Liquid Solution

Solution :→ It is homogeneous mixture of two or more components
eg. air, sugar solⁿ. cold drink, etc.

Solution = Solute + solvent

- **Classification of Solⁿ** :-

A] On the basis of no. of components :

1] Binary solⁿ : 1 solute + 1 solvent

2] Ternary solⁿ : 2 solute + 1 solvent

3] Quarternery solⁿ : 3 solute + 1 solvent

B] On the basis of Phases of solute & solvent :

1] **Solid solution** ,

Solute	Solvent	eg ,
Solid	solid	Brass-alloy
liquid	Solid	Hg-Na (Sod almalgum)
gas	solid	H_2 in Pd

2] **Liquid Solution** ,

Solid	Liquid	NaCl (aq.)
liquid	liquid	C_2H_5OH (l) in water

gas	liquid	$O_{2(g)}$ in water

3] Gaseous solution,

Solid	gas	Camphor in $N_2(g)$
liquid	gas	Chloroform in $N_2(g)$
gas	gas	$O_2 + N_2$ (air)

* Solubility : It is maximum amt. of substance which can be dissolved in specified amt. of solvent at a given temp.

- Factors affecting Solubility :

1) Nature of solute & solvent
2) Temperature
3) Pressure

1] Solubility of solid in liquid :

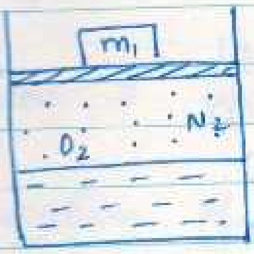
- Effect of temp. : Solⁿ. changes on changing temp.

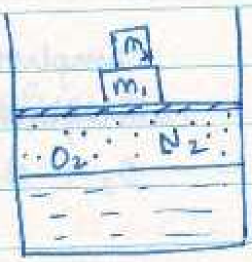
If $\Delta H \geqq 0 \Rightarrow$ Endothermic $\Rightarrow$ Sol. ↑ on ↑ T
$\Delta H \leqq 0 \Rightarrow$ Exothermic $\Rightarrow$ Sol. ↓ on ↑ T

- Effect of Pressure : Pressure has negligible effect on solubility of solid in liquid coz both are almost incompressible

Solubility of gas in liquid :

- Effect of Pressure : on ↑ P , sol. of gas in liq. ↑





Henry's Law :

Partial pressure of gas is directly proportional to mole fraction of gas in liquid sol^n.

$$P_{gas} \propto X_g$$

$$P_{gas} = K_H X_{gas} = K_H \frac{n_{g(aq)}}{n_{g(aq.)} + n_{solvent}}$$

where,

P_g → Partial pressure of gas

X_g → mol fraction of gas in liquid sol^n

K_H → Henry's constant

Henry's constant (K_H) depends on

i) Nature of gas & solvent

ii) Temp. : generally on ↑ temp. K_H ↑

Henry's law is applicable only for highly dilute solution.

$$P = K_H \chi$$

$$P = K_H \times \frac{n_B}{n_A + \xcancel{n_B}^{\to 0}}$$

$$P \propto K_H \times \frac{n_B}{n_A} \approx K_H \times \frac{n_B}{W_A} \times 10^3 \times \frac{M_A}{10^3}$$

$$P = K_H \frac{\times M \times M_A}{1000}$$

- <u>limitations of Henry's law</u> :

- Applicable only for dilute solutions.
- It is not applicable when gas combines with solid

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_3\,(aq.)$$

$$NH_{3(g)} + H_2O\,(l) \longrightarrow NH_4OH(aq.)$$

- If gas dissociates after dissociation then this law cannot be applied.

$$HCl_{(g)} + H_2O\,(l) \longrightarrow H^+\,(aq.) + Cl^-\,(aq.)$$

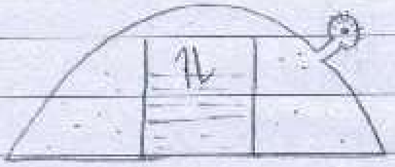
Q. If N_2 (g) is bubbled thru water at 293 K, how many mm of gas would dissolve in water (1L) Assume N_2 exerts a pressure of 1 bar.
Given : $K_H = 75$ k bar at 293 K $\quad \overset{10}{\frac{40}{3 \times 8}}$,

$$\rightarrow \quad 1 = \frac{75 \times 28 \times}{1000} \frac{x}{1L} \qquad x = \frac{1}{75 \times 28} = \frac{1}{2100}$$

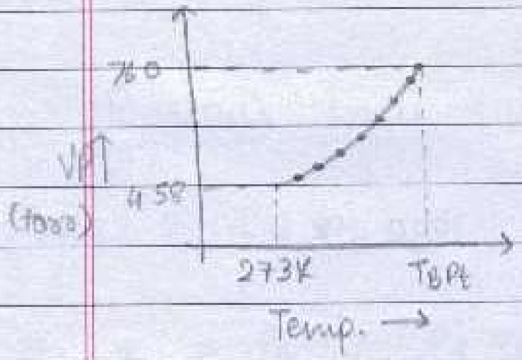
* Vapour Pressure :→

$H_2O_{(l)} \underset{exo}{\overset{endo}{\rightleftharpoons}} H_2O_{(g)}$ $K_p = VP$

As T ↑ K ↑ VP ↑



It is the pressure exerted by vapours of a liquid when liquid & its vapours are in equilibrium

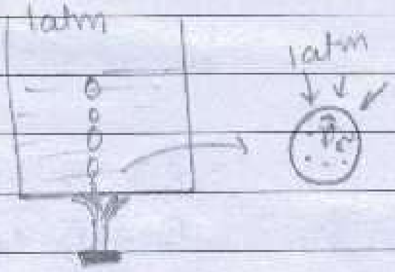


VP of a given liq. can be changed only by changing temperature.

* Boiling Point :→

It is the temp. at which VP of liq. becomes equal t external Pressure.

At BP, KE of gaseous particles will be same as KE of liquid phase particles.



* Claypeyron Equation :

$$\ln \frac{VP_2}{VP_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Q. For a liquid normal BP is $-173^\circ C$. Then at 2 atm pressure its BP should be nearly ___ .

$$\longrightarrow \ln 2 = \frac{200}{2}\left(\frac{1}{100} - \frac{1}{x}\right)$$

$$\Rightarrow \frac{1.4}{200} = \frac{x-100}{100x}$$

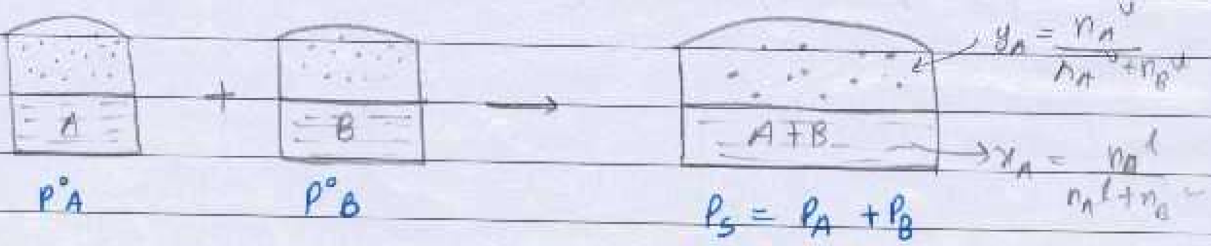
$$\Rightarrow 1.4x = 2x - 200 = x = \frac{2000}{6} = \frac{1000}{3}\ K.$$

* Binary Solutions :-

1] VP of liquid in liquid :

- Rault's Law :

Acc^n to it the partial VP of each component is directly proportional to mole fraction of that component in liq. sol^n.



$P_S = P_A + P_B$

$P_A = P^\circ_A x_A$

$P_B = P^\circ_B x_B$

$P_A \propto x_A$

$P_A = P^\circ_A x_A$

$\|^{ly},$

$P_B = P^\circ_B x_B$

$P_S = P^\circ_A x_A + P^\circ_B x_B$

$P_S = (P^\circ_A - P^\circ_B) x_A + P^\circ_B$

where,

P°_A, P°_B → VP of pure A & B resp.

P_A, P_B → Partial VP of A & B

x_A, x_B → mol fraction of A in liq. solution

P_S → V_P of sol^n.

- **Dalton's law :**

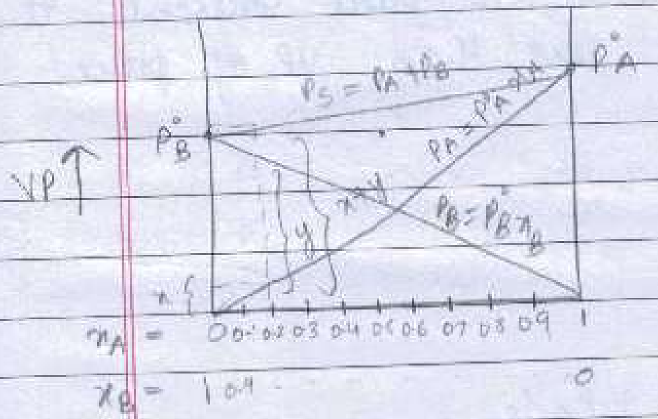
$P_A = y_A P_S$

$$y_A = \frac{P_A}{P_S} = \frac{P^\circ_A x_A}{P^\circ_A x_A + P^\circ_B x_B}$$ (same for y_B)

$$P_S = \underset{\downarrow \atop y}{} \ = P^\circ_B + x_A (P^\circ_A - P^\circ_B)$$

$$\underset{y}{\downarrow} = \underset{c}{\downarrow} + \underset{x}{\downarrow} \ (m)$$

$P^\circ_A > P^\circ_B$



Note : The solutions which obey Raoult's law are called ideal solutions.

- Equilibrium approximation :

Acc^n to it, initial moles of components will be equal to moles of components in liq. sol^n & we will neglect moles of components vapourised.

Q. Find VP of mixture obtained by mixing 2 mol of benzene and 5 mole of toluene at 30°c. (Given : VP of Benzene & toluene are 20 & 30 torr) Also find the mole fraction of benzene & toulene in vapor phase at eq.

→ $P_S = P_A + P_B = \frac{190}{7}$ torr.

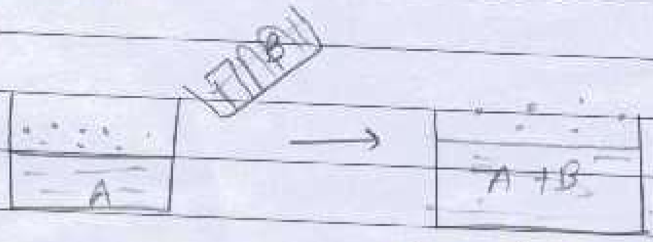
$P_A = 20 \times \frac{2}{7}$

$P_B = 30 \times \frac{5}{7}$

$y_A = \frac{P_A}{P_S} = \frac{4}{19}$ & $y_B = \frac{15}{19}$

2] VP of solid in liquid :-

On add^n of non volatile solute in pure solvent, VP of resulting sol^n will be less than VP of pure solvent.



$P_S = P_A^\circ x_A + P_B^\circ x_B$

$P_S = P_A^\circ x_A$ ($\because P_B^\circ = 0$ (as B is non vol.))

$P_S < P_A^\circ$

Vp Sol < VP of solvent

8. The VP of benzene at certain temp. is 640 torr. A non volatile non electrolyte solute having mass 2.175 g is added to 39 g benzene. Now VP of sol is 600 torr. Find molar mass of solute.

→ ~~640~~ = $600 = 640 \times \frac{0.5}{0.5+x}$ ⇒ $\frac{15}{16} = \frac{0.5}{0.5+x}$

$\Rightarrow 7.5 + 15x = 8$ $\qquad \frac{15}{8} = \frac{1}{0.5+x}$

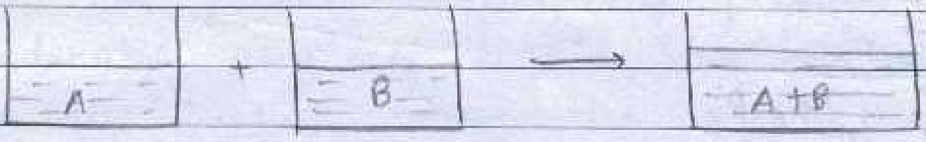
$x = \frac{5}{150} = \frac{1}{30}$

$\frac{2.175}{y} = \frac{1}{30}$ ⇒ $M_{solute} = 65.25$

* Classification of Sol^n on the basis of behaviour :

i] Ideal Solution :→

- These are the solutions which follow rault's law.
- Force of interaction b/w AA, BB & AB are approximately same.



$F_{A-A} \approx f_{B-B} \approx F_{A-B}$

$P^{\circ}_A \qquad P^{\circ}_B$

$P_S = P_A + P_B$

$\left.\begin{array}{l} P_A = P^{\circ}_A x_A \\ P_B = P^{\circ}_B x_B \end{array}\right\}$ Rault's law

- Thermodynamic parameters :

$\Delta_{mix} G < 0 \qquad \Delta_{mix} H = 0$

$\Delta_{mix} S > 0$

$\Delta_{mix} V = 0$

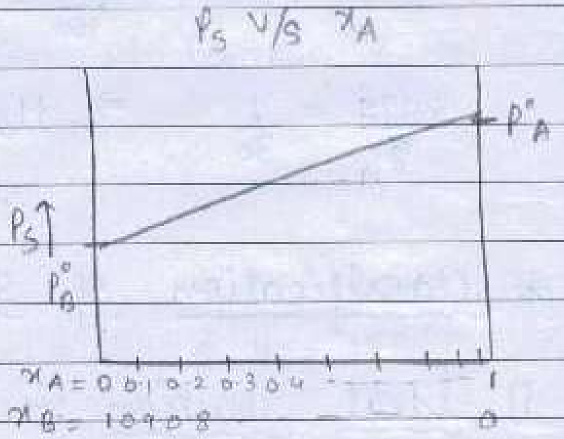
- **Examples :**

  - benzene + toluene
  - ethyl bromide + ethyl iodide
  - ethyl alcohol + methyl alcohol
  - chlorobenzene + bromobenzene
  - n-butyl chloride + n-butyl bromide

- P_S V/S x_A

We assume $P^\circ_A > P^\circ_B$

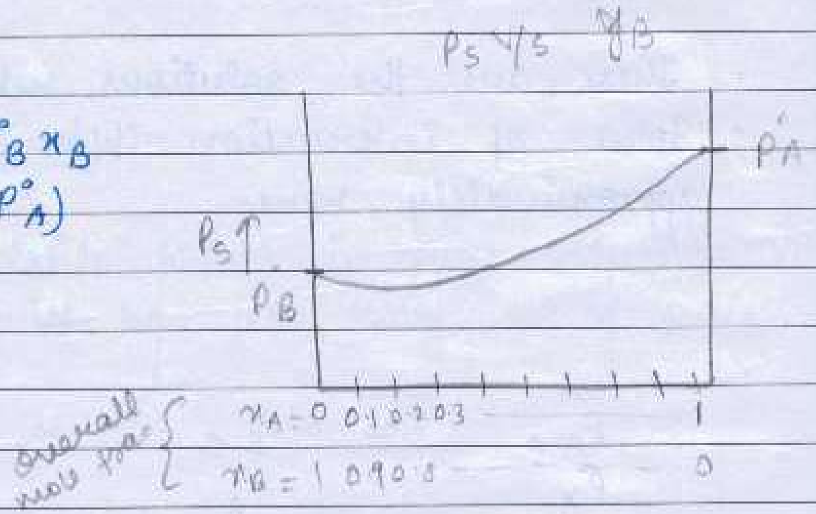
$$P_S = P^\circ_A x_A + P^\circ_B x_B$$
$$P_S = P^\circ_A x_A + P^\circ_B (1 - x_A)$$
$$P_S = P^\circ_B + x_A (P^\circ_A - P^\circ_B)$$
$$y = c + mx$$



P_S v/s x_B

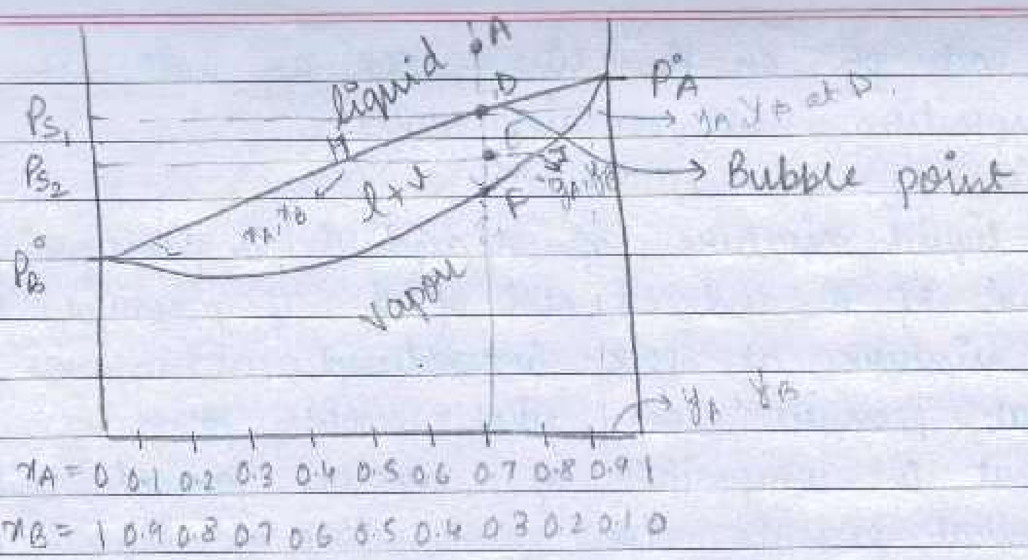
We assume $P^\circ_A > P^\circ_A$

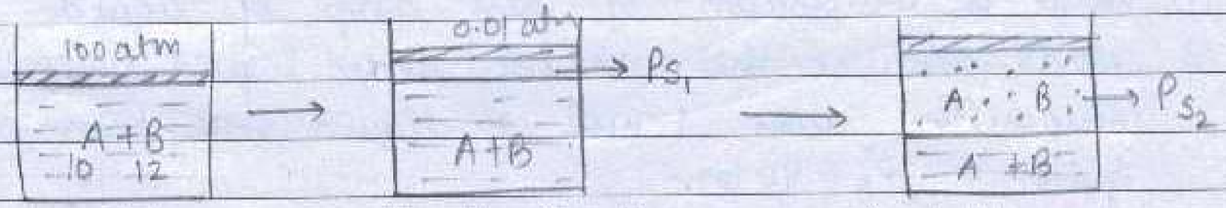
$$P_S = P^\circ_A x_A + P^\circ_B x_B$$
$$P_S = P^\circ_A (1 - x_B) + P^\circ_B x_B$$
$$P_S = P^\circ_A + x_B (P^\circ_B - P^\circ_A)$$
$$y = c + mx$$
$$P_S = \frac{P^\circ_A P^\circ_B}{P^\circ_A - y_A (P^\circ_A - P^\circ_B)}$$



$$x_A = \frac{n_A (\text{Total})}{n_{Total}} = \frac{n_A^l + n_A^v}{n_A^l + n_A^v + n_B^l + n_B^v} \qquad y_A = \frac{n_A^v}{n_A^v + n_B^v}$$

$$x_B = \frac{n_B (\text{Total})}{n_{Total}} = \frac{n_B^l + n_B^v}{n_A^l + n_A^v + n_B^l + n_B^v} \qquad y_B = \frac{n_B^v}{n_A^v + n_B^v}$$





$x_A = 10/22$
$x_B = 12/22$

$x_A = \frac{10}{22}$ $x_B = \frac{12}{22}$

$x_A \neq 10/22$
$x_B \neq 12/22$

- At pt. A only liq. exists
- When we further lower the pressure then at pt. D first drop of liq. will evaporate. This is also called bubble pt. At this pt. only small amt. of liq. has been evaporated.
- When we further lower the pressure till pt. E considerable amt. of liquid has been evaporated.
- When we further lower the pressure till F, at F last drop of liq. will be left.

  Here, $y_A = x_{A_I}$
  $y_B = x_{B_I}$

- Line ADEF is called isopleth. Here overall composition will remain same.
- HEI is called tie line whose end points give composition of two different phases.

At each pt. on the line, liq. as well as vapour composition will remain same.

Q. A liquid mixture of A and B is composed of 1 mol of A and 1 mol of B. If pressure over the mixture at 300 K is reduced, at

i) what pressure does first bubble form
ii) What is composition of vapours formed initially
iii) At what pressure does last drop of liquid disappears
iv) What is composition of last drop of liquid
v) What will be the pressure and liquid vapor composition when 1 mol of liquid has been evap- given : $P^\circ_B = 40$ torr

$P^\circ_A = 100$ torr.

→ i) $P_S = P_A + P_B$

$= 0.5 \times 40 + 0.5 \times 100 = 70$ torr

ii) $y_A = \frac{P_A}{P_S} = \frac{50}{70}$

$y_B = \frac{P_B}{P_S} = \frac{20}{70}$

iii) $P_S = \frac{40 \times 100}{100 - \frac{5}{7}(60)} = \frac{4000}{7}$ torr

iv) ~~0.5, 0.5~~ 4/14, 10/14

v) $P_S = P^\circ_A x_A + P^\circ_B x_B$

4/7, 5/7

$\frac{\frac{1}{2} + \frac{5}{7}}{2}$ $\frac{17}{28}$; $\frac{11}{28}$

$\frac{440}{28} + \frac{1700}{28}$

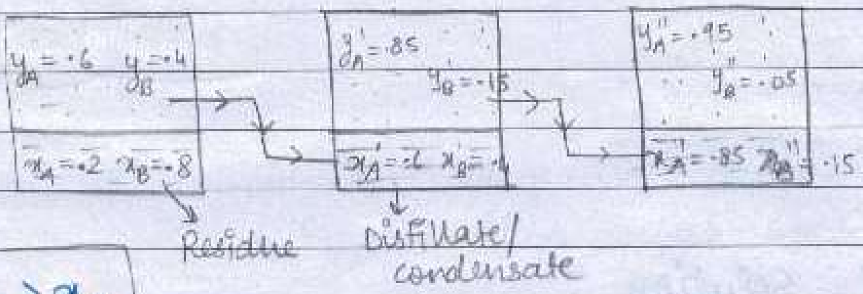
* Fractional Distillation :

It is process of separation of two liquids having diff. boiling points.

1] At constant temperature
2] At constant pressure

- **At constant temperature :→**

Vapours will be richer in the component which is more volatile.



V. imp! $\boxed{y_A > x_A}$

Q. A solution is prepared by mixing 12 mole benzene and 8 mole toluene. If vapours over this sol^n were removed & condensed & again brought to same temp. then what would be the mole fraction of benzene & toluene in vapour state.

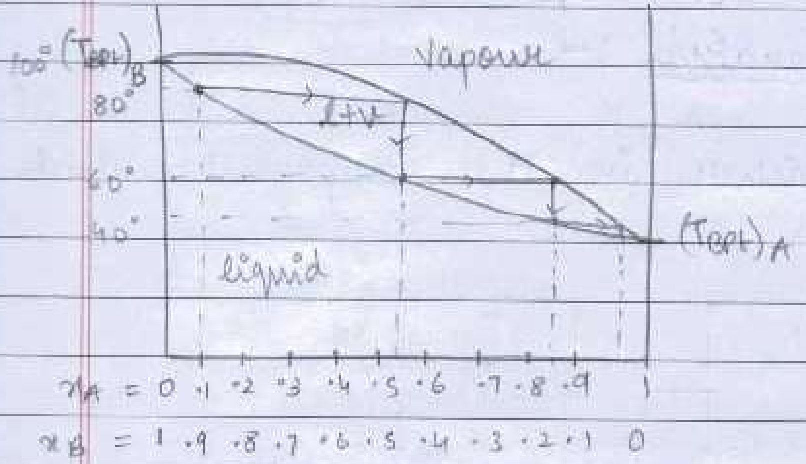
→ $x_B = 3/5$ $\quad y_B = \overset{9/11}{162/198} = x'_B$ $\quad y'_B = P_B/P_S \quad \overset{27/29}{243/261}$

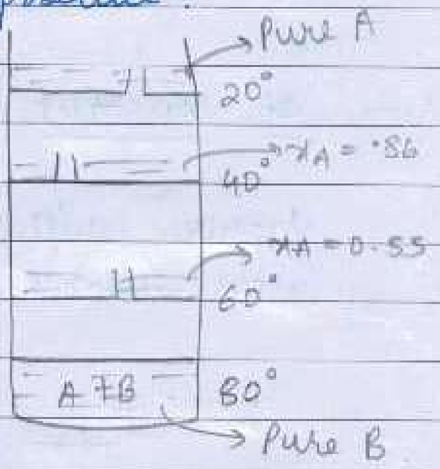
$x_T = 2/5$ $\quad y_T = \underset{2/11}{36/198} = x'_T$ $\quad y'_T = P_T/P_S \quad \underset{2/29}{18/261}$

$\dfrac{2430/11}{2610/11}$

- **At constant Pressure :**

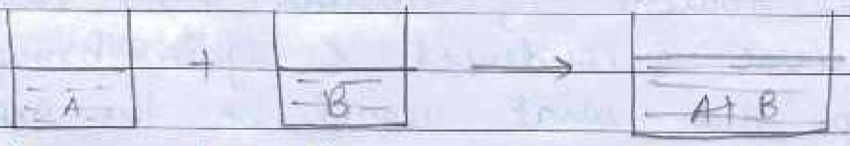
Suppose we take a mixture having composition $x_A = \cdot1$ & $x_B = \cdot9$. As we ↑ temp. from 80°C to 100°C the vapours formed will be richer in more volatile component, however, residue will become richer in less volatile product.





ii] Non-ideal Solution :

- The solutions which do not follow rault's law are called non-ideal solutions.

- 

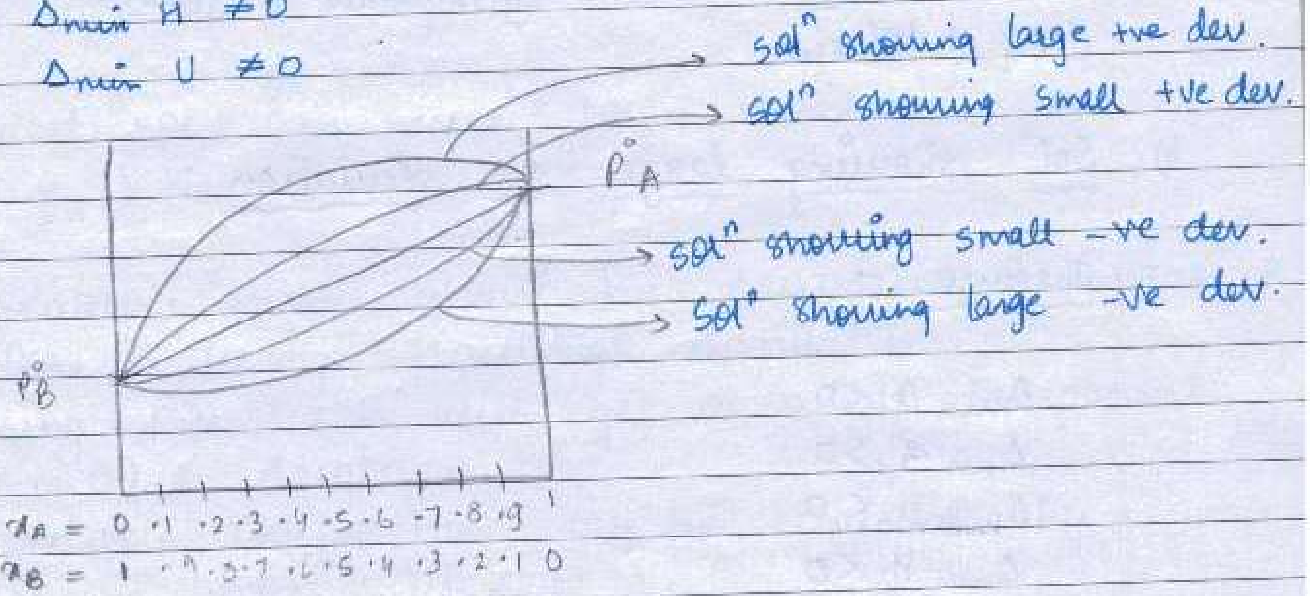
$F_{A-A} \neq F_{B-B} \neq F_{A-B}$

- $P_S = P_A + P_B$ ✓

$P_A \neq P_A^0 x_A$
$P_B \neq P_B x_B$

- Thermodynamics :

$\Delta_{mix} G < 0$
$\Delta_{mix} S > 0$
$\Delta_{mix} H \neq 0$
$\Delta_{mix} U \neq 0$



For sol^n showing large +ve deviation
$(VP)_{sol} > (P)^\circ_A$ (at some comp.)

For sol^n show small +ve dev.
$P^\circ_B \le (VP)_S \le P^\circ_A$

- A sol^n is said to be showing +ve deviation if its VP is greater than expected from ideal behaviour.
- Force of att^r b/w A–B will be weaker than A–A or B–B.
- $P_S = P_A + P_B$
  $P_A > P^\circ_A x_A$
  $P_B > P^\circ_B x_B$
- $\Delta_{mix} G < 0$ $\Delta_{mix} H > 0$
  $\Delta_{mix} S > 0$
  $\Delta_{mix} U > 0$

- Eg,

acetone + ethanol
water + ethanol
acetone + benzene
acetone + CS_2
CCl_4 + toluene

CCl_4 + CH_3OH
water + methanol
CCl_4 + $CHCl_3$
Cyclohexane + ethanol

b) Solⁿ showing large -ve deviation :

- Thermo. :→

$\Delta_{mix} G < 0$
$\Delta_{mix} S > 0$
$\Delta_{mix} V < 0$
$\Delta_{mix} H < 0$

- $P_S = P_A + P_B$
$P_A < P_A^\circ x_A$
$P_B < P_B^\circ x_B$

- Eg,

acetone + aniline
chloroform + diethyl ether
chloroform + benzene
Water + HCl

CH_3OH + CH_3COOH
acetic acid + pyridine
H_2O + HNO_3
acetone + chloroform.

- All mineral acids show -ve deviation

* Azeotrope :

It is a solⁿ which boils like a pure liquid & it will have same composition in vapour state as well as in liquid state.

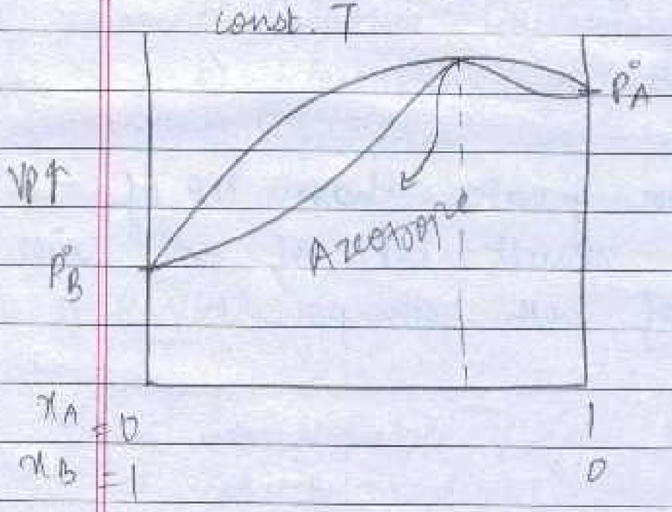
$y_A = x_A$

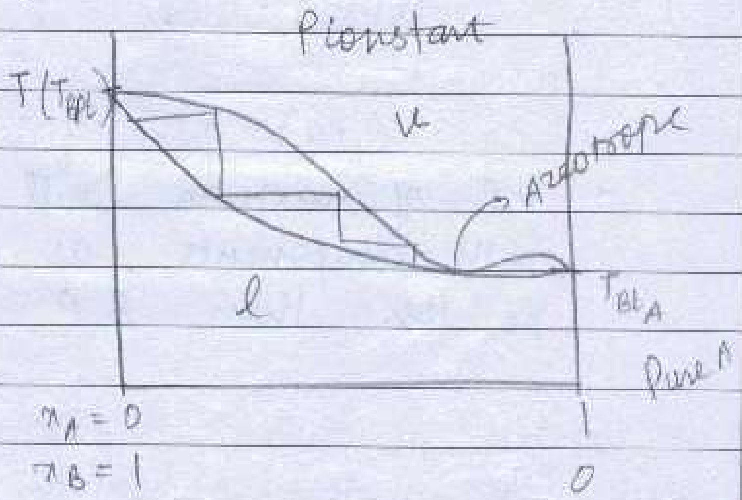
* Ideal solⁿ can never form Azeotrope coz $y_A > x_A$ (always)

- azeotropic mix. cannot be separated in pure A & pure B using fractional distillation.
- Using F.D. we will get a single component (A or B) & Azeotrope.
- Azeotropic composition can be changed by changing ext. pressure
- Types of Azeotrope :

i) min. boiling azeotrope
ii) max. boiling azeotrope

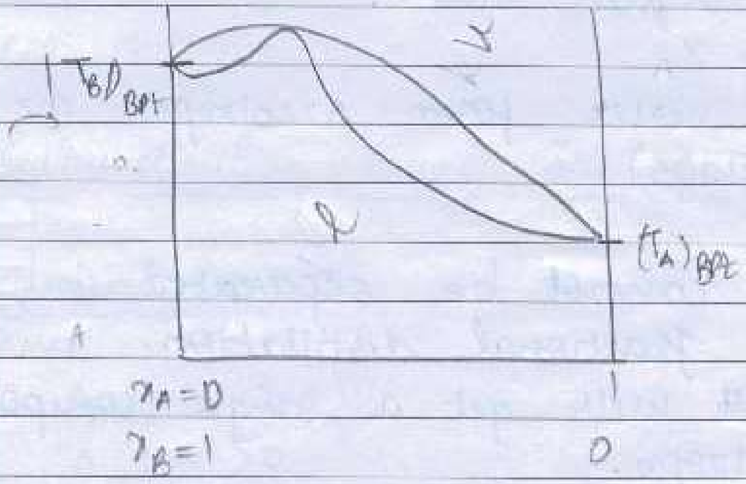
- min. b.a. are obt. from a solⁿ showing +ve deviation
- These azeotropic mixtures will have lower BPt then both of its components.





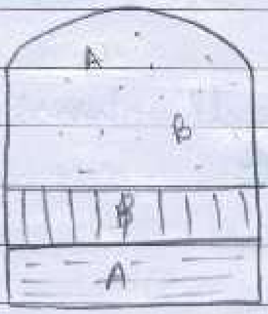
ii) Max. boiling azeotrope :

- Max. b.a. are obt. from a solⁿ showing +ve deviation.



* Rault's law for solⁿ containing two immiscible liquids :

- when two immiscible liquids are mixed then V.P is given by,



$$P_S = P_A + P_B$$
$$= P_A^\circ x_A + P_B^\circ x_B$$
$$= P_A^\circ + P_B^\circ$$

- V.P. of mixture will be greater than V.P of both components, as a result B.P. of solⁿ will be less than B.P. of both components

- This solⁿ will boil only when V.P. of solⁿ (P_s) becomes equal to external pressure.
V.P. of mixture (P_s) will remain constant irrespecti of proportion in which A & B are mixed.

$$P^\circ_A = n_A^v \frac{RT}{V}$$

$$P^\circ_B = n_B^v \frac{RT}{V}$$

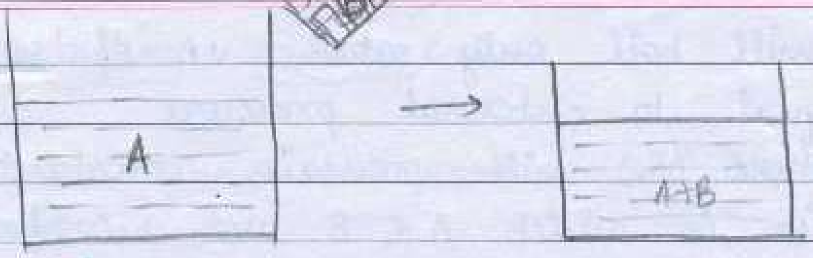
$$\frac{P^\circ_A}{P^\circ_B} = \frac{n_A^v}{n_B^v} = \frac{w_A}{w_B} \times \frac{M_B}{M_A}$$

* Colligative (to collect) Properties :→

- These are the prop which depend on no. of solute particles present in the solⁿ. These do not depend upon nature of particle.
- However, colligative prop. may change on changing solvent.
- Colligative prop. are defined only for non-volatile solute particles and these are additive in nature.
- There are 4 colligative prop :
  a) Relative lowering in VP (RLVP)
  b) Elevation of BP (ΔT_B)
  c) Depression in freezing point (ΔT_f)
  d) Osmotic pressure (π)

1] RLVP :

- If non volatile / non electrolyte solute is added to a volatile solvent then VP of resulting solⁿ will ↓ coz some of the SA will be occupied by solute.



$P^\circ_A = 100$ torr

$P_s = 95$ torr

$P_s = P^\circ_A x_A + \cancel{P^\circ_B x_B}^{\,0}$

lowering in VP = $P^\circ_A - P_s = P^\circ_A x_B$

Relative lowering in VP $= \dfrac{P^\circ_A - P_s}{P^\circ_A} = x_B$

if soln is highly dilute,

$$\frac{P^\circ_A - P_s}{P^\circ_A} = \frac{n_B}{n_A + \cancel{n_B}^{\to 0}} \simeq \frac{n_B}{n_A} = \frac{n_B}{w_A} \times 10^3 \times \frac{M_A}{10^3} \longrightarrow \text{app}^{\text{r}}$$

$$\Rightarrow \boxed{\frac{P^\circ_A - P_s}{P^\circ_A} \simeq \frac{n_B}{n_A} \simeq \frac{m M_A}{10^3}}$$

$P_s = P^\circ_A x_A$

$\dfrac{1}{x_A} = \dfrac{n_A + n_B}{n_A} = \dfrac{P^\circ_A}{P_s}$

$$\boxed{\frac{P^\circ_A - P_s}{P_s} = \frac{n_B}{n_A} = \frac{m M_A}{10^3}} \longrightarrow \text{Exact}$$

$\downarrow$

NOT RLVP

- If more than one non volatile solutes are present,

x_1, x_2, x_3 → mole fraction of solute 1, 2 & 3
M_A → Molar mass of Solvent
m → molality.

→ Till now we have considered non volatile, non electrolyte solutes.
In case of electrolytes due to association/dissociation colligative properties of solution will be different from expected values, such CP are called abnormal or experimental colligative prop. To account for association or dissociation Vant Hoff factor (i) is defined.

- Vant Hoff factor (i) :→ It is mathematically defined as

$$i = \frac{\text{Final moles after ass./diss.}}{\text{Initial moles}} = \frac{\text{Theo. Molar mass}}{\text{observed molar mass}}$$

$$= \boxed{\frac{\text{Obs. CP}}{\text{Th. CP}} = \frac{O\cdot(\Delta T_f)}{T\cdot(\Delta T_f)} = \frac{O}{T}\cdot\frac{\pi}{\pi}} = \frac{O}{T}\frac{RLVP}{RLVP}$$

only for highly dilute sol^n

- Calculation of Vant Hoff factor :

a) For dissociation,

$$A_n \overset{\alpha}{\rightleftharpoons} nA \qquad n_T = a(1-\alpha+n\alpha)$$

$$t=0 \quad a \qquad 0 \qquad i = \frac{n_T}{n_i} \Rightarrow \boxed{\alpha = \frac{i-1}{n-1}}$$

$2A \overset{\alpha}{\rightleftharpoons} 3B$

$t=0 \quad a$

$t=t \quad a-a\alpha \qquad \frac{3\alpha a}{2} \qquad n_T = a\left(1-\alpha+\frac{3\alpha}{2}\right)$

Q. Calculate 'i' for : if $\alpha = 1$

a) $NaCl\,(aq.) \overset{\alpha}{\rightleftharpoons} Na^+ + Cl^-$

$t=0 \quad a$

$a-a\alpha \qquad a\alpha \qquad a\alpha$

$\therefore\ i = \frac{\cancel{a}(1+\alpha)}{\cancel{a}}$ 2

b) $CaCl_2\,(aq.) \overset{\alpha}{\rightleftharpoons} Ca^{2+} + 2Cl^-$

$t=0 \quad a$

$a-a\alpha \qquad a\alpha \qquad 2a\alpha$

$\therefore\ i = 1+2\alpha$ 3

c) $AlCl_3\,(aq.) \overset{\alpha}{\rightleftharpoons} Al^{3+} + 3Cl^-$

$i = 1+3\alpha$ 4

d) $K_4[Fe(CN)_6] \overset{\alpha}{\rightleftharpoons} 4K^+ + [\ ]^{4-}$

$t=0 \quad a$

5

$i = 1+4\alpha$

Note : generally if an electrolyte is given and nothing is mentioned, then take $\alpha = 1$.
For association, α is given.

b) **For Association** :

$$nA \rightleftharpoons A_n$$

$t=0$ $\quad a \qquad 0$

$a - a\alpha \qquad \frac{a\alpha}{n} \qquad n_T = a\left(1 - \alpha + \frac{\alpha}{n}\right)$

$$\therefore i = 1 - \alpha + \frac{\alpha}{n}$$

$i < 1$ for association

eg,

$$2A \overset{\alpha}{\rightleftharpoons} A_2$$

$$i = 1 - \alpha + \frac{\alpha}{2}$$

$72+12+9$
6×12

Q. Find VP of solⁿ obtained by dissolving 30 g of glucos in 360 g of water at 25°c. Given VP of pure water at 25°c is 21 torr.

a) Also find RLVP.

→ $\frac{P_A^\circ - P_s}{P_s} = \frac{n_B}{n_A} \Rightarrow \frac{21 - P_s}{P_s} = \frac{1/6}{20} = \frac{1}{120}$

$\text{RLVP} = x_B.$

2,

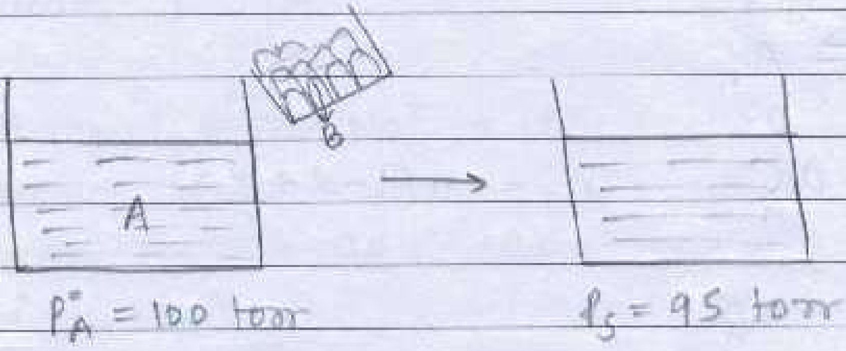
$^{9} i = 1.4$

$\frac{21 - P_s}{P_s} = \frac{1}{200}$ & $\text{RLVP} = \frac{0.1}{20.1}$ | ⓑ Find P_s & RLVP if $\alpha = 2$

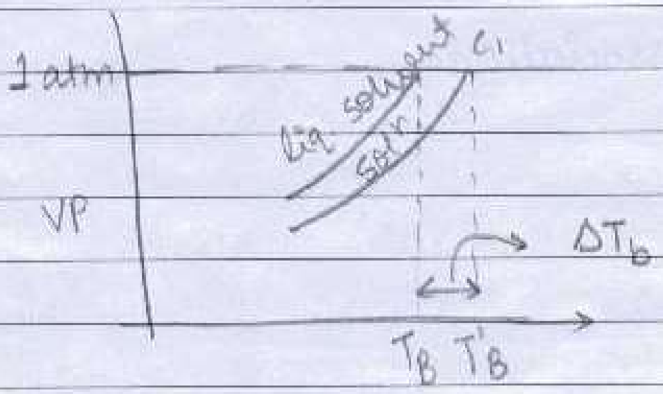
$P_s' = 1.4 P_s$

2) Elevation in Boiling Point :→

When we non volatile solute to a volatile solvent, VP will ↓ as a result BP will ↑ and this increase in BPt. is called elevation in BPt.



$BPt \propto \frac{1}{VP}$



$\Delta T_b = T'_b - T_b$ = Elevation in boiling point

For non volatile non electrolyte solutes

$$\Delta T_b \propto m$$

$$\Delta T_b = K_b m$$

where,

m → molality

K_b → Ebullioscopic constant

K_b is characteristic constant of solvent and its value is independent of temperature.

For more than one solute,

$$\Delta T_b = \Delta T_{b_1} + \Delta T_{b_2} + \dots$$

$$\Delta T_b = K_b m_1 + K_b m_2 + \dots$$

$$= K_b (m_1 + m_2 + \dots)$$

If solute is an electrolyte

$$\Delta T_b = i K_b m$$

For more than solute

$$\Delta T_b = K_b (i_1 m_1 + i_2 m_2 + \dots)$$

$$K_b = \frac{RT_b^2}{1000 L_v} = \frac{RT_b^2 \times M (g/mol)}{1000 \times \Delta_{vap} H}$$

L_v → Latent heat of vap. (Energy/g)

$\Delta_{vap} H$ → Enthalpy of vap. (Energy/mol)

T_b = Boiling point of solvent (in K)

M_A → Molar mass of solvent (in g/mol)

Q. Calculate K_b for water ($L_v = 540$ cal/g)

→ $K_b = \frac{2 \times (373)^2}{1000 \times 540} = 0.5$ K kg mol^{-1}

0·6

7×12

Q. A Sol^n of 122g of benzoic acid in 1000g of benzene shows a bpt elevation of 1·4°C assuming that solute dimerises to extent of 80% calculate BPt of benzene ($\Delta_{vap} H_B = 7.8$ kcal/mol)

→ 1 mol. ; b

$$1.4 = \frac{2 \times \cancel{122}^{78} \times T^2}{1000 \times 7800} \times \frac{73.2}{1000}$$

$$\frac{7}{3} = \frac{2 \times T^2 \times \cancel{78}}{1000 \times \cancel{7800}_{100}}$$

$$\frac{700 \times 1000}{6} = T^2$$

$\sqrt{70}$

NH_2CONH_2 60

Q. 1L of aq. solⁿ of urea having density 1·06 g/ml is found to have $\Delta T_b = 0{\cdot}5°c$. If temp. of this solⁿ increases to 101·5°c, then calculate amt of water which must have gone in vapor state upto this point. ($K_{b(H_2O)} = 0{\cdot}5 \text{ K kg mol}^{-1}$)

→ $0{\cdot}5 = 0{\cdot}5 \times m \Rightarrow m = 1$ 1060 $\boxed{\frac{2000}{3}}$ 101

60 gm urea 1000 gm

$3 = m$

Note :

A pure solvent gets evaporated completely at its boiling pt. while if we take a solⁿ containing non volatile solute & a volatile solvent then on ↑ temp. its BPt will ↑ coz solvent particles will evaporate as a result, molality will increase.

- Derivation of K_b :

$$\ln \frac{VP_2}{VP_1} = \frac{\Delta_{vap.}H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Assume $\Delta_{vap.} H_{soln} = \Delta_{vap.} H_{solvent}$

$$\Rightarrow \ln \frac{p_A^\circ}{p_s} = \frac{\Delta_{vap} H}{R}\left(\frac{1}{T_b} - \frac{1}{T_b'}\right)$$

$$\Rightarrow -\ln \frac{p_s}{p_A^\circ} = \frac{\Delta_{vap.}H}{R}\left(\frac{\Delta T_b}{T_b^2}\right) \quad \{T_b' \approx T_b\}$$

$$\Rightarrow -\ln(1 - x_B) = \frac{\Delta_{vap}H}{R} \times \frac{\Delta T_b}{T_b^2}$$

$$\Rightarrow \frac{m \times M_A}{1000} = x_B \approx \frac{\Delta H}{R} \times \frac{\Delta T_b}{T_b^2}$$

$$\therefore \Delta T_b = \frac{RT_b^2 M_A}{1000 \times \Delta_{vap}H} \times m$$

$$\Delta T_b = K_b \times m.$$

3] Depression in Freezing point : (ΔT_f)

Freezing Pt : Temp. at which VP of substance in liquid phase becomes equal to VP in solid phase

A solⁿ will freeze when its VP becomes equal to vapour pressure of pure solid solvent.

$\Delta T_f = T_f - T_f'$ = Depression in FPt.
For non volatile, non electrolyte solute,
$\Delta T_f \propto m$
$\Delta T_f = K_f m$
where,
$m \rightarrow$ molality
$K_f \rightarrow$ Cryoscopic constant
K_f is characteristic constant of solvent & its value is independent of temp.
unit of $K \rightarrow K\ kg\ mol^{-1}$

For more than one solute,
$\Delta T_f = K_f (m_1 + m_2 + \ldots)$
If solute is an electrolyte,
$\Delta T_f = iK_f m$
For more than one solute
$\Delta T_f = K_f (i_1 m_1 + i_2 m_2 \ldots)$

$$K_f = \frac{RT_f^2}{1000\, L_f} = \frac{RT_f^2 \times M_A}{1000 \times \Delta_{fus} H}$$

L_f → Latent heat of fusion (energy / g)

$\Delta_{fus}H$ → ~~Latent heat~~ enthalpy of fusion (energy / mol)

T_f → Freezing pt. of solvent

M_A → Molar mass of solvent

Q. Calculate the amount of sucrose in moles that must be dissolved in 500 g of water so that diff in FPt & BPt becomes 104°C.
$K_b = 0.52$, $K_f = 1.86$

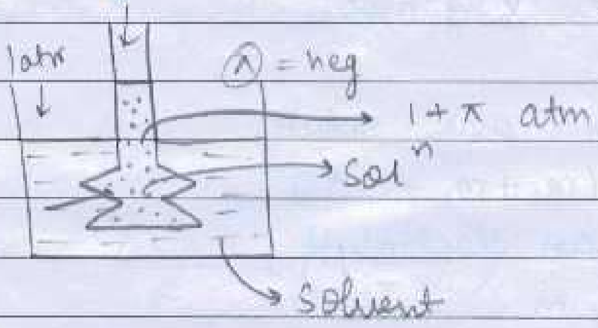
$C_{11}H_{22}O_{12}$

→ $x = 0.52 \times 2n$; $y = 1.86 \times 2n$

$104 = 2.38 \times 2n \Rightarrow n = \frac{2}{2.38} = \frac{200}{238}$

4] Osmotic Pressure :

- **Osmosis** :→ It is a phenomena of movement of solvent particles from low conc. sol^n (w.r.t solute) to high conc. sol^n



- <u>Osmotic pressure</u> (π) : It is the pressure corresp. t
height 'h'.

$$\pi = h \rho g$$

$h \rightarrow$ height of column of liq. sol^n
$\rho \rightarrow$ density of sol^n
$g \rightarrow$ acc^n due to gravity.

It is the pressure that should be applied ~~to~~ on higher conc. sol^n in order to just prevent osmosis.
If,
Applied pressure > Osmotic pressure
then,
<u>Reverse osmosis</u> : If pressure app. is greater then osmotic P then solvent particles will start moving from higher conc. sol^n (w.r.t. solute) to lower conc. sol^n.
Eg,
Desalination of sea water.

- <u>Vant Hoff law</u> :

For non volatile, non electrolyte solute,

$$\pi \propto C$$
$$\pi = CRT$$

where,
$\pi \rightarrow$ Osmotic pressure
$C \rightarrow$ molarity
$R \rightarrow$ gas constant
$T \rightarrow$ Temp. (in K)

If solute is electrolyte,

$$\pi = iCRT$$

$i \rightarrow$ Van't Hoff factor

For more than one solute,

$$\pi = RT(i_1C_1 + i_2C_2 + \text{-----})$$

This colligative property is independent of nature of solvent

- **Isotonic Solution :**

2 sol^n are said to be isotonic if they have same osmotic pressure at same temp.

$$\pi_A = \pi_B$$
$$i_A C_A = i_B C_B$$

- **Hypertonic & Hypotonic Solution :**

A sol^n 'A' is said to be hypertonic w.r.t 'B' if,

$\pi_A > \pi_B$ (at same temp.)

Here 'B' is said to be hypotonic w.r.t 'A'

Q. Which of the following solution is isotonic, hypertonic or hypotonic w.r.t. 0.1M $AlCl_3$

A)	0.1M	$K_4[Fe(CN)_6]$	hyper
B)	0.1M	$NaCl$	hypo
C)	0.2M	KCl	Iso
d)	0.4M	Urea	[illegible]
e)	0.1M	$FeCl_3$	Iso

Q. Calculate π of 0.1M urea solution at 300 K (in atm)

→ $\pi_{urea} = 0.1 \times 0.0821 \times 300 = 2.463$ atm

Q. 200 ml of 0.2M urea is mixed with 300 ml of 0.3 M glucose at 300K. Find π

→ $\pi = \frac{40}{500} \times RT + \frac{90}{500} RT = \frac{13}{50} RT$

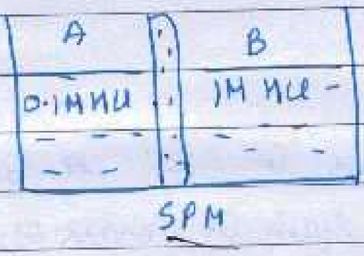
Q. A sol^n having 0.1 M NaCl, 0.2 M Na_2SO_4 & 0.5 M HA ($\alpha = 0.2$). Find π at 300K.

→ $\pi = RT(0.1 \times \cancel{1.4}\, 2 + 0.2 \times \cancel{1.6}\, 3 + 0.5 \times 1.2)$

Q. If 200 ml of 0.2 M $BaCl_2$ sol^n is mixed with 500 ml of 0.1 M Na_2SO_4 sol^n. Calculate π of resulting sol^n at 300K.

→ $2Cl^-$, $2Na^+$
40mm 50mm

$\pi = RT\left(9/70\right)$

Q. 

a) On which side we have to apply osmotic P to stop osm.

b) How much osmotic press we we have to apply?

→ a) on B

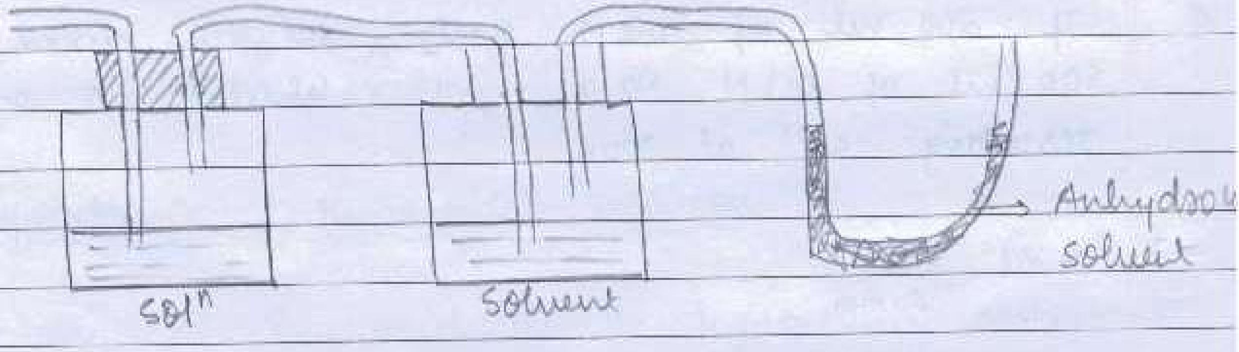
b) $\pi = 0.9 \times 300 R$

* Experimental determination of Colligative Prop. :→

1) Ostwald Walker Dynamic Method :→

It is used to determine relative lowering in VP. In this method, a fixed amount of dry air is passed thru first a sol^n & then thru a solvent. The loss in wt. of sol^n & solvent is calculated.

When air is passed thru sol^n it takes up amt. of vapours which is proportional to VP of sol^n & when it is passed thru pure solvent it takes up amt. of vapours which is proportional to difference in VP of solution and solvent.



$$w_1 \propto P_s$$
$$w_2 \propto P_A^\circ - P_s$$
$$w_1 + w_2 \propto P_A^\circ$$

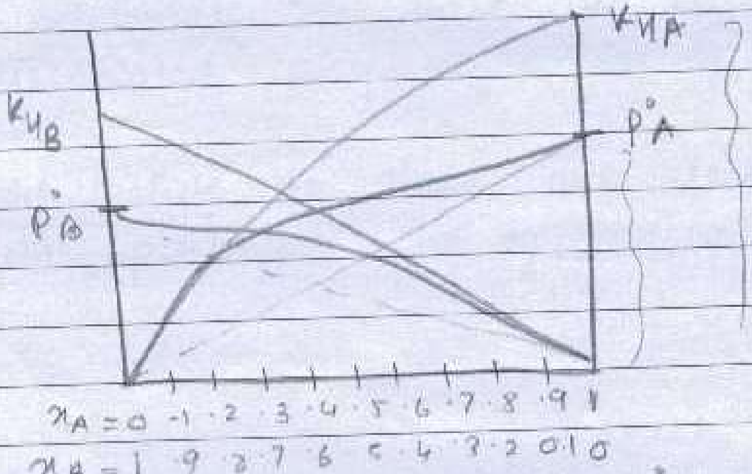
$$RLVP = \frac{P_A^\circ - P_s}{P_A^\circ} = \frac{w_2}{w_1+w_2} = \frac{\text{loss in wt. of solvent}}{\text{gain in mass of } CaCl_2}$$

I, II, III -B&A

- **Relationship between Henry's law & Rault's law :-**

A solⁿ cannot be described by rault's law over all compositions. Such solutions are called non-ideal solutions.

Henry's law is applicable for solute while Rault's law is applicable for solvent.



$P_A = K_{H_A} x_A$
Solute

$P_A = P^\circ_A x_A$
Solvent

For ideal solⁿ $K_{H_A} = P^\circ_A$

1/8/18

Ionic Equilibrium

* Electrolyte : These are substances which on dissolution in suitable solvent produces ions.

Electrolytes are of two types :

i) Strong } on the basis of extent of dissolution
ii) Weak

A] Strong Electrolyte :→ These are electrolytes which get dissociated completely. For eg, NaCl, HCl, etc.

B] Weak Electrolyte :→ These are electrolytes which dissociate partially. For eg, CH_3COOH, NH_4OH, etc.

i) True } on the basis of nature
ii) Potential

A] True Electrolyte :→ These are generally ionic compounds which contain ions in their pure state. For eg, NaCl, $CaCl_2$

B] Potential Electrolytes : These are electrolytes which do not contain ions in their pure state but they can produce ions if dissolved in suitable solvents. For eg, CH_3COOH.

* ACIDS and BASES :→

In 1810, Davy proposed that 'H' was essential part of acid.

- Acids are substances which are sour in taste and can turn blue litmus into red.

Acid : Latin word (Acidus) → sour in taste

- Bases are bitter in taste and can turn red litmus into blue.

- Water soluble bases are called alkali.
  Alkali : al-kali (arabic word) → Ashes of plants

A] Arrhenius Theory (1880-90) :

★ **Acids** : These are the substances which can lose H^+ in water.

eg,

$$HCl_{(aq.)} \longrightarrow H^+_{(aq.)} + Cl^-_{(aq.)}$$

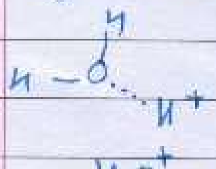
★ **Bases** : These are the substances which lose OH^- in water.

eg,

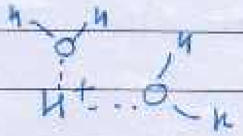
$$NaOH_{(aq.)} \longrightarrow Na^+_{(aq.)} + OH^-_{(aq.)}$$

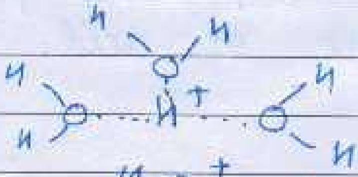
Drawbacks :

i) Due to very ↑ +ve charge density, H^+ cannot exist isolatedly in water. It can exist only in hydrated form as shown



H_3O^+





$H_7O_3^+$

ii) There are certain bases which do not have OH^-

For eg,

$$\underset{Acid}{\underline{HCl}}_{(aq.)} + \underset{Base}{\underline{NH_3}}_{(aq.)} \longrightarrow NH_4Cl_{(aq.)}$$

B] Bronsted Lowry Concept (1923) :

- **Acids** : These are the substances which can donate a proton

- **Bases** : These are substances which can accep a proton.

$$\underset{Acid}{HCl} \overset{H^+}{\curvearrowright} \underset{Base}{H_2O} \longrightarrow \underset{CA}{H_3O^+} + \underset{CB}{Cl^-}$$

$$Acid \xrightarrow{-H^+} Conjugate\ Base$$

Eg,

$C_2H_2 \rightarrow C_2H^-$

$C_6H_5OH \rightarrow C_6H_5O^-$

$NaH_2PO_4 \rightarrow NaHPO_4^-$

$H_2CO_3 \rightarrow HCO_3^-$

$HSO_4^- \rightarrow SO_4^{2-}$

$$\underset{Base}{\ddot{N}H_3} \overset{H^+}{\curvearrowleft} \underset{Acid}{H_2O} \longrightarrow \underset{CA}{NH_4^+} + \underset{CB}{OH^-}$$

$$Base \xrightarrow{+H^+} Conjugate\ Acid$$

Eg,

$CO_3^{2-} \rightarrow HCO_3^-$

$C_2H_5^- \longrightarrow C_2H_6$

$Al(OH)_3 \longrightarrow Al(OH)_2^+$

$C_6H_5NH_2 \longrightarrow C_6H_5NH_3^{\oplus}$

- A strong acid will have weak conjugate base and a weak acid will have strong conjugate base.

$$\underset{SA}{HCl} + \underset{B}{H_2O} \longrightarrow \underset{CA}{H_3O^+} + \overset{H^+}{\underset{CB}{Cl^-}}$$

↳ very weak

$$\underset{WA}{CH_3COOH} + H_2O \longrightarrow \underset{\cancel{S}CA}{H_3O^+} + \overset{H^+}{\underset{SCB}{CH_3COO^-}}$$

c] <u>Lewis Concept</u> (1923) :

★ <u>Acids</u> : These are species which can accept e^- pair.

★ <u>Bases</u> : These are species which can donate an e^- pair.

when protons are not involved, we use this concept.

Eg,

$\ddot{N}H_3 + BF_3 \longrightarrow H_3N \rightarrow BF_3$

Q. True / False

1) Bronsted base is also a lewis base. T
2) Bronsted acid is also a lewis acid. F

* p^H scale :

p^H → Puissance of hydrogen → Power of hydrogen

$p^H = -\log [H^+]$ ← $p^H = -\log a_{H^+}$
$p^{OH} = -\log [OH^-]$ For dilute sol^n
$p^{Ka} = -\log Ka$ $a_{H^+} = [H^+]$
$p^x = -\log x$

- p^H scale can have values -ve or greater than 14. This scale is useful for dilute solutions only.

* Self dissociation or Auto ionisation of water :

$$H_2O(l) \underset{exo}{\overset{endo}{\rightleftharpoons}} \underset{10^{-7}M}{H_3O^+(aq.)} + \underset{10^{-7}M}{OH^-(aq.)} \qquad Kd = \frac{[H^+][OH^-]}{[H_2O]}$$

$$Kw = \underset{\text{dissociation constant}}{\underset{\downarrow}{Kd}} [H_2O] = [H^+][OH^-]$$

$[H_2O] = 55.55\,M$

55 mol → 10^{-7} mol
out of 10^9 molecules
only 2 molecules of H_2O are dissociated

Q. If pure water is taken at 25°c $(Kw = 10^{-14})$. Then calculate

a) $[H_3O^+]$, $[OH^-]$, p^H & p^{OH}
$\downarrow$ $10^{-7}M$, $\downarrow$ $10^{-7}M$, $\downarrow$ 7, $\downarrow$ 7

b) if 0.1 mol of HCl is mixed with 1L of water
i) $[H_3O^+]$ $[OH^-]$
$\downarrow$ $10^{-1}M$ $\downarrow$ $10^{-7}M$
ii) $10^{-7}M$
iii) 1, 7

$$H_2O(l) + H_2O(l) \underset{exo}{\overset{endo}{\rightleftharpoons}} H_3O^+(aq.) + OH^-(aq.)$$

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

At 25°C, $K_w = 10^{-14}$

$p^H = p^{OH} = 7$ (neutral)

If

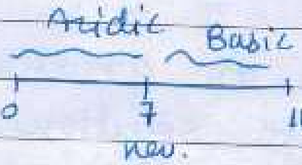
$[H_3O^+] > [OH^-] \Rightarrow$ Acidic

$[H_3O^+] < [OH^-] \Rightarrow$ Basic

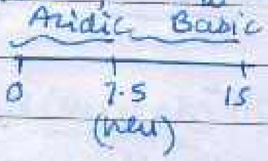
$[H_3O^+] = [OH^-] \Rightarrow$ neutral

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

$p^{K_w} = p^H + p^{OH} = 14$



At 15°C, $K_w = 10^{-15}$



- **Arrhenius Theory :**

Acc^n to it, in case of weak electrolytes there is always a dynamic equilibrium b/w dissociated and undissociated electrolyte.

$$\begin{array}{lcccc} & HA(aq.) & \rightleftharpoons & H^+(aq.) & + & A^-(aq.) \\ t=0 & a & & 0 & & 0 \\ t>t_{eq} & a(1-\alpha) & & a\alpha & & a\alpha \end{array} \qquad K_a = \frac{a\alpha^2}{1-\alpha}$$

if $\underset{(0.05)}{\alpha << 1}$ $\Rightarrow K_a = a\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{c}}$

- if $\frac{K_a}{c} \leq 10^{-3} \Rightarrow \alpha << 1 \Rightarrow$ we can neglect 'α'

if $\frac{K_a}{c} > 10^{-3} \Rightarrow$ we can't neglect 'α'

- **Factors affecting degree of dissociation :-**

i) Nature of solute & solvent
ii) Concentration
iii) Temperature
iv) Common ion effect

- Conc. :

$\alpha \propto \frac{1}{\sqrt{c}}$ (for dilute sol^n^) (weak)

- Ostwald dilution law : As dilution ↑ , α↑ and at infinite dilution, $\alpha \approx 1$, it means even a weak electrolyte will behave like strong electrolyte.

- Temp. :

dissociation is an endothermic process. So on ↑ temp., α ↑.

- common ion effect :

If a mixture of strong & weak electrolyte having at least one common ion is taken then, α of

Ex 1 : 1 to 16

* Dissociation Constants of Acids & Bases :

For acids,

$CH_3COOH_{(aq.)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq.)} + CH_3COO^-_{(aq.)}$

$HCN_{(aq.)} + H_2O_{(l)} \rightleftharpoons CN^-_{(aq.)} + H_3O^+_{(aq.)}$

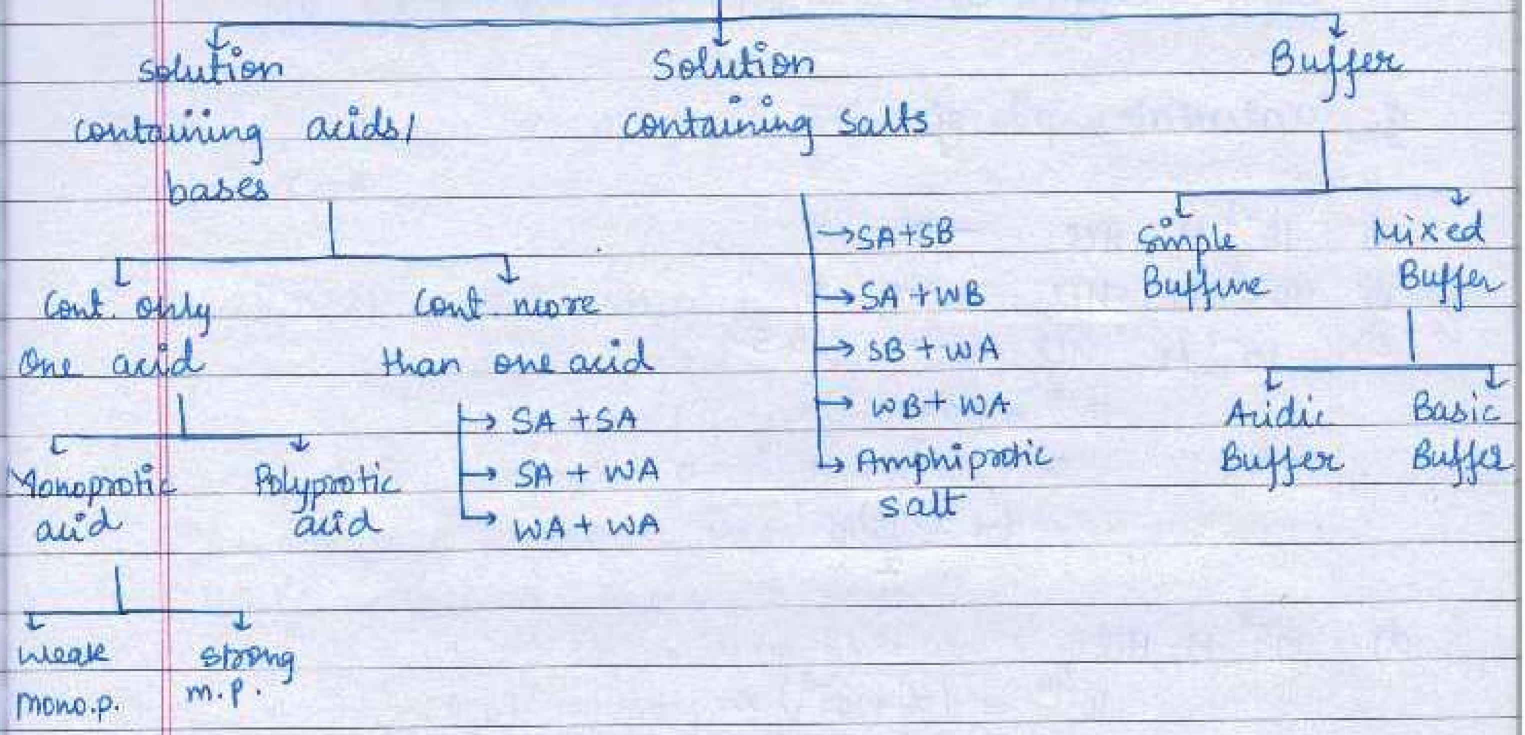
(Same)

$NH_{3(aq.)} + H_2O_{(l)} \rightleftharpoons NH_4^+_{(aq.)} + OH^-_{(aq.)}$

$NH_4OH_{(aq.)} \rightleftharpoons NH_4^+_{(aq.)} + OH^-_{(aq.)}$ $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

6/8/18

p^H Calculation



* p^H of solution containing strong monoprotic acid :→

Case I : If $c > 10^{-6}$ M

Then we can neglect $[H_3O^+]$ due to water

$$\underset{\substack{c\\0}}{H_2O(l) + HCl(aq.)} \longrightarrow \underset{c}{H_3O^+(aq.)} + \underset{c}{Cl^-(aq.)}$$

$[H_3O^+] = c$

$p^H = -\log c$

Case II : If $c \leq 10^{-6}$ M

we have to take conc. due to water

$$\underset{c}{HCl(aq.)} + H_2O(l) \longrightarrow \underset{x+c}{H_3O^+(aq.)} + \underset{c}{Cl^-(aq.)}$$

$$2H_2O(l) \rightleftharpoons \underset{x+c}{H_3O^+} \quad \underset{x}{OH^-}$$

$[H_3O]^+ = x + c$

$p^H = -\log(x+c)$

Q. Calculate p^H of

a) 10^{-3} M HCl $\longrightarrow$ 3

b) 10^{-5} M HCl $\longrightarrow$ 5

c) 10^{-7} M HCl, $\longrightarrow$ 6.45

$$10^{-14} = (x+10^{-7})x$$

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

$$\frac{(-1 \pm \sqrt{5})10^{-7}}{2}$$

d) 10^{-8} M HCl,

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

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

$$\frac{(-10^{-1} \pm 2)\cdot 10^{-7}}{2}$$

Case III : If $c > 10^{-6}$ M & $K_a c > 10^{-12}$

Then we can neglect $[H_3O^+]$ due to water

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

$c-x$ $\qquad x \qquad x$

If,

$$\frac{K_a}{c} < 10^{-3} \Rightarrow K_a = \frac{x^2}{c-\cancel{x}} \Rightarrow x = \sqrt{K_a c}$$

$$[H_3O^+] = x = \sqrt{K_a c}$$

$$p^H = -\frac{1}{2}\log K_a c = \frac{1}{2}(p^{K_a} - \log c)$$

Case IV : If $C > 10^{-6}$ M & $K_a C < 10^{-12}$

we have to take contribution due to water

$$CH_3COOH_{(aq.)} + H_2O(l) \rightleftharpoons CH_3COO^-(aq.) + H_3O^+_{(aq.)}$$

$C - x \qquad x \qquad x + y$

$\downarrow$

$$K_a = \frac{x(x+y)}{(c-x)}$$

$$2H_2O(l) \rightleftharpoons H_3O^+(aq.) + OH^-(aq.)$$

$y + x \qquad y$

$$K_w = (y+x)\,y.$$

$$[H_3O^+] = y + x = \sqrt{K_a C}$$

if $\frac{K_a}{C} < 10^{-3} \Rightarrow K_a C = x(x+y)$

$$K_w = y(x+y)$$

$$[H_3O]^+ = x + y = \sqrt{K_w + K_a C}$$

$$p^H = -\log[H_3O^+] = -\log\sqrt{K_w + K_a C}$$

$* \ \frac{K_a}{C} < 10^{-3}$

$$\frac{-10^{-5} \pm \sqrt{41 \cdot 10^{-5}}}{2}$$

$10^{-10} + 4\,10^{-9}$

Q. Calculate p^H of

a) 0.1M ~~M~~ CH_3COOH

b) 10^{-4}M CH_3COOH at 25°C

given $K_{a\,(CH_3COOH)} = 10^{-5}$

$x^2 - 10^{-9} + x \cdot 10^{-5}$

$5.4 \cdot 10^{-5}$

$2.7 \cdot 10^{-5}$

$-\log 2.7 + 5$

a $\longrightarrow$ $K_a C = 10^{-6}$

$$p^H = -\frac{1}{2}\log 10^{-6} = 3$$

b $\rightarrow$ $K_a C = 10^{-9}$

$$p^H = +\frac{1}{2}(9) \approx \text{~~4/5~~ ~~3rd~~ } 4.5$$

c) 10^{-4} M HCN ($K_a = 10^{-10}$)

$\rightarrow$ $p^H = -\frac{1}{2}\log(10^{-14} + 10^{-14})$

$= ~~7~~ - -\frac{1}{2}(14 \pm 0.3)$ $= ~~30~~ \boxed{6.85}$

Case V : If $c < 10^{-6}$ & $K_a > c$ $\Rightarrow \alpha = 1$

$$\begin{array}{ccccccc} CH_3COOH & + & H_2O & \longrightarrow & CH_3COO^- & + & H_3O^+ \\ c & & & & & & \\ 0 & & & & c & & c \end{array}$$

$$\begin{array}{ccccc} 2H_2O & \rightleftharpoons & H_3O^+ & + & OH^- \\ & & x+c & & x \end{array} \qquad K_w = x(x+c)$$

here, weak acid will behave like strong acid.

Case VI : If $c < 10^{-6}$ & $K_a < c$ $(\alpha < 1)$

$$\begin{array}{ccccccc} CH_3COOH & + & H_2O & \longrightarrow & CH_3COO^- & + & H_3O^+ \\ c & & & & & & \\ c-x & & & & x & & x+y \end{array}$$

$$x = \sqrt{K_a c}$$

$$\left.\begin{array}{l} K_w = (x+y)y \\ K_a = \dfrac{x(x+y)}{c-x} \end{array}\right\} \text{add}.$$

Q. Calculate p^H of 10^{-8} M CH_3COOH $(K_a = 10^{-5})$

→ p^H = $10^{-14} = x(x+10^{-8})$

$$\frac{-10^{-8} + \sqrt{10^{-16} + 4\times10^{-14}}}{2} = 2\times10^{-7}$$

$$0.95\times10^{-7}$$

$$10.5 \times 10^{-8}$$

$p^H = -\log 105 + 8$
$= 6.98$

* p^H of a Solution containing more than one acids:

Case I : SA + SA

$[HCl] = C_1$

$[HBr] = C_2$

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

c_1

$0 \qquad c_1 + c_2 \qquad c_1$

$$HBr + H_2O \longrightarrow H_3O^+ + Br^-$$

c_2

$0 \qquad c_2 + c_1 \qquad c_2$

$[H_3O^+] = c_1 + c_2$

$\therefore p^H = -\log(c_1 + c_2)$

Case II : SA + WA

$[HCl] = C_1$

$[CH_3COOH] = C_2$, K_a

$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

$c_1 \qquad c_1 \qquad c_1$

$$CH_3COOH + H_2O \longrightarrow CH_3COO^- + H_3O^+ \qquad \frac{(c_1+x)x}{c_2-x} = K_a$$

$c_2 - x \qquad x \qquad x + c_1$

$K_w = (x+y)y$

Case III : WA + WA

$[HCN] = C_1 \quad K_{a_1}$

$[CH_3COOH] - C_2 \quad K_{a_2}$

$$K_{a_1} = \frac{x(x+y)}{c_1 - x} \qquad K_{a_2} = \frac{y(x+y)}{c_2 - x}$$

Q. Calculate p^H of a sol. containing 1M CH_3COOH $(K_a = 10^{-5})$ & 10^{-3} M HCl

$x = \sqrt{K_a c}$
$10^{-3} \times \sqrt{10}$

→ $p^H = -\log(10^{-3} + x)$

$= -\log(4.2 \times 10^{-3})$

$= 3 \mp \log 4.2 \approx$ [illegible] 2.4.

<u>Note</u>: We can solve a problem without considering contribution of water if p^H comes out to be 6 to 8, it means we are wrong. We have to take contribution due to water.

* <u>Polyprotic acids</u>:

These are acids which contain more than one protons. for eg, H_2CO_3, H_2SO_4, H_3PO_4, etc.

- Successive dissociation constants of polyprotic acids decreases by $10^4 - 10^6$

$$H_2CO_{3\,(aq.)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq.)} + HCO_3^-{}_{(aq.)} \quad K_1 = 10^{-7}$$

$$HCO_3^-{}_{(aq.)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq.)} + CO_3^{2-}{}_{(aq.)} \quad K_2 = 10^{-11}$$

p^H <u>Calculation</u>:

<u>Case I</u>: If K_1 and K_2 are very large

$[H_2A] = c$

Case II : if K_1 is very large but not K_2

$[H_2A] = c$

$H_2A + H_2O \longrightarrow HA^- + H_3O^+$

$c \qquad c+x$

$HA^- + H_2O \longrightarrow H_3O^+ + A^-$ $\qquad \frac{x(c+x)}{c-x} = K_2$

$c-x \qquad c+x \qquad x$

Case III : if K_1, K_2 & K_3 are all very small

$[H_3PO_4] = c$

$H_3PO_4 + H_2O \longrightarrow H_2PO_4^- + H_3O^+$ $\qquad \frac{(x+y+z)(x-y)}{c-x} = K_1$

$c-x \qquad x-y \qquad x+y+z$

$H_2PO_4^- + H_2O \longrightarrow HPO_4^- + H_3O^+$ $\qquad \frac{(z-y)(x+y+z)}{x-y} = K_2$

$x-y \qquad y-z \qquad y+x$

$HPO_4^- + H_2O \longrightarrow PO_4^- + H_3O^+$ $\qquad \frac{(\cancel{y}\,z)(x+y+z)}{y-z} = K_3$

$y-z \qquad z \qquad x+y+z$

We know,

$K_1 >> K_2 >> K_3$ $\qquad K_1 = \frac{x^2}{c-x}$

$x >> y >> y$ $\qquad K_2 = y$

$[H_3O^+] = x+y+z \simeq x$ $\qquad K_3 = \frac{x \times z}{y}$

$[H_3PO_4] = c-x$

$[H_2PO_4^-] = x-y \simeq x$

$[HPO_4^{2-}] = y-z \simeq y$

$[PO_4^{3-}] \simeq z$

H^+ mainly comes from 1st step so if only pH is asked then we need to write only 1st step.

$-\frac{1}{2}\log K_a C$ $\frac{255\times10^{-3}}{10^{-4}}$ $\frac{1000}{255}^{-1}$

Q. 1 mol of WA HA is added to water to produce 1L solⁿ [$K_a(HA) = 10^{-4}$ M] calculate

a) Its pH. = 2

b) Vol. of H_2O added to double its pH. = 9999 L

c) Vol. of H_2O added to double [OH^-] = 3L

d) " " " evaporated " [H_3O^+] = 750 ml

e) pH if V is ↑ to 100 L = 3·6

f) " " " " " " 10^7 L = 5·5

g) Change in pH if 2L of 0·01 M HCl is added

$10^{-2} + 10^{-2}$ ⟶ 2 − 0·3
= 1·86

$\boxed{0}$

2/-4-86

* Salts :→

These are the substances which are formed along with water when acid-base rxn takes place.

$HCl + NaOH \longrightarrow NaCl + H_2O$
Acid Base Salt

$Na^+ + H_2O_{(l)} \longrightarrow X$
$Cl^- + H_2O_{(l)} \longrightarrow X$

Types of salt

1) Neutral salt (SA + SB)
2) Acidic salt (SA + WB)
3) Basic salt (WA + SB)

- **Neutral salt :**

Neutral salts are formed when strong acid reacts with strong base.
Eg, NaCl, KCl, etc.
Here source of H^+ & OH^- is water.

- **Acidic salt :**

$HCl_{(aq.)} + NH_{3\,(aq.)} \rightleftharpoons NH_4Cl_{(s)} \equiv NH_4^+{}_{(aq.)} + Cl^-{}_{(aq.)}$

$H_2O_{(l)} + HCl_{(aq.)} \longrightarrow H_3O^+{}_{(aq.)} + Cl^-{}_{(aq.)}$

$NH_{3\,(aq.)} + H_2O_{(l)} \rightleftharpoons NH_4^+{}_{(aq.)} + OH^-{}_{(aq.)}$

$H_3O^+{}_{(aq.)} + OH^-{}_{(aq.)} \rightleftharpoons 2H_2O_{(l)}$

$NH_{3\,(aq.)} + HCl_{(aq.)} \rightleftharpoons NH_4^+{}_{(aq.)} + Cl^-{}_{aq.}$ $\quad K = \frac{K_b}{K_w} = 10^9$

$NH_4^+{}_{(aq.)} + H_2O \rightleftharpoons NH_3 + H_3O^+$

- **Basic salt :**

$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O_{(l)}$ $\quad (K_a = 10^{-5})$

$H_2O + CH_3COOH \longrightarrow \underset{K_{a2}}{H_3O^+} + CH_3COO^-$ $\quad K_a = 10^{-5}$

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

$H_3O^+ + OH^- \longrightarrow 2H_2O$ $\quad K = \frac{1}{K_w} = 10^{14}$

$\underset{c-x}{CH_3COOH} + \underset{c}{NaOH} \rightleftharpoons \underset{x}{CH_3COONa}$

CRTI = CR

- **Hydrolysis** : This is phenomena of interactio of cation & anion of a solute with water to produce acidic / basic solⁿ.

It is reverse of neutralisation so it will be endothermic.

Note : From above two cases it is clear that in acid - base rxn if one of them is strong then rxn will be almost completed

* p^H calculation of salts :

Case I : For neutral salts
eg, NaCl, KCl, etc.

$Na^+_{(aq.)} + H_2O_{(l)} \longrightarrow \times$
$Cl^-_{(aq.)} + H_2O_{(l)} \longrightarrow \times$

$p^H = 7$ all $[H_3O^+]$ & $[OH^-]$ will be due to water only.

Case II : For Basic Salt
eg, $CH_3COONa_{(aq.)}$, $NaCN_{(aq.)}$, etc.
$[CH_3COONa] = c$ $\qquad K_{a(CH_3COOH)}$

$$\underset{c-x}{CH_3COO^-} + H_2O \longrightarrow \underset{x}{CH_3COOH} + \underset{y+x}{OH^-} \qquad \frac{(x+y)x}{c-x} = \overset{1}{/}K_a$$

$Na^+ + H_2O \longrightarrow \times$

$$(x+y)\,y = K_w.$$

$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$ $\qquad K_h = \frac{[CH_3COOH][OH^-][H_3O^+]}{[CH_3COO^-][H_3O^+]}$

$c(1-h) \qquad\qquad ch \qquad ch$

$$= \frac{K_w}{K_a} = \frac{ch^2}{1-h}$$

if $\frac{K_h}{c} < 10^{-3} \Rightarrow \frac{K_w c}{K_a} = c^2h^2 = [OH^-]^2$

$-\log[H_3O^+] = -\frac{1}{2}(\log K_w + \log K_a - \log c)$

$p^H = \frac{1}{2}(p^{K_w} + p^{K_a} + \log c)$

Case III : for acidic salt

eg, $NH_4^+Cl^-$, $RNH_3^+Cl^-$

$[NH_4Cl] = c \qquad K_{b(NH_3)}$

$p^{OH} = \frac{1}{2}(p^{K_w} - p^{K_b} - \log c)$

$NH_4^+{}_{(aq.)} + H_2O \longrightarrow NH_4OH + H^+$ $\qquad \frac{K_w}{K_b} = \frac{ch^2}{1-h}$

$c(1-h) \qquad\qquad ch \qquad ch$

if $\frac{K_h}{c} < 10^{-3} \Rightarrow c^2h^2 = \frac{K_w c}{K_b} = [H_3O^+]^2$

h → degree of hydrolysis

K_h → hydrolysis constant

Q. Calculate h, K_h & p^H of 0.25 M NaCN $\qquad h = \frac{1}{50}$

$K_a(HCN) = 10^{-10}$

$K_h = 10^{-4}$

→ $p^H = \frac{-1}{2}(-14 - 10 - \log 25 - \log 10^{-2})$ $\qquad \frac{25\times10^{-2}\times h^2}{1-h} = 1$

$= 11 + \frac{1}{2}\log 5 = 11.6$ $\qquad \frac{h^2}{1-h} = \frac{1}{2500}$

$1 \pm 10^2 \qquad 2500h^2 + h - 1 =$

Case IV : Salt of WA & WB

eg CH_3COONH_4 , NH_4CN, etc.

$[CH_3COONH_4] = c \qquad K_a, K_b$

$$\underset{c(1-h)}{CH_3COO^-} + H_2O \longrightarrow \underset{ch}{CH_3COOH} + \underset{ch}{OH^-} \qquad K_{h_1} = \frac{K_w}{K_a} = \frac{ch^2}{1-h}$$

$$\underset{c(1-x)}{NH_4^+} + H_2O \longrightarrow \underset{cx}{NH_4OH} + \underset{cx}{H_3O^+} \qquad K_{h_2} = \frac{K_w}{K_b} = \frac{cx^2}{1-x}$$

$$H_2O \longrightarrow H_3O^+ + OH^- \qquad \Rightarrow \frac{K_b}{K_a} = \frac{(1-x)h^2}{(1-h)x^2}$$

$$K = \frac{K_w}{K_aK_b} = \frac{(ch)^2}{(c(1-h))^2}$$

$$\frac{h}{1-h} = \sqrt{\frac{K_w}{K_aK_b}}$$

- Here, 'h' changes only on changing temp.

if,

$K_a = K_b \Rightarrow K_{h_1} = K_{h_2} \Rightarrow [H_3O^+] = [OH^-] \Rightarrow$ neutral

$K_a > K_b \Rightarrow K_{h_1} < K_{h_2} \Rightarrow [H_3O^+] > [OH^-] \Rightarrow$ acidic

$K_b > K_a \Rightarrow K_{h_1} > K_{h_2} \Rightarrow [OH^-] > [H_3O^+] \Rightarrow$ basic

We Assume,

$h_1 = h_2 \Rightarrow [CH_3COOH] = [NH_3]$ & $[CH_3COO^-] = [NH_4^+]$

But $[H_3O^+] \neq [OH^-]$

$$\frac{K_b}{K_a} = \frac{[CH_3\cancel{COOH}][OH^-]}{[CH_3\cancel{COO^-}]} \times \frac{[NH_4^+]}{[\cancel{NH_3}][H_3O^+]}$$

$$= \frac{K_w}{[H_3O^+]^2} \Rightarrow [H_3O^+] = \sqrt{\frac{K_wK_a}{K_b}}$$

$$pH = \frac{1}{2}\left(pK_w + pK_a - pK_b\right)$$

- For conjugate Acid / Base pair :→

$K_{a(HF)} \times K_{b(F^-)} = K_w$.

* p^H of a solution containing Polyvalent ions :→

eg, Na_3PO_4 (aq.), Na_2CO_3 (aq.), Na_2SO_4 (aq.), etc.

$[Na_3PO_4] = c$ K_1, K_2, K_3

$$Na_3PO_4 + H_2O \longrightarrow Na_2PO_4^- + Na^+$$

$$\Downarrow$$

$$\underset{\substack{c \\ 0}}{Na_3PO_4} + H_2O \rightarrow \underset{\substack{0 \\ 3c}}{3Na^+} + \underset{\substack{0 \\ 3c}}{PO_4^{3-}}$$

$$\underset{c-x}{PO_4^{3-}} + H_2O \rightleftharpoons \underset{x-y}{HPO_4^{2-}} + \underset{x+y+z}{OH^-} \qquad K_{h_1} = \frac{K_w}{K_3}$$

$$= \frac{[HPO_4^{2-}][OH^-][H_3O^+]}{[PO_4^{3-}][H_3O^+]}$$

$$\underset{x-y}{HPO_4^{2-}} + H_2O \rightleftharpoons \underset{y-z}{H_2PO_4^-} + \underset{y+x+z}{OH^-} \qquad K_{h_2} = \frac{K_w}{K_2}$$

$$= \frac{[H_2PO_4^-][OH^-][H_3O^+]}{[HPO_4^{2-}][H_3O^+]}$$

$$\underset{y-z}{H_2PO_4^-} + H_2O \rightleftharpoons \underset{z}{H_3PO_4} + \underset{x+y+z}{OH^-} \qquad K_{h_3} = \frac{K_w}{K_1}$$

We know,

$K_1 >> K_2 >> K_3$

$x >> y >> z$

$K_{h_1} = \frac{x^2}{c-x}$; $K_{h_2} = y$; $K_{h_3} = \frac{zx}{y}$

$[OH^-] = x+y+z \approx x$

$[PO_4^{3-}] = c-x$

$[HPO_4^{2-}] = x-y \approx x$

$[H_2PO_4^-] = y-z \approx y$

$[H_3PO_4] = z$

If only p^H is asked then we need to write hydrolysis of only 1st step.

* <u>p^H of a sol^n containing amphiprotic salt</u> :→

- <u>Amphiprotic salts</u> : They can accept as well as lose a proton.

eg, $NaHCO_3$, H_2PO_4 , Na_2HPO_4 , etc.

$[NaHCO_3] = c$ $K_1 = 10^{-4}$ $K_2 = 10^{-10}$

$$\begin{array}{lcll} NaHCO_3 + H_2O & \longrightarrow & Na^+_{(aq.)} & + HCO_3^-{}_{(aq.)} \\ c & & 0 & \quad 0 \\ 0 & & c & \quad c \end{array}$$

$$\begin{array}{lcll} HCO_3^- + H_2O & \rightarrow & H_2CO_3 & + OH^- \\ c-x_1-x_2 & & x_1 & \quad x_1 \end{array} \qquad \frac{x_1^2}{c-x_1-x_2} = 10^{-\cancel{10}4}$$

$HCO_3^- + H_2O \rightarrow CO_3^{2-} + [H_3O^+$ $\qquad \frac{x_2^2}{c-x_1-x_2} = 10^{-10}$

$c - x_2 - x_1 \qquad x_2 \qquad x_2$

$H_2O \rightleftharpoons OH^- + [H_3O^+] \qquad K = 10^{-14}$

$HCO_3^- + HCO_3^- \rightleftharpoons CO_3^{2-} + H_2CO_3 \qquad K = 10^{-6}$

$[CO_3^{2-}] \simeq [H_2CO_3]$

$\frac{K_1 K_2}{K_w} = \frac{[\cancel{CO_3^{2-}}][H_3O^+]}{[H\cancel{CO_3^-}]} \times \frac{[H\cancel{CO_3^-}]}{[\cancel{H_2CO_3}][OH^-]}$

$K_1 K_2 = [H_3O^+]^2$

∴ $p^H = \frac{1}{2}(p^{K_1} + p^{K_2})$

Q. Write expression of p^H for

a) $Na_2H_2\cancel{PO_4}A$

b) $NaH_3\cancel{PO_4}A$

c) $Na_3H\cancel{PO_4}A$

d) Na_4A

[Given : K_1, K_2, K_3, K_4 for H_4A]

→ a) $\frac{1}{2}(\cancel{p^{K_1}} + p^{K_2} + p^{K_3} + \cancel{p^{K_4}})$

b) $\frac{1}{2}(p^{K_1} + p^{K_2})$

c) $\frac{1}{2}(p^{K_3} + p^{K_4}]$

d) $\frac{K_w}{K_4} = \frac{x^2}{c-x}$

Q. Write expression of p^H obtained by

i) 100 ml 0.1 M H_3PO_4 + 100 ml 0.1 M NaOH

ii) 100 ml 0.1M H_3PO_4 + 200 ml 0.1M NaOH

iii) 100 ml 0.1 M H_3PO_4 + 300 ml 0.M NaOH

iv) 100 ml 0.1M H_3PO_4 + 400 ml 0.1 M NaOH

→ i) $NaH_2PO_4 \rightarrow \frac{1}{2}(p^{K_2} + p^{K_1})$

ii) $Na_2HPO_4 \rightarrow \frac{1}{2}(p^{K_3} + p^{K_2})$

iii) $Na_3PO_4 \rightarrow \frac{K_w}{K_3} = \frac{x^2}{c-x}$

iv) $12 - \log 2 = 11.7$

$$\frac{K_w}{K_3} = \frac{x\left(x + 1/50\right)}{\left(\frac{1}{50} - x\right)}$$

H.W.

R.B. ⇒ 14 to 21, 37, 38

Ex.1 ⇒ till 27.

3. DPP

26, 27

28, 29 ⇒

RB ⇒ 36-41, 43, 44, 45, 46, 47, 48

* Levelling Effect :-

All the strong acids in aq. sol^n appears to be equally strong so their relative strengths cannot be compared. This phenomena is called levelling effect & water in this case is acting as levelling solvent.
In such case a weak acid like CH_3COOH will act as differentiating solvent.

$$HClO_4\,(aq.) + H_2O\,(l) \xrightarrow{100\%} H_3O^+\,(aq.) + ClO_4^-\,(aq.)$$

$$HNO_3\,(aq.) + H_2O\,(l) \xrightarrow{100\%} H_3O^+\,(aq.) + NO_3^-\,(aq.)$$

$$\underset{\text{Acid}}{HClO_4\,(aq.)} + \underset{\text{Base}}{CH_3COOH\,(aq.)} \rightleftharpoons ClO_4^-\,(aq.) + CH_3COOH_2^+\,(aq.) \quad K = 10^2$$

$$HNO_3 + CH_3COOH \rightleftharpoons NO_3^-\,(aq.) + CH_3COOH_2^+\,(aq.) \quad K = 10$$

* Buffer solution :

It is the sol^n whose p^H does not change significantly on addition of small amt. of acids | bases

Types of Buffer :

1] Simple Buffer
2] Mixed Buffer
  - Acidic Buffer
  - Basic Buffer

- **Simple Buffer :** It is Salt of weak acid and weak base.

- **Mixed buffer :**

1] Acidic : It is mixture of weak acid and its conjugate base

eg,

$CH_3COOH + CH_3COONa$

$HCN + NaCN$

$H_3PO_4 + NaH_2PO_4$

2] Basic : It is mixture of weak base and its conjugate acid

eg,

$NH_3 + NH_4Cl$

$RNH_2 + RNH_3^+Cl^-$

* Mechanism of Buffer Action :

- Suppose we take 1L of pure water at 25°c

$2H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq)$

$pH = 7$

If we add 0.1 mol of HCl to it

$[HCl] = 0.1M$

$pH = 1$

% change in $pH = \frac{7-1}{7} \cong 85\%$.

- If we take a buffer of CH_3COOH & CH_3COONa

  $[CH_3COOH] = 1\ M$ $K_a = 10^{-5}$

  $[CH_3COONa] = 1\ M$

$p^H = 5.$

If we add 0.1 mol HCl to it

$$\frac{(1+x)(0.1+x)}{(1-x)} = 10^{-5}$$

$\Rightarrow$ $0.1 + 1.1x + x^2 = 10^{-5} - 10^{-5}x$

$\Rightarrow$ $x^2 + 1.1x + 0.1 = 0$

$$\frac{-1.1 \pm 0.9}{2}$$

$$\frac{(0.9+x)x}{(1.1-x)} = 10^{-5}$$

$0.9x + x^2 = 1.1 \times 10^{-5}$

$$\frac{-0.9 \pm 0.9}{2}$$

$x = \frac{11}{9} \times 10^{-5}$

$p^H = 5 - \log \frac{11}{9} = 4.98$

% change in $p^H = \frac{5 \cdot 4.98}{5} \times 100 = 0.4\%$

In this case when we add HCl (strong acid) it reacts with conjugate base completely to form a weak acid (CH_3COOH) which cannot provide as much H^+ ions as would have been provided by HCl. (0.1 M)

If we add 0.1 mol NaOH,

$NaOH + CH_3COOH \longrightarrow CH_3COONa + H_2O$

0.1 M 1 M

x 0.9 M 1.1 M

$p^H = 5.02$

* p^H calculation :-

A] For Acidic Buffer :

$[CH_3COOH] = a$ $\quad K_a$

$[CH_3COONa] = S$

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

$$\quad a-x \qquad\qquad\qquad S+x \qquad\quad x$$

$$\frac{x(S+x)}{a-x} = K_a$$

Here we assume,

$S >> x$

$a >> x$

$$p^H = p^{Ka} + \log \frac{S}{a} \longrightarrow \text{Henderson eq}^n.$$

B] For Basic Buffer :

$[NH_3] = b$ $\quad K_b$

$[NH_4^+] = S$

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

$$b-x \qquad\qquad\quad S+x \qquad x$$

$$\frac{x(S+x)}{b-x} = K_b \Rightarrow K_b = \frac{Sx}{b}$$

$$p^H = p^{Kw} - p^{Kb} - \log \frac{S}{b}$$

q For simple Buffer :

eg, $[NH_4^+ CN^-] = a$

$$p^H = \frac{1}{2}(p^{K_w} + p^{K_a} - p^{K_b})$$

q. Write expression of p^H for

a) $\underset{a}{NaH_2PO_4} + \underset{s}{Na_2HPO_4} \rightarrow p^H = p^{K_2} + \log\frac{s}{a}$

b) $\underset{a}{NaHCO_3} + \underset{s}{Na_2CO_3} \rightarrow p^H = p^{K_2} + \log\frac{s}{a}$

c) $\underset{a}{Na_2HPO_4} + \underset{s}{Na_3PO_4} \rightarrow p^H = p^{K_3} + \log\frac{s}{a}$

d) $\underset{a}{H_2CO_3} + \underset{s}{NaHCO_3} \rightarrow p^H = p^{K_1} + \log\frac{s}{a}$

q. Write expression of p^H for a sol. obtained by

a) 100 ml 0.1 M Na_3PO_4 + 50 ml 0.1 M HCl
b) 100 ml 0.1 M Na_3PO_4 + 100 ml 0.1 M HCl
c) 100 ml 0.1 M Na_3PO_4 + 150 ——
d) —〃—— + 200 ml —〃——
e) —〃— + 250 ml —〃—
f) —〃— + 300 ml —〃—
g) —〃— + 350 ml —〃—

a → $p^H = p^{K_3} + \log 5/5$
b → $p^H = \frac{1}{2}(p^{K_3} + p^{K_2})$
c → $p^H = p^{K_2} + \log 5/5$
a → $p^H = \frac{1}{2}(p^{K_2} + p^{K_1})$

e → $p^H = p^{K_1} + 0$
f → $p^H =$ ~~½~~ [illegible]
g →

Q. Calculate p^H of a solution obtained by mixing
i) 100 ml of 0.2 M CH_3COOH + 50 ml of 0.2M NaOH
ii) 100 ml of 0.2 M CH_3COOH + 100 ml of 0.2 M NaO
iii) 100 ml of 0.2 M CH_3COOH + 150 ml of 0.2 M NaOH
$(K_{a(CH_3COOH)} = 10^{-5})$

→ i) $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

CH_3COOH	$NaOH$	CH_3COONa	H_2O
20	10		
10	x	10	0

$p^H = 5$

ii) CH_3COONa ⑨
20

iii) $CH_3COONa \rightarrow 20$ $\Big\}$ $\frac{10}{250}$ 12.6
$NaOH \rightarrow 10$

Q. Find p^H of sol^n obtained by mixing

	H_2CO_3	Na_2CO_3		
a)	1 mol	1 mol	$K_1 = 10^{-6}$	6
b)	2 mol	1 mol	$K_2 = 10^{-10}$	~~7~~ 6
c)	1 mol	2 mol		~~9~~ 9

→ $\underset{1-x}{H_2CO_3}$ + ~~Na_2CO_3~~ $H_2O \longrightarrow \underset{x+y}{HCO_3^-} + \underset{x}{H_3O^+}$ - $\frac{(x+y)x}{1-x} = 1$

$\underset{1-y}{Na_2CO_3} + H_2O \longrightarrow \underset{x+y}{NaHCO_3} + Na^+ + \underset{y}{OH^-}$ $\frac{y(x+y)}{1-y} =$

$xy = 10^{-14}$
10^{-6} 10^{-8}

$\frac{1-x}{1-y} = 10^{2}$

Conclusion : From above ques. it is clear that in an aq. solⁿ only conjugate acid-base pair can exist

* Change in p^H of buffer :

1] Effect of addⁿ of SA/SB on p^H of buffer :

a) If we add x mol of HCl to 1 L Buffer

$$\left.\begin{array}{l}[CH_3COOH] = a \\ [CH_3COO^-] = s\end{array}\right\} p^H = p^{Ka} + \log\frac{s}{a}$$

$$\left.\begin{array}{ccccccc} CH_3COO^- & + & HCl & \longrightarrow & CH_3COOH & + & Cl^- \\ s & & x & & a & & \\ s-x & & 0 & & a+x & & \end{array}\right\} p^H = p^{Ka} + \log\frac{s-x}{a+x}$$

b) If we add x mol of NaOH

$$p^H = p^{Ka} + \log\frac{s+x}{a-x}$$

2] Effect of Dilution :

If a buffer is diluted to a small extent then its p^H will not change.
But if it is diluted to a large extent then its p^H will change & we cannot apply formula.

Q A buffer is prepared by mixing 1 mol of HCOOH with 1 mol of HCOONa in 1L solution calculate

$K_a = 10^{-4}$

a) p^H of sol.
b) p^H if it is diluted 10 times
c) p^H if it is diluted 10^4 times
d) p^H if 1/3 mol of HCl are added to 1L of sol.
e) p^H if 1/3 mol of NaOH " " " " " ".

a) → $p^H = 4$

b) → $p^H = 4$

d) → $p^H = 4 + \log \frac{2/3}{4/3} = 3.7$

e) → $p^H = 4 + \log \frac{4/3}{2/3} = 4.3$

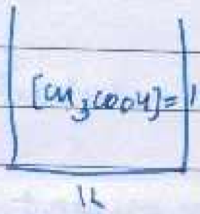
c) →
$$\underset{10^{-4}-x}{HCOOH} + H_2O \longrightarrow \underset{10^{-4}+x}{HCOO^-} + \underset{x}{H_3O^+}$$

$$\frac{(10^{-4}+x)x}{10^{-4}-x} = 10^{-4}$$

$$2\times10^{-4}x + x^2 = 10^{-8}$$

$$x \cancel{=} \cancel{10^{-4}} \frac{-2\times10^{-4} \pm 2\sqrt{2}\cdot10^{-4}}{2}$$

eg,



$$CH_3COOH + H_2O \longrightarrow (CH_3COO^-) + (H_3O^+)$$
$$CH_3COOH + CH_3COOH \rightarrow CH_3COO^- + CH_3COOH_2^+$$

Conditions for an effective Buffer,

- constituents of buffer should be present in large amount.

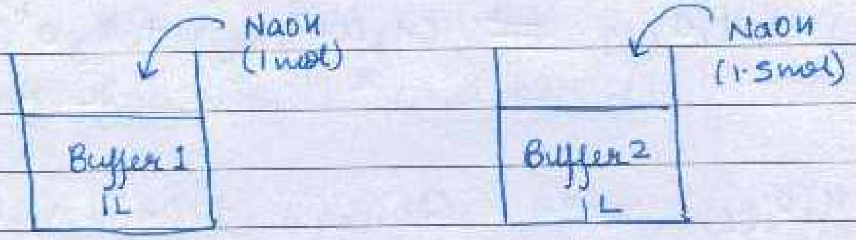
$$\frac{1}{10} \leq \frac{[Salt]}{[Acid]} \leq \frac{10}{1}$$

Q. True / False

1) p^H of acidic buffer at 25°C must be less than 7.
False.

- **Buffer Capacity :**

No. of moles of strong acid / base added to change p^H of 1L of buffer by unity.



p^{H_1}	$= 4$	4
p^{H_2}	$= 5$	5

$$BC = \frac{\text{no. of SA/SB added}}{\text{change in } p^H \text{ of buffer}}$$

$[Salt] + [acid] =$ constant
$a + s = c$

no. of moles of H^+/OH^- added = change in moles of salt

$$p^H = p^{Ka} + \log \frac{s}{a}$$

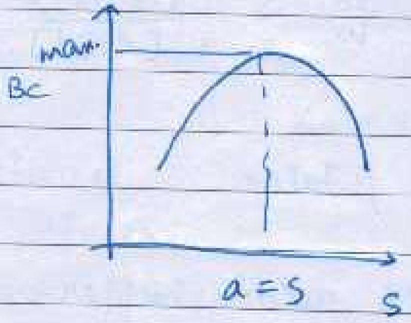
$$p^H = p^{Ka} + \log \frac{s}{c-s} \Rightarrow \frac{dp^H}{ds} = 0 + \frac{c-s}{s} \cdot \frac{c}{(c-s)^2} = \frac{c}{s(c-}$$

$$Bc = \frac{ds}{dp^H} = \frac{\Delta s}{\Delta p^H} = \frac{s(c-s)}{c}$$

$$\frac{d(Bc)}{ds} = c - 2s = 0$$

$$s = c/2$$

$$s = a = c/2$$



Q. Find p^H of

$[CH_3COOH] = a$ $[NaCN] = s$

$K_{a(CH_3COOH)}$ $K_{a(HCN)}$

→ $\cancel{CH_3COOH + NaCN = HCN + CH_3COONa}$

$\cancel{a-x}$ $\cancel{s+x}$ $\cancel{x}$ $\cancel{x}$

$$\underset{a-x}{CH_3COOH}(aq.) + H_2O(l) \rightleftharpoons \underset{x}{CH_3COO^-}(aq.) + \underset{x}{H_3O^+} \quad Ka_1$$

$$\underset{s-y}{CN^-}(aq.) + H_2O(l) \rightleftharpoons \underset{y}{CN^-}(aq.) + \underset{y}{OH^-} \quad K_h = \frac{K_w}{K_{a_2}}$$

<u>we assume</u>,

$x = y$ but $[H_3O^+] = [OH^-]$

$$\frac{Ka_1 Ka_2}{K_w} = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} \times \frac{[CN^-]}{[HCN][OH^-]}$$

$$\Rightarrow Ka_1 Ka_2 = \frac{s}{a} \times [H_3O^+]^2$$

$$CN^- + CH_3COOH \rightleftharpoons CH_3COO^- + HCN$$

$$HCN + H_2O(l) \rightleftharpoons CN^- + H_3O^+$$

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

* Solubility & Solubility products :-

- **Solubility** : Maximum amt. of substance that can be dissolved in specified amt. of solvent at a given temp.

OR

It is maximum no. of moles of a substance which can be dissolved in 1 L of solvent.

For ionic compounds

$$\underset{\underset{x}{1\,mol}}{NaCl_{(s)}} + water \rightarrow \underset{1}{Na^+_{(aq.)}} + \underset{1}{Cl^-_{(aq.)}}$$

For non-ionic compounds

$$C_6H_{12}O_{6\,(s)} + water \rightarrow C_6H_{12}O_{6\,(aq.)}$$

Sparingly soluble salt :

eg, $AgCl_{(s)}$, $BaSO_{4\,(s)}$, $CaCO_{3\,(s)}$

These are the substances which can dissolve to a very small extent.

$$AgCl_{(s)} \rightleftharpoons \underset{S(1-\alpha)}{AgCl_{(aq.)}} \qquad K_1 = S(1-\alpha)$$

$$\underset{S(1-\alpha)}{AgCl_{(aq.)}} \rightleftharpoons \underset{S\alpha}{Ag^+_{(aq.)}} + \underset{S\alpha}{Cl^-_{(aq.)}} \qquad K_2 = \frac{S\alpha^2}{1-\alpha}$$

$$AgCl_{(s)} \rightleftharpoons \underset{S\alpha}{Ag^+_{(aq.)}} + \underset{S\alpha}{Cl^-_{(aq.)}} \qquad K_{sp} = K_1K_2 = (S\alpha)^2$$

Due to very low solubility sol^n will be considered infinitely dilute

$$\alpha \approx 1$$

$$\underset{\text{solubility}}{\underset{\downarrow}{K_{sp}}} = s^2 = [Ag^+]_{aq} \cdot [Cl^-]_{aq}$$

Q. Write impression of K_{sp} for

i) $BaSO_{4}(s) \rightleftharpoons \underset{s}{Ba^{2+}} + \underset{s}{SO_4^{2-}}$ $\quad K_{sp} = [Ba^{2+}][SO_4^{2-}] = s^2$

ii) $CaF_2(s) \rightleftharpoons \underset{s}{Ca^{2+}} + \underset{2s}{2F^-}$ $\quad K_{sp} = [Ca^{2+}][F^-]^2 = 4s^3$

iii) $Ca_3(PO_4)_2(s) \rightleftharpoons \underset{3s}{3Ca^{2+}} + \underset{2s}{2PO_4^{3-}}$ $\quad K_{sp} = 4s^2 \times 27s^3$

iv) $CaCO_3(s) \rightleftharpoons \underset{s}{Ca^{2+}} + \underset{s}{CO_3^{2-}}$ $\quad K_{sp} = s^2$

v) $Ag_2CrO_4(s) \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{CrO_4^{2-}}$ $\quad K_{sp} = 4s^2 \times s$

Q. Solid Ag_2CrO_4 is dissolved and its solution is saturated. Find its solubility. $K_{sp} = 3.2 \times 10^{-11}$

→ $Ag_2CrO_4 \rightleftharpoons \underset{2s}{2Ag^+} + \underset{s}{CrO_4^{2-}}$

$$\Rightarrow 4s^3 = 3.2 \times 10^{-11}$$
$$s = 2 \times 10^{-4}$$

Q. Calculate the solubility product of AgCl if its saturated solⁿ 1.435 mg per litre

→ $M = 10^{-5}$

$K_{sp} = 10^{-10}$

Q. Calculate K_{sp} of PbI_2 if its saturated solⁿ contains 10^{-4} M I^- ions.

→ $\frac{1}{8} \times 10^{-4} \times 4 \times 10^{-8} = K_{sp} = 1/2 \times 10^{-12}$

Q. A particular saturated solution of Ag_2CrO_4 has $[Ag^+] = 5 \times 10^{-5}$ M & $[CrO_4^{2-}] = 4 \times 10^{-4}$ M. What is K_{sp} of Ag_2CrO_4.

→ $\frac{5}{2} \times 10^{-5} \times 4 \times 25 \times 10^{-10}$ / ~~2×10^{-8}~~ . — ×

2.5×10^{-13}

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$= 25 \times 10^{-10} \times 4 \times 10^{-4}$

$= 10^{-12}$

Q. What is the solubility of $Fe(OH)_3$ in aq. solⁿ of $p^H = 8$ $K_{sp} = 10^{-36}$

→ $Fe(OH)_3 \rightleftharpoons \underset{s}{Fe^{3+}} + \underset{10^{-6}}{3OH^-}$

$27 \times s^4 = 10^{-36}$

$s = \frac{1}{3} \times 10^{-6}$

* Application of Solubility product (K_{sp}) :→

- With the help of K_{sp} data we can predict whether pptⁿ will take place or not.

$AgCl_{(s)} \rightleftharpoons Ag^+_{(aq.)} + Cl^-_{(aq.)}$ $K_{sp} = [Ag^+]_{eq} [Cl^-]_{eq}$.
$IP = [Ag^+]_t [Cl^-]_t$

if $IP > K_{sp}$ ⇒ pptⁿ will take place
if $IP < K_{sp}$ ⇒ no pptⁿ will take place
if $K_{sp} = IP$ ⇒ Solution is saturated.

Q. 100 ml of 0.1 M $AgNO_3$ + 900 ml of 0.0001 M NaCl are mixed. Will pptⁿ take place?
$K_{sp} = 10^{-10}$

→ $AgNO_3 + NaCl \longrightarrow AgCl + NaNO_3$
$\quad 10 \qquad 0.09$
$\quad 9.91 \qquad \times \qquad 0.09 \qquad 0.09$

$IP = \frac{\overset{10}{\cancel{9.91}}}{1000} \times \frac{0.09}{1000} = 9 \times 10^{-7}$

As $IP > K_{sp}$ ⇒ pptⁿ will take place.

- K_{sp} data helps in prediction of sequence of pptⁿ or selective pptⁿ.

Q. To a solution which is 0.1 M in Cl^- ions & 0.01 M in CrO_4^{2-} find
a) Sequence of precipitation
b) conc. of already precipitating ion when other ion just starts pptⁿ
c) % of already precipitating ion, when other ion just start

d) Can 100% ion be precipitated.
$K_{sp}(AgCl) = 10^{-10}$ $K_{sp}(Ag_2CrO_4) = 10^{-12}$

a) → $Cl^- > CrO_4^{2-}$
b) → 10^{-5}
c) → 0.01%
d) → No

* Factors affecting solubility :

1) Common ion effect :

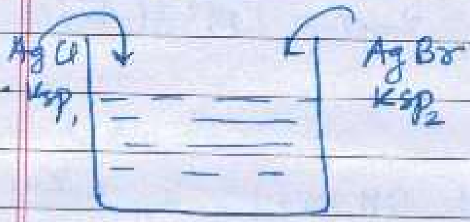
Q. Calculate solubility of MgF_2 ($K_{sp} = 3.2\times10^{-11}$)
a) in Pure water
b) in 0.1 M NaF

→ $MgF_2 \longrightarrow Mg^{2+} + 2F^-$ $K_{sp} = 3.2\times10^{-11}$
a) 2×10^{-4}
b) 3.2×10^{-9}

$(2s+10^{-1})^2(s) = 3.2\times10^{-}$

due to common ion effect, sol. of sparingly soluble salt will decrease.

Q.



→ $(S+x)x = K_{sp_1}$
$(S+x)S = K_{sp_2}$

2) **Effect of hydrolysis :**

due to hydrolysis, solubility will increase.

Note : In case if anion produced from sparingly soluble salt is conjugate base of weak acid or cation produced from salt is conjugate acid of weak base then hydrolysis will take place & solubility of salt will increase.

eg,

$$\underset{}{AgCN_{(s)}} \rightleftharpoons \underset{S}{Ag^+(aq)} + \underset{S-x}{CN^-(aq.)} \qquad K_{sp} = [Ag^+][CN^-]$$

$$\underset{S-x}{CN^-(aq.)} + H_2O(l) \rightleftharpoons \underset{x}{HCN(aq.)} + \underset{x}{OH^-(aq)} \qquad K_h = \frac{K_w}{K_a}$$

In above case solubility will ↓ on ↑ p^H.

In general,

$$MA_{(s)} \rightleftharpoons \underset{S}{M^+(aq.)} + \underset{S-x}{A^-(aq.)} \qquad K_{sp} = [M^+](A^-]$$

$$\underset{S-x}{A^-(aq.)} + H_2O(l) \rightleftharpoons \underset{x}{HA(aq.)} + \underset{x}{OH^-(aq)} \qquad K_h = \frac{K_w}{K_a}$$

$S = (S-x) + x$

$[M^+] = [A^-] + [HA]$

$= [A^-]\left(1 + \underline{K_w}\right)$

$$K_{sp} = \frac{[M^+][M^+]}{\left(1 + \frac{K_w}{K_a[OH^-]}\right)}$$

$$\Rightarrow S = \sqrt{K_{sp}\left(1+\frac{[H_3O^+]}{K_a}\right)}$$

Q. Calculate solubility of AgCN $(K_{sp} = 4\times10^{-16})$ in buffer of $p^H = 3$ $(K_{a\,(HCN)} = 9\times10^{-10})$

$$\rightarrow \quad S = \sqrt{4\times10^{-16}\left(1+\frac{10^{-3}}{9\times10^{-10}}\right)} = \frac{2}{3}\,10^{-9/2}$$

<u>M-II</u> :

$$\underset{}{AgCN} \rightleftharpoons \underset{S}{Ag^+} + \underset{S}{CN^-} \qquad K_{sp} =$$

$$\underset{S}{CN^-} + \underset{10^{-3}}{H_3O^+} \rightleftharpoons HCN + H_2O \qquad K = \frac{10^{10}}{9} = \frac{10^{-3}}{S-10^{-3}}$$

[illegible] [illegible] [illegible]

$x \quad 10^{-3} \quad S$

$x \quad 10^{-3} \quad S-x$

$$\frac{10^{10}}{9} = \frac{(S-x)}{x\times10^{-3}}$$

Q. p^H of a saturated sol^n of silver salt $(AgA_{(s)})$ of monobasic acid (HA) is found to be 9. Find K_{sp}. (given $K_a(HA) = 10^{-10}$]

$$\rightarrow \quad \underset{S-x}{A^-} + H_2O \longrightarrow \underset{x}{HA} + \underset{x}{OH^-} \qquad \Rightarrow \frac{x^2}{S-x} = 10^{-4}$$

$$2\times10^{-4} = S$$

$$\frac{4\times10^{-8}}{11}$$

3) Effect of complex formation :

When sparingly soluble salts are dissolved in solution containing lewis base then their solubility increases considerably

eg,

$$AgCl \rightleftharpoons \underset{x}{Ag^+_{(aq.)}} + \underset{s}{Cl^-_{(aq.)}} \qquad K_{sp} = sx$$

$$Ag^+_{(aq.)} + \ddot{N}H_3 \rightleftharpoons Ag(NH_3)^+_{(aq.)} \qquad K_1 = 2.1 \times 10^3$$

$$Ag(NH_3)^+ + \ddot{N}H_3 \rightleftharpoons Ag(NH_3)^+_2\ (aq.) \qquad K_2 = 8.1 \times 10^3$$

$$Ag^+_{(aq)} + 2\ddot{N}H_{3(aq)} \rightleftharpoons Ag(NH_3)^+_{2\,(aq)} \qquad K_f = K_1 K_2 = 1.7 \times 10^7$$

$s \qquad a$

$0 \qquad a-2s \qquad s$

$x \qquad a-2x+2x \qquad s-x$

larger the value of K_f, more will be stability of complex

$$K_f = \frac{(s-x)}{x(a-2s+2x)^2} = \frac{s}{xa^2}$$

$$K_{instability} = \frac{1}{K_f}$$

Q. Calculate the solubility of $AgCl_{(s)}$ in water ($K_{sp\,(AgCl)} = 10^{-10}$)

b) Cal. the sol. of AgCl in 2M NH_3 solⁿ.
$K_f = 10^7$

→ a) 10^{-5}

b) $\frac{s^2}{a^2} = 10^{-3}$

$s = 2 \times 10^{-3/2}$

Q. What are conc of $Ag^+(aq.)$, $Ag(NH_3)^+(aq.)$, $Ag(NH_3)_2^+$ in solⁿ prepared by mixing 0.1 mol of $AgNO_3$ to 1 L 3.2 M NH_3 (aq.)

$K_1 = 2\times10^3$ $K_2 = 8\times10^3$ $K_f = 16\times10^6$

→ $16\times10^6 = \frac{0.1}{x\times(3.2)^2}$ $\Rightarrow x = \frac{1}{16\times10^7\times10.24}$

$[Ag(NH_3)_2^{2+}] = 0.1\ M$ $\frac{1}{16\times10^7\times3.2}$ $2\times10^3 = \frac{y}{x\cdot s}$

$[Ag(NH_3)^+] = \frac{10^{-4}}{25.6}$

Q. 0.01 M, 500 ml $AgNO_3$ is mixed with 250 ml each NaBr & NaCl having molarity 0.02 M. Find $[Br^-]_{eq.}$ & $[Cl^-]_{eq.}$

$K_{sp}(AgBr) = 5\times10^{-13}$ $K_{sp}(AgCl) = 10^{-10}$

→ $\underset{x\ ~~5~~}{AgNO_3} + \underset{5-x}{NaBr} \longrightarrow \underset{x}{AgBr} + Na^+ + NO_3^-$ 206

$\underset{y}{AgNO_3} + \underset{5-y}{NaCl} \longrightarrow \underset{y}{AgCl} + Na^+ + NO_3^-$ 1000 ml

y. 5 mm Cl^- 200x
5 mm Br^-
5 mm Ag^+

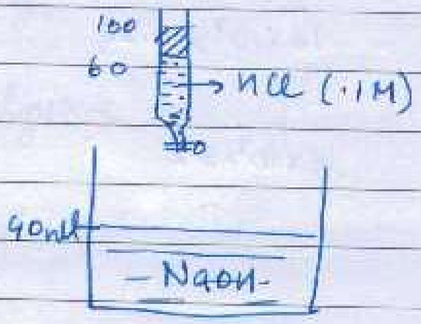
$[Br^-] = \frac{1}{200\times201}$ $\frac{5-x}{1000} = 200z$

$[Cl^-] = \frac{1}{201}$ $\frac{1}{200} - 200z$ $\frac{5-y}{1000} = z$; $x+y = 5$

$z =$

* Indicator Theory :

- **Titration** : It is the process of determination of conc. of unknown solⁿ with the help of known solⁿ.



$NaOH + HCl \longrightarrow NaCl + H_2O(l)$

$M_1V_1 =$ 4mm   4mm   4mm

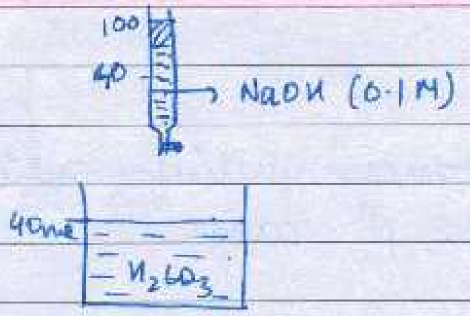
$M_1 = \frac{4}{40} = 0.1$

- **Equivalent point** : It is stage during titration at which a particular step of rxn has been completed.
It is also called stoichiometric point coz at this pt. Stiochiometric amt. of reactant reacts

- **End Point** : It is the pt at which all reactant has been consumed and there is no further scope for any rxn.
During titration there can be more than one equivalent points but there will be only one end point.

2 4 6 8

33, I, III B



$H_2CO_3 + NaOH \longrightarrow NaHCO_3 + H_2O\,(l)$ → I Eq. point

4   4   4

×   ×

$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O\,(l)$ → II Eq. pt. ~~or~~ end pt

4   4

×   ×   4

Q. Calculate p^H at equivalent point when 0.2 M $CH_3COOH_{(aq.)}$ is titrated against 0.2 M $NaOH_{(aq.)}$
[given : $K_a\,(CH_3COOH) = 10^{-5}$]

→ $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$ ⑤

0.2   0.2

×   × $\frac{0.2}{200}$

$\frac{\cancel{0.2}}{20}$ 20

$\cancel{\frac{10}{200}}$ $\frac{20}{300}$ $\frac{1}{15}$

$CH_3COONa + H_2O \longrightarrow CH_3COOH + OH^-$

$\frac{1}{15} - x$ x x

$$K_h = \frac{K_w}{K_a} = \frac{x^2}{\frac{1}{15} - x}$$

Q. Calculate p^H when 100 ml 0.1 M CH_3COOH is titrated against 0.1 M NaOH . when

a) 3
b) 4.6
c) 4.85
d) 9.5

$5 - \frac{2}{3}$

10   4

$\frac{12}{2}$ 10^6 4

10   10

10^{10}

$10^{-9} = \frac{x^2}{\frac{1}{20}}$ $\frac{10}{2000}$

1×10^{-10}

* Indicators :-

- These are the substances which exhibit diff. colours under diff. p^H range.

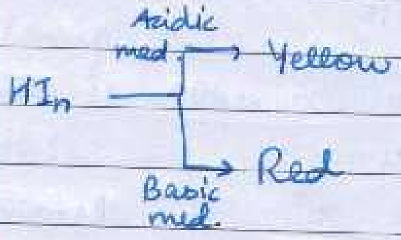
- Indicators are of two types :
  - i) acidic indicator (HIn)
  - ii) Basic indicator (I_nOH)

A] Acidic Indicator :

These are weak acids which exhibit diff. colours in dissociated form & undissociated form.

$$\underset{\text{Yellow}}{HI_n(aq.)} + H_2O(l) \rightleftharpoons H_3O^+(aq.) + \underset{\text{Red}}{I_n^-(aq.)}$$

$$K_{HI_n} = \frac{[H_3O^+][I_n^-]}{[HI_n]}$$



B] Basic Indicator :

$$\underset{\text{Green}}{I_nOH(aq.)} \rightleftharpoons \underset{\text{Violet}}{I_n^+(aq.)} + OH^-(aq. \qquad K_b = \frac{[I_n^+][OH^-]}{[I_nOH]}$$

It is a weak base which exhibits diff. colour in dissociated &

$$\text{InOH}\begin{cases}\xrightarrow{\text{acidic med.}} \text{Violet}\\ \xrightarrow{\text{Basic med.}} \text{green}\end{cases}$$

- **Detection Ratio :**

$$\underset{\text{Yellow}}{HIn_{(aq)}} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \underset{\text{Red}}{In^-_{(aq)}}$$

t=0	100	0	Y
t=t₁	90	10	Y
	60	40	O
	40	60	O
	10	90	R

$$K_{HIn} = \frac{[H_3O^+][In^-]}{[HIn]}$$

$$\Rightarrow [H_3O^+] = K_{HIn}\frac{[HIn]}{[In^-]}$$

$$p^H = p^{K_{In}} + \log\frac{[In^-]}{[HIn]}$$

if $\frac{[In^-]}{[HIn]} \geq 10 \Rightarrow \% [In^-] \approx 91\% \Rightarrow$ Red colour

if $\frac{[In^-]}{[HIn]} \leq \frac{1}{10} = 0.1 \Rightarrow \% [HIn] \approx 91\% \Rightarrow$ Yellow

if $0.1 \leq \frac{[In^-]}{[HIn]} \leq 10 \Rightarrow$ Transition range $\Rightarrow$ Orange

- **Transition range** : This is the p^H range in which an indicator changes its colour

$$p^H = p^{K_{In}} + \log\ [In^-]$$

Case I: if we add an indicator to a solⁿ having
$p^H = p^{K_{In}} - 1 \approx 2$ $(K_{In} = 10^{-3})$

$$p^H = p^{K_{In}} + \log \frac{[In^-]}{[HIn]}$$

$\Rightarrow \% [HIn] = 91\% \Rightarrow$ Yellow colour

Case II: if we add an indicator to a solⁿ having
$p^H = p^{K_{In}} + 1 \approx 4$

$$\frac{[In^-]}{[HIn]} = 10$$

$\Rightarrow \% [In^-] = 91\% \Rightarrow$ Red colour

[illegible]

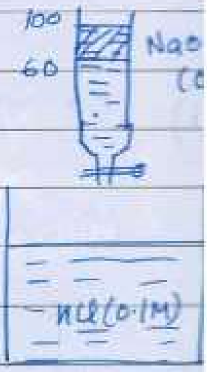
Sr. No.	Indicators	p^H range	color in acidic med.	color in basic med.
1.	Methyl Orange	3.1 – 4.4	Pink	Yellow
2.	Methyl Red	4.2 – 6.3	Red	Yellow
3.	Litmus	5.5 – 7.5	Red	Blue
4.	Phenol Red	6.8 – 8.4	Yellow	Red
5.	Phenolphthalene	8.5 – 10	Colourless	Pink
6.	Thymol Blue	1.2 – 2.8	Red	Yellow

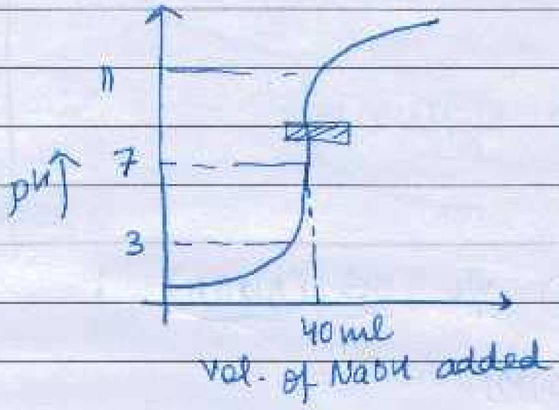
* Types of Titration :

i) SA v/s SB
ii) WA v/s SB
iii) SA v/s WB
iv) SB v/s SA
v) Polyprotic acid (H_2CO_3) v/s SB (NaOH)

A] SA v/s SB (Jump 3 to 11)

So. No.	Vol. of NaOH add.	Vol of soln	mm of H^+	$[H^+]$	pH
1	0	40	4	·1	1
2	10 ml	50	3	·06	1·2
3	10 ml	60	2	2/60	1·5
4	10 ml	70	1	1/70	1·8
5	9 ml	79	0·1	0·1/79	2·3
6	1 ml	80	—	—	7
7	1 ml	81	$[OH^-]=\cdot1$	0·1/81	11

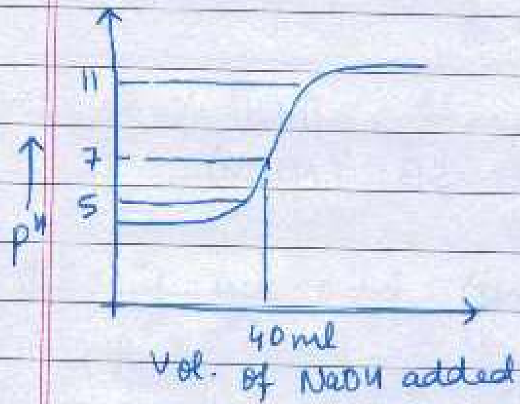




- We can use any indicator which lies on vertical line.
- ~~For~~ Best indicator
  pH at equivalent pt. = $p^{K_{In}}$ of indicator.

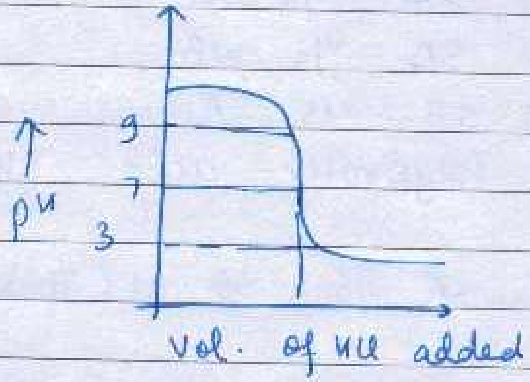
ii) WA v/s SB

(Jump 5 to 11)



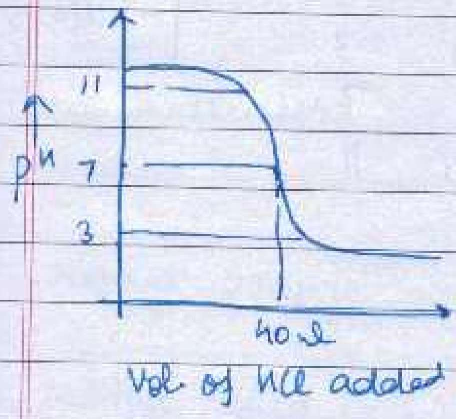
iv) WB v/s SA

(Jump 9 to 3)

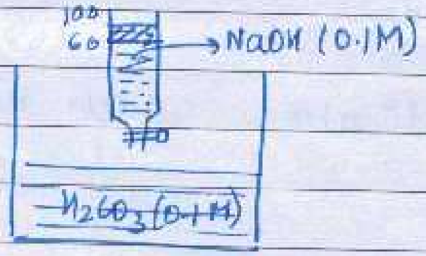


iii) SB v/s SA

(Jump 11 to 3)



v) Polyprotic Acid (H_2CO_3) v/s SB (NaOH) :

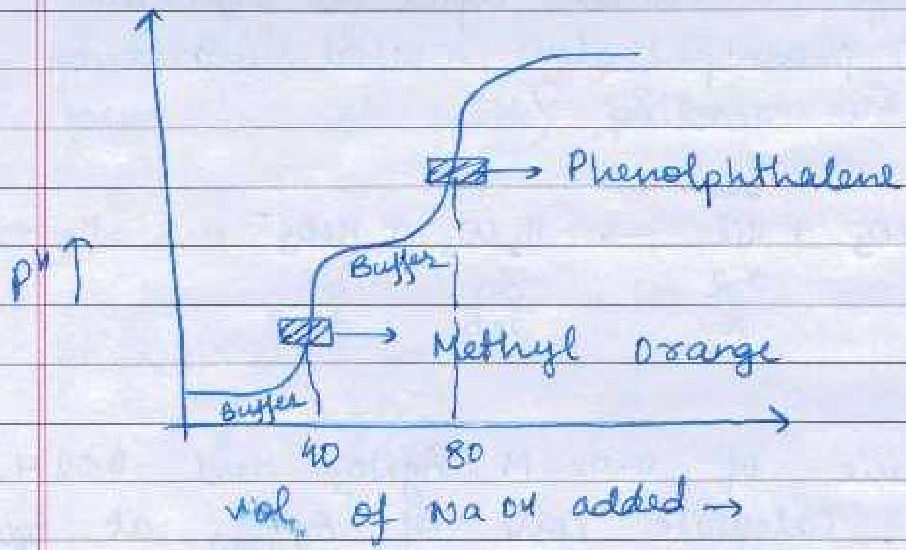


In presence of Methyl orange

$H_2CO_3 (aq.) + NaOH \longrightarrow NaHCO_3 + H_2O$

In presence of phenolphthalene

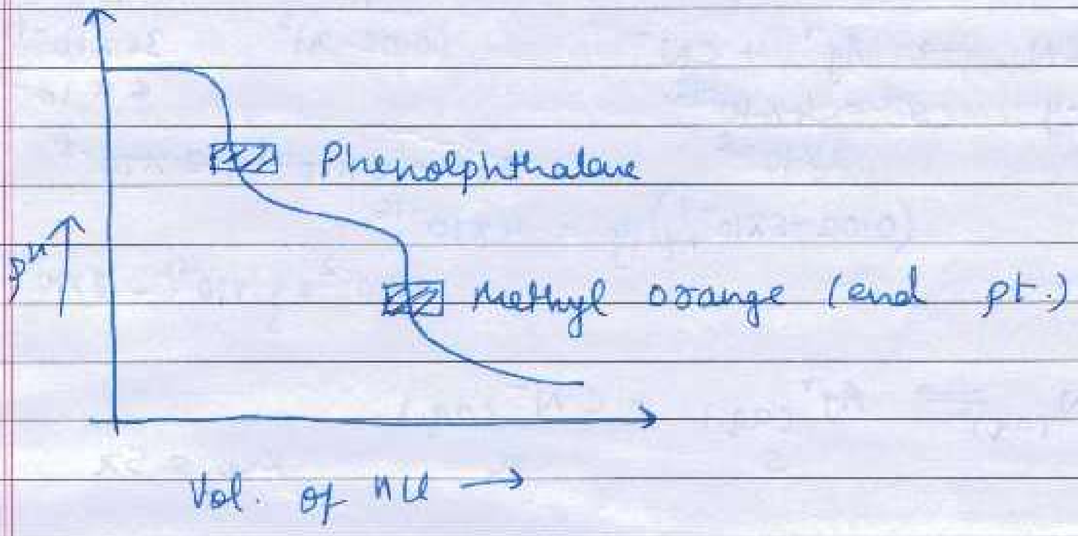
$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$



eg,

$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$

$NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$



Q. Water is added to a mixture containing 0.1 mol of Na_2CO_3 & $NaHCO_3$ each to make 50 ml solution. The solⁿ is titrated with 1 M HCl. What will be the titre reading if

a) Only phenolphthalene is used as indicator

10.

b) Only methyl orange is used as indicator 300

c) Methyl orange is added after I equivalent point with phenolphthalene. What would be 20 the change in reading ?

$\rightarrow$ $$Na_2CO_3 + NaHCO_3 + \overset{200ml}{HCl} \rightarrow H_2CO_3 + HCO_3^-$$

$$\frac{0.1}{\cancel{50}} \quad \frac{0.1}{5\cancel{0}} \quad 0.2 \quad \times \quad \frac{0.1}{200} \quad \frac{0.1}{200}$$

Q. Equal volume of 0.02 M $AgNO_3$ and 0.02 M H
were mixed. Calculate conc of $Ag^+_{(aq.)}$ at Equili
[Take $Ka_{(HCN)} = 9 \times 10^{-10}$ $K_{sp}\,(AgCN) = 4 \times 10^{-16}$]

$\rightarrow$ $$AgNO_3 + HCN \longrightarrow AgCN + HNO_3$$

$$0.02 - x \quad 0.02 - x \quad x \quad x$$

$$\times \quad \times \quad \frac{\cancel{0.02}}{\cancel{4}} \quad \cancel{0.02}$$

$$\frac{x^2}{(0.02 - x)^2} = 9 \times 10^{-10}$$

$$36 \times 10^{-14}$$

$$6 \times 10^{-7}$$

$$AgCN \longrightarrow Ag^+ + CN^-$$

$$x - y \qquad \cancel{s^2 = 4 \times 10^{-16}}$$

$$2 \times 10^{-8}$$

$$\cancel{0.02 - 6 \times 10^{-7} + 2 \times 10^{-8}}$$

$$(0.02 - 6 \times 10^{-7} + y)\, y = 4 \times 10^{-16}$$

$$2 \times 10^{-2} \times \frac{4}{3} \times 10^{-12} - 8 \times 10^{-14}$$

$$AgCN_{(aq.)} \rightleftharpoons Ag^+_{(aq.)} + CN^-_{(aq.)}$$

$$s \qquad x \qquad K_{sp} = sx$$

$$CN^-_{(aq.)} + H_3O^+ \rightleftharpoons HCN_{(aq)} \qquad K = \frac{10^{10}}{9} = \frac{s}{(.1)x}$$

$$s \qquad .1$$

$$\cancel{s} \qquad .1 - s \qquad s$$

$$x \qquad .1 - s + x \qquad s - \cancel{x} \rightarrow 0$$

Q. For the acid indicator Thymol blue, p^H is 2 when half of the indicator is in unionised form. Find the % of indicator in unionised form in sol^n with $[H^+] = 4 \times 10^{-3}$ M

→ $p^H = 2.4$

$2.4 = p^{H_{In}} + \log \frac{1}{2}$ ⇒ $p^{H_{In}} =$ [illegible] 2

$2.4 = 2 + \log$ ___

$\frac{4}{10} = \frac{[In^-]}{[HIn]}$ [illegible] $0.4 = \log \frac{[In^-]}{[HIn]} = \frac{4}{10}$

$\% \, [H_{In}] = \frac{200}{7}$