_5} = \frac{1-x}{1+x} \times P \;;\; P_{Cl_2} = \frac{x}{1+x} \times P \;;\; P_{PCl_3} = \frac{x}{1+x} \times P$$

$$K_P = \frac{P_{PCl_3} \cdot P_{Cl_2}}{P_{PCl_5}}$$

Unit of equilibrium constant :

Unit of K_c = $(\text{Concentration})^{\Delta n}$

Unit of K_p = $(\text{atm})^{\Delta n}$

Δn = no. of moles of gaseous product – no. of moles of gaseous reactant

Relation between K_P & K_c

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

Example I : When $\Delta n = 0$

$K_p = K_c (RT)^0$ $\quad \therefore K_p = K_c$

$N_2 + O_2 \rightleftharpoons 2NO$ $\quad (\Delta n = 0)$

Example II : When $\Delta n = +ve$ $\quad \Delta n > 0$

$K_p > K_c$

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $\quad (\Delta n = +1)$

Example III : When $\Delta n = -ve$ $\quad \Delta n < 0$

$K_p < K_c$

$N_2 + 3H_2 \rightleftharpoons 2NH_3$ $\quad (\Delta n = -2)$

Example 2 :

The unit of K_c for the reaction : $2SO_3 \rightleftharpoons 2SO_2 + O_2$

(A) $\text{mole}^2\ \text{lit}^{-2}$ (B) mole per litre

(C) mole x litre (D) litre per mole

Sol. **(B).** Unit fo $K_c = [M]^{\Delta n}$, where M = mole/litre

Δn = Number of gaseous mole of product – Number of gaseous mole of reactant

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

$\therefore$ unit of $K_c = [\text{mole/litre}]^1$ = mole per litre.

Example 3 :

In which of the following reaction $K_p > K_c$

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

(B) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(C) $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$

(D) $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$

Sol. **(D).** Value of K_p is greater then K_c for those reaction in which $\Delta n > 0$

Here for the reaction

$2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$; $\Delta n = 3 - 2 = 1 > 0$

Therefore $K_p > K_c$ for this reaction

Example 4 :

At 1000K, the value of K_p for the reaction :

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is 20R, then find K_c.

Sol. $K_p = 20R$ (given)

for the reaction $\Delta n = (2 - 1) = 1$

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

$20\,R = K_c (RT)^1$

$$\therefore \quad K_c = \frac{20\,R}{R \times 1000} = 0.02$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

(i) The expression for equilibrium constant, K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.

(ii) The value of equilibrium constant is independent of initial concentration of the reactants and product.

(iii) Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.

(iv) If reaction is performed in multiple steps

$A \rightleftharpoons B$; overall reaction

Step-1 : $A\,(g) \rightleftharpoons C\,(g) + D\,(g)$ $\qquad K_{p_1}$

Step-2 : $C\,(g) \rightleftharpoons E\,(g)$ $\qquad K_{p_2}$

Step-3 : $D\,(g) + E\,(g) \rightleftharpoons B\,(g)$ $\qquad K_{p_3}$

$A\,(g) \rightleftharpoons B\,(g) \quad K_p$ then $K_p = K_{p_1} \cdot K_{p_2} \cdot K_{p_3}$

Factors which influence the equilibrium constant:

(a) **Mode of representation of reaction :**

If we take reaction $2HI \rightleftharpoons H_2 + I_2$

Then, we write the value of equilibrium constant K_{C_1}, for the above reaction as following :

$$K_{C_1} = \frac{[H_2][I_2]}{[HI]^2} \qquad \text{.........}\ (1)$$

Now, if we take reaction $H_2 + I_2 \rightleftharpoons 2HI$

Then, we write the value of equilibrium constant K_{C_2} for above reaction as following

$$K_{C_2} = \frac{[HI]^2}{[H_2][I_2]} = \frac{1}{K_{C_1}} \qquad \text{.........}\ (2)$$

(b) **Stoichiometry of the reaction :**

Method of writing the equation of the reversible reaction is called as stoichiometry of the reaction.

Now, we consider the formation of HI(g) by the combination of H_2(g) and I_2 (g).

$$H_2 + I_2 \xrightleftharpoons{\Delta} 2HI$$

The expression of its equilibrium constant is-

$$K_{C_1} = \frac{[HI]^2}{[H_2][I_2]}$$

If the equation of above reaction is written by following

$$\frac{1}{2}H_2\,(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI\,(g)$$

The expression for the equilibrium constant is -

$$K_{C_2} = \frac{[HI]}{[H_2]^{1/2}\,[I_2]^{1/2}}$$

On the basis of comparing both the equilibrium constant equation. $K_{C_2} = \sqrt{K_{C_1}}$ or $(K_{C_1})^{1/2}$

Note : When we divide a reaction by a factor 'n' in the equation, the value of new equilibrium constant is equal to the root of n of the previous equilibrium constant.

For Example, Suppose, the equilibrium constant for the following reaction : $A + B \rightleftharpoons C + D$ is K_1 then

for the reaction : $\frac{1}{n}A + \frac{1}{n}B \rightleftharpoons \frac{1}{n}C + \frac{1}{n}D$

The value of the equilibrium constant K_2 is equal to

$\sqrt[n]{K_1}$ or $(K_1)^{1/n}$; $K_2 = K_1^{1/n}$

Example 5 :

At a given temperature, the equilibrium constant for the reactions : $NO\,(g) + ½\,O_2\,(g) \rightleftharpoons NO_2\,(g)$ and $2\,NO_2\,(g) \rightleftharpoons 2\,NO\,(g) + O_2\,(g)$ are K_1 and K_2 respectively. If K_1 is 4×10^{-3}, then find K_2.

Sol. $NO\,(g) + \frac{1}{2}\,O_2(g) \rightleftharpoons NO_2(g)$

$$K_1 = \frac{[NO_2]}{[NO][O_2]^{1/2}} = 4 \times 10^{-3}$$

Now for reaction $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$$K_2 = \frac{[NO]^2[O_2]}{[NO_2]^2} = \frac{1}{K_1^2} = \frac{1}{(4 \times 10^{-3})^2} = 6.25 \times 10^4$$

(c) **Temperature :** Increase in temperature favours the endothermic reaction and decrease in temperature favours the exothermic reaction for the forward reaction so for exothermic reactions, the value of K_c and K_p decrease with rise in temperature while for endothermic reactions, the value of K_c and K_p increases with rise in temperature. This type of variation in equilibrium constant with temperature given by Van't Hoff equation as follows :

$$\frac{\Delta H}{RT^2} = \frac{d\,(\ln K)}{dT}$$

After integration,

$$\log K_2 - \log K_1 = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

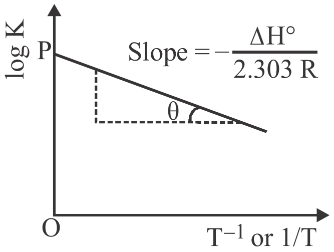
or $$\log\frac{K_2}{K_1}=\frac{\Delta H}{2.303R}\left[\frac{1}{T_1}-\frac{1}{T_2}\right]$$

Where, K_2 = equilibrium constant at temperature T_2

K_1 = equilibrium constant at temperature T_1

ΔH = Energy of reaction of constant temperature

R = Molar gas constant



According to the temperature, reaction are of three types.

(i) Non-thermic reaction means $\Delta H = 0$

$\log K_2 - \log K_1 = 0$; $\log K_2 = \log K_1$

There is no effect of temperature on this type of reaction.

(ii) Endothermic reaction $\Rightarrow \Delta H = (+)$ ve

$\log K_2 - \log K_1 = (+)$ ve, means $K_2 > K_1$

On increasing of temperature, equilibrium constant will also increase for this type of reaction.

(iii) Exothermic reaction $\Rightarrow \Delta H = (-)$ ve

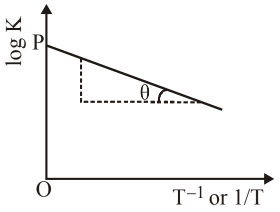
$\log K_2 - \log K_1 = (-)$ ve, means $K_2 < K_1$

On the increase of temperature equilibrium constant will decreases for exothermic reaction.

Example 6 :

Variation of equilibrium constant K with temperature T is given by van't Hoff equation, $\log K = \log A - \frac{\Delta H^\circ}{2.303RT}$.

A graph between log K and T^{-1} was a straight line as shown in the figure and having $\theta = \tan^{-1}(0.5)$ and OP = 10. Calcualte



(a) ΔH° (standard heat of reaction) when T = 300 K

(b) A (pre-exponential factor)

(c) Equilibrium constant K, at 300 K,

(d) K at 900K if ΔH° is independent of temperature.

Sol. (a) $\log_{10}K = \log_{10}A - \frac{\Delta H^\circ}{2.303RT}$

It is an equation of a straight line of the type y = c + mx

$$\text{Slope } m = \tan\theta = \frac{\Delta H^\circ}{2.303R}$$

$$0.5 = \frac{\Delta H^\circ}{2.303\times 8.314}\ ;\ \Delta H^\circ = 9.574\ \text{J mol}^{-1}$$

(b) Intercept 'c' = $\log_{10}A = 10\ \therefore\ A = 10^{10}$

(c) $\log K = 10 - \frac{9.574}{2.303\times 8.314\times 298}$; $K = 9.96\times 10^9$

(d) $$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left\{\frac{1}{T_1}-\frac{1}{T_2}\right\}$$

$$\log\frac{K_2}{9.96\times 10^9} = \frac{9.574}{2.303\times 8.314}\left\{\frac{1}{298}-\frac{1}{798}\right\}$$

On solving, $K_2 = 9.98\times 10^9$

EQUILIBRIUM CONSTANT EXPRESSIONS FOR REACTIONS

Case I : Homogeneous gaseous equilibria when (Δ n = 0)

Synthesis of hydrogen iodide

(a) Calculation of K_c : Suppose the initial concentration of H_2 and I_2 is 'a' and 'b' respectively, x is degree of dissociation and 'v' is volume in litre of container.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial conc.	a	b	0
Moles at equilibrium	a – x	b – x	2x
Active mass	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{2x}{v}$

According to law of mass action.

$$K_c = \frac{[HI]^2}{[H_2][I_2]}\ ;\ K_c = \frac{[2x/v]^2}{\left[\frac{a-x}{v}\right]\left[\frac{b-x}{v}\right]} = \frac{4x^2}{(a-x)(b-x)}$$

(b) Calculation of K_p : The equilibrium constant K_p, can also be calculated considering partial pressure of reactants and products at equilibrium.

	$H_2(g)$ +	$I_2(g)$ $\rightleftharpoons$	$2HI(g)$
Initial concentration	a	b	0
Moles at equilibrium	a – x	b – x	2x

Total number of moles at equilibrium

$= (a-x)+(b-x)+2x = (a+b)$

Let the total pressure of the system at equilibrium be P atmosphere.

Partial pressure of H_2 $\quad P_{H_2} = \frac{(a-x)}{(a+b)}P$

Partial pressure of I_2 $\quad P_{I_2} = \left(\frac{b-x}{a+b}\right)P$

Partial pressure of HI $\quad P_{HI} = \left(\frac{2x}{a+b}\right)P$

$$\text{Therefore, } K_p = \frac{\left(\frac{2x}{a+b}\right)^2 P^2}{\left(\frac{a-x}{a+b}\right)P\times\left(\frac{b-x}{a+b}\right)P} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{4x^2}{(a-x)(b-x)}$$

This also follows the relation $_p = K_c (RT)^{\Delta n}$
Here, $\Delta n = 0 ; K_p = K_c$
i.e. for all gaseous reaction of this type, K_p and K_c are equal and have no units.

(i) Effect of pressure : $K_c \propto \text{pressure}^0$
As the equation does not include volume term, K_c is independent of pressure.

(ii) Effect of adding substances : (Reactant and products)
On adding reactant rate of forward reaction increase on adding product rate of backward reaction increase
Concentration of reactant ↑ Rate of forward reaction ↑
Concentration of product ↑ Rate of backward reaction ↑

(iii) Effect of temperature : The formation of HI from H_2 and I_2 is an exothermic reaction i.e. by increasing temperature the value of K_c decreases.
As $T\uparrow$, $K_c\downarrow$ (exothermic reaction)

Case II : Homogeneous gaseous reactions when $\Delta n > 0$
Dissociation of PCl_5

(a) Calculation of K_c : Let 'a' moles of PCl_5 be taken in a closed vessel of volume 'v' litre. Suppose 'x' mole is dissociated at equilibrium.

	$PCl_5(g)$	$\rightleftharpoons PCl_3(g)$	$+ Cl_2(g)$
Initial concentration	a	0	0
At equilibrium	$a-x$	x	x
Active mass	$\frac{a-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

According to law of mass action

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} \; ; \; K_c = \frac{\frac{x}{v}\times\frac{x}{v}}{\frac{a-x}{v}} = \frac{x^2}{(a-x)v}$$

when a = 1, x becomes degree of dissociation

$$K_c = \frac{x^2}{(1-x)v}$$

(b) Calculation of K_p : Let the total pressure at equilibrium be P. Then total number of moles at equilibrium

$$= (a-x)+x+x = a+x$$

The partial pressure of each reactant and product

$$p_{PCl_5} = \left(\frac{a-x}{a+x}\right)P \; ; \; p_{Cl_2} = \left(\frac{x}{a+x}\right)P \; ; \; p_{PCl_3} = \left(\frac{x}{a+x}\right)P$$

Applying law of mass action

$$K_P = \frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{x}{a+x}\right)P\times\left(\frac{x}{a+x}\right)P}{\left(\frac{a-x}{a+x}\right)P} = \frac{x^2 P}{(a-x)(a+x)}$$

when a = 1, $K_p = \frac{x^2 P}{1-x^2}$

(i) Effect of pressure : $K_p = \frac{x^2 P}{1-x^2}$

Suppose $x <<< 1$ then $1 - x^2 = 1$

$$K_p = x^2 P \; ; x^2 \propto \frac{1}{P} \; ; x \propto \frac{1}{\sqrt{P}} \quad P\downarrow, x\uparrow$$

Degree of dissociation of PCl_5 is inversely proportional to square root of pressure so decrease in pressure increase dissociation of PCl_5

(ii) Effect of concentration :
Concentration of PCl_5 ↑ Rate of forward reaction ↑
Concentration of PCl_3 & Cl_2 ↑Rate of backward reaction ↑

(iii) Effect of temperature : The dissociation of PCl_5 is endothermic reaction. The value of equilibrium constant increase with increase in temperature
K α T As $T\uparrow, K\uparrow$

Case III : Homogeneous gaseous reaction $\Delta n < 0$
Synthesis of Ammonia

(a) Calculation of K_c :

	$N_2(g)$	$+ \; 3H_2(g)$	$\rightleftharpoons \; 2NH_3(g)$
Initial conc.	a	b	0
Moles at eq.	$a-x$	$b-3x$	2x
Active mass	$\frac{a-x}{v}$	$\frac{b-3x}{v}$	$\frac{2x}{v}$

Applying law of mass action

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

$$K_c = \frac{[2x/v]^2}{\left[\frac{a-x}{v}\right]\left[\frac{b-3x}{v}\right]^3} = \frac{4x^2/v^2}{\left[\frac{(a-x)}{v}\right]\left[\frac{b-3x}{v}\right]^3}$$

If a = 1 and b = 3 then $K_c = \frac{4x^2v^2}{27(1-x)^4}$

If $x <<< 1$ then $(1-x)^4 = 1$

$$K_c = \frac{4x^2v^2}{27} \; ; x^2 \propto \frac{1}{v^2} \; ; \; x \propto \frac{1}{v^2}$$

(b) Calculation of K_p :
Let total pressure at equilibrium be P.
Total no. of moles at equilibrium

$$= (a-x)+(b-3x)+2x = (a+b-2x)$$

$$p_{NH_3} = \frac{2x}{(a+b-2x)}\times P \; ; \; p_{N_2} = \frac{a-x}{(a+b-2x)}\times P$$

$$p_{H_2} = \frac{b-3x}{(a+b-2x)}\times P$$

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

If a = 1 and b = 3 then $K_p = \dfrac{16x^2(2-x)^2}{27(1-x)^4P^2}$

Suppose x <<< 1 then $(1-x)^4 = 1;\ (2-x)^2 = 4$

$$K_p = \frac{64x^2}{27P^2}\ ;\ x^2 \propto P^2\ ;\ x \propto P$$

(i) **Effect of pressure :** With increase in pressure the volume term decrease therefore x increase.
$P\uparrow \quad V\downarrow \quad x\uparrow$

(ii) **Effect of temperature :** On increasing temperature value of equilibrium constant decreases.
$T\uparrow \quad K\downarrow$ exothermic reaction

Case IV : Homogeneous liquid system :

Formation of ethyl acetate

$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$

Initial conc.				
	a	b	0	0
Moles at eq.				
	a – x	b – x	x	x
Active mass				
	$\frac{a-x}{v}$	$\frac{b-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

Applying law of mass action

Here V = total volume

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{[x/v]\times[[x/v]}{\left[\frac{a-x}{v}\right]\times\left[\frac{b-x}{v}\right]}$$

$$K_c = \frac{x^2}{(a-x)\,(b-x)}.\quad \text{If } a = b = 1 \text{ then } K_c = \frac{x^2}{(1-x)^2}$$

This does not involve volume term thus K_c is not affected by change in volume $K_c \propto V^0$

Case V : Heterogeneous Equilibrium

The decomposition of solid $NaHCO_3$ to produce solid Na_2CO_3, CO_2 gas and H_2O.

$2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$

Applying law of mass action

$$K_c' = \frac{[Na_2CO_3][H_2O][CO_2]}{[NaHCO_3]^2}$$

It involves two pure solids, Na_2CO_3 and $NaHCO_3$. It is customary not to include concentration of pure solid in equilibrium expression.

$$\frac{K_c'[NaHCO_3]^2}{[Na_2CO_3]} = [CO_2]\,[H_2O]$$

$$K_c = [CO_2]\,[H_2O]$$

Example 7 :

For the reaction $N_2O_4 \rightleftharpoons 2NO$, degree of dissociation is α. Find the number of moles at equilibrium.

Sol.

	N_2O_4	$\rightleftharpoons 2NO$
Initially	1	0
Moles at equilibrium	1 – α	2α

∴ Total number of moles at equilibrium
= 1 – α + 2α = 1 + α

Example 8 :

4 mole of A are mixed with 4 mole of B, when 2 mole of C are formed at equilibrium according to the reaction,
$A + B \rightleftharpoons C + D$. Find the equilibrium constant.

Sol.

	A +	B	C +	D
Initially	4	4	0	0
At equilibrium	4 – α	4 – α	α	α

Given at equilibrium mole of C = 2 (∴ α = 2)

∴ [A] = 4 – 2 = 2 mole; [B] = 4 – 2 = 2 mole
[D] = α = 2 mole

$$K_c = \frac{[C][D]}{[A][B]} = \frac{2\times2}{2\times2} = 1$$

Example 9 :

At a certain temperature, $2HI \rightleftharpoons H_2 + I_2$ only 50% HI is dissociated at equilibrium. Find the equilibrium constant.

Sol.

	2HI $\rightleftharpoons$	H_2 +	I_2
Initially	1	0	0
Moles at equilibrium	1 – α	α/2	α/2

50% of HI is dissociated therefore α = .5

$[HI] = 1 - 0.5 = 0.5\ ;\ [H_2] = 0.5/2\ ;\ [I_2] = 0.5/2$

$$K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.5/2\times0.5/2}{[0.5]^2} = \frac{1}{4} = 0.25$$

Example 10 :

One mole of ethyl alcohol was treated with one mole of acetic acid at 25 °C. 2/3 of the acid changes into ester at equilibrium. Find the equilibrium constant for the reaction of hydrolysis of ester

Sol. $C_2H_5OH(\ell) + CH_3COOH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$

Initially	1	1	0	0
Moles at equilibrium				
	1 – α	1 – α	α	α

Given α = 2/3

Therefore, $C_2H_5OH = 1 - 2/3 = 1/3$
$CH_3COOH = 1 - 2/3 = 1/3$
$CH_3COOC_2H_5 = 2/3,\ H_2O = 2/3$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{2/3\times2/3}{1/3\times1/3} = 4$$

Example 11 :

For the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the partial pressures of CO_2 and CO are 2.0 and 4.0 atm respectively at equilibrium. Find the K_p for the reaction

Sol. $K_p = \dfrac{[p_{co}]^2}{[p_{co_2}]} = \dfrac{[4]^2}{[2]} \quad ∴ \quad K_p = 8$

REACTION QUOTIENT AND EQUILIBRIUM CONSTANT

Consider the following reversible reaction

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

The reaction quotient (Q_c) is the ratio of the product of active masses of the products and product of active masses of the reactants.

$$\therefore \quad Q_c = \frac{[C][D]}{[A][B]}$$

The concentration are not necessarily equilibrium concentration.

[At equilibrium $Q_c = K_c$]

Case I : If $Q_c < K_c$ then : [Reactants] > [Products] then the system is not at equilibrium.

The value of $\frac{[\text{Product}]}{[\text{Reactant}]}$ is small.

$\therefore$ For establishment of equilibrium the reaction will go in forward direction. [Reactants → Products]

Case II : If $Q_c = K_c$ then :

The system is at equilibrium and the concentration of the species C, D, B,A are at equilibrium.

Case III : If $Q_c > K_c$ then : [Products] > [Reactants]

The system is not at equilibrium.

The value of $\frac{[\text{Product}]}{[\text{Reactant}]}$ is large

$\therefore$ For establishment of equilibrium the reaction will go in backward direction [Products → Reactants]

Note : Suppose there are three reaction having equilibrium constant K_1, K_2 and K_3 and $K_1 > K_2 > K_3$

Hence the order of the tendency of the reaction to proceed in forward direction (i.e. formation of product)

Reaction 1 > Reaction 2 > Reaction 3

In short, $K \uparrow$, forward reaction $\uparrow$

Example 12 :

For the reaction $NOBr\,(g) \rightleftharpoons NO\,(g) + \frac{1}{2} Br_2\,(g)$

$K_p = 0.15$ atm at 90°C. If NOBr, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2atm respectively, will Br_2 be consumed or formed ?

Sol. $$Q_p = \frac{[P_{Br_2}]^{1/2}\,[P_{NO}]}{[P_{NOBr}]} = \frac{[0.2]^{1/2}[0.4]}{[0.50]} = 0.36$$

$K_p = 0.15 \quad \therefore \quad Q_p > K_p$

Hence, reaction will shift in backward directioin.

$\therefore$ Br_2 will be consumed

TRY IT YOURSELF-1

Q.1 At 500°C, the equilibrium constant for the reaction, $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$ is 6.02×10^{-2} mol^{-2} L. What is the value of K_p at the same temperature?

Q.2 For the reaction A + 3B ⇌ 2C + D, initial mole of A is twice that of B. If at equilibrium moles of B and C are equal, then percent of B reacted is –

(A) 10% (B) 20%

(C) 40% (D) 60%

Q.3 $N_2 + O_2 \rightleftharpoons 2NO$ has equilibrium constant 2.5×10^{-5}, calculate equilibrium constant for the reaction

$NO \rightleftharpoons \frac{1}{2} N_2 + \frac{1}{2} O_2$.

Q.4 For the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, equilibrium molar concentrations of SO_2 and SO_3 are equal and equilibrium constant is equal to 10. If reaction takes place in a 5 litre vessel then calculate equilibrium mole of O_2.

Q.5 For the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$.

The moles of each component PCl_5 , PCl_3 and Cl_2 at equilibrium were found to be 2. If the total pressure is 3atm. The K_p will be –

(A) 1 atm (B) 2 atm

(C) 3 atm (D) 1.5 atm

Q.6 In a reaction vessel of 2 litre capacity 3 moles of N_2 reacts with 2 moles of O_2 to produce 1 mole of NO. What is the molar concentration of N_2 at equilibrium?

(A) 1.25 (B) 1.50

(C) 0.75 (D) 2.0

Q.7 At 87°C, the following equilibrium is established

$H_2(g) + S\,(s) \rightleftharpoons H_2S\,(g)$; $K_p = 7 \times 10^{-2}$

If 0.50 mole of hydrogen and 1.0 mole of sulphur are heated to 87°C in 1.0 L vessel, what will be the partial pressure of H_2S at equilibrium?

(A) 0.966 atm (B) 1.38 atm

(C) 0.0327 atm (D) 9.66 atm

Q.8 At a certain temperature the equilibrium constant K_c is 0.25 for the reaction $A_2(g) + B_2(g) \rightleftharpoons C_2(g) + D_2(g)$

If we take 1 mole of each of the four gases in a 10 litre container, what would be equilibrium concentration of $A_2(g)$

Q.9 Consider following reactions in equilibrium with equilibrium concentration 0.01 M of every species

(I) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$.

(II) $2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$.

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

Extent of the reactions taking place is –

(A) I > II > III (B) I < II < III

(C) II < III < I (D) III < I < II

Q.10 1 mole N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained. $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$. The equilibrium constant K_p for dissociation of NH_3 is –

(A) $\frac{1}{0.5} \times (1.5)^3\ atm^{-2}$ (B) $0.5 \times (1.5)^3\ atm^2$

(C) $\frac{0.5 \times (1.5)^3}{3 \times 3}\ atm^2$ (D) $\frac{3 \times 3}{0.5 \times (1.5)^3}\ atm^{-2}$

Q.11 For the reaction, $2NO_2\,(g) \rightleftharpoons 2NO\,(g) + O_2\,(g)$.

$K_c = 1.8 \times 10^{-6}$ at 184°C and R = 0.083 $JK^{-1}\,mol^{-1}$. When K_p and K_c are compared at 184°C, it is found that –

(A) $K_p > K_c$ (B) $K_p < K_c$

(C) $K_p = K_c$ (D) $K_p \gtrless K_c$ depends upon pressure of gases

Q.12 A 20.0 litre vessel initially contains 0.50 mole each of H_2 and I_2 gases. These substances react with finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if $K_{eq} = 49$ for the reaction
$H_2 + I_2 \rightleftharpoons 2HI$

(A) 0.78 M (B) 0.039 M
(C) 0.033 M (D) 0.021 M

ANSWERS

(1) 1.5×10^{-5} atm^{-2}. **(2)** (D) **(3)** 2×10^2 **(4)** 0.5 mole
(5) (A) **(6)** (A) **(7)** (A) **(8)** 0.13 **(9)** (B)
(10) (B) **(11)** (A) **(12)** (B)

LECHATELIER'S PRINCIPLE

According to this principle, "If a system at equilibrium is subjected to a change of concentration, pressure or temperature, the equilibrium shift in a direction that tends to undo the effect of the change".

(A) **Effect of change in concentration :** In a chemical equilibrium, increasing the concentration of the reactants result in shifting the equilibrium in favour of products (i.e. equilibrium shift in forward direction). Increasing concentration of the products results in shifting the equilibrium in favour of reactants (i.e in the backward direction).

Concentration	**Equilibrium shift**
Concentration of reactant ↑	Forward direction
Concentration of product ↑	Backward direction

(B) **Effect of change in pressure :** If the pressure is increased reaction will take place in that direction, which will bring lowering of pressure or lowering in number of mole.

(i) Increase of pressure shifts the equilibrium in that direction where number of moles decreases. ($\Delta n < 0$)
eg. $N_2 + 3H_2 \rightleftharpoons 2NH_3$; $\Delta n = 2 - 4 = -2 < 0$
i.e. on ↑ pressure equilibrium shift in forward direction.

(ii) Decrease of pressure shifts the equilibrium in that direction where number of mole increase. ($\Delta n > 0$)
eg. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ $\Delta n = 2 - 1 = +ve$
i.e. ↓ in pressure equilibrium shift in forward direction

(iii) Change of pressure has no effect if $\Delta n = 0$
eg. $H_2 + I_2 \rightleftharpoons 2HI$; $\Delta n = 2 - 2 = 0$

Note : Addition of an inert gas at constant pressure has the same effect as produced by the increased volume of the container. Thus, for equilibrium $\Delta n = 0$, when an inert gas is added at constant pressure, the equilibrium remains unaffected (since V does not appear in the expression of K_p) while for equilibrium having $\Delta n \neq 0$, the addition of an inert gas at constant pressure causes reaction to move in the direction of more moles of the gases.

(C) **Change in temperature :**

(i) **For endothermic reaction :** If we increase the temperature equilibrium shift in forward direction which proceed with absorption of heat.

(ii) **For exothermic reaction :** If we increased the temperature the equilibrium shifts in backward direction which proceed with evolution of the heat.

(D) **Role of Catalyst :** Positive catalyst increase the rate of both the forward and backward reaction equally so the equilibrium will be attained in less time. Negative catalyst decrease the rate of both forward and backward reaction so equilibrium will be attained in more time.

Application of Le Chatelier principle on physical equilibria:

1. **Melting of Ice :**

$$\underset{\substack{\text{Ice}\\ \text{(More volume)}}}{H_2O\,(s)} \overset{0°C}{\rightleftharpoons} \underset{\substack{\text{Water}\\ \text{(Less volume)}}}{H_2O\,(\ell)}$$

With increase in pressure melting point of ice is decreased and equilibrium will be shifted in a direction of less volume.

2. **Vapourisation of liquid :**

$$\underset{\substack{\text{Water}\\ \text{(less volume)}}}{H_2O\,(\ell)} \overset{100°C}{\rightleftharpoons} \underset{\substack{\text{Vapour}\\ \text{(more volume)}}}{H_2O\,(g)}$$

Vaporisation of liquid is endothermic process in the nature i.e. the evaporation of liquid in to its vapour is completed by absorption of heat so rise of temperature will favour vaporisation and equilibrium is shifted in forward direction. On the other hand on increasing the pressure the equilibrium will be shifted in direction of less volume means water cannot be converted in to vapour and boiling point increases.

On ↑ temperature	Vaporisation ↑	forward shift
On ↑ pressure	B.P ↑	Backward shift

3. **Melting of Sulphur :**

$$\underset{\text{Less volume}}{\text{Sulphur (s)}} \rightleftharpoons \underset{\text{More volume}}{\text{sulphur }(\ell)}$$

On increasing pressure the equilibrium will shift towards less volume, means solid will be not converted in to liquid, thus melting point of sulphur increases.

Example 13 :

Describe the effect of (a) Addition of H_2 (b) Addition of CH_3OH (c) Removal of CO (d) Removal of CH_3OH on the equilibrium of the reaction :

$$2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$$

Sol. The equilibrium constant for the given reaction is

$$K_c = \frac{[CH_3OH]}{[H_2]^2\,[CO]}$$

(a) Addition of H_2 will push the reaction in the forward direction.

(b) Addition of CH_3OH will push the reaction in the backward direction.

(c) When CO is removed, the reaction will move in the backward direction.

(d) When CH_3OH is removed, the reaction will move in the forward direction.

Example 14 :

The equilibrium constant of the reaction at 25°C

$$CuSO_4.5H_2O\,(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$$

is 1.084×10^{-4} atm^2. Find out under what conditions of relative humidity, $CuSO_4.5H_2O$ will start loosing its water of crystallization according to above reaction.

(Vapour pressure of water at 25°C is 24mm of Hg).

Relative humidity

$$= \frac{\text{Partial pressure of } H_2O \text{ vapours}}{\text{Vapour pressure of } H_2O \text{ at that temperature}}$$

Sol. $K_p = (P_{H_2O})^2$

$$P_{H_2O} = \sqrt{1.084 \times 10^{-4}} = 1.041 \times 10^{-2}\ \text{atm} \approx 8\text{mm of Hg}$$

In a room, pressure of water is greater than 8mm of Hg then $CuSO_4.3H_2O$ will absorb water from air and will form $CuSO_4.5H_2O$ and will keep absorbing until partial pressure of H_2O becomes 8mm of Hg.

If $P_{H_2O} < 8$mm of Hg then $CuSO_4.5H_2O$ will loose water of crystallization and reaction will move in forward direction.

i.e., if relative humidity $< \frac{8}{24} < 33.33\%$

then $CuSO_4.5H_2O$ will loose water of crystallization.

FREE ENERGY CHANGE AND EQUILIBRIUM CONSTANT

Let Δ G° be the difference in free energy of the reaction when all the reactants and products are in standard state (1 atm pressure and 298 K) and K_c and K_p be the thermodynamic equilibrium constant of the reaction. Both are related to each other at temperature T by following relation.

$$\Delta G° = -2.303\ RT \log K_C \ \ \&\ \ \Delta G° = -2.303\ RT \log K_p$$

Equation relates equilibrium constant of a reaction to a thermochemical property.

where $\Delta G° = \Delta H° - T\,\Delta S°$

here $\Delta H°$ = Standard enthalpy change

$\Delta S°$ = Standard entropy change

Three cases may arise : (i) $\Delta G° = 0$ then $K_c = 1$

(ii) $\Delta G° > 0$ i.e. + ve then $K_c < 1$

In this case reverse reaction is feasible i.e. less concentration of products at equilibrium state.

(iii) $\Delta G° < 0$ i.e. –ve then $K_c > 1$

In this case forward reaction is feasible i.e. large concentration of products at equilibrium state.

In short,

Free energy change	Equilibrium constant	Concentration of reactants and Products
$\Delta G° = 0$	$K_c = 1$	Reactants = Products
$\Delta G° > 0$	$K_c < 1$	Reactants > Products
$\Delta G° < 0$	$K_c > 1$	Reactants < Products

Example 15 :

NO and Br_2 at initial partial pressures of 98.4 and 41.3 torr, respectively, were allowed to react at 300 K. At equilibrium the total pressure was 110.5 torr. Calculate the value of the equilibrium constant and the standard free energy change at 300 K for the reaction $2NO(g) + Br_2\,(g) \rightleftharpoons 2NOBr\,(g)$

Sol.

	$2NO(g)$	$+ Br_2\,(g)$	$\rightleftharpoons 2NOBr\,(g)$
Initial pressure	98.4	41.3	0
At equilibrium	$98.4 - x$	$41.3 - \frac{x}{2}$	x

Total pressure at equilibrium is 110.5 torr

$$\therefore\ \ 98.4 - x + 41.3 - \frac{x}{2} + x = 110.5\ ;\ x = 58.4 \text{ torr}$$

Now, 1 atm = 760 torr $\therefore\ x = 7.68 \times 10^{-2}$ atm

$P_{NOBr} = 7.68 \times 10^{-2}$ atm

$p_{NO} = 98.4 - x = 40 \text{ torr} = 5.26 \times 10^{-2}$ atm

$$P_{Br_2} = 41.3 - \frac{x}{2} = 12.1 \text{ torr} = 1.59 \times 10^{-2}\ \text{atm}$$

$$K_p = \frac{[P_{(NOBr)}]^2}{[P_{(NO)}]^2\,[P_{(Br_2)}]} = \frac{(7.68 \times 10^{-2})^2}{(5.26 \times 10^{-2})^2 (1.59 \times 10^{-2})}$$

$= 134$ atm^{-1}

$\Delta G° = -2.303$ RT log K

$= -2.303\,(1.99) \times 10^{-3}\,(300)\,(\log 134)$

$= -2.92$ k cal $= 12.2$ kJ

[If R is used as 1.99 cal/mol K, then ΔG° will be in cal. If R is used as 8.314 J/mol K, then ΔG° will be in joules. But K_p must be in (atm)$^{\Delta n}$.

DEGREE OF DISSOCIATION BY DENSITY MEASUREMENT

Those type of reactions in which there is change in number of moles after dissociation the extent of dissociation can be determined by vapour density measurement.

Let us consider the following reaction.

	PCl_5	$\rightleftharpoons$	PCl_3	$+ Cl_2$
Initially	1		0	0
Moles at equilibrium	$1 - \alpha$		α	α

($\alpha \rightarrow$ degree of dissociation)

Total no. of moles at equilibrium $= (1 - \alpha) + \alpha + \alpha = (1 + \alpha)$

Now, 'V' is the volume occupied by 1 mole of PCl_5 which have vapour density 'D' before dissociation and after dissociation is 'd'. So under same conditions, the volume occupied by

$(1 + \alpha)$ moles at equilibrium will be $(1 + \alpha)$ V litre.

Since, Density $\propto \frac{1}{\text{Volume}}$. Therefore, $D \propto \frac{1}{V}$

$$d \propto \frac{1}{(1+\alpha)V} \quad \text{or} \quad \frac{D}{d} = 1 + \alpha \quad \text{or}\ \alpha = \frac{D - d}{d}$$

Note : When one mole of reactant on dissociation gives 'n' moles of gaseous products the above equation takes in the form of $\alpha = \frac{D - d}{(n-1)d}$

Example 16 :

At 250°C the vapour density of PCl_5 is 100 calculate the degree of dissociation at this temperature.

Sol. $D \text{ for } PCl_5 = \frac{\text{Molecular mass}}{2} = \frac{208.5}{2} = 104.25$

$d \text{ for } PCl_5 = 100$

$\alpha = \frac{D-d}{d} = \frac{104.25-100}{100} = 0.0425$

TRY IT YOURSELF-2

Q.1 The favourable conditions for melting of ice is –

(A) Low pressure (B) High pressure

(C) Low temperature (D) Absence of catalyst

Q.2 $\Delta G°$ for the dissociation of the dimer ($A \rightleftharpoons 2A$) in benzene solution at 27°C is 6.909 kcal/mol. If 8 moles of A is dissolved in $10 dm^3$ of benzene at 27°C. What is the ratio of equilibrium concentration of monomer to dimer ($[A]/A_2]$? Given : R = 2 cal/mol. K

(A) 1 : 200 (B) 1 : 100

(C) 200 : 1 (D) 800 : 1

Q.3 The exothermic formation of ClF_3 is represented by the equation: $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)$; $\Delta H = -329$ kJ

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3.

(A) Increasing the temperature

(B) Removing Cl_2

(C) Increasing the volume of container

(D) Adding F_2

Q.4 Densities of diamond and graphite are 3.5 and 2.3 gm/mL.

$C(\text{diamond}) \rightleftharpoons C(\text{graphite})$; $\Delta_r H = -1.9$ kJ/mole

favourable conditions for formation of diamond are –

(A) high pressure and low temperature

(B) low pressure and high temperature

(C) high pressure and high temperature

(D) low pressure and low temperature

Q.5 Following two equilibrium is simultaneously established in a container

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$

If some Ni (s) is introduced in the container forming $Ni(CO)_4(g)$ then at new equilibrium

(A) PCl_3 concentration will increase

(B) PCl_3 concentration will decrease

(C) Cl_2 concentration will remain same

(D) CO concentration will remain same

Q.6 The vapour density of N_2O_4 at a certain temperature is 30. What is the %dissociation of N_2O_4 at this temperature?

(A) 53.3% (B) 106.6%

(C) 26.7% (D) None

Q.7 For the equilibrium, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at 298 K, $K = 1.8 \times 10^{-7}$. What is $\Delta G°$ for the reaction?

Q.8 On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(A) K will remain same

(B) K will decrease

(C) K will increase

(D) K will increase initially and decrease when pressure is very high

Q.9 In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?

(A) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

(B) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

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

(D) The equilibrium will remain unaffected in all the three cases

ANSWERS

(1)	(B)	**(2)**	(A)	**(3)**	(D)
(4)	(C)	**(5)**	(B)	**(6)**	(A)
(7)	38.484 kJ	**(8)**	(A)	**(9)**	(D)

IMPORTANT POINTS

*

Characteristics	Equilibrium constant
If reaction is reversed $A + B \rightleftharpoons C + D$	$K' = 1/K$
If reaction is divided by factor n. $\frac{1}{n}A + \frac{1}{n}B \rightleftharpoons \frac{1}{n}C + \frac{1}{n}D$	$K'' = \sqrt[n]{K}$
If reaction is multiplied by factor n. $nA + nB \rightleftharpoons nC + nD$	$K' = K^n$
If reaction is written in n number of steps $A + B \overset{K_1}{\rightleftharpoons} X + Y$; $X + Y \overset{K_2}{\rightleftharpoons} P + Q \ldots$ $\overset{K_n}{\rightleftharpoons} C + D$	$K' = K_1 \times K_2 \times \ldots..$

* K_P is related to K_C as $K_P = K_C(RT)^{\Delta n}$

* **Standard free energy & Equilibrium constant**

$\Delta G = \Delta G^0 + RT \ln Q$; the condition for a system to be at equilibrium is that $\Delta G = 0$

Thus at equilibrium,

$$\Delta G^0 = -RT \ln K \; ; \; \ln K = \frac{-\Delta G^0}{RT}$$

$\Delta G^0 = -ve$ or $K > 1$: forward reaction is feasible, $\Delta G^0 = +ve$ or $K < 1$: reverse reaction is feasible,

$\Delta G^0 = 0$ or $K = 1$: reaction is at equilibrium (very rare).

ADDITIONAL EXAMPLES

Example 1 :

6 gram hydrogen reacts with 9.023×10^{23} chlorine molecules to form HCl. If total pressure of the reaction is 800 mm then find the partial pressure of HCl.

Sol. $H_2 + Cl_2 \rightleftharpoons 2HCl$

3 mole $\quad \frac{9.023 \times 10^{23}}{6.023 \times 10^{23}} \quad$ 0 Initial mole

3 – 1.5 mole 1.5 – 1.5 mole 3.0 Mole at equilibrium

Total mole at equilibrium = 1.5 + 3.0 = 4.5 mole

Partial pressure of HCl = $\frac{3.0}{4.5} \times 800 = \frac{1600}{3} = 533$ mm

Example 2 :

In which case does the reaction go farthest to completion : K=1 ; K = 10^{10} ; K = 10^{-10} and why ?

Sol. The ratio $\frac{[\text{Product}]}{[\text{Reactant}]}$ is maximum when K = 10^{10} and thus reaction goes farthest to completion when K = 10^{10}

Example 3 :

The equilibrium constant K_c for $A_{(g)} \rightleftharpoons B_{(g)}$ is 1.1. Which gas has a molar concentration greater than 1 ?

Sol. For $A_{(g)} \rightleftharpoons B_{(g)}$; $K_c = \frac{[B]}{[A]} = 1.1$

$\Rightarrow$ [B] > [A]. If [B] = 1 ; [A] = 0.91

Case I $\quad 0.91 < [A] \le 1 \quad$ Only [B] > 1

Case II $\quad [A] > 1 \quad$ Both [A] and [B] > 1

Example 4 :

0.1 mole of $N_2O_{4(g)}$ was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of $NO_{2(g)}$ present, if the equilibrium $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}, (K_p = 0.14)$ is reached after some time.

Sol. $N_2O_4 \rightleftharpoons 2NO_2$

0.1 $\quad$ 0

$(0.1 - \alpha) \quad 2\alpha$

$$K_p = \frac{(2\alpha)^2}{(0.1-\alpha)} \times \left[\frac{P}{0.1+\alpha}\right]^1$$

$$\text{or} \quad K_p = \frac{40\alpha^2}{(0.1-\alpha)} \quad \text{or} \quad \frac{40\alpha^2}{(0.1-\alpha)} = 0.14$$

$\therefore \alpha = 0.017 \quad \therefore NO_2 = 0.017 \times 2 = 0.034$ mole

Example 5 :

What concentration of CO_2 be in equilibrium with 2.5×10^{-2} mol litre^{-1} of CO at 100° C for the reaction

$FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$; $K_c = 5.0$

Sol. $K_c = \frac{[CO_2]}{[CO]} \quad \therefore 5 = \frac{[CO_2]}{2.5 \times 10^{-2}}$

$\therefore$ $[CO_2]$ at equilibrium

$= 2.5 \times 10^{-2} \times 5 = 12.5 \times 10^{-2}$ mol litre^{-1}

Example 6 :

What is the % dissociation of H_2S if 1 mole of H_2S is introduced into a 1.10 litre vessel at 1000 K ? K_c for the reaction : $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$ is 1×10^{-6}

Sol. $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$

Mole before dissociation $\quad 1 \quad 0 \quad 0$

Mole after dissociation $\quad (1–\alpha) \quad \alpha \quad \alpha/2$

Where α is degree of dissociation of H_2S

Volume of container = 1.10 litre

$$\therefore \quad K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\left[\frac{\alpha}{1.1}\right]^2\left[\frac{\alpha}{2\times1.1}\right]}{\left[\frac{1-\alpha}{1.1}\right]^2} = 1 \times 10^{-6}$$

Assuming $1 - \alpha = 1$ since α is small because $K_c = 10^{-6}$

$$\therefore \quad \frac{\alpha^3}{2(1.1)} = 10^{-6} \quad ; \alpha = 1.3 \text{ x } 10^{-2} = 1.3\%$$

Example 7 :

In the reaction, $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts, calculate K_P .

Sol. $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$

Gaseous mole before dissociation $\quad$ – $\quad$ 1 $\quad$ 0

Gaseous mole after dissociation $\quad \left(1 - \frac{50}{100}\right) \quad \frac{2 \times 50}{100}$

0.5 $\quad$ 1

$\therefore$ Total mole = 1.5

Total pressure given at equilibrium = 12 atm

Partial pressure of CO = $\frac{1}{1.5} \times 12 = 8$

Partial pressure of $CO_2 = \frac{0.5}{1.5} \times 12 = 4$

$$K_p = \frac{P_{CO}{}^2}{P_{CO_2}} = \frac{(8)^2}{4} = 16 \text{ atm}$$

Example 8 :

When α–d glucose is dissolved in water, it undergoes a partial conversion to β–d glucose to exhibit mutarotation. This conversion stops when 63.6% of glucose is in β from. Assuming that equilibrium has been attained, calculate K_C for mutarotation.

Sol.

$$\begin{array}{lcc} & \alpha\text{–d glucose} \rightleftharpoons & \beta\text{–d glucose} \\ \text{At equilibrium} & 36.4 & 63.6 \end{array}$$

$$\therefore \quad K_c = \frac{63.6}{36.4} = 1.747$$

Example 9 :

What should be the respective active masses of methyl alcohol and carbon tetrachloride, if their densities are 0.5 and 1.2g/ml ?

(1) 15.62 & 7.79	(2) 15.65 & 7.40
(3) 15.46 & 7.80	(4) 15.40 & 6.50

Sol. **(1).** Active mass = number of g molecules per litre

We know that $D = \frac{M}{V}$ and $M = D \times V$

(1) The amount of CH_3OH in one litre = 0.5 × 1000 = 500g

(2) The amount of CCl_4 in one litre = 1.2 × 1000 = 1200g

(a) Active mass of $CH_3OH = \frac{\text{Weight in g}}{\text{Molecular weight } \times \text{Volume}}$

[Molecular weight of $CH_3OH = 12 + 3 + 16 + 1 = 32$]

$$= \frac{500}{32 \times 1} = 15.62\text{g mole/litre}$$

(b) Active mass of $CCl_4 = \frac{1200}{154 \times 1} = 7.79\text{g mole/litre}$

[Molecular weight of $CCl_4 = 12 + 35.5 \times 4] = 12 + 142 = 154$

Example 10 :

For the reaction $A + 2B \rightleftharpoons 2C + D$, initial concentration of A is a and that of B is 1.5 times that of A. Concentration of A and D are same at equilibrium. What should be the concentration of B at equilibrium ?

(A) a/4	(B) a/2
(C) 3a/4	(D) All of the above

Sol. **(B).**

$$\begin{array}{lllll} A\,(g) & +\ 2\,B\,(g) \rightleftharpoons & 2C\,(g) & +\ D\,(g) & \\ a & 1.5\,a & 0 & 0 & \text{No. of initial mole} \\ (a-x) & (1.5\,a-2x) & 2x & x & \text{No. of moles at equilibrium} \end{array}$$

Concentration of A and D are same at equilibrium

$a - x = x\ ;\ 2x = a\ ;\ x = a/2$

Therefore, concentration of B = 1.5 (a) – 2 (a/2)

[B] = 0.5a ; [B] = a/2

Example 11 :

Value of K_c at 300°C for $N_2 + O_2 \rightleftharpoons 2NO$ is 9×10^{-4} and equimolecular amounts of N_2 and O_2 are used. The concentration of NO at equilibrium will be –

(A) 0.0148a	(B) 0.296a
(C) 0.148a	(D) 0.0296a

Sol. **(B).**

$$\begin{array}{lllll} N_2\,(g) & +\ O_2\,(g) & \rightleftharpoons & 2NO\,(g) & K_c = 9 \times 10^{-4} \\ a & a & & 0 & \text{Initial mole} \\ (a-x) & (a-x) & & 2x & \text{Mole at equilibrium} \end{array}$$

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{4x^2}{(a-x)^2} = 9 \times 10^{-4}$$

$$\frac{2x}{a-x} = \sqrt{9 \times 10^{-4}} = 3 \times 10^{-2}$$

$2x = 0.03\,(a - x)\ ;\ 2x = 0.03a - 0.03x$

$2x + 0.03x = 0.03a\ ;\ 2.03x = 0.03a$

$x = 0.0148a\ ;\ 2x = 0.0296a$

Example 12 :

At 87°C, the following equilibrium is established :

$H_2(g) + S\,(s) \rightleftharpoons H_2S\,(g),\ K_c = 8 \times 10^{-2}$

If 0.3 mole hydrogen and 2 mole sulphur are heated to 87°C in a 2L vessel, what will be the partial pressure of H_2S approximately at equilibrium.

[Use R = 0.08 atm.L/mol.K)

(A) 0.32 atm	(B) 0.43 atm
(C) 0.62 atm	(D) 4.0 atm

Sol. **(A).** $K_c = \frac{[H_2S\,(g)]}{[H_2\,(g)]} \Rightarrow 8 \times 10^{-2} = \frac{x}{0.3 - x}$

$0.024 - 0.08 = x\ ;\ 0.024 = 1.08x\ ;\ x = 0.022$

$$P_{H_2S} = \frac{0.022 \times 0.08 \times 360}{2} \approx 0.32\text{ atm}$$

7B

IONIC EQUILIBRIUM

INTRODUCTION

Those compounds which can conduct electricity either in fused state or in solution state in any solvent are called Electrolytes.

Compounds which contain ions in pure solid state and can conduct electricity in the pure liquid state are called True electrolytes e.g. NaCl, KCl etc.

Compounds which do not conduct electricity in fused state but their solution in a solvent can conduct electricity are called potential electrolytes e.g. HCl, CH_3COOH, NaOH, NH_4OH etc.

There are two types of electrolytes –

(a) **Strong Electrolytes :** Compounds which completely ionised in aqueous solution and are good conductor of electricity e.g. HCl, H_2SO_4, HNO_3, NaOH, KOH, CH_3COONa, NH_4Cl etc. ($\alpha = 100\%$)

(b) **Weak Electrolytes :** Compounds which ionise partially in aqueous solution and are poor conductor of electricity e.g. CH_3COOH, HCN, NH_4OH, $Al(OH)_3$ etc. ($\alpha < 100\%$)

Those compounds which do not conduct electricity either in fused state or their solution in any solvent are called Non Electrolytes.

Example 1 :

Identify the non-electrolyte, strong electrolyte and weak electrolytes in aq. medium of the following substance.

NaOH, HCl, NaCl, NH_2CONH_2 (urea), H_2SO_4, H_3PO_4, HCN, NH_4OH, KOH, C_2H_5COOH, NH_4Cl, HNO_3, $C_{12}H_{12}O_{11}$ (sugar), $C_6H_{12}O_6$ (glucose)

Sol. Non-electrolyte : NH_2CONH_2, $C_{12}H_{12}O_{11}$, $C_6H_{12}O_6$

Weak electrolyte : H_3PO_4, HCN, NH_4OH, C_2H_5COOH

Strong electrolytes : NaOH, HCl, NaCl, H_2SO_4, KOH, NH_4Cl, HNO_3.

ARRHENIUS THEORY

(a) When an electrolyte is dissolved in water it breaks into oppositely charged i.e. cations and anions this process is called ionisation.

(b) The solution is electrically neutral, so the number of positive charge is equal to the number of negative charge.

(c) Process of ionisation is reversible. An equilibrium is established between ionised and unionised electrolyte. Hence law of mass action can be applied to this equilibrium

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

$$K_1 = \frac{[A^+][B^-]}{[AB]}$$

K_1 is called ionisation constant or dissociation constant.

(d) Electricity does not help in ionisation of electrolyte. It only causes migration of cation of cathode & anion to anode.

(e) The fraction of total amount of an electrolyte which gets ionised is called its degree of ionisation or degree of dissociation

$$\alpha = \frac{\text{No. of moles of electrolyte ionised}}{\text{Total no of moles before ionisation}}$$

(f) The equivalent conductance of a solution depends upon the number of ions and their charge in solution.

(g) The properties of solution governed by the ions present in the solution i.e. colour of solution.

(h) The colligative properties are effected by ionisation and depend upon number of cations and anions in the solution.

Note: (i) α is always less than 1

(ii) Degree of dissociation is assumed 100% at infinite dilution.

Factors Responsible for degree of ionisation :

1. **Dilution :** When dilution is increased in a weak electrolyte, the degree of ionisation increases and at infinite dilution any substance gets almost completely ionised.
2. **Temperature :** Increase of temperature increases the degree of ionisation, and decrease of temperature decreases the degree of ionisation.
   Kinetic energy of ions increases on increasing temperature and attractive forces between oppositely charged ions become less.
3. **Nature of solute :** Ionic character of electrolyte increase than 'α' increase. e.g. strong acid and base is totally ionised.
4. **Nature of Solvent :** Degree of ionisation depends on the nature of solvent. Solvent molecules weakening the forces of attraction is called dielectric constant. Higher the polarity of the solvent molecule, more is its dielectric constant. Thus degree of ionisation of an electrolyte is high in a solvent of high dielectric constant.
   Degree of ionisation of a compound in different solvents is different, because their dielectric constant are different.
5. **Present of common ion :** The extent or degree of dissociation of an electrolyte is lowered in the presence of a strong electrolyte having a common ion.

Example 2 :

Which is greater α_1 or α_2 for the following equation :

(i) $NH_4OH + H_2O \rightarrow \alpha_1$

(ii) $NH_4OH + D_2O \rightarrow \alpha_2$

Sol. Dielectric constant of D_2O is less than the H_2O so $\alpha_1 > \alpha_2$

OSTWALD DILUTION LAW

Strong electrolytes are almost completely ionised, but the weak electrolytes are partially ionised. Therefore, Ostwald put forward the law for weak electrolytes.

Degree of ionisation can be determined by applying the law of mass action on dilute solutions of weak electrolytes. On the basis of that, equilibrium constant and ionisation constant can be determined.

Take an example of dissociation of a weak acid HA, which takes place as follows.

$$\begin{array}{llll} HA \rightleftharpoons & H^+ + A^- & & \\ 1 & 0 \quad 0 & & \text{Initial mole} \\ 1-\alpha & \alpha \quad \alpha & & \text{Mole at equilibrium} \end{array}$$

If volume is v, then

$$\begin{array}{lll} \frac{1-\alpha}{v} & \frac{\alpha}{v} \quad \frac{\alpha}{v} & \text{Mole at equilibrium} \end{array}$$

$$\text{Therefore,} \quad K_a = \frac{[H^+][A^-]}{[HA]} = \frac{\alpha}{v} \times \frac{\alpha}{v} \times \frac{v}{1-\alpha}$$

$$K_a = \frac{\alpha^2}{(1-\alpha)\,v}$$

K_a is called dissociation constant of the weak acid. Value of x is very low for weak electrolytes, thus $1 - x = 1$. Then

$$K_a = \frac{x^2}{v} \quad ; \; x^2 = K_a \times v$$

$$x \propto \sqrt{v} \text{ or } x \propto \sqrt{1/C}$$

Therefore degree of ionisation of any substance is proportional to the square root of dilution. Thus degree of ionisation increases when dilution is increased. A substance tends to get completely ionised on infinite dilution.

Degree of ionisation increases on decreasing concentration.

* **Application of Dilution Law :** Dissociation constant 'K' and molar concentration 'c' of the electrolyte being known, 'α' can be calculated by using the relation.

* **Limitations of Ostwald's dilution law :** It holds good any for weak electrolytes and falls completely in the case of strong electrolytes.

Example 3 :

What concentration of acetic acid is needed to give a hydrogen ion concentration of 3.5×10^{-4} M ?

($K_a = 1.8 \times 10^{-5}$)

(A) 3.5×10^{-4} M (B) 6.80×10^{-3} M

(C) 4.2×10^{-4} M (D) 7.2×10^{-4} M

Sol. **(B).** Let the concentration of acetic acid be C.

$$\begin{array}{lll} CH_3COOH \rightleftharpoons & CH_3COO^- + & H^+ \\ C - C\alpha & C\alpha & C\alpha \end{array}$$

$$K_a = 1.8 \times 10^{-5} = \frac{C\alpha \cdot C\alpha}{C\,(1-\alpha)} = C\alpha^2$$

$$\text{Now, } \alpha^2 = \frac{K_a}{C} \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{C}} \quad \text{or} \quad C\alpha = \sqrt{K_a \cdot C}$$

$$C\alpha = [H^+] = 3.5 \times 10^{-4}\,M$$

$$\therefore \quad 3.5 \times 10^{-4} = \sqrt{1.8 \times 10^{-5} C}$$

$$\sqrt{C} = \frac{3.5 \times 10^{-4}}{\sqrt{1.8 \times 10^{-5}}}$$

$$C = \frac{(3.5 \times 10^{-4})^2}{1.8 \times 10^{-5}} = \frac{12.25 \times 10^{-8}}{1.8 \times 10^{-5}} = 6.80 \times 10^{-3} \text{ mol L}^{-1}$$

CONCEPT OF ACIDS AND BASES

1. ARRHENIUS CONCEPT

According to Arrhenius concept

(A) **Acid :** The acid is defined as those compounds which given H^+ in aqueous solution.

$$HCl + H_2O \rightleftharpoons H^+ + Cl^-$$

acid

- **(i)** **Strong acids :** Almost completely ionized in water. Hence give more H^+ ions. e.g. : HCl, HNO_3, H_2SO_4, etc.
- **(ii)** **Weak acids :** Feebly ionized in water. Hence give less H^+ ions. e.g. :HCN, CH_3COOH, H_2CO_3, H_2S etc.

(B) **Base :** The base defined are those compounds which give OH^- in aqueous solution.

$$NaOH + H_2O \rightleftharpoons Na^+ + OH^-$$

Base

- **(i)** **Strong bases :** Almost completely ionized in water. Hence give more OH^- ions.
  e.g. : NaOH, KOH, RbOH etc.
- **(ii)** **Weak bases :** Feebly ionized in water. Hence give less OH^- ions. e.g. : NH_4OH, $C_2H_5NH_3^+$, OH^-, $Ba(OH)_2$, $Al(OH)_3$, $Ca(OH)_2$, etc.

Limitations of Arrhenius Theory :

(i) It fails to explain the behaviour of acids and bases in non–aqueous solutions.

(ii) It fails to explain the neutralization giving salt in the absence of a solvent e.g.,

$$CO_2 + CaO \rightarrow CaCO_3 \,;\, NH_3 + HCl \longrightarrow NH_4Cl$$

(iii) It fails to explain the acidic character of certain salts like $AlCl_3$, BF_3 and basic character of NH_3, PH_3 etc.

(iv) It fails to explain as to how H^+ exists in water.

Strength of acid or base:

(i) Strength of acid or base depends on the extent of its ionisation. Hence equilibrium constant K_a or K_b respectively of the following equilibria gives a quantitative measurement of the strength of the acid or base.

(ii) $HA + H_2O \rightleftharpoons H_3O^+ + A^-;\; K_a = \frac{[H_3O^+][A^-]}{[HA]}$

(iii) Similarly, $B + H_2O \rightleftharpoons BH^+ + OH^-;\; K_b = \frac{[BH^+][OH^-]}{[B]}$

Here H_2O is solvent.

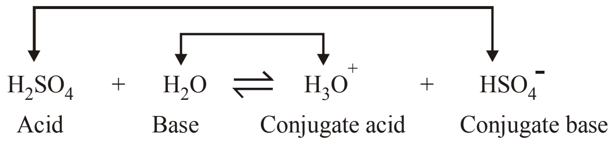
2. BRONSTED-LOWRY CONCEPT

According to this concept, the acid is defined as a substance which give up proton & the base is defined as a substance which accepts proton.

The species B accepts a proton & thus behave as a base, while the species BH^+ gives up a proton & thus acts as an acids. $B + H^+ \rightleftharpoons B^+H$

(Base) (Proton) (acid)

Such related pair of an acid & a base is said to be conjugate to are another so B is a conjugate base of the acid B^+H & B^+H is the conjugate acid of the base B. **eg. :**



$$H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$$

Acid	Base	Conjuate acid	Conjuate base
$HCl +$	$H_2O \rightleftharpoons$	$H_3O^+ +$	Cl^-
$HSO_4^- +$	$NH_3 \rightleftharpoons$	$NH_4^+ +$	SO_4^{2-}
$[Fe(H_2O)_6]^{3+} +$	$H_2O \rightleftharpoons$	$H_3O^+ +$	$[Fe(H_2O)_5(OH)]^{2+}$

* Conjugate acid-base pair differ by only one proton.

* Strong acid will have weak conjugate base and vise versa.

* Reaction will always proceed from strong acid to weak acid or from strong base to weak base.

According to bronsted – Lowry concept, neutralization is a process in which a proton is trasnfered from an acid to a base.

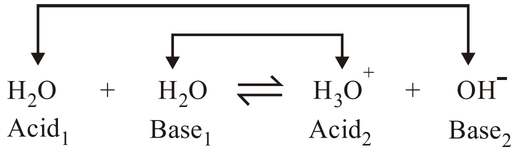
Conclusion of this theory are –

(i) A substance acts as an acid only when another substance capable of accepting a proton is present.

(ii) In aqueous solution H^+ ions exists an hydrated ion H^+H_2O or H_3O^+ & not as free H^+ ion.

(iii) Not only molecules but even ion may act as acids or bases.

(iv) Water, the most common solvent can act both as an acid as well as a base because it can give off a proton as well as can receive. It its dual behaviour may be represented by the following equation.



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

Example 4 :

In which of the following reactions does NH_3 act as an acid?

(A) $NH_3(aq) + H^+(aq) \rightarrow NH_4^+$

(B) $NH_3(\ell) + Na(s) \rightarrow NaNH_2(aq) + \frac{1}{2}H_2(g)$

(C) $NH_3(g) + HCl(g) \rightarrow NH_4Cl(s)$

(D) None of these

Sol. (B). In the following reaction, NH_3 changes to $NaNH_2$ which contains NH_2^- ion. This means that NH_3 has donated a proton to Na and hence acts as an acid.

Example 5 :

Which is the strongest Bronsted base in the following anion-

(A) ClO^- (B) ClO_2^-

(C) ClO_3^- (D) ClO_4^-

Sol. (A). HClO is weakest acid among HClO, $HClO_2$, $HClO_3$ and $HClO_4$.

Behaviour of acids and bases in aqueous solution :

(i) Acids in water : Water functions as a weak base and accepts a proton from the acid, thus

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

A^- can be considered as the conjugate base of anion of salt of the acid HA. So an aqueous solution of an acid contains hydronium (H_3O^+) ions (and not H^+ ions)

(ii) Strong and Weak acids : (Relationship between a conjugate pair). An acid is considered to be a strong acid, it can give up its proton readily. In an aqueous solution of HCl, there is equilibrium $HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$

Since HCl can give up its proton readily, this equilibrium will lie far to the right. Consequently the base Cl^- cannot take up the proton from H_3O^+ readily, i.e., Cl^- is a weak base. In general, the conjugate base of a strong acid will be a week base. In the case of a weak acid like phenol,

$$C_6H_5OH + H_2O \rightleftharpoons H_3O^+ + C_6H_5O^-$$

The equilibrium will lie far to the left. So the conjugate base ($C_6H_5O^-$) of a weak acid (C_6H_5OH) will be moderately strong. Again there is little ionization in the aqueous solution of a weak acid so the acid is weak electrolyte and the solution has a low conductance.

Based on studies of acids it is established that,

$$HClO_4 > HCl > HNO_3$$

(iii) Relationship between the ionization constants of acids and their conjugate bases :

The equilibrium reaction of CH_3COOH in water is :

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

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

The conjugate base of acetic ion ($CH_3CO_2^-$) acts as base in its reaction with water as

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

$$K'_{eq}[H_2O] = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = K_b$$

$$[OH^-] = \frac{K_W}{[H^+]} \quad \text{........ (2)}$$

$$\therefore \quad K_b = \frac{[CH_3COOH]K_W}{[CH_3COO^-][H^+]} \; ; \quad K_b = \frac{K_W}{K_a}$$

Thus, stronger the acid (the larger K_a), weaker will be its conjugate base (the smaller K_b) and vice versa.

Therefore, for an acid-conjugate base pair.

$$K_W = K_a \times K_b$$

3. LEWIS CONCEPT

(A) Lewis acid : Compounds having nature of accepting electron pair are called acids.

e.g. : $AlCl_3$, $ZnCl_2$, $SnCl_2$, $SnCl_4$, BF_3, Ag^+, H^+, Cu^{2+}

Classification of Lewis acids :

(a) Molecule with incomplete octet of its central atom
e.g. : $AlCl_3$, BF_3, $CaCl_2$, $FeCl_3$, $ZnCl_2$, $BeCl_2$

(b) Molecule with central atom containing empty d–orbital.
e.g. : SiF_4, $SnCl_2$, $SnCl_4$, PF_3, PF_5, SF_4, SeF_4

(c) Positively charged ions :
e.g.:Al^{+3},Cu^{+2},Ag^+, NO_2^+, Cl^+, Br^+, RNH_3^-, ROH_2^+ etc.

(d) Molecules having multiple bonds between atoms differing in electronegativities. e.g. : CO_2, SO_2, SO_3 etc.

(e) Atom with electron sextet : e.g. : O, S

(B) Lewis base : Compounds having nature of donating electron pair are called bases.

e.g. : OH^-, Cl^-, CN^-, NH_2^-, $\ddot{N}H_3$, $R\ddot{O}H$, $R-\underset{\cdot\cdot}{\dot{\dot{O}}}-R$

Classification of Lewis bases :

(a) Neutral molecules : Molecules containing atom carrying lone pair of electrons.
e.g. : $\ddot{N}H_3$, $R\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$

(b) Negatively charged ions :
e.g. : Cl^-, Br^-, I^-, $C_2H_5^-$, $C_2H_5O^-$, $C_2H_5S^-$, etc.

(c) Multi bonded compound which is formed coordinate compound with transition element.
e.g. : CO, No, Ethylene, Acetylene etc.

CLASSIFICATION OF SOLVENTS

(I) Protophilic : The solvent which have a greater tendency to accept proton e.g H_2O, alcohol, liquid ammonia. etc.
e.g. : RNH_2, Liquid NH_3, Pyridine, NH_2–NH_2 etc.

(II) Protogenic : The solvent which have a greater tendency to donate proton. e.g. : H_2SO_4, H_2F_2, HCN, HNO_3 H_2O etc.

(III) Amphoteric : The solvents which can both accept & donate a proton. e.g. : H_2O, alcohol etc.
H is always present
H_2O, NH_3, HSO_4^-, OH^-, NH_2-NH_2

(IV) Aprotic : The solvent which can neither accept nor donate a proton. e.g. :Benzene, CS_2, CCl_4 , SO_2, $COCl_2$, BrF_3, N_2O_4.

(V) Levelling solvent : All the strong acids react always completely with water. So all strong acids in aqueous solution appear equally strong. Water so thus called as a leveling solvent because it levels all the acids to the same strength leveling effect.

Note :

* If instead of water solvent, we take mineral acids in pure acetic acid solvent (which is poor proton acceptor as compared to water) it is found acids become weak and can be differentiated.

Ex. $\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{CH_3COOH^-} \rightleftharpoons \underset{\text{Base}}{Cl^-} + \underset{\text{Acid}}{CH_3COOH_2^+}$

In above example acetic acid and Cl^- ions both complete for protons and the former being a poor proton acceptor does it much less effectively than water. Thus HCl in acetic acid solvent appears to be a much weaker acid than that in water.

* Mineral acids in acetic acid solvent follow the following order of their strengths.
$HNO_3 < HCl < H_2SO_4 < HBr < HClO_4$

IONIC PRODUCT OF WATER

Water is a weak electrolyte, which gets ionised to H^+ and OH^- to a very low extent.

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

According to law of mass action

$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Here K is called ionisation constant of water.

Therefore, $K[H_2O] = [H^+][OH^-]$

$K_W = [H^+][OH^-]$ Here $K_W = K[H_2O]$

K_W is called ionic product of water.

In pure water, $\underset{10^{-7}}{[H^+]} = \underset{10^{-7}}{[OH^-]}$

Value of ionic product of water K_W is 1.0×10^{-14} at 25° C

Value of K_W depends on temperature. Value of K_w increases with increase in temperature and decreases with decrease in temperature and decreases with decrease in temperature.

Note :

Effect of Temperature

$T\uparrow \rightarrow K_w\uparrow$

$T\uparrow \rightarrow K\uparrow$ $\qquad -\log[H^+] = P^H$

$K_w = [H^+][OH^-]$ $\qquad -\log[OH^-] = P^{OH}$

$-\log K_w = -\log\left[[H^+][OH^-]\right]$ $\qquad -\log K_w = P^{Kw}$

$-\log K_w = -\log[H^+] - \log[OH^-]$

$P^{Kw} = P^H + P^{OH}$

Effect of temperature on K_w

Temp.	K_w
0°C	0.3×10^{-14}
25°C	1×10^{-14}
50°C	5.3×10^{-14}
90°C	100×10^{-14}

On 25°C $P^H + P^{OH} = 14$ $\Rightarrow$ 7 Neutral P^H

On 90°C $P^H + P^{OH} = 12$ $\Rightarrow$ 6 Neutral P^H

For water increasing the temp. $\Rightarrow \alpha\uparrow, Kw\uparrow, K\uparrow, P^H\downarrow, P^{OH}\downarrow$

pH AND HYDROGEN ION CONCENTRATION

The term pH was given by Sorenson. pH is defined as the negative logarithm to the base 10 of the hydrogen ion concentration i.e. $pH = -\log[H^+]$

pH lies from 0 to 14. For pure water pH = 7. For acidic solution pH is less than 7 and for basic solution pH is more than 7.

* Solution with pH = 0 is acidic

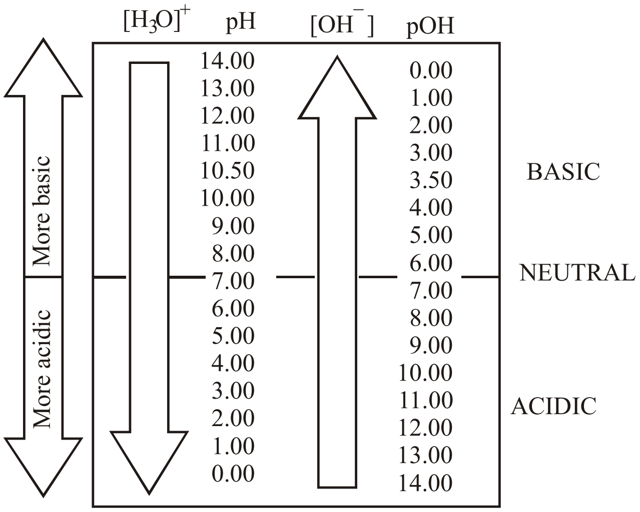
* pH value decreases with heating the solution

* –ve pH value is not possible experimentally (but theoretically it indicate acidic solution)

* Value of pH of acid, base & salts having same concentration is different.

* pH value of solution is determined by universal indicator, EMF method or use of pH meters.

- pH scale extends from 0 to 14
- Mid point of scale is pH = 7, represent neutrality.
- pH values greater than 14 are possible for concentrated strong base and negative pH values are possible for concentrated strong acid.



Example 6 :

What should be the number of OH^- ion one litre water, if concentration of OH^- ion is 10^{-7} gram ions/litre –

Sol. Number of OH^- = Concentration of $[OH^-]$ × Avogadro no.

$= 10^{-7} \times 6.023 \times 10^{23} = 6.023 \times 10^{16}$

Example 7 :

What should be the ionic product of water, if the value of ionisation constant of water is 1.8×10^{-16} ?

Sol. $K_w = K \times [H_2O]$

$= 1.8 \times 10^{-16} \times 55.4 = 1 \times 10^{-14}$

Example 8 :

At 25°C the $[H^+]$ of an acidic solution is 10^{-5} then find out its pH.

Sol. $pH = -\log [H^+]$

$= -\log 10^{-5} = +5 \log 10 = 5$

Example 9 :

At 25°C the $[OH^-]$ is 10^{-9} then find out the value of pH of the solution.

Sol. $pH + pOH = 14$

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

$$[H^+] = \frac{10^{-14}}{10^{-9}} = 10^{-5}$$

$pH = -\log [H^+] = -\log [10^{-5}] = +5 \log 10 = 5$

STRENGTH OF ACID

(i) Oxi acid (Non metal + O–H)

Case I : When non metals are different

Acidic character ∝ Eelectro negativity of non-metal

e.g. :

EN ↓

Acidic character ↓

H_3BO_3	H_2CO_3	HNO_3	
H_2SiO_3	HPO_3	H_2SO_4	$HClO_4$
	$HAsO_3$	H_2SeO_4	$HBrO_4$
		H_2TeO_4	HIO_4

EN ↑, Acidic character ↑

Case–II : When non metal are similar

Acidic character ∝ Oxidation Number

e.g. : $HNO_2 < HNO_3$

(+3) (+5)

$H_2SO_3 < H_2SO_4$

$HClO < HClO_2 < HClO_3 < HClO_4$

(+1) (+3) (+5) (+7)

Exception : $H_3PO_2 > H_3PO_3 > H_3PO_4$

(+1) (+3) (+5)

(ii) In hydride :

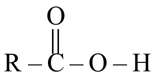
Size ↑

Acidic character ↑

B_2H_6	CH_4	NH_3	H_2O	HF
	SiH_4	PH_3	H_2S	HCl
	GeH_4	AsH_3	H_2Se	HBr
	SnH_4	SbH_3	H_2Te	HI

EN increase, Acidic character increase

(iii) In carbonic acid :



$R-\overset{\overset{O}{\|}}{C}-O-H$

Acidic character ∝ – I group ∝ $\frac{1}{+I \text{ group}}$

e.g. :

(a) $H–COOH > CH_3COOH > CH_3CH_2COOH$

+I group ↑, Acidic character ↓

(b) $CH_3COOH < ICH_2COOH < BrCH_2COOH < FCH_2COOH$

–I group ↑, Acidic character ↑

(iv) Explanation of mathematical acids :

Acidic character ∝ $[H^+] \propto \sqrt{K_a}$

Acidic character↑ = $[H^+]$↑ , pH↓ , $[OH^-]$↓, pOH↑ , K_a↑ , pK_a↓

(v) Oxides (Acidic anhydride) :

$H_2SO_4 \xrightarrow[-H_2O]{} SO_3$

$H_2CO_3 \xrightarrow[-H_2O]{} CO_2$

$H_2SO_3 \xrightarrow[-H_2O]{} SO_2$

$2 \times HNO_3 \xrightarrow[-H_2O]{} N_2O_5$

STRENGTH OF BASE

(i) Hydroxide (metal + O–H)

$$\text{Basic character} \propto \frac{1}{\text{Electro negativity of metal}}$$

LiOH	$Be(OH)_2$		$B(OH)_3$
NaOH	$Mg(OH)_2$	$Al(OH)_3$	
KOH	$Ca(OH)_2$	d–block	$Ga(OH)_3$
RbOH	$Sr(OH)_2$		$In(OH)_3$
CsOH	$Ba(OH)_2$		$Tl(OH)_3$

EN ↓ Basic character ↑

EN ↑ , Basic character ↓

(ii) Basic strength of amine :

$$\text{Basic strength} \propto +\text{I group} \propto \frac{1}{-\text{I group}}$$

e.g. : $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$
$(C_2H_5)_2NH > C_2H_5NH_2 > NH_3 > (C_2H_5)_3N$

(iii) Explanation of mathematical bases :

$$\text{Basic character} \propto [OH^-] \propto \sqrt{K_b}$$

$$\text{Basic character}\uparrow = [OH^-]\uparrow, pOH\downarrow, pH\uparrow, [H^+]\downarrow, K_b\uparrow, pK_b\downarrow$$

(iv) Oxides(Basic anhydride) :

Hydroxide		Alkaline anhydride
$Ca(OH)_2$	$\xrightarrow[-H_2O]{}$	CaO
$Ba(OH)_2$	$\xrightarrow[-H_2O]{}$	BaO
$2 \times NaOH$	$\xrightarrow[-H_2O]{}$	Na_2O'
$2 \times [Al(OH)_3]$	$\xrightarrow[-3H_2O]{}$	Al_2O_3

Relative strength of acids :

$$\frac{\text{Strength of acid 1}}{\text{Strength of acid 2}} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

$pK_a = -\log K_a$; $pK_b = -\log K_b$

Higher pK_a means lower acid strength.

Dissociation constant of poly basic acids :

$H_3PO_4 \rightarrow H^+ + H_2PO_4^{-1}$ (K_{a_1})

$H_2PO_4^{-1} \rightarrow H^+ + H\,PO_4^{-2}$ (K_{a_2})

$H\,PO_4^{-2} \rightarrow H^+ + PO_4^{-3}$ (K_{a_3})

$H_3\,PO_4 \rightarrow 3H^+ + PO_4^{-3}$ (K_a)

$K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$. $K_{a_1} > K_{a_2} > K_{a_3}$

But $pka_1 < pka_2 < pka_3$

Simillarly in poly acidic base.

$$K_b = K_{b_1} \times K_{b_2} \times K_{b_3}$$

$$K_{b_1} > K_{b_2} > K_{b_3}$$

But $p^{K_{b_1}} < p^{K_{b_2}} < p^{K_{b_3}}$

COMMON ION EFFECT

If we consider ionisation of a weak electrolyte say, CH_3COOH, it ionises as : $CH_3COOH \Leftrightarrow CH_3COO^- + H^+$

$$K_a = \frac{\left[CH_3COO^-\right]\left[H^+\right]}{\left[CH_3COOH\right]}$$

A stage will come such that concentration of CH_3COOH, CH_3COO^- and H^+ will not get changed further, their concentrations on a definite mathematical calculation will give a constant called equilibrium constant which will remain constant at same temperature. It does not mean that reaction has stopped only concentration will remain same, ions will continue to change in molecule and molecule will continue to get ionised this is said to be Dynamic Equilibrium. Now suppose some how CH_3COO^- ions are added to the solution to increase CH_3COO^- ions concentration since mathematical calculation will tend to change itself to change that eq. constant, electrolyte (CH_3COOH) will do same thing in order to keep K_a constant because it has to be a constant it will reduce its ionisation thus $[CH_3COOH]$ will increase, $[H^+]$ will decrease and K_a will remain constant.

This is called Common ion Effect that if in a solution of weak electrolyte a solution of strong electrolyte with one of its common ion is added ionisation of weak electrolyte is suppressed.

Applications of Common ion effect :

(a) H_2S is used in presence of HCl as a group reagent for the analysis of second group. HNO_3 cannot be used because it oxidised H_2S to sulphur.

(b) NH_4OH and NH_4Cl are used as group reagent for the analysis of third group.

(c) Purification of common salt by passing HCl gas in a saturated solution of NaCl.

(d) Soap is precipitated from its solution by adding some NaCl.

Example 10 :

Determine the effect on the concentrations of NH_3, NH_4^+ and OH^- when small amounts of each of the following is added to a solution of NH_3 in water.

(a) HCl (b) NH_3 (c) NaOH (d) NH_4Cl (e) KNO_3

Sol. The equilibria of NH_3 in water will be

$$NH_3 + H_2O \rightleftharpoons NH_4^+\,(aq.) + OH^-\,(aq.)$$

(a) If HCl is added it will furnish H and Cl^- ions as it is a strong electrolyte. Now H^+ will form H_2O with OH^- ions (neutralisation) so $[NH_3]$ will decrease, $[NH_4^+]$ & $[OH^-]$ increase since equilibria will shift in forward direction.

(b) If more NH_3 is added, then $[NH_3]$, $[NH_4^+]$ & $[Cl^-]$ will increase.

(c) If NaOH is added it will furnish $[Na^+]$ and $[OH^-]$ ions since it is a strong electrolyte and $[OH^-]$ will suppress the ionisation of weak base NH_3 so $[NH_3]$ increases, $[NH_4^+]$ decreases and $[OH^-]$ increases.

(d) NH_4Cl will also apply common ion effect on NH_4OH but now $[NH_3]$ of increases, $[NH_4^+]$ increases but $[OH^-]$ decreases.

(e) No effect expected.

pH CALCULATION OF DIFFERENT TYPES OF SOLUTIONS

(a) Strong acid solution

(i) If concentration is greater than 10^{-6} M.
In this case H^+ ions coming from water can be neglected.
So, $[H^+]$ = normality of strong acid solution.

(ii) If concentration is less than 10^{-6} M but greater than 10^{-8} M. In this case H^+ ions coming from water cannot be neglect. So, $[H^+]$ = normality of strong acid + H^+ ions coming from water in presence of this strong acid.

(iii) If concentration is less than 10^{-8} M, in this case H^+ ions coming from water is considered only.

Example 11 :

Calculate pH of 10^{-8} M HCl solution.

Sol.
$$\begin{array}{ccccc} H_2O & \rightleftharpoons & H^+ & + & OH^- \\ & & 10^{-8}+x & & x \end{array}$$

$k_w = [H^+][OH^-]$

$10^{-14} = x(x + 10^{-8})$

$x^2 + x \times 10^{-8} - 10^{-14} = 0$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = 0.95 \times 10^{-7}$$

$[H^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7}$

pH = $-\log[H^+]$; pH = $7 - \log 1.05 \approx 7$

(b) Strong base solution :

Calculate the $[OH^-]$ which will be equal to normality of the strong base solution & then use $K_a = [H^+] \times [OH^-] = 10^{-14}$, to calculate $[H^+]$.

Example 12 :

Calculate pH of 10^{-7} M NaOH solution

Sol. $[OH^-]$ from NaOH $= 10^7$

$[OH^-]$ from water $= x < 10^{-7}$ M (due to common ion effect)

$$\begin{array}{ccccc} H_2O & \rightleftharpoons & OH^- & + & H^+ \\ & & (x+10^{-7}) & & x \end{array}$$

$K_w = [H^+][OH^-] = 10^{-14} = x(x + 10^{-7})$

$x^2 + 10^{-7} \times - 10^{-14} = 0$

$$\Rightarrow \quad x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \quad (\sqrt{5} = 2.2336)$$

$[OH^-] = 10^{-7} + 0.618 \times 10^{-7} = 1.618 \times 10^{-7}$

pOH = $7 - \log(1.618) = 6.79$

pH = $14 - 6.79 = 7.21$

(c) pH of mixture of two strong acids : If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of another strong acid solution of normality N_2, then

Number of H^+ ions from I-solution $= N_1V_1$

Number of H^+ ions from II-solution $= N_2V_2$

If final normality is N and final volume of V, then

$NV = N_1V_1 + N_2V_2$

[Dissociation equilibrium of none of these acids will be disturbed as both are strong acid]

$$[H^+] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

(d) pH of mixture of two strong bases:

Similar to above calculation

$$[OH^-] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2} \ ; \quad [H^+] = \frac{10^{-14}}{[OH^-]}$$

Example 13 :

500 mL of 10^{-5} M NaOH is mixed with 500 mL of 2.5×10^{-5}M of $Ba(OH)_2$. To the resulting solution 99 L water is added. Calculate pH.

Sol. Normality of $Ba(OH)_2 = 2 \times 2.5 \times 10^{-5}$

$$[OH^-] = \frac{500 \times 10^{-5} + 500 \times 2 \times 2.5 \times 10^{-5}}{1000} = 3 \times 10^{-5} \text{ M}$$

$M_1 = 3 \times 10^{-5}$ M, $V_1 = 1$L, $V_2 = 100$ L

No. of moles of $[OH^-]$ initially = no. of moles of $[OH^-]$, in final solution.

$3 \times 10^{-5} = M_2 \times 100$

$\because \quad M_2 = 3 \times 10^{-7} < 10^{-6}$

$$\begin{array}{ccc} H_2O & \rightleftharpoons & H^+ + OH^- \\ & & x \quad (x + 3 \times 10^{-7}) \end{array}$$

$K_w = x(x + 3 \times 10^{-7}) = 10^{-14}$

$$\because \quad x = \left(\frac{\sqrt{13}-3}{2}\right) \times 10^{-7} = 0.302 \times 10^{-7}$$

$$[OH^-]_{net} = \left[3 + \frac{\sqrt{13}-3}{2}\right] \times 10^{-7} = \left[\frac{3+\sqrt{13}}{2}\right] \times 10^{-7}$$

$= 3.302 \times 10^{-7}$

(e) pH of mixture of a strong acid and a strong base:

Acid base neutralisation reaction will take place.

The solution will be acidic or basic depending on which component is taken in excess. If V_1 volume of a strong acid solution of normality N_1 is mixed with V_2 volume of a strong base solution normality N_2, then

Number of H^+ ions from I-solution $= N_1V_1$

Number of OH^- ions from II-solution $= N_2V_2$

$$\text{If } N_1V_1 > N_2V_2 \ ; \ [H^+] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

Solution will be acidic in nature.

$$\text{If } N_2V_2 > N_1V_1 \ ; \ [OH^-] = N = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

Solution will be basic in nature.

Example 14 :

Calculate pH of mixture of (400 mL, $\frac{1}{200}$M $Ba(OH)_2$ + (400 mL, $\frac{1}{50}$M HCl) + (200 mL of water)

Sol.
$$[H^+] = \frac{400 \times \frac{1}{50} - 400 \times \frac{1}{200} \times 2}{1000} = 4 \times 10^{-3}$$

So, pH = $3 - 2\log 2 = 2.4$

(f) pH of a weak acid (monoprtoic) solution :

Weak acid does not dissociated 100% therefore we have to calculate the percentage dissociation using (K_a) dissociation constant of the acid.

Using Ostwald's dilution law

$$\begin{array}{lcccc} & HA & \rightleftharpoons & H^+ & + & A^- \\ t=0 & C & & 0 & & 0 \\ \text{At eq.} & C(1-\alpha) & & C\alpha & & C\alpha \end{array}$$

$$K_a=\frac{[H^+][A^-]}{[HA]}=\frac{C\alpha^2}{1-\alpha}$$

$$\text{If } \alpha<<1 \Rightarrow (1-\alpha)\approx 1 \Rightarrow K_a=C\alpha^2 \Rightarrow \alpha=\sqrt{\frac{K_a}{C}}$$

(is valid if $\alpha<0.5$)

$$[H^+]=C\alpha=C\sqrt{\frac{K_a}{C}}=\sqrt{K_a\times C}\text{. So, pH}=\frac{1}{2}(pK_a-\log C)$$

On increasing the dilution $\Rightarrow C\downarrow = a\uparrow$ and $[H^+]\downarrow \Rightarrow pH\uparrow$

Example 15 :

Calculate pH of (a) 10^{-1} M CH_3COOH (b) 10^{-3} M CH_3COOH

$K_a=2\times10^{-5}$

Sol. (a) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$\begin{array}{ccc} C & 0 & 0 \\ C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$K_a=\frac{C\alpha^2}{1-\alpha}\Rightarrow \alpha=\sqrt{\frac{K_a}{C}}=\sqrt{\frac{2\times10^{-5}}{10^{-1}}}=\sqrt{2\times10^{-4}}$$

($\alpha<<0.1$)

$$\text{So, } [H^+]=10^{-1}\times\sqrt{2}\times10^{-2}\Rightarrow pH=3-\frac{1}{2}\log 2=2.85$$

(b) $$\alpha=\sqrt{\frac{K_a}{C}}=\sqrt{\frac{2\times10^{-5}}{10^{-3}}}=\sqrt{2\times10^{-2}} \qquad (\alpha>0.1)$$

Since $\alpha>0.1$, exact calculation is required.

$$K_a=\frac{C\alpha^2}{1-\alpha}\Rightarrow 2\times10^{-5}=\frac{10^{-3}\times\alpha^2}{1-\alpha}\Rightarrow \alpha=13.14\%$$

$[H^+]=10^{-3}\times0.1314=1.314\times10^{-4}$

$\Rightarrow$ $pH=4-\log(1.314)\approx3.8$

(g) pH of a mixture of weak acid (monoprotic) and a strong acid solution :

Weak acid and strong acid both will contribute H^+ ion.

For the first approximation we can neglect the H^+ ions coming from the weak acid solution and calculate the pH of the solution from the concentration of the strong acid only.

To calculate exact pH, we have to take the effect of presence of strong acid on the dissociation equilibrium of the weak acid.

If [SA] = C_1 and [WA] = C_2, then $[H^+]$ from SA= C_1

(SA = Strong acid) ; (WA = Weak acid)

The weak acid will dissociate as follows,

$$\begin{array}{ccccc} HA & \rightleftharpoons & H^+ & + & A^- \\ C_2 & & 0 & & 0 \\ C_2(1-\alpha) & & C_2\alpha+C_1 & & C_2\alpha \end{array}$$

$$K_a=\frac{(C_2\alpha+C_1)\,C_2\alpha}{C_2\,(1-\alpha)} \qquad (\alpha<<<1)$$

(The weak acids dissociation will be further suppressed because of presence of strong acid, common ion effect)

$K_a=(C_2\alpha+C_1)\,\alpha$

To H^+ ion concentration = $C_1+C_2\alpha$

Note : If the total $[H^+]$ from the acid is more than 10^{-6}M, then contribution from the water can be neglected, if comparable then we take $[H^+]$ from water also.

(h) pH of a mixture of two weak acid (both monoprotic) solution:

* Both acids will dissociate partially.

* Let the acid are HA_2 & HA_2 and their final concentrations are C_1 & C_2 respectively, then

$$\begin{array}{lccccc} & HA_1 & \rightleftharpoons & H^+ & + & A_1^- \\ t=0 & C_1 & & 0 & & 0 \\ \text{At eq.} & C_1(1-\alpha_1) & & C_1\alpha_1+C_2\alpha_2 & & C_1\alpha_1 \end{array}$$

$$K_{a_1}=\frac{C_1\alpha_1(C_1\alpha_1+C_2\alpha_2)}{C_1\,(1-\alpha_1)}$$

$$\begin{array}{lccccc} & HA_2 & \rightleftharpoons & H^+ & + & A_2^- \\ t=0 & C_1 & & 0 & & 0 \\ \text{At eq.} & C_2(1-\alpha_2) & & C_2\alpha_2+C_1\alpha_1 & & C_2\alpha_2 \end{array}$$

$$K_{a_2}=\frac{(C_2\alpha_2+C_1\alpha_1)\,C_2\alpha_2}{C_2\,(1-\alpha_1)}$$

(Since α_1, α_2 both are small in comparision to unity)

$$K_{a_1}=(C_1\alpha_1+C_2\alpha_2)\,\alpha_1 : K_{a_2}=(C_1\alpha_1+C_2\alpha_2)\,\alpha_2$$

$$\Rightarrow \frac{K_{a_1}}{K_{a_2}}=\frac{\alpha_1}{\alpha_2}$$

$$[H^+]=C_1\alpha_1+C_2\alpha_2$$

$$=\frac{C_1K_{a_1}}{\sqrt{C_1K_{a_1}+C_2K_{a_2}}}+\frac{C_2K_{a_2}}{\sqrt{C_1K_{a_1}+C_2K_{a_2}}}$$

$$\Rightarrow [H^+]=\sqrt{C_1K_{a_1}+C_2K_{a_2}}$$

Note : If the dissociation constant of one of the acid is very much greater than that of the second acid then contribution from the second acid can be neglected.

So, $[H^+]=C_1\alpha_1+C_2\alpha_2=C_1\alpha_1$

Example 16 :

Calculate pH of solution obtained by mixing vol. of 0.02 M HOCl & 0.2 M CH_3COOH solution given that

$$K_{a_1}[HOCl] = 2\times10^{-4}\,;\ K_{a_2}[CH_3COOH] = 2\times10^{-5}$$

also calculate OH^-, OCl^-, CH_3COO^-.

Sol. Final solution volume become double

$$C_1 = 0.01,\ C_2 = 0.1$$

$$[H^+] = \sqrt{K_{a_1}C_1 + K_{a_2}C_2}$$

$$= \sqrt{2\times10^{-4}\times0.01 + 2\times10^{-5}\times0.1}$$

$$= \sqrt{2\times10^{-6} + 2\times10^{-6}} = 2\times10^{-3}$$

$$pH = 3 - \log 2 = 3 - 0.3010 = 2.69$$

$$\alpha_1 = \frac{2\times10^{-4}}{2\times10^{-3}} = 10^{-1}\ ;\ \alpha_2 = \frac{2\times10^{-5}}{2\times10^{-3}} = 10^{-2}$$

$$\begin{array}{lccc} HOCl & \rightleftharpoons & H^+ & + \ OCl^- \\ C_1(1-\alpha_1) & & C_1\alpha_1 + C_2\alpha_2 & C_1\alpha_1 \end{array}$$

$$[OCl^-] = C_1\alpha_1 = 0.01\times10^{-1} = 1\times10^{-1}$$

$$\begin{array}{lccc} CH_3COOH & \rightleftharpoons & H^+ + & CH_3COO^- \\ C_2(1-\alpha_2) & & C_1\alpha_1 + C_2\alpha_2 & C_2\alpha_2 \end{array}$$

$$[CH_3COO^-] = C_2\alpha_2 = 0.01\times10^{-2} = 1\times10^{-1}$$

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{10^{-14}}{2\times10^{-3}} = 0.5\times10^{-11} = 5\times10^{-12}\,M$$

$$HOCl = 10^{-2}(1-0.01) = 9\times10^{-3}\,M$$

$$[CH_3COOH] = 10^{-1}(1-0.01) \approx 10^{-1}$$

ISOHYDRIC SOLUTIONS

(i) Solution of electrolytes are said to be isohydric if the concentration of the common ion present in them is the same and on mixing such solution, there occurs no change in the degree of dissociation of either of the electrolyte.

(ii) Let the isohydric solution is made by HA_1 and HA_2 acids, then $[H^+]$ of both should be equal i.e.

$$\sqrt{K_{a_1}C_1} = \sqrt{K_{a_2}C_2} \quad \text{or} \quad \frac{K_{a_1}}{K_{a_2}} = \frac{C_2}{C_1}$$

TRY IT YOURSELF-1

Q.1 What molar concentration of ammonia will provide a hydroxyl ion concentration of 1.5×10^{-3} ? ($K_b = 1.8\times10^{-5}$)

(A) 0.125 M (B) 0.12 M
(C) 0.13 M (D) 0.14 M

Q.2 The hydrolysis constant for $ZnCl_2$ will be –

(A) $K_h = \dfrac{K_w}{K_b}$ (B) $K_h = \dfrac{K_w^2}{K_b}$

(C) $K_h = \dfrac{K_w^2}{K_b^2}$ (D) $K_h = \dfrac{K_b}{K_w^2}$

where, K_b is effective dissociation constant of base Zn^{++}.

Q.3 1cc of 0.1 N HCl is added to 99 cc solution of NaCl. The pH of the resulting solution will be –

(A) 7 (B) 3
(C) 4 (D) 1

Q.4 The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be –

(A) 5.0×10^{-5} (B) 5.0×10^{15}
(C) 5.0×10^{-15} (D) 5.0×10^{5}

Q.5 The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C?

(A) Equal to 7.0 (B) Greater than 7.0
(C) Less than 7.0 (D) Equal to zero

Q.6 Acidity of BF_3 can be explained on the basis of which of the following concepts?

(A) Arrhenius concept
(B) Bronsted Lowry concept
(C) Lewis concept
(D) Bronsted Lowry as well as Lewis concept.

Q.7 The ionisation of hydrochloric in water is given below:

$$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$$

Label two conjugate acid-base pairs in this ionisation.

Q.8 CH_3NH_2 (0.1 mol, $K_b = 5\times10^{-4}$) is mixed with 0.08 mol of HCl and the solution is diluted to 1 litre. The H^+ ion concentration of the resulting solution will be –

(A) 1.6×10^{-11} (B) 8×10^{-11}
(C) 3×10^{-5} (D) 1.25×10^{-4}

Q.9 If CO_2 be passed into water, what will remain present in solution –

(A) $CO_2, H_2CO_3, CO_3^{2-}, HCO_3^-$ (B) H_2CO_3, CO_2
(C) HCO_3^-, CO_3^{2-} (D) CO_2, HCO_3^-

Q.10 Given: $Ag^+ + NH_3 \rightleftharpoons Ag(NH_3)^+$; $K_1 = 3.5\times10^{-3}$; $Ag(NH_3)^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $K_2 = 1.7\times10^{-3}$
The equilibrium constant for the reaction
$Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$ is

(A) 6.08×10^{-6} (B) 6.08×10^{6}
(C) 6.08×10^{-9} (D) 6.08×10^{9}

Q.11 The initial rate of hydrolysis of methyl acetate (1 M) by a weak acid (HA, 1M) is 1/100th of that of a strong acid (HX, 1M), at 25°C. The K_a of HA is –

(A) 1×10^{-4} (B) 1×10^{-5}
(C) 1×10^{-6} (D) 1×10^{-3}

ANSWERS

(1) (C) **(2)** (B) **(3)** (B)
(4) (C) **(5)** (C) **(6)** (C)

(7)

HCl	Cl^-
acid	conjugate base
H_2O	H_3O^+
base	conjugate acid

(8) (B) **(9)** (A) **(10)** (A) **(11)** (A)

CLASSIFICATION OF SALTS

Salt : A substance which ionises in water to produce ions other than H^+ and OH^- is called a salt. Salts are produced by the neutralisation reaction.

(a) Normal salt : In case the acid and base neutralise completely the salt formed is a normal salt. In case both acid and base are strong or weak, the salt is neutral, when the constituent acid is strong, the salt is acidic and when the constituent base is strong, the salt is alkaline.

Example : NaCl, Na_2HPO_3, Na_3PO_4, NaH_2PO_2 and KNO_3

(b) Acidic salt : If a polybasic acid (e.g., H_2SO_4, H_3PO_4, H_2SO_3 etc.) is neutralised partly by a base, the salt formed is acidic.

Examples : $NaHSO_3$, $NaHCO_3$, NaH_2PO_4, $Ca(H_2PO_4)_2$ etc.

(c) Basic salt : If a polyacidic base [e.g $Ba(OH)_2$, $Bi(OH)_3$, $Fe(OH)_3$ etc.] is neutralised partly by an acid, the salt formed is basic salt.

Example : Mg(OH)Cl, Zn(OH)Cl, $Al(OH)Cl_2$, $Pb(OH)NO_3$, Ba(OH)Cl, $Bi(OH)_2Cl$, Ca(OH)Cl, etc.

(d) Mixed salt : Salts formed by the simultaneous neutralisation of one acid by two bases or one base by two acids are called mixed salts.

Example : $NaKSO_4$, ZnBrCl, $Al(Cl_2)Br$, $Al(NO_3)Cl.Br$, Ca(OCl)Cl etc.

(e) Double salt : A compound of two salts whose solution gives tests for all the constituent ions is called a double salt or lattice complex .

Example : $FeSO_4.(NH_4)_2SO_4.6H_2O$, $[K_2SO_4.Al_2(SO_4)_3.24H_2O]$

(f) Complex salt : A compound whose solution does not give tests for the constituent ions is called a complex salt, e.g., $K_4[Fe(CN)_6]$.

Strong Acid	Weak Acid	Strong Base	Weak Base
$HClO_4$	all R – COOH	NaOH	LiOH
H_2SO_4	HCOOH	KOH	$Be(OH)_2$
HNO_3	CH_3COOH	RbOH	$Mg(OH)_2$
HCl, HI, HBr	C_2H_5OH	CsOH	$Ca(OH)_2$
Picric Acid	H_2S	$Ba(OH)_2$	$Sr(OH)_2$
H_2PtCl_6	HCN		NH_4OH
H_2AuCl_6	H_2CO_3		$Zn(OH)_2$
	$\begin{array}{c}COOH\\ \vert\\ COOH\end{array}$		$Al(OH)_3$
	H_3PO_4		AgOH
	H_3PO_3		
	H_2PO_3		
	$B(OH)_2$		

HYDROLYSIS OF SALT

1. Salt of Weak acid and Strong base [CH_3COONa, HCOONa]

Let AB be salt i.e. HA is weak acid and BOH is strong base.

$$A^- + B^+ + H_2O \Leftrightarrow HA + BOH$$

After hydrolysis BOH will again get ionised to give B^+ and OH^- ions $\qquad BOH \Leftrightarrow B^+ + OH^-$

Thus only A^- ions are hydrolysed to give weak acid HA & OH^- ions. This is known as Anionic Hydrolysis

$$A^- + H_2O \Leftrightarrow HA + OH^-$$

$$K_h = \frac{[AH][OH^-]}{[A^-]} \qquad \text{........ (1)}$$

Weak acid HA further ionised partially and set a reversible equation formally to attain equilibrium

$$HA \Leftrightarrow H^+ + A^-$$

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{........ (2)}$$

$$K_W = [H^+][OH^-] \qquad \text{....... (3)}$$

Eq. (1), (2) and (3), $K_h = \dfrac{K_w}{K_a}$

As earlier, let C was the concentration (mole lit^{-1}) taken initially and 'h' be the degree of hydrolysis (mole ionised per mole of salt) then,

$$\begin{array}{lccl} A^- + H_2O \Leftrightarrow & HA & + \;\; OH^- & \\ C & 0 & 0 & \text{(initially)} \\ C(1-h) & Ch & Ch & \text{(at equilibrium)} \end{array}$$

$$K_h = \frac{[AH][OH^-]}{[A^-]} = \frac{Ch.Ch}{C\,(1-h)} = \frac{Ch^2}{1-h}$$

if $h <<< 1$ so $1 - h \approx 1$

$$\Rightarrow K_h = Ch^2 \quad \Rightarrow h = \sqrt{\frac{K_h}{C}}$$

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

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

$$pOH = \left[7 - \frac{1}{2}pK_a - \frac{1}{2}\log C\right] < 7$$

$$pH = 14 - pOH$$

$$pH = \left[7 + \frac{1}{2}pK_a + \frac{1}{2}\log C\right] > 7$$

Result :

(a) Solution will be basic

(b) Hydrolysis is anionic.

(c) pH of solution is > 7.

(d) Red litmus change in to blue litmus.

Example 17 :

Find out pH, h and $[OH^-]$ of milli molar solution of KCN if the dissociation constant of HCN is 10^{-7}.

Sol. (i) $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C = 7 + \frac{1}{2} \times 7 + \frac{1}{2}\log 10^{-3}$

$$= 7 + \frac{7}{2} - \frac{3}{2}\log 10 = \frac{14 + 7 - 3}{2} = \frac{21 - 3}{2} = 9$$

(ii) $$h=\sqrt{\frac{K_h}{C}}=\sqrt{\frac{10^{-14}\times10^{-3}}{10^{-7}}}=10^{-5}$$

(iii) $$[OH^-]=\sqrt{\frac{K_w\times C}{K_a}}=\sqrt{\frac{10^{-14}\times10^{-3}}{10^{-7}}}=10^{-5}$$

2. Salt of a strong acid and a weak base :

$NH_4Cl, NH_4NO_3, (NH_4)_2SO_4)$

Let AB be salt, HA is strong acid and BOH is weak base.

$$A^-+B^++H_2O \Leftrightarrow HA+BOH$$

Only B^+ ion is hydrolysed so it is known as cationic hydrolysis.

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

$$K_h=\frac{[BOH][H^+]}{[B^+]} \qquad \text{................ (1)}$$

Weak base BOH further ionised partially and set a reversible equation formally to attain equilibrium

$$BOH \Leftrightarrow B^++OH^-$$

$$K_h=\frac{[BOH][H^+]}{[B^+]}$$

Weak base BOH further ionised partially and set a reversible equation formally to attain equilibrium

$$BOH \Leftrightarrow B^++OH^-$$

$$K_b=\frac{[B^+][OH^-]}{[BOH]} \qquad \text{..... (2)}$$

$$K_w=[H^+][OH^-] \qquad \text{..... (3)}$$

By eq. (1), (2) and (3), $K_h=\frac{K_w}{K_b}$

As earlier , let C was the concentration (mole lit^{-1}) taken initially and 'h' be the degree of hydrolysis (mole ionised per mole of salt) then,

$$\begin{array}{lllll} B^+ + & H_2O \Leftrightarrow & BOH + & H^+ & \\ C & & 0 & 0 & \text{(initially)} \\ C(1-h) & & Ch & Ch & \text{(at equilibrium)} \end{array}$$

$$K_h=\frac{[BOH][H^+]}{[B^+]}=\frac{Ch.Ch}{C(1-h)} \;;\; K_h=\frac{Ch^2}{1-h}$$

If $h <<< 1$ so $1-h \approx 1$

$$\Rightarrow K_h = Ch^2 \Rightarrow h=\sqrt{\frac{K_h}{C}}$$

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

$$[H^+]=Ch=C\sqrt{\frac{K_w}{K_b\times C}}=\sqrt{\frac{K_w\times C}{K_b}}$$

$$pH=\left[7-\frac{1}{2}pK_b-\frac{1}{2}\log C\right] < 7$$

Result :

(a) Hydrolysis is cataionic

(b) Nature of solution is acidic.

(c) P^H of solution is less than 7.

(d) Blue litmus change into red litmus.

Example 18 :

How many grams of NH_4Cl should be dissolved per litre of solution to have a pH of 5.13 ? K_b for NH_3 is 1.8×10^{-5}.

Sol. NH_4Cl is a salt of strong acid and weak base for solutions of such salts.

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

$$\Rightarrow 10.26=14-\log C-4.74$$

$$\Rightarrow \log C=9.26-10.26=-1.0 \quad \therefore C=10^{-1}\,M$$

$$NH_4Cl=10^{-1}\,M$$

$$W_{NH_4Cl}=10^{-1}\times53.5g\,L^{-1}=5.35\,gL^{-1}$$

3. Salt of a weak acid and a weak base

Let AB be salt i.e. HA and BOH both are weak acid and weak base respectively. Here both A^- and B^+ ions will get hydrolysed because neither of HA and BOH are completely ionisable.

$$A^-+B^++H_2O \Leftrightarrow HA + BOH$$

$$K_h=\frac{[HA][BOH]}{[A^-][B^+]} \qquad \text{..... (1)}$$

$$HA \Leftrightarrow H^++A^-$$

$$K_a=\frac{[H^+][A^-]}{[HA]} \qquad \text{..... (2)}$$

$$BOH=B^++OH^-$$

$$K_b=\frac{[B^+][OH^-]}{[BOH]} \qquad \text{..... (3)}$$

From equation (1), (2) & (3) we have

$$K_h=\frac{K_W}{K_a.K_b}$$

Let degree of hydrolysis be h

$$\begin{array}{lllllllll} A^- & + & B^+ & + & H_2O & \Leftrightarrow & AH & + & BOH \\ C & & C & & & & 0 & & 0 \\ C(1-h) & & C(1-h) & & & & Ch & & Ch \end{array}$$

$$K_h=\frac{Ch.Ch}{C(1-h).C(1-h)}=\frac{h^2}{(1-h)^2}$$

if $h <<< 1$

$$K_h=h^2 \Rightarrow h=\sqrt{K_h}$$

$$h=\sqrt{\frac{K_W}{K_a.K_b}}$$

It is very important to note that here degree of hydrolysis is independent of concentration of salt taken initially. It just depends upon K_a and K_b.
h increases on increasing temperature.

$$\Leftrightarrow \quad A^{-} + H^{+}$$

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

$$[H^+] = K_a . h \Rightarrow [H^+] = K_a \cdot \sqrt{\frac{K_W}{K_a . K_b}} = \sqrt{\frac{K_W . K_a}{K_b}}$$

$$[H^+] = \left(\frac{K_W . K_a}{K_b}\right)^{1/2}$$

$$pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} pK_b$$

Conclusions :

Condition	Behaviour of solution	pH	Hydrolysis
$K_b > K_a$	basic	>7	anionic
$K_a > K_b$	acidic	<7	cataionic
$K_a = K_b$	neutral	$=7$	neutral

Example 19 :

Calculate pH and degree of hydrolysis of 10^{-2} M NH_4CN solution. Given that K_a of HCN $= 5 \times 10^{-10}$ and K_b of (aq. NH_3) $= 2 \times 10^{-5}$.

Sol. $pH = \frac{1}{2}[14 + pK_a - pK_b]$

$$= \frac{1}{2}[14 + 10 - \log 5 - 5 + \log 2] = \frac{1}{2}[18.6] = 9.3$$

$$\frac{h}{1-h} = \sqrt{K_h} = \sqrt{\frac{K_W}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{5 \times 10^{-10} \times 2 \times 10^{-5}}} = 1$$

$\Rightarrow$ $2h = 1$ $\Rightarrow h = 1/2 = 0.5$

4. Salt of strong acid & strong base

(a) Here HA and BOH both are strong acid and strong base respectively.

(b) As A^- will get hydrolysed to HA, HA will again get ionised in to A^- ions. The same thing happens with B^+ ions so hydrolysis of both A^- and B^+ ions is not possible.

(c) Also after coming into solution A^- and B^+ ions do not have tendency to react with each other they want to remain free so only A^- and B^+ are present in solution.

Result :

(a) The solution of such salts remain neutral, i.e. pH = 7

(b) It is not a process of hydrolysis.

(c) No effect on litmus.

5. Salt of a weak polyprotic acid and strong base

(i) Salt containing multivalent cation or anion :

Hydrolysis of multivalent cation or anion takes place in stepwise manner and more than one hydrolytic products are formed. For example the hydrolysis of Fe^{2+} ions will occur in following steps :

$Fe^{2+} + 2H_2O \rightleftharpoons Fe(OH)^+ + H_3O^+$

$Fe(OH)^+ + 2H_2O \rightleftharpoons Fe(OH)_2 + H_3O^+$

The hydrolysis constants K_{h_1} and K_{h_2} are

$$K_{h_1} = \frac{[Fe(OH)^+][H_3O^+]}{[Fe^{2+}]} = \frac{K_w}{K_{b_2}}$$

$$K_{h_2} = \frac{[Fe(OH)_2][H_3O^+]}{[Fe(OH)^+]} = \frac{K_w}{K_{b_1}}$$

where K_{b_1} and K_{b_2} are dissociation constants of $Fe(OH)_2$. Since $K_{b_1} >>>> K_{b_2}$ thus $K_{h_1} >>> K_{h_2}$ hence the hydrolysis of $Fe(OH)^+$ in comparision can be neglected and

$$[H_3O^+] = \sqrt{K_{h_1} C} \quad \text{or} \quad pH = 7 - \frac{1}{2} pk_{b_2} - \frac{1}{2} \log C$$

(ii) Salt containing weak conjugate cation and an amphiprotic cation: When a salt like $NaHCO_3$, NaHS, NaH_2PO_4, Na_2HPO_4 etc. is dissolved in water the amphiprotic anion can either accept a proton from water (Hydrolysis) or can donate a proton to water. The pH of the solution can be calculated as

$$pH = \frac{1}{2}(pK_1 + pK_{a_2})$$

(iii) Salt containing strong conjugate cation and an amphiprotic cation :

Examples of such salts are NH_4HCO_3, NH_4HS etc. The $[H_3O^+]$ of the solution can be calculated as

$$[H_3O^+] = \sqrt{\frac{K_{a_1} K_w}{K_b} - K_{a_1} K_{a_2}}$$

(iv) Hydrolysis of amphiprotic anion :

Let us consider hydrolysis of amphiprotic anion only, i.e., when counter cation is not hydrolysed, example of some salts of this category are $NaHCO_3$, NaHS, Na_2HPO_4, NaH_2PO_4.
Here, $H_2PO_4^-$ and HPO_4^{2-} are amphiprotic anions. pH after their hydrolysis can be calculated as,

$$\text{pH of } H_2PO_4^- \text{ in aqueous medium} = \frac{pK_{a_1} + pK_{a_2}}{2}$$

$$\text{pH of } H_2PO_2^{-4} \text{ in aqueous medium} = \frac{pK_{a_2} + pK_{a_3}}{2}$$

Here, $H_2PO_4^{2-}$ is conjugate base of $H_2PO_4^-$ and H_3PO_4 is conjugate acid of $H_2PO_4^-$.

Similarly, PO^{3-}_4 isconjugate base of HPO^{-2}_4 and HPO^{-}_4 is conjugate acid of PO^{3-}_4.
When these salts are dissolved in water, $[H_3O^+]$ concentration can be determined as,

$$[H_3O^+] = \sqrt{K_{a_1}(K_w / k_b + K_{a_2})}$$

$$pH = -\log\sqrt{K_{a_1}(K_w / k_b + K_{a_2})}$$

BUFFER SOLUTION

A solution that resists change in pH upon addition of small amount of strong acid and strong base is called Buffer Solution. Capacity of a solution to resist alteration in its pH value is known as buffer capacity.

Salient features of buffer solutions

(i) Its pH does not change on standing for long.
(ii) Its pH is slightly changed by the addition of small amount of acid & base.
(iii) It has definite pH.
(iv) It has reverse acidity or alkalinity.

Types of buffer solution

(i) **Simple buffers :**
- **(a)** A salt of weak acid & weak base in water example CH_3COONH_4, NH_4CN
- **(b)** Proteins & Amino acids.
- **(c)** A mixture of an acid salt & normal salt of a poly basic acid example $Na_2HPO_4 + Na_3PO_4$

(ii) **Mixed buffers :** These are of two types

(a) **Acidic buffer mixtures :** Solution of a weak acid and its salt with strong base is acid buffer.
e.g. : $NaHCO_3 + H_2CO_3, CH_3COOH + CH_3COONa$, Boric acid (H_3BO_3) + Borax $(Na_2B_4O_7)$

Acidic buffer action : It is shown by following equilibrium.

(1) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ (partly ionised)
(2) $CH_3COONa \longrightarrow CH_3COO^- + Na^+$ (fully ionised)
(3) $H_2O \rightleftharpoons H^+ + OH^-$

pH of an acidic buffer :

Let in acidic buffer $CH_3COOH + CH_3COONa$

(1) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

(2) In the above equation we will have to assume two things

* Since CH_3COOH is a weak acid it's ionisation may be neglected so at equilibrium, it's concentration may be assumed the same as it was before ionisation

* CH_3COO^- ions concentration may be assumed totally due to CH_3COONa because it is highly ionised as compared to CH_3COOH
So, $[CH_3COO^-] = [CH_3COONa] = [Salt]$

$$\Rightarrow K_a = \frac{[Salt][H^+]}{[Acid]} \; ; \quad [H^+] = \frac{K_a[Acid]}{[Salt]}$$

$$-\log[H^+] = \log[Salt] - \log[Acid] - \log K_a$$

$$\text{or} \quad pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

These equation are called **Handerson equations.**

(b) **Basic buffer mixture :** A weak base with it's salt with strong acid.
e.g. : $NH_4OH + NH_4Cl$, glycine + Glycine Hydrochloride

Basic buffer action :

The best known example is a mixture of ammonium hydroxide and ammonium chloride.

$NH_4OH \rightleftharpoons NH_4^+ + OH^-$ (weakly ionised)
$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$ (Highly ionised)

The NH_4^+ ions from completely ionised NH_4Cl suppress the ionisation of NH_4OH which is already a weak ionisable substance. Thus the concentration of OH^- ions remains constant.

When a few drops of a base (say NaOH) are added, the OH^- ions (from NaOH) combine with NH_4^+ ions to form nearly unionised NH_4OH & thus the concentration of OH^- ions and hence PH value remains constant.

$$\underset{\text{(from buffer)}}{NH_4^+} + \underset{\text{(from added base)}}{OH^-} \longrightarrow NH_4OH$$

On the other hand, when a few drops of acid (say HCl) are added, the H^+ ions (from acid) combine with the excess of NH_4OH to form H_2O ammonium ions.

$$\underset{\text{(from buffer)}}{NH_4OH} + \underset{\text{(from added acid)}}{H^+} \longrightarrow NH_4^+ + H_2O$$

Thus the addition acid does not increase H^+ ion concentration and hence again pH remains unchanged. pOH and pH values of basic buffers can be determined from the following Henderson's equation.

$$pOH = pK_b + \log\frac{[Salt]}{[Base]}$$

Application of buffer solutions

(i) Qualitative analysis of mixture
(ii) Quantitative analysis or estimations
(iii) Industrial process such as manufacture of paper, dyes, inks, paint, drugs etc.
(iv) Digestion of food
(v) Preservation of foods & Fruits
(vi) Agriculture & Dairy products preservation.

Buffer capacity : May be defined as change in concentration of buffer acid required for changing its p^H value by one unit.

$$B.C. = \frac{\text{Change in concentration or number of moles of acid or base added to litre of Buffer}}{\text{Change in pH}}$$

Example 20 :

Calculate the pH of a buffer prepared by mixing 300 cc of 0.3M NH_3 & 500 cc of 0.5 NH_4Cl K_b for $NH_3 = 1.8 \times 10^{-5}$

(A) 8.11 (B) 9.81
(C) 8.82 (D) None of these

Sol. **(C).** Total volume of the buffer solution

$= 300\text{ cc} + 500\text{ cc} = 800\text{ cc}$

Number of milli moles of $NH_3 = 300 \times 0.3 = 90$

Molarity of NH_3 (Base) in the buffer = 90/800 M

Number of milli moles of $NH_4Cl = 500 \times 0.5 = 250.0$

Molarity of [salt] in the buffer = 250/800 M

Henderson's equation for basic buffer is:

$$pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{250/800}{90/800}$$

$$= 4.74 + \log(250/90) = 4.74 + 0.44 = 5.18$$

$pH = 14 - pOH = 14 - 5.18 = 8.82$

Example 21 :

In which case pH will not change on dilution

(A) 0.01 M CH_3COONa + 0.01 M CH_3COOH buffer
(B) 0.01 M CH_3COONH_4
(C) 0.01 M NaH_2PO_4
(D) in all cases

Sol. **(D).** Mixture of Sodium acetate and acetic acid is a buffer of pH value equal to pKa so its buffer capacity is maximum and hence its pH will not change significantly while CH_3COONH_4 is a salt of weak acid CH_3COOH and weak base NH_4OH whose magnitude of K_a and K_b are equal. So its pH does not depend upon concentration. Further more, NaH_2PO_4 is, in fact, a single solute buffer.

TRY IT YOURSELF-2

Q.1 The pH of a solution prepared by mixing 50.0 mL of 0.02M NaOH and 50mL of 0.04 M CH_3COOH is ($K_a = 1.8 \times 10^{-5}$)

(A) 4.74 (B) 5.74
(C) 3.74 (D) 7.45

Q.2 The pK_b of NH_4OH is 4.75. An aqueous solution of NH_4OH is titrated with HCl. The pH of the solution at a point when half of NH_4OH is neutralised is –

Q.3 Which of the following will produce a buffer solution when mixed in equal volumes?

(A) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(B) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(C) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl
(D) 0.1 mol dm^{-3} CH_4COONa and 0.1 mol dm^{-3} NaOH

Q.4 HX is weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is –

(A) 0.01% (B) 0.0001%
(C) 0.1% (D) 0.5%

Q.5 The pH of 0.1 M solution of the following salts increases in the order of :

(A) NaCl < NH_4Cl < NaCN < HCl
(B) HCl < NH_4Cl < NaCl < NaCN
(C) NaCN < NH_4Cl < NaCl < HCl
(D) HCl<NaCl< NaCN < NH_4Cl

Q.6 What will be the pH of the buffer solution containing 0.15moles of NH_4OH and 0.25 moles of NH_4Cl. K_b for NH_4OH is 1.8×10^{-5}.

(A) 9.08 (B) 10.03
(C) 9.05 (D) 9.03

ANSWERS

(1) (A) **(2)** 9.25 **(3)** (C)
(4) (A) **(5)** (B) (6) (D)

SOLUBILITY & SOLUBILITY PRODUCT

Solubility : At a constant temperature the mass of a solute present in 100g of solvent in its saturated solution is called its Solubility.

In numerical question, solubility of a substance is expressed in mole lit^{-1} it is number of moles of solute present in one litre of solvent.

$$\text{Number of moles} = \frac{\text{amount in grams}}{\text{mol wt. in grams}}$$

$$\text{Solubility} = \frac{\text{Number of moles}}{\text{Litres of the solution}}$$

Solubility Product : Solubility product of a sparingly soluble electrolyte is equal to the product of ionic concentrations in a saturated solution at a given temperature.

Ionisation of compound A_xB_y may be shown as

$$A_xB_y \Leftrightarrow xA^{y+} + yB^{x-}$$

$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Let solubility of compound A_xB_y is S mol lit^{-1} equilibrium

$$A_xB_y \Leftrightarrow xA^{y+} + yB^{x-}$$

$$S \qquad xS \quad yS$$

$$K_{sp} = (xS)^x(yS)^y$$

$$K_{sp} = x^xy^y\,S^{x+y}$$

* In a saturated solution $K_{sp} = [A^+][B^-]$

* In an unsaturated solution of AB, $K_{sp} > [A^+][B^-]$ i.e. more solute can be dissolved.

* In a super saturated solution $K_{sp} < [A^+]\,[B^-]$ i.e precipitation will start to occur.

* For AB type (in case of AgCl, $PbSO_4$, $BaSO_4$) ; $K_{sp} = S^2$

* For AB_2 or A_2B type (in case of $PbCl_2$, $CaCl_2$, Na_2SO_4, $Pb(NO_3)_2$) $K_{sp} = 4S^3$

* For A_3B or AB_3 type [$AlCl_3$, $FeCl_3$, Na_3PO_4)] ; $K_{sp} = 27S^4$

* For A_3B_2 or A_2B_3 type [$Al_2(SO_4)_3$, $Ba_3(PO_4)_2$] ; $K_{sp} = 108S^5$

Note : K_{sp} increases with increase in temperature.

Example 22 :

Given the solubility product of F_3B_2 is 2×10^{-30}. What will be the solubility in moles/litre.

(A) $1.85 \times 10^{-32})^{1/5}$

(B) $\left(\frac{2 \times 10^{-30}}{108}\right)^{1/5}$

(C) $\left(\frac{2 \times 10^{-28}}{5400}\right)^{1/5}$

(D) All of these

Sol. **(B).** K_{sp} of $A_3B_2 = 2 \times 10^{-30}$.

$A_3B_2 \rightleftharpoons 3A^{+2} + 2B^{-3}$

Assume s is the solution of A_3B_2 then

$K_{sp} = (3s)^3\,(2s)^2 = 108\,s^5$

$$s = \sqrt[5]{\frac{K_{sp}}{108}} = \left(\frac{2 \times 10^{-30}}{108}\right)^{1/5}$$

Example 23 :

If the solubility product of $BaSO_4$ is 1.44×10^{-12} then find out the solubility of SO_4^{-2}.

Sol. $BaSO_4 \rightleftharpoons Ba^{+2} + SO_4^{-2}$

$$S = \sqrt{K_{sp}} = \sqrt{1.44 \times 10^{-12}} = 1.2 \times 10^{-6}$$

Effect of Common ion on Solubility:

For a saturated solution product of concentration of ions should not exceed a constant called solubility product. Now suppose, extra common ions are added to increase concentration of ions it will tend to increase the value of K_{sp}, but it can not increase so ions will react to form molecule and get precipitated e.g. let solubility of AB in water be s moles L^{-1}. It is dissolved in solution CB having a common ion B^- let concentration of CB be C.

$$\begin{array}{ccccc} AB & \rightleftharpoons & A^+ & + & B^- \\ s & & s & & s \end{array}$$

$K_{sp} = s^2 = [A^+]\,[B^-]$ .... (1)

(Product should not exceed s^2 otherwise precipitation will start) Now. Let solubility of AB in CB be S_1.

$$\begin{array}{ccccc} CB & \rightleftharpoons & C^+ & + & B^- \\ C & & C & & C \\ AB & \rightleftharpoons & A^+ & + & B^- \\ s_1 & & s_1 & & s_1 \end{array}$$

$[A^+] = s_1$; $[B^-] = s_1 + C$; $K_{sp} = (s_1)\,(s_1 + C)$

If $s_1 <<< C$, $K_{sp} = s_1C = s^2$, from eq. (1)

or $s_1 = s^2/C$. So, solubility gets reduced.

APPLICATION OF K_{sp}

(1) In purification of common salt :

In a saturated solution of NaCl & imparities, by passing HCl gas through it increase the Cl^- ion concentration which shifts the equilibrium $NaCl \Leftrightarrow Na^+ + Cl^-$ to left & causes the precipitation of NaCl

(2) In preparation of $NaHCO_3$ by solvay method :

Precipitation of $NaHCO_3$ from it's saturated solution is done by addition of NH_4HCO_3, HCO_3 as common ion.

(3) Predicting precipitation in ionic reaction :

Precipitation in an ionic reactions could be predicted by comparing K_{sp} to the ionic concentration product of ions

(4) Salting out action of soap :

When NaCl is added to saturated solution of soap (RCOONa) concentration of Na^+ increases & causes to precipitation of soap it is due to $[Na^+][RCOO^-] > K_{sp}$

(5) In qualitative analysis :

Qualitative analysis of mixtures is based on the principle of solubility product. Some important applications are as follows:

Group	Radical	Condition of Precipitate
Zero	NH_4^+, K^+, Na^+	dissolve 1, 2 drop of CH_3COOH solution
Ist	Ag^{+2}, Pb^{+2}, Hg_2^{+2}	dissolve dil. HCl, precipitated as Cl^{-1}
IInd	IIA = Cu^{+2},Cd^{+2}, Bi^{+3},Hg^{+2},Pb^{+2} IIB = As^{+3}, Sb^{+3}, Sn^{+2}, Sn^{+4}	presence of HCl in acidic medium precipited as S^{-2} dissolve H_2S
IIIrd	Fe^{+3}, Al^{+3}, Cr^{+3}	in presence of NH_4Cl dissolve NH_4OH precipitated as OH^-
IV	Mn^{+2}, Ni^{+2} Co^{+2}, Zn^{+2}	presence of H_2S, in basic medium precipitated as S^{-2}
V	Ba^{+2}, Sr^{+2}, Ca^{+2} (BSC)	presence of NH_4Cl dissolve $(NH_4)_2CO_3$,precipited as CO_3^{-2}
VI	Mg^{+2}	dissolve Na_24PO_4 precipitated as HPO_4^{-2}

Precipitation of II group radicals : Group reagent is H_2S. In presence dilute HCl the ionic product of H_2S is suppressed due to common ion(H^+) and only ionic product of the sulphides of II radicals exceeds their solubility product and get precipitated.

II and IV precipitated $H_2S \rightleftharpoons 2H^+\downarrow + s^{-2}\downarrow$ common ion effect.

Precipitation of IV group radicals : Group reagent is H_2S in presence of NH_4OH. The presence of NH_4OH enhances the dissociation of H_2S. Thus due to high ionisation of H_2S the concentrations of S^{-2} ions increases and ionic product of sulphides of IV group radicals exceeds corresponding solubility product and get precipitated.

Precipitation of III group radicals : Group reagent is NH_4OH in presence of NH_4Cl the presence of NH_4Cl suppresses the ionisation of NH_4OH, NH_4^+ as common ion. Thus the ionic product of hydroxides of III group radicals exceeds corresponding solubility products and get precipitated.

Example 24 :

You are given 10^{-5} M NaCl solution and 10^{-8} M $AgNO_3$ solution, they are mixed in 1 : 1 volume ratio, predict whether AgCl will be precipitated or not, if solubility product of AgCl is 10^{-10}.

Sol. Ionic product $= \frac{10^{-5}}{2} \times \frac{10^{-8}}{2} = 25 \times 10^{-15} < K_{sp}$

Hence, no precipitation will take place.

Example 25 :

What $[H^+]$ must be maintained in a saturated H_2S (0.1 M) to precipitate CdS but not ZnS, if $[Cd^{2+}] = [Zn^{2+}] = 0.1$ initially?

$K_{sp}(CdS) = 8 \times 10^{-27}$, $K_{sp}(ZnS) = 1 \times 10^{-21}$,

$K_a(H_2S) = 1.1 \times 10^{-21}$

Sol. In order to prevent precipitation of ZnS,

$[Zn^{2+}][S^{2-}] < K_{sp}(ZnS) = 1 \times 10^{-21}$

(Ionic product)

or $(0.1)[S^{2-}] < 1 \times 10^{-21}$

$[S^{2-}] < 1 \times 10^{-20}$ M

This is the maximum value of $[S^{2-}]$ before ZnS will precipitate. Let $[H^+]$ to maintain this $[S^{2-}]$ be x.

Thus for $H_2S \rightleftharpoons 2H^+ + S^{2-}$

$$K_a = \frac{[H^+][S^{2-}]}{[H_2S]} = \frac{x^2(1 \times 10^{-20})}{0.1} = 1.1 \times 10^{-21}$$

or $x = [H^+] = 0.105$ M

$\therefore$ No ZnS will precipitate at a concentration of H^+ greater than 0.105 M.

ACID–BASE INDICATOR

Indicators are organic compound of complex structure that change colour in solution as the pH changes.

Hence acid-base indicator is useful in deciding end point in titration. Indicator does not change colour at particular pH but it changes for a specific pH range.

Suitable indicator for pH titration :

Type	**Indicator**	**pH range near the end point**
Strong acid strong base	Methyl orange or Phenolphthalein	4 – 10
Strong acid Weak base	Methyl orange	4 – 7
Weak acid strong base	Phenolphthalein	7 – 10
Weak base acid	Phenol Red	6.5 – 7.5

Colour change interval (sensitive range or useful range):

Generally indicator are weak organic acid or weak organic base.

Consider the dissociation of the indicator HIn [Weak organic acid] $HIn \rightleftharpoons H^+ + In^-$

HIn – (different colour)

In^- – (different colour)

By applying law of mass action

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \; ; \; [H^+] = \frac{K_{In} \times [HIn]}{[In^-]}$$

K_{In} = dissociation constant of indicator

$$pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$$

Solution assumes colour of HIn, when

$$\frac{[HIn]}{[In^-]} = 10, \; pH = pK_{In} - 1$$

Solution assumes colour of In^-, when

$$\frac{[HIn]}{[In^-]} = 0.1, \; pH = pK_{In} \pm 1$$

pH range $= pK_{In} \neq 1$

Indicator	**pH range**	**Colour change**
(a) Phenolphthalein	8.3 – 10.0	Colourless – Red
(b) Methyl orange	3.1 – 4.4	Red – orange
(c) Methyl red	4.2 – 6.3	Red – Blue
(d) Litmus	5.0 – 8.0	Red – Blue
(e) Phenol red	6.8 – 8.4	Yellow – Red

OSTWALD'S THEORY

Indicators are very weak organic acid or bases. There exists an equilibrium, e.g.

$HIn \rightleftharpoons In^- + H^+$, $InOH \rightleftharpoons In^+ + OH^-$

One colour different colour One colour different colour

Phenolphthalein : $HPh \rightleftharpoons H^+ + Ph^-$

In acidic medium : Due to common ion effect of H^+

$[HPh] > [Ph^-]$, the solution would be colourless

In basic medium : $OH^- + H^+ \rightarrow H_2O$

$[Ph^-] > [HPh]$

The solution would be pink

Methyl orange : $MeOH \rightleftharpoons Me^+ + OH^-$

In basic medium : Due to common ion effect of OH^- :

$[MeOH] > [Me^+]$

the solution would be light yellow

In acidic medium : $H^+ + OH^- \rightarrow [H_2O]$

Hence $[Me^+] > [MeOH]$

The solution would be red

pH of the indicator :

or $HIn \rightleftharpoons H^+ + In^-$

$$pH = pK_{In} + \log \frac{[In^-]}{[HIn]}$$

Where K_{In} = dissociation constant of the indicator.

$pH = pK_{In}$

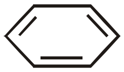
Then, $[HIn] = [In^-]$

Thus indicator changes its colour at this pH.

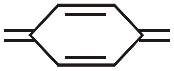
QUINONOID & BENZENOID THEORY

Indicator is an equilibrium mixture of two tautomeric forms. One is of structure benzenoid and other of quinonoid structure.

Benzenoid form colourless or light colour


B–form

Quinonoid form deep colour


Q–form

Equilibrium : Between two tautomeric forms

$$\text{B–from} \rightleftharpoons \text{Q–from}$$

Example :

$HPh \rightleftharpoons Ph^- + H^+$

HPh B–form .... acidic medium (colourless)

Ph^- Q–form .... basic medium (pink)

$MeOH \rightleftharpoons Me^+ + OH^-$

MeOH B–form...............basic medium (light yellow)

Me^+ Q–form .... acidic medium (red)

(i) Choice of indicator : For a particular titration the indicator is chosen on reviewing two factors :

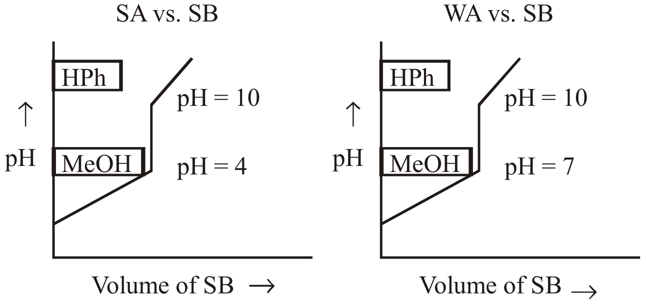
(a) pH near the end point in the neutralization curve [pH vs volume of alkali added graph]

(b) Colour change interval of the indicator

HPh pH [8.3 – 10.0] MeOH pH[3.1 – 4.4]

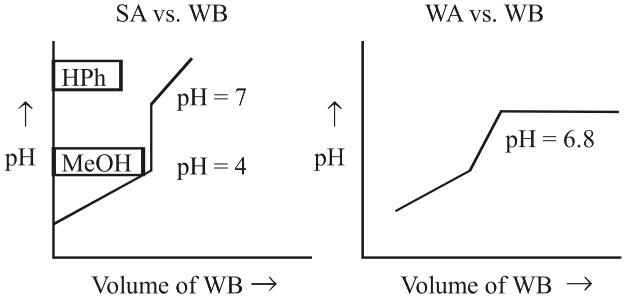
Ph Red pH[6.8 – 8.4]

Acid–Base Titration


SA vs. SB

WA vs. SB

Acid–Base Titration


SA vs. WB

WA vs. WB

Titration of strong acid with strong base :

Sharp change of pH near the end point [4 – 10]

suitable indicator : HPh (8.3 – 10) and MeOH (3.1 – 4.4)

Titration of a strong acid with week base :

Sharp change of pH near the end point [4 – 7]

Suitable indicator : MeOH (3.1 – 4.4) HPh can not be used (8.3 – 10)

Titration of weak acid with strong base :

Sharp change of pH near the end point [7 – 10].

Suitable indicator : HPh ; MeOH can not be used (3.1 – 4.4)

Titration of a weak acid with a weak base :

No sharp change of pH [6.5 – 7.5]

For rough titration the indicator is : Phenol red (6.8 – 8.4)

Titration of sodium carbonate with HCl :

Suitable indicator : MeOH

Example 26 :

The pH at which an acid indicator with $K_a = 1 \times 10^{-5}$ changes colours when indicator concentration is 1×10^{-5} M is –

(A) 4 (B) 5 (C) 6 (D) 3

Sol. **(B).** For acid indicator HIn

$$\underset{\text{Colour (A)}}{HIn} \rightleftharpoons \underset{\text{Colour (B)}}{H^+ + In^-}$$

$K_{In} = \dfrac{[H^+][I_n^-]}{[HI_n]}$ when $[I_n^-] = [HI_n]$ indicator changes colour.

$\therefore$ $K_{In} = [H^+] = 1 \times 10^{-5}$ $\therefore$ pH = 5

TRY IT YOURSELF-3

Q.1 $Mg(OH)_2$ has a solubility product equal to 1.2×10^{-11}. A solution contains 0.10 moles of magnesium ions per litre. The maximum pH of the solution from which $Mg(OH)_2$ will not precipitate is –

(A) 4.96 (B) 9.04

(C) 12.13 (D) 6.94

Q.2 Given the solubility product of $Pb_3(PO_4)_2$ is 1.5×10^{-32}. Determine the solubility in gms/litre.

Q.3 If K_{sp} for $HgSO_4$ is 6.4×10^{-5}, then solubility of this substance in moler per m^3 is –

(A) 8×10^{-3} (B) 6.4×10^{-5}

(C) 8×10^{-6} (D) None of these

Q.4 50 litre of a solution containing 10^{-5} mole of is mixed with 50 litre of a 2×10^{-7} M HBr solution. $[Ag^+]$ in resultant solution is [Given : K_{sp} (AgBr) = 5×10^{-13}]

(A) 10^{-5} M (B) 10^{-6} M

(C) 10^{-7} M (D) None of these

Q.5 0.1 M of HA is titrated with 0.1 M NaOH, Calculate the pH at end point. Given $K_a(HA) = 5 \times 10^{-6}$ and $\alpha << 1$

Q.6 2.5 mL of (2/5) M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with (2/15) M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_2 = 1 \times 10^{-14}$ at 25°C)

(A) 3.7×10^{-13} M (B) $3.2\ 10^{-7}$ M

(C) 3.2×10^{-2} M (D) 2.7×10^{-2} M

Q.7 In 1 L saturated solution of AgCl $[K_{sp}(AgCl) = 1.6 \times 10^{-10}]$, 0.1 mol of CuCl $[K_{sp}(CuCl) = 1.0 \times 10^{-6}]$ is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}. Value of x is

Q.8 The K_{sp} of Ag_2CrO_4 is 1.1×10^{-12} at 298K. The solubility (in mol/L) of Ag_2CrO_4 in a 0.1M $AgNO_3$ solution is –

(A) 1.1×10^{-11} (B) 1.1×10^{-10}

(C) 1.1×10^{-12} (D) 1.1×10^{-9}

ANSWERS

(1) (B) **(2)** 2.92×10^{-7} **(3)** (D)

(4) (C) **(5)** 9 **(6)** (D)

(7) 7 **(8)** (B)

IMPORTANT POINTS

*

Concept	Acid	Base
Arrhenius	give hydrogen ions in aqueous solutions e.g. HCl, H_2SO_4, HNO_3.	give hydroxyl ions in aqueous solutions e.g., KOH, NaOH,$Ca(OH)_2$
Bronsted-Lowry concept	Proton donors e.g. CH_3COOH, HCl, HNO_3	Proton acceptors e.g., NH3, Cl^-, CO_3^{2-}
Lewis concept	Electron acceptor e.g., H^+, SO_3, SO_2, $AlCl_3$, Ag^+	Electron donor e.g. O_2^-, $\ddot{N}H_3$, $H_2\ddot{\underset{..}{O}}$

* Strong acids : HCl, HNO_3, H_2SO_4, $HClO_4$, etc.

* Weak acids : HCN, H_2CO_3, H_3PO_4, CH_3CHOOH, H_2S, etc.

* Strong bases : NaOH, KOH, CsOH, $Ba(OH)_2$

* Weak bases : $Mg(OH)_2$, NH_4OH, $Ca(OH)_2$, LiOH, etc.

* Conjugate acid = Given species + H^+

* Conjugate base = Given species – H^+.

* If the acid is strong its conjugate base will be weak and vice versa.

* Water posseses a high dielectric constant and high dipole moment. It is amphoteric in character.

* When water functions as an acid, its conjugate base is OH^-. When it functions as a base, its conjugate acid is H_3O^+ ion.

* Strength of all strong acids (HCl, H_2SO_4, HNO_3, $HClO_4$ etc.) in water is same and become equal to the strength of H_3O^+ ion. This is called levelling effect of water.

* The strength of hydracids increases as we go down a group because of increase in the size of the atom or anion. For example, $HF < HCl < HBr < HI$

and $H_2O < H_2S < H_2Se < H_2Te$.

* In the case of oxyacids of the same element, the acidic nature increases as the oxidation number increases.

$HClO_4 > HClO_3 > HClO_2 > HClO$.

(+7) (+5) (+4) (+1)

* Among oxyacids of the same type formed by different elements. acidic nature increases as the electronegativity increases.

$HIO_4 < HBrO_4 < HClO_4$

(2.5) (2.8) (3.0)

* Among oxyacids of an element. acidic strength increases as the number of non-hydrogenated oxygen atoms increases or oxidation number increases.

$HClO_4 > HClO_3 > HClO_2 > HClO$

Oxidation No. +7 +5 +3 +1

Non hydrogenated

oxygen atoms 3 2 1 0

* Acidic nature of the hydride increases as the electronegativeity of the central atom increases.

$CH_4 < NH_3 < H_2O < HF$

(2.5) (3.5) (3.5) (4.0)

* The basic nature of hydroxides and oxides of IA and IIA group elements increases with increase in electropositivity.

$LiOH < NaOH < KOH < RbOH < CsOH$.

$Be(OH)_2 < Mg(OH)_2 < Ca(OH)_2 < Sr(OH)_2 < Ba(OH)_2$

* The basic nature of hydrides of same group decreases with the size of the central atom. This is because of decrease in the ability to donate the lone pair.

$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$

* All Lewis bases are also the Bronsted Lowry bases, but all Lewis acids are not Bronsted Lowry acids. Lewis acids are electron deficient molecules such as BF_3, $AlCl_3$, $GaCl_3$ etc.

* Some examples of Lewis acids are Na^+, Ag^+, Cu^{2+}, Al^{3+}, Fe^{3+}, O = C = O, O = S = O, BF_3, $AlCl_3$, $ZnCl_2$, $SnCl_2$ etc. Some examples of Lewis bases are Cl^-, Fe^-, Br^-, H_2O, NH_3, ROH, R_2O, R_2S, CO, NO, C_2H_4, C_2H_2 etc.

* K_w :

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

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

$K_w = [H_3O^+]^2 = [H^+]^2 = [OH^-]^2$

* Heat of neutralisation :

1. $S_A + S_B =$ Maximum heat
2. $S_A + W_B =$ Less
3. $W_A + W_B =$ Lessed
4. $^{+} + OH^{-} \longrightarrow H_2O + 13.6$ Kcal

$\Rightarrow 13.6 \times$ No. of Equivalent of water

* Ionic product of water is the product of concentration of H^+ ions and OH^- ions in pure water. It is constant at constant temperature.

* The ionic product of water increases with increase in temperature

* Salt hydrolysis is reverse of neutralisation

* The aqueous solution of salts of weak acid and strong base is alkaline in nature (pH > 7).

* The aqueous solution of strong acid and weak base is acidic in nature (pH < 7).

* The nature of salts of weak acid and weak base on hydrolysis depends upon the relative hydrolysis of the cation or anion of the salt.

* The aqueous solution of salts of strong acid and strong base is neutral

* Solubility product is defined as the product of ionic concentration of sparingly soluble electrolyte in a saturated solution and is constant at constant temperature.

- * A solution is saturated when ionic product is equal to solubility product.
- * When ionic product exceeds the solubility product the precipitation takes place.
- * HF is a strong acidic solvent.
  A strong acid in HF behave like weak base.
- * Concentration of [Salt] should in $\frac{\text{Mole}}{\text{litre}}$
- * Strength of acid
  $HClO_4 > H_2SO_4 > HCl > HNO_3 > H_3O^+ > HSO_4^- > H_3PO_4 > CH_3COOH > H_2CO_3 > H_2S > NH_4^+ > HCN > C_6H_5OH > H-OH > R-OH > NH_3 > R-NH_2 > H_2 > CH_4$
- * Solubility of sparingly soluble in acids or bases :
  There are many salts of weak acids or weak bases which are almost insoluble in water but their solubility increases with decreasing P^H. The salts containing Carbonates, Phosphates, Fluorids acetates etc. are soluble at low P^H. The salts of weak bases similarly dissolve at higher P^H (low acidity) CaF_2 is insoluble in water but it goes into solution when some acid is added.

ADDITIONAL EXAMPLES

Example 1 :

Explain CaC_2O_4 is insoluble in CH_3COOH but soluble in dilute HCl.

Sol. CH_3COOH being weaker acid than oxalic acid does not decompose CaC_2O_4; on the other hand HCl being stronger acid forms Ca^{+2} and oxalate ion to pass CaC_2O_4 in solution state. $CaC_2O_4 + 2HCl \rightarrow CaCl_2 + H_2C_2O_4$

Example 2 :

Find out solubility of $AgCl_{(Ksp)}$ in solution of NaCl (conc. C)

Sol. $AgCl \rightleftharpoons Ag^+ + Cl^-$

First, S S S

$K_{SP} = [Ag^+][Cl^-]$; $K_{SP} = S^2$

$AgCl \rightleftharpoons Ag^+ + Cl^-$ $\quad$ $NaCl \rightleftharpoons Na^+ + Cl^-$

$S^1 \quad (S^1 + C)$ $\quad$ C C

$$K_{SP} = [S^1]\,[S^1 + C]$$

$$K_{SP} = {S^1}^2 + S^1C$$

$$K_{SP} = S^1C$$

$$S^1 = \frac{K_{sp}}{C}$$

Example 3 :

Find out solubility of KCl (K_{SP}) in solution of $CaCl_2$ (conc. C)

Sol. $KCl \rightleftharpoons K^+ + Cl^-$

S S S

$K_{SP} = S^2$

$CaCl_2 \rightleftharpoons Ca^{+2} + 2Cl$

C C 2C

$KCl \rightleftharpoons K^+ + Cl^-$

$S^1 \quad S^1 + 2C$

$$K_{SP} = [S^1]\,[S^1 + 2C]$$

$$K_{SP} = {S^1}^2 + 2S^1C$$

$$S^1 = \frac{K_{sp}}{2C}$$

Example 4 :

What should be the concentration of H^+ and OH^- ions in a solution having 4g of NaOH dissolve 100ml of water at 25°C?

Sol. $$\text{Normality} = \frac{\text{Weight of substance}}{\text{Equivalent weight } \times \text{Volum}} = \frac{4}{40 \times 0.1} = 1\text{ N}$$

When normality is 1N,

$[OH^-] = 1$ gram equivalent ion/litre

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1} = 10^{-14} \text{ gram mole ion/litre}$$

Example 5 :

Find out the pOH of 10^{-3} M NH_4OH if $K_b = 10^{-5}$

Sol. $[OH^-] = \sqrt{K_b \times C} = \sqrt{10^{-5} \times 10^{-3}} = \sqrt{10^{-8}} = 10^{-4}$

$pOH = -\log[OH^-] = -\log[10^{-4}] = 4\log 10 = 4$

Example 6 :

Find out the K_h of centi normal $[10^{-2}\text{N}]$ solution of NH_4Cl [SA-WB) if dissociation constant of NH_4OH is 10^{-6} and $K_w = 10^{-14}$. Find out degree of hydrolysis and also find $[H^+]$, pH of solution ?

Given : $K_w = 10^{-14}$, $K_b = 10^{-6}$

Sol. (i) $K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{10^{-6}} = 10^{-8}$

(ii) $h = \sqrt{\frac{K_h}{K_C}} = \sqrt{\frac{10^{-8}}{10^{-2}}} = \sqrt{10^{-6}} = 10^{-3}$

(iii) $[H^+] = Ch = 10^{-2} \times 10^{-3} = 10^{-5}$

(iv) $pH = -\log[H^+] = -\log[10^{-5}] = +5\log 10 = +5 \times 1 = 5$

Example 7 :

Find out pH, h and $[OH^-]$ of milli molar solution of KCN $[10^{-3}\text{ M}]$. If the dissociation constant of HCN is 10^{-7}.

Sol. (i) $pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C = 7 + \frac{1}{2} \times 7 + \frac{1}{2}\log 10^{-3}$

$$= 7 + \frac{7}{2} - \frac{3}{2}\log 10 = \frac{14 + 7 - 3}{2} = \frac{21 - 3}{2} = \frac{18}{2} = 9$$

(ii) $h = \sqrt{\frac{K_h}{c}} = \sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{10^{-14}}{10^{-7} \times 10^{-3}}}$

$$= \sqrt{10^{-14} \times 10^{10}} = \sqrt{10^{-4}} = 10^{-2}$$

(iii) $[OH^-] = \sqrt{\dfrac{K_w \times C}{K_a}} = \sqrt{\dfrac{10^{-14} \times 10^{-3}}{10^{-7}}}$

$$= \sqrt{10^{-17} \times 10^{+7}} = \sqrt{10^{-10}} = 10^{-5}$$

Example 8 :

Hydrolysis constant of salts, M_1X and M_2X formed from strong acid and weak base, are 10^{-7} and 10^{-4}, respectively. For the base, M_3OH, $K_b = 10^{-4}$. What will be the decreasing order of strength of the base ?

(1) M_3OH, M_1OH, M_2OH (2) M_2OH, M_3OH, M_1OH

(3) M_1OH, M_2OH, M_3OH (4) Equal for all

Sol. **(1).** Strength of base $\propto K_b$

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

(i) $M_1x = K_b = \dfrac{10^{-14}}{10^{-7}} = 10^{-7}$

(ii) $M_2x = K_b = \dfrac{10^{-14}}{10^{-4}} = 10^{-10}$

(iii) $M_3x = K_b = 10^{-4}$

Therefore, $M_3OH > M_1OH > M_2OH$

Example 9 :

What should be the percentage of hydrolysis and pH of $\dfrac{N}{100}$ KCN, if the dissociation constant of HCN = 1.3×10^{-9} and $K_w = 1 \times 10^{-14}$?

Sol. $x = \sqrt{\dfrac{K_w}{K_a \times C}}$; $K_w = 10^{-14}$, $K_a = 1.3 \times 10^{-9}$, $C = \dfrac{N}{100} = 0.01$

$$x = \sqrt{\frac{10^{-14}}{1.3 \times 10^{-9} \times 0.01}} = 2.77 \times 10^{-2}$$

$\% = 2.77 \times 10^{-2} \times 100 = 2.77\%$

$K_a = 1.3 \times 10^{-9}$, $pK_a = 8.8$

$$pH = 7 + \frac{1}{2}pK_a + \frac{1}{2}\log C$$

$$pH = 7 + \frac{1}{2} \times 8.8 + \frac{1}{2}\log 10^{-2} = 7 + 4.4 - 1.00 = 10.4$$

Example 10 :

Solubility product of AgCl is 2.8×10^{-10} at 25°C. Calculate solubility of the salt in 0.1 M$AgNO_3$ solution

(A) 2.8×10^{-9} mole/litre (B) 2.8×10^{-10} mole/litre

(C) 3.2×10^{-9} mole/litre (D) 3.2×10^{-12} mole/litre

Sol. **(A).** In 0.1 M $AgNO_3$

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$,

$AgCl \rightleftharpoons Ag^+ + Cl^-$

$K_{sp} = [Ag^+][Cl^-]$

Now $[Ag^+]$ can be taken as $[AgNO_3]$

while $[Cl^-]$ is the solubility of AgCl

$$\therefore \quad Cl = \frac{K_{sp}}{[Ag^+]} = \frac{2.8 \times 10^{-10}}{0.1}$$

$\therefore$ Solubility of AgCl = 2.8×10^{-9} mole/litre

Example 11 :

If K_{sp} of saturated solution of $Mg(OH)_2$ is 4×10^{-12}, then find out its pH.

Sol. $Mg(OH)_2 \rightleftharpoons Mg^{+2} + 2OH^-$

$\quad 1 \qquad\qquad s \qquad 2s$

$K_{sp} = 4s^3$; $4 \times 10^{-12} = 4s^3$; $10^{-12} = s^3$

$s = (10^{-12})^{1/3} = 10^{-4}$

$OH^- = 2s = 2 \times 10^{-4}$

$pOH = -\log(2 \times 10^{-4}) = -\log 2 + 4 = -0.3010 + 4 = 3.7$

$pH = 14 - 3.7 = 10.3$

Example 12 :

The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5M $NaHCO_3$ solution should be mixed with 10mL of blood which is 2M in H_2CO_3 in order to maintain pH of 7.4. K_a for H_2CO_3 in blood is 7.8×10^{-7} ?

Sol. Let the volume of $NaHCO_3$ solution mixed = x mL

Number of moles of $NaHCO_3$ in x mL of 5M $NaHCO_3$ solution = $\dfrac{5 \times x}{1000} = 0.005 \times$ mol

Number of moles of H_2CO_3 in 10 mL of 2M H_2CO_3 solution = $\dfrac{2 \times 10}{1000} = 0.02$ mol

pH of the solution = 7.4

K_a for $H_2CO_3 = 7.8 \times 10^{-7}$

According to Henderson's equation

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

$$7.4 = -\log(7.8 \times 10^{-7}) + \log\left(\frac{0.005x}{0.02}\right)$$

$$7.4 = (7 - 0.892) + \log(0.25x)$$

$7.4 = 6.108 + \log(0.25x)$

$\log(0.25x) = 7.4 + 6.108 = 1.292$

$0.25\,x = \text{Antilog } 1.292 = 19.59 \quad \therefore \; x = \frac{19.59}{0.25} = 78.36$

Thus, the volume of 5M $NaHCO_3$ solution to be mixed = 78.36 mL.

Example 13 :

Find the pH of a 2 litre solution which is 0.1 M each with respect to CH_3COOH and $(CH_3OO)_2Ba$.

Sol. $pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$

$pK_a = -\log(1.8 \times 10^{-5}) = 4.7447$

$[CH_3COO^-] = 2 \times [(CH_3COO)_2Ba) = 0.2\text{ M}$

$[CH_3COOH] = 0.1\text{ M}$

$pH = 4.7447 + \log\frac{0.2}{0.1} = 5.046$

Example 14 :

When a decinormal solution of acetic acid gets 1.3% ionised, then find the value of ionisation constant.

Sol. Ionisation of acetic acid $\frac{1.3}{100} \times 0.1 = 0.0013$

(Decinormal = 0.1 N)

	$CH_3COOH \rightleftharpoons$	H^+ +	CH_3COO^-
Initial conc.	C	0	0
Conc. at equ.	$(1-0.0013)C$	$(0.0013)C$	$(0.0013)C$
	$0.9987C$	$0.0013\,C$	$0.0013\,C$

$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$; $K_a = \frac{0.0013 \times 0.1 \times 0.0013}{0.9987}$

$K_a = 1.71 \times 10^{-7}$

Example 15 :

Hydrolysis of NaCl does not take place, because –

(A) Na^+ ions are surrounded by negative ends of water molecules.

(B) Na^+ and Cl^- are present in ionic state.

(C) It is a monovalent salt

(D) Na^+ is a weak acid and Cl^- is a weak base.

Sol. **(4).** The weak acid Na^+ will not react with negative OH^-. Similarly, the weak base Cl^- will not react with H^+. Therefore, hydrolysis will not occur.

Example 16 :

KCN in solution gets 3.7% hydrolysed at 100 litre dilution at 100 litre dilution. If the dissociation constant of HCN is 7.2×10^{-10}, find the value of K_w.

Sol. KCN is formed from KOH (strong base) & HCN (weak acid) $x = \sqrt{\frac{K_w}{K_a} \times v}$; $x = \frac{3.7}{100} = 0.037$

$K_a = 7.2 \times 10^{-10}$, $v = 100$, $x^2 = \frac{K_w}{K_a} \times v$

$(0.037)^2 = \frac{K_w \times 100}{7.2 \times 10^{-10}}$

$K_w \times 100 = (0.037)^2 \times 7.2 \times 10^{-10}$

$K_w = \frac{0.037 \times 0.037 \times 7.2 \times 10^{-10}}{100} = 0.986 \times 10^{-14}$

Example 17 :

A solution is 0.1 molar in relation to AcOH and is 0.2 molar in relation to AcONa. What should be the concentration of Ac^{-1}, if x = 0.2 ?

(A) 0.202 (B) 0.1

(C) 0.3 (D) 0.15

Sol. **(A).**

	$AcOH \rightleftharpoons$	H^+ +	AcO^{-1}
Initial mole	1	0	0
Conc. at equilibrium	$\frac{1-x}{v}$	$\frac{x}{v}$	$\frac{x}{v}$
Conc. at equilibrium	$(1-x)\,C$	Cx	Cx
	$(1-0.02)\,0.1$	0.1×0.02	0.1×0.02

(AcOH, i.e. acetic acid is weak acid. Therefore, it does not ionise completely)

$AcOH \rightleftharpoons Na^+ + AcO^{-1}$

0.2 0.2

Here, AcONa will ionise completely.

AcO^{-1} obtained from AcOH = 0.002

AcO^{-1} obtained from AcONa = 0.2

Total AcO^{-1} obtained = 0.202

Example 18 :

K_a for acid HA is 2.5×10^{-8} calculate for its decimolar solution at 25°C. (i) % dissociation (ii) pH (iii) OH^- ion concentration

Sol.

$HA \rightleftharpoons$	H^+	+	A^-
C	0		0
$C(1-\alpha)$	$C\alpha$		$C\alpha$

$K_a = \frac{[H^+][A^-]}{[HA]} \Rightarrow \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2$

(i) $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2.5 \times 10^{-8}}{1/10}}$ (C = 1/10 M)

$= 5 \times 10^{-4} = 0.05\%$

(ii) $[H^+]=C\alpha=\frac{1}{10}\times5\times10^{-4}$ mol/L. So, pH=5 – log 5 = 4.30

(iii) $[H^+]\,[OH^-]=1\times10^{-14}$

$$\therefore\quad [OH^-]=\frac{10^{-14}}{5\times10^{-4}}=2\times10^{-10}\,\text{mol}/\text{L}$$

Example 19 :

The degree of dissociation of pure water at 25°C is found to be 1.8×10^{-9}. Find K_w and K_d at 25°C.

(A) 3.24×10^{-18}; 5.83×10^{-20} (B) 1×10^{-14} ; 1.8×10^{-15}

(C) 1.8×10^{-16}; 1×10^{-14} (D) 1×10^{-14}; 1×10^{-14}

Sol. **(B).** Since $\alpha=1.8\times10^{-14}$

and for water C = 1000/18 = 55.56

$[H^+]=[OH^-]=C\alpha=55.56\times1.8\times10^{-9}=1\times10^{-7}$ M

$K_w=[H^+]\times[OH^-]=(1\times10^{-7})^2=10^{-14}$

$$K_d=\frac{[H^+]\,[OH^-]}{[H_2O]}=\frac{K_W}{[H_2O]}=\frac{10^{-14}}{55.56}=1.8\times10^{-16}$$

Example 20 :

Calculate pH of the mixture (25 mL of 0.1 M NH_4OH + 25 mL of 0.1 M CH_3COOH)

Given that $K_a=1.8\times10^{-5}$, and $K_b=1.8\times10^{-5}$

Sol.

	NH_4OH	+ CH_3COOH	$\rightarrow CH_3COONH_4$	+ H_2O
Initially milli moles	25 × 0.1 = 2.5	25 × 0.1 = 2.5	0	0
Final milli moles	0	0	2.5	2.5

As salt is formed (salt of weak acid and weak base) and pH will be decided by salt hydrolysis

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

$$=\frac{1}{2}(-\log10^{-14}-\log1.8\times10^{-5}+\log1.8\times10^{-5})=7$$

Example 21 :

Find out the concentration of $[H^+]$ in 0.1 M CH_3COONa solution $[K_a=10^{-5}]$

Sol. Salt is [WA – SB]

$$[H^+]=\sqrt{\frac{K_W\times K_a}{C}}=\sqrt{\frac{10^{-14}\times10^{-5}}{10^{-1}}}$$

$$=\sqrt{10^{-19}\times10^{+1}}=\sqrt{10^{-18}}=10^{-9}$$

Example 22 :

Calculate degree of hydrolysis of a mixture containing 0.1 N NH_4OH and 0.1 N HCN.

Sol. Salt is [WA – WB]

$$h=\sqrt{\frac{K_w}{K_a\times K_b}}=\sqrt{\frac{10^{-14}}{10^{-5}\times10^{-5}}}=\sqrt{10^{-14}\times10^{+10}}=\sqrt{10^{-4}}=10^{-2}$$

Example 23 :

What should be the pH of 0.018 M sodium acetate, its $K_a=1.8\times10^{-5}$?

(A) 8.5 (B) 7.5

(C) 6.5 (D) 9.5

Sol. **(A).** $pH=7+\frac{1}{2}pK_a+\frac{1}{2}\log C$

If $K_a=1.8\times10^{-5}$; $pK_a=4.75$

$$=7+\frac{1}{2}\times4.75+\frac{1}{2}\log1.8\times10^{-2}=7+2.37-0.87=8.5$$

Example 24 :

Calculate degree of hydrolysis, K_h and pH of 1 M urea hydrochloride solution in water, K_b (Urea) = 1.5×10^{-14}.

Sol. NH_2CONH_3Cl is a salt of (SA + WB)

$$\text{So,}\quad h=\sqrt{\frac{K_W}{K_b\cdot C}}=\sqrt{\frac{10^{-14}}{1.5\times10^{-14}\times1}}$$

or h = 0.816 > 0.1, so we use actual relation

$$K_h=\frac{K_w}{K_b}=\frac{10^{-14}}{1.5\times10^{-14}}=6.667\times10^{-1}$$

$$K_h=\frac{K_w}{K_b}=\frac{Ch^2}{1-h}=\frac{1}{1.5}$$

$1.5\,h^2+h-1=0\Rightarrow h=0.55$

$[H^+]=ch=0.55$ M ; pH = 0.26

Example 25 :

Calculate degree of hydrolysis (h) and pH of solution obtained by dissolving 0.1 mole of CH_3COONa in water to get 100 lt. of solution (Take K_a of acetic acid = 2×10^{-5})

Sol.
$$c=\frac{0.1}{100}=1\times10^{-3}\,M$$

$$K_h=\frac{K_w}{K_a}=\frac{10^{-14}}{2\times10^{-5}}=5\times10^{-10}$$

$$\Rightarrow\quad h=\sqrt{\frac{K_h}{c}}=\sqrt{\frac{5\times10^{-10}}{2\times10^{-5}}}=5\times10^{-3}=0.5\%$$

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

$$=\frac{1}{2}[14+5-\log2+\log10^{-3}]=\frac{1}{2}[15.7]=7.85$$

QUESTION BANK

CHAPTER 7 : EQUILIBRIUM

EXERCISE - 1 [LEVEL-1]

PART-1 : EQUILIBRIUM IN PHYSICAL PROCESSES

Q.1 $CO_2\text{ (gas)} \rightleftharpoons CO_2\text{ (in solution)}$

This equilibrium is governed by

(A) Raoult's law (B) Charles' law

(C) Boyle's law (D) Henry's law

Q.2 Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows

(A) liquid – liquid equilibrium

(B) liquid – vapour equilibrium

(C) solid –liquid equilibrium

(D) solid – gas equilibrium

Q.3 Which of the following statement is correct?

(A) Boiling point of the liquid depends on the atmospheric pressure.

(B) Boiling point depends on the altitude of the place.

(C) At high altitude the boiling point decreases.

(D) All of the above

Q.4 $H_2O(\ell) \rightleftharpoons H_2O\text{ (vap.)}$

Point out the correct statement for this equilibrium.

(A) Rate of condensation = rate of sublimation

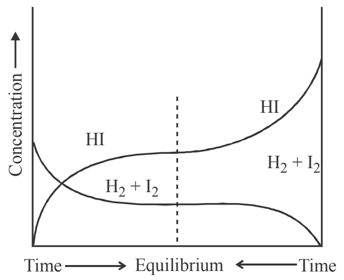
(B) Rate of sublimation = rate of evaporation

(C) Rate of evaporation = rate of condensation

(D) None of the above

PART-2 : EQUILIBRIUM IN CHEMICAL PROCESSES - DYNAMIC EQUILIBRIUM

Q.5 Consider the following graph,



The correct statement is

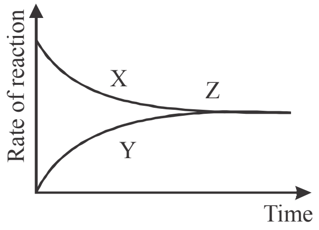
(A) Chemical equilibrium in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$ can be attained from forward direction.

(B) Chemical equilibrium in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$ can be attained from backward direction.

(C) Chemical equilibrium in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$ can be attained from either direction.

(D) Chemical equilibrium in the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$ can not be attained from either direction.

Q.6 Study the given figure and label X, Y and Z.



(A) X-Backward reaction, Y-Forward reaction, Z-Products

(B) X-Forward reaction, Y-Backward reaction Z-Equilibrium

(C) X-Reversible reaction, Y-Irreversible reaction Z-Equilibrium

(D) X-Forward reaction, Y-Forward reaction Z-Backward reaction

PART-3 : LAW OF CHEMICAL EQUILIBRIUM AND EQUILIBRIUM CONSTANT

Q.7 For these reactions,

I. $H_2\ (g) + I_2(g) \rightleftharpoons 2HI(g);\ K_c = \dfrac{[HI]^2}{[H_2][I_2]}$

II. $2HI\ (g) \rightleftharpoons H_2\ (g) + I_2(g);\ K'_c = \dfrac{[H_2][I_2]}{[HI]^2}$

K_c and K'_c are related as

(A) $K = K_c \times K'_c$ (B) $K = K_c + K'_c$

(C) $K = K'_c - K_c$ (D) $K'_c = 1/K_c$

Q.8 If the equilibrium constant for the reaction, $2XY \rightleftharpoons X_2 + Y_2$ is 81,

what is the value of equilibrium constant for the reaction

$XY \rightleftharpoons \frac{1}{2}X_2 + \frac{1}{2}Y_2$

(A) 81 (B) 9

(C) 6561 (D) 40.5

Q.9 For the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ What is K_c when the equilibrium concentration of $[SO_2] = 0.60$ M, $[O_2] = 0.82$ M and $[SO_3] = 1.90$ M ?

(A) 12.229 L mol^{-1} (B) 24.5 L mol^{-1}

(C) 36.0 L mol^{-1} (D) 2.67×10^3 L mol^{-1}

Q.10 The following concentrations were obtained for the formation of NH_3 from N_2 and H_2 at equilibrium at 500K. $[N_2] = 1.5 \times 10^{-2}$ M, $[H_2] = 3.0 \times 10^{-2}$ M and $[NH_3] = 1.2\times10^{-2}$ M. Calculate equilibrium constant.

(A) 1.06×10^3 (B) 0.06×10^3

(C) 1.06×10^5 (D) 3.06×10^3

Q.11 At a certain temperature only 50% HI is dissociated into H_2 and I_2 at equilibrium. The equilibrium constant is

(A) 1.0 (B) 3.0
(C) 0.5 (D) 0.25

Q.12 If the value of equilibrium constant K_c for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 7. The equilibrium constant for the reaction $2N_2 + 6H_2 \rightleftharpoons 4NH_3$ will be –

(A) 49 (B) 7
(C) 14 (D) 28

Q.13 At equilibrium, the concentrations of $N_2 = 3.0 \times 10^{-3}$ M, $O_2 = 4.2 \times 10^{-3}$ M and $NO = 2.8 \times 10^{-3}$ M in a sealed vessel at 800K. What will be K_c for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO\,(g)$

(A) 0.912 (B) 0.122
(C) 0.622 (D) 0.214

PART-4 : HOMOGENEOUS EQUILIBRIA

Q.14 For which of the following reactions, $K_p = K_c$

(A) $PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g)$
(B) $H_2\,(g) + Cl_2\,(g) \rightleftharpoons 2HCl\,(g)$
(C) $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$
(D) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$

Q.15 In a homogeneous system, all the reactants and products are in the

(A) different phase (B) same phase
(C) gaseous state only (D) liquid and gas state

Q.16 For the equilibrium, $2\,NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2(g)$ the value of the equilibrium constant, K_c is 3.75×10^{-6} at 1069 K. Calculate the K_p for the reaction at this temperature?

(A) 0.112 (B) 0.033
(C) 0.33 (D) 0.098

Q.17 In the system $X + 2Y \rightleftharpoons Z$, the equilibrium concentrations are, $[X] = 0.06$ mol L^{-1} $[Y] = 0.12$ mol L^{-1}, $[Z] = 0.216$ mol L^{-1}
Find the equilibrium constant of the reaction.

(A) 250 (B) 500
(C) 125 (D) 273

Q.18 Which of the following is an example of homogeneous equilibrium?

(A) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3\,(g)$
(B) $C(s) + H_2O\,(g) \rightleftharpoons CO(g) + H_2(g)$
(C) $CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2(g)$
(D) $NH_4HS\,(s) \rightleftharpoons NH_3(g) + H_2S(g)$

Q.19 What is the relation between K_p and K_c for a general reaction, $aA + bB \rightleftharpoons cC + dD$?

(A) $K_p = K_c\,(RT)^{\Delta n}$ (B) $K_c = K_p\,(RT)^{\Delta n}$
(C) $K_p = \dfrac{1}{K_c(RT)^{\Delta n}}$ (D) $K_c = \dfrac{1}{K_p(RT)^{\Delta n}}$

Q.20 5 moles of PCl_5 are heated in a closed vessel of 5 litre capacity. At equilibrium 40% of PCl_5 is found to be dissociated. What is the value of K_c?

(A) 0.266 M (B) 0.133 M
(C) 2.5 M (D) 0.20 M

Q.21 For a reaction, $NH_4COONH_2\,(s) \rightleftharpoons 2NH_3\,(g) + CO_2(g)$, the equilibrium pressure is 3 atm. K_p for the reaction will be –

(A) 27 (B) 4
(C) 3 (D) 9

PART-5 : HETEROGENEOUS EQUILIBRIA

Q.22 The equilibrium constant for the following reaction will be : $P_4(s) + 5O_2\,(g) \rightleftharpoons P_4O_{10}\,(s)$

(A) $K_c = \dfrac{[P_4][O_2]^5}{[P_4O_{10}]}$ (B) $K_c = \dfrac{1}{[O_2]^5}$

(C) $K_c = \dfrac{[P_4O_{10}]}{[P_4][O_2]^5}$ (D) $K_c = [O_2]^5$

Q.23 Which of the following reaction(s) show(s) heterogeneous equilibria?

(A) $N_2(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$
(B) $H_2O(\ell) \rightleftharpoons H_2O\,(g)$
(C) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$
(D) Both (B) and (C)

Q.24 The expression for equilibrium constant, K_c for the following reaction is
$2Cu(NO_3)_2\,(s) \rightleftharpoons 2CuO\,(s) + 4NO_2(g) + O_2(g)$

(A) $K_c = \dfrac{[CuO\,(s)]^2[NO_2(g)]^4[O_2(g)]}{[Cu(NO_3)_2(s)]^2}$

(B) $K_c = \dfrac{[NO_2(g)]^4\,[O_2(g)]}{[Cu(NO_3)_2(s)]^2}$

(C) $K_c = [NO_2(g)]^4\,[O_2(g)]$

(D) $K_c = \dfrac{[CuO(s)]^2}{[Cu(NO_3)_2(s)]^2}$

PART-6 : APPLICATIONS OF EQUILIBRIUM CONSTANTS

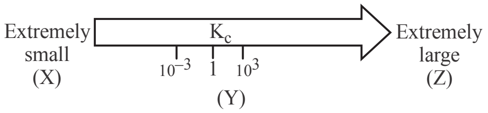
Q.25 Important features of equilibrium constants are as follows:

I. Expression for the equilibrium constant is not applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.
II. The value of equilibrium constant is dependent on initial concentration of the reactants and products.
III. Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.
IV. The equilibrium constant for the reverse reaction is directly proportional to the equilibrium constant for the forward reaction.

Choose the correct statement(s) is/are

(A) I and II (B) II and III
(C) Only III (D) I, II, III and IV

Q.26 Study the figure given below and mark the correct statement about K, and dependence of extent of reaction on it.



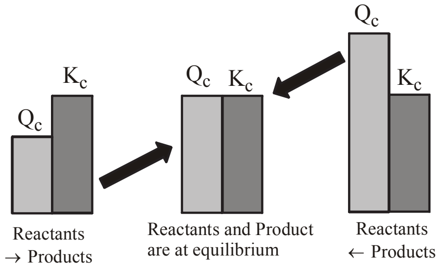
(A) X-Reaction does not occur
Y-Reaction proceeds to completion
Z-Reaction does not occur

(B) X-Reaction completes
Y-Reaction does not occur
Z-Reactants and products are at equilibrium.

(C) X-Reaction hardly occurs
Y-Reactants and products are at equilibrium.
Z-Reaction proceeds to completion

(D) X-Reaction proceeds to completion
Y-Reactants and products are at equilibrium.
Z-Reaction hardly occurs

Q.27 Consider the following graph which shows the prediction the direction of the reaction.



Point out the correct statement(s) for the above graph.

(A) If $Q_c < K_c$, net reaction goes from left to right (forward reaction).

(B) If $Q_c > K_c$ net reaction goes from right to left (reverse reaction)

(C) If $Q_c = K_c$ no net reaction occurs

(D) All of the above

Q.28 In the following reaction:

$2NO\,(g) + Cl_2\,(g) \rightleftharpoons 2NOCl\,(g)$

it is observed that equilibrium is not attained and the rate of forward reaction is greater than rate of backward reaction. Which of the following is true for the reaction?

(A) $K_p = Q_p$ (B) $Q_p > K_p$
(C) $Q_p < K_p$ (D) $Q_p = 0$

Q.29 The reaction quotient Q is used to –

(A) predict the extent of a reaction on the basis of its magnitude.

(B) predict the direction of the reaction

(C) calculate equilibrium concentrations

(D) calculate equilibrium constant

Q.30 Which of the following is/are important application(s) of equilibrium constant?

(A) To predict the extent of a reaction on the basis of its magnitude

(B) To predict the direction of the reaction

(C) To calculate equilibrium concentrations

(D) All of the above

PART-7 : RELATIONSHIP BETWEEN EQUILIBRIUM CONSTANT K, REACTION QUOTIENT Q AND GIBBS ENERGY G

Q.31 Equilibrium constant (K) is directly related to the thermodynamics of the reaction and to the change in Gibbs energy, ΔG. If

I. ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.

II. ΔG is positive, then reaction is considered non–spontaneous. Instead, as reverse reaction would have a negative ΔG, the products of the forward reaction shall be converted to the reactants.

III. ΔG is 0, reaction has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

Choose the correct statement(s).

(A) I and II (B) II and III
(C) I and III (D) I, II and III

Q.32 The correct relationship between free energy change in a reaction and the corresponding equilibrium constant, K_c is

(A) $\Delta G = RT \ln K_c$ (B) $-\Delta G = RT \ln K_c$
(C) $\Delta G° = RT \ln K_c$ (D) $-\Delta G° = RT \ln K_c$

Q.33 Which of the following equation represent relationship between reaction quotient, Q, and Gibbs energy, G?

(A) $\Delta G^{\ominus} = \Delta G + RT \ln Q$ (B) $\Delta G = \Delta G^{\ominus} + RT \ln Q$

(C) $\Delta G = \dfrac{1}{\Delta G^{\ominus} + RT \ln Q}$ (D) $\Delta G^{\ominus} = \dfrac{1}{\Delta G + RT \ln Q}$

PART-8 : FACTORS AFFECTING EQUILIBRIA

Q.34 Le-Chatelier's principle is applicable to all

(A) physical equilibria

(B) chemical equilibria

(C) physical or chemical equilibria

(D) physical and chemical equilibria

Q.35 Which of the following reactions will not get affected on increasing the pressure?

(A) $2H_2(g) + CO(g) \rightleftharpoons CH_3OH(g)$

(B) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$

(C) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S\,(g)$

(D) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2(g)$

Q.36 Which of the following statements is incorrect?

(A) In equilibrium mixture of ice and water kept in perfectly insulated flask, mass of ice and water does not change with time.

(B) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.

(C) On addition of catalyst, the equilibrium constant value is not affected.

(D) Equilibrium constant for a reaction with negative ΔH value decreases as the temperature increases.

Q.37 Consider the following statements,

I. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.
II. The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.
III. The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.
IV. Temperature changes affect the equilibrium constant and rates of reactions.

Choose the correct statement(s).

(A) I and II
(B) III and IV
(C) I, II and III
(D) I, II, III and IV

Q.38 On increasing the pressure, in which direction will the gas phase reaction proceed to reestablish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?

(A) K will remain same.
(B) K will decrease.
(C) K will increase.
(D) K will increase initially and decrease when pressure is very high.

Q.39 When I_2 dissociates to its atomic form the following reaction occurs: $I_2(g) \rightleftharpoons 2I(g)$; $\Delta_f H^\circ = +150$ kJ
The reaction is favoured at

(A) low temperature
(B) high temperature
(C) no change with temperature
(D) high pressure.

Q.40 Which of the following statement(s) is/are correct?

(A) Addition of hydrogen in the formation of HI at equilibrium results in the value of Q_c being less than K_c. Thus, in order to attain equilibrium again reaction moves in the forward direction.
(B) In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction.
(C) In the large scale production of CaO (used as important building material) from $CaCO_3$, constant removal of CO_2 from the kiln drives the reaction to completion.
(D) All of the above

Q.41 The reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ + Heat, will be favoured by

(A) high temperature and low pressure.
(B) low temperature and high pressure.
(C) high temperature and high pressure.
(D) low temperature and low pressure.

Q.42 Effect of a catalyst on a equilibrium reaction.

I. A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products.
II. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium.
III. It lowers the activation energy for the forward and reverse reactions by exactly the same amount.

Which of the above statement(s) is (are) correct?

(A) Only I
(B) I and II
(C) I, II and III
(D) II and III

Q.43 The following reaction is at equilibrium,
$Fe^{3+}(aq) + SCN(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$
Yellow Colourless Deep red

$$K_c = \frac{[Fe(SCN)]^{2+}}{[Fe^{3+}][SCN^-]}$$

In the above reaction, colour intensity of red colour can be increased by

(A) addition of KSCN
(B) addition of oxalic acid which reacts with Fe^{3+} ions
(C) addition of Hg^{2+} ions which react with SCN^- ion.
(D) red colour intensity cannot be changed.

PART-9 : IONIC EQUILIBRIUM IN SOLUTION

Q.44 __(X)__ classified electrolytes into strong and weak electrolytes __(Y)__ electrolytes on dissolution in water are ionised almost completely, while the __(Z)__ electrolytes are only partially dissociated. Correct words for X, Y, Z is –

(A) Faraday, weak, strong
(B) Arrhenius, weak, strong
(C) Arrhenius, strong, weak
(D) Faraday, strong, weak

PART-10 : ACIDS, BASES AND SALTS

Q.45 Sodium chloride (common salt) is an important component of our diet and is formed by the reaction between

(A) dichlorine and sodium hydride
(B) hydrochloric acid and sodium hydride
(C) hydrochloric acid and sodium hydroxide
(D) dichlorine and sodium hydroxide

Q.46 Fill in the blanks in the given table with the appropriate choice.

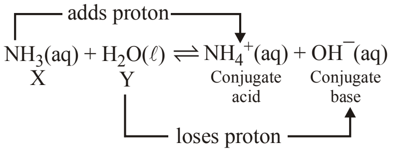
Species	**Conjugate acid**	**Conjugate base**
HCO_3^-	__p__	CO_3^{2-}
HSO_4^-	H_2SO_4	__q__
NH_3		__r__
__s__		
H_2O		__t__
OH^-		

(A) $p = H_2CO_3$, $q = SO_4^{2-}$, $r = NH_4^+$, $s = NH_2^-$, $t = H_3O^+$
(B) $p = HCO_3^-$, $q = H_2SO_3$, $r = NH_2^-$, $s = NH_4^+$, $t = H_3O^+$
(C) $p = H_2CO_3$, $q = HSO_4^-$, $r = NH_4^+$, $s = NH_2^-$, $t = H_2O$
(D) $p = HCO_3^-$, $q = H_2SO_4$, $r = NH_2^+$, $s = NH_2^-$, $t = OH^-$

Q.47 Point out the species which acts as Lewis acids.
(A) Mg^{2+}, H_2O, NH_3 (B) NH_3, OH^-, Co^{3+}
(C) $AlCl_3, Co^{3+}, Mg^{2+}$ (D) $AlCl_3, H_2O, Co^{3+}$

Q.48 Acidity of BF_3 can be explained on the basis of which of the following concepts?
(A) Arrhenius concept
(B) Bronsted–Lowry concept
(C) Lewis concept
(D) Bronsted–Lowry as well as Lewis concept

Q.49



$$\underset{X}{NH_3(aq)} + \underset{Y}{H_2O(\ell)} \rightleftharpoons \underset{\text{Conjugate acid}}{NH_4^+(aq)} + \underset{\text{Conjugate base}}{OH^-(aq)}$$

(X) and (Y) in the above figure are
(A) neutral, acid (B) acid, base
(C) base, acid (D) base, neutral

Q.50 According to Lewis concept, an acid is a/an
(A) proton donor (B) electron pair donor
(C) proton acceptor (D) electron pair acceptor.

Q.51 "An acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+".
The above statement is justified by
(A) Arrhenius concept
(B) Bronsted–Lowry theory
(C) Lewis concept
(D) All of these

Q.52 Point out the conjugate acids for the following Bronsted bases : NH_2^-, NH_3 and $HCOO^-$
(A) NH_2^-, NH_4^+ and HCOOH
(B) NH_3, NH_4^+ and HCOOH
(C) N^{3-}, NH^{2-} and HCOOH
(D) NH_3, NH_2^- and HCOOH

PART-11 : IONIZATION OF ACIDS AND BASES

Q.53 Strong acid dissociates completely in water, the resulting base formed would be very weak. The reason is that
(A) strong acids have strong conjugate bases.
(B) strong acids have strong conjugate acids.
(C) strong acids have very weak conjugate bases.
(D) strong acids have very weak conjugate acids.

Q.54 The pH of neutral water at 25°C is 7.0. As the temperature increases, ionisation of water increases, however, the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C?
(A) Equal to 7.0 (B) Greater than 7.0
(C) Less than 7.0 (D) Equal to zero

Q.55 Which of the following salts does not show its correct nature mentioned against it?
(A) KBr solution – Neutral
(B) NaCN solution – Acidic
(C) NH_4NO_3 solution – Acidic
(D) KF solution – Basic

Q.56 For a polybasic acid, the dissociation constants have a different values for each step, e.g.,

$$H_3A \rightleftharpoons H^+ + H_2A^-;\ K = K_{a_1}$$

$$H_2A^- \rightleftharpoons H^+ + HA^{2-};\ K = K_{a_2}$$

$$HA^{2-} \rightleftharpoons H^+ + A^{3-};\ K = K_{a_3}$$

What is the observed trend of dissociation constants in successive stages?
(A) $K_{a_1} > K_{a_2} > K_{a_3}$ (B) $K_{a_1} = K_{a_2} = K_{a_3}$
(C) $K_{a_1} < K_{a_2} < K_{a_3}$ (D) $K_{a_1} = K_{a_2} + K_{a_3}$

Q.57 What is the value of pK_w of water?
(A) 7 (B) 10
(C) 12 (D) 14

Q.58 Match the Column I with Column II and choose the correct option from the codes given below.

	Column I (Aqueous solutions)	**Column II (Relativevalue of H_3O^+ and OH^-)**
a.	Acidic	1. $[H_3O^+] < [OH^-]$
b.	Neutral	2. $[H_3O^+] > [OH^-]$
c.	Basic	3. $[H_3O^+] = [OH^-]$

Codes
(A) a-2, b-1, c-3 (B) a-1, b-2, c-3
(C) a-1, b-3, c-2 (D) a-2, b-3, c-1

Q.59 What will be the pH of 1×10^{-4} M H_2SO_4 solution?
(A) 10.4 (B) 3.70
(C) 3 (D) 13

Q.60 The ionisation of weak base MOH can be represented by equation $MOH\,(aq) \rightleftharpoons M^+\,(aq) + OH^-(aq)$

$$K_b = [M^+]\,[OH^-]\,/\,[MOH]$$

Where K_b is represented as
(A) base ionisation constant
(B) acid ionisation constant
(C) ionic product of water
(D) Both (A) and (B)

Q.61 If the pH of a solution is 2, the hydrogen ion concentration in moles per litre is
(A) 1×10^{-14} (B) 1×10^{-2}
(C) 1×10^{-7} (D) 1×10^{-12}

Q.62 Point out the correct relation between K_a, K_b and K_w.
(A) $K_a + K_b = K_w$ (B) $K_a - K_b = K_w$
(C) $\frac{K_a}{K_b} = K_w$ (D) $K_a \times K_b = K_w$

Q.63 $$\underset{\text{acid}}{H_2O(\ell)} + \underset{(X)}{H_2O\,(\ell)} \rightleftharpoons \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{(Y)}{OH^-(aq)}$$

Here, (X) and (Y) refer to
(A) base and conjugate acid
(B) acid and conjugate base
(C) base and conjugate base
(D) acid and conjugate acid

Q.64 Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the –

(A) pH scale
(B) pOH scale
(C) ionic product of water
(D) Both (A) and (B)

Q.65 What will be the pH of a soft drink if hydrogen ion concentration in sample is 3.8×10^{-3} M?

(A) 3.8
(B) 5.04
(C) 2.42
(D) 9.2

PART-12 : BUFFER SOLUTIONS

Q.66 An acidic buffer solution can be prepared by mixing the solution of

(A) sodium acetate and acetic acid
(B) ammonium acetate and ammonium hydroxide
(C) sodium chloride and sodium hydroxide
(D) potassium sulphate and sulphuric acid.

Q.67 Which of the following will produce a buffer solution when mixed in equal volumes?

(A) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(B) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl
(C) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl
(D) 0.1 mol dm^{-3} CH_3COONa and 0.1 mol dm^{-3} NaOH

Q.68 The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called –

(A) homogeneous solutions
(B) heterogeneous solutions
(C) ionic solutions
(D) buffer solutions

PART-13 : SOLUBILITY EQUILIBRIA OF SPARINGLY SOLUBLE SALTS

Q.69 The solubility of salts of weak acids like phosphates increases at –

(A) higher pOH
(B) lower pOH
(C) higher pH
(D) lower pH

Q.70 Solubility product expression of salt MX_4 which is sparingly soluble with a solubility 's' can be given as –

(A) $256s^5$
(B) $16s^3$
(C) 5s
(D) $25s^4$

Q.71 Match the column I with column II and mark the appropriate choice.

Column I	Column II
(a) $Fe(OH)_3$	(i) $K_{sp} = s^2$
(b) Ag_2CrO_4	(ii) $K_{sp} = 27s^4$
(c) CH_3COOAg	(iii) $K_{sp} = 108\ s^5$
(d) $Ca_3(PO_4)_2$	(iv) $K_{sp} = 4s^3$

(A) (a) – (iii), (b) – (ii), (c) – (iv), (d) – (i)
(B) (a) – (ii), (b) – (iv), (c) – (i), (d) – (iii)
(C) (a) – (i), (b) – (iii), (c) – (ii), (d) – (iv)
(D) (a) – (iv), (b) – (i), (c) – (iii), (d) – (ii)

Q.72 The solubility product of AgCl is 1.5625×10^{-10} at 25°C. Its solubility in grams per litre will be

(A) 143.5
(B) 108
(C) 1.57×10^{-8}
(D) 1.79×10^{-3}

Q.73 What is the range of solubility of slightly soluble salts?

(A) 0.001 M – 0.01 M
(B) 0.01 M – 0.1 M
(C) 0.1 M – 1.0 M
(D) 1.0 M – 10.0 M

Q.74 For a reaction, $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$, K_{sp} can be represented as

(A) $[A^{y+}]^x [B^{x-}]^y$
(B) $[A]^y [B]^x$
(B) $[A]^x [B]^y$
(D) $[A]^{x+y} [B]^{x-y}$

Q.75 The values of K_{sp} of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble?

(A) $Ni(OH)_2$ is more soluble than AgCN.
(B) AgCN is more soluble than $Ni(OH)_2$.
(C) Both $Ni(OH)_2$ and AgCN soluble to same extent.
(D) $Ni(OH)_2$ is soluble but AgCN is insoluble.

Q.76 Solubility product of radium sulphate is 4×10^{-11}. What will be the solubility of Ra^{2+} in 0.10 M Na_2SO_4?

(A) 4×10^{-10} M
(B) 2×10^{-5} M
(C) 4×10^{-5} M
(D) 2×10^{-10} M

Q.77 $BaSO_4(s) \xrightleftharpoons[\text{in water}]{\text{saturated solution}} Ba^{2+}(aq) + SO_4^{2-}(aq).$

The solubility product of the above reaction is

(A) $K[BaSO_4] = [Ba^{2+}][SO_4^{2-}]$
(B) $K[Ba^{2+}] = [BaSO_4]$
(C) $K[Ba^{2+}][SO_4^{2-}] = [BaSO_4]$
(D) $K[SO_4^{2-}] = [BaSO_4]$

Q.78 The solubility product of AgCl is 1.8×10^{-10}. Precipitation of AgCl will occur by mixing which of the following solutions in equal volumes?

(A) 10^{-8} M Ag^+ and 10^{-8} M Cl^- ions
(B) 10^{-3} M Ag^+ and 10^{-3} M Cl^- ions
(C) 10^{-6} M Ag^+ and 10^{-6} M Cl^- ions
(D) 10^{-10} M Ag^+ and 10^{-10} M Cl^- ions

Q.79 From Le-Chatelier's principle that if we __(i)__ the concentration of anyone of the ions, it should combine with the ion of its __(ii)__charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$. Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again __(iii)__. Correct words for (i), (ii) and (iii) are –

(A) decrease, same, $K_{sp} > Q_{sp}$
(B) increase, opposite, $K_{sp} = Q_{sp}$
(C) increase, same, $K_{sp} > Q_{sp}$
(D) decrease, opposite, $K_{sp} > Q_{sp}$

Q.80 Let the solubilities of AgCl in pure H_2O, 0.01 M $CaCl_2$, 0.01 M NaCl and 0.05 M $AgNO_3$ be s_1, s_2, s_3, s_4 M respectively. The correct relationship between these quantities would be

(A) $s_1 > s_2 > s_3 > s_4$
(B) $s_1 > s_2 = s_3 > s_4$
(C) $s_1 > s_3 > s_2 > s_4$
(D) $s_4 > s_2 > s_3 > s_1$

EXERCISE - 2 [LEVEL-2]

Choose one correct response for each question.

Q.1 Choose the correct statement(s)

(A) There are an infinite number of equilibrium positions at a given temperature depending on the initial concentrations

(B) The size of K has no relationship to the speed at which equilibrium is achieved.

(C) A pure liquid or solid is never included in the equilibrium expression.

(D) All of these

Q.2 For the reaction $2NO_2(g) \rightleftharpoons N_2O_4(g)$, K_p/K_c; is equal to

(A) $\frac{1}{RT}$ (B) $\sqrt{RT}$

(C) RT (D) $(RT)^2$

Q.3 The pH of a 10^{-10} M HCl solution is approximately –

(A) 10 (B) 7

(C) 1 (D) 14

Q.4 The expression for equilibrium constant, K_c for the following reaction is

$Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

(A) $K_c = \frac{[Fe(OH)_3]}{[Fe^{3+}][OH^-]^3}$ (B) $K_c = \frac{[Fe(OH)_3]}{[Fe^{3+}][OH^-]}$

(C) $K_c = \frac{1}{[Fe^{3+}][OH^-]^3}$ (D) $K_c = [Fe(OH)_3]$

Q.5 pH of a solution is 10. The OH^- ion concentration in the solution would be

(A) 10^{-4} mol/litre (B) 10^{-6} mol/litre

(C) 10^{-8} mol/litre (D) 10^{-10} mol/litre

Q.6 Calculate the molar solubility of $Ni(OH)_2$ in 0.10M NaOH. The ionic product of $Ni(OH)_2$ is 2.0×10^{-15}.

(A) 6.0×10^{-12} M (B) 8.0×10^{-13} M

(C) 2.0×10^{-13} M (D) 5.0×10^{-12} M

Q.7 Using the equation ($K = e^{-\Delta G^\ominus/RT}$), the reaction spontaneity can be interpreted in terms of the value of $\Delta G^\ominus$ is/are

(A) If $\Delta G^\ominus < 0$, then $-\Delta G^\ominus/RT$ is positive, and $e^{-\Delta G^\ominus/RT} > 1$, making K > 1, which implies a spontaneous reaction or the reaction which proceeds in the forward direction to such an extent that the products are present predominantly.

(B) If $\Delta G^\ominus > 0$, then $-\Delta G^\ominus/RT$ is negative, and $e^{-\Delta G^\ominus/RT} < 1$, that is, K < 1, which implies a non-spontaneous reaction or a reaction which proceeds in the forward direction to such a small degree that only a very minute quantity of product is formed.

(C) Both (A) and (B)

(D) None of the above

Q.8 For pure water

(A) pH increases and pOH decreases with rise in temperature.

(B) pH decreases and pOH increases with rise in temperature.

(C) both pH and pOH increases with rise in temperature.

(D) both pH & pOH decreases with rise in temperature.

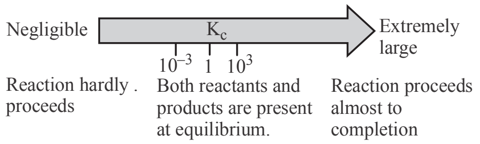
Q.9 PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K with concentration 2.1 M PCl_3, 2.1 M Cl_2 and 1.9 M PCl_5. The equilibrium constant for the given reaction is

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(A) 2.32 (B) 1.79

(C) 4.2 (D) 3.8

Q.10 Consider the following figure which shows dependence of extent of reaction on K_c.



Point out of the correct statement(s) for the above graph.

(A) If $K_c > 10^3$, products predominate over reactants, i.e., K_c is very large, the reaction proceeds nearly to completion.

(B) If $K_c < 10^{-3}$, reactants predominate over products, i.e., if K_c is very small, the reaction proceeds rarely.

(C) If K_c is in the range of 10^{-3} to 10^3, appreciable concentrations of both reactants and products are present.

(D) All of the above

Q.11 At 350 K, K_p for the reaction given below is 3.0×10^{10} bar^{-1} at equilibrium. What will be the value of K_c at this temperature? $2N_2(g) + O_2(g) \rightleftharpoons 2N_2O(g)$

(A) 7.4×10^{11} L mol^{-1} (B) 8715×10^{10} L mol^{-1}

(C) 0.08 L mol^{-1} (D) 8.715×10^{11} L mol^{-1}

Q.12 At 90°C, pure water has $H_3O^+ = 10^{-6}$ mol/litre. The value of K_w at 90°C is

(A) 10^{-6} (B) 10^{-12}

(C) 10^{-14} (D) 10^{-8}

Q.13 What is the molar solubility S of a solid salt with general formula $M_x^{p+}X_y^{q-}$?

(A) $\left(\frac{K_{sp}}{x^y \cdot y^x}\right)^{1/x+y}$ (B) $\left(\frac{K_{sp}}{x^x \cdot y^y}\right)^{x+y}$

(C) $\left(\frac{K_{sp}}{x^x \cdot y^y}\right)^{1/x+y}$ (D) $\left(\frac{K_{sp}}{x^y \cdot y^x}\right)^{x+y}$

Q.14 For the reaction $a + b \rightleftharpoons c + d$, initially concentrations of a and b are equal and at equilibrium the concentration of d will be twice of that of a. What will be the equilibrium constant for the reaction?

(A) 2 (B) 9

(C) 4 (D) 3

Q.15 At 473 K, K_c for the reaction $PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g)$ is 8.3×10^{-3}. What will be the value of K'_c for the formation of PCl_5 at the same temperature?

(A) 8.3×10^{3} (B) 120.48

(C) 8.3×10^{-3} (D) 240.8

Q.16 Correct statements for Sulphuric acid :

(A) It is a strong acid in the first dissociation step (is very large).

(B) It is a weak acid in the second step.

(C) It is a strong acid in the second step.

(D) Both (A) and (B)

Q.17 Production of ammonia according to the reaction, $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$; $\Delta H = -92.38$ kJ mol^{-1} is an exothermic process. At low temperature, the reaction shifts in

(A) forward direction

(B) backward direction

(C) either forward or backward direction

(D) None of the above

Q.18 For the reaction, $H_2\,(g) + I_2(g) \rightleftharpoons 2HI\,(g)$;
$K_c = 57.0$ at 700 K The molar concentration of $[H_2]_t = 0.10$ M, $[I_2]_t = 0.20$ M and $[HI]_t = 0.40$M Calculate the reaction quotient, Q_c of the reaction.

(A) 10.0 (B) 7.0

(C) 8.0 (D) 12.0

Q.19 The value of K_c for the following equilibrium is

$$CaCO_3\,(s) \rightleftharpoons CaO(s) + CO_2(g)$$

Given $K_p = 167$ bar at 1073 K.

(A) 1.896 mol L^{-1} (B) 4.38×10^{-3} mol L^{-1}

(C) 6.3×10^{4} mol L^{-1} (D) 6.626 mol L^{-1}

Q.20 Formation of ClF_3 from Cl_2 and F_2 is an exothermic process. The equilibrium system can be represented as $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3$; $\Delta H = -329$ kJ
Which of the following will increase quantity of ClF_3 in the equilibrium mixture?

(A) Increase in temperature, decrease in pressure, addition of Cl_2.

(B) Decrease in temperature and pressure, addition of ClF_3.

(C) Increase in temperature and pressure, removal of Cl_2.

(D) Decrease in temperature, increase in pressure, addition of F_2

Q.21 Nucleophiles are __ while electrophiles are ____

(A) Lewis bases, Lewis acids

(B) Lewis acids, Lewis bases

(C) Bronsted acids, Bronsted bases

(D) Lewis acids, Bronsted bases

Q.22 In which of the following reactions the increase in pressure will favour the increase in products?

(A) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(B) $PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g)$

(C) $PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g)$

(D) $2CO_2\,(g) \rightleftharpoons 2CO(g) + O_2\,(g)$

Q.23 Equimolar solutions of HF, HCOOH and HCN at 298 K have the values of K_a as 6.8×10^{-4}, 1.8×10^{-4} and 4.8×10^{-9} respectively. What will be the order of their acidic strength?

(A) HF > HCN > HCOOH (B) HF > HCOOH > HCN

(C) HCN > HF > HCOOH (D) HCOOH > HCN > HF

Q.24 In which of the following solvents is silver chloride most soluble?

(A) 0.1 mol dm^{-3} $AgNO_3$ solution

(B) 0.1 mol dm^{-3} HCl solution

(C) H_2O

(D) Aqueous ammonia

Q.25 Which of the following salts with a concentration 0.1 M will give a basic solution?

(A) Ammonium acetate (B) Ammonium chloride

(C) Ammonium sulphate (D) Sodium acetate

Q.26 Consider the equilibrium set up:

$2H_2\,(g) + CO(g) \rightleftharpoons CH_3OH(g)$

What will be the effect of the following on the equilibrium of the reaction?

(i) Addition of H_2 (ii) Addition of CH_3OH

(iii) Removal of CO (iv) Removal of CH_3OH

(A) (i)-Forward, (ii)-Backward, (iii)-Backward, (iv)-Forward

(B) (i)-Backward, (ii)-Backward, (iii)-Forward, (iv)-Forward,

(C) (i)-Forward, (ii)-Forward, (iii)-Backward, (iv)-Backward

(D) (i)-Backward, (ii)-Forward, (iii)-Forward, (iv)-Backward

Q.27 K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constants for the following reactions:

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

$HS^- \rightleftharpoons H^+ + S^{2-}$

$H_2S \rightleftharpoons 2H^+ + S^{2-}$

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is

(A) $K_{a_3} = K_{a_1} \times K_{a_2}$ (B) $K_{a_3} = K_{a_1} + K_{a_2}$

(C) $K_{a_3} = K_{a_1} - K_{a_2}$ (D) $K_{a_3} = K_{a_1} / K_{a_2}$

Q.28 At 500 K, equilibrium constant, K_c, for the following reaction is 5. $\frac{1}{2}H_2\,(g) + \frac{1}{2}I_2\,(g) \rightleftharpoons HI\,(g)$

What would be the equilibrium constant K_c for the reaction: $2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$?

(A) 0.04 (B) 0.4

(C) 25 (D) 2.5

Q.29 1 mole N_2 and 3 mol H_2 are placed in a closed container at a pressure of 4 atm. The pressure falls to 3 atm at the same temperature when the following equilibrium is attained. $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$. The equilibrium constant K_p for dissociation of NH_3 is –

(A) $\frac{1}{0.5} \times (1.5)^3\,\text{atm}^{-2}$ (B) $0.5 \times (1.5)^3\,\text{atm}^2$

(C) $\frac{0.5 \times (1.5)^3}{3 \times 3}\,\text{atm}^2$ (D) $\frac{3 \times 3}{0.5 \times (1.5)^3}\,\text{atm}^{-2}$

Q.30 For the reaction: $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, the standard free energy is $\Delta G° > 0$.

The equilibrium constant (K) would be –

(A) $K = 0$
(B) $K > 1$
(C) $K = 1$
(D) $K < 1$

Q.31 pK_a of a weak acid is 5.76 and pK_b of a weak base is 5.25. What will be the pH of the salt formed by the two?

(A) 7.255
(B) 7.005
(C) 10.225
(D) 4.255

Q.32 Which of the following species can act both as an acid as well as a base?

(A) SO_4^{2-}
(B) HSO_4^-
(C) PO_4^{3-}
(D) O^{2-}

Q.33 What is pOH of an aqueous solution with hydrogen ion concentration equal to 3×10^{-5} mol L^{-1}?

(A) 9.47
(B) 4.52
(C) 12.69
(D) 11.69

Q.34 What will be the ionisation constant of formic acid if its 0.01 M solution is 14.5% ionised?

(A) 2.1×10^{-4}
(B) 14.5
(C) 0.145
(D) 1.45×10^{-4}

Q.35 PCl_5, PCl_3 and Cl_2 are at equilibrium at 500 K in a closed container and their concentrations are 0.8×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1} respectively. The value of K_c for the reaction:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ will be

(A) 1.8×10^{3}
(B) 1.8×10^{-3}
(C) 1.8×10^{-4}
(D) 0.55×10^{-4}

Q.36 A 20.0 litre vessel initially contains 0.50 mole each of H_2 and I_2 gases. These substances react with finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if $K_{eq} = 49$ for the reaction

$H_2 + I_2 \rightleftharpoons 2HI$

(A) 0.78 M
(B) 0.039 M
(C) 0.033 M
(D) 0.021 M

Q.37 If CO_2 be passed into water, what will remain present in solution –

(A) CO_2, H_2CO_3, CO_3^{2-}, HCO_3^-
(B) H_2CO_3, CO_2
(C) HCO_3^-, CO_3^{2-}
(D) CO_2, HCO_3^-

Q.38 What will be the solubility of AgCl in 0.05 M NaCl aqueous solution if solubility product of AgCl is 1.5×10^{-10}?

(A) 3×10^{-9} mol L^{-1}
(B) 1.5×10^{-5} mol L^{-1}
(C) 0.05 mol L^{-1}
(D) 3×10^{9} mol L^{-1}

Q.39 Consider following reactions in equilibrium with equilibrium concentration 0.01 M of every species

(I) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.
(II) $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$.
(III) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

Extent of the reactions taking place is –

(A) I > II > III
(B) I < II < III
(C) II < III < I
(D) III < I < II

Q.40 50 litre of a solution containing 10^{-5} mole of is mixed with 50 litre of a 2×10^{-7} M HBr solution. $[Ag^+]$ in resultant solution is [Given : $K_{sp}(AgBr) = 5 \times 10^{-13}$]

(A) 10^{-5} M
(B) 10^{-6} M
(C) 10^{-7} M
(D) None of these

EXERCISE - 3 (NUMERICAL VALUE BASED QUESTIONS)

NOTE : The answer to each question is a NUMERICAL VALUE.

Q.1 A sample of HI(g) is placed in flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI(g) is 0.04 atm. What is K_P for the given equilibrium ?

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

Q.2 In a gaseous system of the type, $AB(g) \rightleftharpoons A(g) + B(g)$, at a given temperature 50% of AB is dissociated at equilibrium. The value of P at equilibrium in terms of the equilibrium constant is x K_p. Find the value of x.

Q.3 25 mL of H_2 and 18 mL of I_2 vapours were heated in a sealed glass tube at 465ºC and at equilibrium 30.8 mL of HI was formed. Calculate the approximate percentage degree of dissociation of HI at 465ºC.

Q.4 For the reaction : $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$.

Degree of dissociation of NH_3 is given as :

$\alpha = \left[1 + \frac{3\sqrt{3}}{4}\frac{P}{K_p}\right]^{-1/2}$, where 'P' is equilibrium pressure. If K_p of the above reaction is 78.1 atm at 400°C, K_c is (A + 0.413) moles litre^{-1}. Find the value of A.

Q.5 The pressure of iodine gas at 1273 K is found to be 0.112atm whereas the expected pressure is 0.074 atm. The increased pressure is due to the dissociation of $I_2 \rightleftharpoons 2I$. K_p is 15.75×10^{-A}. Find the value of A.

Q.6 A diprotic acid H_2A undergoes the following dissociation reaction :

$$H_2A \rightleftharpoons HA^- + H^+ ; \qquad K_1 = 1.0 \times 10^{-7}$$
$$NA \rightleftharpoons A^{2-} + H^+ ; \qquad K_2 = 1.0 \times 10^{-11}$$

A 20.0 ml of a solution containing a mixture of Na_2A and NaHA is titrated with 0.300 M hydrochloric acid, the progress of the titration is followed with a glass electrode pH meter.

ml of HCl added	**pH**
1.0	10.33
10.00	9.00

Calculate the total volume (in ml) of HCl required to reach the second equivalence point.

Q.7 A solution contains 0.1 M H_2S and 0.3 M HCl. The concentration of S^{2-} is 1.44×10^{-A} M. Find the value of A. Given K_{a_1} and K_{a_2} for H_2S are 10^{-7} and 1.3×10^{-13} respectively.

Q.8 In above quesiton concentration of HS^- ions in solution is 3.3×10^{-A} M. Find the value of A.

Q.9 50 mL of 0.1 M NaOH is added to 75 mL of 0.1 M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, Calculate the integral part of pH value.

Q.10 The dissociation constants for aniline and acetic acid at 25°C are 3.83×10^{-10} M and 1.75×10^{-5} M respectively and K_w of water at 25°C is 1.008×10^{-14} M^2. The degree of hydrolysis of anilinium acetate in a decinormal solution is 5.5/A. Find the value of A.

Q.11 Calculate the integral part of pH value of a solution that is 0.050 M in ammonium ion.

EXERCISE - 4 [PREVIOUS YEARS AIEEE / JEE MAIN QUESTIONS]

SECTION-A (CHEMICAL EQUILIBRIUM)

Q.1 For the reaction $CO + \frac{1}{2} O_2 \rightarrow CO_2$, the value of $\frac{K_P}{K_C}$ is **[AIEEE-2002]**

(A) $\frac{1}{RT}$ (B) $\sqrt{RT}$ (C) $\frac{1}{\sqrt{RT}}$ (D) RT

Q.2 Which of the following equilibria is not affected by change in volume of the flask – **[AIEEE-2002]**

(A) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

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

(C) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

(D) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

Q.3 For the reaction equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1} respectively. The value of K_C for the reaction is – **[AIEEE-2003]**

(A) 3×10^{-3} mol L^{-1} (B) 3×10^{3} mol L^{-1}

(C) 3.3×10^{2} mol L^{-1} (D) 3×10^{-1} mol L^{-1}

Q.4 Consider the reaction equilibrium

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H° = -198$ kJ

On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is - **[AIEEE-2003]**

(A) Lowering the temperature and increasing the pressure.

(B) Any value of temperature and pressure.

(C) Lowering of temperature as well as pressure.

(D) Increasing temperature as well as pressure.

Q.5 What is the equilibrium expression for the reaction

$P_{4(S)} + 5O_{2(g)} \rightleftharpoons P_4O_{10(s)}$? **[AIEEE-2004]**

(A) $K_C = [P_4O_{10}] / [P_4][O_2]^5$

(B) $K_C = [P_4O_{10}] / 5[P_4][O_2]$

(C) $K_C = [O_2]^5$

(D) $K_C = 1/[O_2]^5$

Q.6 For the reaction $CO_{(g)} + Cl_{2(g)} \rightleftharpoons COCl_{2(g)}$ the K_p/K_c is equal to - **[AIEEE-2004]**

(A) 1/RT (B) RT

(C) $\sqrt{RT}$ (D) 1.0

Q.7 The equilibrium constant for the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ at temperature T is 4×10^{-4}. The value of K_C for the reaction

$NO_{(g)} \rightleftharpoons \frac{1}{2} N_{2(g)} + \frac{1}{2} O_{2(g)}$ at the same temperature is

(A) 2.5×10^2 (B) 50 **[AIEEE-2004]**

(C) 4×10^{-4} (D) 0.02

Q.8 For the reaction : $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$, ($K_c = 1.8 \times 10^{-6}$ at 184°C) (R = 0.0831 kJ/(mol.K))

When K_p and K_c are compared at 184°C it is found that

(A) K_p is less than K_c **[AIEEE-2005]**

(B) K_p is greater than K_c

(C) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure.

(D) $K_p = K_c$

Q.9 The exothermic formaton of ClF_3 is represented by the equation : $Cl_{2(g)} + 3F_{2(g)} \rightleftharpoons 2ClF_{3(g)}$; $\Delta_rH = -329$ kJ

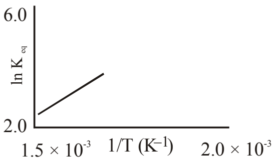
Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3 ?

(A) Removing Cl_2 **[AIEEE-2005]**

(B) Increasing the temperature (C) Adding F_2

(D) Increasing the volume of the container

Q.10 A schematic plot of ln K_{eq} versus inverse of temperature for a reaction is shown below **[AIEEE-2005]**



The reaction must be

(A) endothermic

(B) exothermic

(C) highly spontaneous at ordinary temperature

(D) one with negligible enthalpy change

Q.11 An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm ? The equilibrium constant for NH_4HS decomposition at this temperature is– **[AIEEE-2005]**

(A) 0.18 (B) 0.30

(C) 0.11 (D) 0.17

Q.12 Phosphorus pentachloride dissociates as follows, is a closed reaction vessel, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be – **[AIEEE 2006]**

(A) $\left(\frac{2x}{1-x}\right)P$ (B) $\left(\frac{x}{x-1}\right)P$

(C) $\left(\frac{x}{1-x}\right)P$ (D) $\left(\frac{x}{x+1}\right)P$

Q.13 The equilibrium constant for the reaction

$SO_3(g) \rightleftharpoons SO_2(g) + ½ O_2(g)$ is $K_c = 4.9 \times 10^{-2}$. The value of K_c for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ will be **[AIEEE 2006]**

(A) 2.40×10^{-3} (B) 9.8×10^{-2}

(C) 4.9×10^{-2} (D) 416

Q.14 For the following three reactions a, b and c, equilibrium constants are given - **[AIEEE 2008]**

(a) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g); K_1$

(b) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g); K_2$

(c) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g); K_3$

Which of the following relations is correct ?

(A) $K_2 K_3 = K_1$ (B) $K_3 = K_1 K_2$
(C) $K_3 K_2^3 = K_1^2$ (D) $K_1\sqrt{K_2} = K_3$

Q.15 The equilibrium constants Kp_1 and Kp_2 for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is -
(A) 1 : 1 (B) 1 : 3 **[AIEEE 2008]**
(C) 1 : 9 (D) 1 : 36

Q.16 A vessel at 1000 K contains CO_2 with a pressure of 0.5atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is – **[AIEEE 2011]**
(A) 1.8 atm (B) 3 atm
(C) 0.3 atm (D) 0.18 atm

Q.17 The equilibrium constant (K_c) for the reaction
$N_2(g) + O_2(g) \rightarrow 2NO\,(g)$ at temperature T is 4×10^{-4}.
The value of K_c for the reaction **[AIEEE 2012]**

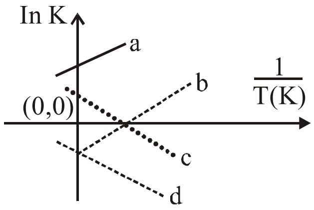
$NO(g) \rightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is
(A) 0.02 (B) 2.5×10^2
(C) 4×10^{-4} (4) 50.0

Q.18 For the reaction, $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$, If $Kp = K_C(RT)^x$ where the symbols have ususal meaning then value of x is (assuming ideality) **[JEE MAIN 2014]**
(A) 1/2 (B) 1
(C) –1 (D) –1/2

Q.19 The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is [A] = 1/2, [B] = 2 and [C] = 1/2. The reaction proceeds in the :
[R = 8.314 J/K/mol, e = 2.718] **[JEE MAIN 2015]**
(A) Reverse direction because $Q > K_C$
(B) Forward direction because $Q < K_C$
(C) Reverse direction because $Q < K_C$
(D) Forward direction because $Q > K_C$

Q.20 The equilibrium constant at 298 K for a reaction $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1M each, then equilibrium concentration of D (in mol L^{-1}) will be **[JEE MAIN 2016]**
(A) 0.818 (B) 1.818
(C) 1.182 (D) 0.182

Q.21 Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction? **[JEE MAIN 2018]**



(A) c and d (B) a and d
(C) a and b (D) b and c

Q.22 Consider the following reversible chemical reactions :

$A_2(g) + Br_2(g) \xrightleftharpoons{K_1} 2AB(g)$ .....(1)

$6AB(g) \xrightleftharpoons{K_2} 3A_2(g) + 3B_2(g)$ .....(2)

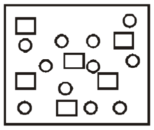
The relation between K_1 and K_2 is : **[JEE MAIN (JAN) 2019]**
(A) $K_2 = K_1$ (B) $K_2 = K_1^{-3}$
(C) $K_1K_2 = 3$ (D) $K_1K_2 = 1/3$

Q.23 For the following reactions, equilibrium constants are given
$S(s) + O_2(g) \rightleftharpoons SO_2(g); K_1 = 10^{52}$
$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); K_2 = 10^{129}$
The equilibrium constant for the reaction,
$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is
[JEE MAIN 2019 (APRIL)]
(A) 10^{181} (B) 10^{154}
(C) 10^{25} (D) 10^{77}

Q.24 For the reaction, $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -57.2\,kJ\,mol^{-1}$ and $K_c = 1.7 \times 10^{16}$.
Which of the following statement is INCORRECT?
[JEE MAIN 2019 (APRIL)]
(A) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.
(B) The equilibrium will shift in forward direction as the pressure increase.
(C) The equilibrium constant decreases as the temperature increases.
(D) The addition of inert gas at constant volume will not affect the equilibrium constant.

Q.25 In which one of the following equilibria, $K_p \neq K_c$?
[JEE MAIN 2019 (APRIL)]
(A) $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$
(B) $2\,HI\,(g) \rightleftharpoons H_2(g) + I_2(g)$
(C) $2NO\,(g) \rightleftharpoons N_2(g) + O_2(g)$
(D) $2C\,(s) + O_2(g) \rightleftharpoons 2CO(g)$

Q.26 In the figure shown below reactant A (represented by square) is in equilibrium with product B (represented by circle). $A \rightleftharpoons B$.
The equilibrium constant is : **[JEE MAIN 2020 (JAN)]**



(A) 2 (B) 1
(C) 8 (D) 4

SECTION-B (IONIC EQUILIBRIUM)

Q.1 The solubility of $Mg(OH)_2$ is x mole/ltr. then its solubility product is - **[AIEEE-2002]**
(A) x^3 (B) $5x^3$
(C) $4x^3$ (D) $2x^2$

Q.2 The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol L^{-1}. Its solubility product will be – **[AIEEE-2003]**

(A) 1×10^{-15} (B) 1×10^{-10}

(C) 4×10^{-15} (D) 4×10^{-10}

Q.3 The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{SP}. 's' is given in terms of K_{sp} by the relation - **[AIEEE-2004]**

(A) $s = (K_{SP}/128)^{\frac{1}{4}}$ (B) $s = (128K_{SP})^{\frac{1}{4}}$

(C) $s = (256K_{SP})^{\frac{1}{5}}$ (D) $s = (K_{SP}/256)^{\frac{1}{5}}$

Q.4 The solubility product of a salt having general formula MX_2, in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **[AIEEE-2005]**

(A) 1.0×10^{-4} M (B) 2.0×10^{-6} M

(C) 4.0×10^{-10} M (D) 1.6×10^{-4} M

Q.5 The first and second dissociation constants of an acid H_2A are 1.0×10^{-5} & 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be -**[AIEEE-2007]**

(A) 5.0×10^{-5} (B) 5.0×10^{15}

(C) 5.0×10^{-15} (D) 0.2×10^{5}

Q.6 The pK_a of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is- **[AIEEE-2007]**

(A) 4.5 (B) 2.5

(C) 9.5 (D) 7.0

Q.7 In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is : $AgIO_{3(s)} \rightleftharpoons Ag^{+}_{(aq)} + IO_3^{-}{}_{(aq)}$

If the solubility product K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 ml of its saturated solution ? **[AIEEE-2007]**

(A) 28.3×10^{-2} g (B) 2.83×10^{-3} g

(C) 1.0×10^{-7} g (D) 1.0×10^{-4} g

Q.8 The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be - **[AIEEE-2008]**

(A) 4.79 (B) 7.01

(C) 9.22 (D) 9.58

Q.9 Solid $Ba(NO_3)$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{2+} will a precipitate begin to form ? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$) **[AIEEE-2009]**

(A) 5.1×10^{-5} M (B) 8.1×10^{-8} M

(C) 8.1×10^{-7} M (D) 4.1×10^{-5} M

Q.10 In aqueous solution the ionization constants for carbonic acid are $K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$.
Select the correct statement for a saturated 0.034 M solution of the carbonic acid. **[AIEEE 2010]**

(A) The concentration of CO_3^{2-} is 0.034 M.

(B) The concentration of CO_3^{2-} is greater than that of HCO_3^{-}

(C) The concentration of H^+ & HCO_3^- are approximately equal.

(D) The concentration of H^+ is double that of CO_3^{2-}

Q.11 Solubility product of silver bromide is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120g of mol^{-1}) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **[AIEEE 2010]**

(A) 1.2×10^{-10} g (B) 1.2×10^{-9} g

(C) 6.2×10^{-5} g (D) 5.0×10^{-8} g

Q.12 At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ? **[AIEEE 2010]**

(A) 9 (B) 10

(C) 11 (D) 8

Q.13 The degree of dissociation (α) of a weak electrolyte, A_xB_y is related to van't Hoff factor (i) by the expression: **[AIEEE 2011]**

(A) $\alpha = \dfrac{i-1}{(x+y-1)}$ (B) $\alpha = \dfrac{i-1}{x+y+1}$

(C) $\alpha = \dfrac{x+y-1}{i-1}$ (D) $\alpha = \dfrac{x+y+1}{i-1}$

Q.14 The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant, K_a of the acid is : **[AIEEE 2012]**

(A) 3×10^{-1} (B) 1×10^{-3}

(C) 1×10^{-5} (D) 1×10^{-7}

Q.15 How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? **[JEE MAIN 2013]**

(A) 0.1 L (B) 0.9 L

(C) 2.0 L (D) 9.0 L

Q.16 pK_a of weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is: **[JEE MAIN 2017]**

(A) 1.0 (B) 7.2

(C) 6.9 (D) 7.0

Q.17 Which of the following salts is the most basic in aqueous solution? **[JEE MAIN 2018]**

(A) $FeCl_3$ (B) $Pb(CH_3COO)_2$

(C) $Al(CN)_3$ (D) CH_3COOK

Q.18 An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination? **[JEE MAIN 2018]**

	Base	**Acid**	**End point**
(A)	Weak	Strong	Yellow to pinkish red
(B)	Strong	Strong	Pink to colourless
(C)	Weak	Strong	Colourless to pink
(D)	Strong	Strong	Pinkish red to yellow

Q.19 An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 mL of a 1 M solution of Na_2SO_4 is added, $BaSO_4$ just begins to precipitate. The final volume is 500 mL. The solubility product of $BaSO_4$ is 1×10^{-10}. What is the original concentration of Ba^{2+}

[JEE MAIN 2018]

(A) 1.1×10^{-9} M (B) 1.0×10^{-10} M

(C) 5×10^{-9} M (D) 2×10^{-9} M

Q.20 An aqueous solution contains 0.10 M H_2S and 0.20M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that S^{2-} from HS^- ions is 1.2×10^{-13} then the concentration of S^{2-} ions in aqueous solution is : **[JEE MAIN 2018]**

(A) 6×10^{-21} (B) 5×10^{-19}

(C) 5×10^{-8} (D) 3×10^{-20}

Q.21 20 mL of 0.1 MH_2SO_4 solution is added to 30 mL of 0.2M NH_4OH solution. The pH of the resulatant mixture is :

[pK_b of $NH_4OH = 4.7$]. **[JEE MAIN 2019 (JAN)]**

(A) 9.4 (B) 5.0

(C) 9.0 (D) 5.2

Q.22 If solubility product of $Zr_3(PO_4)_4$ is denoted by K_{sp} and its molar solubility is denoted by S, then which of the following relation between S and K_{sp} is correct

[JEE MAIN 2019 (APRIL)]

(A) $S = \left(\frac{K_{sp}}{929}\right)^{1/9}$ (B) $S = \left(\frac{K_{sp}}{216}\right)^{1/7}$

(C) $S = \left(\frac{K_{sp}}{144}\right)^{1/6}$ (D) $S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$

Q.23 The pH of a 0.02M NH_4Cl solution will be

[Given $K_b(NH_4OH) = 10^{-5}$ and $\log 2 = 0.301$]

[JEE MAIN 2019 (APRIL)]

(A) 4.65 (B) 5.35

(C) 4.35 (D) 2.65

Q.24 Two solutions A and B, each of 100 L was made by dissolving 4g of NaOH and 9.8 g of H_2SO_4 in water, respectively. The pH of the resultant solution obtained from mixing 40 L of solution A and 10 L of solution B is_______. **[JEE MAIN 2020 (JAN)]**

Q.25 3 gram of acetic acid is mixed in 250 mL of 0.1 M HCl. This mixture is now diluted to 500 mL. 20mL of this solution is now taken in another container.

(1/2) mL of 5 M NaOH is added to this. Find the pH of this solution. ($\log 3 = 0.4771$, $pK_a = 4.74$)

[JEE MAIN 2020 (JAN)]

Q.26 The K_{sp} for the following dissociation is 1.6×10^{-5}

$PbCl_2 (s) \rightleftharpoons Pb^{2+} (aq) + 2Cl^- (aq)$

Which of the following choices is correct for a mixture of 300 mL 0.134 M $Pb(NO_3)_2$ and 100mL 0.4 M NaCl ?

[JEE MAIN 2020 (JAN)]

(A) $Q < K_{sp}$ (B) $Q > K_{sp}$

(C) $Q = K_{sp}$ (D) Not enough data provided

Q.27 The solubility product of $Cr(OH)_3$ at 298 K is 6.0×10^{-31}. The concentration of hydroxide ions in a saturated solution of $Cr(OH)_3$ will be :

[JEE MAIN 2020 (JAN)]

(A) $(18 \times 10^{-31})^{1/4}$ (B) $(2.22 \times 10^{-31})^{1/4}$

(C) $(4.86 \times 10^{-29})^{1/4}$ (D) $(18 \times 10^{-31})^{1/2}$

EXERCISE - 5 (PREVIOUS YEARS AIPMT/NEET EXAM QUESTIONS)

Choose one correct response for each question.

Q.1 What is the correct relationship between the pHs of isomolar solutions of sodium oxide (pH_1), sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4) ? **[AIPMT 2005]**

(A) $pH_1 > pH_2 > pH_3 > pH_4$
(B) $pH_1 > pH_2 \approx pH_3 > pH_4$
(C) $pH_1 < pH_2 < pH_3 < pH_4$
(D) $pH_1 < pH_2 < pH_3 \approx pH_4$

Q.2 At 25°C, the dissociation constant of a base, BOH, is 1.0×10^{-12}. The concentration of hydroxyl ions in 0.01M aqueous solution of the base would be – **[AIPMT 2005]**

(A) 1.0×10^{-5} mol L^{-1} (B) 1.0×10^{-6} mol L^{-1}
(C) 2.0×10^{-6} mol L^{-1} (D) 1.0×10^{-7} mol L^{-1}

Q.3 H_2S gas when passed through a solution of cations containing HCl precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because **[AIPMT 2005]**

(A) Presence of HCl decreases the sulphide ion concentration.
(B) Sulphides of group IV cations are unstable in HCl.
(C) Solubility product of group II sulphides is more than that of group IV sulphides.
(D) Presence of HCl increases the sulphides ion concentration.

Q.4 Equilibrium constants K_1 and K_2 for the following equilibria : **[AIPMT 2005]**

(i) $NO(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO_2(g), K_1$

(ii) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g), K_2$

The equilibrium constants K_1 and K_2 are related as –

(A) $K_2 = 1/K_1$ (B) $K_2 = K_1^{1/2}$
(C) $K_2 = 1/K_1^2$ (D) $K_2 = K_1^2$

Q.5 For the reaction : $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(\ell)$ $\Delta_rH = -170.8$ kJ mol^{-1} **[AIPMT 2006]**

Which of the following statement is not true –

(A) The equilibrium constant for the reaction is given by $K_p = \frac{[CO_2]}{[CH_4][O_2]}$.
(B) Addition of $CH_4(g)$ or $O_2(g)$ at equilibrium will cause a shift to the right.
(C) The reaction is exothermic.
(D) At equilibrium, the conentration of $CO_2(g)$ and $H_2O(\ell)$ are not equal.

Q.6 The hydrogen ion concentrated of a 10^{-8} M HCl aqueous solution at 298 K ($K_w = 10^{-14}$) is **[AIPMT 2006]**

(A) 11×10^{-8} M (B) 9.525×10^{-8} M
(C) 1.0×10^{-8} M (D) 1.0×10^{-6} M

Q.7 Which of the following pairs constitutes a buffer **[AIPMT 2006]**

(A) NaOH and NaCl (B) HNO_3 and NH_4NO_3
(C) HCl and KCl (D) HNO_2 and $NaNO_2$

Q.8 A weak acid, HA, has a K_a of 1.00×10^{-5} if 0.100 mole of this acid dissolved in one litre of water, the percentage of acid dissociated at equilibrium is closest to –

(A) 1.00% (B) 99.9% **[AIPMT 2007]**
(C) 0.100% (D) 99.0%

Q.9 The following equilibrium constants are given

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1
$N_2 + O_2 \rightleftharpoons 2NO$; K_2
$H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$; K_3

The equilibrium constant for the oxidation of NH_3 by oxygen to give NO is – **[AIPMT 2007]**

(A) $\frac{K_2K_3^2}{K_1}$ (B) $\frac{K_2^2K_3}{K_1}$

(C) $\frac{K_1K_2}{K_3}$ (D) $\frac{K_2K_3^3}{K_1}$

Q.10 Calculate the pOH of a solution at 25°C that contains 1×10^{-10} M of hydronium ions, i.e., H_3O^+. **[AIPMT 2007]**

(A) 4.000 (B) 9.0000
(C) 1.000 (D) 7.000

Q.11 The value of equilibrium constant of the reaction

$HI(g) \rightleftharpoons \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g)$ is 8.0.

The equilibrium constant of the reaction

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ will be: **[AIPMT 2008]**

(A) 1/8 (B) 1/16
(C) 1/64 (D) 16

Q.12 Equal volumes of three acid solutions of pH 3, 4 and 5 are mixed in a vessel. What will be the H^+ ion concentration in the mixture ? **[AIPMT 2008]**

(A) 1.11×10^{-3} M (B) 1.11×10^{-4} M
(C) 3.7×10^{-4} M (D) 3.7×10^{-3} M

Q.13 The values of Kp_1 and Kp_2 for the reactions

$X \rightleftharpoons Y + Z$ ....(i) and
$A \rightleftharpoons 2B$ ....(ii)

are in ratio of 9:1. If degree of dissociation of X and A be equal, then total pressure at equilibrium (i) and (ii) are in the ratio : **[AIPMT 2008]**

(A) 1 : 1 (B) 3 : 1
(C) 1 : 9 (D) 36 : 1

Q.14 If the concentration of OH^- ions in the reaction

$Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$ is decreased by 1/4 times, then equilibrium concentration of Fe^{3+} will increase by: **[AIPMT 2008]**

(A) 4 times (B) 8 times
(C) 16 times (D) 64 times

Q.15 The dissociation equilibrium of gas AB_2 can be represented as : $2AB_2\,(g) \rightleftharpoons 2AB\,(g) + B_2\,(g)$
The degree of dissociation is 'x' and is small compared to 1. The expression relating the degree of dissociation(x) with equilibrium constant Kp and total pressure P is: **[AIPMT 2008]**

(A) (K_p/P)
(B) $(2K_p/P)$
(C) $(2K_p/P)^{1/3}$
(D) $(2K_p/P)^{1/2}$

Q.16 The dissociation constants for acetic acid and HCN at 25°C are 1.5×10^{-5} and 4.5×10^{-10} respectively. The equilibrium constant for the equilibrium
$CN^- + CH_3COOH \rightleftharpoons HCN + CH_3COO^-$ would be: **[AIPMT 2009]**

(A) 3.0×10^{-5}
(B) 3.0×10^{-4}
(C) 3.0×10^{4}
(D) 3.0×10^{5}

Q.17 Which of the following molecules acts as a Lewis acid? **[AIPMT 2009]**

(A) $(CH_3)_2O$
(B) $(CH_3)_3P$
(C) $(CH_3)_3N$
(D) $(CH_3)_3B$

Q.18 The ionization constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is: **[AIPMT 2009]**

(A) 6.50×10^{-12}
(B) 5.65×10^{-13}
(C) 5.65×10^{-12}
(D) 5.65×10^{-10}

Q.19 What is the $[OH^-]$ in the final solution prepared by mixing 20.0 mL of 0.050 M HCl with 30.0 mL of 0.10 M $Ba(OH)_2$ **[AIPMT 2009]**

(A) 0.40 M
(B) 0.0050M
(C) 0.12 M
(D) 0.10 M

Q.20 If pH of a saturated solution of $Ba(OH)_2$ is 12, the value of its K_{sp} is: **[AIPMT (PRE) 2010]**

(A) $4.00 \times 10^{-6}\,M^3$
(B) $4.00 \times 10^{-7}\,M^3$
(C) $5.00 \times 10^{-6}\,M^3$
(D) $5.00 \times 10^{-7}\,M^3$

Q.21 In a buffer solution containing equal concentration of B^- & HB, the K_b for B^- is 10^{-10}. The pH of buffer solution: **[AIPMT (PRE) 2010]**

(A) 10
(B) 7
(C) 6
(D) 4

Q.22 What is $[H^+]$ in mol/L of a solution that is 0.20M in CH_3COONa and 0.10 M in CH_3COOH?
(K_a for $CH_3COOH = 1.8 \times 10^{-5}$) **[AIPMT (PRE) 2010]**

(A) 3.5×10^{-4}
(B) 1.1×10^{-5}
(C) 1.8×10^{-4}
(D) 9.0×10^{-6}

Q.23 In which of the following equilibrium K_c and K_p are not equal? **[AIPMT (PRE) 2010]**

(A) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$
(B) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
(C) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(D) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$

Q.24 The reaction, $2A\,(g) + B\,(g) \rightleftharpoons 3C\,(g) + D\,(g)$ is begun with the concentrations of A and B both at an initial value of 1.00 M. When equilibrium is reached, the concentration of D is measured and found to be 0.25 M. The value for the equilibrium constant for this reaction is given by the expression : **[AIPMT (MAINS) 2010]**

(A) $[(0.75)^3\,(0.25)] \div [(1.00)^2\,(1.00)]$
(B) $[(0.75)^3\,(0.25)] \div [(0.50)^2\,(0.75)]$
(C) $[(0.75)^3\,(0.25)] \div [(0.50)^2\,(0.25)]$
(D) $[(0.75)^3\,(0.25)] \div [(0.75)^2\,(0.25)]$

Q.25 Match List I (Equations) with List II (Types of processes) and select the correct option. **[AIPMT (MAINS) 2010]**

List I **Equations**	**List II** **Types of process**
(a) $K_p > Q$	(i) Non-spontaneous
(b) $\Delta G^\circ < RT \ln Q$	(ii) Equilibrium
(c) $K_p = Q$	(iii) Spontaneous and endothermic
(d) $T > \dfrac{\Delta H}{\Delta S}$	(iv) Spontaneous

(A) a - (i), b - (ii), c - (iii), d - (iv)
(B) a - (iii), b - (iv), c - (ii), d - (i)
(C) a - (iv), (b -(i), c - (ii), d - (iii)
(D) a - (ii), b - (i), c - (iv), d - (iii)

Q.26 For the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$, the equilibrium constant is K_1. The equilibrium constant is K_2 for the reaction : $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$.

What is K for the reaction :$NO_2\,(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$ **[AIPMT (PRE) 2011]**

(A) $\dfrac{1}{(K_1K_2)}$
(B) $\dfrac{1}{(2K_1K_2)}$
(C) $\dfrac{1}{(4K_1K_2)}$
(D) $\left[\dfrac{1}{K_1K_2}\right]^{1/2}$

Q.27 The value of ΔH for the reaction
$X_2(g) + 4Y_2\,(g) \rightleftharpoons 2XY_4\,(g)$ is less than zero.
Formation of $XY_4(g)$ will be favoured at **[AIPMT (PRE) 2011]**

(A) High pressure and low temperature
(B) High temperature and high pressure
(C) Low pressure and low temperature
(D) None of these

Q.28 A buffer solution is prepared in which the concentration of NH_3 is 0.30 M and the concentration of NH_4^+ is 0.20M. If the equilibrium constant, K_b for NH_3 equals 1.8×10^{-5}, what is the pH of this solution?
[log 1.8 = 0.255, log 2 = 0.3010, log 3 = 0.477] **[AIPMT (PRE) 2011]**

(A) 8.73
(B) 9.08
(C) 9.44
(D) 11.72

Q.29 Which is least likely to behave is Lewis base? **[AIPMT (PRE) 2011]**

(A) OH^-
(B) H_2O
(C) NH_3
(D) BF_3

Q.30 Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value ? **[AIPMT (PRE) 2012]**

(A) $BaCl_2$ (B) $AlCl_3$

(C) LiCl (D) $BeCl_2$

Q.31 Buffer solutions have constant acidity and alkalinity because : **[AIPMT (PRE) 2012]**

(A) these give unionised acid or base on reaction with added acid or alkali.

(B) acids and alkalies in these solution are shielded from attack by other ions.

(C) they have large excess of H^+ or OH^- ions

(D) they have fixed value of pH.

Q.32 Given that the equilibrium constant for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ has a value of 278 at a particular temperature. What is the value of the equilibrium constant for the following reaction at the same temperature? $SO_3(g) \rightleftharpoons SO_2(g) + ½O_2(g)$ **[AIPMT (MAINS) 2012]**

(A) 1.8×10^{-3} (B) 3.6×10^{-3}

(C) 6.0×10^{-2} (D) 1.3×10^{-5}

Q.33 Given the reaction between 2 gases represented by A_2 and B_2 to give the compound AB (g).

$$A_2(g) + B_2(g) \rightleftharpoons 2\,AB\,(g).$$

At equilibrium, the concentration

of $A_2 = 3.0 \times 10^{-3}$ M

of $B_2 = 4.2 \times 10^{-3}$ M

of $AB = 2.8 \times 10^{-3}$ M.

If the reaction takes place in a sealed vessel at 527°C, then the value of K_C will be : **[AIPMT (MAINS) 2012]**

(A) 2.0 (B) 1.9

(C) 0.62 (D) 4.5

Q.34 Which of these is least likely to act as a Lewis base?

(A) PF_3 (B) CO **[NEET 2013]**

(C) F^- (D) BF_3

Q.35 Which of the following salts will give highest pH in water? **[AIPMT 2014]**

(A) KCl (B) NaCl

(C) Na_2CO_3 (D) $CuSO_4$

Q.36 For the reversible reaction,

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

The equilibrium shifts in forward direction **[AIPMT 2014]**

(A) By increasing the concentration of $NH_3(g)$

(B) By decreasing the pressure

(C) By decreasing the concentrations of $N_2(g)$ and $H_2(g)$

(D) By increasing pressure and decreasing temperature.

Q.37 For a given exothermic reaction, K_p and K'_p are the equilibrium constants at temperatures T_1 and T_2, respectively ($T_2 > T_1$). Assuming that heat of reaction is constant in temperature range between T_1 and T_2, it is readily observed that – **[AIPMT 2014]**

(A) $K_p > K'_p$ (B) $K_p < K'_p$

(C) $K_p = K'_p$ (D) $K_p = 1/K'_p$

Q.38 If the value of an equilibrium constant for a particular reaction is 1.6×10^{12}, then at equilibrium the system will contain? **[AIPMT 2015]**

(A) mostly reactant.

(B) mostly products

(C) similar amounts of reactants and products.

(D) all reactants.

Q.39 The K_{sp} of Ag_2CrO_4, AgCl, AgBr and AgI are respectively, 1.1×10^{-12}, 1.8×10^{-10}, 5.0×10^{-13}, 8.3×10^{-17}. Which one of the following salts will precipitate last if $AgNO_3$ solution is added to the solution containing equal moles of NaCl, NaBr, NaI and Na_2CrO_4 ? **[AIPMT 2015]**

(A) AgCl (B) AgBr

(C) Ag_2CrO_4 (D) AgI

Q.40 If the equilibrium constant for $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is K, the equilibrium constant for $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$ will be

(A) K (B) K^2 **[RE-AIPMT 2015]**

(C) $K^{1/2}$ (D) K/2

Q.41 Which one of the following pairs of solution is not an acidic buffer ? **[RE-AIPMT 2015]**

(A) H_2CO_3 and Na_2CO_3 (B) H_3PO_4 and Na_3PO_4

(C) $HClO_4$ and $NaClO_4$ (D) CH_3COOH & CH_3COONa

Q.42 Aqueous solution of which of the following compounds is the best conductor of electric current?

(A) Ammonia, NH_3 **[RE-AIPMT 2015]**

(B) Fructose, $C_6H_{12}O_6$

(C) Acetic acid, $C_2H_4O_2$

(D) Hydrochloric acid, HCl

Q.43 What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed ? **[RE-AIPMT 2015]**

(A) 7.0 (B) 1.04

(C) 12.65 (D) 2.0

Q.44 MY and NY_3, two nearly insoluble salts, have the same K_{SP} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3 ? **[NEET 2016 PHASE 1]**

(A) The molar solubility of MY & NY_3 in water are identical.

(B) The molar solubility of MY in water is less than that of NY_3.

(C) The salts MY and NY_3 are more soluble in 0.5 M KY than in pure water.

(D) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities.

Q.45 Consider the following liquid-vapour equilibrium.

Liquid $\rightleftharpoons$ Vapour

Which of the following relations is correct? **[NEET 2016 PHASE 1]**

(A) $\frac{d\ln G}{dT^2} = \frac{\Delta H_V}{RT^2}$

(B) $\frac{d\ln P}{dT} = \frac{-\Delta H_V}{RT}$

(C) $\frac{d\ln P}{dT^2} = \frac{-\Delta H_V}{T^2}$

(D) $\frac{d\ln P}{dT} = \frac{\Delta H_V}{RT^2}$

Q.46 The percentage of pyridine (C_5H_5N) that forms pyridinium ion ($C_5H_5N^+H$) in a 0.10 M aqueous pyridine solution (K_b for $C_5H_5N = 1.7 \times 10^{-9}$) **[NEET 2016 PHASE 2]**

(A 0.0060%

(B) 0.013%

(C) 0.77%

(D) 1.6%

Q.47 The solubility of AgCl(s) with solubility product 1.6×10^{-10} in 0.1 M NaCl solution would be **[NEET 2016 PHASE 2]**

(A) 1.26×10^{-5} M

(B) 1.6×10^{-9} M

(C) 1.6×10^{-11} M

(D) Zero

Q.48 The equilibrium constant of the following are :

$N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1 **[NEET 2017]**

$N_2 + O_2 \rightleftharpoons 2NO$; K_2

$H_2 + ½O_2 \rightarrow H_2O$; K_3

The equilibrium constant (K) of the reaction :

$2NH_3 + (5/2)\,O_2 \xrightleftharpoons{K} 2NO + 3H_2O$, will be –

(A) $K_2K_3^3 / K_1$

(B) K_2K_3 / K_1

(C) $K_2^3K_3 / K_1$

(D) $K_1K_3^3 / K_2$

Q.49 Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol L^{-1}. Solubility product of $Ag_2C_2O_4$ is **[NEET 2017]**

(A) 2.66×10^{-12}

(2) 4.5×10^{-11}

(C) 5.3×10^{-12}

(D) 2.42×10^{-8}

Q.50 Which of the following statements is not correct? **[NEET 2017]**

(A) The value of equilibrium constant is changed in the presence of a catalyst in the reaction at equilibrium.

(B) Enzymes catalyse mainly bio-chemical reactions.

(C) Coenzymes increase the catalytic activity of enzyme.

(D) Catalyst does not initiate any reaction.

Q.51 A 20 litre container at 400 K contains CO_2(g) at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be (Given that : $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)$, $K_p = 1.6$atm) **[NEET 2017]**

(A) 10 litre

(B) 4 litre

(C) 2 litre

(D) 5 litre

Q.52 Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations

(a) 60 mL $\frac{M}{10}$ HCl + 40 mL $\frac{M}{10}$ NaOH **[NEET 2018]**

(b) 55 mL $\frac{M}{10}$ HCl + 45 mL $\frac{M}{10}$ NaOH

(c) 75 mL $\frac{M}{10}$ HCl + 25 mL $\frac{M}{5}$ NaOH

(d) 100 mL $\frac{M}{10}$ HCl + 100 mL $\frac{M}{10}$ NaOH

pH of which one of them will be equal to 1?

(A) d

(B) a

(C) b

(D) c

Q.53 The solubility of $BaSO_4$ in water is 2.42×10^{-3} gL^{-1} at 298 K. The value of its solubility product (K_{sp}) will be

(Given molar mass of $BaSO_4$ = 233 g mol^{-1}) **[NEET 2018]**

(A) 1.08×10^{-14} mol^2L^{-2}

(B) 1.08×10^{-12} mol^2L^{-2}

(C) 1.08×10^{-10} mol^2L^{-2}

(D) 1.08×10^{-8} mol^2L^{-2}

Q.54 Which one of the following conditions will favour maximum formation of the product in the reaction,

$A_2(g) + B_2(g) \rightleftharpoons X_2(g)\ \Delta_rH = -X$ kJ? **[NEET 2018]**

(A) High temperature and high pressure

(B) Low temperature and low pressure

(C) Low temperature and high pressure

(D) High temperature and low pressure

Q.55 pH of a saturated solution of $Ca(OH)_2$ is 9. The solubility product (K_{sp}) of $Ca(OH)_2$ is: **[NEET 2019]**

(A) 0.5×10^{-15}

(B) 0.25×10^{-10}

(C) 0.125×10^{-15}

(D) 0.5×10^{-10}

Q.56 Conjugate base for Bronsted acids H_2O and HF are :

(A) OH^- and H_2F^+, respectively. **[NEET 2019]**

(B) H_3O^+ and F^-, respectively.

(C) OH^- and F^-, respectively.

(D) H_3O^+ and H_2F^+, respectively.

Q.57 Which will make basic buffer? **[NEET 2019]**

(A) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH

(B) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH

(C) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH.

(D) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH

ANSWER KEY

EXERCISE - 1

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	D	C	D	C	C	B	D	B	A	A	A	A	C	B	B	B	A	A	A	A	B	B	D	C	C
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50
A	C	D	C	B	D	D	D	B	D	C	B	D	A	B	D	B	C	A	D	C	A	C	C	C	D
Q	51	52	53	54	55	56	57	58	59	60	61	62	63	64	65	66	67	68	69	70	71	72	73	74	75
A	B	B	C	C	B	A	D	D	B	A	B	D	C	A	C	A	C	D	D	A	B	D	B	A	A
Q	76	77	78	79	80																				
A	A	A	B	B	C																				

EXERCISE - 2

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25
A	D	A	B	C	A	C	C	D	A	D	D	B	C	C	B	D	D	C	A	D	A	B	B	D	D
Q	26	27	28	29	30	31	32	33	34	35	36	37	38	39	40										
A	A	A	A	B	D	A	B	A	A	B	B	A	A	B	C										

EXERCISE - 3

Q	1	2	3	4	5	6	7	8	9	10	11
A	4	3	25	1	2	28	20	8	9	10	5

EXERCISE - 4 (SECTION-A)

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26
A	C	C	A	A	D	A	B	B	C	B	C	D	D	B	D	A	D	D	A	B	C	B	C	A	D	A

EXERCISE - 4 (SECTION-B)

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
A	C	C	D	A	C	C	B	B	A	C	B	B	A	C	D	C	D	A	A	D	C	D	B	11	5.2	B	A

EXERCISE - 5

Q	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29	30
A	A	D	A	C	A	A	D	A	A	A	C	C	D	D	C	C	D	D	D	D	D	D	D	B	C	D	A	C	D	A
Q	31	32	33	34	35	36	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54	55	56	57			
A	A	C	C	D	C	D	A	B	C	C	C	D	C	B	D	B	B	A	C	A	D	D	C	C	A	C	C			

CHEMICAL EQUILIBRIUM

TRY IT YOURSELF-1

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

$K_p = (6.02 \times 10^{-2}\ L^{-2}\ mol^{-2}) \times (0.082\ L\ atm\ K^{-1}\ mol^{-1} \times 773\ K)^{-2}$

$= 1.5 \times 10^{-5}\ atm^{-2}$.

(2) (D)

(3) The reaction is reversed and then multiplied by 1/2, therefore relation between K_c and K'_c will be

$$K'_c = \sqrt{\frac{1}{K_c}} = \sqrt{\frac{1}{2.5 \times 10^{-5}}} = \frac{1}{5 \times 10^{-3}} = 2 \times 10^2$$

(4) Given, $[SO_2] = [SO_3]$, let O_2 is x mole at equilibrium

$V = 5$ litre, $K_c = 10$

$$K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$K_c = \frac{1}{[O_2]} \quad [\text{Since, } [SO_2] = [SO_3]]$$

$$10 = \frac{1}{x/5} \Rightarrow x = 0.5 \text{ mole}$$

(5) **(A).** Total moles = 2 + 2 + 2 = 6

$$P_{PCl_3} = \frac{2}{6} \times 3,\ P_{PCl_5} = \frac{2}{6} \times 3,\ P_{Cl_2} = \frac{2}{6} \times 3$$

$$K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{1 \times 1}{1} = 1 \text{ atm}$$

(6) **(A).**

$$\begin{array}{ccccc} N_2 & + & O_2 & \rightleftharpoons & 2NO \\ 3 & & 2 & & 0 \\ 3-x & & 2-x & & 2x \end{array}$$

$\because \quad 2x = 1\ ;\ x = 0.5$

$$[N_2] = \frac{3 - 0.5}{2} = 1.25$$

(7) **(A).** $H_2(g) + S(s) \rightleftharpoons H_2S(g)$

Conc. at equ. $0.5 - x \quad - \quad x$

$$K_c = \frac{[H_2S]}{[H_2]} \Rightarrow 7 \times 10^{-2} = \frac{x}{0.5 - x}\ ;\ x = 0.0327$$

$$P_{H_2S} = \left(\frac{n_{H_2S}}{V}\right) RT$$

$\Rightarrow\ 0.0327 \times 0.0821 \times 360 = 0.966$ atm

(8) $Q = \dfrac{1 \times 1}{1 \times 1} = 1$

$\because\ Q > K_c$ so reaction will proceed in backward direction

$A_2(g) + B_2(g) \rightleftharpoons C_2(g) + D_2(g)$

concen. at equlib. $\dfrac{1.0 + x}{10} \quad \dfrac{1.0 + x}{10} \quad \dfrac{1.0 - x}{10} \quad \dfrac{1.0 - x}{10}$

$$\Rightarrow \quad 0.25 = \frac{\left(\frac{1-x}{10}\right)^2}{\left(\frac{1+x}{10}\right)^2} \Rightarrow 0.5 = \frac{1-x}{1+x}$$

$\Rightarrow\ 0.5 + 0.5x = 1 - x$

$1.5x = 0.5 \Rightarrow x = 0.333$

$$[A_2(g)] = \frac{1+x}{10} \Rightarrow \frac{1.333}{10} = 0.13$$

(9) **(B).** (I) $K_c = \dfrac{0.01 \times 0.01}{0.01} = 10^{-2}$

(II) $K_c = \dfrac{0.01 \times 0.01}{[0.01]^2} = 1$

(III) $K_c = \dfrac{[0.01]^2}{0.01 \times [0.01]^3} = 100$

(10) **(B).**

$$\begin{array}{lccc} & N_2(g) + & 3H_2(g) \rightleftharpoons & 2NH_3(g) \\ \text{At } t = 0 & 1 & 3 & \\ \text{At eq.} & 1 - x & 3 - 3x & 2x \end{array}$$

$4 - 2x = 3$

$x = 0.5$

$$K_p \text{ for dissociation of } NH_3 = \frac{(0.5)\,(1.5)^3}{1}$$

(11) **(A).** $\Delta n = 1,\ K_p = K_c (RT)^{\Delta n}$ or $K_p > K_c$

(12) **(B).**

$$\begin{array}{lccc} & H_2 + & I_2 \rightleftharpoons & 2HI \\ \text{At } t = 0, & 0.5 & 0.5 & 0 \\ \text{At eq.,} & 0.5 - x & 0.5 - x & 2x \end{array}$$

$$49 = \frac{\frac{[2x]^2}{20 \times 20}}{\left(\frac{0.5 - x}{20}\right)\frac{(0.5 - x)}{20}} = K = 0.039$$

TRY IT YOURSELF-2

(1) (B)

(2) **(A).** $\Delta G^\circ = -RT \ln K_{eq}$

$6.909 \times 1000 = -2 \times 300 \times 2.303 \log K_c$

$-5 = \log K_c$ or $K_c = 10^{-5}$

$K'_c = 1/K_c = 10^5$

$$\begin{array}{ccc} 2A & \rightleftharpoons & A_2 \\ 0.8 - 2x & & x \end{array}$$

$\because\ K'_c$ is very high, so $2x \approx 0.8 \Rightarrow x \approx 0.4$

$\therefore\ 0.8 - 2x \approx y$

$$10^5 = \frac{0.4}{(y)^2}\ ;\ y = (0.4 \times 10^{-5})^{1/2} = 2 \times 10^{-3}$$

$$\frac{[A]}{[A_2]}=\frac{y}{x}=\frac{2\times10^{-3}}{0.4}=\frac{5}{1000}=\frac{1}{200}$$

(3) **(D).** Addition of F_2 shits equilibrium in forward direction.

(4) **(C).** Formation of diamond is endothermic reaction and at high pressure density increases.

(5) **(B).** Ni combines with CO and produced $Ni(CO)_4$ so concentration Cl_2 increases and eq. in Ist reaction shifts in backward direction.

$\therefore$ Concentration PCl_3 decreases.

(6) **(A).** $\alpha=\dfrac{D-d}{d\,(n-1)}\times100=\dfrac{46-30}{30\,(2-1)}\times100=53.3\%$

(7) We know that $\Delta G^\circ=-2.303\ RT\log K$

Now, $R=8.314\ JK^{-1}, T=298\ K, K=1.8\times10^{-7}$

Putting these value in the above expression, we have

$$\Delta G^\circ=-2.303\times8.314\ JK^{-1}\times298\ K\times\log(1.8\times10^{-7})$$
$$=-5705.85\times(-6.7447)=38484\ J=38.484\ kJ$$

(8) (A)

(9) (D)

IONIC EQUILIBRIUM

TRY IT YOURSELF-1

(1) **(C).** The reaction is $NH_3+H_2O\rightleftharpoons NH_4{}^++OH^-$

$$K_b=1.8\times10^{-5}=\frac{[NH_4^+][OH^-]}{[NH_3]}$$

$$=\frac{(1.5\times10^{-3})\,(1.5\times10^{-3})}{[NH_3]}=1.8\times10^{-5}$$

Equilibrium conc. of ammonia $[NH_3]=0.125\ M$

Total $[NH_3]=1.5\times10^{-3}+0.125=0.13\ M$

(2) **(B).** $Zn^{++}+H_2O\rightleftharpoons Zn(OH)_2+2H^+$

$$\therefore\quad K_h=\frac{[Zn(OH)_2][H^+]^2}{[Zn^{++}]}\qquad\text{.........}\ (1)$$

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

$$\therefore\quad K_b=\frac{[Zn^{++}][OH^-]^2}{[Zn(OH)_2]}$$

$$K_w=[H^+][OH^-]\quad\therefore\quad\frac{K_w^2}{K_b}=K_h$$

(3) **(B).** $[H^+]=\dfrac{0.1}{100}=10^{-3}$; $pH=3$

(4) **(C).** $H_2A\rightleftharpoons H^++HA^-$; $k_1=1\times10^{-5}$

$HA^-\rightleftharpoons H^++A^{2-}$; $k_2=5\times10^{-10}$

$H_2A\rightleftharpoons 2H^++A^{2-}$; $k=k_1\,.\,k_2=5\times10^{-15}$

(5) (C)

(6) (C)

(7)

HCl	Cl^-
acid	conjugate base
H_2O	H_3O^+
base	conjugate acid

(8) **(B).**

$$\begin{array}{lccc} & CH_3NH_2 + & HCl \longrightarrow & CH_3\overset{\oplus}{N}H_3 + Cl^- \\ \text{Initially} & 0.1 & 0.08 & - \\ \text{In solution} & 0.02 & - & 0.08 \end{array}$$

$$[OH^-]=K_b\frac{[CH_3NH_2]}{[CH_3NH_3^+]}$$

$$[OH^-]=\frac{5\times10^{-4}\times0.02}{0.08}=\frac{5}{4}\times10^{-4}$$

$$[H^+]=\frac{K_w}{[OH^-]}=\frac{10^{-14}\times4}{5\times10^{-4}}=8\times10^{-11}$$

(9) **(A).** $CO_2+H_2O\rightleftharpoons H_2CO_3\rightleftharpoons H^++HCO_3{}^-$

$$\rightleftharpoons H^++CO_3{}^{-2}$$

(10) **(A).** $Ag^++NH_3\rightleftharpoons Ag(NH_3)^+$; $K_1=3.5\times10^{-3}$;

$Ag(NH_3)^++NH_3\rightleftharpoons[Ag(NH_3)_2]^+$; $K_2=1.7\times10^{-3}$

Adding :

$Ag^++2NH_3\rightleftharpoons[Ag(NH_3)_2]^+$

$K=K_1\times K_2=5.95\times10^{-6}$

(11) **(A).** Rate in weak acid $=\dfrac{1}{100}$ (rate in strong acid)

$$\therefore\quad[H^+]_{\text{weak acid}}=\frac{1}{100}\,[H^+]_{\text{strong acid}}$$

$$\therefore\quad[H^+]_{\text{weak acid}}=\frac{1}{100}\,M=10^{-2}\,M$$

$\therefore\quad C\alpha=10^{-2}$

$\therefore\quad K_a=10^{-4}$

TRY IT YOURSELF-2

(1) **(A).** 50mL of 0.02 M NaOH contains 1 milli moles of OH^-.

50mL of 0.04 M CH_3COOH contains 2 millimoles of H^+.

The combination of the two solutions will give 1 milli mole of salt, and 1 milli mole of acid will be left behind.

By using Henderson equation

$$pH=pK_a+\log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or}\quad pH=pK_a+\log\frac{[0.1\ \text{milli mole per 100mL of soln.}]}{[0.1\ \text{milli mole per 100mL of soln.}]}$$

$$\text{or}\quad pH=-\log K_a=-\log(1.8\times10^{-5})=4.74$$

(2) When half of NH_4OH is neutralised.

$[NH_4OH]=NH_4Cl]$.

By using the Henderson equation,

$$pOH = pK_b + \log\frac{[Salt]}{[Base]} \quad \text{or } pOH = 4.75$$

$pH = 14 - 4.75 = 9.25$

(3) (C)

(4) **(A).** The degree of hydrolysis of a salt of weak acid and strong base is given by

$$\alpha_h = \sqrt{\frac{K_w}{K_aC}} = \sqrt{\frac{1\times10^{-4}}{1\times10^{-5}\times0.1}} = \sqrt{\frac{1\times10^{-4}}{1\times10^{-6}}} = 1\times10^{-4}$$

or $100\alpha_h = 100 \times 1 \times 10^{-4} = 10^{-2} = 0.01$

So, the degree of hydrolysis of NaX (0.1 M) is 0.01%.

(5) **(B).** HCl is strong acid.

NH_4Cl is a salt of weak base and strong acid - NH_4^+ hydrolysis to give acid solution.

NaCl is a salt of strong acid and strong base - No hydrolysis neutral solution.

NaCN is a salt of strong base and weak acid - CN^- hydrolysis to give basic solution.

(6) **(D).** Since it is a basic buffer so

$pOH = pK_b + \log [Salt]/[Base]$

$pOH = -\log K_b + \log [Salt]/[Base]$

$= -\log (1.8 \times 10^{-5}) + \log (0.25/0.15)$

$= 4.74 + 0.22 = 4.96$

or $pOH = 4.97$

$pH = 14 - pOH = 14 - 4.97 = 9.03$

TRY IT YOURSELF-3

(1) **(B).** $Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$; $K_{sp} = 1.2 \times 10^{-11}$.

$[OH^-]$ higher than that contained in a saturated solution will cause precipitation. Therefore, the solution must be at the point of attaining equilibrium and the concentration of ions in solution must be no greater than those required to satisfy the solubility product constant. In this solution, $[Mg^{2+}] = 0.10$ M and $[Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$.

$$[OH^-]^2 = \frac{1.2\times10^{-11}}{0.10} = 1.2 \times 10^{-10}.$$

or $[OH^-] = 1.1 \times 10^{-5}$ or $pOH = 4.96$ or $pH = 9.04$

(2) Solubility product of $Pb_3(PO_4)_2 = 1.5 \times 10^{-32}$.

$Pb_3(PO_4)_2 \rightleftharpoons 3Pb2+ + 2PO_4^{3-}$

If x is the solubility of $Pb_3(PO_4)_2$

Then $K_{sp} = (3x)^3 (2x)^2 = 108x^5$

$$x = 5\sqrt{\frac{K_{sp}}{108}} = \left(\frac{1.5\times10^{-32}}{108}\right)^{1/5}$$

$x = 1.692 \times 10^{-7}$ moles/lit.

Molecular mass of $Pb_3(PO_4)_2 = 811$

$x = 1.692 \times 10^{-7}$ m × 811 g/lit = 1.37 × 10–4 g/lit

Solubility product is

$K_{sp}(SrC_2O_4) = [Sr^{2+}][C_2O_4^{2-}]$

$= (5.4 \times 10^{-4})^2 = 2.92 \times 10^{-7}$

(3) **(D).** $HgSO_4 \rightleftharpoons Hg^{2+} + SO_4^{2-}$

$K_{sp} = [Hg^{2+}][SO_4^{2-}] = S^2 = 6.4 \times 10^{-5}$

$S = 8 \times 10^{-3}$ mole/lit = 8 mole/m^3.

(4) **(C).** 50 lit 10^{-5} mole AgCl + 50 lit of 2×10^{-7} M HBr

$$[Ag^+] = \frac{10^{-5}}{100} = 10^{-7}\,M + 10^{-7}\,M\ Br^-$$

$K = 10^{-7} \times 10^{-7} = 10^{-14} < K_{sp} = 5 \times 10^{-3}$

So, no. precipitation and $[Ag^+] = 10^{-7}$ M

(5) **9.** $HA + NaOH \rightarrow NaA + H_2O$

At the end point, the solution contains only NaA whose concentration is 0.1/2 = 0.05 M.

Since the salt NaA is formed by strong alkali (NaOH) and weak acid HA (indicated by its low K_a value), its pH can be evaluated by the following reaction:

$$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

$$= \frac{1}{2}(14 + 5.3010 + (-1.3010)) = 9$$

(6) **(D).** $BOH + HCl \longrightarrow \underset{C}{BCl} + H_2O$

$$\underset{C(1-h)}{B^+} + H_2O \rightleftharpoons \underset{Ch}{BOH} + \underset{Ch}{H^+}$$

$$\text{Volume of HCl used} = \frac{2.5\times(2/5)}{2/15} = 7.5 \text{ ml.}$$

$$\text{Concentration of Salt, } C = \frac{2.5\times(2/5)}{10} = 0.1\,M$$

$$\therefore \frac{Ch^2}{1-h} = \frac{K_w}{K_b} \quad \text{Solving, } h = 0.27$$

$[H^+] = Ch = 0.1 \times 0.27 = 2.7 \times 10^{-2}$ M

(7) **7.** $\underset{Z}{AgCl\,(s)} \rightleftharpoons \underset{Z+Y}{Ag^+} + Cl^-$; $K_{sp}(AgCl) = 1.6 \times 10^{-10}$

$\underset{Y}{CuCl\,(s)} \rightleftharpoons \underset{Z+Y}{Cu^+} + Cl^-$; $K_{sp}(CuCl) = 10^{-6}$

$Z(Z + Y) = 1.6 \times 10^{-10}$

$Y(Z + Y) = 10^{-6}$

$\Rightarrow (Z + Y)^2 = 1.6 \times 10^{-10} + 10^{-6}$

$\Rightarrow (Z + Y)^2 \approx 10^{-6}$

$\Rightarrow Z + Y = 10^{-3} \Rightarrow Z(Z + Y) = 1.6 \times 10^{-10}$

$\Rightarrow Z \times 10^{-3} = 1.6 \times 10^{-10}$

$\Rightarrow Z = 1.6 \times 10^{-7}$

$\Rightarrow 1.6 \times 10^{-x} = 1.6 \times 10^{-7} \Rightarrow x = 7$

(8) **(B).** $K_{sp} = 1.1 \times 10^{-12} = [Ag^+]^2 [CrO_4^{-2}]$

$1.1 \times 10^{-12} = [0.1]^2 [s]$

$s = 1.1 \times 10^{-10}$

CHAPTER-7 : EQUILIBRIUM

EXERCISE-1

(1) **(D).** $CO_2\,(gas) \rightleftharpoons CO_2\,(in\ solution)$
This equilibrium is governed by Henry's law which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

(2) **(C).** Ice and water kept in a perfectly insulated thermos flask (no exchange of heat between its contents and the surroundings) at 273K and the atmospheric pressure are in equilibrium state and the system shows interesting characteristic features. The system shows solid-liquid equilibrium.

(3) **(D).** Boiling point of the liquid depends on the atmospheric pressure. It depends on the altitude of the place; at high altitude the boiling point decreases.

(4) **(C).** $H_2O\,(\ell) \rightleftharpoons H_2O\,(vap.)$
Rate of evaporation = Rate of condensation

(5) **(C).** Chemical equilibrium in the reaction
$H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$ can be attained from either direction.

(6) **(B).** The concentration of reactants decreases and that of products increases with time. Rate of reaction increases with time.
At equilibrium, $R_f = R_b$

(7) **(D).** Let us write equilibrium constant for the reaction,
$H_2\,(g) + I_2(g) \rightleftharpoons 2HI(g);$

$$\text{as } K_c = \frac{[HI]^2}{[H_2][I_2]} = x$$

The equilibrium constant for the reverse reaction $2HI\,(g) \rightleftharpoons H_2\,(g) + I_2(g)$, at the same temperature is

$$K'_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{x} = \frac{1}{K_c}\text{. Thus, } K'_c = \frac{1}{K_c}$$

Equilibrium constant for the reverse reaction is the inverse the equilibrium constant for the reaction in the forward direction.

(8) **(B).** $2XY \rightleftharpoons X_2 + Y_2\,;\,K_c = 81$

$$XY \rightleftharpoons \frac{1}{2}X_2 + \frac{1}{2}Y_2\,;\,K'_c = ?;\ K'_c = \sqrt{K_c} = \sqrt{81} = 9$$

(9) **(A).** $K_c = \dfrac{[SO_3]^2}{[SO_2]^2\,[O_2]} = \dfrac{(1.9)^2}{(0.6)^2(0.82)} = 12.229\,L\,mol^{-1}$

(10) **(A).** The equilibrium constant for the reaction,
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3\,(g)$ can be written as,

$$K_c = \frac{[NH_3(g)]^2}{[N_2(g)][H_2(g)]^3} = \frac{(1.2\times10^{-2})^2}{(1.5\times10^{-2})\,(3.0\times10^{-2})^3}$$

$$= 0.106 \times 10^4 = 1.06 \times 10^3$$

(11) **(A).**

$$\begin{array}{lccc} & 2HI & \rightleftharpoons\ H_2 & +\ I_2 \\ \text{Initial} & a & 0 & 0 \\ \text{At equilibrium} & a/2 & a/2 & a/2 \end{array}$$

$$K = \frac{(a/2)\,(a/2)}{(a/2)^2} = 1$$

(12) **(A).** If reaction is multiplied by 2, the equilibrium constant becomes square of the previous value.
$K = 7^2 = 49$

(13) **(C).** For the reaction equilibrium constant, K_c can be written as,

$$K_c = \frac{[NO]^2}{[N_2][O_2]} = \frac{(2.8\times10^{-3}M)^2}{(3.0\times10^{-3}M)\,(4.2\times10^{-3}M)} = 0.622$$

(14) **(B).** When $\Delta n_g = 0,\ K_p = K_c$

(15) **(B).** In a homogeneous system, all the reactants and products are in the same phase.

(16) **(B).** We know that, $K_p = K_c(RT)^{\Delta n}$
For the above reaction, $\Delta n = (2 + 1) - 2 = 1$
$K_p = 3.75 \times 10^{-6}\,(0.0831 \times 1069) = 0.033$

(17) **(A).**

$$\begin{array}{ccc} X & +\,2Y \rightleftharpoons & Z \\ 0.06 & 0.12 & 0.216 \end{array}$$

$$K_c = \frac{[Z]}{[X][Y]^2} = \frac{0.216}{0.06\times0.12\times0.12} = 250$$

(18) **(A).** All the reactants and products are in same physical state.

(19) **(A).** For a general reaction, $aA + bB \rightleftharpoons cC + dD$

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

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

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

where Δn = (number of moles of gaseous products) – (number of moles of gaseous reactants) in the balanced chemical equation.

(20) **(A).**

$$\begin{array}{lccc} & PCl_5\,(g) \rightleftharpoons & PCl_3(g) & +\ Cl_2\,(g) \\ \text{Initial conc.} & \frac{5}{5} = 1 & 0 & 0 \\ \text{At equilibrium} & 1 - 0.4 & 0.4 & 0.4 \end{array}$$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{0.4M\times0.4M}{0.6M} = 0.266\,M$$

(21) **(B).** $NH_4COONH_2\,(s) \rightleftharpoons 2NH_3\,(g) + CO_2(g)$
$\qquad 2p \quad p$
When volume and temperature are constant, the number of moles of a gas is proportional to its partial pressure. So, $2p + p = 3\,;\ \ 3p = 3\ \ \therefore p = 1$ atm
$K_p = (2p)^2 \times p = 4p^3 = 4 \times (1)^3 = 4\ atm^3$

(22) **(B).** $P_4(s) + 5O_2\,(g) \rightleftharpoons P_4O_{10}\,(s)$
Since concentration of solids is taken as 1, expression for equilibrium constant involves only oxygen.

$$K_c = \frac{1}{[O_2]^5}$$

(23) **(D).** The equilibrium between water vapour and liquid water in a closed container is an example of heterogeneous equilibrium. $H_2O(\ell) \rightleftharpoons H_2O(g)$

In this example there is a gas phase and a liquid phase. In the same way, equilibrium between two solid phases and a gas phase.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

(24) **(C).** $2Cu(NO_3)_2(s) \rightleftharpoons 2CuO(s) + 4NO_2(g) + O_2(g)$

Since conc. of solids is taken as 1, the expression for K_c becomes

$K_c = [NO_2(g)]^4 [O_2(g)]$

(25) **(C).** Important features of equilibrium constant as follows:

(i) Expression for equilibrium constant is applicable only when concentrations of the reactants and products have atttained constant value at equilibrium state.

(ii) The value of equilibrium constant is independent of initial concentrations of the reactants and products.

(iii) Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.

(iv) The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.

(26) **(C).** Value of K_c predicts the extent of the reaction.

(27) **(D).** All three statements are correct.

(28) **(C).** When $Q_p < K_p$, the rate of forward reaction is more than rate of backward reaction.

(29) **(B).** The equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage. For this purpose, we calcualte the reaction quotient Q. The reaction quotient, Q (Q_c with molar concentration and Q_p with partial pressures) is defined in the same way as the equilibrium constant K_c except that the concentrations in Q_c are not necessarily equilibrium values.

(30) **(D).** Important applications of equilibrium constant to

- predict the extent of a reaction on the basis of its magnitude.
- predict the direction of the reaction, and
- calculate equilibrium concentrations.

(31) **(D).** The value of K_c for a reaction does not depend on the rate of the reaction.

It is directly related to the thermodynamics of the reaction and in particular, to the change in Gibbs energy ΔG. If,

- ΔG is negative, then the reaction is spontaneous and proceeds in the forward direction.
- ΔG is positive, then reaction is considered non–spontaneous. Instead, as reverse reaction would have a negative ΔG, the products of the forward reaction shall be converted to the reactants.
- ΔG is 0, reactions has achieved equilibrium; at this point, there is no longer any free energy left to drive the reaction.

(32) **(D).** $-\Delta G° = RT \ln K_c$

(33) **(B).** A mathematical expression of the thermodynamic view of equilibrium can be described by the following equation $\Delta G = \Delta G^{\ominus} + RT \ln Q$

where, $\Delta G^{\ominus}$ is standard Gibbs energy.

(34) **(D).** Le–Chatelier's principle is applicable to all physical and chemical equilibria.

(35) **(C).** Since number of moles of gaseous reactants and products are same, the reaction will not be affected by changing the pressure.

(36) **(B).** $Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons [Fe(SCN)]^{2+}(aq)$

YellowColourless Deep red

When oxalic acid is added, it reacts with Fe^{3+} ions to form stable complex ion $[Fe(C_2O_4)_3]^{3-}$, thus decreasing the conc. of free $Fe^{3+}(aq)$. Now, according to Le Chatelier's principle, the reaction will shift in backward direction to increase the conc, of free $Fe^{3+}(aq)$. Thus, conc. of $[Fe(SCN)]^{2+}$ decreases, so the intensity of red colour decreases.

(37) **(D).** In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

- The equilibrium constant for an exothermic reaction (negative ΔH) decreases as the temperature increases.
- The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

Temperature changes affect the equilibrium constant and rates of reaction.

(38) **(A).** Equilibrium constant (K) is temperature dependent as temperature is constant thus, K will remain same.

(39) **(B).** Endothermic reaction is favoured at high temperature.

(40) **(D).** Addition of hydrogen at equilibrium results in value of Q_c being has less than K_c. Thus, in order to attain equilibrium again reaction moves in the forward direction.

Similarly, we can say that removal of a product also boosts the forward reaction and increases the concentration of the products and this has great commercial application in cases of reactions, where the product is a gas or a volatile substance. In case of manufacture of ammonia, ammonia is liquified and removed from the reaction mixture so that reaction keeps moving in forward direction. Similarly, in the large scale production of CaO (used as important building material) from $CaCO_3$, constant removal of CO_2 from the kiln drives the reaction to completion. It should be remembered that continuous removal of a product maintains Q_c at a value less than K_c and reaction continues to move in the forward direction.

(41) **(B).** Since reaction is exothermic it is favoured at low temperature. There is a decrease in number of moles hence reaction is favoured at high pressure.

(42) **(C).** A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reaction that pass through the same transition state and does not affect equilibrium.

Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount.

(43) **(A).** Addition of KSCN increases the colour intensity the solution as it shifts the equilibrium to right. Addition of reagents like oxalic acid or Hg^{2+} ions which remove Fe^{3+} or SCN^- ions shift the equilibrium to the left and colour intensity decreases.

(44) **(D).** **Faraday** classified electrolytes into strong and weak electrolytes. **Strong** electrolytes on dissolution in water are ionised almost completely, while the **weak** electrolytes are only partially dissociated.

(45) **(C).** Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide.

(46) **(A).**

Species	Conjugate acid	Conjugate base
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-
H_2O	H_3O^+	OH^-

(47) **(C).** Electron deficient species like $AlCl_3$, Co^{3+}, Mg^{2+} etc. can act as Lewis acids while species like H_2O, NH_3, OH^- etc. which can donate a pair of electrons, can act as Lewis bases.

(48) **(C).** BF_3 is an electron deficient compound and hence is a Lewis acid.

(49) **(C).** (X) and (Y) in the given figure are base and acid.

(50) **(D).** Lewis acid is acceptor of a pair of electrons while Lewis base is donor of a pair of electrons.

(51) **(B).** According to Bronsted–Lowry theory, acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+. In short, acids are proton donors and bases are proton acceptors.

(52) **(B).** The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are NH_3, NH_4^+ and HCOOH respectively.

(53) **(C).** Strong acid dissociates completely in water, the resulting base formed would be very weak, i.e., strong acids have very weak conjugate bases.

(54) **(C).** The pH of neutral water at 25°C is 7.0.

$\therefore\ [H^+] = [OH^-] = 10^{-7}$

$(pH = -\log[H^+])$

Now, $K_w = [H^+][OH^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14}$

As the temperature increases, ionisation of water increases, thus $[H^+]$ and $[OH^-]$ increases equally. Now

$K_w = [H^+][OH^-] > 1 \times 10^{-14} \quad (\because [H^+] = [OH^-])$

or $[H^+]^2 > 1 \times 10^{-14}\ \therefore\quad [H^+] > 1 \times 10^{-7}$ and $pH < 7$

(55) **(B).** NaCN solution is basic in nature since HCN formed is a weak acid and does not hydrolyse.

$NaCN + H_2O \rightleftharpoons NaOH + HCN$

$NaOH \rightleftharpoons Na^+ + OH^-$ (Basic solution)

(56) **(A).** The values of dissociation constants for successive stages decrease.

(57) **(D).** Consider the equation of water at 298 K

$K_w = [H_3O^+][OH^-] = 10^{-14}$

Taking negative logarithm on both sides of equation, we obtain

$-\log K_w = -\log\{[H_3O^+][OH^-]\}$

$= -\log[H_3O^+] - \log[OH^-] = -\log 10^{-14}$

$pK_w = pH + pOH = 14$

(58) **(D).** We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations.

Acidic $[H_3O^+] > [OH^-]$

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

Basic, $[H_3O^+] < [OH^-]$

(59) **(B).** $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$

$[H^+] = 2 \times 1 \times 10^{-4}$ M

$pH = -\log(2 \times 10^{-4}) = 3.70$

(60) **(A).** $MOH\ (aq) \rightleftharpoons M^+\ (aq) + OH^-(aq)$

The equilibrium constant for base ionization is called base ionization constant and is represented by K_b. It can be expressed in terms of concentration in molarity of various species in equilibrium by the following equation $K_b = \frac{[M^+][OH^-]}{[MOH]}$

Alternatively, if C = initial concentration of base and α = degree of ionisation of base. The equilibrium constant can be written as

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

(61) **(B).** $pH = -\log[H^+]$

$2 = -\log[H^+]\ ;\ [H^+] = 1 \times 10^{-2}$

(62) **(D).** In case of a conjugate acid–base pair, $K_a \times K_b = K_w$ Knowing one, the other can be obtained. It should be noted that a strong acid will have a weak conjugate base and vice-versa.

(63) **(C).** $H_2O(\ell) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

acid base conjugate acid conjugate base

(64) **(A).** Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the pH scale. The pH of a solution is defined as the negative logarithm to base 10 of the activity (a_{H^+}) of hydrogen ion.

(65) **(C).** $pH = -\log[H^+] = -\log(3.8 \times 10^{-3}) = 2.42$

(66) **(A).** A mixture of acetic acid and sodium acetate acts as a buffer with pH around 4.75.

(67) **(C).** In 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl, total amount of HCl reacts with NH_4OH to form NH_4Cl and some NH_4OH will be left unreacted. Thus, the resultant solution contains NH_4Cl and NH_4OH which will produce a buffer solution.

(68) **(D).** The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called buffer solutions.

(69) **(D).** The solubility of salts of weak acids like phosphates increases at lower pH. This is because at lower pH the concentration of the anion decreases due to its protonation. This in turn increase the solubility of the salt so that $K_{sp} = Q_{sp}$.

(70) **(A).** $MX_4 \rightleftharpoons M^+ + 4X^-$

$s \quad 4s$

$K_{sp} = s \times (4s)^4 = 256s^5$

(71) **(B).**

(a) $Fe(OH)_3 \rightleftharpoons Fe^{3+} + 3OH^-$; $K_{sp} = 27s^4$

$s \quad (3s)^3$

(b) $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$; $K_{sp} = 4s^3$

$(2s)^2 \quad s$

(c) $CH_3COOAg \rightleftharpoons CH_3COO^- + Ag^+$; $K_{sp} = s^2$

$s \quad s$

(d) $Ca_3(PO_4)_2 \rightleftharpoons 3Ca^{2+} + 2PO_4^{3-}$; $K_{sp} = 108\ s^5$

$(3s)^3 \quad (2s)^2$

(72) **(D).** $AgCl \rightleftharpoons Ag^+ + Cl^-$

$s \quad s$

$s^2 = 1.5625 \times 10^{-10}$

$s = 1.25 \times 10^{-5}$ mol L^{-1}

Solubility in g L^{-1} = Molar mass × s

$= 143.5 \times 1.25 \times 10^{-5} = 1.79 \times 10^{-3}$ g L^{-1}

(73) **(B).**

Category I	Soluble salt	Solubility > 0.1 M
Category II	Slightly soluble salt	0.01 M < Solubility < 0.1 M
Category III	Sparingly soluble salt	Solubility < 0.01 M

(74) **(A).** $A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$

$K_{sp} = [A^{y+}]^x\,[B^{x-}]^y$

(75) **(A).** $AgCN \rightleftharpoons Ag^+ + CN^-$

$K_{sp} = [Ag^+]\,[CN^-] = 6 \times 10^{-17}$

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

$K_{sp} = [Ni^{2+}]\,[OH^-]^2 = 2 \times 10^{-15}$

Let $[Ag^+] = S_1$, then $[CN^-] = S_1$

Let $[Ni^{2+}] = S_2$, then $[OH^-] = 2S_2$

$S_1{}^2 = 6 \times 10^{-17}$, $S_1 = 7.8 \times 10^{-9}$

$(S_2)\,(2S_2)^2 = 2 \times 10^{-15}$, $S_2 = 7.9 \times 10^{-4}$

$Ni(OH)_2$ is more soluble than AgCN.

(76) **(A).** $RaSO_4 \rightleftharpoons Ra^{2+} + SO_4{}^{2-}$

$K_{sp} = [Ra^{2+}]\,[SO_4{}^{2-}]$

Concentration of $SO_4{}^{2-}$ from $Na_2SO_4 = 0.10$ M

$$Ra^{2+} = \frac{4 \times 10^{-11}}{0.10} = 4 \times 10^{-10}\text{ M}$$

(77) **(A).** The equilibrium between the undissolved solid and the ions in a saturated solution can be represented by the equation

$$BaSO_4\,(s) \underset{\text{in water}}{\overset{\text{saturated solution}}{\rightleftharpoons}} Ba^{2+}(aq) + SO_4{}^{2-}(aq).$$

The equilibrium constant is given by the equation

$$K = \frac{[Ba^{2+}]\,[SO_4^{2-}]}{[BaSO_4]}$$

For a pure solid substance the concentration remains constant and we can write

$K_{sp} = K\,[BaSO_4] = [Ba^{2+}]\,[SO_4{}^{2-}]$

We call K_{sp} the solubility product constant or simply solubility product.

(78) **(B).** For precipitation, ionic product > solubility product. In all other options, ionic product is less than solubility product.

(79) **(B).** From Le-Chatelier's principle that if we **increase** the concentration of anyone of the ions, it should combine with the ion of its **opposite** charge and some of the salt will be precipitated till once again $K_{sp} = Q_{sp}$. Similarly, if the concentration of one of the ions is decreased, more salt will dissolve to increase the concentration of both the ions till once again $\mathbf{K_{sp} = Q_{sp}}$.

(80) **(C).** Solubility of a salt in a solution containing common ion is less than the solubility of the salt in pure water. More is the concentration of the common ion, lesser would be the solubility of salt. Thus, the order of solubility of AgCl in various solutions would be

$s_1 > s_3 > s_2 > s_4$

EXERCISE-2

(1) **(D).** There are an infinite number of equilibrium positions at a given temperature depending on the initial concentrations.

The size of K has no relationship to the speed at which equilibrium is achieved.

A pure liquid or solid is never included in the equilibrium expression.

(2) **(A).** $2NO_2\,(g) \rightleftharpoons N_2O_4(g),\ \Delta n = 1 - 2 = -1$

$$K_p = K_c\,(RT)^{\Delta n}\,;\ \frac{K_p}{K_c} = (RT)^{-1}$$

(3) **(B).** In presence of 10^{-10} M HCl, the common ion effect exerted by H^+ ions contributed by HCl on dissociation of water would be negligible. Thus, the $[H^+]$ coming from water would be about 1×10^{-7} M.

$$\therefore\ [H^+]_{Total} = [H^+]_{H_2O} + [H^+]_{HCl}$$

$$= 10^{-7} + 10^{-10} \approx 10^{-7}\,M$$

$\therefore$ pH = 7

(4) **(C).** For $Fe^{3+}(aq) + 3OH^-(aq) \rightleftharpoons Fe(OH)_3(s)$

$$K_c = \frac{1}{[Fe^{3+}][OH^-]^3}$$

(5) **(A).** pH = 10, $[H^+] = 1 \times 10^{-10}$ M $\therefore$ $[OH^-] = 1 \times 10^{-4}$ M

(6) **(C).** Let the solubility of $Ni(OH)_2$ be equal to S. Dissolution of S mol/L of $Ni(OH)_2$ provides S mol/L, of Ni^{2+} and 2S mol/L of OH^-, but the total concentration of OH^- = (0.10 + 2S) mol/L because the solution already contains 0.10 mol/L of OH^- from NaOH.

$K_{sp} = 2.0 \times 10^{-15} = [Ni^{2+}]\,[OH^-]^2 = (S)\,(0.10 + 2S)^2$

As K_{sp} is small, 2S << 0.10, thus, (0.10 + 2S) ≈ 0.10

Hence, $2.0 \times 10^{-15} = S\,(0.10)^2$

$S = 2.0 \times 10^{-13}\ M = [Ni^{2+}]$

(7) **(C).** Both (A) & (B) are correct for the equation, $K = e^{-\Delta G^{\Theta}/RT}$.

(8) **(D).** $2H_2O\,(\ell) \rightleftharpoons H_3O^+\,(aq) + OH^-\,(aq)$

The dissociation reaction of H_2O being endothermic, with the increase of temperature, equilibrium constant (K_w) increases, as reaction is favoured in the forward direction. Thus, concentration of H_3O^+ as well as OH^- increases and pH and pOH decreases with increase of temperature.

(9) **(A).** $K_c = \dfrac{[PCl_3][Cl_2]}{[PCl_5]} = \dfrac{2.1 \times 2.1}{1.9} = 2.32$

(10) **(D).** All the three statements are correct.

(11) **(D).** $K_p = K_c(RT)^{\Delta n}$; $\Delta n = 2 - 3 = -1$

$T = 350\text{ K}, R = 0.083\text{ bar L K}^{-1}\text{ mol}^{-1}$

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

$$K_c = \frac{3 \times 10^{10}\ \text{bar}^{-1}}{(0.083\ \text{L bar K}^{-1}\text{mol}^{-1} \times 350\text{ K})^{-1}}$$

$= 8.715 \times 10^{11}\text{ L mol}^{-1}$

(12) **(B).** K_w at 90°C $= [H_3O^+]\,[OH^-]$

$= 10^{-6} \times 10^{-6} = 10^{-12}$

(13) **(C).** A solid salt of the general formula $M_x^{p+}X_y^{q-}$ with molar solubility S in equilibrium with its saturated solution may be represented by the equation

$M_xX_y(s) \rightarrow xM^{p+}(aq) + yX^{q-}(aq)$

(where $x \times p^+ = y \times q^-$)

And its solubility product constant is given by K_{sp} $= [M^{p+}]^x\,[X^{q-}]^y = (xS)^x\,(yS)^y$

$K_{sp} = x^x \,.\, y^y \cdot S^{(x+y)}$

$$S^{(x+y)} = \frac{K_{sp}}{x^x \cdot y^y}\ ; \quad S = \left(\frac{K_{sp}}{x^x \cdot y^y}\right)^{1/x+y}$$

(14) **(C).** $a + b \rightleftharpoons c + d$

$x \quad x \qquad 2x \quad 2x$

$$K_c = \frac{2x \times 2x}{x \times x} = \frac{4x^2}{x^2} \Rightarrow K_c = 4$$

(15) **(B).** $PCl_5\,(g) \rightleftharpoons PCl_3(g) + Cl_2\,(g)$; $K_c = 8.3 \times 10^{-3}$.

For $PCl_3\,(g) + Cl_2\,(g) \rightleftharpoons PCl_5\,(g)$;

$$K_c' = \frac{1}{8.3 \times 10^{-3}} = 120.48$$

(16) **(D). Sulphuric acid :**

* It is a strong acid in the first dissociation step (is very large)

* It is a weak acid in the second step.

(17) **(D).** Production of ammonia according to the reaction, $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$; $\Delta H = -92.38\text{ kJ mol}^{-1}$ is an exothermic process. According to LeChatelier′s principle, raising the temperature shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia, but practically very low temperatures slow down the reaction and thus a catalyst is used.

(18) **(C).** Consider the gaseous reaction of H_2 with I_2 :

$H_2\,(g) + I_2(g) \rightleftharpoons 2HI\,(g)$; $K_c = 57.0$ at 700 K

Suppose we have molar concentrations

$[H_2]_t = 0.1\text{ M}, [I_2]_t = 0.20\text{ M}$ and

$[HI]_t = 0.40\text{ M}$ (the subscript t on the concentration symbols means that the concentrations were measured at some arbitrary time t, not necessarily at equilibrium). Thus, the reaction quotient, Q_c at this stage of the reaction is given by,

$$Q_c = \frac{[HI]_t^2}{[H_2]_t[I_2]_t} = \frac{(0.40)^2}{(0.10) \times (0.20)} = 8.0$$

(19) **(A).** $K_p = K_c(RT)^{\Delta n}$; $\Delta n = 1$

$K_p = 167$ bar,

$$K_c = \frac{167\text{ bar}}{0.0821\ \text{L bar K}^{-1}\text{mol}^{-1} \times 1073\text{K}}$$

$= 1.896\text{ mol L}^{-1}$

(20) **(D).** Exothermic reaction, decrease in number of moles, increase in concentration of reactants.

(21) **(A).** Nucleophiles are Lewis bases while electrophiles are Lewis acids.

(22) **(B).** Decrease in number of moles in the reaction makes it favourable at high pressure.

(23) **(B).** Acidic strength $\propto \sqrt{K_a}$

(24) **(D).** $AgCl + 2NH_3 \rightarrow \underset{\text{(Soluble)}}{[Ag(NH_3)_2]Cl}$

Thus, AgCl is most soluble in aqueous ammonia.

(25) **(D).** $CH_3COONa + H_2O \rightleftharpoons CH_3COOH + NaOH$

$NaOH \rightleftharpoons Na^+ + OH^-$ (Basic solution)

(26) **(A).**

(i) Increase in concentration of reactants favours forward reaction.

(ii) Increase in concentration of products favours backward reaction.

(iii) Removal of CO will favour backward reaction (decrease in concentration of reactants).

(iv) Removal of CH_3OH will favour forward reaction (increase in concentration of products).

(27) **(A).** For the reaction:

$H_2S \rightleftharpoons H^+ + HS^-$; K_{a_1}

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} \qquad \text{... (i)}$$

For the reaction: $HS^- \rightleftharpoons H^+ + S^{2-}$; K_{a_2}

$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]} \qquad \text{... (ii)}$$

For the reaction: $H_2S \rightleftharpoons 2H^+ + S^{2-}$; K_{a_3}

$$K_{a_3} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \quad \text{... (iii)}$$

By multiplying eqn. (i) and eqn. (ii), we get

$$K_{a_1} \times K_{a_2} = \frac{[H^+][HS^-]}{[H_2S]} \times \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$= \frac{[H^+]^2[S^{2-}]}{[H_2S]} = K_{a_3}$$

(28) **(A).** $\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g) \quad ; K_c = 5 \quad \text{...(i)}$

Multiply eqn (i) by 2,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)\,;\ K_c = (5)^2 \quad \text{...(ii)}$

Now, reverse the reaction

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)\ ;\ K_c = \frac{1}{(5)^2}$$

$$\therefore \quad K_c = \frac{1}{25} = 0.04$$

(29) **(B).** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At t = 0 $\quad 1 \quad 3$

At eq. $\quad 1 - x \quad 3 - 3x \quad 2x$

$4 - 2x = 3$

$x = 0.5$

$$K_p \text{ for dissociation of } NH_3 = \frac{(0.5)(1.5)^3}{1}$$

(30) **(D).** $\Delta G° = -RT \ln K$

If ln K = –ve then only

$\Delta G° = +\text{ve} \ (\text{or} > 0)$. Thus, $K < 1$

(31) **(A).** $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

$$pH = 7 + \frac{1}{2}(5.76 - 5.25) = 7.255$$

(32) **(B).** $HSO_4^- \rightarrow H_2SO_4$

$\downarrow$

SO_4^{2-}

HSO_4^- can accept or give a proton.

(33) **(A).** $pH = -\log[H^+]$

$= -\log(3 \times 10^{-5}) = 4.5229$

$pOH = 14 - pH,$

$14 - 4.5229 = 9.47$

(34) **(A).** $K_a = c\,\alpha^2$

$$\alpha = \frac{14.5}{100} = 0.145$$

$K_a = 0.01 \times (0.145)^2 = 2.1 \times 10^{-4}$

(35) **(B).** For the reaction:

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(1.2 \times 10^{-3})^2}{0.8 \times 10^{-3}} = 1.8 \times 10^{-3}$$

(36) **(B).** $H_2 + I_2 \rightleftharpoons 2HI$

At t = 0, $\quad 0.5 \quad 0.5 \quad 0$

At eq., $\quad 0.5 - x \quad 0.5 - x \quad 2x$

$$49 = \frac{\dfrac{[2x]^2}{20 \times 20}}{\left(\dfrac{0.5 - x}{20}\right)\dfrac{(0.5 - x)}{20}} = K = 0.039$$

(37) **(A).** $CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

$\rightleftharpoons H^+ + CO_3^{-2}$

(38) **(A).** $K_{sp} = [Ag^+][Cl^-]$

$[Cl^-] = NaCl = 0.05\ M$

$$Ag^+ = \frac{1.5 \times 10^{-10}}{0.05} = 3 \times 10^{-9}\ M$$

$[Ag^+] = \text{solubility} = 3 \times 10^{-9}\ M$

(39) **(B).** (I) $\quad K_c = \frac{0.01 \times 0.01}{0.01} = 10^{-2}$

(II) $\quad K_c = \frac{0.01 \times 0.01}{[0.01]^2} = 1$

(III) $\quad K_c = \frac{[0.01]^2}{0.01 \times [0.01]^3} = 100$

(40) **(C).** 50 lit 10^{-5} mole AgCl + 50 lit of 2×10^{-7} M HBr

$$[Ag^+] = \frac{10^{-5}}{100}$$

$K = 10^{-7} \times 10^{-7} = 10^{-14} < K_{sp} = 5 \times 10^{-3}$

So, no precipitation and $[Ag^+] = 10^{-7}$ M

EXERCISE-3

(1) **4.** We can write, $\quad 2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

Initial pressure : $\quad 0.2$ atm $\quad 0 \quad 0$

Equilibrium partial pressure : 0.04 atm

$$\frac{(0.2 - 0.04)}{2} \qquad \frac{(0.2 - 0.04)}{2}$$

$= 0.08 \qquad 0.08$

$$\text{Then, } K_p = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.08 \times 0.08}{(0.04)^2} = 4.0$$

(2) **3.** $\quad AB(g) \rightleftharpoons A(g) + B(g)$

Initial $\quad$ 1 mole $\quad 0 \quad 0$

At equilibrium $\quad 1–0.5 \quad 0.5 \quad 0.5$

Total number of moles = 1.5

Equilibrium pressure = P

$$\therefore\ K_p = \frac{\left(\frac{0.5}{1.5}P\right)^2}{\left(\frac{0.5}{1.5}\right)P} = \frac{0.5}{1.5}P = \frac{1}{3}P \qquad \therefore\ P = 3K_p$$

(3) **25.** Since the number of moles in a gas under the same conditions of temperature and pressure are proportional to volumes (Avogadro's Law), the volumes in mL of gases may be used instead of concentrations in the case of reversible reactions in which there is no change in the number of molecules of reactants and products.

Given : $2x = 30.8$ mL So, $x = 15.4$ mL

Vol. of H_2 at equilibrium $= (25 - 15.4) = 9.6$ mL.

Vol. of I_2 at equilibrium $= (18 - 15.4) = 2.6$ mL.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(30.8)^2}{9.6 \times 2.6} = 38.0$$

Consider the equation : $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$

Let the degree of dissociation be x

$$K_c' = \frac{x^2}{4(1-x)^2} \qquad \left\{K_c' = \frac{1}{K_c} = \frac{1}{38}\right\}$$

$$\frac{1}{38} = \frac{x^2}{4(1-x)^2} \quad \text{or} \quad \frac{1}{6.1644} = \frac{x}{2(1-x)}$$

or $x = 0.245$ i.e., 24.5% dissociated.

(4) **1.** $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$. Total moles

Initial moles t = 0

$1 \qquad 0 \qquad 0 \qquad 1$

Moles equilibrium

$1-\alpha \qquad \alpha/2 \qquad 3\alpha/2 \qquad 1+\alpha$

Partial pressure

$$\left\{\frac{1-\alpha}{1+\alpha}\right\}p \qquad \left\{\frac{\alpha}{2(1+\alpha)}\right\}p \qquad \left\{\frac{3\alpha}{2(1+\alpha)}\right\}p$$

$$K_p = \frac{[N_2]^{1/2}[H_2]^{3/2}}{[NH_3]}$$

$$= \frac{\left[\frac{\alpha}{2(1+\alpha)}p\right]^{1/2}\left[\frac{3\alpha}{2(1+\alpha)}p\right]^{3/2}}{\left[\frac{1-\alpha}{1+\alpha}p\right]} = \frac{p\alpha^2\sqrt{27}}{4(1-\alpha^2)}$$

Solving for 'α' we get : $\alpha = \left[1 + \frac{3\sqrt{3}}{4}\frac{p}{K_p}\right]^{-1/2}$

We know, $K_p = K_c(RT)^{\Delta n}$; $78.1 = K_c(0.0821 \times 673)^1$

$K_c = 1.413$ moles litre^{-1}

(5) **2.**

	I_2	$\rightleftharpoons$	$2I^-$
Initial mole	1		–
At equilibrium	$1-x$		$2x$

Total moles $= 1 - x + 2x = 1 + x$

Pressure is proportional to number of moles,

$$\frac{\text{Experimental value of pressure}}{\text{Expected value of pressure}} = \frac{1+x}{1}$$

$$\frac{0.112}{0.074} = \frac{1+x}{1} \quad \text{or } x = 0.51$$

$$K_p = \frac{P_{I^-}^2}{P_{I_2}} = \frac{\left(\frac{2x}{1+x}\right)^2 P^2}{\left(\frac{1-x}{1+x}\right)P} = \frac{4x^2P}{(1-x^2)} = \frac{4 \times (0.51)^2 \times 0.112}{(1-0.51^2)}$$

$= 0.1575$ atm.

(6) **28.** A^{2-} will react first and product is HA^-

m mol of product $= 1.00 \times 0.300 = 0.300$

$HA^- + H_2O \rightleftharpoons H_2A + OH^-$

at pH 9.00 which is equal to $\dfrac{pKa_1 + pK_{a_2}}{2}$

All A^{2-} are protonated as HA^-

Number of A^{2-} initially present in the solution

$= 0.300 \times 10.0 = 3.00$ m mol

at pH 10.33 the system is a buffer in which the ratio of A^{2-} and HA^- is equal to 1

$[HA^-]_{initial} + [HA^-]_{formed} = [A^{2-}]_{initial} - [HA^-]_{formed}$

$[HA^-]_{initial} = 3.00 - 0.300 - 0.300 = 2.40$ m mol

m mol of $Na_2A = 3.00$

m mol of $NaHA = 2.40$

Total volume of HCl required $= \dfrac{2 \times 3.00 + 2.40}{0.30} = 28.00$ ml

(7) **20. & (8) 8.**

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

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]} \qquad \text{.......(i)}$$

Further $HS^- = H^+ + S^{2-}$

$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]} \qquad \text{.......(ii)}$$

Multiplying both the equations

$$K_{a_1} \times K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

Due to common ion, the ionisation of H_2S is suppressed and the $[H^+]$ in solution is due to the presence of 0.3 M HCl.

$$[S^{2-}] = \frac{K_{a_1} \times K_{a_2}[H_2S]}{[H^+]^2} = \frac{1.0 \times 10^{-7} \times 1.3 \times 10^{-13} \times (0.1)}{(0.3)^2}$$

$$= 1.44 \times 10^{-20}\ M$$

Putting the value of $[S^{2-}]$ in Eq. (ii)

$$1.3 \times 10^{-13} = \frac{0.3 \times 1.44 \times 10^{-20}}{[HS^-]}$$

$$\text{or } [HS^-] = \frac{0.3 \times 1.44 \times 10^{-20}}{1.3 \times 10^{-13}} = 3.3 \times 10^{-8}\ M$$

(9) **9.** Using Handerson equation for basic buffer

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

$$\because \text{ For } NH_4OH,\ (pK_a)_{NH_4^+} + (pK_b)_{NH_4OH} = 14$$

$$\therefore\ (pK_b)_{NH_4OH} = 14 - 9.26 = 4.74$$

	NH_4Cl	$+NaOH$	$\longrightarrow NH_4OH$	$+NaCl$
$t=0$	7.5	5		
$t=t$	2.5	–	5	5

$$\therefore\ pOH = 4.74 + \log\frac{2.5}{5} = 4.44$$

$$\therefore\ pH = 14 - 4.44 = 9.56$$

(10) **10.** Let h be the degree of hydrolysis of the salt (anilinium acetate).

$$\begin{array}{llll} C_6H_5NH_3^+(aq) + CH_3CO_2^-(aq) + H_2O \rightleftharpoons & C_6H_5NH_3OH + & CH_3CO_2H & \\ 0.1\ (1-h) \qquad 0.1\ (1-h) & 0.1\ h & 0.1\ h & \end{array}$$

$$K_h = \frac{[C_6H_5NH_3OH][CH_3CO_2H]}{[C_6H_5NH_3^+][CH_3CO_2^-]} = \frac{K_w}{K_a \times K_b}$$

$$\frac{K_w}{K_a \times K_b} = \frac{(0.1h)^2}{[0.1(1-h)]^2}$$

$$\sqrt{\frac{1.008 \times 10^{-14}}{1.75 \times 10^{-5} \times 3.83 \times 10^{-10}}} = \frac{h}{(1-h)}$$

$$h = 0.55$$

(11) **5.** First, write the chemical equation.

$$NH_4^+(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + NH_3(aq)$$

Calculate K_a from K_b for ammonia.

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

Now, write the iCe [initial concentration (i), change due to the reaction (C) and the equilibrium concentration (e)] table.

	NH_4^+	$+H_2O$	$\rightleftharpoons H_3O^+$	$+NH_3$
initial, M	0.050		0	0
Change, M	–y		+y	+y
equilibrium, M	0.050 – y		y	y

Substitute into the equilibrium constant expression and solve for y.

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^+]}\ ;\ 5.6 \times 10^{-10} = \frac{(y)(y)}{0.050 - y}$$

$$\text{If } y << 0.050 \text{ then } 5.6 \times 10^{-10} \approx \frac{y^2}{0.050}$$

$$y^2 = 0.050 \times 5.6 \times 10^{-10} = 2.8 \times 10^{-11}$$

$$y = 5.3 \times 10^{-6}$$

Check the assumption. Is $5.3 \times 10^{-6} << 0.050$? Yes, it is. The assumption is good and we can accept the value.

$$[H_3O^+] = 5.3 \times 10^{-6}\ ;\ pH = -\log[5.6 \times 10^{-6}] = 5.28$$

EXERCISE-4

SECTION - A [CHEMICAL EQUILIBRIUM]

(1) **(C).** We know that, $K_p = K_c(RT)^{\Delta n}$ $[\because \Delta n = n_P - n_R]$

From the reaction, $CO + \frac{1}{2}O_2 \longrightarrow CO_2$

$$n_R = 1 + \frac{1}{2} = 1\frac{1}{2}\ ;\ n_P = 1\ ;\ \Delta n = 1 - 1\frac{1}{2} = -\frac{1}{2}$$

$$K_P = K_C \cdot (RT)^{-1/2} = \frac{K_C}{(RT)^{1/2}} = \frac{K_C}{\sqrt{RT}}\ ;\ \frac{K_P}{K_C} = \frac{1}{\sqrt{RT}}$$

(2) **(C).** Volume of reactant = Volume of product so, then equilibria is not affected by change in volume of the flask.

(3) **(A).** $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$$K_C = \frac{[NO_2]^2}{[N_2O_4]}$$

Given value

$[NO_2] = 1.2 \times 10^{-2}$ mol/lit

$[N_2O_4] = 4.8 \times 10^{-2}$ mol/lit

$$\text{So, } K_C = \frac{(1.2 \times 10^{-2})^2}{(4.8 \times 10^{-2})} = \frac{1.44 \times 10^{-4}}{4.8 \times 10^{-2}} = 0.3 \times 10^{-2}$$

$$= 3 \times 10^{-3} \text{ mol/lit}$$

(4) **(A).** The reaction

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)\ ;\ \Delta H^\circ = -198$ kJ

Since the reaction is exothermic so, high temp. is unfavourable, similarly in forward direction, the volume is low so pressure is high.

(5) **(D).** $P_4(S) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$

$K_C = \dfrac{1}{[O_2]^5}$; $[P_4] = [P_4O_{10}] = 1$, due to solid state

(6) **(A).** $CO + Cl_2 \rightleftharpoons COCl_2$

$n_R = 2 \qquad n_P = 1$

$K_P = K_C\,(RT)^{\Delta n}$, $K_P = K_C\,(RT)^{-1}$

$\dfrac{K_P}{K_C} = \dfrac{1}{RT}$

(7) **(B).** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$K_C = \frac{[NO]^2}{[N_2][O_2]} = 4 \times 10^{-4}$$

For the reaction, $NO(g) \rightleftharpoons \frac{1}{2}N_2 + \frac{1}{2}O_2$

$$K'_C = \frac{[N_2]^{1/2}.[O_2]^{1/2}}{[NO]}$$

$$K'_C = \frac{1}{[K_C]^{1/2}} = \frac{1}{\sqrt{K_C}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = \frac{1}{2 \times 10^{-2}} = 50$$

(8) **(B).** $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$K_C = 1.8 \times 10^{-6}$, $T = 184°C = 184 + 273 = 475\,K$

$R = 0.0831$ kJ/mol k,

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

$K_P = K_C.(RT)$

$\dfrac{K_P}{K_C} = RT$. So, $K_P > K_C$

(9) **(C).** $Cl_{2(g)} + 3F_{2(g)} \rightleftharpoons 2ClF_{3(g)}$; $\Delta_r H = -329$ kJ
From the above reaction, the quantity of ClF_3 increase with adding F_2.

(10) **(B).** With decrease in temperature (increase in 1/T), the value of K_{eq} is increasing. Thus the reaction must be exothermic.

(11) **(C).** $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

$\qquad\qquad\qquad\qquad x \qquad\quad x$

Already present $NH_3 = NH_3(g)$ 0.50 atm

So, at equilibrium total pressure $= 0.5 + 2x = 0.84$

$x = 0.17$. So, at equilibrium,

$P_{NH_3} = (0.50 + 0.17) = 0.67$; $P_{H_2S} = 0.17$

Hence, $K_P = P_{NH_3} \times P_{H_2S} = 0.67 \times 0.17 = 0.1139$

(12) **(D).** $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Initial $\qquad a$

At equilibrium $\qquad (a - ax) \qquad ax \qquad ax$

Total moles at equilibrium $= a + ax = a\,(1 + x)$

Mole fraction of $PCl_3 = \dfrac{ax}{a\,(1+x)} = \dfrac{x}{(1+x)}$

$$P_{PCl_3} = \left(\frac{x}{1+x}\right) P$$

(13) **(D).** $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

$$K_C = \frac{[SO_2][O_2]^{1/2}}{[SO_3]} = 4.9 \times 10^{-2}$$

For the reaction, $2SO_2\,(g) + O_2\,(g) \rightleftharpoons 2SO_3\,(g)$

$$K'_C = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]}$$

$$K'_C = \frac{1}{[K_C]^2} = \frac{1}{4.9 \times 10^{-2} \times 4.9 \times 10^{-2}}$$

$= 4.16 \times 10^2 = 416$

(14) **(B).** From the equation,

$$K_1 = \frac{[CO_2][H_2]}{[CO][H_2O]}, K_2 = \frac{[CO][H_2]^3}{[CH_4][H_2O]},$$

$$K_3 = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2}$$

On multiplying K_1 and K_2

$$K_1.K_2 = \frac{[CO_2][H_2]}{[CO][H_2O]}.\frac{[CO][H_2]^3}{[CH_4][H_2O]} = \frac{[CO_2][H_2]^4}{[CH_4][H_2O]^2} = K_3$$

i.e., $K_3 = K_1.K_2$

(15) **(D).** $X \rightleftharpoons 2Y$

$1 \qquad\qquad 0$

$(1 - x) \qquad 2x$

$$K_{p_1} = \frac{(2x)^2}{(1-x)}\left(\frac{P_1}{1+x}\right)$$

$Z \rightleftharpoons P + Q$

$1 \qquad\qquad 0 \quad 0$

$(1 - x) \qquad x \quad x$

$$K_{p_2} = \frac{x^2}{(1-x)}\left(\frac{P_2}{1+x}\right) ; \quad \frac{4 \times P_1}{P_2} = \frac{1}{9} \Rightarrow \frac{P_1}{P_2} = \frac{1}{36}$$

(16) **(A).** $CO_2\,(g) + C\,(s) \rightleftharpoons 2CO\,(g)$

0.5 atm

$0.5 - p \qquad\qquad 2p$

Total pressure $= 0.5 - P + 2P = 0.8$

$P = 0.3$

$$K_p = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(2P)^2}{(0.5-P)} = \frac{(0.6)^2}{(0.5-0.3)} ; \; K_p = 1.8$$

(17) **(D).** $N_2 + O_2 \rightarrow 2NO$; $\quad K = 4 \times 10^{-4}$

$$NO \rightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2 ; K' = \frac{1}{\sqrt{K}} = \frac{1}{\sqrt{4 \times 10^{-4}}} = 50$$

(18) **(D).** For reaciton : $SO_2(g)+\frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

$$\Delta n_g = -\frac{1}{2} = x$$

(19) **(A).** $2A \rightleftharpoons B + C$; $\Delta G° = 2494.2$ J

As we know $\Delta G° = -2.303\ RT \log K_C$

$\Rightarrow$ $2494.2 = -2.303 \times 8.314 \times 300 \log K_C$

$\Rightarrow$ $-0.434 = \log K_C$

$\Rightarrow$ $K_C = \text{anti}\log(-0.434) = 0.367$

Now $[A] = 1/2$, $[B] = 2$ and $[C] = 1/2$

$$\text{Now,}\quad Q_C = \frac{[C][B]}{[A]^2} = \frac{(1/2)(2)}{(1/2)^2} = 4$$

$Q_C > K_C$, reaction will shift in backward direction.

(20) **(B).** Initially at equilibrium

$$\begin{array}{ccccccc} A & + & B & \rightleftharpoons & C & + & D \ ;\ K_{eq} = 100 \\ 1 & & 1 & & 1 & & 1 \quad Q = 1 \\ (1-x) & & (1-x) & & (1+x) & & (1+x) \end{array}$$

$$K_{eq} = \frac{[C][D]}{[A][B]} = \frac{(1+x)(1+x)}{(1-x)(1-x)} = \frac{(1+x)^2}{(1-x)^2}$$

$10 = \frac{1+x}{1-x}$. On solving, $x = 9/11$, $[D] = 1.818$

(21) **(C).** $\Delta G = \Delta H - T\Delta S$; $-RT \ln k = \Delta H - T\Delta S$

$$\ln k = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}\ ;\ \text{Slope is } \frac{-\Delta H}{R}$$

Since ΔH is – ve $\quad\therefore$ Slope is positive.

(22) **(B).** $A_2(g) + Br_2(g) \xrightleftharpoons{K_1} 2AB(g)$ .....(1) $\Rightarrow$ eq. (1) × 3

$$6AB(g) \xrightleftharpoons{K_2} 3A_2(g) + 3B_2(g)$$

$$\Rightarrow \left(\frac{1}{k_1}\right)^3 = k_2 \Rightarrow k_2 = (k_1)^{-3}$$

(23) **(C).** $S(s) + O_2(g) \rightleftharpoons SO_2(g)$; $K_1 = 10^{52}$ ...(1)

$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g)$; $K_2 = 10^{129}$ ...(2)

$2SO_2(g) + O_2(g) \rightleftharpoons SO_3(g)$; $K_3 = x$

Multiplying equation (1) by 2;

$2SO(s) + 2O_2(g) \rightleftharpoons 2SO_2(g)$; $K_1' = 10^{104}$ ...(3)

Substracting (3) from (2); we get

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$;

$K_{eq} = 10^{(129-104)} = 10^{25}$

(24) **(A).** In option (B)- Δn_g is –ve therfore increase in pressure will bring reaction in forward direction.

In option (C)- as the reaction is exothermic therefore increase in temperature will decrease the equilibrium constant.

In option (D)- Equillibrium constant changes only with temperature.

Hence, option (B), (C) and (D) are correct therefore option (A) is incorrect choice.

(25) **(D).** If $\Delta n_g \neq 0$

$K_p \neq K_c$

(26) **(A).** $K = \frac{[B]}{[A]} = \frac{11}{6} = 2$

SECTION - B [IONIC EQUILIBRIUM]

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

$\qquad\qquad x \qquad 2x$

$K_{sp} = [Mg^{+2}][OH]^{-2} = (x)(2x)^2 = 4x^3$

(2) **(C).** For AB_2 type

Solubility product $= 4x^3 = 4 \times (1.0 \times 10^{-5})^3$

$= 4 \times 10^{-15}$

(3) **(D).** $MX_4 \rightleftharpoons M^{4+} + 4X^-$

$\quad s \qquad\qquad 4s$

$K_{sp} = [M^{4+}][X^-]^4$

$= (s)\ (4s)^4 = 256s^5$

$$s = \left(\frac{K_{sp}}{256}\right)^{1/5}$$

(4) **(A).** For the salt,

$MX_2 \rightleftharpoons M^{+2} + 2X^-$

$\qquad\qquad (s) \quad (2s)$

$K_{sp} = 4s^3$

$4 \times 10^{-12} = 4s^3$

$s = 1 \times 10^{-4}$ M

$[M^{+2}] = s = 1 \times 10^{-4}$ M

(5) **(C).** $H_2A \xrightarrow{k_a} H^+ + HA^-$

$$HA^- \xrightarrow{k_b} H^+ + A^{2-}$$

(6) **(C).** Given value, $pKa = 4.5$

$$pH = pKa + \log\frac{[A^-]}{[HA]} = 4.5 + \log\frac{[A^-]}{[A]} = 4.5$$

$pOH = 14 - pH = 14 - 4.5 = 9.5$

(7) **(B).** $AgIO_{3(s)} \rightleftharpoons Ag^+_{(aq)} + IO_3^-{}_{(aq)}$

$K_{sp} = 1.0 \times 10^{-8}$

Now, $K_{sp} = [Ag^+][IO_3^-]$

$\Rightarrow$ $[Ag^+] = \sqrt{K_{sp}} = 10^{-4}$ mol/lit.

So, no. of Ag^+ moles in 100ml $= 10^{-5}$ mole

Weight of $AgIO_3$ dissociation in 100ml solution

$= 283 \times 10^{-5} = 283 \times 10^{-3}$ gm

(8) **(B).** $pH = \frac{1}{2}(pK_a - pK_b) + 7 = \frac{1}{2}(4.80 - 4.78) + 7$

$$= \frac{1}{2}(0.02) + 7 = 0.01 + 7 = 7.01$$

(9) **(A).** Concentration of Ba^{2+} needed to precipitate $BaCO_3$

$$= \frac{K_{sp}\ \text{of}\ BaCO_3}{[CO_3^{2-}]} = \frac{5.1 \times 10^{-9}}{1.0 \times 10^{-4}} = 5.1 \times 10^{-5}\ M$$

(10) **(C).** $A \rightarrow H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$; $K_1 = 4.2 \times 10^{-7}$

$B \rightarrow HCO_3^- \rightleftharpoons H^+ + CO_3^{2-}$; $K_2 = 4.8 \times 10^{-11}$

As $K_2 << K_1$

All major $[H^+]_{total} = [H^+]_A$

and from I equilibrium, $[H^+]_A \approx [HCO_3^-] \approx [H^+]_{total}$

$[CO_3^{2-}]$ is negligible compared to $[HCO_3^-]$ or $[H^+]_{total}$

(11) **(B).** $Ag^+ + Br^- \rightleftharpoons AgBr$

Precipitation starts when ionic product just exceeds solubility product $K_{sp} = [Ag^+][Br^-]$

$$[Br^-] = \frac{K_{sp}}{[Ag^+]} = \frac{5 \times 10^{-3}}{0.05} = 10^{-11}$$

i.e., precipitation just starts when 10^{-11} moles of KBr is added to 1L of $AgNO_3$ solution.

No. of moles of KBr to be added $= 10^{-11}$

$\therefore$ Weight of KBr to be added $= 10^{-11} \times 120 = 1.2 \times 10^{-9}$ g

(12) **(B).** $Mg^{2+} + 2OH^- \rightleftharpoons Mg(OH)_2$

$K_{sp} = [Mg^{2+}][OH^-]^2$

$$[OH^-] = \sqrt{\frac{K_{sp}}{[Mg^{2+}]}} = 10^{-4}$$

$\therefore$ $p^{OH} = 4$ and $p^H = 10$

(13) **(A).**

$A_xB_y \longrightarrow$	xA^{y+} +	yB^{x-}
$1-\alpha$	$x\alpha$	$y\alpha$

$i = 1 - \alpha + x\alpha + y\alpha$

$i = 1 + \alpha(x + y - 1)$

$$\alpha = \frac{i-1}{(x+y-1)}$$

(14) **(C).**

HQ $\rightleftharpoons$	H^+ +	Q^-
0.1		
0.1 – x	x	x

pH = 3, $[H^+] = 10^{-3}$, $x = 10^{-3}$

$$K_a = \frac{(x)\times(x)}{(0.1-x)} = \frac{(10^{-3})^2}{0.1-10^{-3}} = \frac{10^{-6}}{0.1} = 10^{-5}$$

(15) **(D).** pH = 1 : $[H^+] = 10^{-1} = 0.1$ M

pH = 2 : $[H^+] = 10^{-2} = 0.01$ M

For dilution of HCl $M_1V_1 = M_2V_2$

$0.1 \times 1 = 0.01 \times V_2$

$V_2 = 10$ lt

Volume of water added = 10 – 1 = 9 litre.

(16) **(C).** pH of a salt made up of weak acid and weak base is calculated by using expression

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b = 7 + \frac{3.2}{2} - \frac{3.4}{2} = 6.9$$

(17) **(D).** CH_3COOK is a salt of a weak acid and a strong base

$\therefore$ Most basic

(18) **(A).** Methyl orange is used for titration of strong acid and weak base.

(19) **(A).** $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$; $K_{sp} = 10^{-10}$

$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-}$

Conc. of SO_4^{2-} in final solution $= \frac{50 \times 1}{500} = 0.1$ M

For final solution, $[Ba^{2+}][SO_4^{2-}] = 10^{-10}$

$[Ba^{2+}] = 10^{-9}$ M ; $M_iV_i = M_fV_f$

$C \times 450 = 10^{-9} \times 500$; $C = 1.1 \times 10^{-9}$M

(20) **(D).** $HCl \rightarrow H^+ + Cl^-$

0.2M 0.2 M

$_2S \rightleftharpoons H^+ + HS^-$; $K_1 = 10^{-7}$

$HS^- \rightleftharpoons H^+ + S^{2-}$; $K_2 = 1.2 \times 10^{-13}$

$H_2S \rightleftharpoons 2H^+ + S^{2-}$; $K = K_1.K_2 = 1.2 \times 10^{-20}$

$$K = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \ ; [H^+] = 0.2\,M,\ [H_2S] = 0.1$$

$$1.2 \times 10^{-20} = \frac{(0.2)^2[S^{2-}]}{0.1} \ ; \ [S^{2-}] = 3 \times 10^{-20}\,M$$

(21) **(C).** 20 ml 0.1 M $H_2SO_4 \Rightarrow \eta_{H^+} = 4$

30 ml 0.2 M $NH_4OH \Rightarrow \eta_{NH_4OH} = 6$

NH_4OH +	$H^+ \rightleftharpoons$	$NH_4^{\oplus}$ +	H_2O
6	4	0	0
2	0	4	4

Solution is basic buffer $pOH = pK_b + \log\frac{NH_4^+}{NH_4OH}$

$= 4.7 + \log 2 = 4.7 + 0.3 = 5$; pH = 14 – 5 = 9

(22) **(D).** $Zr_3(PO_4)_4(s) \rightleftharpoons 3Zr^{4+}(aq.) + 4\,PO_4^{3-}(aq.)$

3S M 4S M

$K_{sp} = [Zr^{4+}]^3[PO_4^{3-}]^4 = (3S)^3.(4S)^4 = 6912\,S^7$

$$\therefore \quad S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$$

(23) **(B).** For the salt of strong acid and weak base

$$H^+ = \sqrt{\frac{K_w \times C}{K_b}} \ ; \ [H^+] = \sqrt{\frac{10^{-14} \times 2 \times 10^{-2}}{10^{-5}}}$$

$$-\log[H^+] = 6 - \frac{1}{2}\log 20 \qquad \therefore pH = 5.35$$

(24) **10.60**

$$M_{H_2SO_4} = \frac{9.8}{98 \times 100} = 10^{-3}$$

$$M_{NaOH} = \frac{4}{40 \times 100} = 10^{-3} = \frac{40 \times 10^{-3} - 10 \times 10^{-3} \times 2}{50} = \frac{20}{50} \times 10^{-3}$$

$$[OH^-] = \frac{2}{5} \times 10^{-3} \ ; \ pOH = 3.397 \ ; \ pH = 10.603$$

(25) **5.22.**

m mole of acidic acid in 20 mL = 2

m mole of HCl in 20 mL = 1

m mole of NaOH = 2.5

CH_3COOH +	NaOH (remaining) $\rightarrow$	CH_3COONa +	water
2	3/2	0	0
0.5	0	3/2	-

$$pH = pK_a + \log\left(\frac{3/2}{2}\right) = 4.74 + \log 3$$

$= 4.74 + 0.48 = 5.22$

(26) **(B).** $[Pb^{2+}] = \frac{300 \times 0.134}{400} = 1.005 \times 10^{-1}$ M

$[Cl^-] = \frac{100 \times 0.4}{400} = 10^{-1} M$

$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$

$Q = [Pb^{2+}] \times [Cl^-]^2 = 1.005 \times 10^{-3} > k_{sp}$

(27) **(A).** $\underset{}{Cr(OH)_3(s)} \rightleftharpoons \underset{(s)}{Cr^{3+}(aq.)} + \underset{(3s)}{3OH^-(aq.)}$

$K_{sp} = 27(s)^4 = 6 \times 10^{-31}$

$[3(s)]^4 = 18 \times 10^{-31}$

$[OH^-] = 3(s) = [18 \times 10^{-31}]^{1/4}$

EXERCISE-5

(1) **(A).** The solution formed from isomolar solutions of sodium oxide, sodium sulphide, sodium selenide and sodium telluride are H_2O, H_2S, H_2Se and H_2Te respectively. As the acidic strength increases from H_2O to H_2Te thus pH decreases and hence the correct of pHs is : $pH_1 > pH_2 > pH_3 > pH_4$

(2) **(D).** Given : $K_b = 1.0 \times 10^{-12}$.

$[BOH] = 0.01$ M, $[OH] = ?$

$$\begin{array}{lccc} & BOH & \rightleftharpoons B^+ & + OH^- \\ t = 0 & c & 0 & 0 \\ t_{eq} & c(1-x) & cx & cx \end{array}$$

$$K_b = \frac{c^2x^2}{c(1-x)} = \frac{cx^2}{(1-x)} \;;\; 1.0 \times 10^{-12} = \frac{0.01\,x^2}{0.01\,(1-x)}$$

On calculation, we get, $x = 1.0 \times 10^{-5}$

Now $[OH^-] = cx = 0.01 \times 10^{-5} = 1.0 \times 10^{-7}$ mol L^{-1}

(3) **(A).** In qualitative analysis of cations of second group H_2S gas is passed in presence of HCl, therefore due to common ion effect, lower concentration of sulphide ions is obtained which is sufficient for the precipitation of second group cations in the form of their sulphides due to lower value of their solubility product (K_{sp}). Here, fourth group cations are not precipitated because it require more sulphide ions for exceeding their ionic product to their solubility products which is not obtained here due to common ion effect.

(4) **(C).** For equation (i), $NO(g) + \frac{1}{2} O_2(g) \rightleftharpoons NO_2(g)$

$$K_1 = \frac{[NO_2]}{[NO][O_2]^{1/2}} \qquad \text{........ (1)}$$

For equation (ii), $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$

$$K_2 = \frac{[NO]^2[O_2]}{[NO_2]^2} \qquad \text{........ (2)}$$

Now, on reversing eq. (1), we get

$$\frac{1}{K_1} = \frac{1}{\dfrac{[NO_2]}{[NO][O_2]^{1/2}}} = \frac{[NO][O_2]^{1/2}}{[NO_2]}$$

$$\left(\frac{1}{K_1}\right)^2 = \left\{\frac{[NO][O_2]^{1/2}}{[NO_2]}\right\}^2 = \frac{[NO]^2[O_2]}{[NO_2]^2} = K_2$$

$$\frac{1}{K_1^2} = K_2$$

(5) **(A).** $CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(\ell)$

$\Delta_rH = -170.8$ kJ mol^{-1}

$$K_c = \frac{[CO_2]}{[CH_4][O_2]^2} \;;\; K_p = \frac{p_{CO_2}}{p_{CH_4}\,{p_{O_2}}^2}$$

The reaction is an example of exothermic reaction.

(6) **(A).** For a solution of 10^{-8} M HCl $[H^+] = 10^{-8}$

$[H^+]$ of water $= 10^{-7}$

Total $[H^+] = 10^{-7} + 10^{-8} = 10 \times 10^{-8} + 10^{-8}$

$10^{-8}(10 + 1) = 11 \times 10^{-8}$

(7) **(D).** (D) is the answer as HNO_2 is a weak acid and $NaNO_2$ is salt of that weak acid and strong base (NaOH).

(8) **(A).** $K_a = 1.00 \times 10^{-5}$, $C = 0.100$ mol for a weak electrolyte.

Degree of dissociation (α)

$$= \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1 \times 10^{-5}}{0.100}} = 10^{-2} = 1\%$$

(9) **(A).** The required equation for the oxidation of NH_3 by oxygen to give NO is :

$$2NH_3 + \frac{5}{2}O_2 \xrightarrow[800°C]{\text{Pt (gauze)}} 2NO + 3H_2O$$

For this $K = \frac{[NO]^2[H_2O]^3}{[NH_3]^2[O_2]^{5/2}}$

For getting the K we must do

$$K_1^2 = \frac{[NH_3]^4}{[N_2]^2[H_2]^6} \;;\; K_2^2 = \frac{[NO]^4}{[N_2]^2[O_2]^2}$$

$$K_3^6 = \frac{[H_2O]^6}{[H_2]^6[O_2]^3} \;;\; K^2 = \frac{K_2^2 \times K_3^6}{K_1^2} \quad \text{or} \quad K = \frac{K_2K_3^3}{K_1}$$

(10) **(A).** Given $[H_3O^+] = 1 \times 10^{-10}$ M

At 25°C $[H_3O^+][OH^-] = 10^{-14}$

$\therefore$ $[OH^-] = \frac{10^{-14}}{10^{-10}} = 10^{-4}$

Now, $[OH^-] = 10^{-p^{OH}} = 10^{-4} = 10^{-p^{OH}}$

$\therefore$ $p^{OH} = 4$

(11) **(C).** $HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$; $K = 8$

then, $H_2 + I_2 \rightleftharpoons 2HI$

$$K = \left[\frac{1}{8}\right]^2 = \frac{1}{64}$$

(12) **(C).** $[H^+] = M = \dfrac{10^{-3}\times 1 + 10^{-4}\times 1 + 10^{-5}\times 1}{3}$

$$= \frac{10^{-3}[1+10^{-1}+10^{-2}]}{3} = \frac{10^{-3}[1.11]}{3} = \frac{1.11\times 10^{-3}}{3}$$

$$= 3.7\times 10^{-4}\ M$$

(13) **(D).** $X \rightleftharpoons Y + Z$

1	0	0	Initial mole
$1-\alpha$	α	α	Mole at equilibrium

$$K_{p_1} = \frac{p_Y \times p_Z}{p_X} = \frac{\left[\frac{\alpha\times p_1}{1+\alpha}\right]\left[\frac{\alpha\times p_1}{1+\alpha}\right]}{\left[\frac{1-\alpha}{1+\alpha}\right]p_1}$$

$$K_{p_1} = \frac{\alpha^2 p_1}{1-\alpha^2} \qquad ....(1)$$

For equation,

$A \rightleftharpoons 2B$

1	0	Initial mole
$1-\alpha$	2α	Mole at equilibrium

$$K_{p_2} = \frac{\left[\frac{2\alpha}{1+\alpha}\cdot p_2\right]^2}{\left[\frac{1-\alpha}{1+\alpha}\right]\cdot p_2} = \frac{4\alpha^2 p_2}{1-\alpha^2} \qquad ....(2)$$

From eqs. (1) and (2),

$$\frac{K_{p_1}}{K_{p_2}} = \frac{p_1}{4p_2} \Rightarrow \frac{9}{1} = \frac{p_1}{4p_2} \quad \therefore \quad \frac{p_1}{p_2} = \frac{36}{1}$$

(14) **(D).** $Fe(OH)_3(s) \rightleftharpoons Fe^{3+}(aq) + 3OH^-(aq)$

$K_c = [Fe^{+3}][OH^-]^3$

Since, K_c depends only on temperature

$[Fe^{+3}][OH^-]_i^3 = [Fe^{+3}][OH^-]_F^3$

$x \times y^3 = x' \times (y/4)^3$

$x = x' \times \dfrac{1}{64} \Rightarrow x' = 64x$

(15) **(C).** $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$

1		
$1-\alpha$	α	$\alpha/2$

$$K_p = \frac{\alpha^2 . \frac{\alpha}{2}}{(1-\alpha)^2}\left(\frac{P}{1+\frac{\alpha}{2}}\right)^1$$

As $\alpha << 1$; $1-\alpha \approx 1$; $2+\alpha \approx 2$

$$K_p = \frac{\alpha^3 P}{2} \Rightarrow \alpha = \left(\frac{2K_p}{P}\right)^{1/3}$$

(16) **(C).** $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$;

$$K_1 = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} = 1.5\times 10^{-5}$$

$HCN \rightleftharpoons H^+ + CN^-$

$$K_2 = \frac{[CN^-][H^+]}{[HCN]} = 4.5\times 10^{-10}$$

$CN^- + CH_3COOH \rightleftharpoons CH_3COO^- + HCN$

$$K = \frac{[HCN][CH_3COO^-]}{[CN^-][CH_3COOH]} = \frac{K_1}{K_2} = 3.33\times 10^4$$

(17) **(D).** $(CH_3)_3\,B$ – is electron deficient

(18) **(D).** $K_h = \dfrac{K_w}{K_b} = \dfrac{1\times 10^{-14}}{1.77\times 10^{-5}} = 5.65\times 10^{-10}$

(19) **(D).** No. of m. equivalent of HCl $= 20\times 0.05 = 1.0$

No. of m. equivalent of $Br(OH)_2 = 30\times 0.1\times 2 = 6.0$

After neutralization, no. of milli equivalents in 50 ml. of solution $= (6-1) = 5$

No. of m. equivalent of OH^- is 5 in 50 ml

$$[OH^-] = \frac{5}{50} = 0.1\ M$$

(20) **(D).** Given, pH of $Ba(OH)_2 = 12$

$\therefore\ [H^+] = [1\times 10^{-12}]$

and $[OH^-] = \dfrac{1\times 10^{-14}}{1\times 10^{-12}} = 1\times 10^{-2}$ mol/L

$\because [H^+][OH^-] = 1\times 10^{-14}]$

$Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$

$\qquad\qquad s \qquad 2s$

$K_{sp} = [Ba^{2+}][OH^-]^2 = [s][2s]^2$

$$= \left[\frac{1\times 10^{-2}}{2}\right](1\times 10^{-2})^2$$

$= 0.5\times 10^{-6} = 5.0\times 10^{-7}\ M^3$

(21) **(D).** (i) For basic buffer

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

(ii) $pH + pOH = 14$

Given, $K_b = 1\times 10^{-10}$, $[salt] = [base]$

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

$\therefore\ pOH = -\log(1\times 10^{-10}) + \log 1 = 10$

$pH + POH = 14$; $pH = 14 - 10 = 4$

(22) **(D).** CH_3COOH (weak acid) and CH_3COONa (conjugated salt) form acidic buffer and for acidic buffer,

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

and $[H^+] = -\text{antilog } pH$

$$pH = -\log K_a + \log \frac{[salt]}{[acid]} \; [\because pK_a = -\log K_a]$$

$$= -\log(1.8 \times 10^{-5}) + \log \frac{0.20}{0.10}$$

$= 4.74 + \log 2 = 4.74 + 0.3010 = 5.041$

Now, $[H^+] = \text{antilog}(-5.045) = 9.0 \times 10^{-6}$ mol/L

Alternative :

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$C - x \qquad x \qquad x$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

$0.2\text{ M} \qquad 0.2\text{ M} \qquad 0.2\text{ M}$

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$[CH_3COOH] = C - x \approx 0.1\text{ M}$

$[CH_3COO^-] = 0.2 + x \approx 0.2\text{ M}$

[Acitic acid is a weak acid so, dissociation is minimum]

$$\therefore \; [H^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]} = \frac{1.8 \times 10^{-5} \times 10^{-1}}{2 \times 10^{-1}} = 9 \times 10^{-6}\text{ M}$$

(23) **(D).** $K_p = K_c(RT)^{\Delta n}$.

For $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$;

$\Delta n = 2 - 1 = 1 \neq 0$

(24) **(B).** $2A(g) + B(g) \rightleftharpoons 3C(g) + D(g)$

Initial moles : $1 \qquad 1 \qquad 0 \qquad 0$

Moles of eq. :

$1-(2\times0.25) \qquad 1 - 0.25 \qquad 3 \times 0.25 \qquad 0.25$

$= 0.5 \qquad = 0.75 \qquad = 0.75 \qquad = 0.25$

Equilibrium constant,

$$K = \frac{[C]^3[D]}{[A]^2[B]} = \frac{(0.75)^3(0.25)}{(0.5)^2(0.75)}$$

(25) **(C).** When $K_p > Q$,

rate of forward reaction > rate of backward reaction.

$\therefore$ Reaction is spontaneous.

When $\Delta G^\circ < RT \ln Q$, ΔG° is positive, reverse reaction is feasible, thus reaction is non-spontaneous.

When $K_p = Q$, rate of forward reaction = rate of backward reaction

$\therefore$ Reaction is in equilibrium.

When $T\Delta S > \Delta H$, ΔG will be –ve only when $\Delta H = +$ ve.

(26) **(D).** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) ; K_1$

$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g) ; K_2$

$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g) ; \; K = K_1 \times K_2$

$$\therefore \text{ For } NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g); \; K' = \left[\frac{1}{K_1K_2}\right]^{1/2}$$

(27) **(A).** $\Delta n_g = -$ve and $\Delta H = -$ve

The forward reaction is favoured at high pressure and low temperature.

(28) **(C).** $pOH = pK_b + \log \frac{[Salt]}{[Base]} = 4.74 + \log \frac{0.20}{0.30}$

$= 4.74 + (0.301 - 0.477) = 4.74 - 0.176 = 4.56$

$\therefore \; pH = 14 - 4.56 = 9.44$

(29) **(D).** BF_3 is an electron deficient species.

(30) **(A).** ($AlCl_3$, LiCl & $BeCl_2$) all these solution are acidic due to cationic Hydrolysis, where $BaCl_2$, is salt of strong base & strong acid.

(31) On adding small amount of acid (H^+) and base(OH^-), weak acid or weak base will be formed respectively.

(32) **(C).** $2SO_2 + O_2 \rightleftharpoons 2SO_3$; $K = 278$

$$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2$$

$$K' = \sqrt{\frac{1}{278}} = \sqrt{35.97 \times 10^{-4}} = 6 \times 10^{-2}$$

(33) **(C).** $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

$$K_C = \frac{(2.8 \times 10^{-3})^2}{3 \times 10^{-3} \times 4.2 \times 10^{-3}} = \frac{(2.8)^2}{3 \times 4.2} = 0.62$$

(34) **(D).** BF_3 is a Lewis acid.

(35) **(C).** Na_2CO_3 is a salt of strong base and weak acid will produce a basic solution with pH > 7.

(36) **(D).** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$

It is an exothermic reaction so decreasing temperature is favorable because dissociation $(x) \propto 1/T$

& dissociation $x \propto (1/P)^{-2/2}$ $\qquad \therefore x \propto P$

So increasing pressure is favorable for forward reaction

(37) **(A).** According to Vant Hoff equation

$$\log \frac{K'_p}{K_p} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

For exothermic reaction on increasing temperature equilibrium constant decreases means $T_2 > T_1$ then $K'_p < K_p$

(38) **(B).** $K = 1.6 \times 10^{12} = \left[\frac{\text{Product}}{\text{Reactant}}\right]$

K have high value so products have very high conc. than reactant.

(39) **(C).** K_{sp} of $Ag_2CrO_4 = 1.1 \times 10^{-12}$

K_{sp} of $AgCl = 1.8 \times 10^{-10}$

K_{sp} of $AgBr = 5.0 \times 10^{-13}$

K_{sp} of $AgI = 8.3 \times 10^{-17}$

$[Ag^+]^2\,[C] = 1.1\times10^{-12}$

$$[Ag^+] = \sqrt{\frac{1.1\times10^{-12}}{[C]}}$$

If we take [C] = 1 then the maximum requirement of $[Ag^+]$ will be in case of Ag_2CrO_4.

(40) **(C).** $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$; K

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)\,;\ K'$$

When a reaction is multiplied by 1/2 then $K' = (K)^{1/2}$.

(41) **(C).** $HClO_4$ is a strong acid.

Acidic buffer is a mixture of a weak acid and its salt with a strong base.

(42) **(D).** Aqueous solution of HCl is the best conductor of electric current because HCl is strong acid, so it dissociates completely into ions.

(43) **(C).** One mole of NaOH is completely neutralised by one mole of HCl. Hence, 0.01 mole of NaOH will be completely neutralised by 0.01 mole of HCl.

NaOH left unneutralised = 0.1 – 0.01 mol = 0.09 mol

As equal volumes of two solutions are mixed,

$$[OH]^- = \frac{0.09}{2} = 0.045\text{ M}$$

$\Rightarrow\ pOH = -\log(0.045) = 1.35$

$\therefore\ pH = 14 - 1.35 = 12.65$

(44) **(B).** For MY, $K_{SP} = S^2 \quad \therefore\ S = (6.2\times10^{-13})^{1/2}$

For NY_3, $K_{SP} = 27\,S^4\ \therefore\ S = \left(\frac{6.2\times10^{-13}}{27}\right)^{1/4}$

(45) **(D).** Vant Hoff's equation is $\frac{\Delta H}{RT^2} = \frac{d(\ln K)}{dT}$

$$\log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_2T_1}\right]$$

(46) **(B).** $C_5H_5N + H_2O \rightleftharpoons C_5H_5N^{\oplus}H + OH^{\ominus}$

t = 0 $\quad$ C

t = eq $\quad C(1-\alpha) \qquad C\alpha \qquad C\alpha$

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

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.7\times10^{-9}}{0.1}} = 1.3\times10^{-4}$$

$\%\,\alpha = 1.3\times10^{-4}\times100 = 0.013\%$

(47) **(B).** $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$\qquad\qquad S \qquad\qquad S$

$NaCl \rightleftharpoons Na^+(aq) + Cl^-(aq)$

$\qquad\qquad 0.1\text{ M} \qquad 0.1\text{ M}$

$\therefore\ K_{sp(AgCl)} = S(S + 0.1)$

$\therefore\ S << 0.1 \quad \therefore\ S + 0.1 \approx 0.1$

$\therefore\ 1.6\times10^{-10} = S\times0.1\ \therefore\ S = 1.6\times10^{-9}\text{ M}$

(48) **(A).** $N_2 + 3H_2 \rightleftharpoons 2NH_3\ ;\ K_1 \to (1)$

$N_2 + O_2 \rightleftharpoons 2NO\ ;\ K_2 \to (2)$

$H_2 + ½\,O_2 \to H_2O\ ;\ K_3 \to (3)$

For reaction

$$2NH_3 + (5/2)\,O_2 \xrightleftharpoons{K} 2NO + 3H_2O \to (4)$$

Equation (4) = equation (2) + 3 × eq. (3) – equation (1)

$$K = \frac{K_2\cdot K_3^3}{K_1}$$

(49) **(C).** $Ag_2C_2O_4 \rightleftharpoons 2Ag^+ + C_2O_4^{2-}$

$\qquad 2.2\times10^{-4}\text{ M} \quad 1.1\times10^{-4}\text{ M}$

$K_{sp} = [Ag^+]^2\,[C_2O_4^{2-}] = [2.2\times10^{-4}]^2\,.\,[1.1\times10^{-4}]$

$K_{sp} = 5.3\times10^{-12}$

(50) **(A).** Equilibrium constant is not affected by presence of catalyst hence statement (A) is incorrect.

(51) **(D).** $SrCO_3(s) \rightleftharpoons SrO(s) + CO_2(g)\ ;\ K_p = P_{CO_2}$

Maximum pressure of CO_2 = 1.6 atm

$P_1V_1 = P_2V_2\,;\ 0.4\times20 = 1.6\,V_2\ ;V_2 = 5L$

(52) **(D).** Meq of HCl = $75\times\frac{1}{5}\times1 = 15$

Meq of NaOH = $25\times\frac{1}{5}\times1 = 5$

Meq of HCl in resulting solution = 10

Molarity of $[H^+]$ in resulting mixture $= \frac{10}{100} = \frac{1}{10}$

$$pH = -\log[H^+] = -\log\left[\frac{1}{10}\right] = 1.0$$

(53) **(C).** Solubility of $BaSO_4$,

$$s = \frac{2.42\times10^{-3}}{233} = 1.04\times10^{-5}\,(\text{mol L}^{-1})$$

$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$

$\qquad\qquad s \qquad\qquad s$

$K_{sp} = [Ba^{2+}][SO_4^{2-}] = s^2$

$= (1.04 \times 10^{-5})^2 = 1.08 \times 10^{-10}\ mol^2\ L^{-2}$

(54) **(C).** $A_2\,(g) + B_2\,(g) \rightleftharpoons X_2\,(g)\ \Delta_rH = -X$ kJ?

On increasing pressure equilibrium shifts in a direction where pressure decreases i.e. forward direction. On decreasing temperature, equilibrium shifts in exothermic direction i.e., forward direction.

So, high pressure and low temperature favours maximum formation of product.

(55) **(A).** $Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$

pH = 9 Hence, pOH = 14 – 9 = 5 ; $[OH^-] = 10^{-5}$ M

Hence $[Ca^{2+}] = \dfrac{10^{-5}}{2}$

$$K_{sp} = [Ca^{2+}][OH^-]^2 = \left(\frac{10^{-5}}{2}\right)(10^{-5})^2 = 0.5 \times 10^{-15}$$

(56) **(C).**

$$\begin{tikzcd} & OH^{\ominus}\ \text{Conjugate base} \\ H_2O \arrow[ur] \arrow[dr] & \\ & H_3O^{\oplus}\ \text{Conjugate acid} \end{tikzcd}$$

HF on loss of H^+ ion becomes F^- is the conjugate base of HF

Example :

$$HF + H_2O \rightleftharpoons F^- + H_3O^+$$

Acid	Base	Conjugate base	Conjugate acid

(57) **(C).**

(A) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Before	25 mL × 0.1 M = 2.5 mmol	50 mL × 0.1M = 5 mmol	0
After	0	2.5 mmol	2.5 mmol

This is basic solution due to NaOH.

This is not basic buffer.

(B) $CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

Before	100 mL × 0.1 M = 10 mmol	100 mL × 0.1M = 10 mmol	0
After	0	0	10 mmol

Hydrolysis of salt takes place.

This is not basic buffer.

(C) $HCl + NH_4OH \rightarrow NH_4Cl + H_2O$

Before	100 mL × 0.1 M = 10 mmol	200 mL × 0.1 M = 20 mmol	0
After	0	10 mmol	10 mmol

This is basic buffer

(D) $HCl + NaOH \rightarrow NaCl + H_2O$

Before	100 mL × 0.1 M = 10 mmol	100 mL × 0.1 M = 10 mmol	0
After	0	0	10 mmol

∴ Neutral solution