Fill Ups, True False of Equilibrium

Fill in the Blanks

Q.1. The conjugate base of HSO_4^- in aqueous solution is ....   (1982 - 1 Mark)

Ans. SO_4^{2-}

Solution. SO_4^{2-} ; Conjugate base = Acid – H^+

∴ Conjugate base of HSO_4^- is SO_4^{2-}

Q.2. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be ....   (1984 - 1 Mark)

Ans. amphoteric

Solution. amphoteric ; because amphoteric substances show properties of both acids and basic

Q.3. For a given reversible reaction at a fixed temperature, equilibrium constants K_p and K_c are related by........   (1994 - 1 Mark)

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

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

Here Δn = No. of moles of gaseous products – no. of moles of gaseous reactants

R = gas constant, and T = absolute temperature.

Q.4. A ten - fold increase in pressure on the reaction , $N_2(g)+3H_2(g) \rightleftharpoons 2NH_3(g)$ at equilibrium results in .... in K_P.   (1996 - 1 Mark)

Ans. no change

Solution. no change; (K_p of an equilibrium reaction is independent of the pressure of the system.)

Q.5. In the reaction $I^-+I_2 \rightarrow I_3^-$, the Lewis acid is .... **(1997 - 1 Mark)**

Ans. I_2

Solution. I_2. ∵ electron acceptors are Lewis acids.

True/False

Q.1. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons. **(1982 - 1 Mark)**

Ans. F

Solution. False : $AlCl_3$ is a Lewis acid (although they do not have a proton, aprotic) because it accepts electrons (octet being incomplete).

Q.2. If equilibrium constant for the reaction $A_2+B_2 \rightleftharpoons 2AB,$ is K, then for the backward reaction $AB \rightleftharpoons \frac{1}{2}A_2+\frac{1}{2}B_2,$ the equilibrium constant is 1/K. **(1984 - 1 Mark)**

Ans. F

Solution. False :

$$K \text{ for } A_2+B_2 \rightleftharpoons 2AB \text{ is } \frac{[AB]^2}{[A_2][B_2]}$$

$$K' \text{ for } AB \rightleftharpoons \tfrac{1}{2}A_2+\tfrac{1}{2}B_2 \text{ is } \frac{[A_2]^{1/2}\,[B_2]^{1/2}}{[AB]}$$

$$\text{or} \quad (K')^2=\frac{[A_2][B_2]}{[AB]^2}=\frac{1}{K} \quad \therefore \quad K'=\sqrt{\frac{1}{K}}$$

Q.3. When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs. **(1984 - 1 Mark)**

Ans. T

Solution. True : Lower the pressure, lower will be boiling point. More liquid will vapourise and temperature decreases.

Q.4. Solubility of sodium hydroxide increases with increase in temperature. (1985 - ½ Mark)

Ans. F

Solution. TIPS/Formulae : Dissolution of NaOH is exothermic.

False : When a solute like NaOH is added to a solvent exothermic dissolution takes place. An increase in temperature always favour endothermic process. So solutes having exothermic dissolution shows a decrease in their solubility with temperature

Subjective Questions of Equilibrium, (Part -1)

Q.1. A solution contains Na_2CO_3 and $NaHCO_3$. 10 ml of solution requires 2.5 ml of 0.1 M H_2SO_4 for neutralisation using phenolphthalein as an indicator. Methyl orange is then added when a further 2.5ml of 0.2M H_2SO_4 was required. Calculate the amount of $Na_2CO_3$and $NaHCO_3$ in one litre of the solution.

Ans. 5.3 g/l; 4.2 g/l;

Solution. Phenolphthalein indicates half neutralization.

$Na_2CO_3 + H^+ \rightarrow NaHCO_3 + Na^+$ ...(i)

Methyl orange indicates complete neutralisation

$NaHCO_3 + H^+ \rightarrow Na^+ + H_2O + CO_2$ ...(ii)

$\therefore$ Volume of 0.1M H_2SO_4 required for complete neutralisation = 2 × 2.5 = 5.0 ml

0.1 M $H_2SO_4 \equiv 0.2\ NH_2SO_4$

[For H_2SO_4 molarity = 2 × normality]

($\because$ Mol. wt. of H_2SO_4 = 98, and eq. wt. of H_2SO_4 = 49)

$\therefore$ 0.2 M $H_2SO_4 \equiv 0.4\ NH_2SO_4$

N_1 = normality of Na_2CO_3, V_1 = volume of Na_2CO_3 = 10 ml,

N_2 = normality of H_2SO_4 = 0.2, V2 = volume of H_2SO_4 = 5.0 ml

$$\therefore N_1V_1 = N_2V_2 \Rightarrow N_1 \times 10 = 0.2 \times 5$$

$$\therefore N_1 = \frac{0.2\times5}{10} = 0.1\,\text{N}$$

$\therefore$ Eq. wt. of $Na_2CO_3 = \frac{1}{2} \times \text{molecular weight} = \frac{106}{2} = 53$

Strength of Na_2CO_3 = 53 × 0.1 = 5.3 g/l

[$\therefore$ strength = normality × Eq. wt]

For neutralization with methyl orange, volume of 0.2 M

H_2SO_4 used = 2.5 ml = 2.5 ml of 0.4 N H_2SO_4

= 5 ml of 0.2 N H_2SO_4 [$\therefore N_1V_1 = N_2V_2$]

From 5 ml of 0.2 N H_2SO_4, 2.5 ml is used for neutralising $NaHCO_3$ formed during first half neutralization Na_2CO_3

$\therefore$ Volume of 0.2N H_2SO_4 used for neutralisation of $NaHCO_3$ present in original solution = 5.0 – 2.5 = 2.5 ml

$\therefore N_1V_1 = N_2V_2$

where N_1 = Normality of $NaHCO_3$,

N_2 = Normality of H_2SO_4 = 0.2,

V1 = Volume of $NaHCO_3$ = 10 ml, V_2 = Volume of H_2SO_4 = 2.5 ml

$N_1V_1 = N_2V_2 \Rightarrow N_1 \times 10 = 0.2 \times 2.5$

$$N_1 = \frac{0.2 \times 2.5}{10} = 0.05\,\mathrm{N}$$

Eq. wt. of $NaHCO_3$ = 84

$\therefore$ Strength of $NaHCO_3$ = 84 × 0.05 = 4.2 g/l

Q.2. How many moles of sodium propionate should be added to one litre of an aqueous solution containing 0.020 mole of propionic acid to obtain a buffer solution of pH 4.75? What will be pH if 0.010 mole of hydrogen chloride is dissolved in the above buffer solution. Compare the last pH value with the pH of 0.010 molar HCl solution. Dissociation constant of propionic acid, K_a at 25ºC = 1.34×10^{-5}.

Ans. 1.5072×10^{-2} mol, 4.09, 2

Solution. Suppose the number of moles of sodium propionate = x

$$\text{Then } pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4.75 = -\log(1.34 \times 10^{-5}) + \log\left(\frac{x}{0.02}\right)$$

$$\text{or } 4.75 = 5 - 0.1271 + \log \frac{x}{0.02}$$

$$\text{or } 4.75 = 4.8729 + \log \frac{x}{0.02}$$

$$\log \frac{x}{0.02} = -0.1229$$

$$\text{or } \frac{x}{0.02} = \text{Antilog}\,[-0.1229] \quad \text{or } \frac{x}{0.02} = 0.7536$$

$$x = 0.7536 \times 0.02 = \mathbf{1.5072 \times 10^{-2}\ mol}$$

$$\begin{array}{llll} \text{HCl} & \rightleftharpoons & H^+ & + \ Cl^- \\ 0.01 \text{ mole} & & 0.01 \text{ mole} & \end{array}$$

When 0.01 mole of HCl is added, there is (0.01 + 0.02) M of propionic acid and (0.015 – 0.010) M of propionate. Therefore

$$pH = -\log(1.34 \times 10^{-5}) + \log \frac{0.005}{0.03} = \mathbf{4.09}$$

The pH of a 0.010 molar HCl solution = –log 10^{-2} = 2

Q.3. One mole of nitrogen is mixed with three moles of hydrogen in a 4 litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction

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

calculate the equilibrium constant (Kc) in concentration units. What will be the value of Kc for the following equilibrium ?

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(ag)$$

Ans. 1.48 × 10^{-5} l2 mol^{-2}, 3.82 × 10^{-3} litre mol^{-1}

Solution.

$$\begin{array}{lccccc} \text{Initial moles} & 1 & & 3 & & 0 \\ & N_2(g) & + & 3H_2(g) & \rightleftharpoons & 2NH_3(g) \\ \text{Eq. moles} & 1 - 0.0025 & & 3 - 0.0075 & & 2 \times 0.0025 \\ \text{Eq. conc.} & \dfrac{1 - 0.0025}{4} & & \dfrac{3 - 0.0075}{4} & & \dfrac{2 \times 0.0025}{4} \end{array}$$

Now we know that $K_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

Since 0.0025 and 0.0075 are very small, 1–0.0025 and 3–0.0075 may be taken as 1 and 3 respectively.

Substitute the various values

$$K_c = \frac{\left(\dfrac{2 \times 0.0025}{4}\right)^2}{\left[\dfrac{1}{4}\right]\left[\dfrac{3}{4}\right]^3} = \frac{0.0025 \times 0.0025}{4} \times \frac{4 \times 4 \times 4 \times 4}{3 \times 3 \times 3}$$

$= 1.48 \times 10^{-5}$ litre^2 mol^{-2}

For the equilibrium,

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \rightleftharpoons NH_3(g)$$

$$K_c' = \frac{[NH_3]}{[N_2]^{1/2}[H_2]^{3/2}} = \sqrt{K_c}$$

$$= \sqrt{(1.48 \times 10^{-5} \text{ litre}^2 \text{ mol}^{-2})}$$

$$= \mathbf{3.82 \times 10^{-3} \text{ litre mol}^{-1}}$$

Q.4. Twenty ml. of 0.2 M sodium hydroxide is added to 50 ml. of 0.2 M acetic acid to give 70 ml of the solution. What is the pH of this solution? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. The ionization constant of acetic acid is 1.8 × 10^{-5}.

Ans. 4.5686, 4.86 ml

Solution. TIPS/Formulae :

(i) Find the moles of each species after reaction.

(ii) $pH = -\log K_a + \log\left[\dfrac{\text{salt}}{\text{Acid}}\right]$

Given, NaOH 0.2 M, 20 ml; CH_3COOH 0.2 M, 50 ml $K_a = 1.8 \times 10^{-5}$

V of 0.2M NaOH required to make pH = 4.74 =?

From the chemical reaction

$$\underset{50\text{ ml}}{CH_3COOH} + \underset{20\text{ ml}}{NaOH} \longrightarrow \underbrace{CH_3COONa + H_2O}_{20\text{ ml}}$$

It is evident that 70 ml of the product will contain

(i) 30 ml of 0.2 M unused CH3COOH

[unused CH_3COOH = 50 – 20 = 30 ml]

(ii) 20 ml of CH_3COONa.

∴ No. of moles of CH_3COOH in solution

$$= \frac{0.2}{1000} \times 30 = 0.006\text{ mole}$$

Similarly, No. of moles of CH_3COONa solution

$$= \frac{0.2}{1000} \times 20 = 0.004\text{ moles}$$

$$pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

Substituting the values of the various values

$$pH = -\log 1.8 \times 10^{-5} + \log \frac{0.004}{0.006}$$

$$= 4.7447 - 0.1761 = \mathbf{4.5686}$$

Calculation of the additional volume of 0.2 M NaOH required to make pH of solution 4.74.

$$pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 4.74 = -\log 1.8 \times 10^{-5} + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 4.74 = 4.7447 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore \log \frac{[\text{Salt}]}{[\text{Acid}]} = 0.0047 \quad \text{or} \quad \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{1}{1.011}$$

NOTE THIS STEP : Let x ml. be the volume of additional 0.2 M NaOH added to make the pH of the solution 4.74. This will further neutralise x ml. of 0.2 M CH_3COOH and produce x ml. of 0.2 M sodium acetate. The resulting solution (70 + x) will now contain

(i) (30 – x) ml of 0.2 M acetic acid.

(ii) (20 + x) ml of 0.2 M sodium acetate.

Number of moles of acetic acid in (70 + x) ml. solution

$$= \frac{0.2}{1000} \times (30-x) = 2 \times 10^{-4}(30-x)$$

Number of moles of CH_3COONa in (70 + x) ml. solution

$$= \frac{0.2}{1000} \times (20+x) = 2 \times 10^{-4}(20+x)$$

$$\text{Therefore, } \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{2 \times 10^{-4}\,(20+x)}{2 \times 10^{-4}\,(30-x)} = \frac{20+x}{30-x}$$

$$\frac{1}{1.011} = \frac{20+x}{30-x} \text{ or } 20.22 + 1.011x = 30 - x$$

or 1.001 x + x = 30 – 20.22; 2.011x = 9.78 or x = 4.86

Therefore, the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74 is 4.86 ml.

Q.5. The dissociation constant of a weak acid HA is 4.9 × 10^{-8}. After making the necessary approximations, calculate (i) percentage ionization, (ii) pH and (iii) OH^- concentration in a decimolar solution of the acid. Water has a pH of 7.

Ans. (i) $7 \times 10^{-2\%}$, (ii) 4.1549, (iii) 1.43×10^{-10} mol/l

Solution. (i) From the dissociation of weak acid HA,

$$HA \rightleftharpoons H^+ + A^-$$

It α is the degree of ionization of the acid HA,
then $[H^+] = 0.1\ \alpha$ [∵ the acid is decimolar]
$[A^-] = 0.1\ \alpha$; $[HA] = 0.1\ (1 - \alpha)$

Therefore,

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{0.1\alpha \times 0.1\alpha}{0.1(1-\alpha)}$$

$$= \frac{0.1\alpha \times 0.1\alpha}{0.1} \quad \text{(since acid is weak, } 1 - \alpha = 1\text{)}$$

$$K_a = 0.1\,\alpha^2 \text{ or } 4.9 \times 10^{-8} = 0.1\,\alpha^2$$

$$\text{or } \alpha^2 = \frac{4.9 \times 10^{-8}}{0.1} \text{ or } \alpha = 7 \times 10^{-4}$$

∴ Percentage ionization = $100 \times 7 \times 10^{-4}$ = 7 × 10–2%

(ii) Calculation of pH

$[H^+] = 0.1a = 0.1 \times 7 \times 10^{-4}$ mole/litre [∵ $\lambda = 7 \text{ x } 10^{-4}$]

$= 7 \times 10^{-5}$ mole/litre

Now since pH = – log $[H^+]$ = – log $[7 \times 10^{-5}]$

= 5 – log 7 = 5 – 0.8451 = 4.1549

(iii) Concentration of OH^- in decimolar solution

$[H^+] = 7 \times 10^{-5}$ mole per litre

Now, $K_w = [H+]\,[OH–]$ or $1.0 \times 10^{-14} = 7 \times 10^{-5} \times [OH^-]$

$$\therefore [OH^-] = \frac{1 \times 10^{-14}}{7 \times 10^{-5}} = 1.43 \times 10^{-10} \text{ mole per litre}$$

Q.6. A solution contains a mixture of Ag (0.10 M) and Hg_2^{++} (0.10 M) which are to be separated by selective precipitation.

Calculate the maximum concentration of iodide ion at which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated?

[K_{sp} : AgI = 8.5×10^{-17}; Hg_2I_2 = 2.5×10^{-26}]

Ans. 5.0×10^{-13} M, 99.83%

Solution. TIPS/Formulae :

For precipitation to occur ionic product > K_{sp}.

Mixture solution contains 0.1 M Ag+ and 0.1 Mg Hg_2^{2+}.

K_{sp} of $Hg_2I_2 = 2.5 \times 10^{-26}$ is much smaller than K_{sp} of AgI which is 8.5×10^{-17}.

$[I^-]$ concentration needed to precipitate Hg_2I_2 is calculated as :

$$Hg_2I_2 \rightleftharpoons Hg_2^{2+} + 2I^-$$

$$[I^-] = \sqrt{\frac{K_{sp}}{[Hg_2^{2+}]}} = \sqrt{\frac{2.5 \times 10^{-26}}{0.1}} = \mathbf{5.0 \times 10^{-13}\ M}$$

Similarly, $[I^-]$ concentration needed to precipitate AgI is :

$$AgI \rightleftharpoons Ag^- + I^-$$

$$[I^-] = \frac{K_{sp}}{[Ag^+]} = \frac{8.5 \times 10^{-17}}{0.1} = 8.5 \times 10^{-16}\,M$$

NOTE : Since $[I^-]$ concentration needed to ppt. AgI is smaller than that needed to ppt. Hg_2I_2, AgI is completely precipitated first. AgI starts precipitation with $[I^-] = 8.5 \times 10^{-16}$ M.

However, Hg_2I_2 starts precipitating with AgI only when molar concentration of I^- reaches 5.0×10^{-13}M.

$[Ag^+]$ left when Hg_2I_2 begins to ppt. is given by

$$\frac{K_{sp} \text{ of AgI}}{[I^-]_{Hg_2I_2}} = \frac{8.5 \times 10^{-17}}{5.0 \times 10^{-13}} = 1.7 \times 10^{-4}\,M$$

Thus % $[Ag^+]$ left unprecipitated $= \dfrac{1.7 \times 10^{-4}}{0.1} \times 100$

= 0.17%

Hence % Ag+ precipitated = 99.83%

Q.7. One mole of Cl_2 and 3 moles of PCl_5 are placed in a 100 litre vessel heated to 227°C. The equilibrium pressure is 2.05 atmosphere. Assuming ideal behaviour, calculate the degree of dissociation for PCl_5 and K_p for the reaction :

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

Ans. 33.3%, 0.41

Solution. Let x be the degree of dissociation of $PCl_5(g)$, then

	$PCl_5(g)$	$\rightleftharpoons$	$PCl_3(g)$	+	$Cl_2(g)$
Initial	3		0		1
At equilibrium	$3(1-x)$		$3x$		$1+3x$

$\therefore$ Total number of moles at equilibrium

$= 3(1-x) + 3x + 1 + 3x = 3(1+x) + 1$

Using the gas equation : $PV = nRT$

$$\therefore n = \frac{PV}{RT}$$

Here, $P = 2.05$ atm., $V = 100$ litres, $R = 0.082$ atm/deg.,

$T = 273 + 227 = 500$ K

$$\therefore \quad n = \frac{2.05 \times 100}{0.082 \times 500} = 5 \quad \therefore 3(1+x) + 1 = 5$$

or $3 + 3x + 1 = 5$ or $3x = 5 - 4$ or $x = \frac{1}{3} = 0.333$

Hence perecentage dissociation of $PCl_5 = 0.333 \times 100 = 33.3\%$

Calculation of K_P for the reaction :

$$K_p = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\left[\frac{3xP}{3(1+x)+1}\right]\left[\frac{(1+3x)P}{3(1+x)+1}\right]}{\left[\frac{3(1-x)}{3(1+x)+1}P\right]}$$

$$= \frac{3x\,(3x+1)}{4+3x} \times \frac{1\mathrm{P}}{3(1-x)}$$

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

Substituting, $x = 1/3$ and $P = 2.05$ atm., we get

$$K_p = \frac{\frac{1}{3}\left(3\times\frac{1}{3}+1\right)\times 2.05}{\left(4+3\times\frac{1}{3}\right)\left(1-\frac{1}{3}\right)} = \frac{4.1}{10} = 0.41$$

Q.8. Arrange the following in :

(i) increasing bond length : F_2, N_2, Cl_2, O_2

(ii) increasing acid strength : $HClO_3$, $HClO_4$, $HClO_2$, $HClO$

(iii) increasing basicity : H_2O, OH^-, CH_3OH, CH_3O^-

(iv) Arrange the following oxides in the decreasing order of Bronsted basicity :

BaO, SO_3, CO_2, Cl_2O_7, B_2O_3

Ans. (i) $N_2 < O_2 < F_2 < Cl_2$,

(ii) $HClO < HClO_2 < HClO_3 < HClO_4$

(iii) $H_2O < CH_3OH < OH- < CH_3O^-$

(iv) $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$

Solution. (i) $N_2 < O_2 < F_2 < Cl_2$

i.e., $N \equiv N$;O <O ; F,F ; Cl,Cl

NOTE :

As the number of bonds increases the bond length decreases.

So $N_2 < O_2 <$ halogens. Among F_2 and Cl_2 bond length of Cl_2 will be higher because of higher atomic radii.

(ii) Among oxyacids of the same element, acidic nature increases with its oxidation number, e.g.,

$$\begin{array}{lcccccccc} & HOCl & < & HOClO & < & HOClO_2 & < & HOClO_3 \\ \text{O.N. of Cl} & +1 & & +3 & & +5 & & +7 \end{array}$$

(*iii*) $H_2O < CH_3-\ddot{O}H < {}^{-}OH < {}^{-}OCH_3$

Weaker the base stronger is its conjugate acids

$H_3O^+ > CH_3\overset{+}{O}H_2 > H_2O > CH_3OH$ (Decreasing acidic order of the conjugate bases.)

(iv) $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$

Basicity increases with increase in oxidation state

(Ba = +2, B = +3, C = +4, S = +6, Cl = +7).

Q.9. The $[H^+]$ in 0.2 M solution of formic acid is 6.4×10^{-3} mole litre^{-1}. To this solution sodium formate is added so as to adjust the concentration of sodium formate to one mole litre^{-1}. What wil be pH of this solution? K_a for HCOOH is 2.4×10^{-4} and degree of dissociation of HCOONa is 0.75.

Ans. 4.19

Solution. TIPS/Formulae :

For acidic buffer $pH = -\log K_a + \log \dfrac{[\text{Salt}]}{[\text{Acid}]}$

Calculation of concentration of HCOOH.

Here, c = 0.2 M; $[H^+] = 6.4 \times 10^{-3}$

$$[H^+] = c\alpha \text{ or } \alpha = \frac{[H^+]}{c} \quad \Rightarrow \alpha = \frac{6.4 \times 10^{-3}}{0.2} = 3.2 \times 10^{-2}$$

NOTE : Thus the degree of dissociation of HCOOH is very low which on addition of sodium formate is further suppressed due to common ion effect.

Since the degree of dissociation is very low (3.2×10^{-2}), it can be neglected and hence [HCOOH] can be taken as 0.2 M.

Calculation of concentration of $HCOO^-$, $[HCOO^-]$

It can be obtained in the following manner :

	$HCOONa$	$\rightleftharpoons$	$HCOO^-$	$+$	Na^+
At start	1		0		0
At equb.	0.25		0.75		0.75

$\therefore [HCOO^-] = 0.75$

For acidic buffer $pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{acid}]}$

$$= -\log 2.4 \times 10^{-4} + \log \frac{0.75}{0.20} = \mathbf{4.19}$$

Q.10. The equilibrium constant of the reaction

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

at 100°C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two mole of B_2, how many mole of AB will be formed at 373°C?

$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

Ans. 1.886

Solution.

	$A_2(g)$	$+$	$B_2(g)$	$\rightleftharpoons$	$2AB(g)$
At start	1		2		0
At equ.	$1-x$		$2-x$		$2x$

$$\therefore [A_2] = \frac{1-x}{3}, [B_2] = \frac{2-x}{3}, [AB] = \frac{2x}{3}$$

$$\therefore K = \frac{(2x/3)^2}{[(1-x)/3][2-x)/3]} = 50$$

On solving we get, $23x^2 - 75x + 50 = 0$; $x = 2.317$ or 0.943

The value 2.317 is inadmissable because initial concentration of reactants is 2 moles and so $x = 0.943$

$\therefore$ Moles of AB formed $= 2 \times 0.943 = 1.886$

Q.11. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g/litre. Calculate its solubility (in g/litre) in 0.02 M $Mg(NO_3)_2$ solution.

Ans. 8.7×10^{-4} g/litre

Solution. Solubility of $Mg(OH)_2$ in water

$$S = 9.57 \times 10^{-3} \text{ g/litre} = \frac{9.57 \times 10^{-3}}{58} = 1.65 \times 10^{-4} \text{ mole/litre}$$

$[\because \text{M for } Mg(OH)_2 = 58]$

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

$K_{sp} = (S)(2S)^2 = 4S3 = 4(1.65 \times 10^{-4})^3 = 1.8 \times 10^{-11}$ approx.

Calculation of solubility of $Mg(OH)_2$, say, x, in $Mg(NO_3)_2$ or $[Mg^{2+}] = x + 0.02$; $[OH^-] = x$

$K_{sp} = [Mg^{2+}][2OH^-]^2$ or $1.8 \times 10^{-11} = (x + 0.02)(2x)^2$

Neglecting x in comparison to 0.02 (common ion effect)

$$\Rightarrow 4x^2 = \frac{1.8 \times 10^{-11}}{0.02} = 9 \times 10^{-10} \quad \text{or } 2x = 3 \times 10^{-5}$$

$x = 1.5 \times 10^{-5}$ moles/litres

$= 1.5 \times 58 \times 10^{-5} = 8.7 \times 10^{-4}$ g/litre.

Q.12. What is the pH of the solution when 0.20 mole of hydrochloric acid is added to one litre of a solution containing.

(i) 1 M each of acetic acid and acetate ion?

(ii) 0.1 M each of acetic acid and acetate ion?

Assume the total volume is one litre.

K_a for acetic acid = 1.8×10^{-5}.

Ans. 4.5686, 1

Solution. (i) Amount of HCl added = 0.20 mole

$[H^+] = 0.2$ g litre^{-1}

NOTE : Added H^+ ions will combine with the acetate ions forming acetic acid with the result concentration of acetate ions will decrease while that of acetic acid will increase.

$$CH_3COO^- + HCl \longrightarrow CH_3COOH + Cl^-$$

	CH_3COO^-	HCl	CH_3COOH	Cl^-
before reaction	1	0.2	1	0
after reaction	0.8	0	1.2	0.2

∴ Concentration of acetate ions after adding 0.20 mole of HCl.

$[CH_3COO^-] = 1.0 - 0.2 = 0.8$ mole

Similarly, concentration of acetic acid,

$[CH_3COOH] = 1.0 + 0.2 = 1.2$ mole

$$\text{Now, } pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log 1.8 \times 10^{-5} + \log \frac{0.8}{1.2}$$

pH = 4.7447 + 0.3010 – 0.4771 = 4.5686

(ii) Amount of HCl added = 0.20 mole

Out of 0.2 mole of $[H^+]$ added, 0.1 mole will combine with 0.1 mole of CH_3COO^- forming 0 mole of CH_3COOH.

$$CH_3COO^- + H^+ \rightarrow CH_3COOH + Cl^-$$

	CH_3COO^-	H^+	CH_3COOH	Cl^-
before reaction	0.1	0.2	0.1	0
after reaction	0	0.1	0.2	0.1

∴ Total concentration of acetic acid $[CH_3COOH]$

= 0.1 + 0.1 = 0.2 mole

In presence of $[H^+]$, CH_3COOH will not ionize.

Therefore, pH of the solution will be due to the presence of H^+ of HCl, i.e. 0.2 – 0.1 = 0.1 mole HCl

$pH = -\log [H^+] = -\log [0.1] = 1$

Q.13. At a certain temperature equilibrium constant (K_c) is 16 for the reaction.

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mole each of all the four gases in a one litre container, what would be the equilibrium concentrations of NO(g) and NO_2(g)?

Ans. 1.6 moles, 0.4 moles

Solution. Initial concentration of each gas = 1 mole

Let the No. of moles of NO_2 reacted at equilibrium = x

$$\begin{array}{lcccc} \text{Then,} & SO_2(g) + & NO_2(g) \rightleftharpoons & SO_3(g) + & NO_2(g) \\ \text{At equilibrium} & (1-x) & (1-x) & (1+x) & (1+x) \end{array}$$

$$\text{Now we know that, } \frac{[SO_3][NO]}{[SO_2][NO_2]} = K_c$$

$$\text{or } \frac{(1+x/V)(1+x/V)}{(1-x/V)(1-x/V)} = 16 \quad \text{or } \frac{(1+x)^2}{(1-x)^2} = 16 \ (\because V = 1L)$$

$$\text{or } \frac{1+x}{1-x} = 4 \quad \text{or } 1+x = 4-4x \quad \text{or } 5x = 3$$

$$x = \frac{3}{5} = 0.6$$

∴ Thus the concentration of NO at equilibrium

= 1 + x = 1 + 0.6 = 1.6 moles

Concentration of NO_2 at equilibrium

= 1 – x = 1 – 0.6 = 0.4 moles

Q.14. N_2O_4 is 25% dissociated at 37°C and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C.

Ans. 0.266 atm, 64%

Solution. (i)

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Before dissociation	1		0
After dissociation	$1 - \alpha$		2α

$\therefore$ Total moles $= 1 - \alpha + 2\alpha = 1 + \alpha$

$$\therefore K_p = \frac{(p_{NO_2})^2}{p_{N_2O_4}} = \frac{\left(\frac{2\alpha}{1+\alpha} \times P\right)^2}{\left(\frac{1-\alpha}{1+\alpha} \times P\right)}$$

where P is total pressure

$$K_p = \frac{\left(\frac{2 \times 0.25 \times 1}{1 + 0.25}\right)^2}{\left(\frac{1 - 0.25}{1 + 0.25} \times 1\right)} = \mathbf{0.266\ atm} \quad [\because a = 0.25]$$

$$\text{(ii)} \quad K_p = \frac{4\alpha^2 P^2 \times (1+\alpha)}{(1+\alpha)^2 (1-\alpha) \times P} = \frac{4\alpha^2 P}{(1+\alpha)(1-\alpha)}$$

$$0.266 = \frac{4\alpha^2 \times 0.1}{1 - \alpha^2} \Rightarrow \alpha = 0.64$$

$\therefore$ Percentage dissociation = 63 %

Q.15. How many gram-mole of HCl will be required to prepare one litre of buffer solution (containing NaCN and HCl) of pH 8.5 using 0.01 gram formula weight of NaCN?

K dissociation (HCN) = 4.1×10^{-10}.

Ans. 8.85 × 10–3 M

Solution. TIPS/Formulae :

$$pH = pK_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)$$

If x moles of HCl are added then they will combine with

NaCN to form x moles of very weak acid HCN.

$$\begin{array}{lccccccc} & NaCN & + & HCl & \rightarrow & NaCl & + & HCN \\ \text{At equilibrium :} & (0.01-x) & & x & & x & & x \end{array}$$

For an acidic buffer,

$$pH = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\therefore\ 8.5 = -\log 4.1 \times 10^{-10} + \log\left(\frac{0.01-x}{x}\right)$$

$$\text{or}\quad 8.5 = (10 - \log 4.1) + \log\left(\frac{0.01-x}{x}\right)$$

$$\log\left(\frac{0.01-x}{x}\right) = -0.8872 \qquad [\log 4.1 = 0.6128]$$

$$\frac{0.01-x}{x} = 0.1296$$

$x = 8.85 \times 10^{-3}$ M = 8.85 × 10−3 moles of HC

Q.16. The equilibrium constant K_p of the reaction :

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

is 900 atm. at 800 K. A mixture containing SO_3 and O_2 having initial partial pressure of 1 and 2 atm. respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K.

Ans. P_{SO_2} = 0.0236 atm, P_{O_2} = 2.0118 atm, P_{SO_3} = 0.9764 atm

Solution. NOTE : Since the reaction is carried out at constant volume, change in partial pressure of a species will be directly proportional to the change in its amount. Hence, we can write

$$\begin{array}{lccccc} & 2SO_2(g) & + & O_2(g) & \rightleftharpoons & 2SO_3(g) \\ \text{Initial pressure} & 0 & & 2\text{ atm} & & 1\text{ atm} \\ \text{Equb. pressure} & 2x & & 2\text{ atm} + x & & 1\text{ atm} - 2x \end{array}$$

Where 2 x is th e change in par tial pr essure of SO_3 at equilibrium.

Substituting the expression of partial pressure in the expression. For K_b, we get

$$K_p = \frac{(p_{SO_3})^2}{(p_{SO_2})^2\,(p_{O_2})}$$

or $900\ \text{atm}^{-1} = \dfrac{(1\ \text{atm} - 2x)^2}{(2x)^2\ (2\ \text{atm} + x)}$

Assuming x is very small as compared to 1

$900\ \text{atm}^{-1} = \dfrac{1\ \text{atm}^2}{(4x^2)\ (2\ \text{atm})}$

On usual calculations, x = 0.0118 atm

Thus p_{SO_2} = 2x = 2 × 0.0118 atm = 0.0236 atm

p_{O_2} = 2 atm + x = 2 + 0.0118 = 2.0118 atm

p_{SO_3} = 1 atm – 2x = 1 – 0.0236 = 0.9764 atm

Q.17. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mole/l of ammonium chloride and 0.05 mole/l of ammonium hydroxide. Calculate the concentration of aluminium and magnesium ions in solution:

$K_b[NH_4OH] = 1.80 \times 10^{-5}$
$K_{sp}\ [Mg(OH)_2] = 6 \times 10^{-10}$
$K_{sp}\ [Al(OH)_3] = 6 \times 10^{-32}$

Ans. 46.29 mol ion/l, 1.286×10^{-15} mol ion/l

Solution. TIPS/Formulae :

p(OH) for basic buffer $= pK_b + \log\left(\dfrac{\text{Salt}}{\text{Base}}\right)$

We know that $\text{pOH} = pK_b + \log\dfrac{[\text{Salt}]}{[\text{Base}]}$ or $-\log 1.8 \times 10^{-5} + \log\dfrac{0.25}{0.05}$

pOH = 5 – log 1.8 + log 5 = 5.6989 – 0.2552

$-\log[OH^-] = 5.4437;\ \log[OH^-] = -5.4437$

$[OH^-] = 3.5999 \times 10^{-6}$ [Taking antilog]

K_{sp} for $Mg(OH)_2 = [Mg^{2+}][OH^-]^2$
$6 \times 10^{-10} = [Mg^{2+}][3.5999 \times 10^{-6}]^2$

$$[Mg^{2+}] = \frac{6 \times 10^{-10}}{12.9598 \times 10^{-12}} = 0.4629 \times 10^2$$

= 46.29 mole ion per litre

K_{sp} for $Al(OH)_3 = [Al^{3+}] [OH^-]3$

$6 \times 10^{-32} = [Al^{3+}] (3.5999 \times 10^{-6})^3$

$$[Al^{3+}] = \frac{6 \times 10^{-32}}{(3.5999 \times 10^{-6})^3} = 1.286 \times 10^{-15} \text{ mol ion/l}$$

Q.18. For the reaction : $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO(g) and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of $CH_3OH(g)$ is formed. Calculate the equilibrium constant, K_p and K_c.

Ans. 277.78 $mol^{-2}\ l^2$, 0.1144 atm^{-2}

Solution. Let the total number of moles of all gases at equilibrium point = n

P = 4.92 atm.   V = 5l

R = 0.0821 atm. l mol^{-1} K^{-1} T = 273 + 327 = 600K

By applying the formula   PV = nRT

$$n = \frac{PV}{RT} = \frac{4.92 \times 5}{0.0821 \times 600} = 0.5 \text{ moles}$$

(i) Calculation of the number of moles of the individual gases at equilibrium point.

No. of moles of CH3OH formed = 0.1 (Given)

∴ No. of moles of CO (also) = 0.1

[∴ moles of CO = moles of CH_3OH formed]

Hence No. of moles of H_2 = 0.5 – (0.1 + 0.1) = 0.3

∴ Molar concentration of various species will be

$$[CH_3OH] = [CO] = \frac{0.1}{5} = 0.02;\ [H_2] = \frac{0.3}{5} = 0.06$$

$$\therefore K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{0.02}{0.02 \times (0.06)^2} = \mathbf{277.78\ mol^{-2}\ l^2}$$

(ii) Calculation of K_p. We know that

$$K_p = K_c \times (RT)^{\Delta n} = 277.78 \times (0.0821 \times 600)^{-2}\ (\Delta n = 1 - 3 = -2)$$

$$= \frac{277.78}{2426.54} = \mathbf{0.1144\ atm^{-2}}$$

Q.19. What is the pH of 1.0 M solution of acetic acid? To what volume must one liter of this solution be diluted so that the pH of the resulting solution will be twice the original value? Given : Ka = 1.8 × 10^{-5}.

Ans. 2.3724, 2.78 × 10^4 litres

Case I.	CH_3COOH	$\rightleftharpoons$	CH_3COO^-	+	H^+
At start	1		0		0
At equib.	$1 - \alpha$		α		α

$$[H^+] = c\alpha = c\sqrt{\frac{K_a}{c}} = \sqrt{K_a c}$$

$$\therefore [H^+] = \sqrt{1.8 \times 10^{-5} \times 1} = 4.24 \times 10^{-3}\ M$$

Thus pH = – log H^+ = –log 4.24 × 10^{-3} = 2.3724

Case II. pH after dilution = 2 × original pH

= 2 × 2.3724 = 4.7448

Let conc. after dilution = c_1

and degree of dissociation = α_1

Since pH = – log $[H^+]$

$4.7448 = -\log [H^+]$

$[H^+] = 1.8 \times 10^{-5} = c_1\alpha_1 \therefore c_1\alpha_1 = 1.8 \times 10^{-5}$

Dissociation constant

$$\text{Since } K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$= \frac{(c_1\alpha_1)(c_1\alpha_1)}{c_1[1-\alpha_1]} = \frac{c_1\alpha^2}{(1-\alpha_1)}$$

$$1.8 \times 10^{-5} = \frac{1.8 \times 10^{-5} \times \alpha_1}{1-\alpha_1} \quad \therefore \alpha_1 = 0.5$$

Substituting the value of α_1 in the following relation

$$c_1\alpha_1 = [H^+];\ c_1 \times 0.5 = 1.8 \times 10^{-5}$$

$$c_1 = \frac{1.8 \times 10^{-5}}{0.5} = 3.6 \times 10^{-5}\ M$$

Since the number of moles of CH_3COOH before and after dilution will be same

∴ Mole of CH_3COOH before dilution = Mole of CH_3COOH after dilute

$$(\because \text{Mole} = M \times V_{\text{in litre}})$$
$$1 \times 1 = 3.6 \times 10^{-5} \times V \Rightarrow V = \mathbf{2.78 \times 10^4\ litres}$$

Q.20. The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} mol^3 l^{-3}. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 ml water is shaken at 25°C with excess of Ag_2CO_3 till the following equilibrium is reached :

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium the solution contains 0.0358 mole of K_2CO_3.
Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3.

Ans. 3.794×10^{-12} mol^3 l^{-3}

Solution.

	Ag_2CO_3 +	$K_2C_2O_4$	→	$Ag_2C_2O_4$ +	K_2CO_3
Moles at start	Excess	0.1520		0	0
Moles after reaction		0.1520–0.0358 = 0.1162		0.0358	0.0358

Molar concentration of $K_2C_2O_4$ or $C_2O_4^{2-}$ left unreacted

$$= \frac{0.1162}{0.5} = 0.2324 \text{ moles } l^{-1} \; [\because \; 500 \text{ ml} = 0.5 \text{ L}]$$

$$[K_2CO_3] = [CO_3^{2-}] \text{ at equilibrium}$$

$$= \frac{0.0358}{0.5} = 0.07156 \text{ moles } l^{-1}$$

Given that K_{sp} for $Ag_2C_2O_4 = 1.29 \times 10^{-11}$ mol^3 l^{-3} at 25°C

So, $[Ag^+]^2[C_2O_4^{2-}] = 1.29 \times 10^{-11}$

or $[Ag^+]^2 \times 0.2324 = 1.29 \times 10^{-11}$

Hence $[Ag^+]^2 = \dfrac{1.29}{0.2324} \times 10^{-11}$

Then K_{sp} for Ag_2CO_3

$$= [Ag^+]^2[CO_3^{2-}] = \frac{1.29 \times 10^{-11}}{0.2324} \times 0.0716$$

$= \mathbf{3.974 \times 10^{-12}}$ **mol^3 l^{-3}**

Subjective Questions of Equilibrium, (Part -2)

Q.21. A 40.0 ml solution of weak base, BOH is titrated with 0.1N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after adding 5.0 ml and 20.0 ml of the acid respectively. Find out the dissociation constant of the base.

Ans. 1.828×10^{-5}

Solution. Case I. Write the concerned chemical reaction

	BOH +	HCl $\longrightarrow$	BCl +	H_2O
Moles before reaction	x	$0.1 \times 5 = 0.5$	0	0
Moles after reaction	$(x - 0.5)$	0	0.5	0.5
$\therefore$ Molar concentration	$\frac{x-0.5}{V}$		$\frac{0.5}{V}$	$\frac{0.5}{V}$

Since the solution represents a basic buffer, following Hendersen equation can be applied.

$$pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$14 - 10.04 = -\log K_b + \log \frac{0.5}{(x - 0.5)} \qquad ...(i)$$

Case II.

	BOH +	HCl $\longrightarrow$	BCl +	H_2O
Moles at start	x	$0.1 \times 20 = 2$	0	0
Moles after adding 20 ml. of 0.1N HCl	$(x - 2)$	0	2	2
$\therefore$ Molar concentration	$\frac{x-2}{V_1}$	0	$\frac{2}{V_1}$	$\frac{2}{V_1}$

Again the solution is acting as basic buffer

$$\therefore pOH = -\log K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

$$14 - 9.14 = -\log K_b + \log \frac{2}{(x - 2)} \qquad ...(ii)$$

$$\frac{3.96}{4.86} = \frac{0.5}{(x - 0.5)} \times \frac{(x - 2)}{2} \Rightarrow x = 0.088 \text{ mol } l^{-1}$$

Substituting x in (i) and solving for K_b

$$3.96 = -\log K_b + \log \frac{0.5}{0.088 - 0.5}$$

$$K_b = 1.828 \times 10^{-5}$$

Q.22. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is 4.42×10^{-5}. A 500 ml. of saturated solution of $Ca(OH)^2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in milligrams is precipitated?

Ans. 743.3 mg

Solution. Let the solubility of Ca(OH)2 in pure water = S moles/litre

$$Ca(OH)_2 \rightleftharpoons \underset{S}{Ca^{2+}} + \underset{2S}{2OH^-}$$

Then $K_{sp} = [Ca^{2+}]\,[OH^-]^2$

$4.42 \times 10^{-5} = S \times (2S)^2$; $4.42 \times 10^{-5} = 4S^3$

$S = 2.224 \times 10^{-2} = 0.0223$ moles $litre^{-1}$

∴ No. of moles of Ca^{2+} ions in 500 ml. of solution = λ

$$= \frac{0.0223 \times 500}{4000} = 0.01115$$

NOTE THIS STEP : Now when 500 ml. of saturated solution is mixed with 500 ml of 0.4M NaOH, the resultant volume is 1000 ml. The molarity of OH– ions in the resultant solution would therefore be 0.2 M.

$$\therefore [Ca^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{4.42 \times 10^{-5}}{(0.2)^2} = 0.001105\,M$$

Thus, No. of moles of Ca^{2+} or $Ca(OH)_2$ precipitated = 0.01115 – 0.001105 = 0.010045

Mass of $Ca(OH)_2$ precipitated

= 0.010045 × 74 = 0.7433 g = 743.3 mg

[mole wt. of $Ca(OH)_2$ = 74]

Q.23. 0.15 mole of CO taken in a 2.5 l flask is maintained at 750 K along with a catalyst so that the following reaction can take place :

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

Hydrogen is introduced until the total pressure of the system is 8.5 atmosphere at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction does not take place.

Ans. (i) 0.05 atm^{-2}, 187.85 $mol^{-2}\ l^2$, (ii) 12.438 atm

Solution. (i)

	$CO(g)$ +	$2H_2(g)$ $\rightleftharpoons$	CH_3OH
Moles at start	0.15	a	0
Moles at equb.	$(0.15 - x)$	$(a - 2x)$	0.08
or	$(0.15 - 0.08)$	$(a - 0.16)$	0.08

$$\therefore \text{Total moles at equb.} = 0.15 - 0.08 + a - 0.16 + 0.08$$
$$= a - 0.01$$

Total moles at equilibrium can also be calculated from the following relation

$$n = \frac{PV}{RT} = \frac{8.5 \times 2.5}{0.0821 \times 750} = 0.345$$

$\therefore$ 0.345 = a – 0.01 [Comparing (i) and (ii)]

or a = 0.355

Thus, Moles of CO at equilibrium = 0.15 – 0.08 = 0.07

Moles of H_2 at equilibrium = 0.355 – 0.16 = 0.195

Moles of CH_3OH at equilibrium = 0.08

Substituting the values in the relation,

$$K_c = \frac{[CH_3OH]}{[H_2]^2\,[CO]} = \frac{0.08/2.5}{(0.195/2.5)^2 \times (0.07/2.5)}$$

= 187.85 $mole^{-2}$ litre2 [$\because$ V = 2.5 L]

Calculation of K_p

$K_p = K_c (RT)^{\Delta n} = 187.85 \times (0.0821 \times 750)^{-2} = 0.05\ \text{atm}^{-2}$

[∵ $\Delta n = -2$]

(ii) Calculation of final pressure when there is no reaction

Moles of CO = 0.15; Moles of H_2 = 0.355

∴ Total moles = 0.15 + 0.355 = 0.505

PV = nRT

$P \times 2.5 = 0.505 \times 0.0821 \times 750 \Rightarrow P = 12.438$ atm.

Q.24. 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 a 10 ml sample of blood which is 2M in H_2CO_3 in order to maintain a pH of 7.4 ? K_a for H_2CO_3 in blood is 7.8×10^{-7}.

Ans. 78.36 ml

Solution. Volume of blood = 10 ml. (given)

$[H_2CO_3]$ in blood = 2 M (given)

$[NaHCO_3]$ to be added = 5 M (given)

Let volume of $NaHCO_3$ added in 10 ml blood = V ml

$$\therefore [H_2CO_3] \text{ in blood mixture } = \frac{2 \times 10}{(V+10)}$$

$$[NaHCO_3] \text{ in blood mixture } = \frac{5 \times V}{(V+10)}$$

$$\therefore pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\text{or } 7.4 = -\log 7.8 \times 10^{-7} + \log \frac{5V/(V+10)}{20/(V+10)} \quad \therefore V = \mathbf{78.36\ ml}$$

Q.25. An aqueous solution of a metal bromide MBr_2 (0.05M) is saturated with H_2S. What is the minimum pH at which MS will precipitate?

K_{sp} for MS = 6.0 x 10^{-21}; concentration of saturated H_2S = 0.1 M

$K_1 = 10^{-7}$ and $K_2 = 1.3$ x 10^{-13} , for H_2S.

Ans. 0.983

Solution.

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

$$\text{Further, } HS^- \rightleftharpoons H^+ + S^{2-} \quad \therefore K_2 = \frac{[H^+][S^{2-}]}{[HS^-]}$$

Dissociation constant of H_2S, $K = K_1 \times K_2$

i.e. $K = 1 \times 10^{-7} \times 1.3 \times 10^{-13} = 1.3 \times 10^{-20}$

Now we know that

$$K_{sp} = [M^{2+}][S^{2-}] \quad \Rightarrow 6 \times 10^{-21} = 0.05 \times [S^{2-}]$$

$$[S^{2-}] = \frac{6 \times 10^{-21}}{0.05} = 1.2 \times 10^{-19}$$

Substituting the various values in the following relation

$$K = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$1.3 \times 10^{-20} = \frac{[H^+]^2[1.2 \times 10^{-19}]}{0.1} \quad \because [H_2S] = 0.1\,M$$

$$[H^+]^2 = \frac{1.3 \times 10^{-20} \times 0.1}{1.2 \times 10^{-19}}$$

$$[H^+] = \sqrt{\frac{1.3 \times 10^{-20} \times 0.1}{1.2 \times 10^{-19}}} = 1.04 \times 10^{-1}$$

$$pH = -\log[H^+];\ pH = -\log(1.04 \times 10^{-1})$$

$$= 1.0 - \log 1.04 = 1.0 - 0.017 = \mathbf{0.983}$$

Q.26. At temperature T, a compound AB_2 (g) dissociates according to the reaction

$$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$$

with a degree of dissociation x which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant K_p and the total pressure, P.

Ans. $\left[\frac{2K_p}{P}\right]^{1/3}$

Solution.

	$2AB_2(g)$	$\rightleftharpoons$	$2AB(g)$	$+$	$B_2(g)$
Initial mole	1		0		0
Moles at equb	$1-x$		x		$\frac{x}{2}$

Total moles at equb. $=1-x+x+\frac{x}{2}=1+\frac{x}{2}=\frac{2+x}{2}$

$$p_{AB_2}=\frac{(1-x)}{2+x/2}P=\frac{2(1-x)}{2+x}P$$

$$p_{AB}=\frac{x}{2+x/2}P=\frac{2x}{2+x}P$$

$$p_{B_2}=\frac{x/2}{2+x/2}P=\frac{x}{2+x}P$$

$$\therefore K_p=\frac{(p_{AB})^2\,(p_{B_2})}{(p_{AB_2})^2}=\frac{\left(\frac{2x}{2+x}P\right)^2\left(\frac{x}{2+x}P\right)}{\left[\frac{2(1-x)}{(2+x)}P\right]^2}$$

$$=\frac{x^3P}{(2+x)\,(1-x)^2}$$

$$K_p\approx\frac{x^3}{2}P \quad \text{or} \quad x=\left[\frac{2K_p}{P}\right]^{1/3}$$

Q.27. For the reaction

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

the equilibrium constant, at 25°C , is 4.0 x 10^{-19} . Calculate the silver ion concentration in a solution which was originally 0.10 molar in KCN and 0.03 molar in $AgNO_3$.

Ans. 7.5×10^{-18} M

Solution. TIPS/Formulae : Consider common ion effect

Conc. of Ag+ ions = Conc. of AgNO3 = 0.03 M

Most of these Ag+ ions will be present in the form of $[Ag(CN)_2]^-$.

0.03 M $AgNO_3$ requires 2 × 0.03 M

= 0.06 M CN^- to form $[Ag(CN)_2]^-$

∴ Conc. of free CN^- at equilibrium will be 0.1 – 0.06 = 0.04 M

$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

$$\therefore\ K = \frac{[Ag^+][CN^-]^2}{[Ag(CN)_2]} ; 4.0 \times 10^{-9} = \frac{[Ag^+][0.04]^2}{0.03}$$

$$[Ag^+] = \frac{4.0 \times 10^{-19} \times 0.03}{(0.04)^2} = \mathbf{7.5 \times 10^{-18}\ M}$$

Q.28. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissociation.

(pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8.)

Ans. 6.5

Solution. For ammonium formate which is a salt of weak acid with weak base, we know that

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b] = \frac{1}{2}[14 + 3.8 - 4.8] = \mathbf{6.5}$$

Q.29. What is the pH of a 0.50 M aqueous NaCN solution? pKb of CN^- is 4.70.

Ans. 11.5

Solution.

$pK_b = 4.70,\ \therefore\ K_b = 10^{-4.7}$

Now we know that

$$[OH^-] = \sqrt{K_b \times c}$$

$$\therefore [OH^-] = \sqrt{10^{-4.7} \times 0.5} = 3.158 \times 10^{-3} M$$

Now we know that

$pOH = -\log[OH-]$

$pOH = -\log 3.158 \times 10^{-3} = 2.5$

or, $pH = 14 - 2.5 = 11.5$

Q.30. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl ($K_{sp}(Ag_2CO_3) = 8.2 \times 10^{-12}$).

Ans. 1.71×10^{-10}

Solution. The concerned chemical reaction is

$2AgCl + Na_2CO_3 \rightarrow Ag_2CO_3 + 2\ NaCl$

Calculation of $[Ag^+]$ left in the solution :

$$K_{sp}(Ag_2CO_3) = [Ag^+]^2 [CO_3^{2-}]$$

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

Concentration of Cl– left = 0.0026 g/l

$$= \frac{0.0026}{35.5} mol/l = 7.33 \times 10^{-5} M$$

$\therefore K_{sp}(AgCl) = [Ag^+][Cl^-] = (2.34 \times 10^{-6})(7.33 \times 10^{-5})$

$= 1.71 \times 10^{-10}$

Q.31. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio$[In^-]/[HIn]$ is greater than 10 or smaller than. 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ($K_a=1.0\times10^{-5}$)?

Ans. 2

Solution. Given $K_a = 1 \times 10^{-5}$

$\therefore pK_a = 5$

The two conditions when colour indicator will be visible are derived by

$$pH = pK_a + \log \frac{[In^-]}{[HIn]}$$

(i) pH = 5 + log 10 = 6

(ii) pH = 5 + log 0.1 = 4

Thus minimum change in pH = 2

Q.32. Given : $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3, K_c = 6.2 \times 10^{-8}$ and K_{sp} of AgCl = 1.8×10^{-10} at 298 K. If ammonia is added to a water solution containing excess of AgCl(s) only, calculate the concentration of the complex in 1.0 M aqueous ammonia.

Ans. 0.0538 M

Solution.

For AgCl; $AgCl \rightleftharpoons Ag^+ + Cl^-$

$\therefore K_{sp} = [Ag^+][Cl^-]$ .....(i)

Again it is given that

$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3 ; K_c = 6.2 \times 10^{-8}$

or $Ag^+ + 2NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ ;$

$$K_f = \frac{1}{6.2 \times 10^{-8}} = \frac{10^8}{6.2}$$

$$\therefore K_f = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} \quad \text{or} \quad [Ag^+] = \frac{[Ag(NH_3)_2]^+}{K_f[(NH_3)_2]}$$

NOTE THIS STEP : Since the formation constant of the complex is very high, most of the $[Ag^+]$ which dissolves must be converted into complex and each Ag^+ dissolved also requires dissolution of Cl^-.

$\therefore [Cl^-] = [Ag(NH_3)_2]^+$ and let it be c M

Equation (i) becomes

$$K_{sp} = \frac{[\mathrm{Ag(NH_3)_2}]^+}{\mathrm{K_f[NH_3]^2}} \times c \Rightarrow K_{sp} = \frac{c}{K_f[1]^2} \times c$$

$$c^2 = K_{sp} \times K_f[1]^2 = 1.8 \times 10^{-10} \times \frac{10^8}{6.2} \times (1)^2$$

$$c^2 = \frac{1.8 \times 10^{-2}}{6.2} = 0.2903 \times 10^{-2}$$

$$\text{or } c = 0.538 \times 10^{-1} = \mathbf{0.0538\ M}$$

Q.33. What will be the resultant pH when 200mL of an aqueous solution of HCl (pH = 2.0) is mixed with 300 mL of an aqueous solution of NaOH (pH = 12.0) ?

Ans. 11.3010

Solution.

	HCl	$+ NaOH$	$\longrightarrow NaCl$	$+ H_2O$
Meq. before reaction	200×10^{-2}	300×10^{-2}		
Meq. after reaction	0	100×10^{-2}	200×10^{-2}	200×10^{-2}

pH of HCl = 2, pH of NaOH = 12

$\therefore [HCl] = 10^{-2}$ M, $\therefore [NaOH] = 10^{-2}$ M

$$\therefore [OH^-] = \frac{100 \times 10^{-2}}{500} = 2 \times 10^{-3} \text{ or } p[OH] = -\log(2 \times 10^{-1})$$

$$\therefore pOH = 2.6989; \therefore pH = \mathbf{11.3010} \qquad [pH = 14 - p(OH)]$$

Q.34. When 3.06 g of solid NH_4HS is introduced into a two litre evacuated flask at 27° C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. (i) Calculate Kc and Kp for the reaction at 27°C. (ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask ?

Ans. 8.1×10^{-5} mol^2 l^{-2}, 4.90×10^{-2} atm^2

Solution.

$$NH_4HS_{(s)} \rightleftharpoons NH_{3(g)} + H_2S_{(g)}$$

Initial moles	$\frac{3.06}{51}$	0	0
Moles at eq.	$\frac{3.06}{51}\times\frac{70}{100}$	$\frac{3.06}{51}\times\frac{30}{100}$	$\frac{3.06}{51}\times\frac{30}{100}$

Given $V = 2$ litre, $T = 300\text{K}$, $\Delta n = 2 - 0 = 2$

$$\therefore K_c = [NH_3][H_2S] = \frac{3.06\times30}{51\times100\times2}\times\frac{3.06\times30}{51\times100\times2}$$

$$= \mathbf{8.1 \times 10^{-5}\ mol^2\ litre^{-2}}$$

$$\text{Also } K_p = K_c(RT)^{\Delta n} = 8.1\times10^{-5}\,(0.082\times300)^2$$

$$= \mathbf{4.90\times10^{-2}\ atm^2}$$

NOTE : Addition of more NH_4HS on this equilibrium will cause no effect because concentration of NH_4HS is not involved in formula of K_p or K_c.

Q.35. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.

Ans. 1.203×10^{-3} mol litre^{-1}

Solution.

	$Pb(OH)_2$	$\rightleftharpoons$	Pb^{2+}	+	$2OH^-$
(given)	6.7×10^{-6}M		6.7×10^{-6}M		$2\times6.7\times10^{-6}$M

$\therefore K_{sp} = [Pb^{2+}][OH^-]^2 = (6.7\times10^{-6})\,(2\times6.7\times10^{-6})^2$

$= 1.203 \times10^{-15}$

The buffer solution pH = 8 (given)

$\therefore$ pOH = 6 or $[OH^-] = 10^{-6}$

Thus in this buffer we have, $[Pb^{2+}][OH^-]^2 = 1.203 \text{ x } 10^{-15}$

or $[Pb^{2+}] \times [10^{-6}]^2 = 1.203 \text{ x } 10^{-15}$

$\therefore [Pb^{2+}] = 1.203 \text{ x } 10^{-3}$ mol litre^{-1}

Q.36. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.3653 moles litre^{-1} and the pKa of H_2SO_3 is 1.92, estimate the pH of rain on that day.

Ans. 4.865

Solution. Amount of SO_2 in atmosphere = $= \frac{10}{10^6} = 10 \times 10^{-6}$

Molar concentration of SO_2 present in water = Amount of SO_2 × Solubility of SO_2 in water = $10 \times 10^{-6} \times 1.3653$ mole $L^{-1} = 1.3653 \times 10^{-5}$ M

Writing the concerned chemical equation

	H_2SO_3	$\longrightarrow$	H^+	+	HSO_3^-
Initial conc.	1.3653×10^{-5}		0		0
Molar conc. at equb.	$1.3653 \times 10^{-5} - x$		x		x

$$\text{Therefore } K_a = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

$$\Rightarrow \quad 10^{-1.92} = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

$(pK_a = 1.92, \therefore K_a = 10^{-1.92})$

$$\Rightarrow 1.2 \times 10^{-2} = \frac{x^2}{(1.3653 \times 10^{-5} - x)}$$

$x^2 = 1.2 \times 10^{-2} (1.3653 \times 10^{-5} - x)$ On solving, $x = 1.364 \times 10^{-5}$

Therefore, pH = $-\log (1.364 \times 10^{-5}) = 4.865$

Q.37. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH. [Assume there is no change in volume on mixing; K_a of acetic acid is 1.75×10^{-5} mol L^{-1}].

Ans. 1.75×10^{-4}, 1, 4.75

Solution. (i) The volume being doubled by mixing the two solutions, the molarity of each component will be halved i.e.

$[CH_3COOH] = 0.1$ M, $[HCl] = 0.1$ M.

NOTE :

HCl being a strong acid will remain completely ionised and hence H^+ ion concentration furnished by it will be 0.1 M. This would exert common ion effect on the dissociation of acetic acid, (a weak acid.)

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

	CH_3COOH	CH_3COO^-	H^+
At start	C	0	0
At equilibrium	C (1 - α)	Cα	Cα + 0.1

$$K_a = \frac{C\alpha(C\alpha + 0.1)}{C(1-\alpha)} = \frac{C\alpha^2 + 0.1\alpha}{(1-\alpha)}$$

Since α is very very small, Ca^2 can be neglected and 1 – α can be taken as unity

$$\therefore K_a = 0.1\,\alpha$$

$$\text{or } \alpha = \frac{K_a}{0.1} = \frac{1.75\times10^{-5}}{0.1} = \mathbf{1.75\times10^{-4}}$$

$$[H^+]_{Total} = 0.1 + C\alpha,$$

Cα is negligible as compared to 0.1.

$$\therefore [H^+]_{Total} = 0.1 \qquad \therefore \; pH = \mathbf{1}$$

$$\text{(ii)}\;\; 6g\ NaOH = \frac{6}{40} = 0.15 mol$$

0.1 mole of NaOH will be consumed by 0.1 mole of HCl.

Thus, 0.05 mole of NaOH will react with acetic acid according to the equation.

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

	CH_3COOH	$NaOH$	CH_3COONa	H_2O
Initial moles	0.1 mol	0.05 mol	0	0
At equilibrium	0.05 mol	0 mol	0.05 mol	0.05mol

Thus, solution of acetic acid and sodium acetate will become acidic buffer. So pH of the buffer will be

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

$$= -\log\left(1.75\times10^{-5}\right) + \log 1 = \mathbf{4.75}$$

Q.38. Match the following if the molecular weights of X, Y and Z are same.

	Boiling Point	K_b
X	**100**	**0.63**
V	**27**	**0.53**
z	**253**	**0.98**

Ans. x = 0.63, y = 0.53, z = 0.98

Solution. TIPS/Formulae :

Higher the value of dipole-dipole interaction higher is b.p.
Higher value of K_b of a solvent suggests larger polarity of solvent molecules which in turn leads to higher dipole – dipole interaction implies higher boiling point due to dipole – dipole interaction. Therefore, the correct order of K_b values of the three given solvents is

Mathematically $K_b = \frac{M_A R T_b^2}{\Delta H_{vap} \times 1000}$

or $K_b \propto T_b$ (b.pt.)

Solvents	**Boiling point**	**K_b values**
X	100°C	0.63
Y	27°C	0.53
Z	283°C	0.98

Integer Type Question of Equilibrium

Q. 1. 0.1 M NaOH is titrated with 0.1 M HA till the end point; K_a for HA is 5.6 × 10^{-6} and degree of hydrolysis is less compared to 1. Calculate pH of the resulting solution at the end point.

Ans. 9

Solution. HA + NaOH → 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 relation.

$$pH = \frac{1}{2}(pK_w + pK_a + \log C)$$

$$= \frac{1}{2}(14 + 5.3010 + (-1.3010)] = 9$$

Q. 2. The dissociation constant of a substituted benzoic acid at 25°C is 1.0 × 10^{-4}. The pH of a 0.01 M solution of its sodium salt is

Ans. 8

Solution. pH of sodium salt of weak acid

$$= \frac{1}{2}(pK_w + pK_a + \log C) = \frac{1}{2}(14 + 4 - 2) = 8$$

Q. 3. Amongst the following, the total number of compounds whose aqueous solution turns red litmus paper blue is

KCN, K_2SO_4, $(NH_4)_2C_2O_4$, NaCl, $Zn(NO_3)_2$, $FeCl_3$, K_2CO_3, NH_4NO_3 and LiCN

Ans. 3

Solution. KCN, K_2CO_3 and LiCN are the salts of weak acid and strong base. So, their aqueous solutions turns red litmus paper blue.

Q. 4. The total number of diprotic acids among the following is:

H_3PO_4, H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_3BO_3, H_3PO_2, H_2CrO_4 and H_2SO_3.

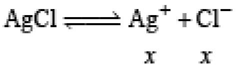
Ans. 6

Solution. Diprotic acids are H_2SO_4, H_3PO_3, H_2CO_3, $H_2S_2O_7$, H_2CrO_4 and H_2SO_3.

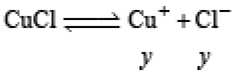
Q. 5. In 1 L saturated solution of AgCl [Ksp(AgCl) = 1.6×10^{-10}], 0.1 mol of CuCl [K_{sp}(CuCl) = 1.0×10^{-6}] is added. The resultant concentration of Ag^+ in the solution is 1.6×10^{-x}.
The value of "x" is

Ans. 7

Solution. Let the solubility of AgCl is x mol litre^{-1} and that of CuCl is y mol litre^{-1}



$$AgCl \rightleftharpoons \underset{x}{Ag^+} + \underset{x}{Cl^-}$$



$$CuCl \rightleftharpoons \underset{y}{Cu^+} + \underset{y}{Cl^-}$$

$\therefore K_{sp}$ of AgCl = $[Ag^+][Cl^-]$

$1.6 \times 10^{-10} = x(x + y)$ ....(i)

Similarly, K_{sp} of CuCl = $[Cu^+][Cl^-]$

$1.6 \times 10^{-6} = y(x + y)$ … (ii)

On solving, (i) and (ii)

$[Ag^+] = 1.6 \times 10^{-7} \therefore x = 7$