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CHAPTER-7
EQUILIBRIUM

In chemistry, all equilibrium are [dynamic equilibrium.]
[Rate of forward reaction = Rate of backward reaction]

Sign of equilibrium = $\rightleftharpoons$ or $\rightleftarrows$

At equilibrium → Temperature is constant
→ Partial Pressure is constant
→ Concentration constant

Equilibrium
- Physical Eqm
  (NO reaction)
  - $S \rightleftharpoons L$ (T is constant) M.P.
  - $L \rightleftharpoons G$ (B.P.)
  - $S \rightleftharpoons G$ (sublimation Point)
  - $A \rightleftharpoons A(aq)$ [dissolution].
- chemical Eqm.
  - Molecular chemical Eqm.
    (No Ion Involved)
    - $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
    - $CH_3COOCH_3 + H_2O \overset{H^+}{\rightleftharpoons} CH_3COOH + CH_3OH$
  - Ionic chemical eqm.
    (Ions Involved)
    - $CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$
    - $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Chemical Eqm.
- Homogenous Chemical Eqm.
  All Species in same phase
  1) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$
- Heterogneous Chemical Eqm.
  Atleast 2 different phase
  1) $H_2N-\overset{O}{\overset{\parallel}{C}}-O\,NH_4(s) \overset{\Delta}{\rightleftharpoons} 2NH_3(g) + CO_2(g)$
  (Ammonium Carbamate)
  2) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

* PHYSICAL EQUILIBRIUM.

1) Melting or Freezing

$S \rightleftharpoons L$ T is constant, conc. is constant

Partial Pressure (vapour Pressure is constant)

2) Boiling or Condensation

$L \rightleftharpoons G$ T, conc., VP is constant

3) sublimation or desublimation/deposition

$S \rightleftharpoons G$ T. conc. VP is constant

4) Saturation of solution.

T is constant. $A(s) \rightleftharpoons A(aq)$.

$\boxed{\text{Conc. is constant}}$

Saturated Solution At a particular temperature when no more solid is further dissolved or at a particular temperature solution having maximum amount of soluble substance is called saturated solution.

If we add more substance, it will remain as solid.

"NO MORE SOLID CAN BE DISSOLVED AT SAME TEMPERATURE".

When temperature is increased then more solid can be dissolved in a saturated solution. If at this higher temp. sol^n. reaches max solubility then this is called super saturated solution. If temp is brought to room temp then some solid will precipitate out.

* LAW OF MASS ACTION

According to this law, rate of chemical reaction is directly proportional to active masses of reactants raised to the power of their respective stoichiometric coefficients.

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

k_f Rate of forward reaction $\propto (a_A)^a (a_B)^b$

k_b Rate of reverse reaction $\propto (a_C)^c (a_D)^d$

Active masses of A, B, C, D are a_A, a_B, a_C, a_D.

$$\boxed{\text{active mass of substance} \simeq \text{Molarity of substance (for dilute solutions)}}$$

Active mass of solid substance or pure liquids are taken as unity (equal to 1) ...

if molar concentration of A, B, C & D are respectively [A] [B], [C], [D] so

$$\therefore R_f \propto [A]^a[B]^b \Rightarrow R_f = k_f [A]^a [B]^b$$
$$R_b \propto [C]^c [D]^d \Rightarrow R_b = k_b [C]^c [D]^d$$

where $\underbrace{k_f \text{ and } k_b}_{\text{small } k}$ are $\boxed{\text{rate constants}}$ of forward and backward direction

or
specific rate
or specific velocity

Rate constant of reaction is defined as the rate of reaction when molar concentration of all reactants equal to 1.

At equilibrium, $R_f = R_b$

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

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

New constant called Equilibrium constant K_{eq} or K [capital K]

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

Q when will eq^m reaction complete under normal conditions?

Equilibrium reaction never completes 100%.

$A(g) + 3B(g) \longrightarrow 2C(g) + D(g)$

t=0 $\quad 2 \quad 2 \quad 0 \quad 0$

eqm $\quad 2-x \quad 2-3x \quad 2x \quad x$

At eqm, moles of B = moles of C

$\Rightarrow 2-3x = 2x \Rightarrow x = 0.4$

equil moles $\quad 2-x = 1.6 \quad 2-3x = 0.8 \quad 2x = 0.8 \quad 0.4$

eqm molar concentration $\quad \frac{1.6}{2} = 0.8, \quad \frac{0.8}{2} = 0.4, \quad \frac{0.8}{2} = 0.4, \quad \frac{0.4}{2} = 0.2$

$$K_c = \frac{[C]^2[D]^1}{[A][B]^3} = \frac{\cancel{(0.4)^2} \times \cancel{0.2}}{0.8 \times \cancel{(0.4)^3}_2} = \frac{1}{1.6} = \boxed{0.625}$$

Q. $A(g) + 3B(g) \longrightarrow 2C(g) + D(g)$

initial concentration of A and B is 2 mol/litre. At eqm. concentr of B & C were found equal. Calculate value of K_c and % of B reacted?

$A(g) + 3B(g) \longrightarrow 2C(g) + D(g)$

t=0 $\quad 2\,\text{mol}\,l^{-1} \quad 2\,\text{mol}\,l^{-1} \quad 0 \quad 0$

eqm. $\quad 2-x \quad 2-3x \quad 2x \quad x$

At eqm. $[B] = [C]$

$\Rightarrow 2-3x = 2x \Rightarrow x = 0.4$

Concentraty $\quad 1.6 \quad 0.8 \quad 0.8 \quad 0.4$

$$K_c = \frac{[C]^2 [D]}{[A][B]^3} = \frac{\cancel{(0.8)^2}\, \cancel{(0.4)}}{1.6 \times \cancel{(0.8)^3}_2} = \frac{1}{2 \times 1.6} = \frac{1}{3.2}$$

$$= \boxed{0.3125}$$

% B reacted $= \frac{1.2}{2} \times 100 = \boxed{60\%}$

K_p calculation "we need partial pressure of each gaseous species".

1) Initial Moles are given

a) using initial moles calculate moles at eqm.

b) calculate total moles of gas at eqm.

c) Calculate mole fraction of each gaseous species.

d) using [Partial Pressure = mole fraction × Ptotal]

calculate partial pressures of all gases.

Put the value to calculate kp.

Q $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ at T K.

At eq^m total pressure was found to be 4 atm. If two moles of PCl_5 was initially taken and it shows 50% dissociation. calculate value of Kp.

	$PCl_5(g)$	$\rightleftharpoons$ $PCl_3(g)$ +	$Cl_2(g)$	
t = 0	2 mol	0	0	
eq^m	(2-1) = 1 mol (50% dissociation).	1 mol	1 mol	eq^m.
e fraction	1/3	1/3	1/3	
ial Pres.	4/3 atm	4/3 atm	4/3 atm	

$$K_p = \frac{(P_{PCl_3}) \times P_{Cl_2}}{P_{PCl_5}} = \frac{4/3 \times 4/3}{\cancel{4/3}} = \boxed{4/3}$$

Q Calculate Total pressure when 80% dissociation occurs at T K. (for above Question).

After 50% diss., n_{Total} = 3.

After 80% disso., PCl_5 = 2 − 1.6 = 0.4

PCl_3 = 1.6

Cl_2 = 1.6

} = 3.6

3 − 4

3.6 − $\frac{4 \times 3.6}{3}$ = ~~4.8~~

Kp = same.

mole fraction. $\frac{0.4}{3.6} = \frac{1}{9}$, $\frac{1.6}{3.6} = \frac{4}{9}$.

let new P_{Total} = P.

∴ Partial Pressure. P/9. 4P/9 4P/9

$$K_p = \frac{4P/9 \times 4P/\cancel{9}}{P/\cancel{9}} = \frac{\cancel{16}^{4}P}{\cancel{9}_{3}} = \frac{4}{3}$$

$$\Rightarrow \boxed{P = 3/4}$$

② If initial partial pressure is given :
using initial partial pressure, calculate value of Partial Pressure.
Put value of Partial Pressure to calculate K_p.

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

$t=0$ P_0 0 0

Partial Press. $P_0 - x$ x x

Q66. 15 mol H_2 5.2 mol I_2, attain eq^m. at 500°C. At eq^m. conc. of $HI = 10$ mol
eq. constant is →

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

$2x = 10$
$x = 5$

$t=0$ 15 5.2 0

eq^m. $(15-x)$ $(5.2-x)$ 10

$$K_{eq} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(10)^{\cancel{2}}}{\cancel{(10)}(0.2)} = \boxed{50}$$

* DEGREE OF DISSOCIATION (α)

It is defined as fraction of molecule dissociated per mole.

$$\alpha = \frac{\text{Moles dissociated}}{\text{Total moles taken (initial)}}$$

α ⇒ value lies b/w 0 to 1.

$\alpha = 0$ No dissociation $\alpha = 1$. 100% dissociation

$$\boxed{\alpha = \frac{\%\ \text{dissociation}}{100}}$$

* VAPOUR DENSITY RELATION WITH DEGREE OF DISSOCIATION →

$$A(g) \rightleftharpoons nB(g)$$

From one gas particle dissociation we get n gas particle.

$t=0$ 1 0

eq^m $1-\alpha$ $n\alpha$

At eq^m. total moles $= 1 - \alpha + n\alpha$.

Vapour density (VD) $= \frac{MW}{2}$

Suppose initial VD = D

eqm. VD = d

$$\boxed{\frac{D}{d} = 1-\alpha+n\alpha} \Rightarrow \frac{D}{d} - 1 = (n-1)\alpha$$

$$\Rightarrow \boxed{\alpha = \frac{D-d}{d(n-1)}}$$

Proof - ∵ density of gas = $\frac{\text{Mass}}{\text{Volume}}$

Volume ∝ moles of gas & mass is constant

$$D = \frac{M}{V_{initial}} = \frac{M}{mol_{initial}} = \frac{M}{1}$$

$$d = \frac{M}{V_{final}} = \frac{M}{mol_{final}} = \frac{M}{1-\alpha+n\alpha}$$

$$\therefore \boxed{\frac{D}{d} = 1-\alpha+n\alpha}$$

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

eqm VD = 100, then calculate α of PCl_5 if P & Cl atomic mass are 31 & 35.5.

$d = 100$ $\quad D = \frac{31+(35.5)5}{2} = \frac{31+177.5}{2} = \frac{208.5}{2}$

$\underline{n=2}$ $\quad \therefore \frac{D}{d} = 1-\alpha+2\alpha = 1+\alpha$

$$\Rightarrow \alpha = \frac{208.5}{200} - 1 = 1.0425 - 1$$

$$= \boxed{0.0425}$$

* LE CHATELIER'S PRINCIPLE

It states that whenever equilibrium is disturbed due to change in temperature, pressure, volume, etc., the reaction ~~equilibrium~~ tries to ~~adjust in such a manner~~ re-establish the state of equilibrium.

Effect of Temperature

$$\log K_{eq} = \frac{-\Delta H^\circ}{2.303\,RT} + \frac{\Delta S^\circ}{2.303\,R}$$

$$\boxed{\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]}$$ Van't Hoff Equation

where $K_2 = K_{eq}$ at T_2 K.
$K_1 = K_{eq}$ at T_1 K.

Endothermic Reaction $\Delta H = ⊕$	Exothermic Reaction $\Delta H = ⊖$
T↑ K_{eq}↑	T↑ K_{eq}↓
T↑ equil. shift $\longrightarrow$ forward direction	T↑ equil. shift ⟵

only temperature can change K_{eq}. K_{eq} doesn't change due to change in pressure, volume, Conc., catalyst, etc.

$A \longrightarrow B \quad \Delta H = -x \Rightarrow B \longrightarrow A \quad \Delta H = +x$.

Effect of Pressure Change

It affects only those eq^m which contains atleast 1 gaseous species.

$$nRT = PV \Rightarrow \overset{\text{Conc.}}{\left(\frac{n}{V}\right)} = \frac{P}{RT} \Rightarrow C = \frac{P}{RT} \Rightarrow C \propto P$$

P↑ ⇒ C↑ ⇒ Equilibrium shift to side with less moles of gas.

P↓ ⇒ C↓ ⇒ Equilibrium shifts to side with more moles of gas

eg. $\overbrace{N_2(g) + 3H_2(g)}^{4} \rightleftharpoons \overbrace{2NH_3(g)}^{2}$

P↑ ⟶ eq^m shift

eg $\underbrace{H_2(g) + Cl_2(g)}_{2} \rightleftharpoons \underbrace{2HCl(g)}_{2}$

P↓ ~~No shift~~ in concentration.

eg. $CaCO_3(s) \rightleftharpoons CaO(s) + \underbrace{CO_2(g)}_{1\,mol}$.

P↓ ⟶ eqm shift

eg $A(aq) \rightleftharpoons 2B(aq) + 3C(aq)$

No moles of gas ⇒ No effect of P change.

$$\overbrace{3A(aq)}^{\text{zero mole}} \rightleftharpoons \overbrace{B(aq) + 2C(g)}^{\text{2 mole}}$$

P↑ ← eqm shift.

Effect of Volume

It affects aqueous as well as gaseous equilibrium.

$conc = \frac{n}{v}$. $\boxed{conc \propto \frac{1}{vol}}$

vol↓ ⇒ conc↑ ⇒ eqm shifts to side with less moles

vol↑ ⇒ conc↓ ⇒ Eqm shifts to side with more moles.

eg. $$\overbrace{N_2(g) + 3H_2(g)}^{4} \rightleftharpoons \overbrace{2NH_3(g)}^{2}$$

V↑ ⇒ conc↓ ⇒ $\boxed{\leftarrow}$ eqm shift.

$$\overbrace{H_2(g) + Cl_2(g)}^{2} \rightleftharpoons \overbrace{2HCl(g)}^{2}$$

V↓ No shift.

zero $CaCO_3(s) \rightleftharpoons CaO(s) + \overset{1}{CO_2}(g)$

V↓ ⇒ conc↑ ⇒ $\boxed{\leftarrow \text{eqm shift}}$

$$\overbrace{A(aq)}^{1} \rightleftharpoons \overbrace{2B(aq) + 3C(aq)}^{5}$$

V↑ $\boxed{\rightarrow \text{eqm. shift}}$

$$\overbrace{3A(aq)}^{3\text{ mol.}} \rightleftharpoons \overbrace{B(aq) + 2C(g)}^{3\text{ mol}}$$

$\boxed{\text{No shift}}$

Effect of change in concentration

	eqm. shift
Reactant added	→
Reactant removed	←
Product added	←
Product removed	→

Effect of catalyst

catalyst doesn't affect equilibrium. It only decreases time to reach equilibrium.

It decreases Activation Energy of reaction.

catalyst increases K_f and K_b by same factor.

Addition of Inert Gases → gases that don't participate in rxn.

a) addition of inert gas at constant volume.

conc. is constant ∵ V is constant

⇒ No effect on equil.

b) addition of inert gas at Constant Pressure.

As inert gas at constant P and T will increase volume.

∴ conc ↓.

∴ Rxn. goes in direction having more moles.

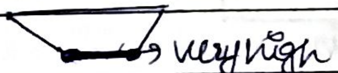
only applicable for gaseous reaction.

$Q > K_{eq}$ ← (eqm shift)

$Q = K_{eq}$ No shift.

$Q < K_{eq}$ → (eqm shift)

Ice skating shoes.



Ice water

$H_2O(s) \rightleftharpoons H_2O(l)$

If P↑ $\rightarrow$

⇓

eqm shift.

* ANY REACTION INVOLVING GAS CAN ONLY ATTAIN EQUILIBRIUM IN A CLOSED VESSEL.

* THEORY OF ACIDS AND BASES.

1. ARRHENIUS Acid - Base Theory

Arrhenius acid are substance that can give H^+ ions in aqueous solution. eg - HCl, HNO_3, H_2SO_4, H_3PO_4, ~~H_3BO_3~~, ~~SO_2~~	Arrhenius bases are species that can give $\bar{O}H$ ions in aqueous solⁿ. eg - NaOH, KOH, $Ca(OH)_2$, ~~$B(OH)_3$~~, NH_4OH, ~~NH_3~~, ~~Na_2O~~ Boric Acid (H_3BO_3).

2. BRONSTED LOWRY Acid Base Theory

B.L. Acid = $\boxed{H^+ \text{ donor}}$ in their aqueous solution.	B.L. Base - $\boxed{H^+ \text{ acceptor}}$ in aqueous sol.
eg. same as Arrhenius Acid.	eg All arrhenius base + Some more examples like NH_3, H_2O, etc. which can accept H^+.
$\underbrace{H_2\ddot{O}: + H^+ \longrightarrow H_3O^+}_{\text{conjugate Acid \& Base pair}}$	$\underbrace{\ddot{N}H_3 + H^+ \longrightarrow \overset{\oplus}{N}H_4}_{\text{Conjugate Acid Base pair}}$

CONJUGATE ACID BASE PAIR.

Conjugate acid & conjugate base pair $\boxed{\text{differ by one } H^\oplus}$

$$\overset{\text{CA of } Cl^\ominus}{HCl} + \overset{\text{CB of } H_3O^+}{H_2O} \rightleftharpoons \overset{\text{CA of } H_2O}{H_3O^+} + \overset{\text{CB of HCl}}{Cl^-}$$

$\boxed{\text{conjugate Acid-Base}}$ Pair

Conjugate acid base pair

Conjugate Acid (CA) of species A = A + H^+ = AH^+

Conjugate Base (CB) of species B = $BH - H^+$ = $B^\ominus$.

eg. Phosphoric Acid

$$\underset{\left(\substack{\text{CA of}\\ H_2PO_4^-}\right)}{H_3PO_4} \xrightleftharpoons{-H^+} \underset{\left(\substack{\text{CB of}\\ H_3PO_4}\right) \text{ or } \left(\substack{\text{CA of}\\ HPO_4^{2-}}\right)}{H_2PO_4^-} \xrightleftharpoons{-H^+} \underset{(\text{CA of } PO_4^{3-}) \text{ or } (\text{CB of } H_2PO_4^-)}{HPO_4^{2-}} \xrightleftharpoons{-H^+} \underset{(\text{CB of } HPO_4^{2-})}{PO_4^{3-}}$$

Carbonic Acid $H_2CO_3 \underset{}{\overset{-H^+}{\rightleftharpoons}} HCO_3^- \overset{-H^+}{\rightleftharpoons} CO_3^{2-}$

(CA of HCO_3^-) (CB of H_2CO_3)

or (CA of CO_3^{2-}) (CB of HCO_3^-)

Amphoteric species can behave as acid as well as base.

eg. $H_2PO_4^-$, HPO_4^{2-}, HCO_3^- etc.

Important rules

1. conjugate Base of strong ~~base~~ acid will be weak base & vice versa.
2. conjugate Acid of strong base will be weak acid & vice versa.

Q. Predict order of Basic nature →

i) $F^\ominus > Cl^\ominus > Br^\ominus > I^\ominus$ (HI is strongest acid) } acidic character increases down the group → Bond length increases → strength decreases → easy to give H^+

ii) $\overset{\ominus}{C}H_3$ $\overset{\ominus}{N}H_2$ $\overset{\ominus}{O}H$ $F^\ominus$

$CH_4 \longrightarrow \overset{\ominus}{C}H_3 + H^\oplus$

$NH_3 \longrightarrow \overset{\ominus}{N}H_2 + H^\oplus$

$H_2O \longrightarrow \overset{\ominus}{O}H + H^\oplus$

$H\text{-}F \longrightarrow H^\oplus + F^\ominus$

$F^\ominus < \overset{\ominus}{O}H < \overset{\ominus}{N}H_2 < \overset{\ominus}{C}H_3$

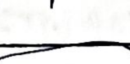
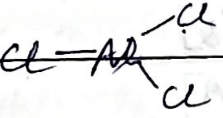
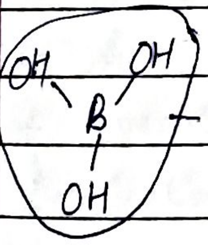
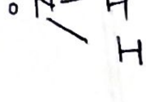
Q. Predict acidic nature order.

H_3O^+ NH_4^+ $CH_3-\overset{\oplus}{N}H_3$

Basic Nature of $H_2O < NH_3 < CH_3NH_2$.

$\Rightarrow$ Acidic of $H_3O^+ > NH_4^\oplus > CH_3\text{-}\overset{\oplus}{N}H_3$

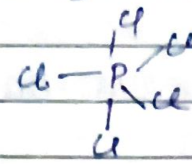
3. LEWIS ACID BASE THEORY:

Lewis Acid	Lewis Base
are e^- pair acceptors.	are $\boxed{e^- \text{ pair}}$ donors.
eg ⇒  , F-Be-F  } central atom with Incomplete octet	eg. all anions. $:\ddot{Cl}:^-$, Br^-, $\overset{\ominus}{O}H$, $\overset{\ominus}{N}H_2$, PO_4^{3-}, etc. All species with 8 or more electron & have atleast one e^- pair on Central Atom.
	eg. $H-\ddot{\underset{..}{O}}-H$, 

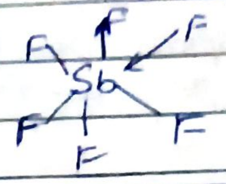
Ag^+ Cu^+ Zn^{2+}, etc can accept e^- in vacant d orbitals

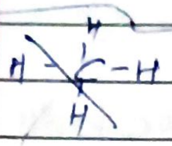
CO_2, SO_2, SO_3, etc. O=C=O ⟷ $\overset{\ominus}{O}-\overset{\oplus}{C}=O$ ↳ only 6e⁻

SbF_5, PCl_5, etc.



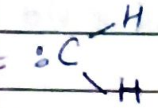
$SbF_5 + F^{\ominus} \longrightarrow SbF_6^{\ominus}$





is not Lewis base as it has no lonepair

Carbene



is not Lewis base. e^- lone pair present but octet isn't complete.

Non metal oxides ⇒ generally acid

but N_2O, NO, CO are neutral.

* VARIATION OF K(Eq) during multiplication, division, etc. operations

multiplication or division by any number

$A \rightleftharpoons B$. $K_1 = \frac{[B]}{[A]}$ — ①

Multiply eqn ① by n.

$nA \rightleftharpoons nB$. $K_2 = \frac{[B]^n}{[A]^n} = \left(\frac{[B]}{[A]}\right)^n = (K_1)^n$.

$\therefore \boxed{K_2 = (K_1)^n}$

Whenever eqm ~~eqn~~ multiplied by 'n' new K_{eq} ~~eq~~ = (old K_{eq})^n

dition of ve eqm

$A \rightleftharpoons B$ $K_1 = \frac{[B]}{[A]}$

$P \rightleftharpoons Q$ $K_2 = \frac{[Q]}{[P]}$

Product of old Keq

$A+P \rightleftharpoons B+Q$ $K_{new} = \frac{[B][Q]}{[P][A]}$

$\boxed{K_{new} = K_1 \times K_2}$

[illegible] eq^m

$A \rightleftharpoons B \quad \left(K_1 = \frac{[B]}{[A]}\right)$

$P \rightleftharpoons Q \quad \left(K_3 = \frac{[Q]}{[P]}\right)$

$\Rightarrow A + Q \rightleftharpoons P + B \qquad K_{new} = \frac{[B][P]}{[A][Q]}$

$= \boxed{K_1/K_3}$

$K_{new} = \frac{K_{old}}{K_{old} \text{ of subtracted } eq^m}$.

If reaction is reversed $\boxed{K_{new} = \frac{1}{K_{old}}}$

$A \rightleftharpoons B \; (K_1) \quad K_1 = \frac{[B]}{[A]}$. $\qquad B \rightleftharpoons A \quad K_{new} = \frac{[A]}{[B]} = \frac{1}{K_1}$.

eg $Rxn_4 = Rxn_1 + \frac{1}{2} Rxn_2 - 3 Rxn_3$

$\Rightarrow \boxed{K_4 = \frac{K_1 \cdot K_2^{1/2}}{K_3^{3}}}$

* Electrolytes Species that conduct electricity either in molten or aqueous solution or both.

Strong electrolyte
'complete ionisation'
eg HCl, HNO_3, H_2SO_4.
$NaOH$, KOH, $NaCl$, Na_2SO_4.

Weak electrolyte
incomplete ionisation.
eg HCN, H_3PO_4, CH_3COOH,
H_2CO_3, $HCOOH$.
$NH_3(aq) = NH_4OH(aq)$
$PbCl_2$.

Note: water is almost non-electrolyte.

* OSTWALD'S DILUTION LAW of WEAK ELECTROLYTE.
As per this law, on dilution or decrease in concentration of weak electrolyte, its degree of dissociation (α) or ionisation increases.

Suppose AB is a weak electrolyte ~~(weak acid)~~.

$$AB(s) + H_2O \rightleftharpoons A^+(aq) + B^-(aq)$$

$$\Rightarrow AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$$

Suppose initial concentration of AB (weak electrolyte) = c

& degree of dissociation = α

$$\begin{array}{llll} t=0 & c & 0 & 0 \\ eqm & c(1-\alpha) & \alpha & \alpha \end{array}$$

$$K_{eq} = \frac{[A^+][B^+]}{[AB]}$$

$$\Rightarrow K_{eq} = \frac{c\alpha\, c\alpha}{\cancel{c}(1-\alpha)} = \boxed{\frac{c\alpha^2}{1-\alpha}}$$

Suppose $\alpha << 1$, $1-\alpha \simeq 1$

$$K_{eq} \simeq c\alpha^2$$

$$\Rightarrow \boxed{\alpha = \sqrt{\frac{K_{eq}}{c}}}$$

dilution $c\downarrow \Rightarrow \alpha\uparrow$

Weak Monoprotic Acid (weak acid that can give 1 H^+).

$$HA(aq) + H_2O(l) \rightleftharpoons H^+(aq) + A^-(aq).$$

$$\begin{array}{llll} t=0 & c & 0 & 0 \\ equi. & c(1-\alpha) & c\alpha & c\alpha . \end{array}$$

$$K_{eq} = \frac{[H^+][A^-]}{[HA][H_2O]}.$$

As H_2O is in large excess. Amount of H_2O almost constant.

∴ $[H_2O]$ constant = 55.55 mol l^{-1}.

$$\underbrace{K_{eq}[H_2O]}_{\text{New constant}} = \frac{[H^+][A^-]}{[HA]}.$$

$$\boxed{K_a = \frac{[H^+][A^-]}{[HA]}}$$

Dissociation or ionisation constant of weak Acid.

$$K_a = \frac{\cancel{c}\alpha \cdot c\alpha}{\cancel{c}(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

when $\alpha << 1$, $1-\alpha \simeq 1$

$$K_a \simeq c\alpha^2$$

$$\rightarrow \boxed{\alpha \simeq \sqrt{\frac{K_a}{c}}}$$

for weak monoprotic acid $\leftarrow$ $[H^+] = c\alpha$

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

$\boxed{pK_a = -\log K_a}$

Note $\boxed{\begin{array}{l} pH = -\log[H^+] \\ pOH = 14 - pH \quad (\text{at } 25^\circ C) \end{array}}$

stronger acid. $K_a \uparrow \Rightarrow pK_a \downarrow$

ASSIGNMENT ~~set~~ level 1:

1. which reaction almost completes:

$A + B \rightleftharpoons C$ ✓ Because $K = 10^4$.

2. At constant pressure, addition of Argon in Haber's process

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

add Ar. $\Rightarrow$ Volume increases $\Rightarrow$ concentration $\downarrow$.

$\Rightarrow$ shifts toward ~~less~~ more moles $\Rightarrow$ NH_3 formation reduced.

3. $A(s) \rightleftharpoons 2B(g) + 3C(g)$.

$[C]$ at eqm is doubled, after eqm re established, conc. of B will be $\rightarrow$

K_c = constant $\Rightarrow [C]_i^3[B]_i^2 = [C]_f^3[B]_f^2$

$$\Rightarrow [C]^3[B]_i^2 = (2[C])^3[B]_f^2 \Rightarrow [B_f]^2 = [B]^2/8$$

$$\Rightarrow [B_f] = 2\sqrt{2}[B]$$

$$[B_f] = \boxed{\frac{[B]}{2\sqrt{2}}}$$

$\boxed{P_2 = 2.4\,\text{atm}}$

* pH. (continuous) →:

$$pH = -\log[H^+] = -\log(c\alpha)$$

$$\Rightarrow \boxed{pH = -\log\sqrt{K_a \cdot c}}$$

$$pH = -\log(K_a \cdot c)^{1/2}$$

$$pH = \frac{1}{2}\left[-\log K_a - \log c\right]$$

$$\boxed{pH = \frac{1}{2}\left[pK_a - \log c\right]} \quad (pK_a = -\log K_a).$$

for same concentration (c), strong Acid will have

$$\boxed{\begin{array}{l} \rightarrow \text{more } [H^+] \\ \Rightarrow \text{higher } K_a \\ \Rightarrow \text{lower } pK_a \end{array}}$$

* WEAK MONOACIDIC BASE:

$$BOH \rightleftharpoons B^+(aq) + \bar{O}H\,(aq)$$

$t=0$. $\quad c \quad\quad 0 \quad\quad 0$

equilibrium $\quad c(1-\alpha) \quad\quad c\alpha \quad\quad c\alpha$

Dissociation constant of weak base $\Rightarrow K_b = \dfrac{c\alpha^2}{1-\alpha}$.

$\alpha << 1 \Rightarrow 1-\alpha \simeq 1$.

$\therefore K_b = c\alpha^2 \Rightarrow \boxed{\alpha \simeq \sqrt{\frac{K_b}{c}}}$

$[OH^-] = c\alpha$.

Put $\alpha \simeq \sqrt{\frac{K_b}{c}}$

$$\Rightarrow \boxed{[OH^-] \simeq \sqrt{K_b \cdot c}}$$

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

$$\boxed{pOH = -\log(c\alpha)}$$

$$\boxed{pOH = -\log\sqrt{K_b \cdot c}}$$

$$= -\log(K_b \cdot c)^{1/2}$$

$$= \frac{1}{2}(-\log K_b - \log c)$$

$$\Rightarrow \boxed{pOH = \frac{1}{2}(pK_b - \log c)} \quad pK_b = -\log K_b.$$

At 25°C $pH + pOH = 14$

$$\Rightarrow \boxed{pH = 14 - pOH}.$$

for same concentration; stronger base will have →

$\rightarrow$ more $[\bar{O}H]$
$\rightarrow$ Higher K_b
$\rightarrow$ lower pK$_b$

Q. calculate pH of following sol. at 25°C.

1) HCl. 0.01M. $= -\log[H^+] = -\log[0.01] = \boxed{2}$
2) 0.01M H_2SO_4 $= -\log[H^+] = \boxed{-\log[0.02]} = \boxed{1.7}$
3) 0.01M CH_3COOH $(pK_a = 4.74) = \frac{1}{2}(4.74 + 2) = \boxed{3.37}$
4) 0.04M NH_4OH $(pK_b = 4.8)$ $= 14 - \frac{1}{2}(4.8 - \log 0.04) = \boxed{10.9}$
5) 0.01M NaOH $14 - (-\log[OH^-]) = 14 - (-\log(0.01)) = \boxed{12}$.
6) 0.01 M $Ca(OH)_2$. $14 - (-\log[\bar{O}H]) = \boxed{14 - (-\log(0.02))} = \boxed{12.3}$

7) 100 ml 0.01 M HCl + 100 ml 0.01 M H_2SO_4

$$\Rightarrow [H^+] = \frac{0.01 \times 100 + 0.01 \times 2 \times 100}{200} = \left(\frac{3}{200}\right).$$

$$pH = -\log(3/200) = -(\log 3 - \log 200)$$
$$= -(0.48 - 2.3) = 2.3 - 0.48$$
$$= \boxed{1.82}$$

8) 100 ml 0.01 M NaOH + 100 ml 0.01 M $Ca(OH)_2$.

$$[\bar{O}H] = \frac{0.01 \times 100 + 0.01 \times 2 \times 100}{200} = 3/200.$$

$$\therefore pOH = -\log[\bar{O}H] = 1.82$$
$$\therefore pH = 14 - 1.82 = \boxed{12.18}$$

9) 100 ml 0.01 M HCl + 100 ml 0.01M $Ca(OH)_2$
meq = 1. meq = 100 × 0.02 = 2.

$$\therefore [OH^-] = \frac{2 - 1}{200} = \frac{1}{200}.$$

$$pOH = -\log[\bar{O}H]$$
$$= -\log(1/200)$$
$$= -\underset{0}{\cancel{\log 1}} + \log 200$$
$$= \log 2 + \log 100$$
$$= 0.3 + 2 = 2.3$$

$\therefore$ $pH = 14 - 2.3 = \boxed{11.7}$.

10. 100 ml 0.01 M H_2SO_4 + 100 ml 0.01 M NaOH

Meq = 2   Meq = 1.

$$\therefore [H^+] = \frac{2-1}{200} = \frac{1}{200}$$

$$pH = -\log(1/200) = \boxed{2.3}$$

11. which has highest pK_b?

F^- Cl^- Br^- I^- ✓

HI = strong acid ⇒ I^- = weak base ⇒ $\boxed{\text{highest } pK_b}$

HF = weak ⇒ F^- = strong base

highest pK_b.

12. Higher pKa among H_2O and H_2S?

H_2S – stronger acid ⇒ Higher pKa.

✓ H_2O – weak acid ⇒ $\boxed{\text{Higher pKa}}$

* for strong Acid

$[H^+] = n_f \times M_{acid} = N_{acid}$.

Mixture of strong acids $= \dfrac{n_1M_1V_1 + n_2M_2V_2}{V_1 + V_2}$.

n_1 & n_2 = n_f of Acid 1 & Acid 2

M_1 & M_2 = Molarity of Acid 1 & Acid 2.

V_1 & V_2 = Volume of Acid 1 and Acid 2

* for strong base

$[OH^-] = n_f \times M_{base} = N_{base}$.

Mixture of strong bases, $[OH^-] = \frac{n_1M_1V_1 + n_2M_2V_2}{V_1+V_2}$

n_1 and n_2 = n_f of Base 1 & Base 2

V_1 and V_2 = Volume of Base 1 & Base 2

M_1 and M_2 Molarity of Base 1 & Base 2.

when Strong Acid & strong base is mixed -

Case 1. Meq Acid = Meq Base

$[H^+] = [OH^-] \Rightarrow pH = pOH = 7$.

Case 2. Meq Acid > Meq Base

Acid will be finally left

$[H^+] = \frac{\text{Meq Acid} - \text{Meq Base}}{V_1+V_2}$

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

Case 3 Meq Acid < Meq Base

Base will be finally left.

$[OH^-] = \frac{\text{Meq Base} - \text{Meq Acid}}{V_1+V_2}$.

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

$\Rightarrow pH = 14 - pOH$.

At 25°C.

pH of Base > 7
pH of Acid < 7
pH of neutral = 7

Date
Page

* DISSOCIATION CONSTANT OF WATER Kw

Water undergoes auto ionisation or self ionisation.

$$2H_2O \rightleftharpoons H_3O^+ + \bar{O}H$$

$$H_2O(l) \rightleftharpoons H^+(aq) + \bar{O}H(aq)$$

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

$$\Rightarrow K_{eq}[H_2O] = [H^+][\bar{O}H].$$

$$[H_2O] = \text{constant} = 55.56$$

$$\Rightarrow K_{eq}[H_2O] = \text{New constant called } K_w.$$

$$\Rightarrow \boxed{K_w = K_{eq}[H_2O]}$$

$$\boxed{K_w = [H^+][\bar{O}H]}$$

Experimentally it was found that $\boxed{\text{at } 25°C}$ from H_2O we get $[H^+] = 10^{-7}\,M$ $[\bar{O}H] = 10^{-7}\,M.$

$$\Rightarrow K_w = [H^+][\bar{O}H]$$

$$\Rightarrow K_w = 10^{-7} \times 10^{-7}.$$

$$\Rightarrow \boxed{K_w = 10^{-14}} \text{ at } 25°C.$$

$$-\log K_w = pK_w.$$

$$pK_w = -\log 10^{-14}.$$

$$\boxed{pK_w = 14} \text{ at } 25°C.$$

Now, $K_w = [H^+][\bar{O}H]$

Taking log both sides

$$\log K_w = \log[H^+] + \log[\bar{O}H].$$

$$\Rightarrow -\log K_w = -\log[H^+] + (-\log[\bar{O}H])$$

$$\Rightarrow \boxed{pK_w = pH + pOH}$$

$$\boxed{14 = pH + pOH}. \text{ at } 25°C.$$

At 25°C, $[H^+][\bar{O}H] = K_w = 10^{-14}$

$$\Rightarrow \boxed{[H^+] = \frac{10^{-14}}{[OH^-]}} \text{ and } \boxed{[\bar{O}H] = \frac{10^{-14}}{[H^+]}}$$

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

$$pOH = -\log[\bar{O}H] \Rightarrow \boxed{[\bar{O}H] = 10^{-pOH}}$$

* pH scale

pH scale = 0 to pK_w.
Neutral pH = $\frac{pK_w}{2}$

At 25° C, $pK_w = 14$.
⇒ at 25°C, pH scale = 0 to 14.
neutral pH = $14/2 = \boxed{7}$

pH scale at 25°C.

$[H^+] = 1$	$[H^+] = 7$	$[H^+] = 10^{-14}$
$[\bar{O}H] = 10^{-14}$.	$[\bar{O}H] = 7$	$[\bar{O}H] = 1$
pH = 0	pH = 7	pH = 14
pOH = 14.	pOH = 7	pOH = 0
$[H^+] > [\bar{O}H]$ Acidic solution pH < 7 ; pOH > 7	⇓ Neutral solution ⇒ $[H^+] = [\bar{O}H]$	Basic solution $[\bar{O}H] > [H^+]$ pH > 7 pOH < 7.

At T > 25°C. Suppose $K_w = 10^{-13}$.
$pK_w = 13$ ⇒ Neutral pH = $\frac{pK_w}{2} = \frac{13}{2} = 6.5$.

* Pure water is always neutral at whatever temperature because $[\bar{O}H] = [H^+]$.

Q. pH = 2 find $[\bar{O}H]$
Acidic solution. pOH = 14 − 2 = 12.
∴ 12 = − log $[\bar{O}H]$ ⇒ $\boxed{[\bar{O}H] = 10^{-12}}$

H.W. Q. Calculate the pH of

i) 10^{-8} M HCl
ii) 10^{-7} M HCl
iii) 10^{-8} M NaOH
iv) Final pH when equal volume of solutions pH = 2 and pH = 3 are mixed.

I If temperature is more than 25°C. then

i) value of $K_w > 10^{-14}$ [Ionisation increases on increasing temperature]

ii) $pK_w < 10^{-14}$

iii) Neutral solⁿ $pH = \frac{pK_w}{2} < 7$

iv) pH of pure water. < 7

* Important Point.

In Aqueous solution at 25°C, 10^{-7} M H^+ and 10^{-7} OH^- form water.

∴ Always $[H^+]_{total} = [H^+]_{acid} + [H^+]_{water}$.

$[H^+]_{total} = [H^+]_{acid} + 10^{-7}$.

Similarly, always $[\bar{OH}]_{total} = [OH^-]_{base} + [\bar{OH}]_{water}$.

$\Rightarrow [\bar{OH}]_{total} = [\bar{OH}]_{base} + 10^{-7}$.

Remember $[H^+]_{acid} \leq 10^{-5}$, add 10^{-7} to $[H^+]_{acid}$

Remember $[\bar{OH}]_{base} \leq 10^{-5}$, add 10^{-7} to $[\bar{OH}]_{base}$

HW 10^{-8} M HCl. $[H^+] = 10^{-8} + 10^{-7}$

$= 10^{-8}(10+1) = 10^{-8} \cdot 11$

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

$= -\log 10^{-8} - \log 11$

$= 8 - 1.05 = \boxed{6.95}$

10^{-8} M NaOH. $[\bar{OH}] = 10^{-8} + 10^{-7} = 10^{-8} \cdot 11$

$pOH = 6.95$

$\Rightarrow pH = 14 - 6.95 = \boxed{7.05}$.

10^{-7} M HCl $[H^+] = 2 \cdot 10^{-7}$

$pH = -\log 2 - \log 10^{-7}$

$= 7 - 0.3 = \boxed{6.7}$

equal volumes of $pH = 2$ & $pH = 3$.

$[H^+] = 10^{-2}$ $[H^+] = 10^{-3}$.

$$N = \frac{N_1V + N_2V}{2V} = \frac{N_1 + N_2}{2} \Rightarrow [H^+] = \frac{[H^+] + [H^+]}{2}$$

$$\Rightarrow [H^+] = \frac{10^{-2} + 10^{-3}}{2} = (10^{-3}) \times \frac{11}{2}$$

$$pH = -\log 10^{-3} - \log 11 + \log 2$$
$$= 3 + 0.3 - 1.05 = 3.3 - 1.05 = \boxed{2.35}$$

Dilution factor pH changed to 4 from 2.

$N_1V_1 = N_2V_2$

$\Rightarrow [H^+]_1V_1 = [H^+]_2V_2 \Rightarrow [10^{-2}]V_1 = [10^{-4}]V_2$

$\Rightarrow \frac{V_2}{V_1} = 10^2 \Rightarrow \boxed{V_2 = 100}$

dilution factor = 100.

* ~~POLYTROPIC~~ - WEAK ACID.

* COMMON ION EFFECT.

when we have an equilibrium reaction and we get common ion from another equil reaction or simple reaction, then we will have common ion effect.

Concentration of common ion must be same in all reactions.

example: Calculate pH of soln obtained by 0.01M CH_3COOH $K = 10^{-5}$ with 0.01M HCl.

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

(aq) (aq) (aq)

t=0 C_1 0 0

equil $C_1(1-\alpha)$ $C_1\alpha$ $C_1\alpha + C_2$ ⟸ equil shifts backward

$$HCl \longrightarrow H^+ + Cl^-$$

strong electrolyte dissociates completely.

C_2 $C_1\alpha + C_2$ C_2

$\boxed{H^+ \text{ is common ion}}$

Due to common ion, concn of product (H^+) ion increases. ⇒ common ion shifts equil backward.

⇒ ionisation of weak acid decreases.

⇒ α decreases.

$pH = -\log(c_1\alpha + c_2)$

But $c_2 >> c_1\alpha \Rightarrow c_2 + c_1\alpha \simeq c_2$

$\therefore \; pH = -\log c_2 = -\log 0.01 = \boxed{2}$

* POLYPROTIC WEAK ACIDS.

Acids with n-factor > 1

eg H_2CO_3, | H_3PO_4. etc

$\Downarrow$ | $\Downarrow$

dibasic & diprotic acid (H_2A) | Tribasic & Triprotic Acid (H_3A)

$$H_2CO_3 \rightleftharpoons H^+(aq) + HCO_3^- \quad (ka_1)$$
$$HCO_3^- \rightleftharpoons H^+(aq) + CO_3^{2-} \quad (ka_2)$$
$$H_2CO_3 \rightleftharpoons 2H^+ + CO_3^{2-} \quad \text{(overall ka)}.$$

$\boxed{ka_1 \gg ka_2}$

overale $ka = ka_1 \times ka_2$

$pKa = pka_1 + pka_2$

$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \quad ka_1$$
$$H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \quad ka_2$$
$$HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-} \quad ka_3$$
$$H_3PO_4 \rightleftharpoons 3H^+ + PO_4^{3-} \quad ka \text{ overall}.$$

$ka_1 \gg ka_2 > ka_3$.

overall $ka = ka_1 * ka_2 * ka_3$

$pKa = pKa_1 + pKa_2 + pKa_3$.

Similarly for weak polyprotic base.

$Kb_1 \gg Kb_2 > kb_3$.

and $Kb = kb_1 \cdot kb_2 \cdot kb_3$.

calculate concentration of ions in H_2A (weak Acid)

$$H_2A\,(aq) \rightleftharpoons H^+ + HA^-\,(aq) \qquad Ka_1$$

t=0 $\quad c \qquad 0 \qquad 0$

$c(1-\alpha_1) \qquad \cancel{c\alpha_1} \qquad \cancel{c\alpha_1}$

eqm $\quad c\alpha_1 + c\alpha_1\alpha_2 \qquad c\alpha_1(1-\alpha_2)$

$$HA^{\ominus}\,(aq) \rightleftharpoons H^+ + A^{2-}\,(aq) \qquad Ka_2$$

$c\alpha_1(1-\alpha_2) \qquad \cancel{c\alpha_1\alpha_2} \qquad c\alpha_1\alpha_2$

$c\alpha_1 + c\alpha_1\alpha_2$.

Note. we have 2 different $\boxed{\text{common ions}}$

i) H^+ → conc Same everywhere

ii) HA^- → conc. same everywhere.

$$Ka_1 = \frac{[H^+][HA^-]}{[H_2A]} \Rightarrow Ka_1 = \frac{(c\alpha_1 + c\alpha_1\alpha_2)\cancel{c}\alpha_1(1-\alpha_2)}{\cancel{c}(1-\alpha_1)}$$

$$Ka_2 = \frac{[H^+][A^{2-}]}{[HA^-]} \Rightarrow Ka_2 = \frac{(c\alpha_1 + c\alpha_1\alpha_2)(\cancel{c}\alpha_1\alpha_2)}{\cancel{c}\alpha_1(1-\alpha_2)}$$

using these 2 eqns. calculate α_1 and α_2.

for conjugate Acid Base pair → like H_2O, H_3O^+

NH_3, NH_4^+

pyridine, pyridinium

$$Ka \times Kb = Kw = 10^{-14}$$

$$\boxed{pKa + pKb = pKw = 14}$$

** HYDROLYSIS OF SALT OF ACID AND BASE

There are 4 types of Acid base salt →

i) strong acid strong base salt
ii) weak Acid strong base salt
iii) strong acid weak base salt
iv) weak acid weak base salt

when salt react with H_2O, then salt hydrolysis (Breaking of compound on reacting with H_2O) takes place.

HYDROLYSIS OF SALT OF STRONG ACID & STRONG BASE

eg. NaCl, KCl, $NaNO_3$, Na_2SO_4, K_2SO_4, etc.

Cation of strong base
Na^+, K^+, etc.
Anion of strong acid
Cl^-, NO_3^-, SO_4^{2-}, etc.
} These aren't hydrolysed. (they don't react with H_2O).

∴ No effect on pH.

∴ pH of salt of SA & SB = $\boxed{7}$

HYDROLYSIS OF SALT OF WEAK ACID AND STRONG BASE.

eg. $\boxed{CH_3COONa}$, NaCN, KCN, etc.

WA = CH_3COOH → SB = NaOH.

In such salt base is strong ⇒ overall salts are basic

for salts of WA & SB, $\boxed{pH > 7}$

Na^+ = cation of strong base ⇒ No hydrolysis

$CH_3COO^\ominus$ · Anion of weak acid will get hydrolysed.

$\boxed{\text{ANIONIC HYDROLYSIS}}$ · salt conc = C ⇒ $[CH_3COO^-] = c$

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + \bar{O}H$$

	CH_3COO^-		CH_3COOH	$\bar{O}H$
t=0	c		0	0
	c(1-h)		ch	ch

h = degree of hydrolysis ⇒ h value = b/w 0 to 1.

K_h = equili. constant called $\boxed{\text{hydrolysis constant}}$

$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \rightarrow K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{1-h}$.

$\boxed{K_h = \frac{ch^2}{1-h}}$ $\quad h << 1 \Rightarrow 1-h \simeq 1$

$\Rightarrow \boxed{K_h = ch^2}$

$\Rightarrow h = \sqrt{\frac{K_h}{c}}$. $\quad c\downarrow \Rightarrow h\uparrow$.

(ostwald Dilution law)

we have following equil. constant.

$K_w = K_h \times K_a$

$K_h = \frac{K_w}{K_a}$. $\quad \boxed{h = \sqrt{\frac{K_w}{K_a \cdot c}}}$.

$h^2 = \frac{K_w}{K_a c}$

$c = \frac{K_w}{K_a h^2}$

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

$= -\log ch$.

$= -\log c\sqrt{\frac{K_w \cancel{c}}{K_a \cdot \cancel{c}\, c}}$

$= -\log\sqrt{\frac{K_w c}{K_a}}$

$pOH = ch = \frac{\cancel{K_w}\, h}{K_a h^2} = \frac{K_w}{K_a h}$

$\Rightarrow pH = 14 - pOH = 14 + \log\left(\frac{K_w c}{K_a}\right)^{1/2}$

$\Rightarrow \boxed{pH = 7 + \frac{1}{2}(pK_a + \log c)}$ at 25°C.

$\boxed{pH = \frac{1}{2}(pK_w + pK_a + pc)}$ (at any temperature).

level I assignment.

conjugate Acid of PO_4^{3-} $\quad HPO_4^{2-}$

Ka for acids A, B, C are $10^{-4}, 10^{-6}, 10^{-10}$. $c = 0.1M$.

increasing pH order

$pH = \frac{1}{2}(pK_a - \log c)$ $\quad \log c$ is constant.

$\Rightarrow pH \propto pK_a \Rightarrow pH \propto \frac{1}{K_a}$

$\therefore \boxed{A < B < C}$ (pH)

250 ml of $\frac{M}{50}$ H_2SO_4, 4g NaOH added, resulting solⁿ. diluted to 1.0L. pH of resulting solution →

HYDROLYSIS OF SALT OF STRONG ACID AND WEAK BASE

Example: NH_4Cl, pyridinium hydrochloride ($C_5H_5\overset{\oplus}{N}HCl^-$)

$\boxed{pH < 7}$

$$NH_4Cl \rightarrow \underset{(WB)}{NH_4OH} \quad \underset{(SA)}{HCl}$$

$$NH_4Cl \begin{cases} \rightarrow NH_4^+ \text{ (cation of WB – hydrolysis occurs)} \\ \rightarrow Cl^- \text{ (anion of SA – no hydrolysis)} \end{cases}$$

Concentration of salt = C.

This is called $\boxed{\text{CATIONIC HYDROLYSIS}}$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH(aq) + H^+$$
$$c \qquad\qquad 0 \qquad\qquad 0$$
$$c(1-h) \qquad\qquad ch \qquad\qquad ch$$

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} = \frac{ch \cdot ch}{c(1-h)} = \boxed{\frac{ch^2}{1-h}}$$

as $h \ll 1 \Rightarrow 1-h \simeq 1$

So, $\boxed{K_h = ch^2} \Rightarrow \boxed{h = \sqrt{\frac{K_h}{c}}}$

OSTWALD dilution law. $c\uparrow \; h\downarrow$

$\boxed{K_w = K_h \cdot K_b}$

$$(K_h)\quad NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$
$$(K_b)\quad NH_4OH \rightleftharpoons \overset{\oplus}{N}H_4 + OH^-$$
$$K_w \quad H_2O \rightleftharpoons H^+ + OH^-$$

$$\Rightarrow \boxed{K_w = K_h K_b}$$

$$[H^+] = ch = c\sqrt{\frac{K_h}{c}} = \sqrt{K_h c}$$

$$\Rightarrow [H^+] = \sqrt{\frac{K_w \cdot c}{K_b}}$$

$$\Rightarrow -\log[H^+] = -\log\sqrt{\frac{K_w c}{K_b}}$$

$$\therefore pH = -\log\left(\frac{K_w c}{K_b}\right)^{\frac{1}{2}}$$

$$\boxed{pH = 7 - \frac{1}{2}[pK_b + \log c]} \rightarrow \text{at } 25°C.$$

$$\boxed{pH = \frac{1}{2}(pK_w - pK_b - \log c)}$$ at any temperature.

HYDROLYSIS OF SALT OF WEAK ACID AND WEAK BASE

examples. CH_3COONH_4, NH_4CN

CH_3COOH NH_4OH NH_4OH HCN

$$CH_3COONH_4 \rightarrow CH_3COO^-$$ (Anion of WA will hydrolyse)

$$\rightarrow NH_4^+$$ (cation of WB will hydrolyse)

$\boxed{\text{CATIONIC AND ANIONIC HYDROLYSIS}}$

$\boxed{\text{pH is close to 7}}$.

$$\underset{c}{CH_3COO^{\ominus}} + \underset{c}{NH_4^{\oplus}} + H_2O \rightleftharpoons \underset{0}{NH_4OH(aq)} + \underset{0}{CH_3COOH(aq)} \quad K_h.$$

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

$$K_h = \frac{[CH_3COOH][NH_4OH]}{[CH_3COO^-][NH_4^+]} = \frac{\cancel{c}h \cdot \cancel{c}h}{\cancel{c}(1-h)\cdot\cancel{c}(1-h)}$$

$$\Rightarrow \boxed{K_h = \frac{h^2}{(1-h)^2}}$$

$$h << 1 \Rightarrow 1-h \simeq 1 \Rightarrow \boxed{K_h = h^2} \Rightarrow \boxed{h = \sqrt{K_h}}$$

(Degree of Hydrolysis doesn't change on dilution or change of salt concentration.)

$$\boxed{K_w = K_h \cdot K_a \cdot K_b}$$

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

At 25°C, $pK_w = 14 \Rightarrow$ $\boxed{pH = 7 + \frac{1}{2}(pK_a - pK_b)}$

Solution of salt of weak Acid and weak base is called buffer solution.

Q1. Calculate pH of final solution obtained by mixing ~~[illegible]~~ 100 ml 0.1M CH_3COOH and 100ml 0.1M NaOH. $pK_a = 4.74$.

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ii) 100 ml 0.1M NH_4OH and 100 ml 0.1 M HCl. ($pK_b = 9.2$)

iii) 100 ml, 0.1M CH_3COOH and 100ml 0.1 M NH_4OH.

$pK_b = \boxed{14 - 9.2}$

Q2. ~~When salt solution concentration was diluted to 100 times~~

Salt with 0.1M concentration has 10% hydrolysis, upon dilution to 0.01M, its hydrolysis increases. The salt can't be →

a) $C_6H_5\overset{\oplus}{N}HCl^-$ b) NH_4Cl ✓c) CH_3COONH_4 d) CH_3COONa

e) None of these.

1. i)

$$\underset{(10\,m\cdot m)}{CH_3COOH} + \underset{(10\,m\cdot m)}{NaOH} \longrightarrow \underset{(10\,m\cdot mole)}{CH_3COONa} + H_2O$$

$$H_2O + CH_3COO^{\ominus} \rightleftharpoons CH_3COOH + \overset{\ominus}{O}H \qquad Ka = (4.74)$$

$$c = [CH_3COO^-] = \frac{10}{200} = \frac{1}{20}$$

$$pH = 7 + \frac{1}{2}(pK_a + \log c)$$

$$= 7 + \frac{1}{2}(\cancel{\log}\,4.74 + \log \tfrac{1}{20})$$

$$\cancel{= 7 + \frac{1}{2}\left(\log\left(\frac{1}{20\times4.74}\right)\right) = 7 + \frac{1}{2}(\log 20 + \log 4.74)}$$

$$= 7 + \frac{1}{2}(4.74 - \log 20) = 7 + \frac{1}{2}(4.74 - \log 2 - \log 10)$$

$$= 7 + \frac{1}{2}(4.74 - 0.3 - 1) = 7 + \frac{1}{2}(3.44)$$

$$= 7 + 1.72 = \boxed{8.72}$$

ii)

$$\underset{(10\,mm)}{NH_4OH} + \underset{(10\,mm)}{HCl} \longrightarrow \underset{(10\,m\cdot mole)}{NH_4Cl} + H_2O$$

$$NH_4^{\oplus} + H_2O \rightleftharpoons NH_4OH + H^{\oplus}$$

$$c = [NH_4^+] = \frac{10}{200} = \frac{1}{20}$$

$$pH = 7 - \frac{1}{2}(pK_b + \log c) = 7 - \frac{1}{2}(9.2 + \log \tfrac{1}{20})$$

$pK_b = 14 - 9.2$
$= \textcircled{4.8}$

$$= 7 - \frac{1}{2}(4.80 - 1.30) = 7 - \frac{1}{2}(3.5)$$

$$= 7 - 1.75 = \cancel{\boxed{3.26}}\ \boxed{5.25}$$

iii) $CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$.

(10 m mole) (10 m mole) (10 m mole)

$CH_3COO^{\ominus} + NH_4^{\oplus} + H_2O \rightleftharpoons CH_3COOH + NH_4OH$.

$C = (\frac{1}{20})$ $C = \frac{1}{20}$

$pH = 7 + \frac{1}{2}(pKa - pKb)$

$= 7 + \frac{1}{2}(4.74 - 4.8) = 7 + \frac{1}{2}(-0.06) = \boxed{6.97}$

BUFFER SOLUTION

* Solution whose pH doesn't change due to addition of small amount of acid or base are called buffer solutions.

Buffer solutions resist change of pH.

$$\boxed{\text{Buffer capacity} = \frac{\text{No. of moles of } H^+ \text{ or } \bar{O}H \text{ added to } 1l \text{ buffer sol}^n.}{\text{change in pH}}}$$

Higher Buffer capacity ⇒ Better buffer solution.

examples i) blood ii) saliva iii) soil iv) sea water.

Blood is $\boxed{\text{basic buffer}}$ (7.4 = pH)

There are 3 types of Buffer solution →

A) Acidic Buffer → pH < 7. pH ≃ between 4 to 7.

B) Basic Buffer → pH > 7 pH ≃ between 7 to 10

Acidic buffer - Mixture of weak acid and salt of weak Acid & strong base.

eg. CH_3COOH and CH_3COONa

HCN and $NaCN$.

$$\boxed{pH = pKa + \log\frac{[salt]}{[WA]}}$$ Henderson and Haselblanck equation

If [salt] = [WA], then $\log\frac{[salt]}{[WA]} = 0$

⇒ $\boxed{pH = pKa}$ - max buffer capacity.

for good buffer (acidic) $\boxed{pH = pka \pm 1}$

CH_3COOH consumes $\overset{\ominus}{OH}$]

CH_3COO^- consumes $\overset{\ominus}{H}$]

**** Basic buffer** Mixture of weak base and salt of strong acid & weak base

eg NH_4OH and NH_4Cl, NH_4NO_3, etc.

pyridine and pyridiam hydrochloraide

C_5H_5N $\qquad$ $C_5H_5\overset{\oplus}{N}HCl^-$.

$$\boxed{pOH = pK_b + \log\frac{[salt]}{[WB]}}$$ (henderson haselblanck equation)

If $[salt] = [Wb]$

~~[pH]~~ $\boxed{pOH = pK_b}$ (max buffer capacity)

Good basic buffer, $\boxed{pOH = pK_b \pm 1}$.

NH_4OH consumes $H^{\oplus}$]

$\overset{\oplus}{NH_4}$ consumes $\overset{\ominus}{OH}$]

Salt of weak Acid & weak base in Buffer solution.

It is single compound Buffer.

$$pH = \boxed{7 + \frac{1}{2}(pk_a - pk_b)}$$

* pH of Amphoteric Ions :-

Amphoteric ion solⁿ. is also called buffer solution.

(pH of solⁿ is constant, doesn't depend on concentration)

$$\underset{(Acid)}{H_2CO_3} \underset{}{\overset{ka_1}{\rightleftharpoons}} \underset{(Amphoteric\ ion)}{HCO_3^-} \overset{ka_2}{\rightleftharpoons} \underset{(base)}{CO_3^{2-}}$$

HCO_3^- amphoteric ← $\boxed{\text{pH of } NaHCO_3 \text{ sol.} = \frac{pka_1 + pka_2}{2}}$

$$\underset{\text{acid}}{H_3PO_4} \xrightleftharpoons{Ka_1} \underset{\text{(Amphoteric)}}{H_2PO_4^{\ominus}} \xrightleftharpoons{Ka_2} \underset{\text{(Amphoteric)}}{HPO_4^{2-}} \xrightleftharpoons{Ka_3} \underset{\text{Base}}{PO_4^{3-}}$$

$H_2PO_4^{\ominus}$ amphoteric ← $$\boxed{\text{pH of } NaH_2PO_4 = \frac{pKa_1 + pKa_2}{2}}$$

HPO_4^{2-} amphoteric ← $$\boxed{\text{pH of } Na_2HPO_4 = \frac{pKa_2 + pKa_3}{2}}$$

Q. Identify which can be used to prepare buffer solution →. Also calculate pH →.

i) 0.1M 100 ml CH_3COOH + 0.1 M 50 ml NaOH
$pKa = 4.74$

ii) 100 ml 0.1M NH_4OH + 500 ml 0.1 M HCl $pK_b = 4.8$

iii) 100 ml 0.1M CH_3COONa + 50 ml 0.1M HCl

iv) 100 ml 0.1 M NH_4Cl + 50 ml 0.1M NaOH.

v) Initially 0.2 mol each NH_4Cl & NH_3 were present. If we add 4g NaOH to this mixture. Calculate pH.

i)
	CH_3COOH +	NaOH	⟶	CH_3COONa +	H_2O
t=0	10 mmole	5 mmole		0	0
finally	5 mmole			5 mmole	

∴ Acidic Buffer ⇒ $pH = pK_a + \log\frac{[salt]}{[WA]}$

$$= 4.74 + \log\left(\frac{5/v}{5/v}\right) = \boxed{4.74}$$

ii)
	NH_4OH +	HCl	⟶	NH_4Cl +	H_2O
t=0	10 mmole	5 mmole			
finally	5 mmole	0		5 mmole	

Basic buffer ⇒ $pOH = pK_b + \log\frac{[salt]}{[WB]} = 4.8 + \log\frac{[5/v]}{[5/v]} = 4.8$

$$\Rightarrow pH = 14 - 4.8 = \boxed{9.2}$$

iii) $CH_3COONa + HCl \longrightarrow CH_3COOH + NaCl$

t=0   10 m mol   5 mmole

finally   5 m mol   0   5 m mole

∴ Acidic Buffer ⇒ $pH = pK_a + \log\frac{[salt]}{[WA]}$

$= 4.74 + \log\frac{[5/V]}{[5/V]} = \boxed{4.74}$

iv) $NaOH + NH_4Cl \longrightarrow NaCl + NH_4OH$

t=0   5 m mole   10 m mole

finally   0   5   5   ⑤

Basic Buffer ⇒ $pOH = pK_b + \log\frac{[salt]}{[WB]}$

$= 4.8 + \log\frac{[5/V]}{[5/V]} = 4.8$

∴ $pH = 14 - 4.8 = \boxed{9.2}$

v) 0.2 mol each of NH_4Cl and NH_4OH.   0.2

⇒ initially it is basic buffer. ⇒ $pOH = pK_b = 4.8$

$NH_4Cl + NaOH \longrightarrow NaCl + NH_4OH$.

t=0   (0.2 mole)   (0.1 mole)

finally   0.1 mole   0   0.1 mole

Now, it is a buffer with NH_4Cl and NH_4OH'

$\Rightarrow pOH = pK_b + \log\frac{[0.1/V]}{[0.3/V]} = pK_b + \log\frac{1}{3}$

∴ ~~$\boxed{pH = 9.2}$~~ $= 4.8 + (-0.50)$

$= 4.3$.

∴ $pH = 14 - 4.3 = (9.7)$

Q. You have to make basic buffer $pH = 8.9$ using $NH_4OH(aq)$ and $HCl(aq)$. What is the molarity of $HCl(aq)$ if 50 ml $HCl(aq)$ is added to 0.1M 100 ml NH_4OH to make required buffer.

$pOH = 14 - 8.9 = 5.1$

Let Molarity be M.

$$HCl + NH_4OH \longrightarrow NH_4Cl + H_2O$$

t=0 (50M) m.mole (10 m. mole)

finally (10 − 50M) m.mole 50M.

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

$$\Rightarrow 5.1 = 4.8 + \log\frac{[50M]}{[10-50M]}$$

$$\Rightarrow 0.3 = \log\left[\frac{50M}{10-50M}\right]$$

$$\Rightarrow 10^{(0.3)} = \frac{50M}{10-50M} \Rightarrow 2 = \frac{50M}{10-50M}$$

$$\Rightarrow 20 - 100M = 50M \Rightarrow 20 = 150M$$

$$\Rightarrow \boxed{M = 2/15}$$

Mains Q. At 25°C, pH of pure water = 7. If 1 drop of 0.1M NaOH (aq) is added to 100 ml H_2O, what will be new pH. (vol of 1 drop = 0.05ml)

a) about 7 b) about 7.5 c) about 8 [✓ d) about 9]

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

$$[OH^+] = \frac{M_1V_1 + M_2V_2}{V_1+V_2} = \frac{(10^{-7})\,100 + (0.1)(0.05)}{100}$$

$$= \frac{10^{-5} + 0.005}{100} = \frac{10^{-5} + 500\times10^{-5}}{100}$$

$$= \frac{500\times10^{-5}}{100.05} = 5\times10^{-5}$$

$$\therefore pOH = -\log 5 + (-\log 10^{-5})$$

$$= 5 - 0.7 = 4.3$$

$$\Rightarrow pH = 14 - 4.3 = \text{[illegible]} \; 8 \; \boxed{9.7}$$

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* TITRATION

It is a process to determine the concentration of solution with the help of another solution whose concentration is already known. This process is part of Volumetric Analysis.

Equivalence Point

It is defined as the point at which reaction is 100% complete.

or Equivalents of all reactants become equal at this point.

Equivalence point ⟶ 100% rxn completed
$\frac{1}{3}$ Equivalence point ⟶ $\frac{1}{3}$rd rxn completed
$\frac{2}{3}$ Equivalence point ⟶ $\frac{2}{3}$rd rxn completed
Half ~~50%~~ Equivalence point ⟶ 50% rxn completed

End Point

- The point at which reaction completion is marked by visual change (like colour change) or some other measurable change (like conductance) is called end point.
- At end point visual indicator changes its colour.
- End point is usually arrived just after the equivalence point (Numerically, equivalence point is approximately equal to end point).

* Indicators (of Acid Base titrations)

These are usually weak organic acids. for example, phenolphthalein indicator, methyl orange indicator, litmus paper or soln.

These indicators have different colours in different medium or different pH range.

Phenolphthalein Indicator

Neutral	Acidic Medium	Alkaline	highly alkaline
Colourless	Colourless	Pink	Colourless

Indicator colour is determined based on the pH of solution and value of pK_{In}.

Phenolphthalein indicator $\Longrightarrow$ weak Acid
(HIn).

$$\underset{\text{Colour A}}{HIn_{(aq)}} \rightleftharpoons H^{+}(aq) + \underset{\text{colour B}}{In^{-}(aq)} \qquad \underset{\text{Equilibrium Constant}}{(K_{In})}$$

exist in Acidic Medium or Neutral form

exist in Basic Medium or Ionic form.

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

$$\Rightarrow \log K_{In} = \log[H^+] + \log[In^-] - \log[HIn].$$

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

$$\Rightarrow \boxed{pH = pK_{In} + \log\frac{[In^-]}{[HIn]}}$$

When we will have colour A $\longrightarrow$

$$\boxed{[HIn] \geq 10[In^-]}$$

$$\log\frac{[In^-]}{[HIn]} = \log\frac{1}{10} = -1.$$

$$\therefore \boxed{pH = pK_{In} - 1}.$$

Minimum % of HIn for colour A $= \dfrac{[HIn]}{[HIn]+[In^-]} \times 100$

$$= \frac{10x \times 100}{11x} = \boxed{\frac{1000}{11}\%}$$

when we will have colour B

$\boxed{[In^-] \geq 10[HIn]}$

$\log\frac{[In^-]}{[HIn]} = \log 10 = 1.$

$\Rightarrow \boxed{pH = pK_{In}+1}$

min. percentage of $[In^-]$ for colour B.

$= \frac{10x}{11x} \times 100 = \boxed{\frac{1000}{11}\%}$

$pK_{In}-1$ or more $\Leftarrow pK_{In} \Rightarrow$ $pK_{In}+1$ or more.

(Colour A of Acidic form of HIn) (colour B of Basic/Ionic form of In^-)

$\boxed{pK_{In} \pm 1}$

Phenolphthalein $pK_{In} = 8.3$

$pH = pK_{In}-1 = \boxed{7.3}$ $pH = pK_{In}+1 = 9.3$

colour of Acidic form — Colour of Basic form

$\boxed{\text{colourless}}$ — Pink.

* TYPES OF ACID BASE TITRATIONS

for monoprotic acid & base, 4 types of acid base titrations -

At equivalence point, we will have salt & H_2O.

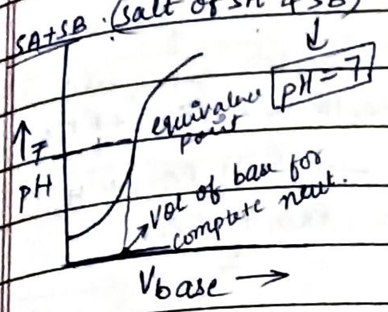
1) SA + SB. equivalence point pH = 7 (Salt of SA & SB)
2) SA + WB equivalence point pH < 7 (Salt of SA & WB)
3) WA + SB equivalence point pH > 7 (Salt of WA & SB)
4) WA + WB equivalence point pH → close to 7. (salt of WA & WB)

Besides, polyprotic Acid Titrations are also possible.
(like H_2CO_3., H_3PO_4, etc)

ACID BASE TITRATION CURVE

* pH vs 'volume of Base solution added' is plotted.

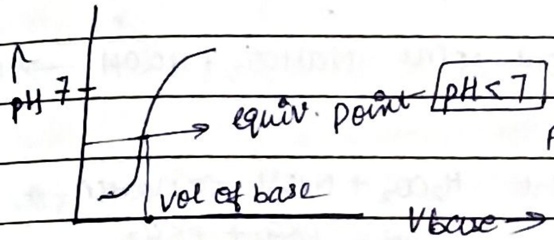
Ⓐ SA+SB (Salt of SA & SB)



Near end point, pH change is very sharp

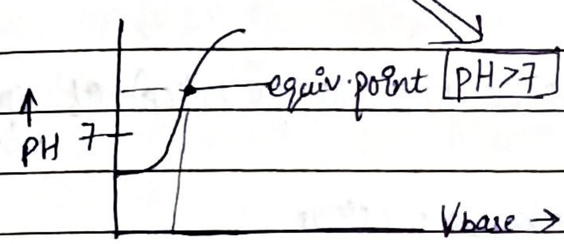
Base solution is added slowly to an acid solution. so, $\boxed{\text{initial pH} < 7}$

Ⓑ SA + WB ⇒ salt of (SA & WB)



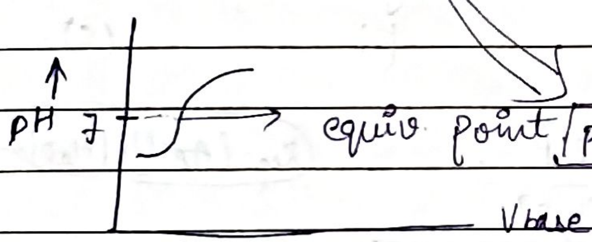
$pH = 7 - \frac{1}{2}(pK_b + \log c)$

Ⓒ WA + SB ⇒ salt of (WA & SB)



$pH = 7 + \frac{1}{2}(pKa + \log c)$

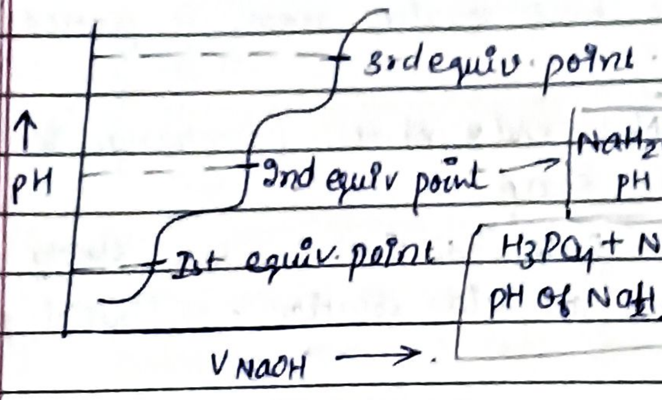
Ⓓ WA + WB ⇒ salt of (WA & WB)



$\boxed{pH = \text{close to } 7} = \boxed{7 + \frac{1}{2}(pka - pk_b)}$

Note : If pH versus volume of Acid solⁿ added is plotted, then graph might change'

H_3PO_4 + NaOH Titration curve →

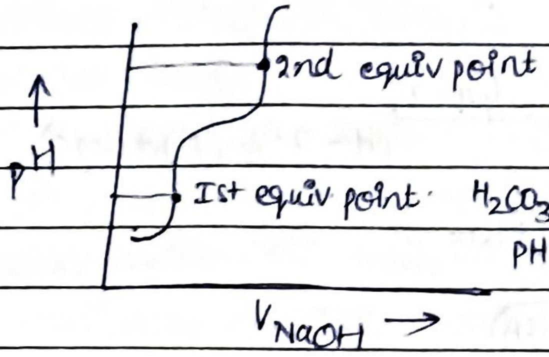


$Na_2HPO_4 + NaOH \rightarrow Na_3PO_4 + H_2O$

$\boxed{NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O \quad \text{pH of } Na_2HPO_4 = \frac{pKa_2 + pKa_3}{2}}$

$\boxed{H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O \quad \text{pH of } NaH_2PO_4 = \frac{pKa_1 + pKa_2}{2}}$

H_2CO_3 + NaOH Titration curve



$NaHCO_3 + NaOH \rightarrow Na_2CO_3 + H_2O$

$H_2CO_3 + NaOH \rightarrow NaHCO_3 + H_2O$

$pH = \frac{pKa_1 + pKa_2}{2}$

* SOLUBILITY (s) and SOLUBILITY PRODUCT (K_{sp}) of sparingly (or partially) soluble compounds.

solubility is taken in mol/litre.

Ksp is a type of Keq ⇒ it only changes with T.

$AgCl(s)$ (ppt) $\underset{}{\overset{H_2O}{\rightleftharpoons}}$ $\underset{(s)}{Ag^+(aq)}$ + $\underset{(s)}{Cl^-(aq)}$.

(sparingly soluble compound)

$K_{eq} = \frac{[Ag^+][Cl^-]}{[AgCl][H_2O]}$

$K_{eq} \cdot [AgCl] \cdot [H_2O]$ — constant = K_{sp}

$\Rightarrow \boxed{K_{sp} = [Ag^+][Cl^-]}$.

AgCl. $K_{sp} = s \cdot s = s^2$

$\Rightarrow \boxed{K_{sp} = s^2}$ or $s = \sqrt{K_{sp} \text{ of } AgCl}$

General Expression for Ksp.

$A_xB_y(s) \rightleftharpoons xA^{y+}_{(aq.)} + y\,B^{x-}_{(aq.)}$

(sparingly soluble) $\quad xs \quad\quad ys$

Ksp of $A_xB_y = [A^{y+}]^x\,[B^{x-}]^y$

$= (xs)^x\,(ys)^y$

$\Rightarrow \boxed{\text{Ksp of } A_xB_y = x^x \cdot y^y \cdot s^{x+y}}$

Type of salt (with eqn)	$K_{sp} = x^x y^y s^{x+y}$	Solubility (s)
AB type. ($x=1$ $y=1$) AgCl, AgBr, AgI, $CaCO_3$ $BaSO_4$, etc.	$K_{sp} = s^2$	$s = \sqrt{K_{sp}}$
A_2B type $x=2$ $y=1$ Ag_2CrO_4, $Ag_2C_2O_4$, Ag_2S AB_2 type $x=1$ $y=2$. $Mg(OH)_2$. $PbCl_2$.	$K_{sp} = 4s^3$ $(2^2 \cdot 1^1 \cdot s^{2+1})$	$s = \sqrt[3]{\frac{K_{sp}}{4}}$
AB_3 type. $x=1$ $y=3$ $Al(OH)_3$	$K_{sp} = 27s^4$ $= (3^3 \cdot 1^1 \cdot s^{3+1})$	$\Rightarrow s = \sqrt[4]{\frac{K_{sp}}{27}}$
A_3B_2 $x=3$ $y=2$ $Ca_3(PO_4)_2$	$K_{sp} = 3^3 2^2 s^{2+3}$ $= \boxed{108s^5}$	$s = \sqrt[5]{\frac{K_{sp}}{108}}$

$Hg_2Cl_2 \longrightarrow Hg_2^{2+} + 2Cl^-$

$AB_2 \Rightarrow \boxed{K_{sp} = 4s^3}$

III) Q.

		Ksp
AX	(1)	10^{-12}
BX_2	(2)	4×10^{-15}
CX_3	(3)	2.7×10^{-19}

Arrange in increasing order of solubility.

$S(1) = \sqrt{K_{sp}} = \sqrt{10^{-12}} = \boxed{10^{-6}}$ $\Rightarrow AX < BX_2 = CX_3$

$S(2) = \sqrt[3]{\frac{K_{sp}}{4}} = \sqrt[3]{\frac{4\times10^{-15}}{4}} = \boxed{10^{-5}}$

$S(3) = \sqrt[4]{\frac{K_{sp}}{27}} = \sqrt[4]{\frac{2.7\times10^{-19}}{\cancel{27}0\,10}} = \boxed{10^{-5}}$

* IONIC PRODUCT (IP)

Its value can be used to determine when precipitate formation starts

IP is like reaction Quotient (Q).

	Solution
$IP < K_{sp}$	unsaturated
$IP = K_{sp}$	saturated
$\boxed{IP > K_{sp}}$	ppt formation starts

formula of IP is same as K_{sp}.

Q. Solution contains

$A^+ = 0.01M$

$B^+ = 0.01M$

$C^+ = 0.01M$

To this solution, NaCl is added slowly. which ppt will form first.

	K_{sp}
ACl	10^{-18}
BCl	10^{-12}
CCl	10^{-16}

Determine min. concentration of $[Cl^-]$ when ACl ppt formation starts.

$K_{sp} = IP_{ACl} = [A^+][Cl^-]$

$\Rightarrow 10^{-18} = [A^+][Cl^-]$

$\Rightarrow [Cl^-] = \frac{10^{-18}}{[A^+]} = \frac{10^{-18}}{0.01} = \textcircled{10^{-16}}$

BCl $\rightarrow [Cl^-] = \frac{10^{-12}}{0.01} = 10^{-10}$

CCl $[Cl^-] = \frac{10^{-14}}{0.01} = 10^{-12}$

$\boxed{ACl}$ needs least $[Cl^-]$ value to form ppt. first.

Exercise 7.4

20. Aqueous soln. of Aluminium Chloride is acidic due to →
CATIONIC HYDROLYSIS

Different factors affecting solubility

Effect of common ion.

Presence of common ion usually decrease the solubility.

Common ion must have equal concentration in all reactions.

Calculate the ratio of solubility of AgCl in water ~~is~~ to new solubility in presence of 0.1M $CaCl_2$ aqueous ($CaCl_2$ is completely ionised). [K_{sp} of AgCl $= 4\times10^{-12}$]

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-(aq) \qquad \text{(Pure water)}$$

$$K_{sp} = s^2 \Rightarrow s = \sqrt{K_{sp}} = \sqrt{4\times10^{-12}} = 2\times10^{-6}.$$

In presence of common ion →

$$AgCl(s) \rightleftharpoons Ag^+ + \underset{s'+0.2}{Cl^-}$$

(Solubility decreases) $\xleftarrow[\text{backward}]{\text{Eqm shifts}}$

$$CaCl_2(aq) \longrightarrow Ca^{2+}(aq) + \underset{(0.2M)+s'}{2Cl^-(aq)}.$$

Cl^- is common ion in both rxn.

⇒ $[Cl^-]$ equal in both eqn

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

$$= s'(0.2+s')$$

$$s' \lll 0.2 \Rightarrow s'+0.2 \simeq 0.2$$

$$4\times10^{-12} = s'\times0.2$$

$$\Rightarrow s' = \frac{4\times10^{-12}}{0.2} \Rightarrow \boxed{s' = 2\times10^{-11}}$$

$$\text{Ratio} = \frac{s}{s'} = \frac{2\times10^{-6}}{2\times10^{-11}} = \boxed{10^{5}}$$

B) SIMULTANEOUS SOLUBILITY

When in same solution, we have two or more partially soluble compounds having common ion among them, then we will get simultaneous solubility.

Due to simultaneous solubility, solubility of all partially soluble compounds decreases.

Q. In 1l pure water AgCl and AgBr are added, calculate the total solubility. Ksp of AgCl is 4×10^{-12} Ksp of AgBr is 12×10^{-12}.

$$\underset{\xleftarrow{\text{eqm shift}}}{AgCl(s)} \rightleftharpoons \underset{(S_1+S_2)}{Ag^+(aq)} + \underset{(S_1)}{Cl^-(aq)}$$

$$\underset{\xleftarrow{\text{eqm shift}}}{AgBr(s)} \rightleftharpoons \underset{S_2+S_1}{Ag^+(aq)} + \underset{S_2}{Br^-(aq)}$$

common ion ⇒ $[Ag^+]$ same in both soln.

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

$$\Rightarrow 4\times10^{-12} = (S_1+S_2)S_1. \quad — ①$$

$$K_{sp}\ AgBr = [Ag^+][Br^-]$$

$$\Rightarrow 12\times10^{-12} = (S_1+S_2)S_2 \quad — ②$$

① + ②, $4\times10^{-12} + 12\times10^{-12} = (S_1+S_2)S_1 + (S_1+S_2)S_2$

$$\Rightarrow Ksp_1 + Ksp_2 = (S_1+S_2)^2$$

$$\Rightarrow 16\times10^{-12} = (S_1+S_2)^2$$

$$\Rightarrow \boxed{(S_1+S_2) = 4\times10^{-6}}$$

Divide ① by ②, $\frac{Ksp_1}{Ksp_2} = \frac{S_1}{S_2}$

$$\Rightarrow \frac{4\times10^{-12}}{12\times10^{-12}} = \frac{S_1}{S_2} \Rightarrow \boxed{\frac{S_1}{S_2} = \frac{1}{3}}$$

c) Effect of complex formation on solubility

Due to formation of complex involving ion of partially soluble compound, solubility $\boxed{\text{increases}}$

we will have 2 eq^{n}s.

1) for partially soluble compound → (K_{sp})

2) for complex formation ⟶ (K_f or $K_{stability}$) = $\frac{1}{K_{instability}}$

(Higher K_f indicates more stable complex)

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

Calculate the new solubility of AgCl in presence of 0·2M $NH_3(aq)$.

K_{sp} of $AgCl = 4\times10^{-12}$ $\quad$ K_f of $[Ag(NH_3)_2]^+ = 10^6$

$$AgCl \rightleftharpoons \underset{s'}{Ag^+(aq)} + \underset{s'}{Cl^-(aq)}$$

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

t=0 $\quad s' \quad 0\cdot2 \quad$ zero

eq^m $\quad (s'-x) \quad (0\cdot2-2x) \quad x$

Ag^+ common ion ⇒ $[Ag^+]$ value same in both.

$$K_f = \frac{[[Ag(NH_3)_2]]}{[Ag^+][NH_3]^2} = \frac{x}{(s'-x)(0\cdot2-2x)^2}$$

since $x < s' \leq 0\cdot2 \Rightarrow 0\cdot2-2x \simeq 0\cdot2$

$$\therefore K_f = \frac{x}{(s'-x)(0\cdot2)^2} = 10^6 \quad — ①$$

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

$$\Rightarrow 4\times10^{-12} = (s'-x)s' \quad — ②$$

① × ② $\quad 10^{-8}\times16 = s'x$.

∴ eq^n ②

$$4\times10^{-12} = (s')^2 - s'x$$

$$\Rightarrow 4\times10^{-12} = (s')^2 - 16\times10^{-8}$$

$$\Rightarrow (s')^2 = (4\times10^{-12}) + (16\times10^{-8})$$

$4\times10^{-12} \ll 16\times10^{-8} \Rightarrow (s')^2 \simeq 16\times10^{-8}$

$$\Rightarrow (s') = 4\times10^{-4}$$

$$\Rightarrow \boxed{s' = 0\cdot0004}$$