

027/07/17

Ionic Equilibrium

* Ionic equilibrium :

On the basis of Providing ion
Substance can be of two type.

Substance

Electrolyte
(Provide ion)

Non-Electrolyte
(do not provide ions)

Ex: $C_6H_{12}O_6$

Strong electrolyte
Complete dissociate

Weak electrolyte
(Partially dissociate
in ion)

⇒ Strong Acid!
 $HCl, HBr, HI, HClO_4$
 HNO_3, H_2SO_4

⇒ Strong base! $NaOH, KOH$
 $Ca(OH)_2, Ba(OH)_2,$
 $Sr(OH)_2$

⇒ Salt - By default
All salts are considered
as strong electrolytes.

⇒ weak acid! HCN, CH_3COOH

⇒ weak base! $NH_4OH, Zn(OH)_2$

SBG STUDY

* Degree of Ionisation of strong Electrolyte will
be 100% or 1 and degree of Ionisation of
weak electrolyte less than 100% or less than 1.

Common ion \rightarrow Priority For
odd ion \rightarrow decr

dielectric \propto Polar

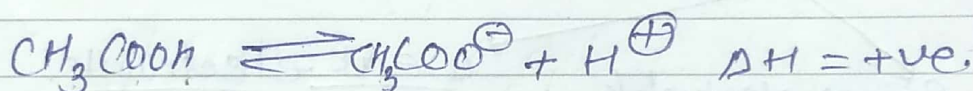
* Factors affecting degree of ionisation of weak electrolyte:

(i) Nature of weak electrolyte

(ii) Nature of solvent:

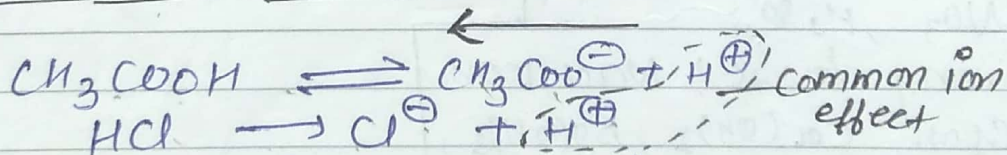
on increasing dielectric constant of solvent degree of ionisation of weak electrolyte increase

(iii) Effect of temperature:



In general on increasing temp. degree of ionisation increase
 $\uparrow \quad \uparrow$

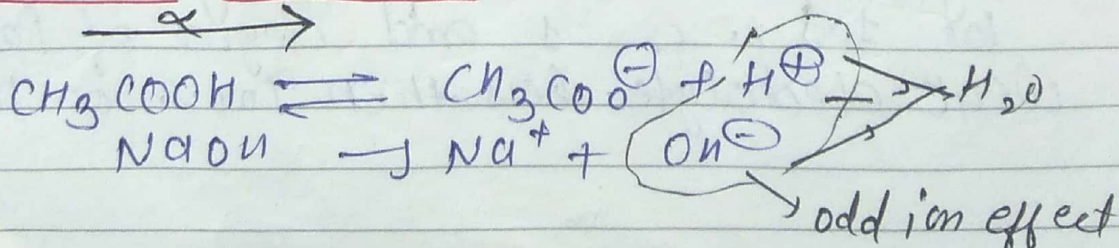
(iv) Common ion effect:



Due to common ion effect degree of ionisation decrease

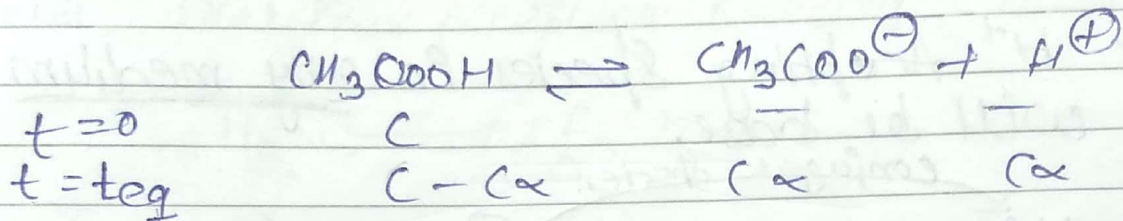
(v) odd ion effect:

Due to odd ion effect degree of ionisation increase



(vi) Effect of dilution (Ostwald dilution)

Acc. to Ostwald dilution law on dilution degree of ionisation of weak electrolyte increase



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

$$K_a = \frac{C\alpha^2}{1 - \alpha}$$

$$K_a = C\alpha^2 \quad \alpha \ll 1$$

$$\alpha^2 = \frac{K_a}{C}$$

$$\alpha = \sqrt{\frac{K_a}{C}}$$

$$\alpha \propto \frac{1}{\sqrt{C}}$$

$$\uparrow \alpha \propto \sqrt{V} \uparrow$$

★ Different Acid base Concept

1) Arrhenius Concept

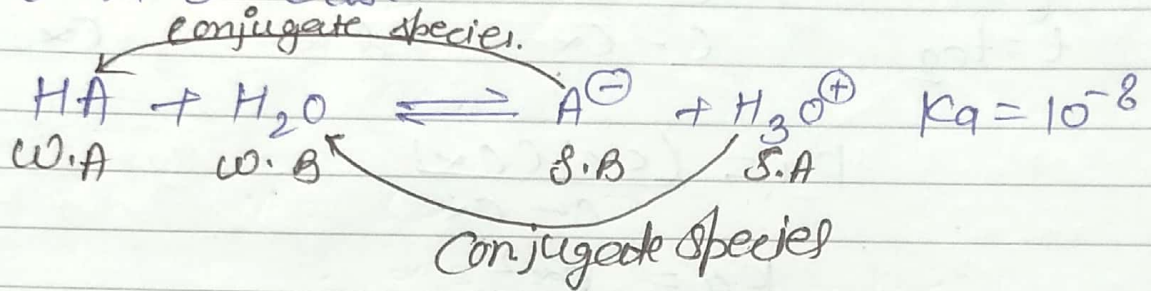
= Acid: H^+ releasing species in aqueous medium

Base: OH^\ominus releasing species in aqueous medium

2) Bronsted-Lowry Concept:

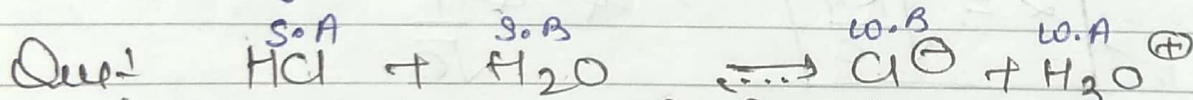
Acid: H^+ releasing species in any medium will be acid

Base: H^+ Accepting species in any medium will be base.



(1) There will be difference of only one H^+ ion b/w conjugate acid base

(2) Conjugate of strong will be weak and conjugate of weak acid will be base



Behaviour of H_3O^+ in given pt. be

(A) s.A

(B) s.B

~~(C) w.A~~

(D) w.B

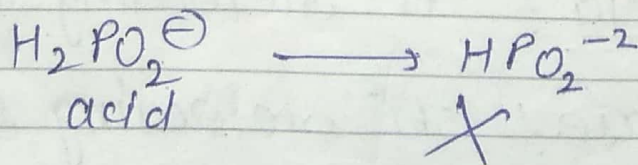
Que: Conjugate base of $H_2PO_3^-$ will be

(A) HPO_2^{-2}

(B) H_3PO_2

(C) PO_2^{-3}

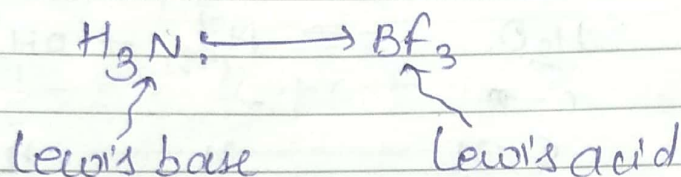
~~(D) Not possible.~~



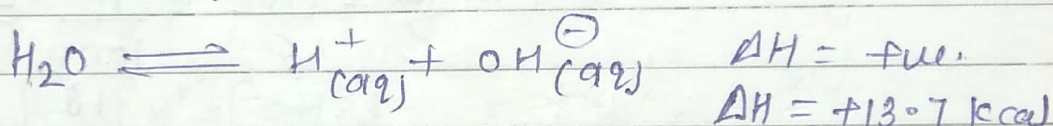
* Lewis Acid Base concept :

Base: lone pair donating species called base.

Acid: lone pair accepting species called acid.



* Ionic Product of H₂O : (K_w) :



$$\Delta H = +13.7 \text{ kcal}$$

$$K_w = [\text{H}^+][\text{OH}^-]$$

$$\boxed{K_w = [\text{H}^+][\text{OH}^-]} \quad T \uparrow \quad K_w \uparrow$$

$$\begin{array}{l} \text{at } 25^\circ\text{C} \quad K_w = 10^{-14} \\ \text{at } 40^\circ\text{C} \quad K_w = 10^{-12} \end{array}$$

* Value of K_w depend only on temp. on increasing temp. value of K_w increase.

$$T_1 \text{ --- } K_{w1} \quad T_2 \text{ --- } K_{w2}$$

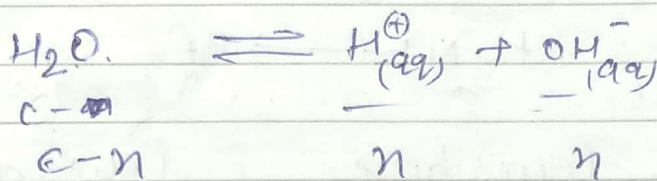
$$\boxed{\ln \left(\frac{K_{w2}}{K_{w1}} \right) = -\frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)}$$

Pure $\frac{1000}{18}$

In pure H_2O $H^+ = OH^- = \sqrt{K_w}$ and at $25^\circ C$
 $\sqrt{K_w} = 1.8 \times 10^{-7}$

Ques: Calculate % degree of dissociation of pure H_2O at $25^\circ C$

- (A) 1.8×10^{-7}
- (B) 1.8×10^{-9}
- (C) 10^{-7}
- (d) 10^{-9}



$$n = C\alpha = 10^{-7}$$

$$\alpha = \frac{10^{-7}}{c} = \frac{10^{-7}}{\frac{1000}{18}} = 1.8 \times 10^{-9}$$

% dissociation = 1.8×10^{-7} Ans.

Ques: Dissociation Const. of H_2O is defined as

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

the calculate value of K_d at $25^\circ C$.

Ans:

$$K_d = \frac{[H^+][OH^-]}{(H_2O)}$$

$$K_d = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{\frac{1000}{18}} = \frac{18 \times 10^{-14}}{1000} = 1.8 \times 10^{-14}$$

* ϕ

pH

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

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

$pH \uparrow [H^+] \downarrow$

$$pK_a = -\log K_a$$

$$pK_b = -\log K_b$$

$$pK_w$$

$T \uparrow K_w \uparrow pK_w \downarrow$

* Relation b/w p^H and p^{OH} for neutral aqueous solution:

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

$$pK_w = p^H + p^{OH}$$

at $25^\circ C$ $K_w = 10^{-14}$

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

$$pK_w = -\log K_w = -\log 10^{-14} = +14 \log 10 = +14$$

$$K_d = \frac{[H^+][OH^-]}{[H_2O]} = \frac{K_w}{[H_2O]} = \frac{10^{-14}}{\frac{1000}{18}}$$

* p^H of aqueous neutral solution:

$$[H^+] = [OH^-] \Rightarrow p^H = p^{OH}$$

$$pK_w = p^H + p^{OH} \Rightarrow pK_w = p^H + p^H$$

$$2p^H = pK_w$$

$$p^H = \frac{pK_w}{2}$$

at $25^\circ C$ $p^H = 7$

* p^H scale:

$$p^H < \frac{pK_w}{2}$$

$$p^H = \frac{pK_w}{2}$$

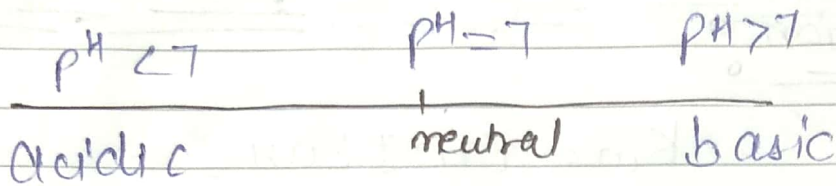
$$p^H > \frac{pK_w}{2}$$

acidic

neutral point

basic

at 25°C.



Q. for Acidic aqueous solution Select Correct options.

~~A~~ $[H^+] > \sqrt{K_w} > [OH^-]$

(B) $[H^+] < \sqrt{K_w} < [OH^-]$

~~C~~ $pH < \frac{1}{2} pK_w < pOH$

(D) $pH > \frac{1}{2} pK_w > pOH$

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

for neutral solution $[H^+] = [OH^-]$

$$K_w = [H^+]^2$$

$$[H^+] = \sqrt{K_w} = [OH^-]$$

for acidic solution

$$\Rightarrow [H^+] > \sqrt{K_w} > [OH^-]$$

$$pH < \frac{1}{2} pK_w < pOH$$

Ques: At 80°C pH of an aqueous solution is 7 the nature of solution will be

(a) neutral

(b) Acidic

~~(c) Basic~~

(d) Cannot will predict

at 25°C $pK_w = 14$

at 80°C $pK_w = 14 \downarrow$

$$pH = \frac{pK_w}{2} = 7 \downarrow$$

$$[H^+] = n \times 10^{-y}$$

$$pH = y - \log n$$

* pH calculation for different Acid base in an aqueous solution at 25°C

(i) pH calculation of Strong Acid and Strong base:

(i) 10^{-3} M HCl

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

$$pH = -\log 10^{-3} = 3$$

(ii) 10^{-4} M HNO_3

$$[H^+] = 10^{-4}$$

$$pH = 4$$

$$[OH^-] = 2 \times 10^{-3}$$

$$-\log [OH^-] = -\log 2 \times 10^{-3}$$

$$= -\log 2 - \log 10^{-3}$$

$$= -\log 2 + 3$$

$$= 3 - \log 2$$

(iii) 10^{-3} M $Ba(OH)_2$

$$[OH^-] = 2 \times 10^{-3}$$

$$pOH = 3 - \log 2 = 2.7$$

$$pH + pOH = 14$$

$$pH = 14 - 2.7$$

(iv) 10^{-4} N $Sr(OH)_2$

$$N = M \times V.F$$

$$M = \frac{10^{-4}}{2}$$

$$[OH^-] = \frac{10^{-4}}{2} \times 2 = 10^{-4}$$

$$pOH = 4$$

$$pH = 10$$

Ques:

10^{-7} M HCl

$$[H^+] = 10^{-7}$$

$$pH = 7$$

Ans

X

$$\frac{p_a}{c} > 10^{-6}$$

$$< 10^{-6}$$

Therms are 98-1 comple

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

$$= 10^{-7} + 10^{-7}$$

$$[H^+] = 2 \times 10^{-7}$$

$$pH = 7 - \log 2$$

$$= 6.7$$

* If concn of H^+ and OH^- from acid and base less than or equal to 10^{-6} the concn of H^+ and OH^- from water will be considered.

$[H^+]_{acid}$	$[H^+]_{water}$
$10^{-4} + 10^{-7}$	$\approx 10^{-4}$
$10^{-5} + 10^{-7}$	$\approx 10^{-5}$
$10^{-6} + 10^{-7}$	$\approx 1.1 \times 10^{-6}$
$10^{-7} + 10^{-7}$	$\approx 2 \times 10^{-7}$
$10^{-8} + 10^{-7}$	$\approx 1.1 \times 10^{-7}$
$10^{-9} + 10^{-7}$	$\approx 10^{-7}$
$10^{-10} + 10^{-7}$	$\approx 10^{-7}$

Q. $10^{-7} M HCl$

$$[H^+] = 10^{-7}$$

$$pH = 7$$

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

$$= 10^{-7} + 10^{-7}$$

$$[H^+] = 2 \times 10^{-7}$$

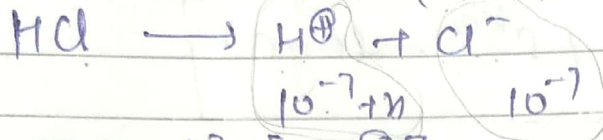
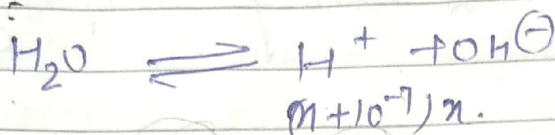
$$pH = 7 - \log 2$$

$$= 6.7$$

Acid Replacable H \Rightarrow Valency factor
 $n =$

OH
 Chemistry

Exact Process:



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

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

$$n = 0.8 \times 10^{-7}$$

$$[H^+] = 10^{-7} + n$$

$$= 10^{-7} + 0.8 \times 10^{-7}$$

$$[H^+] = 1.8 \times 10^{-7}$$

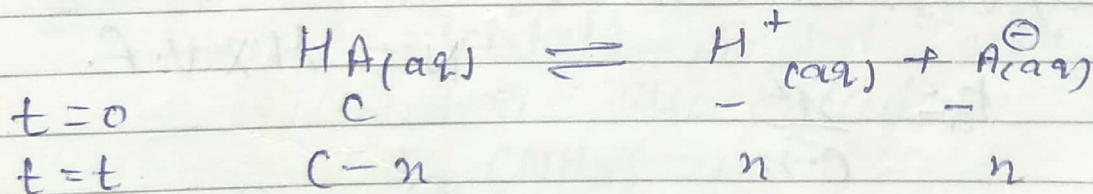
$$pH = 7 - \log(1.8)$$

$$= 6.8$$

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

★

* pH calculation of weak acid OR weak base



approx \rightarrow $K_a = \frac{n^2}{c-n}$

$$\frac{K_a}{c} < 10^{-2}$$

$$c-n \approx c$$

$$K_a = kac$$

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

$$\frac{c}{n} > 10 \Rightarrow \frac{1}{10} > \frac{n}{c}$$

$$0.1 > \frac{\sqrt{K_a c}}{c} \Rightarrow 0.1 > \sqrt{\frac{K_a}{c}}$$

$$10^{-2} > \frac{K_a}{c}$$

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

Applicable
if $\frac{K_a}{c} < 10^{-2}$

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

for weak base

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

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

if $\frac{K_b}{c} < 10^{-2}$

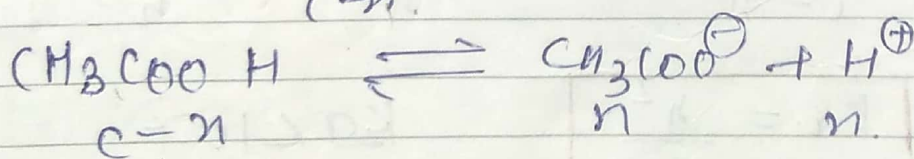
$$pH = 14 - pOH$$

$$N = 4 \times V \cdot f$$

Ques: Calculate pH of 0.1 N CH_3COOH solution.
 $K_a (CH_3COOH) = 10^{-5}$

$$N = M \times V \cdot f$$

$$K_a = \frac{x^2}{c-x}$$



$$K_a = \frac{x^2}{c-x}$$

$$10^{-5} = \frac{x^2}{0.1-x}$$

$$x = 10^{-3}$$

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

$$\therefore \frac{K_a}{c} = 10^{-4} < 10^{-2}$$

$$= \frac{10^{-5}}{1 \times 10^{-1}} = 10^{-4}$$

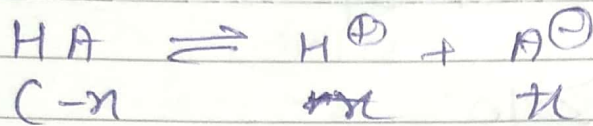
w.A or w.B \Rightarrow

$$\boxed{\frac{K_a}{c} < 10^{-2}}$$

10^{-3}

Que: Concn of H^+ ion is solution of 0.1 M HA solution is 10^{-3} mol/100 ml. then calculate value of K_a for weak acid HA?

$$K_a = \frac{n^2}{c-n}$$



$$n = 10^{-2} \text{ mol/litre}$$

$$K_a = \frac{n^2}{c-n}$$

$$K_a = \frac{(10^{-2})^2}{0.1 - 10^{-2}}$$

$$\frac{K_a}{c} = \frac{10^{-3}}{0.1} = 10^{-2} < 10^{-2}$$

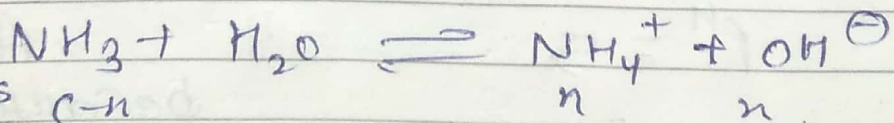
$$K_a = \frac{10^{-4}}{0.1 - 0.01}$$

Solve.

Que: pH of an aqueous solution of NH_3 is 11.5 then calculate initial Concn of NH_3 in solution also calculate pOH .
 $K_b(NH_3) = 10^{-5}$.

$$pOH = 2.5$$

$$[OH^{\ominus}] = 10^{-2.5} \quad c-n$$



$$x = [OH^{\ominus}] = 10^{-2.5}$$

$$K_b = \frac{n^2}{c-n}$$

$$K_b = \frac{n^2}{c-n}$$

$$10^{-5} = \frac{n^2}{11.5 - n}$$

$$10^{-5} = \frac{(10^{-2.5})^2}{c - 10^{-2.5}}$$

$$\frac{K_b}{c} = \frac{10^{-5}}{1} = 10^{-5} < 10^{-2}$$

$$c = 1$$

~~Not Imporant~~

$$10^4 \frac{K_a}{c} > 10$$

$$> 10^{-2}$$

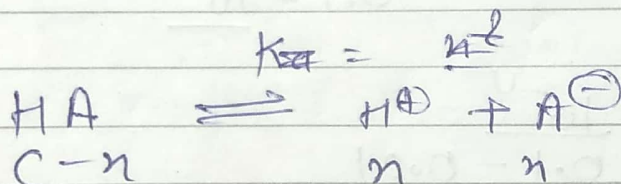
* Very dilute solⁿ of weak acid behaves just like solution of Strong Acid because on dilution degree of dissociation increases.
Our solⁿ of weak acid is very diluted this constⁿ is check by

$$\text{If } \frac{K_a}{c} \geq 10$$

Ques: Calculate pH of 10^{-5} M HA solution if

$$K_a(\text{HA}) = 10^{-2}$$

Ans:



$$K_a = \frac{n^2}{c-n}$$

$$\frac{K_a}{c} = \frac{10^{-2}}{10^{-5}} = 1000$$

$$1000 \geq 10$$

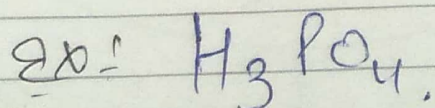
It means this will ^{just like} behave strong Acid

because its solⁿ is very diluted

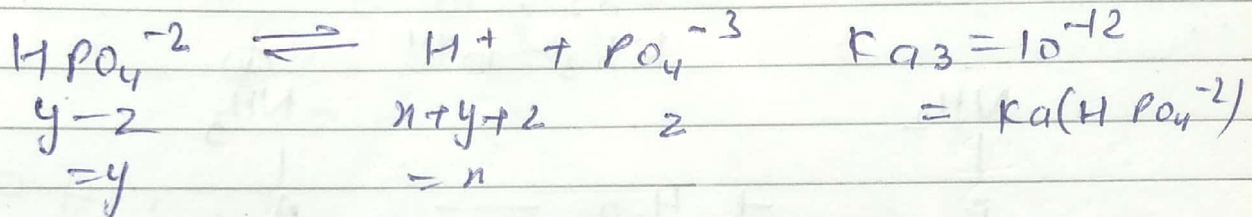
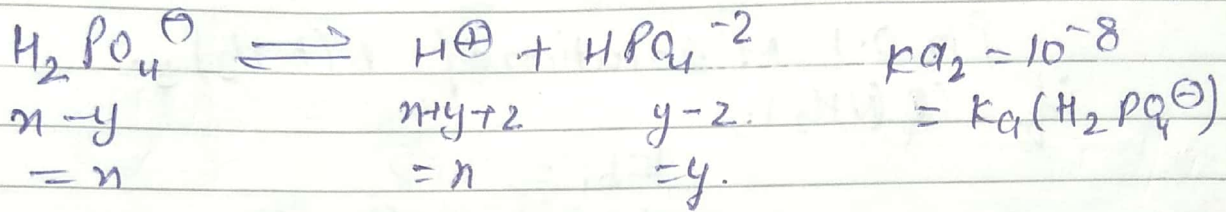
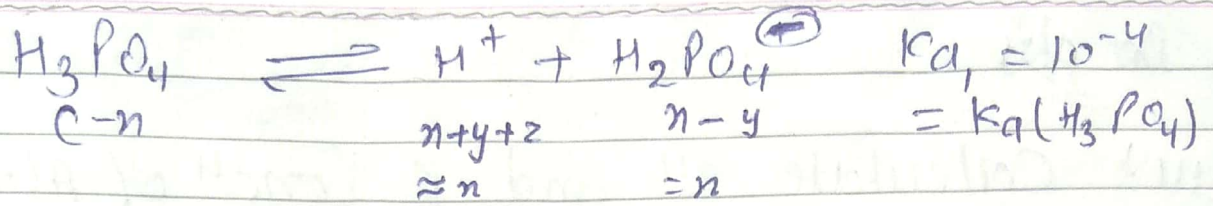
$$\left\{ \begin{array}{l} [\text{H}^{\oplus}] = x \approx c = 10^{-5} \\ \text{pH} = 5 \end{array} \right.$$

* pH calculation of weak Polyprotic acid:

If a acid has more than one replaceable H^{\oplus} ion then it is called Polyprotic acid



$$\left[\frac{K_a < 10^{-2}}{c} \right] \text{ poly.}$$



$$K_{a1} \gg \gg \gg K_{a2} \gg \gg \gg K_{a3}$$

$$n \gg \gg \gg y \gg \gg \gg z$$

$$K_{a1} = \frac{n^2}{c-n} \quad \frac{K_{a1}}{c} < 10^{-2}$$

$$c-n \approx c$$

$$K_{a2} = \frac{ny}{n} = y.$$

$$K_{a3} = \frac{nz}{y}$$

* For pH calculation only 1st eqn is sufficient

In dissociation of H_3PO_4

$$* \quad \begin{array}{l} K_{a1} = K_a(\text{H}_3\text{PO}_4) \\ K_{a2} = K_a(\text{H}_2\text{PO}_4^-) \\ K_{a3} = K_a(\text{HPO}_4^{2-}) \end{array}$$

* Pro ch's

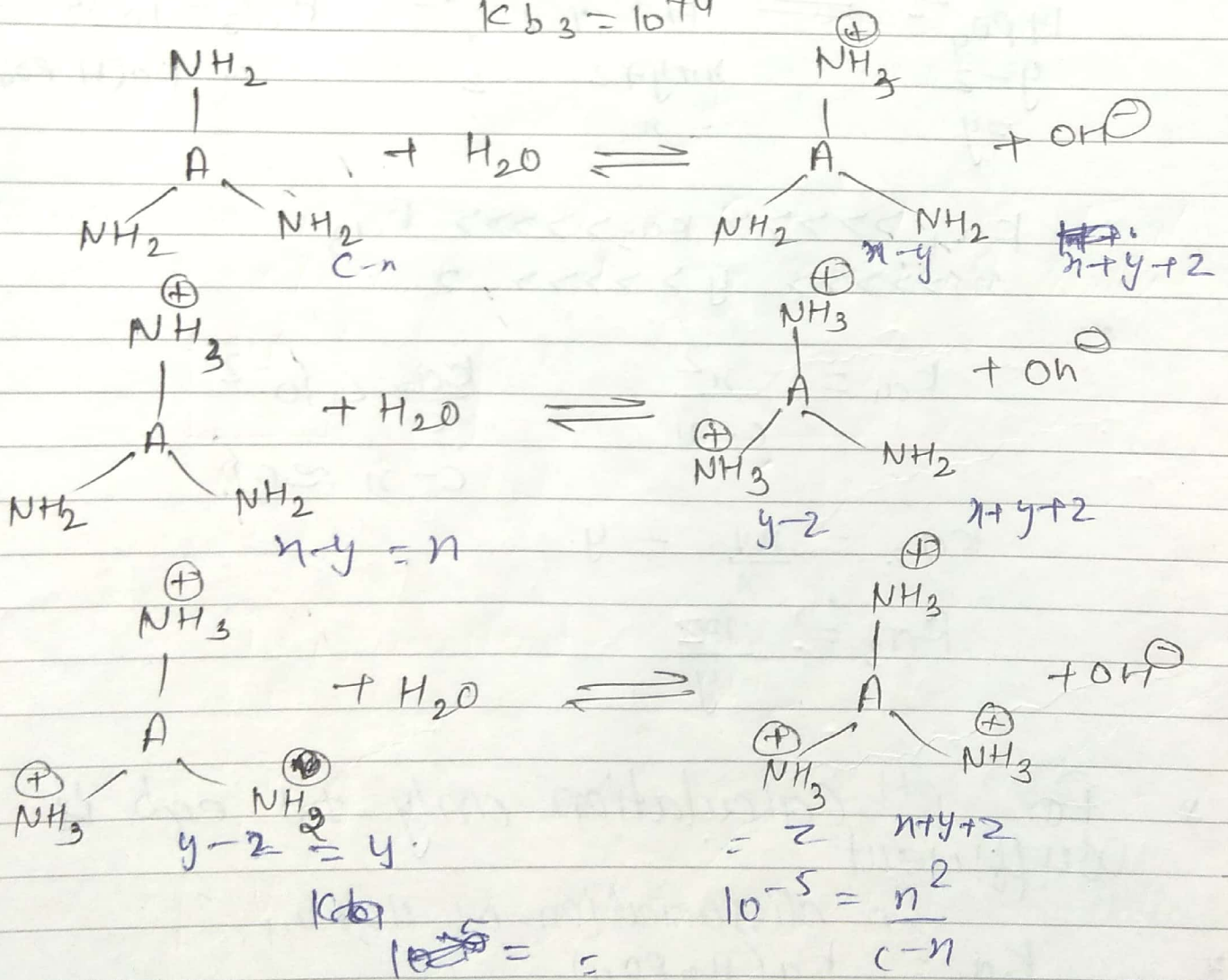
Ques: Calculate pH and ρ concⁿ of $A(NH_3)^{+3}$

In 0.1 M solution of $A(NH_2)_3$
 if $(A(NH_2)_3)$

$$K_{b1} = 10^{-5}$$

$$K_{b2} = 10^{-9}$$

$$K_{b3} = 10^{-14}$$



$$K_{b1} = \frac{n^2}{c-n}$$

$$10^{-5} = \frac{n^2}{0.1 - n}$$

$$[\text{OH}^\ominus] = n = 10^{-3}$$

$$p\text{OH} = 3$$

$$p\text{H} = 11$$

$$K_{b2} = \frac{ny}{n} = y = 10^{-9}$$

$$K_{b3} = \frac{nz}{y}$$

$$10^{-14} = \frac{(10^{-3})z}{(10^{-9})}$$

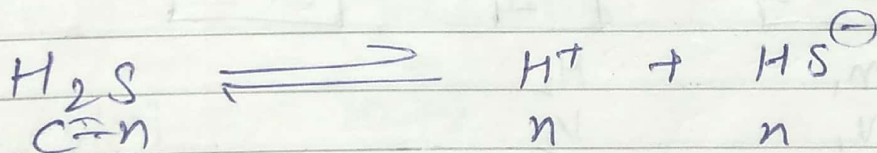
$$z = 10^{-20}$$

Que: Calculate pH of 0.1 M H_2S solution

$$K_{a1}(\text{H}_2\text{S}) = 9 \times 10^{-7}$$

$$K_{a2}(\text{HS}^\ominus) = 10^{-13}$$

$$K_a(\text{HS}^\ominus)$$



only H^+
not HS^\ominus

$$K_{a1} = \frac{n^2}{c-n}$$

$$9 \times 10^{-7} = \frac{n^2}{0.1-n}$$

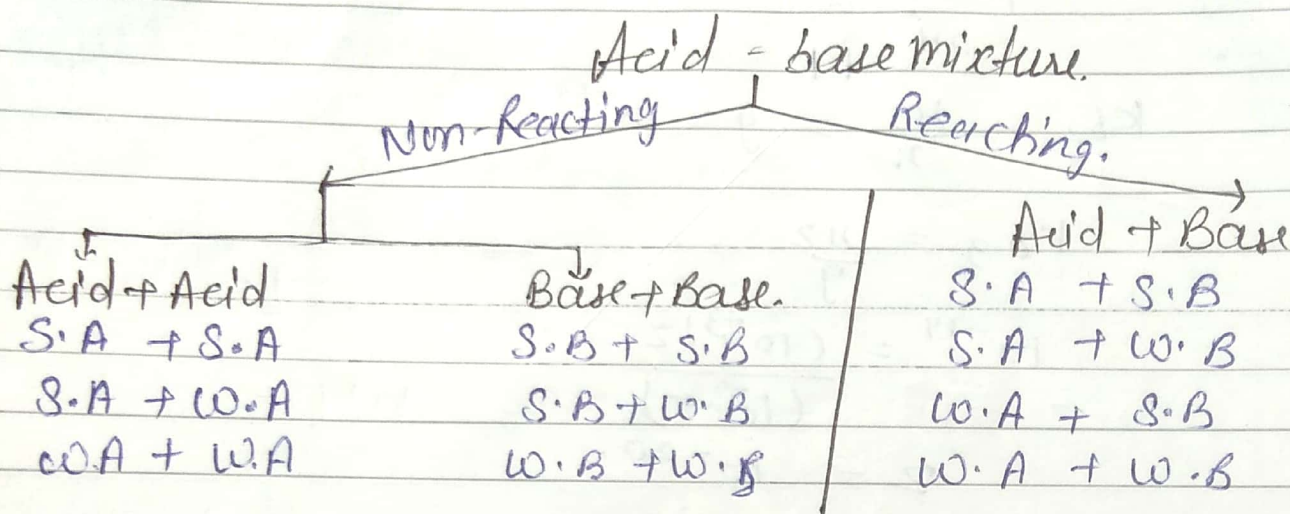
$$n^2 = 9 \times 10^{-8}$$

$$[\text{H}^+] = n = 3 \times 10^{-4}$$

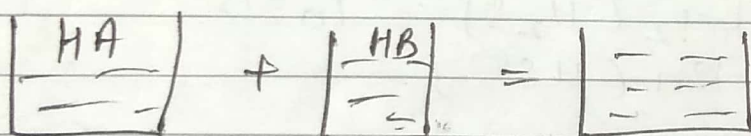
$$p\text{H} = 4 - \log 3$$

H.W: 0-1 JIAJ Complete.

* PH Calculation of Acid base mixture!



Question of mixing will be processed by final concⁿ of components in resultant solution.



$$\begin{array}{cc} m_1 & m_2 \\ v_1 & v_2 \end{array}$$

$$[\text{HA}]_{\text{resultant}} = \frac{M_1 V_1}{V_1 + V_2}$$

$$[\text{HB}]_{\text{resultant}} = \frac{M_2 V_2}{V_1 + V_2}$$

If $V_1 = V_2 = v$ if equal vol. is mixed.

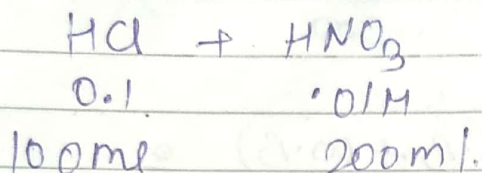
$$[\text{HA}]_{\text{resultant}} = \frac{M_1}{2}$$

$$[\text{HB}]_{\text{resultant}} = \frac{M_2}{2}$$

* pH calculation of non-reacting mixture!

$n = M + V$

(1) $\frac{(S.A + S.A)}{(S.B + S.B)}$



$N = M \times V.f$

$\frac{M \times \text{Volume}}{\text{Total vol.}}$

$[HCl]_{\text{resultant}} = \frac{0.1 \times 100}{300} = \frac{0.1}{3}$

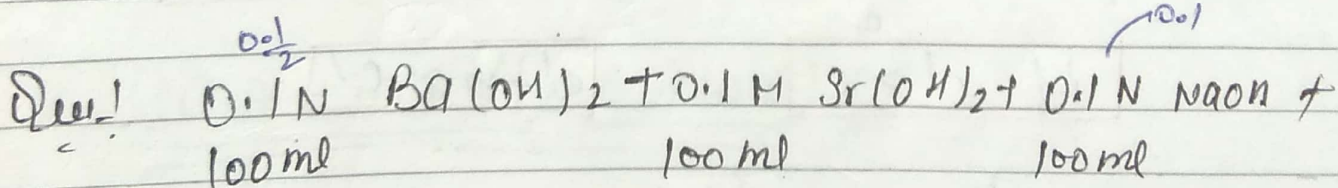
$[HNO_3]_{\text{resultant}} = \frac{0.1 \times 200}{300} = \frac{0.02}{3}$

$[H^+] = \frac{0.1}{3} + \frac{0.02}{3}$

(4.2)

$[H^+] = \frac{\text{mole of HCl} + \text{mole of HNO}_3}{\text{Total Volume}}$

$[H^+] = \frac{10 + 2}{300}$



Calculate concⁿ of OH⁻ ion in resultant solⁿ. 200ml pure H₂O

Ans

mole $0.1 \times 5 = 0.5 = \frac{0.1}{2}$

$= 0.5 + 10 + 10 +$

$\frac{0.1M \times 100 \times 2 + (0.1 \times 100 \times 2) + (0.1 \times 100)}{2}$

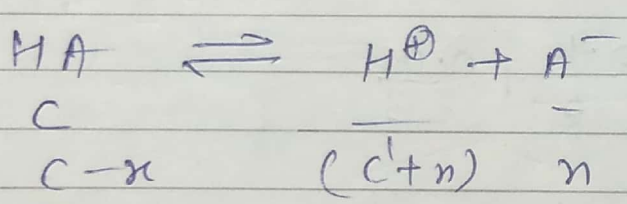
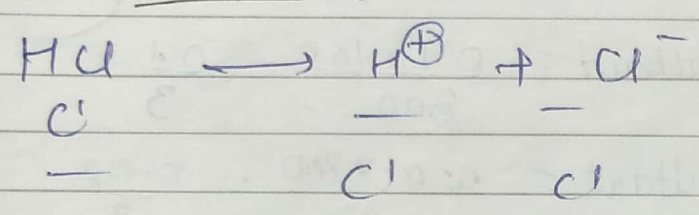
500

$$\boxed{\frac{K_a}{c} < 10^{-2}}$$

Ques: $10^{-1} M$ $(P^H=1)$ HCl + 10^{-2} $(P^H=2)$ HNO₃
100ml 100 ml.

$$[H^+] = \frac{10 + 1}{200} = \frac{11}{200}$$

$$* \frac{(S.A + w.A)}{(S.B + w.B)} \circ$$



$$K_{eq} = \frac{(c+n)(n)}{c-n}$$

$$\boxed{\frac{K_a}{c} < 10^{-2}} \\ \boxed{c-n \approx c}$$

$$K_a = \frac{(c+n)(n)}{c}$$

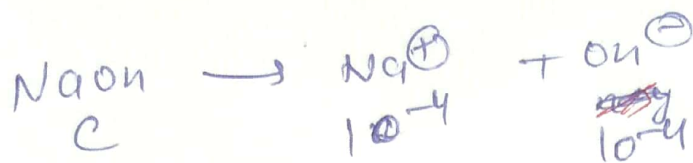
$$\boxed{\text{if } c' \geq c}$$

$$\boxed{c'+n \approx c'}$$

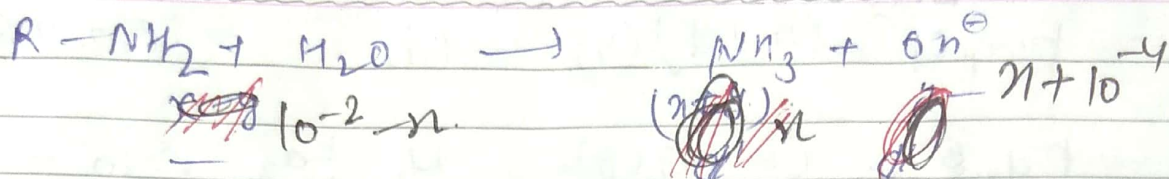
$$K_{eq} = \frac{c'(n)}{c}$$

Ques: In an aqueous solution $10^{-2} M$ R-NH₂ present with $10^{-4} M$ NaOH - then calculate concn of $[OH^{\ominus}]$ ion in the solution?

$$K_b (R-NH_2) = 2 \times 10^{-6}$$



$$\left[\frac{K_{a1}}{c_1} < 10^{-2} \right]$$



$$K_{eq} = \frac{(c-x)(x)}{c-x}$$

$$= K_{eq} = \frac{(c-x)x}{c-x}$$

$$K_{eq} = \frac{(10^{-2} - x)x}{(10^{-2} - x)}$$

$$= 2 \times 10^{-6} = \frac{(10^{-2} - x)x}{(10^{-2} - x)}$$

$$2 \times 10^{-6} = \frac{10^{-4}x + x^2}{10^{-2}}$$

$$\left[x = 2 \times 10^{-4} \right]$$

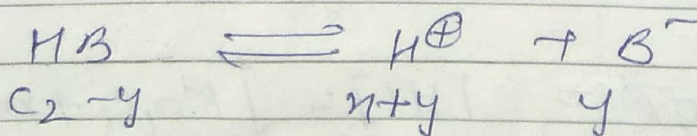
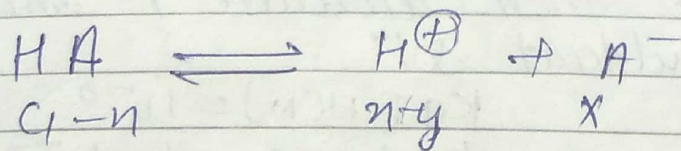
$$2 \times 10^{-8} = 10^{-4}x + x^2$$

$$x = 10^{-4} \quad \& \quad 2 \times 10^{-4}$$

$$[\text{OH}^-] = 10^{-4} + x$$

$$[\text{OH}^-] = 10^{-4} + 10^{-4} = 2 \times 10^{-4}$$

$$\times \frac{(w \cdot A + w \cdot A)}{(w \cdot B + w \cdot B)} \circ$$



$$K_{a1} = \frac{(x+y)(x)}{c_1 - x} \rightarrow 0$$

$$\text{if } \frac{K_{a1}}{c_1} < 10^{-2}$$

$$K_{a1} C_1 = (n+y)(n) \quad \text{--- (i)} \quad C_1 - n \approx C_1$$

$$K_{a2} C_2 = \frac{(n+y)(y)}{C_2 - y} \quad \text{if } \frac{K_{a2}}{C_2} < 10^{-2}$$

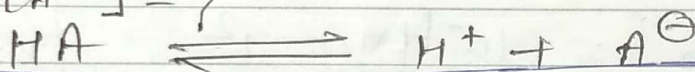
$$K_{a2} = (n+y)(y) \quad \text{--- (ii)} \quad C_2 - y \approx C_2$$

$$\begin{aligned} & \text{(i) + (ii)} \\ (n+y)(n+y) &= K_{a1} C_1 + K_{a2} C_2 \end{aligned}$$

$$[H^+] = (n+y) = \sqrt{K_{a1} C_1 + K_{a2} C_2}$$

for $[A^-] = ?$

~~HA~~



$$K_{a1} = \frac{[H^+][A^-]}{[HA]} \quad ?$$

$\swarrow \sqrt{K_{a1} C_1 + K_{a2} C_2}$
 $\searrow C_1 - n \approx C_1$

Ques? 0.2 Molar aqueous solⁿ of CH_3COOH is mixed with equal volume of 0.2 molar HCN. ~~Solⁿ~~ acid then calculate pH and con^t of $[CN^-]$ in resultant solⁿ

$$K_a(HCN) = 10^{-8}$$

$$K_a(CH_3COOH) = 10^{-5}$$

Ans:

$$10^{-7} = [H^+] = \sqrt{K_{a1} C_1 + K_{a2} C_2}$$

$$[H^+] = \sqrt{(10^{-8} \times 0.1) + (10^{-5} \times 0.1)}$$

$$[H^+] = \sqrt{10^{-9} + 10^{-6}}$$

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

$$pH = 3$$

$$10^{-8} = \frac{10^{-3} [CN^{\ominus}]}{0.1}$$

$$10^{-8} = \frac{10^{-3} [CN^{\ominus}]}{0.1}$$

Ques: H_3PO_4 + H_2A Calculate

$$0.2 M$$

$$100 ml$$

$$K_{a1} = 10^{-4}$$

$$K_{a2} = 10^{-8}$$

$$K_{a3} = 10^{-12}$$

$$0.2 M$$

$$100 ml$$

$$K_{a1} = 10^{-5}$$

$$K_{a2} = 10^{-9}$$

Calculate pH of resultant solution.

$$[H^+] = \sqrt{K_{a1} C_1 + K_{a2} C_2 + K_{a3} C_3}$$

$$= \sqrt{(10^{-4} \times 0.2) + (10^{-5} \times 0.1)}$$

$$[H^+] = \sqrt{10^{-5} + 10^{-6}} = \sqrt{10^{-5} \left(1 + \frac{1}{10}\right)}$$

$$[H^+] = \sqrt{11 \times 10^{-6}}$$

$$pH = \frac{1}{2} (6 - \log 11)$$

$$= \sqrt{10^{-5} \left(\frac{11}{10}\right)}$$

$$= \sqrt{10^{-5} (11 \times 10^{-1})}$$

$$= \sqrt{11 \times 10^{-6}}$$

* pH Calculation of Reacting mixture:

To calculate a pH of reacting mixture first we have to study hydrolysis of ions and Buffer solution.

(i) Relation b/w K_a and K_b of conjugate acid base:



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

$$K_b(\text{CN}^-) = \frac{[\text{HCN}][\text{H}^+][\text{OH}^-]}{[\text{H}^+][\text{CN}^-]}$$

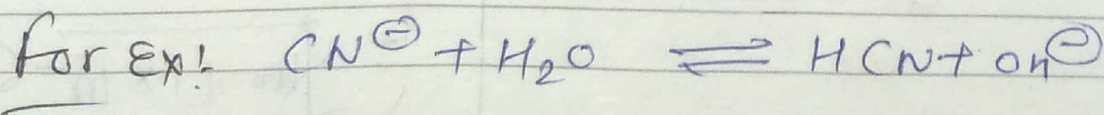
$$K_b(\text{CN}^-) = \frac{K_w}{K_a(\text{HCN})}$$

$$K_a(\text{HCN}) \cdot K_b(\text{CN}^-) = K_w$$

$$\boxed{pK_a + pK_b = pK_w}$$

* Hydrolysis of Ion:

Reaction of ion with water called hydrolysis of ion for ex. CN^-



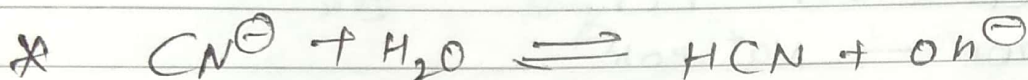


Ch. Ther. 02 6 to 17
 S-1 = Ionic Eq. 1 to 5

$$K_H = K_b(CN^\ominus) = \frac{K_w}{K_a(HCN)}$$

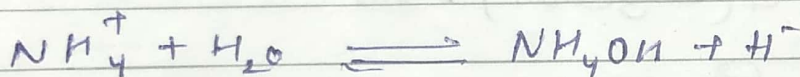


$$K_a(NH_4^+) = K_H = \frac{K_w}{K_b(NH_4OH)}$$



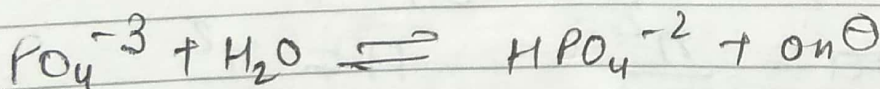
$$K_b(CN^\ominus) = K_H = \frac{K_w}{K_a(HCN)} = \frac{n^2}{c-n} \quad \frac{K_H}{c} < 10^{-2}$$

$c - n \approx c$
 $n = \sqrt{K_H c} = [OH^\ominus]$

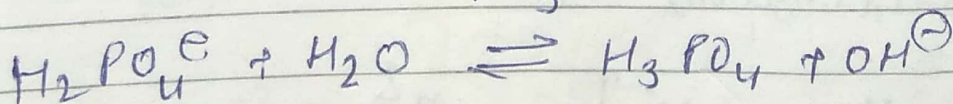


$$K_a(NH_4^+) = K_H = \frac{K_w}{K_b(NH_4OH)} = \frac{n^2}{c-n}$$

$$\frac{K_H}{c} < 10^{-2} \quad n = \sqrt{K_H c} = [H^+]$$



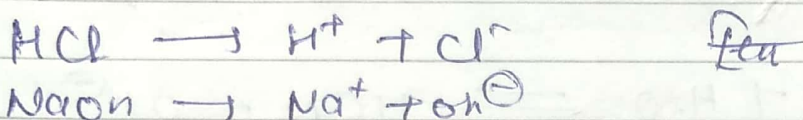
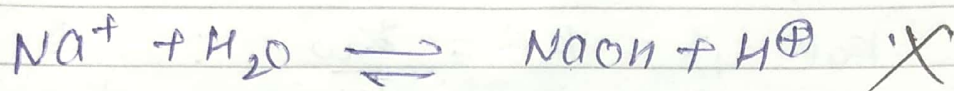
$$K_H = \frac{K_w}{K_{a3}}$$



$$K_H = \frac{K_w}{K_{a1}}$$

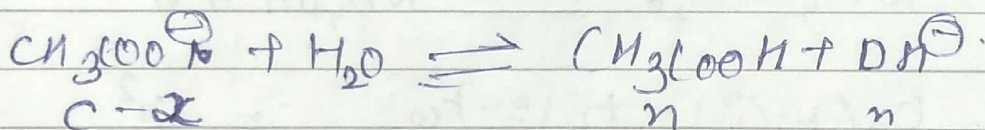
Important Point

* Hydrolysis of ions of strong Acid or strong Base do not occur in their aqueous solution



Ques: Calculate pH of 0.1 M CH_3COO^- or CH_3COONa solution

$$K_a(\text{CH}_3\text{COOH}) = 10^{-5}$$



$$K_a = \frac{n^2}{c-n}$$

$$10^{-5} = \frac{n^2}{0.1-n}$$

$$K_a = \frac{n^2}{c-n} \quad \text{H} = \frac{n^2}{c-n}$$

$$\frac{K_w}{K_a(\text{CH}_3\text{COOH})} = \frac{n^2}{c-n}$$

$$K_b = 10^{-9} = \frac{n^2}{0.1-n} \quad \frac{K_b}{c} < 10^{-2}$$

$$n^2 = 10^{-10}$$

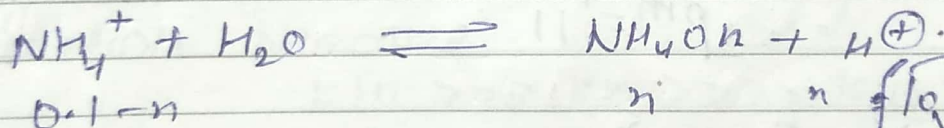
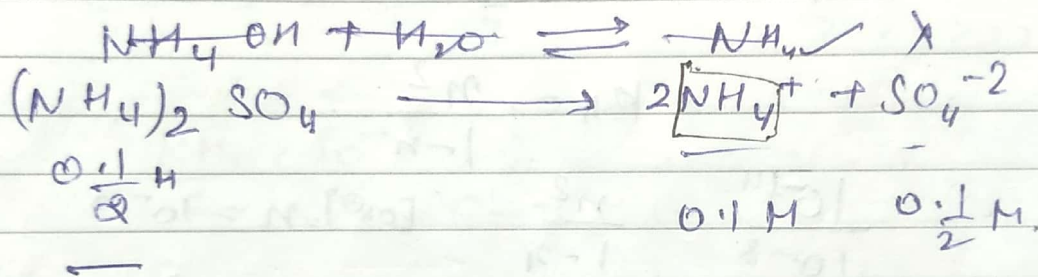
$$[\text{OH}^-] = n = 10^{-5}$$

$$\text{pOH} = 5$$

$$\alpha = h = \frac{x}{C} = \frac{10^{-5}}{0.1}$$

Q. Calculate pH and % degree of hydrolysis of
~~0.02~~ 0.1 M $(\text{NH}_4)_2\text{SO}_4$ solution

$$K_b = \left(\frac{\text{NH}_4\text{OH}}{\text{NH}_3} \right) = 10^{-5}$$



$$0.1 - x$$

$$x$$

$$x$$

$$\boxed{10^{-5} = \frac{x^2}{0.1 - x}}$$

$$\frac{K_w}{K_b(\text{NH}_4\text{OH})} = \frac{x^2}{0.1 - x}$$

$$= \frac{10^{-14}}{10^{-5}} = \frac{x^2}{0.1 - x}$$

$$10^{-9} = \frac{x^2}{0.1 - x}$$

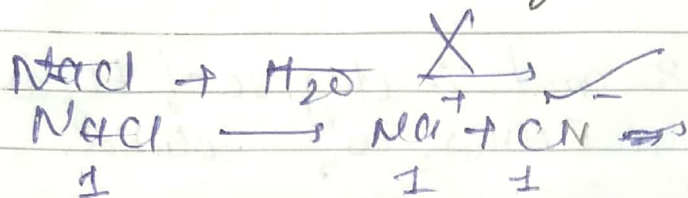
$$[\text{H}^+] = x = 10^{-5}$$

$$\text{pH} = 5$$

$$\% \text{ h} = \frac{x}{C} = \frac{10^{-5}}{0.1} \times 100$$

$$K_a(\text{HCN}) = 10^{-8}$$

Q. Calculate pH of 1 mol NaCN solution.
also calculate % degree of solution.



No



$$K_a = \frac{n^2}{1-n}$$

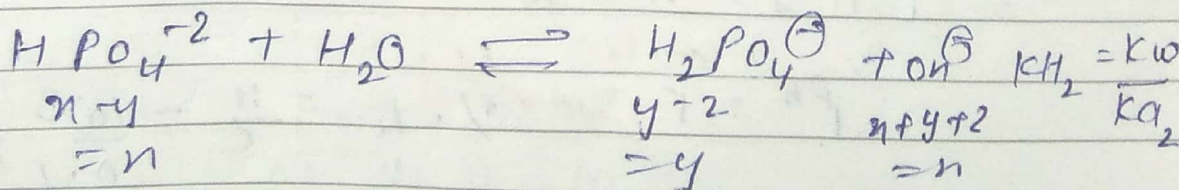
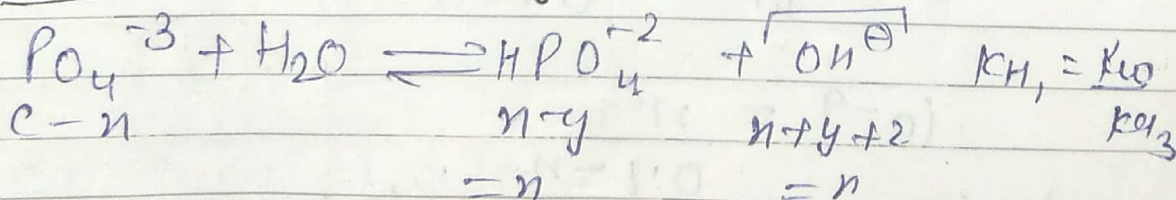
$$\frac{10^{-14}}{10^{-8}} = \frac{n^2}{1-n} \quad [\text{OH}^-] = n = 10^{-3}$$

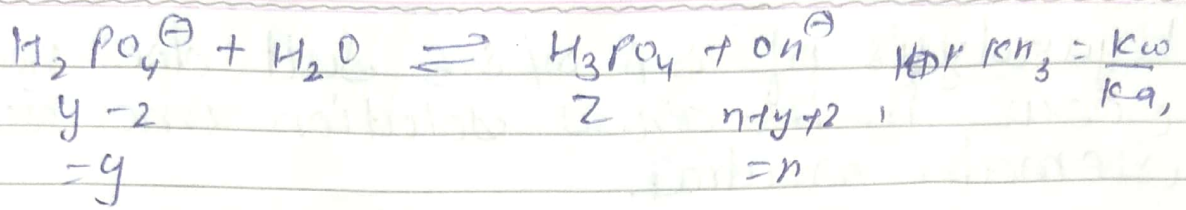
$$\text{pH} = 11$$

$$\% \text{ } n = \frac{n}{1} \times 100$$

$$= 10^{-3} \times 100 = 0.1\%$$

* Hydrolysis of Polyvalent Ions!





$$\frac{K_w}{K_{a3}} = K_{H1} = \frac{n^2}{c-n}$$

$$\frac{K_w}{K_{a2}} = K_{H2} = \frac{ny}{n}$$

$$\frac{K_w}{K_{a1}} = K_{H3} = \frac{ny}{z}$$

$$K_{a1} \gg \gg K_{a2} \gg \gg K_{a3}$$

$$\frac{K_w}{K_{a3}} \gg \gg \frac{K_w}{K_{a2}} \gg \gg \frac{K_w}{K_{a1}}$$

$$K_{H1} \gg \gg K_{H2} \gg \gg K_{H3}$$

$$n \gg \gg y \gg \gg z$$

$$\frac{K_{H1}}{c} < 10^{-2} \qquad c-n \approx c$$

Imp. point

* Only 1st eqn will be sufficient for pH calculation because

$$K_{H1} \gg \gg K_{H2} \gg \gg K_{H3}$$

$$n \gg \gg y \gg \gg z$$

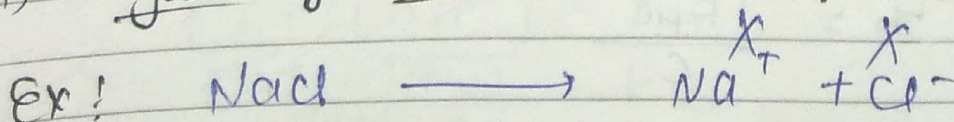
$$K_{H1} = K_H(\text{PO}_4^{3-})$$

$$K_{H2} = K_H(\text{HPO}_4^{2-})$$

$$K_{H3} = K_H(\text{H}_2\text{PO}_4^-)$$

* Salt Hydrolysis: Reaction of salt with water (H₂O) called salt hydrolysis.

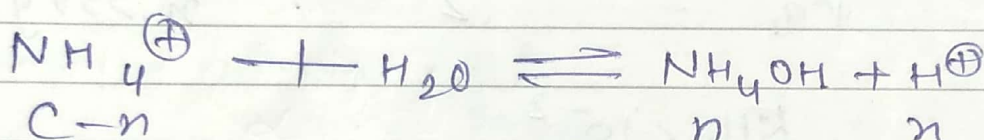
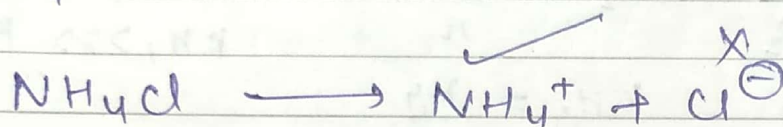
* 1) Hydrolysis of SA + Strong Base salt!



Hydrolysis of S.A or S.B salt does not occur in its aqueous solution and solution remain neutral.

(ii) Hydrolysis of (S.A + W.B) salt:

Ex! NH_4Cl



$$\frac{K_w}{K_b(\text{NH}_4\text{OH})} = K_h = \frac{n^2}{c-n}$$

$$\frac{K_h}{c} < 10^{-2}$$

$$n^2 = K_h c$$

$$c-n \approx c$$

$$[\text{H}^+] = n = \sqrt{K_h c}$$

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

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

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

$$\frac{K_h}{c} < 10^{-2}$$

* Degree of Hydrolysis:

$$\alpha = h = \frac{n}{c}$$

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

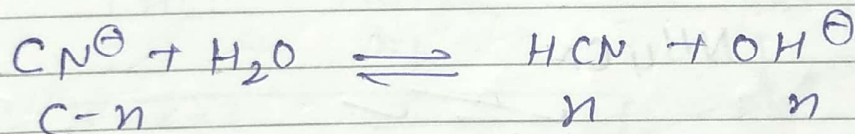
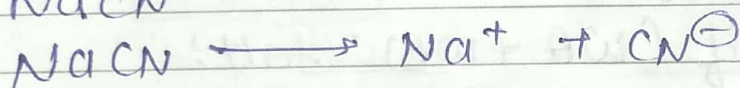
$$h = \sqrt{\frac{K_h}{c}}$$

$$\% h = \sqrt{\frac{K_h}{c}} \times 100$$

* Nature of SA + WB salt solution will be Acidic.

* Hydrolysis of (W.A + S.B) salt :

Ex:



$$\frac{K_w}{K_a(HCN)} = K_h = \frac{x^2}{c-x} \quad \frac{K_h}{c} < 10^{-2}$$

$c-x \approx c$

$$x^2 = K_h c$$

$$[OH^-] = x = \sqrt{K_h c}$$

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

$$[OH^-] = \sqrt{\frac{K_w}{K_a} c}$$

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

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

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

$$\frac{K_H}{c} < 10^{-2}$$

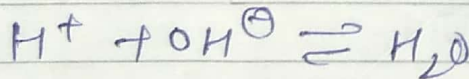
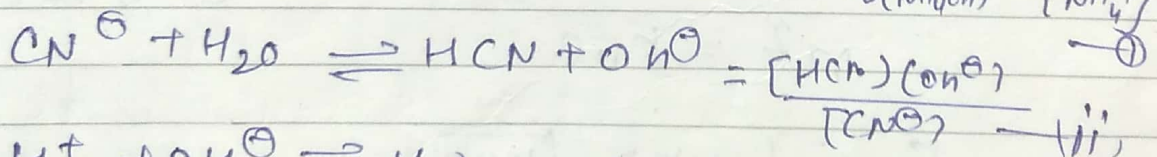
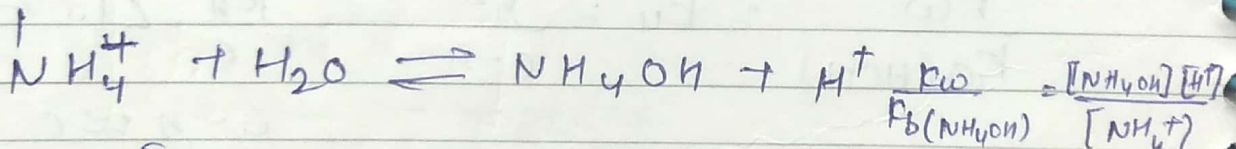
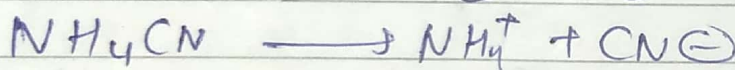
$$p^H = \frac{1}{2} (pK_w + pK_a + \log c)$$

* Nature of SA + WB salt
WA + SB salt solution will be basic

degree of hydrolysis:
 $\alpha = \frac{A}{A+B}$

* Hydrolysis of (WA + WB) salt:

Example: NH_4CN



$$\frac{1}{K_w} = \frac{1}{[H^+][OH^-]} \quad \text{--- (iii)}$$

(9) Nature of WA + WB salt solution can be acidic, basic or neutral it depends on extent of hydrolysis of anion and cation

$n \approx y$

* for derivation purpose it is assumed that extent of hydrolysis of anion and cation are almost equal

$$(i) \div (ii)$$

$$\frac{K_a}{K_b} = \frac{[NH_4OH] \cdot [CN^\ominus]}{[HCN] \cdot [NH_4^+]} \cdot \frac{[H^+]}{[OH^\ominus]}$$

$$\frac{K_a}{K_b} = \frac{[H^+]^2}{[H^+][OH^\ominus]}$$

$$\frac{K_a}{K_b} = \frac{[H^+]^2}{K_w}$$

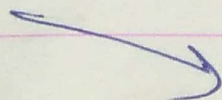
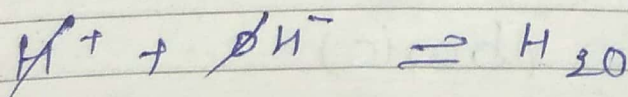
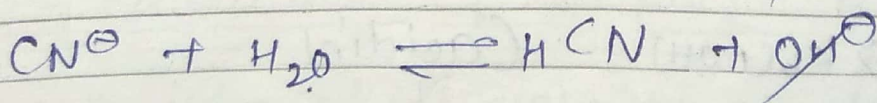
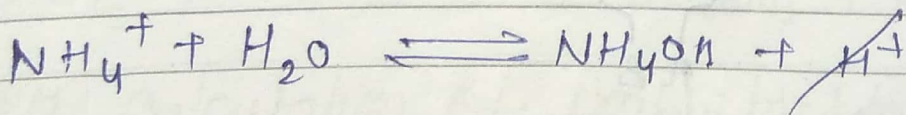
$$[H^+]^2 = \frac{K_w K_a}{K_b}$$

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

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

Important
learn this
formula

* Overall Rxn of Hydrolysis of (wA + wB) salt and its hydrolysis constant.

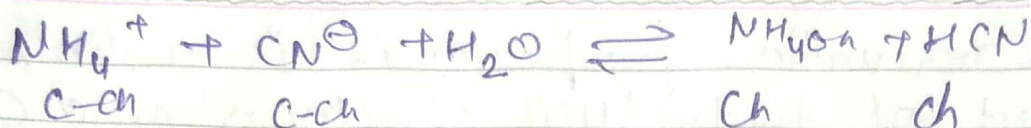


6 to 16

0-1

S-1

1 to 5



$$K_H = \frac{K_w}{K_a(\text{HCN}) \cdot K_b(\text{NH}_4\text{OH})}$$

$$K_H = \frac{(\text{CH})^2}{(\text{C-CH})^2} =$$

extent of hydrolysis or degree of hydrolysis ~~will not~~ of (WA + WB) will not depend on concentration

$$\sqrt{K_H} = \frac{\text{CH}}{\text{C-CH}}$$

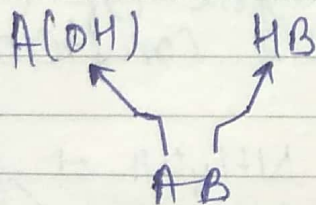
$$\sqrt{\text{CH}} = \frac{h}{1-h}$$

$$h \ll 1$$

$$1-h \approx 1$$

$$h = \sqrt{K_H}$$

* Nature of WA + WB salt solution



$K_a(\text{HB}) > K_b(\text{A(OH)})$ (acidic)

$K_a(\text{HB}) < K_b(\text{A(OH)})$ (basic)

Strong

$$K_a(\text{HB}) = K_b(\text{AOH}) \quad (\text{neutral})$$

Ex! $\text{CH}_3\text{COONH}_4 \rightleftharpoons K_a(\text{CH}_3\text{COOH}) = K_b(\text{NH}_4\text{OH})$

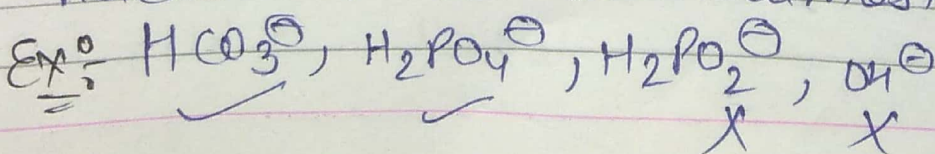
	Nature	K_H	* $[\text{H}^+]$	pH	h
S.A + W.B Ex: NH_4Cl	acidic	$\frac{K_w}{K_b}$	$\sqrt{\frac{K_w c}{K_b}}$	$\frac{1}{2}(pK_w - pK_b - \log c)$	$\sqrt{\frac{K_H}{c}}$
W.A + S.B Ex: NaCN	basic	$\frac{K_w}{K_a}$	$\sqrt{\frac{K_w K_a}{c}}$	$\frac{1}{2}(pK_w + pK_a + \log c)$	$\sqrt{\frac{K_H}{c}}$
W.A + W.B Ex: NH_4CN	$K_a > K_b$ (acidic) $K_b > K_a$ (basic) $K_a = K_b$ (neutral)	$\frac{K_w}{K_a K_b}$	$\sqrt{\frac{K_w K_a}{K_b}}$	$\frac{1}{2}(pK_w + pK_a - pK_b)$	$\sqrt{\frac{K_H}{c}}$

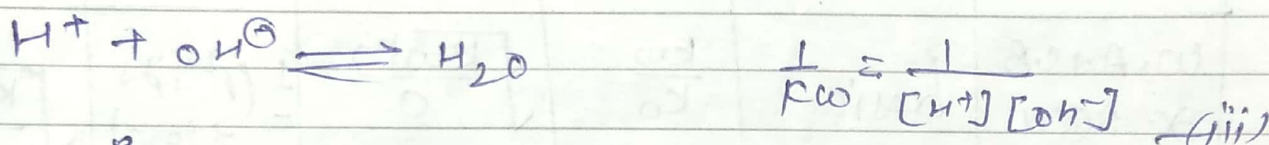
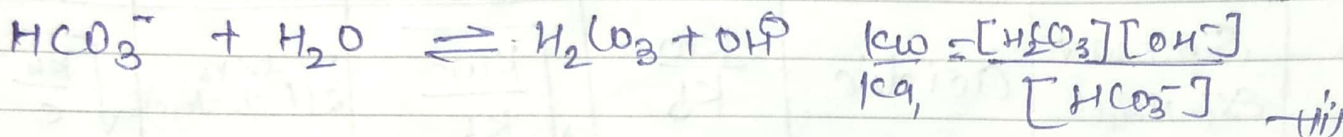
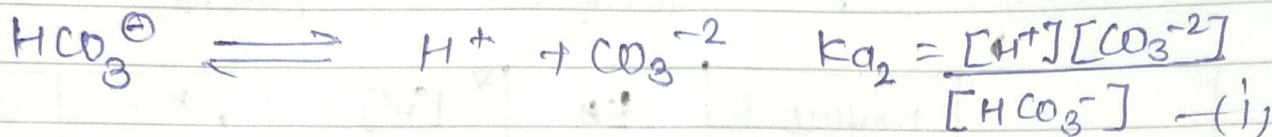
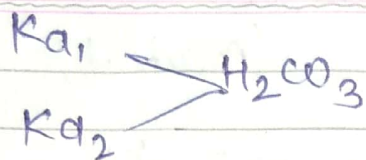
Qw! what will be nature of solution of following salts!

- (i) KCN \Rightarrow basic
- (ii) $\text{FeCl}_3 \Rightarrow$ acidic $\rightarrow \text{Fe}(\text{OH})_3 + \text{HCl}$
- (iii) $\text{BaCl}_2 \Rightarrow$ Neutral $\rightarrow \text{Ba}(\text{OH})_2 + \text{HCl}$

* pH Calculation of Amphiprotic species:

These type of species can accept as well as release H^+ ion with almost equal strength





(i) \div (iii)

$$\frac{K_{a2} \cdot K_{a1}}{K_w} = \frac{[CO_3^{2-}]}{[H_2CO_3]} \cdot \frac{[H^+]}{[OH^-]}$$

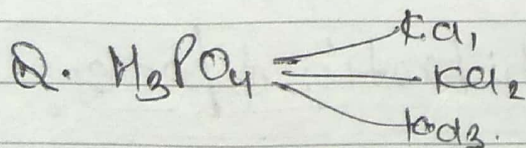
$$\frac{K_{a1} \cdot K_{a2}}{[H^+][OH^-]} = \frac{[H^+]}{[OH^-]}$$

$$[H^+]^2 = K_{a1} \cdot K_{a2}$$

$$[H^+] = \sqrt{K_{a1} \cdot K_{a2}}$$

$$\boxed{pH = \frac{1}{2}(pK_{a1} + pK_{a2})}$$

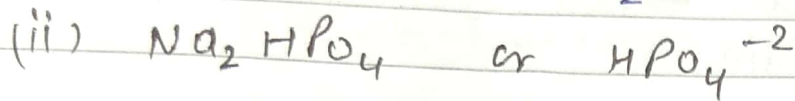
~~Answer~~
~~Ans~~



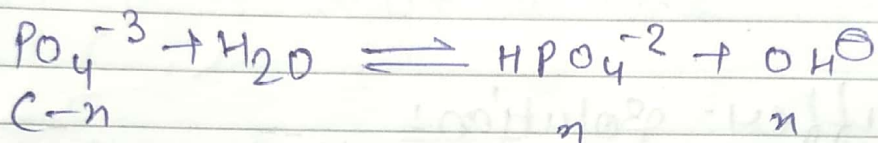
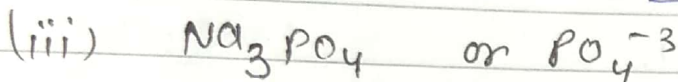
then calculate pH of given solution
(i) NaH_2PO_4 or $H_2PO_4^-$?

A B → React
 A A → non reacting

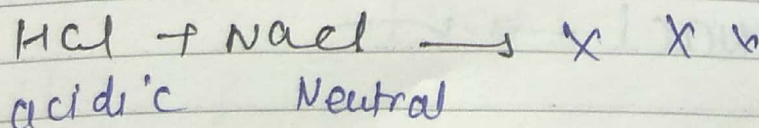
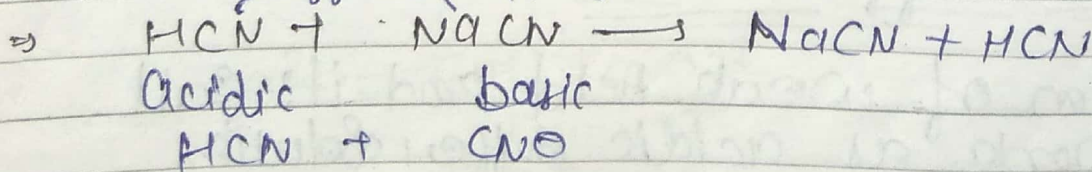
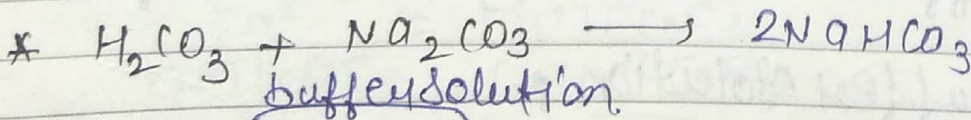
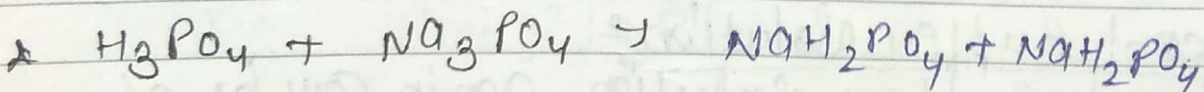
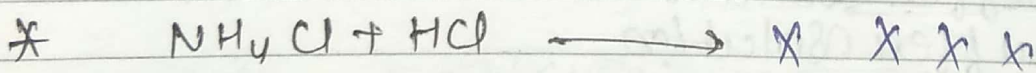
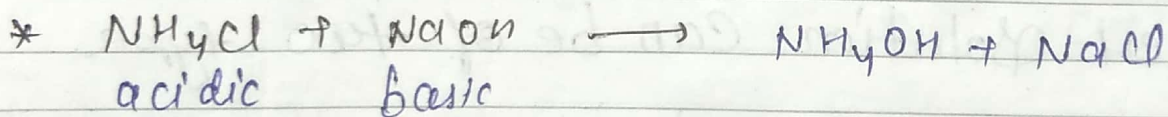
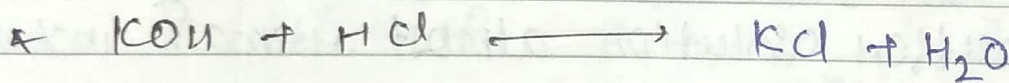
$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$



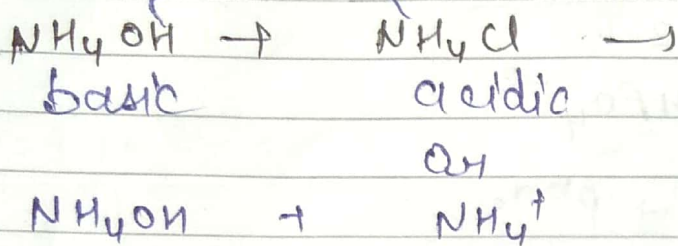
$$pH = \frac{pK_{a2} + pK_{a3}}{2}$$



$$\frac{K_w}{K_{a3}} = pH_1 = \frac{x^2}{c-n}$$



Buffer solution



not a buffer solution.

* Buffer solution!

Buffer solution resist its pH change on dilution or addition of acid or base externally. If very minute amount of acid or base add or externally the pH of buffer solution almost remain unchanged.

* Buffer solution can be of two type.

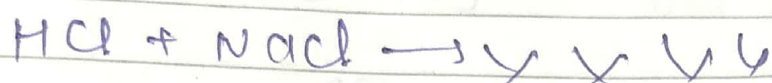
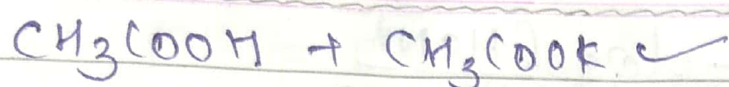
- (i) mixed Buffer solution
- (ii) Simple Buffer solution

(i) Mixed Buffer solution :-
mixed Buffer solution again can be of two type.

(a) Acidic Buffer solution :-

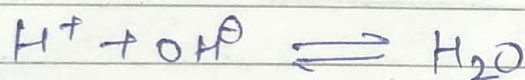
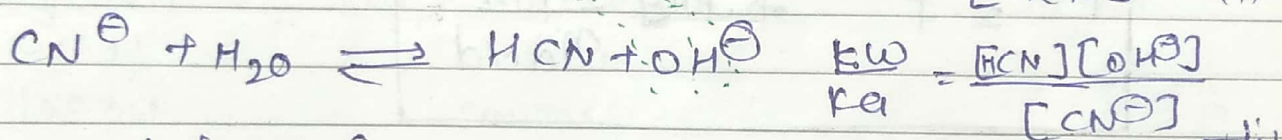
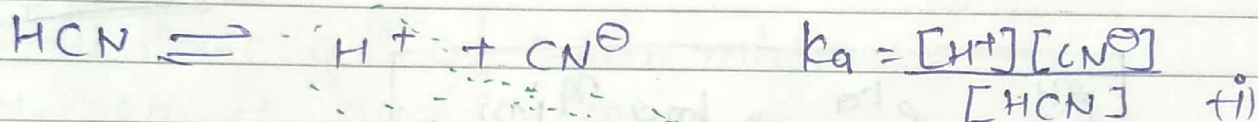
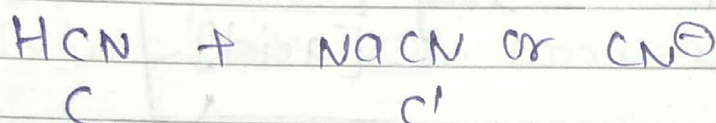
Solution of weak acid and its salt will work as acidic Buffer solution.

for ex! $\text{HCN} + \text{NaCN} \rightarrow \checkmark$



because strong acid

Example!



$$\frac{K_w}{K_a} = \frac{1}{[\text{H}^+][\text{OH}^\ominus]} \quad \text{(iii)}$$

(i) \div (ii)

$$\frac{K_a^2}{K_w} = \frac{[\text{H}^+][\text{CN}^\ominus]^2}{[\text{HCN}]^2[\text{OH}^\ominus]}$$

$$\frac{K_a^2}{[\text{H}^+][\text{OH}^\ominus]} = \frac{[\text{H}^+][\text{CN}^\ominus]^2}{[\text{HCN}]^2[\text{OH}^\ominus]}$$

$$K_a^2 = \frac{[\text{H}^+]^2[\text{CN}^\ominus]^2}{[\text{HCN}]^2}$$

$$K_a = \frac{[\text{H}^+][\text{CN}^\ominus]}{[\text{HCN}]}$$

$$[\text{H}^+] = K_a \frac{[\text{HCN}]}{[\text{CN}^\ominus]}$$

A.B.S: Nature:

$$pH = pK_a - \log \frac{[HCN]}{[CN^-]}$$

$$pH = pK_a + \log \frac{[CN^-]}{[HCN]}$$

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

c' from salt

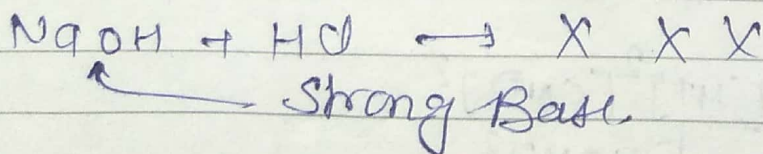
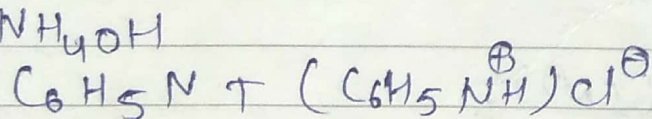
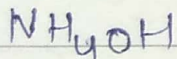
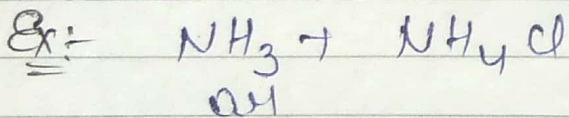
c from acid

Levey

$$pH = pK_a + \log \frac{n_{ion}}{n_{acid}}$$

* Basic Buffer Solution:

Mixture of weak base and its salt work as basic Buffer solution



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

mixed buffer prob

SH \Rightarrow 16-26 +
OT \Rightarrow 6 to 8.

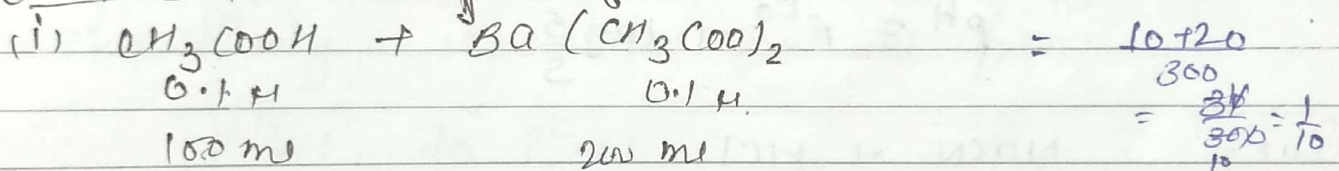
$$pOH = pK_b + \log \frac{n_{ion}}{n_{base}}$$

N/B

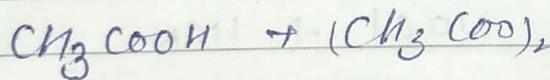
* Simple buffer solution : ^{Nov}

Solution of amphiprotic species or weak acid weak base salt can work as simple buffer solution.

Ques: Calculate pH of given mixture.



$$K_a(CH_3COOH) = 10^{-5}$$

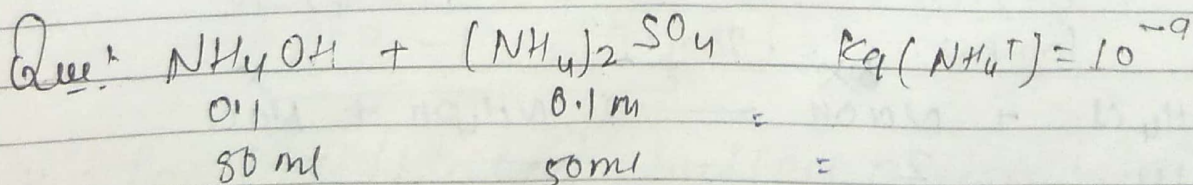


$$pH = pK_a + \log \frac{n_{ion}}{n_{acid}}$$

$$pH = 5 + \log 4$$

$$pH = 5 + \log 2$$

$$pH = 5.6$$

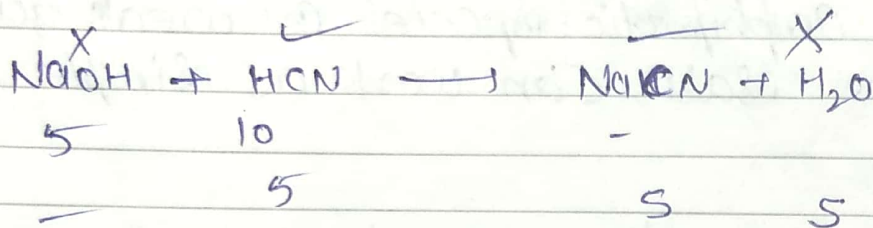
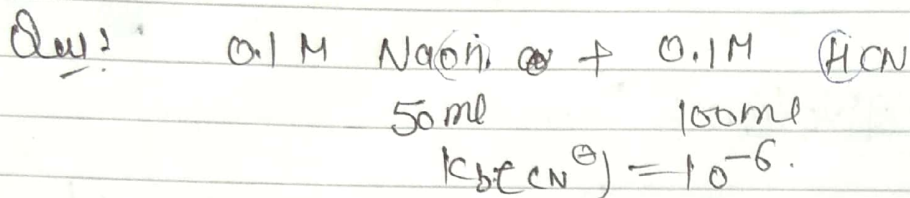


$$pOH = pK_b + \log \frac{10}{5}$$

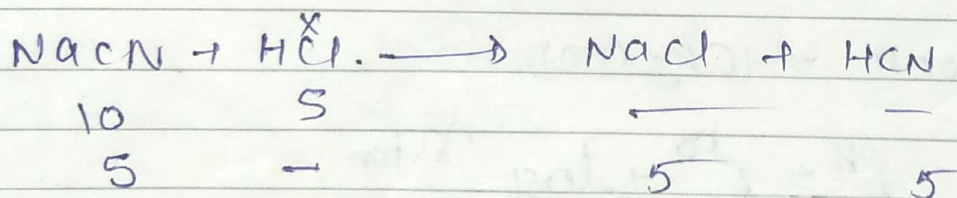
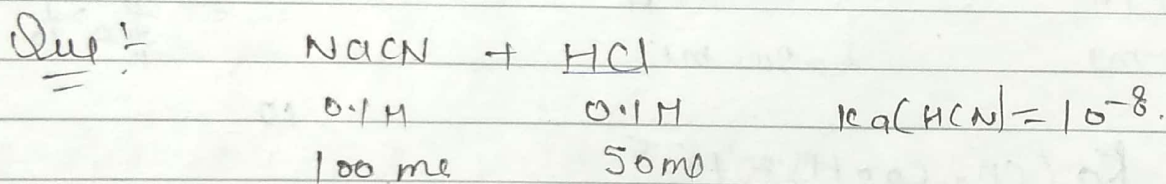
$$pOH = 5 + \log 2$$

$$p^{OH} = 5.3$$

$$pH = 14.5.3 = 8.7$$

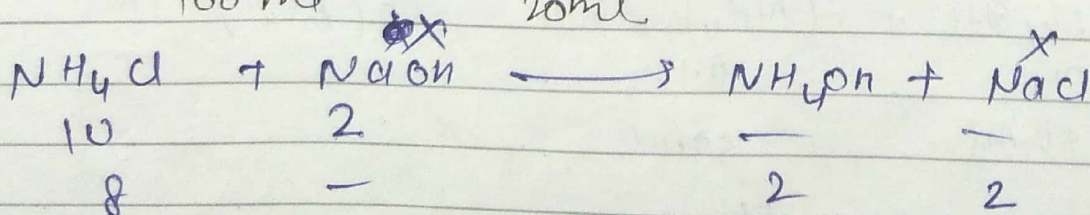
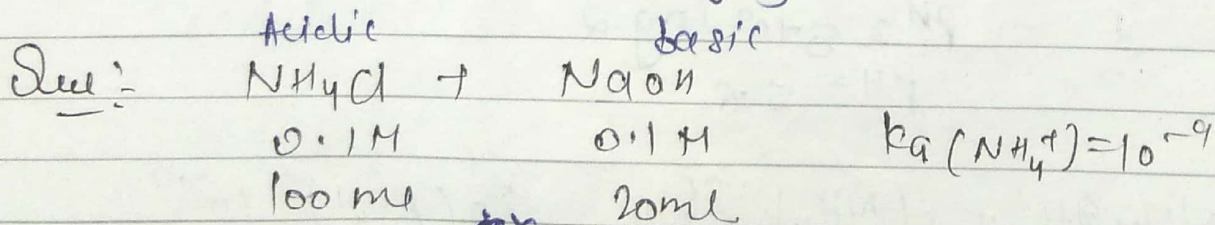


$$pH = pK_a + \log \frac{5}{5}$$



$$pH = pK_a$$

$$pH = 8 + \log \frac{5}{5}$$



$$p^{OH} = pK_b + \log \frac{8}{2}$$

\downarrow
 10^{-5}

Important point Regarding Buffer solution:

* Buffer Capacity of buffer solⁿ (ϕ) :-

$$\phi \uparrow \quad \text{quality of buffer} \uparrow$$

B.C of B.S = $\frac{\text{mol of } H^+ / OH^- \text{ added in buffer solution}}{\text{change in } pH \text{ of buffer solution}}$

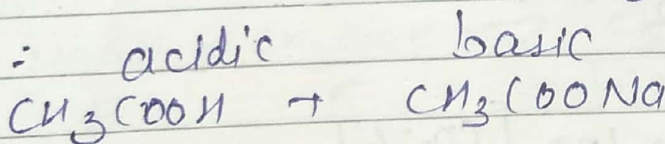
(iii) pH Range of Buffer solution:

It is the pH interval in which buffer solⁿ ~~is~~ works effectively its value will be from

$$pK_a - 1 \quad \text{to} \quad pK_a + 1$$

Theoretically it is based on concept that

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



$$\begin{aligned} \frac{[CH_3COOH]}{[CH_3COO^-]} &< 10 \\ \frac{1}{10} &< \frac{[CH_3COO^-]}{[CH_3COOH]} \end{aligned}$$

$$pK_a - 1 < pH$$

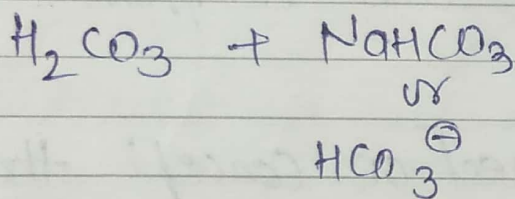
$$\frac{[CH_3COO^-]}{[CH_3COOH]} < 10$$

$$pH < pK_a + 1$$

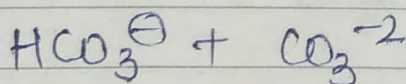
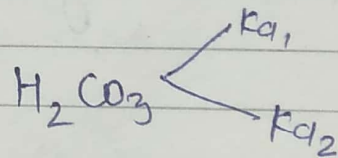
* for best/highest buffer action $\frac{[ion]}{[acid]} = 1$

1^o diff
com + the
1^o carbon

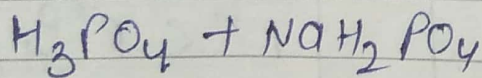
- * ON dilution buffer capacity of buffer solⁿ will always decrease
- * Nature of Acidic buffer solution can be acidic, basic or neutral
- * Nature of basic buffer solⁿ can be basic, acidic or neutral.
- * Solution of two conjugate species will always work as a buffer solution.



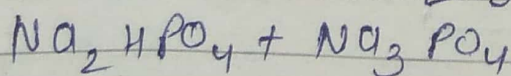
$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$



$$\text{pH} = \text{p}K_{a2} + \log \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]}$$



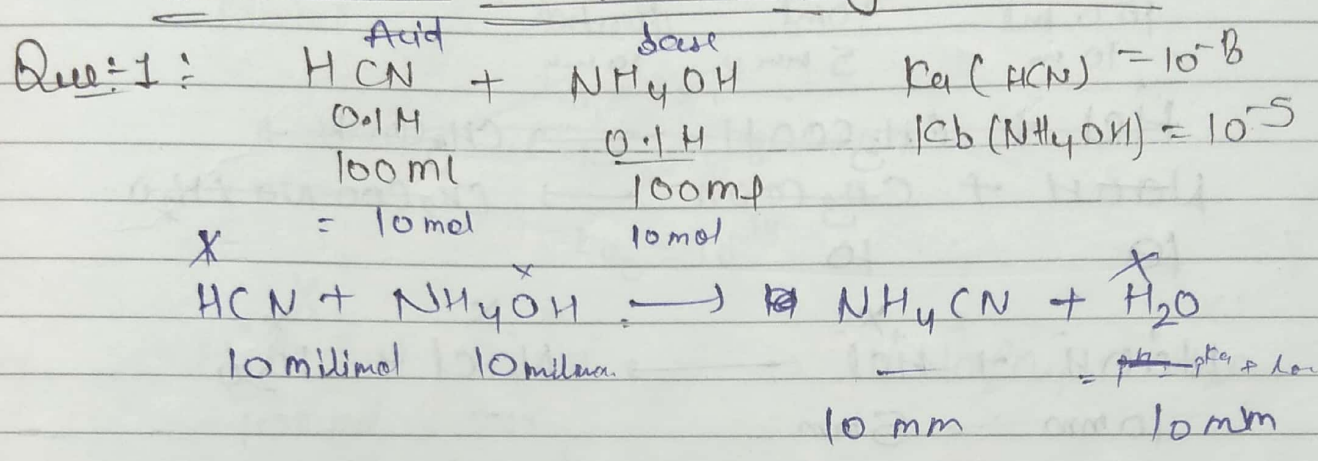
$$\text{pH} = \text{p}K_{a1} + \log \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]}$$



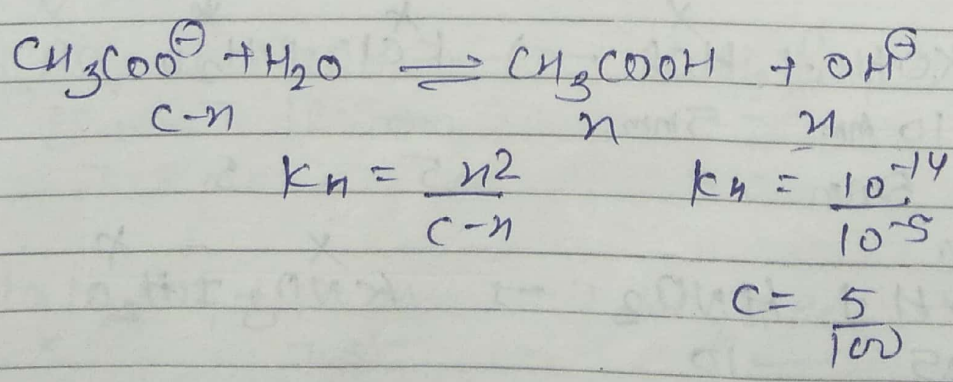
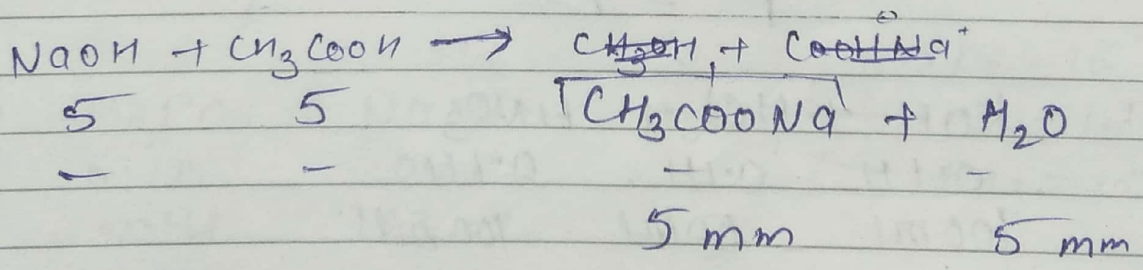
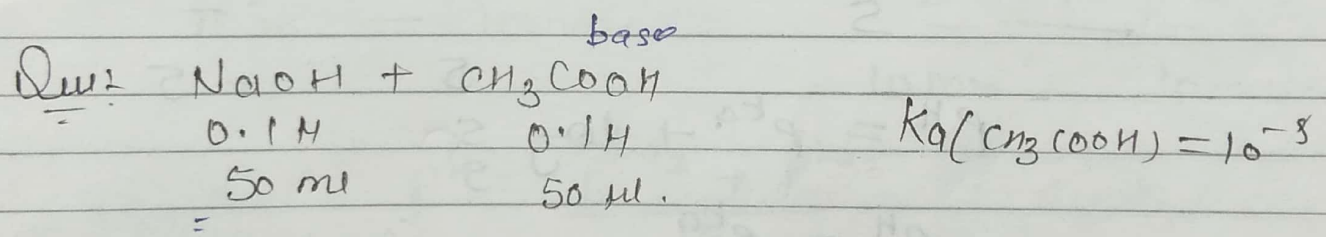
$$\text{pH} = \text{p}K_{a3} + \log \frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^{2-}]}$$

React M & B. \rightarrow amphiprotic
 Buff. \rightarrow w.A.w.B. }
 Buffer amphiprotic }

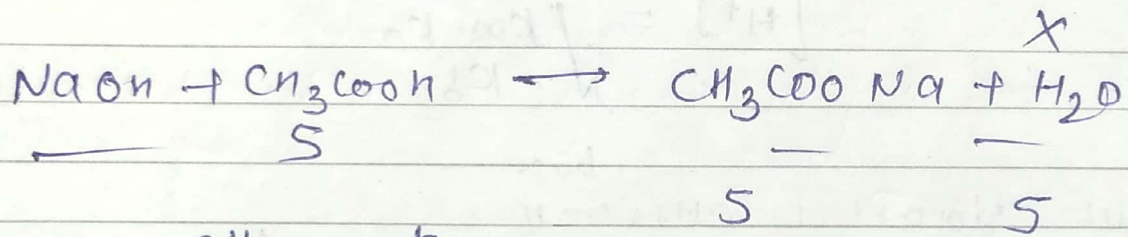
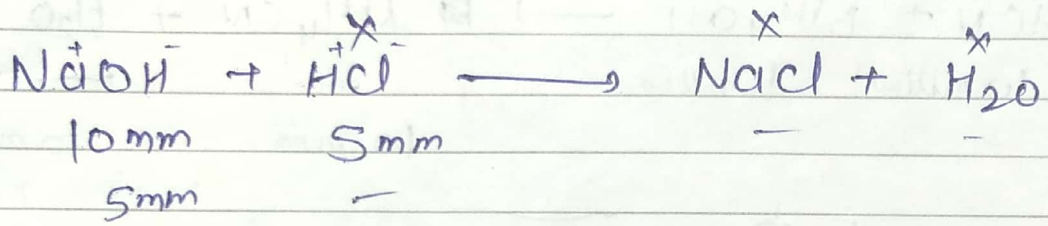
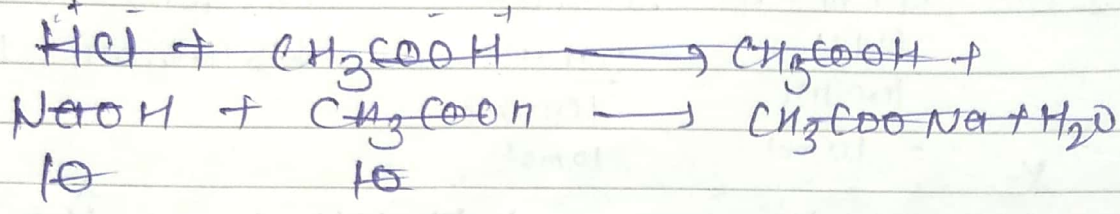
Ques: PH Calculation of Reacting Mixture



$$[\text{H}^+] = \sqrt{\frac{K_w \cdot K_a}{K_b}}$$



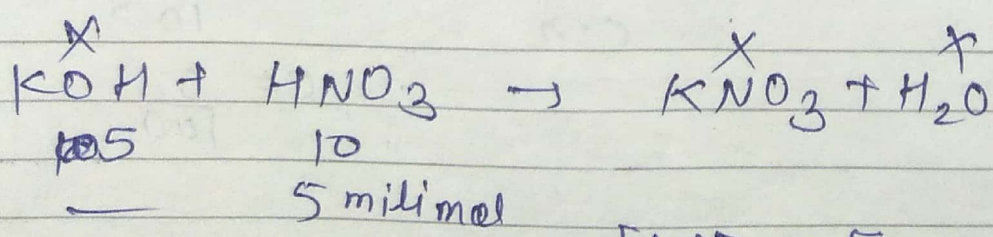
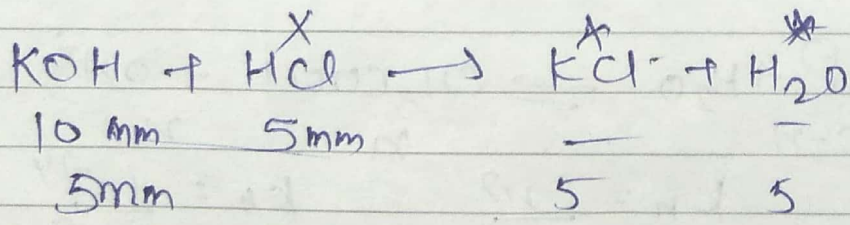
Ques) $\text{NaOH} + \text{HCl} + \text{CH}_3\text{COOH}$ $K_a(\text{CH}_3\text{COOH}) = 10^{-5}$
 0.1 M 0.1 M 0.1 M
 100 ml 50 ml 100 ml
 = 10 mm 5 mm 10 mm



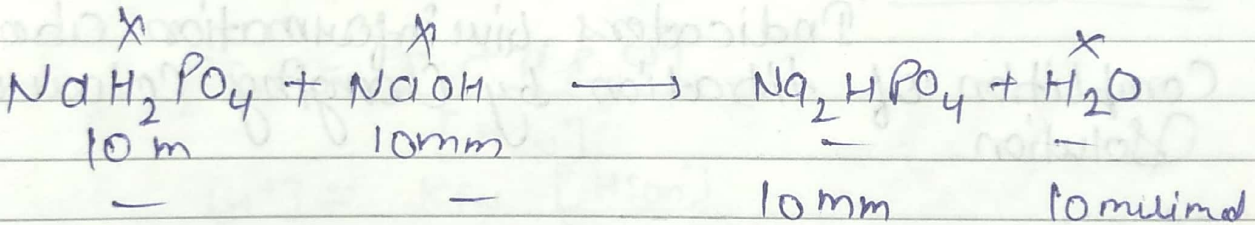
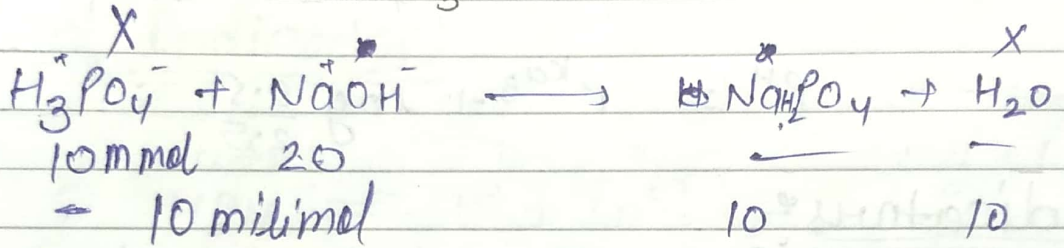
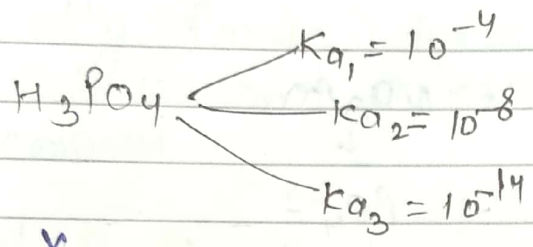
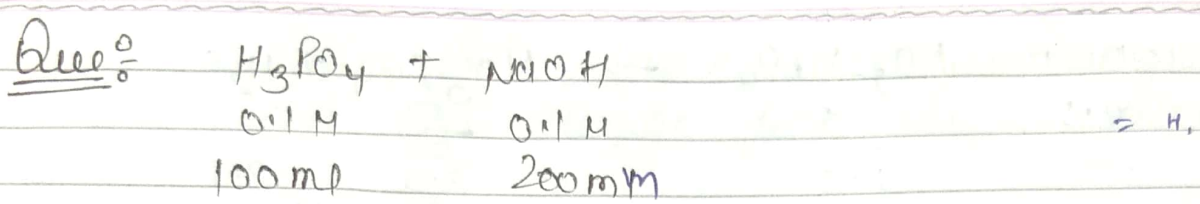
$\text{pH} = \text{p}K_a + \log \frac{5}{5}$

$\text{pH} = \text{p}K_a$

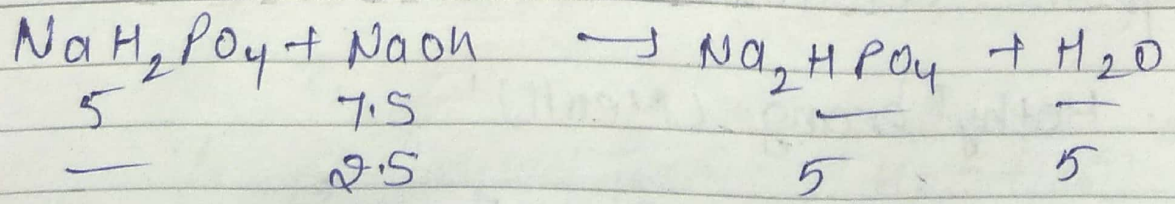
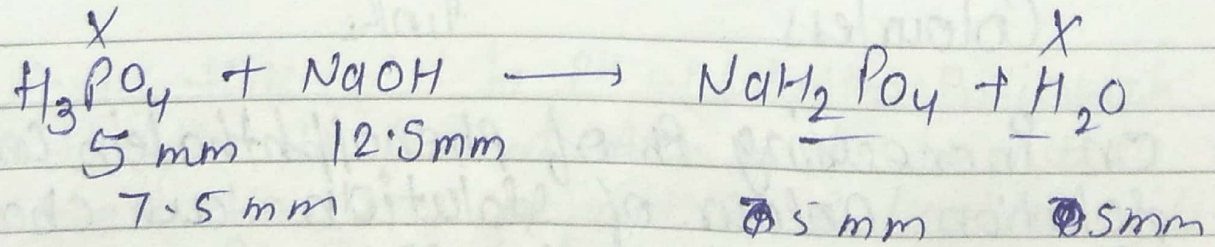
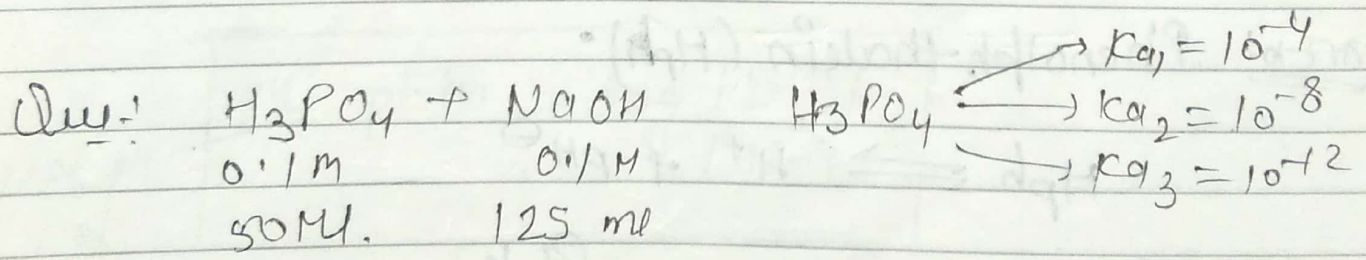
Ques) $\text{KOH} + \text{HCl} + \text{HNO}_3$
 0.1 M 0.1 M 0.1 M
 100 ml 50 ml 100 ml

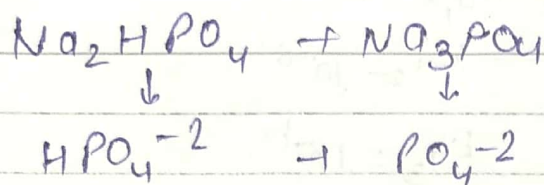
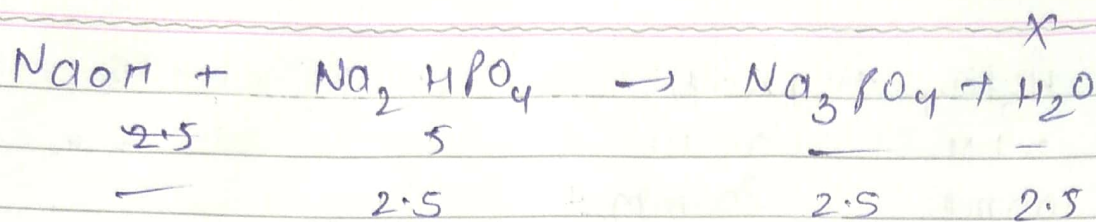


$[\text{H}^+] = \frac{5}{250}$



$$pH = \frac{pK_{a2} + pK_{a3}}{2}$$





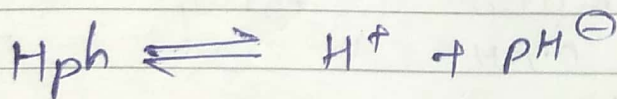
$$\text{pH} = \text{p}K_{a3} + \log \frac{2.5}{2.5}$$

* Indicators

Indicators give information about completion of titration by changing colour of solution

Indicators used in Acid-base titration generally are weak organic acid or weak organic base

Ex: Phenolphthalein (Hph)

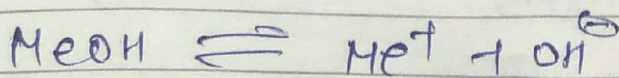


Colourless

Pink.

⇒ On increasing Ph of phenolphthalein containing solution colour of solution are changed from colourless to pink.

Ex Methyl orange (MeOH)



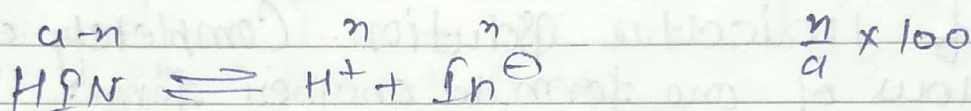
Yellow

Red.

on increasing pH colour of methylorange containing solution can change from red to yellow.

Generally ionised form of Indicator represent dark colour and unionised form represent light colour.

x pH of Indicator:



$$K_{In} = \frac{[H^+][In^{\ominus}]}{[H_nIn]}$$

$$[H^+] = K_{In} \frac{[H_nIn]}{[In^{\ominus}]}$$

$$pH = pK_{ion} - \log \frac{[H_nIn]}{[In^{\ominus}]}$$

ph of ph of

$$pH = pK_{ion} + \log \frac{[In^{\ominus}]}{[H_nIn]}$$

x Basically this will be pH of solution in which indicator is present. Acc. to it, it will be decided how much part of indicator will remain in ionised form and unionised form.

$$\% \text{ of Ionised form} = \frac{[In^{\ominus}]}{[H_nIn] + [In^{\ominus}]} \times 100$$

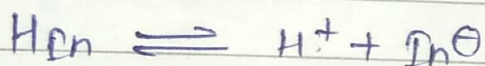
$$\% \text{ of unionised form} = \frac{[HIn]}{[HIn] + [In^-]} \times 100$$

$$\text{or } \frac{\alpha}{a} \times 100.$$

* pH Range of Indicator:

The pH is the pH interval in which colour of indicator solution completely changed from colour of one form to another form.

Theoretically it is based on the concept of that



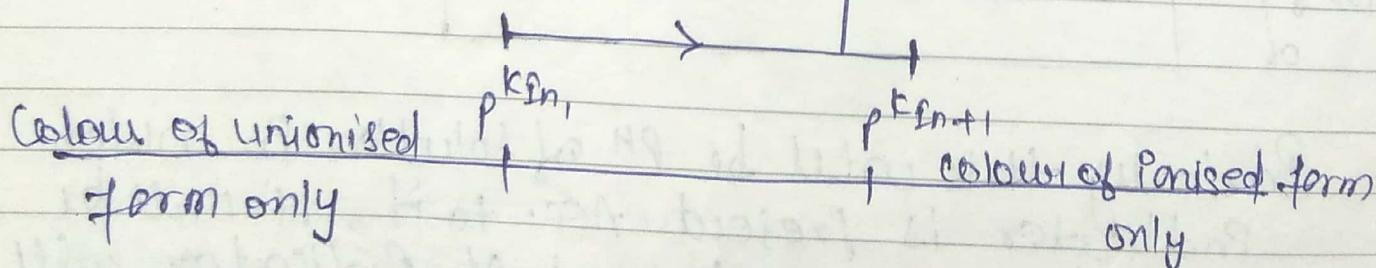
$$\frac{[HIn]}{[In^-]} > 10$$

indicator will represent colour of unionised form only

$$\frac{[In^-]}{[HIn]} > 10 \left[\begin{array}{l} \text{indicator will} \\ \text{represent colour} \\ \text{of ionised form} \end{array} \right.$$

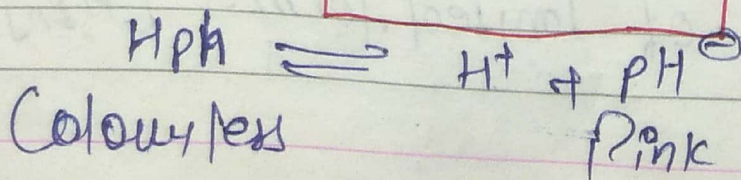
$$\frac{1}{10} > \frac{[In^-]}{[HIn]} \quad pH < pK_{In-1}$$

$$pH > pK_{In+1}$$



* Practical value of pH interval of some indicator:

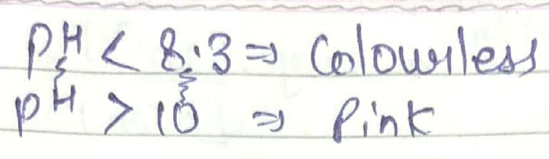
Phenolphthalein (8.3 to 10)



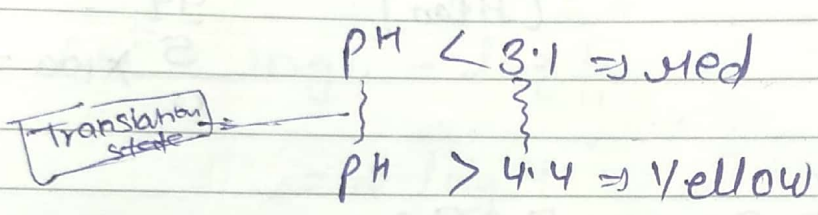
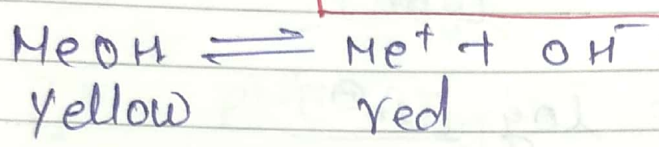
Learn

Remember

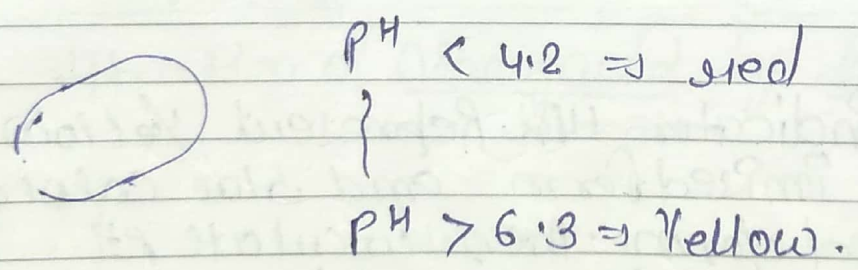
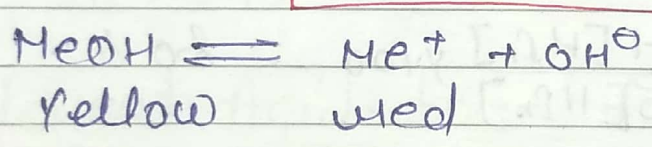
~~Ans~~



Methyl orange \Rightarrow (3.1 to 4.4)

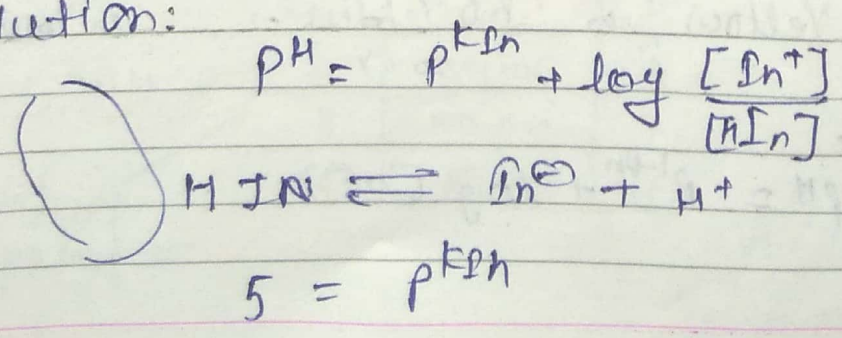


Methyl red \Rightarrow (4.2 to 6.3)



Que:

If an acidic Indicator is mixed in $pH = 5$ solution then its 50% part remain in ionised form then calculate % of ionised form of Indicator if this Indicator is mixed in $pH = 5.6$ solution:



0.6 - log 4
0.3 - log 2

$$5.6 = pK_{In} + \log \frac{[In^{\ominus}]}{[HIn]}$$

$$5.6 = 5 + \log \frac{[In^{\ominus}]}{[HIn]}$$

$$0.6 = \log \frac{[In^{\ominus}]}{[HIn]}$$

$$\frac{[In^{\ominus}]}{[HIn]} = 4$$

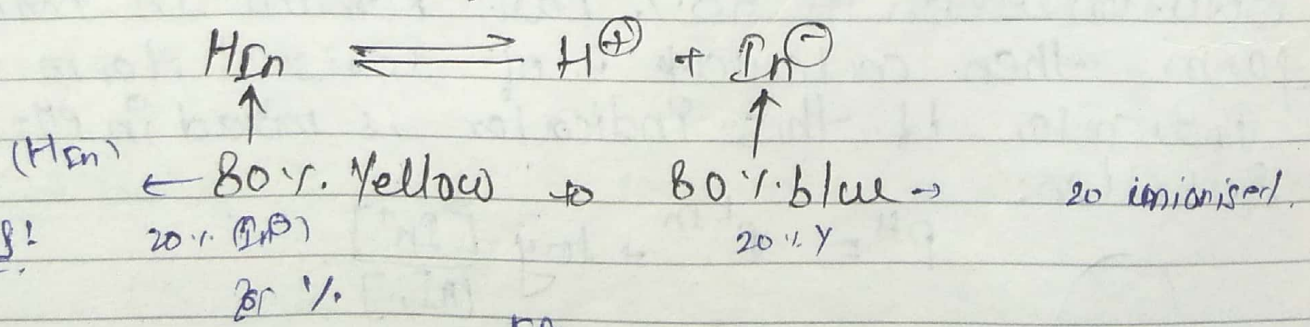
$$\frac{4}{5} \times 100 = 80\%$$

$$\% \text{ of } [In^{\ominus}] = \frac{[In^{\ominus}]}{[HIn] + [In^{\ominus}]} \times 100$$

$$\frac{4[HIn]}{5[HIn]} \times 100 = 80\%$$

Ques:

An acidic indicator HIn represent yellow colour in its unionised form and blue colour in its ionised form then calculate pH interval of a solution in which colour of solution will change from 80% yellow to 80% blue.



Ans:

$$pH = pK_{In} + \log \frac{[In^{\ominus}]}{[HIn]}$$



p_{1H} 80% 20%
 p_{2H} 20% 80%

$$pH_1 = pK_{In} + \log \frac{1}{4}$$

$$pH_2 = pK_{In} + \log \frac{4}{1}$$

$$\Delta pH = \log 4 - \log \frac{1}{4}$$

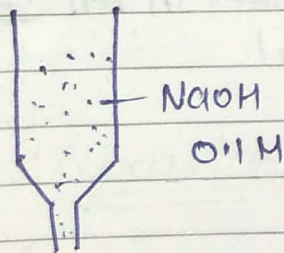
$$= 2 \log 4$$

$$= 4 \log 2$$

$$\Delta pH = 1.2$$

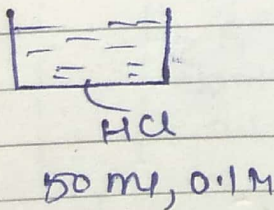
* Different Acid-base titration:

d) titration of strong acid by strong base
 beaker burette



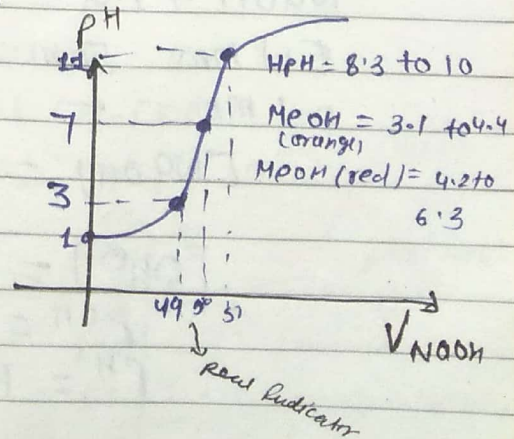
burette \rightarrow 0.1M NaOH

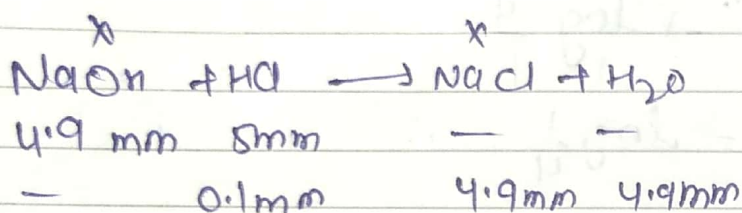
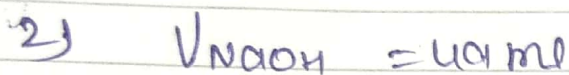
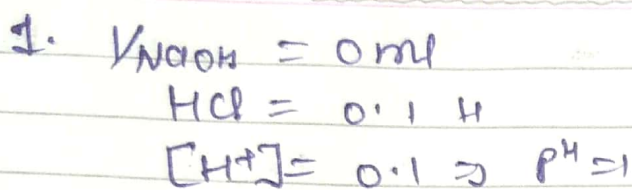
beaker \rightarrow 0.1M HCl
50 ml



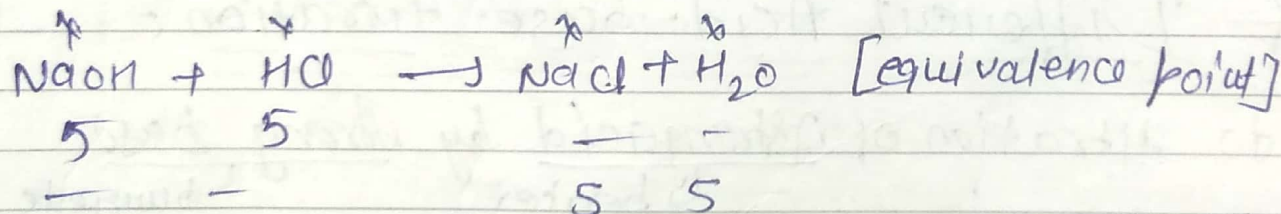
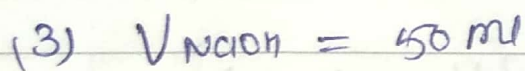
equivalence point \rightarrow

	V NaOH	pH
1	0 ml	1
2	49 ml	3
3	50 ml	7
4	51 ml	11

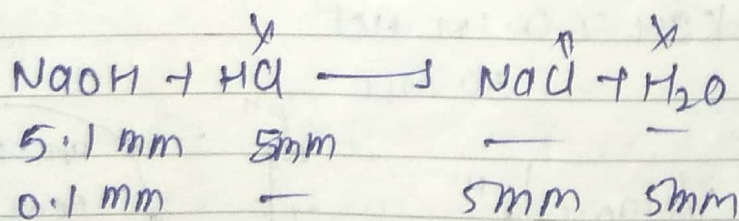
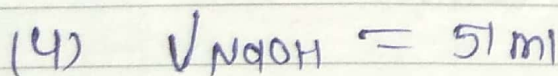




$[HCl] = 10^{-3}$
 $pH = 3$



$pH = 7$ [No working species left in rxn so it is neutral.]



$[NaOH] = \frac{0.1}{101} \approx 10^{-3}$

$[OH^-] = 10^{-3}$

$pOH = 3$

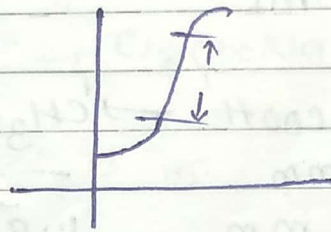
$pH = 11$

(i) Equivalence point in titration?

Point at which acid or base taken in beaker neutralised completely called equivalence point.

(ii) pH Range of titration:

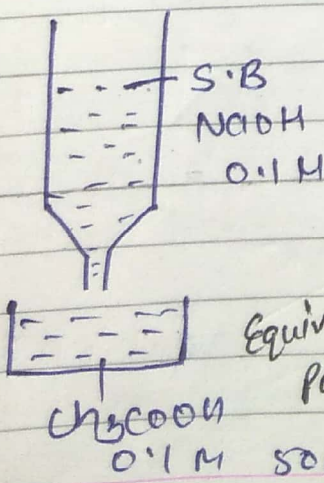
Sudden change in pH in close reason of equivalence point called pH range of titration.



If pH range of indicator exist with in pH range of titration then this type of indicator can be used for titration

* Best indicator for the titration will be indicator which have pK_{in} equal to pH at equivalence point

* Titration of W.A by S.B:



burette \Rightarrow NaOH 0.1 M

beaker \Rightarrow 0.1 CH₃COOH

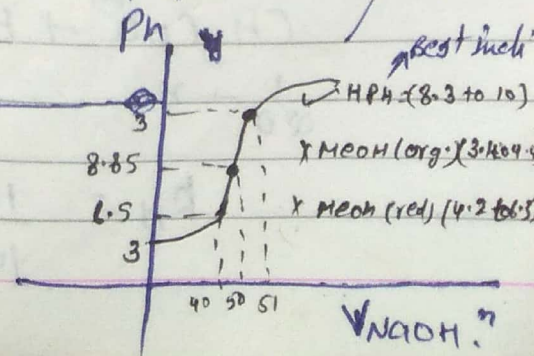
50 ml

$K_a = 10^{-5}$

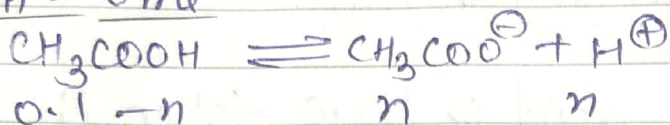
$\frac{8.3+10}{2} = 9.15$

V_{NaOH}	pH
0 ml	3
49 ml	6.5
50 ml	8.85
51 ml	11

Equivalence Point \rightarrow some



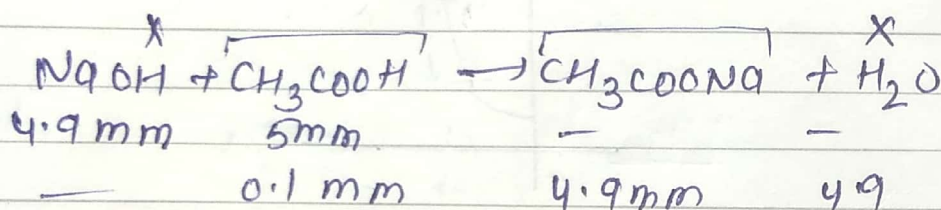
(1) $V_{NaOH} = 0 \text{ ml}$



$$10^{-5} = \frac{n^2}{0.1 - n} \Rightarrow n = 10^{-3}$$

$$[\text{H}^+] = x = 10^{-3} \Rightarrow \text{pH} = 3$$

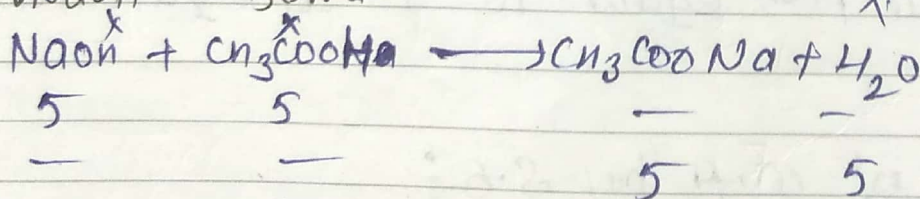
(2) $V_{NaOH} = 4.9 \text{ ml}$



$$\text{pH} = \text{p}K_a + \log \frac{4.9}{0.1}$$

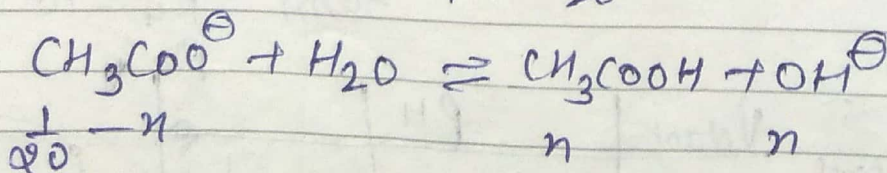
$$\text{pH} = 6.5$$

(3) $V_{NaOH} = 50 \text{ ml}$



$$\text{CH}_3\text{COONa} = 5 \text{ mmol}$$

$$C = \frac{5}{100} = \frac{1}{20}$$



$$K_b = \frac{10^{-14}}{10^{-5}} = \frac{n^2}{\frac{1}{20} - n}$$

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

$$[\text{OH}^\ominus] = x = \frac{1}{\sqrt{2}} \times 10^{-5}$$

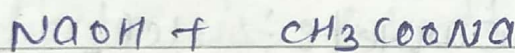
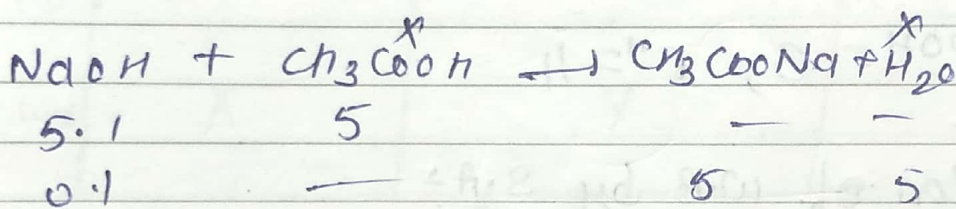
$$p\text{OH} = 5 - \log \frac{1}{\sqrt{2}} = 5 + \log \sqrt{2}$$

$$p\text{OH} = 5.15, \quad p\text{H} = 8.85$$

Handwritten notes in the top right corner, including the word "प्रश्न" (Question) and some illegible scribbles.

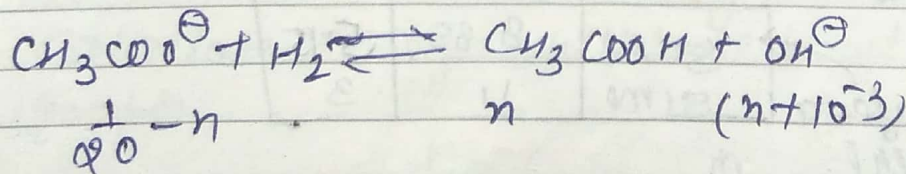
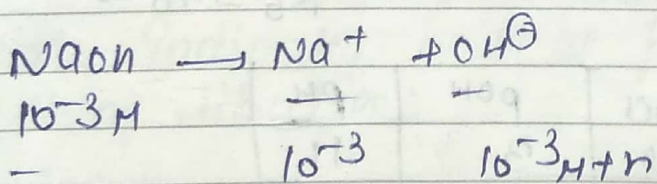


(4) $\sqrt{NaOH} = 5 \text{ mM}$



0.1 mM 5 mM

$$\frac{0.1}{100} \approx \frac{0.1}{100} \approx 10^{-3} \quad \rightarrow \quad \frac{5}{101} \approx \frac{5}{100} \approx \frac{1}{20}$$



$$K_b = \frac{K_w}{K_a} = \frac{x(x + 10^{-3})}{\frac{1}{20} - x}$$

$$10^{-9} = \frac{x(x + 10^{-3})}{\frac{1}{20} - x}$$

$$10^{-9} = \frac{n(n+10^{-3})}{1/20}$$

$$\rightarrow \left(\begin{aligned} 10^{-9} &= \frac{n \times 10^{-3}}{1/20} \\ n &= \frac{1}{2} \times 10^{-7} \end{aligned} \right)$$

$$n = \frac{1}{2} \times 10^{-7}$$

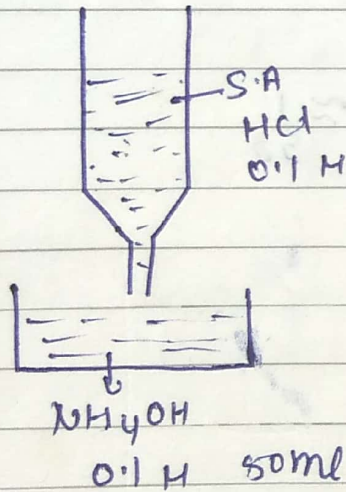
$$\begin{aligned} [\text{OH}^{\ominus}] &= n + 10^{-3} \\ &= \frac{1}{2} \times 10^{-7} + 10^{-3} \end{aligned}$$

neglect

$$[\text{OH}^{\ominus}] \approx 10^{-3}$$

$$p\text{OH} = 3, \quad p\text{H} = 11$$

* titration of w.B by S.A

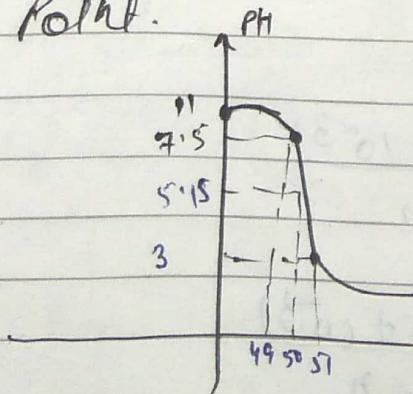


Burette: HCl
0.1 M

Beaker: 0.1 M NH₄
50 ml
K_b = 10⁻⁵

V _{HCl}	pOH	pH
0 ml	3	11
49 ml	6.5	7.5
50 ml	8.85	5.15
51 ml	11	3

Equivalence Point.



$$X \text{ pH} = 8.3 \pm 0.10$$

MEOH = 3.1 to 4.4
(orange)

MEOH = 4.2 to 6.3
(red)

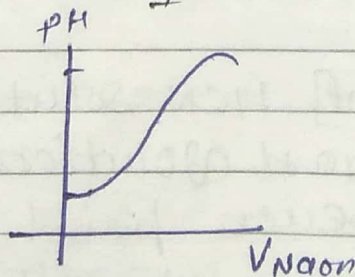
Best Indicator

Titration	HPH (8.3 to 10)	Meon (orange) 3.1 to 4.4	Meon (red) 4.2 to 6.3
Q.A + S.B (3 to 11)	✓	✓	✓
W.A + S.B (6.5 to 11)	✓	X	X
W.B + S.A (3 to 7.5)	X	✓	✓
W.A + W.B	X	X	X

⇒ Indicator is selected acc. to the strong component in the burette.

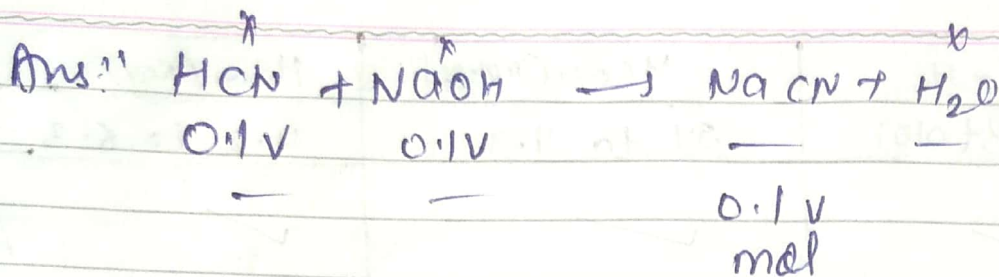
* W.A + W.B Titration: These type of titration is not done because there are no suitable indicator will be present for these types of titration's

Q.1 0.1 M HCN is titrated by 0.1 M NaOH solution. Then calculate pH at equivalence point and also plot graph.



05/08/17

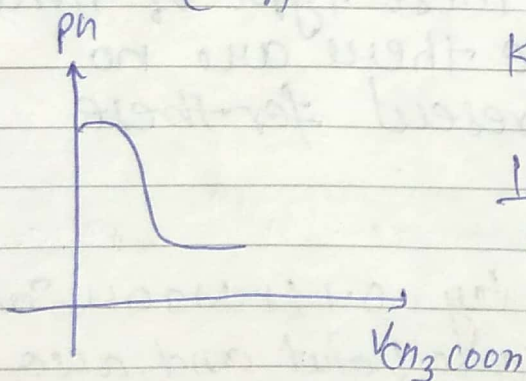
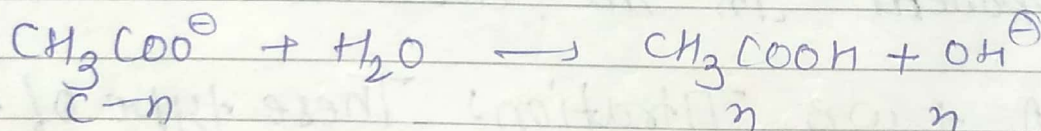
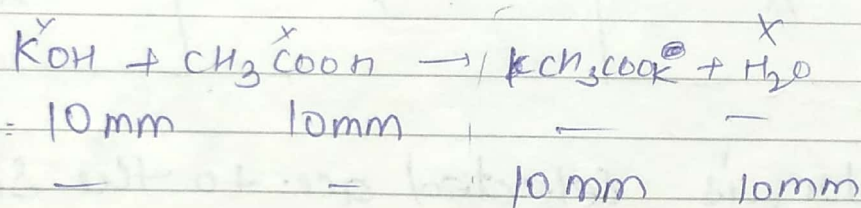
WA + WB salt
amphiprotic
buffer. } → formula



$$[\text{NaCN}] = \frac{0.1\text{V}}{2\text{V}} = \frac{0.1}{2}$$

Que: 0.1 M 100 ml KOH solution is titrated by 0.1 M CH₃COOH solution calculate pH at equivalence point
K_a(CH₃COOH) = 10⁻⁵

Ans:

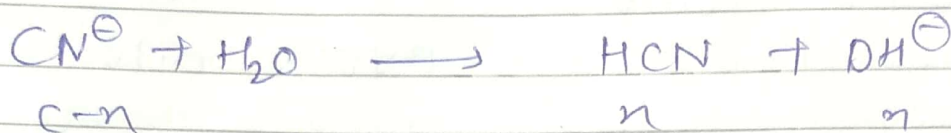
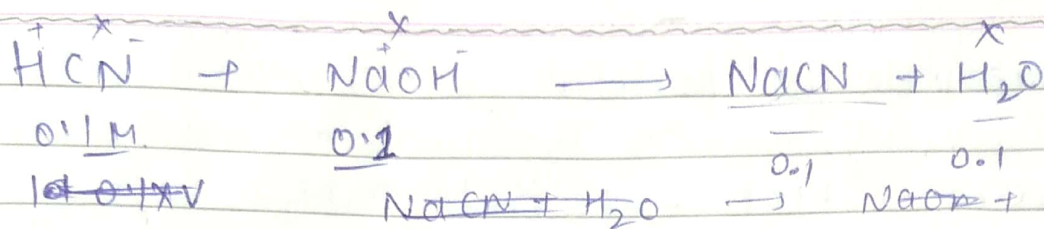


$$K_H = \frac{n^2}{C-n}$$

$$\frac{10^{-14}}{10^{-5}} = \frac{n^2}{\frac{1}{20} - n} \quad C = \frac{10}{200} = \frac{1}{20}$$

Que: 0.1 M 50 ml HCN solution is titrated by 0.2 M NaOH solution calculate pH at equivalence point

$$K_a(\text{HCN}) = 10^{-8}$$



$$\frac{10^{-14}}{10^{-8}} = \frac{n^2}{c-n} \quad 0.1\text{V} = 0.02\text{V}'$$

$$V' = 5V'$$

$$10^{-6} = \frac{n^2}{\frac{0.1}{6} - \frac{n}{6}}$$

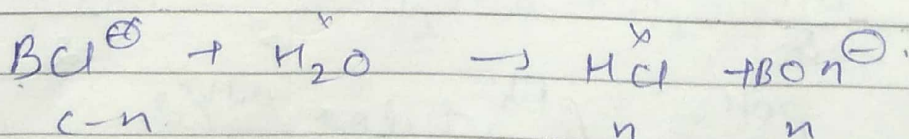
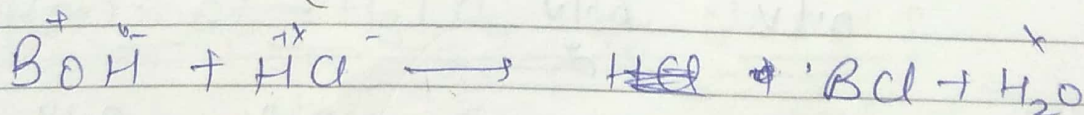
$$[\text{NaCN}]_{\text{residual}} = \frac{0.1\text{V}}{6\text{V}} = \frac{0.1}{6}$$

$$\frac{10^{-7}}{6} = n^2$$

$$[\text{OH}^{\ominus}] = \sqrt{\frac{10^{-7}}{6}}$$

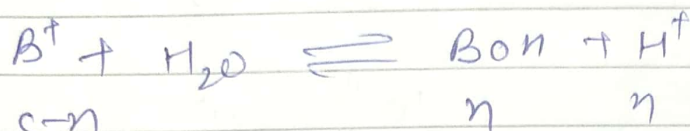
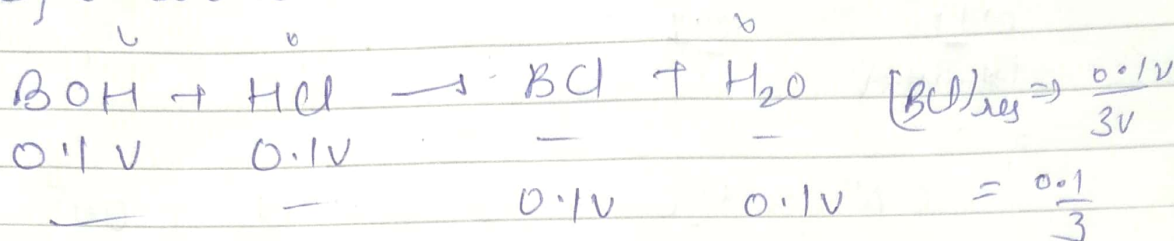
$$p^{\text{OH}} = \frac{1}{2}(7 - \log 6)$$

Ques! 0.1 M solution of W.B. BOH is titrated by 0.05 M HCl solution then calculate pH at equivalence and half eq. valence point



$$\log 3 = \frac{10^{-14}}{10^{-7}} = n^2$$

For Equivalence Point



$$K_n = \frac{n^2}{c-n}$$

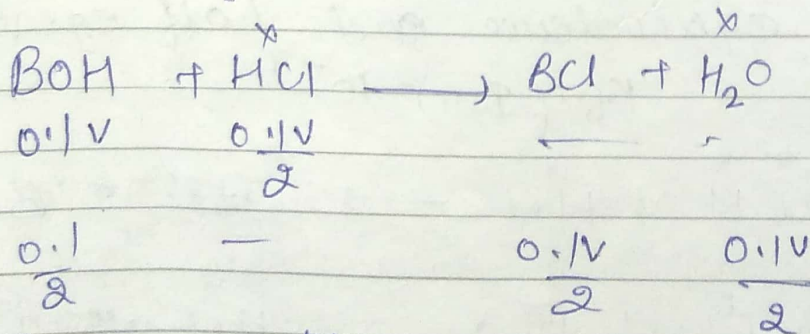
$$\frac{10^{-14}}{10^{-7}} = \frac{n^2}{\frac{0.1}{3} - n} \rightarrow 0.$$

$$10^{-7} = \frac{n^2}{0.1/3}$$

$$\frac{10^{-8}}{3} = n^2 \qquad [\text{H}^+] = \frac{10^{-4}}{\sqrt{3}}$$

$$pH = 4 + \frac{1}{2} \log 3.$$

* \Rightarrow for Half Equivalence Point



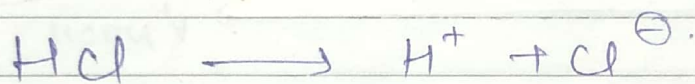
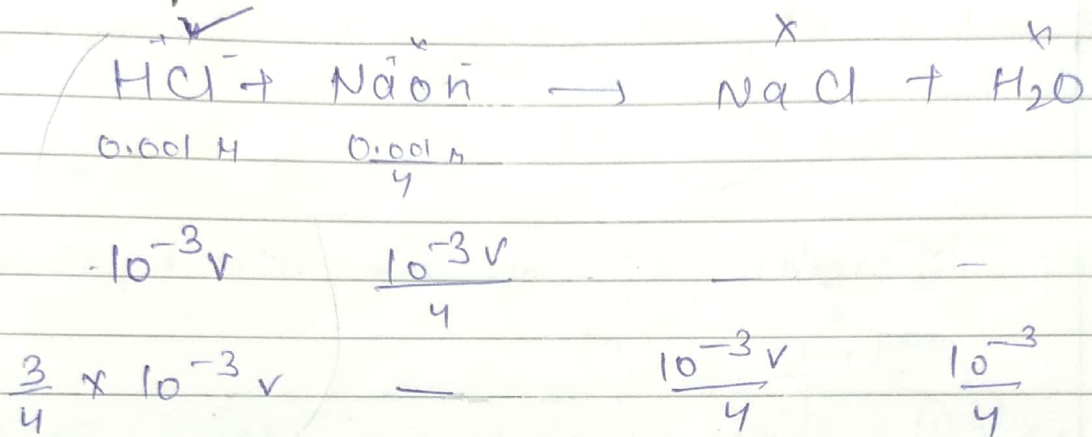
$$pOH = pK_b + \log \frac{0.1V/2}{0.1V/2}$$

$$pOH = pK_b$$

$$\frac{1}{1000M} \times \frac{1}{4000}$$

Ques) 0.001 M HCl is treated by 0.01 M NaOH solution calculate pH at $\frac{1}{4}$ th equivalence point.

Ans:



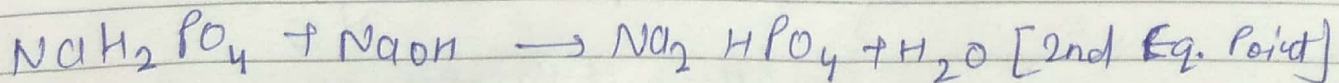
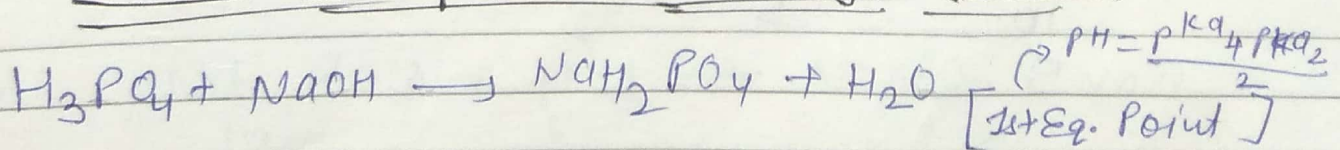
10^{-3}

$$[\text{HCl}]_{\text{residual}} = \frac{\frac{3}{4} \times 10^{-3} \times V}{V + \frac{V}{40}}$$

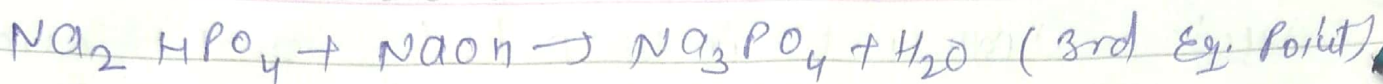
$$\frac{10^{-3}}{4} V = 10^{-2} V'$$

$$V' = \frac{V}{40}$$

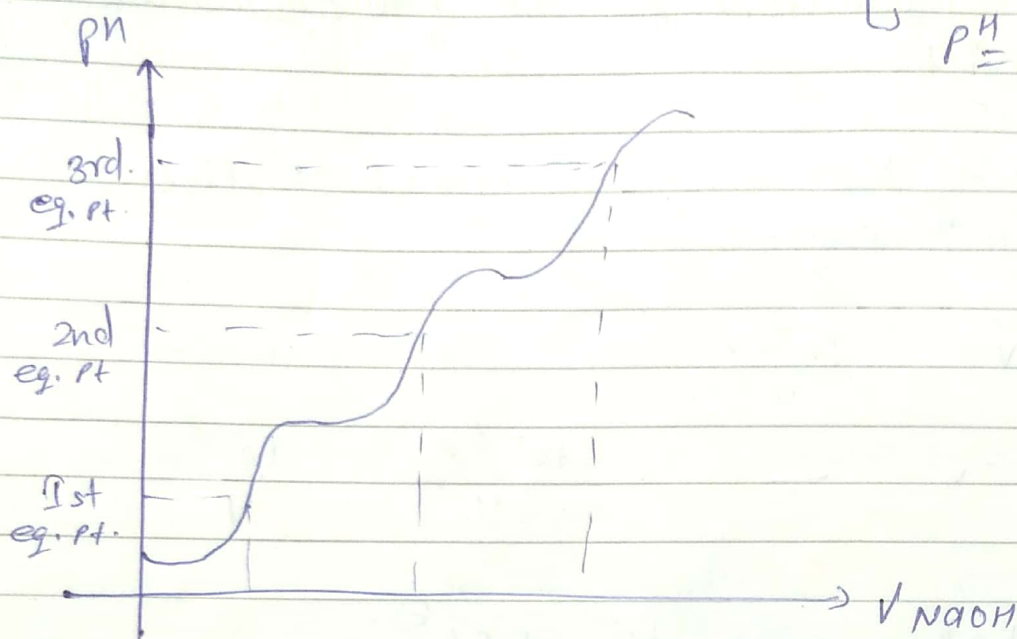
* Titration of H_3PO_4 by NaOH:



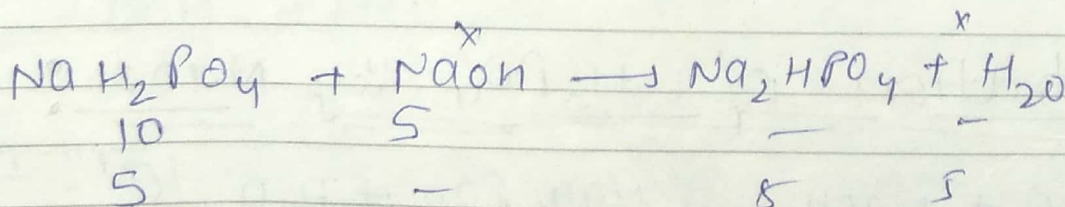
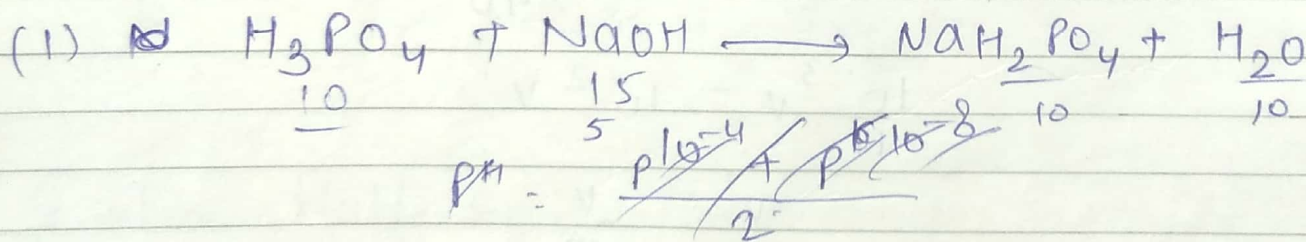
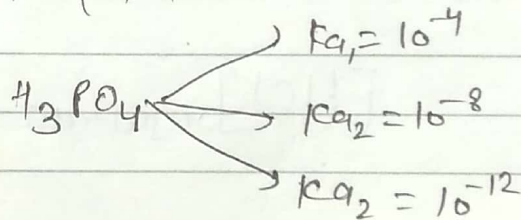
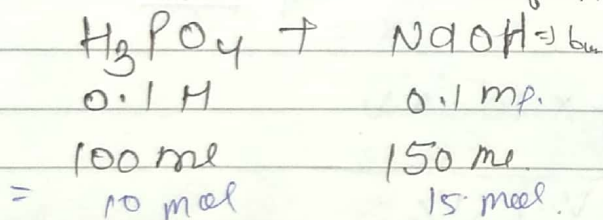
$$\text{pH} = \frac{\text{p}K_{a2} + \text{p}K_{a3}}{2}$$



↳ pH by hydrolysis of PO_4^{3-}



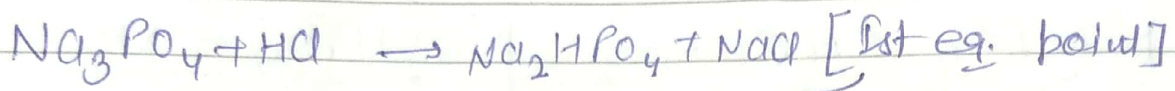
Q. Calculate the pH of resultant solution.



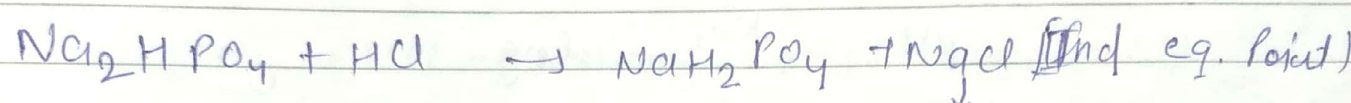
$$\text{pH} = \text{pK}_2 + \log \frac{5}{5}$$

$$\text{pH} = \text{pK}_2 + 0 = 8.$$

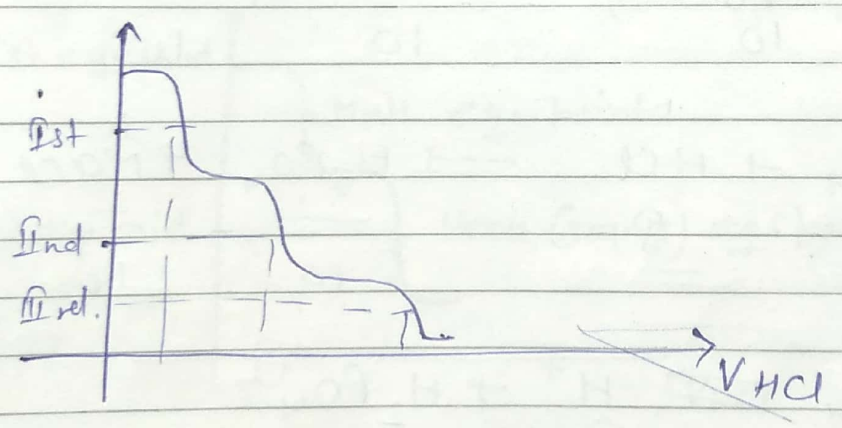
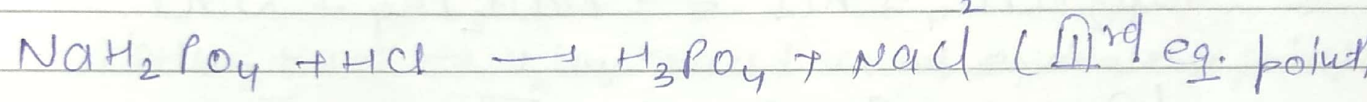
* Titration of Na_3PO_4 by HCl :



$$\text{pH} = \frac{\text{p}K_{a2} + \text{p}K_{a3}}{2}$$

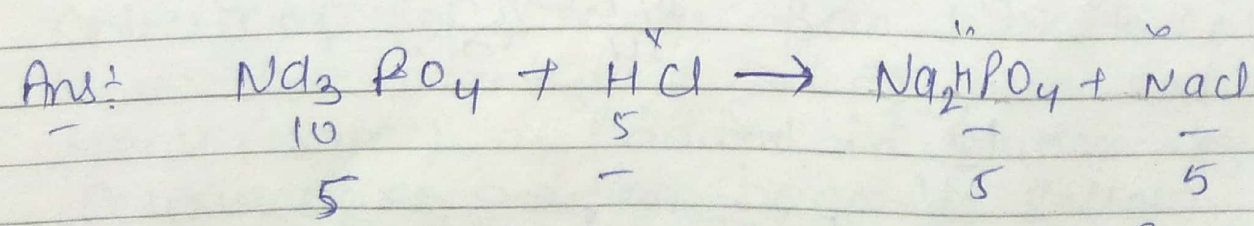


$$\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2}$$

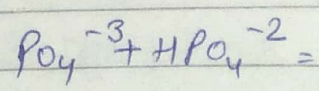


pH will be calculated by H_3PO_4

Ques: 0.1 M Na_3PO_4 + 0.1 M HCl H_3PO_4
 100 ml 50 ml $\left\{ \begin{array}{l} K_{a1} = 10^{-4} \\ K_{a2} = 10^{-8} \\ K_{a3} = 10^{-12} \end{array} \right.$
 Calculate pH of

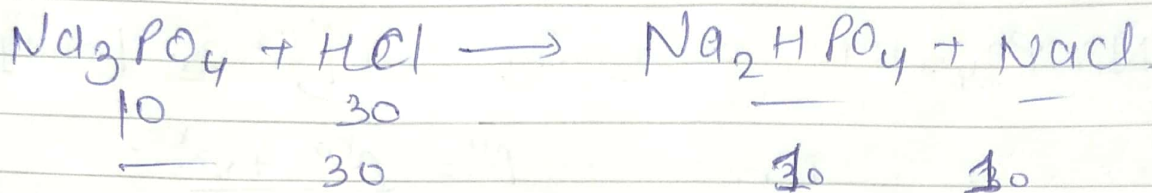


$$\text{pH} = \text{p}K_{a1} + \log \frac{\text{PO}_4^{-3}}{\text{HPO}_4^{-2}}$$

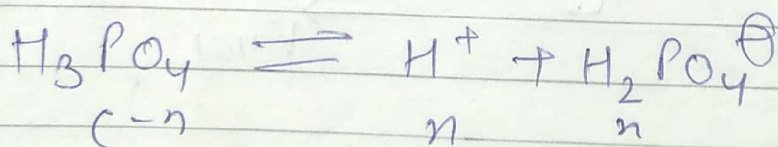
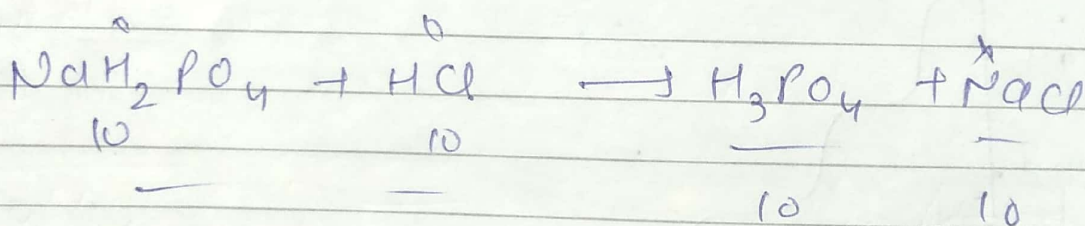
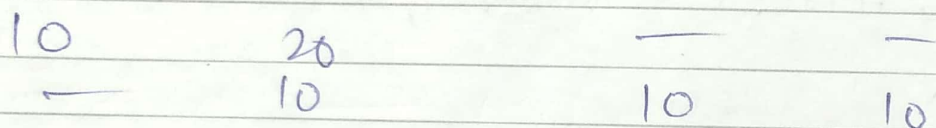
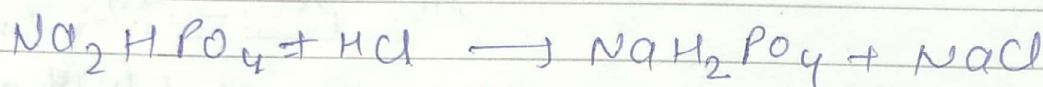


(10⁻¹²)

Ques: $0.1\text{M Na}_3\text{PO}_4 + 0.1\text{M HCl}$ $\text{H}_3\text{PO}_4 = \begin{cases} K_{a1} = 10^{-4} \\ K_{a2} = 10^{-8} \\ K_{a3} = 10^{-12} \end{cases}$
 100ml 300ml



$$\text{pH} = \text{p}K_{a2} + \log$$



$$K_{a1} = \frac{n^2}{c-n}$$

$$[\text{H}_3\text{PO}_4]_{\text{res}} = \frac{10}{400}$$

$$10^{-4} = \frac{n^2}{\frac{0.1}{4} - n}$$

$$\frac{10^{-5}}{4} = n^2$$

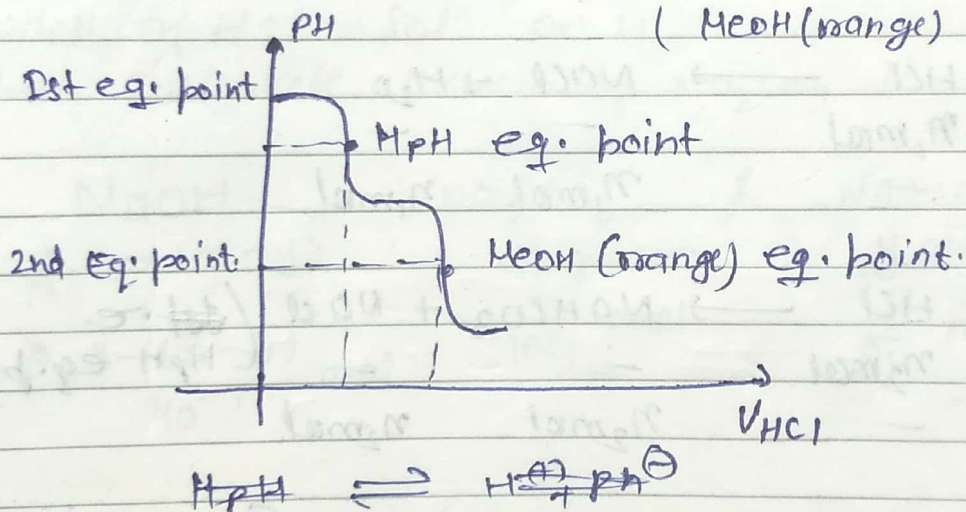
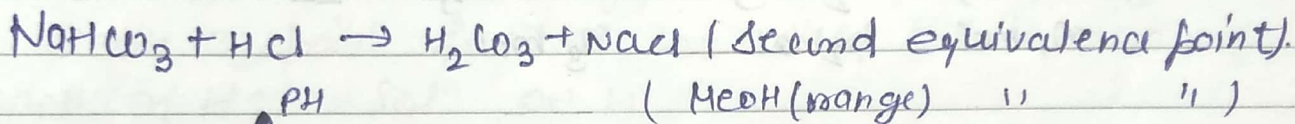
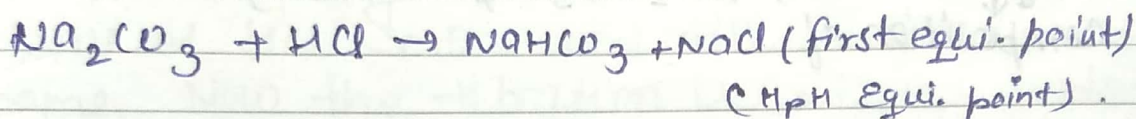
$$[\text{H}^+] = n = \sqrt{\frac{10^{-5}}{4}} = \sqrt{\frac{10^{-2.5}}{2}}$$

Race: 9.
SH = 34-40

$$pH = 2.5 + \log 2 \\ = 2.8. \quad \text{Ans}$$

* Titration of Na_2CO_3 by HCl
↳ beaker ↳ burette

Also called double indicator titration



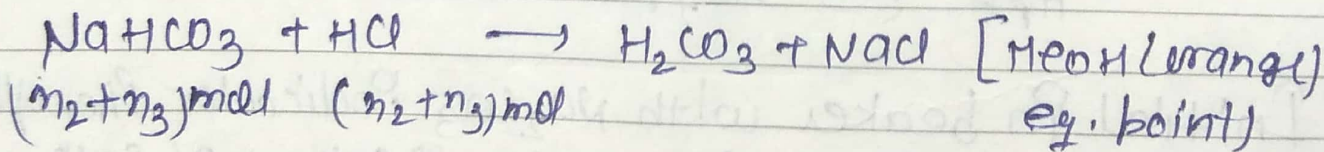
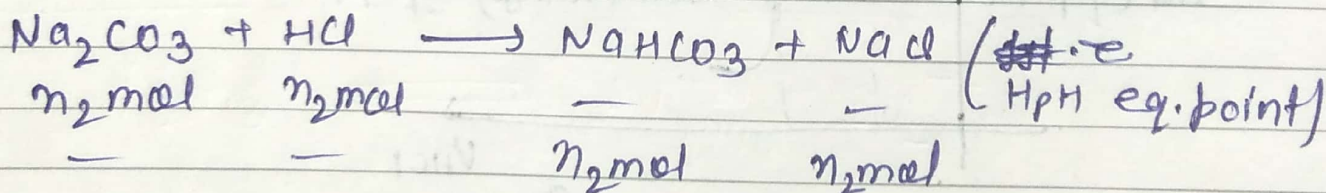
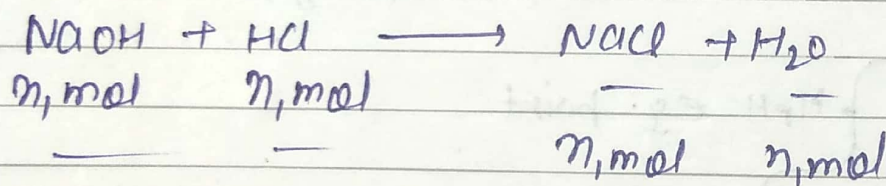
Initial pH in beaker with Na_2CO_3 indicator Phenolphthalein is mixed it turn by this $\$$ colour of solⁿ becomes pink. Now titration is started by adding HCl from burette tube at 1st eq. point colour of solⁿ change from pink to colourless. Now for identifying 2nd eq. point indicator MeOH (orange) is added in solution by this colour of ~~ss~~ solution becomes yellow. Now we again start adding HCl from burette tube ~~cmel~~ at 2nd eq. point due to

Indicator MeOH (orange) colour of Solⁿ is changed yellow to red.

* Application of double Indicator titration

can be used for finding out the composition of NaOH, Na₂CO₃ & NaHCO₃ mixture.

NaOH, Na₂CO₃ & NaHCO₃
n₁ mol, n₂ mol, n₃ mol.



⇒ titration of Na₂CO₃ by HCl
↳ beaker ↳ burette

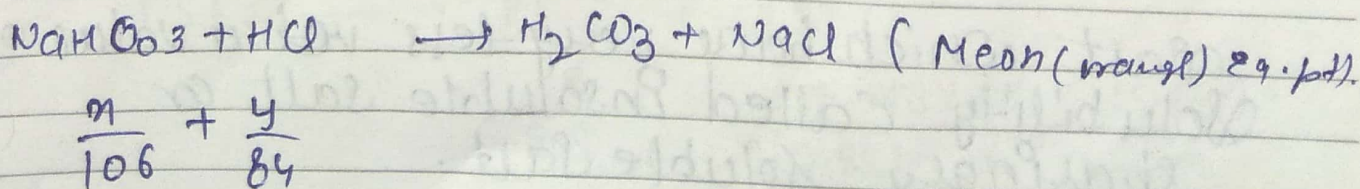
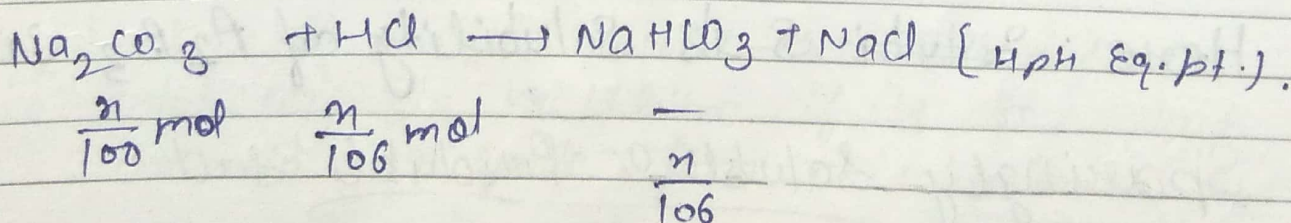
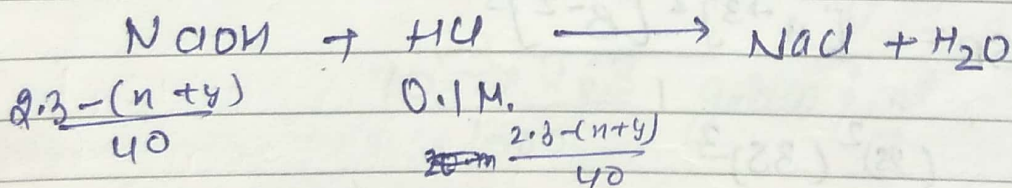
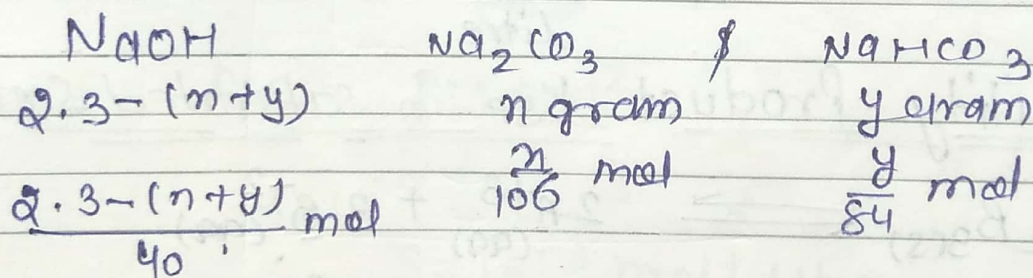
total used mol of HCl till H⁺ equivalence point = n₁ + n₂

used mol of HCl after H⁺ equivalence to MeOH eq. point = n₂ + n₃

total used mol of HCl from starting till 1st eq. point.

$$= n_1 + 2n_2 + n_3$$

Q. 2.3 g mixture of NaOH, Na_2CO_3 & NaHCO_3 is titrated by 0.1 M HCl soln. Total volume of HCl soln. used till 1st eq. point is 200 ml. Now the titration is continued adding indicator MeOH (orange). Now after 1st eq. point till 2nd eq. point further 200 ml of HCl is used if concn of HCl soln 0.1 M. then calculate mass % of Na_2CO_3 in initial mixture.



$$\frac{2.3 - (n+y)}{40} + \frac{n}{106} = \frac{0.1 \times 200}{1000}$$

$$\frac{n}{106} + \frac{y}{84} = 0.1 \times \frac{200}{1000}$$

∴ max y. of $\text{Na}_2\text{CO}_3 = \frac{2.3}{2.3} \times 100$

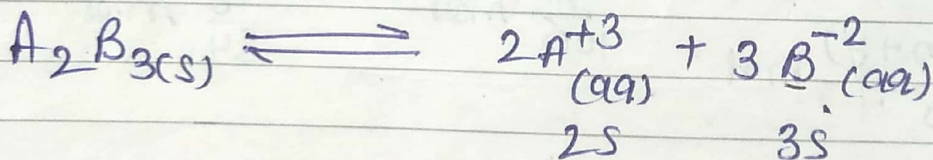
∴ Important

∗ ∗ ∗ Solubility (S)

It is the concn of solute in its saturated solⁿ. Highest concn solⁿ of solute called its saturated solutiⁿ solution.

$$S = \frac{\text{mol}}{\text{litre}}$$

⇒ Solubility Product K_{sp} in saturated solⁿ



$$K_{sp} = [A^{+3}]^2 [B^{-2}]^3$$

$$K_{sp} = (2s)^2 (3s)^3$$

Here ~~Solubi~~ S is solubility of A_2B_3 salt

∗ Sparingly Soluble or Insoluble salt

Salt which have very less val a value of solubility called insoluble salt or sparingly soluble salt.

In our syllabus we will study only about insoluble salt.

Ex: AgCl, AgI, AgBr

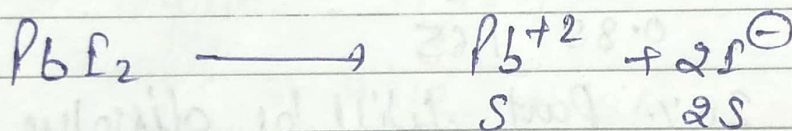
PbF₂, PbBr₂, BaCO₃, PbSO₄

Ques: K_{sp} of PbF₂ is 4×10^{-9} . then calculate its solubility in gram/ml.

↳ Molecular weight of PbF₂ is 463

Ans:

$$\frac{463}{1000} = 10^{-3}$$



$$K_{sp} = (S)(2S)^2$$

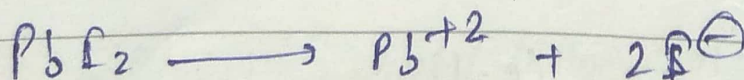
$$4 \times 10^{-9} = 4 \cdot S^3$$

$$S = 10^{-3} \text{ mol/litre}$$

$$= 10^{-3} \times 463 \text{ gm/litre}$$

$$\frac{10^{-3} \times 463}{1000} \text{ gram/ml.}$$

Ques: K_{sp} of PbF₂ is 4×10^{-9} then calculate its solubility in mol/litre if its 80% part remain in ionic form in solution

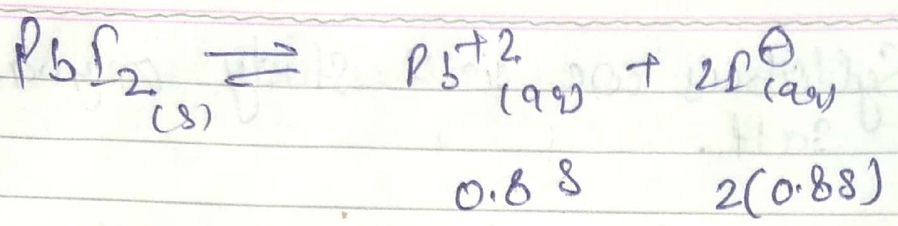


$$0.8S$$

$$2(0.8S) \quad \frac{(S)(8S)^2}{4 \times 10^{-9}}$$

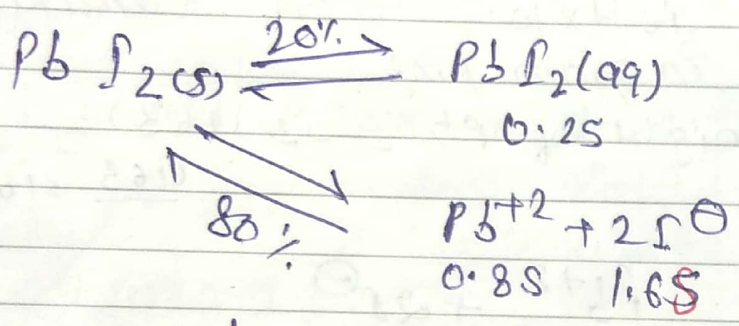
sl.

8-1 ³⁴⁻⁴²
0-2 1 to 10



$$K_{sp} = (0.8S)(7.65)^2$$

$$4 \times 10^{-9} = (0.8S)(1.65)^2 \quad S$$

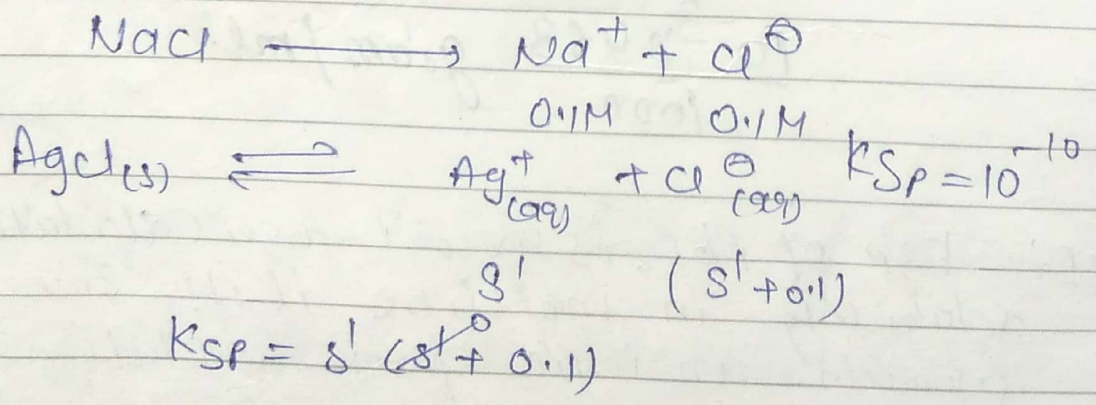


remaining 20% part will be dissolve in molecular form directly

* Solubility in different condition:

(i) Solubility due to common ion effect:

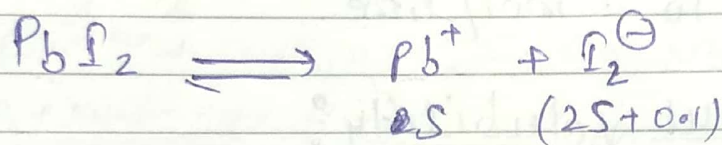
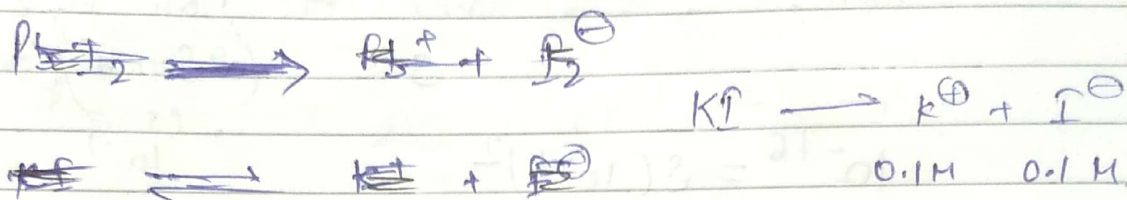
Due to common ion effect solubility will decrease



$$10^{-10} = S'(0.1)$$

$$S' = 10^{-9}$$

Q. Calculate solubility of PbI_2 in gm/ml in solution of $0.1M$ KI (aq).
 $K_{sp}(PbI_2) = 4 \times 10^{-9}$ Mwt of $PbI_2 = 463$

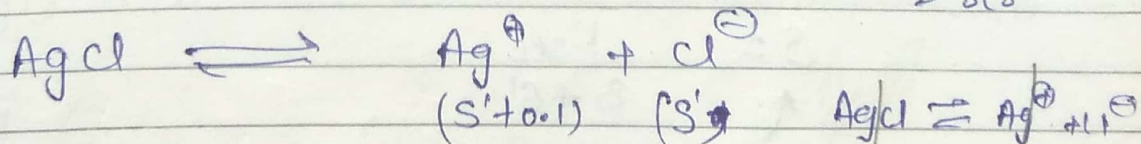
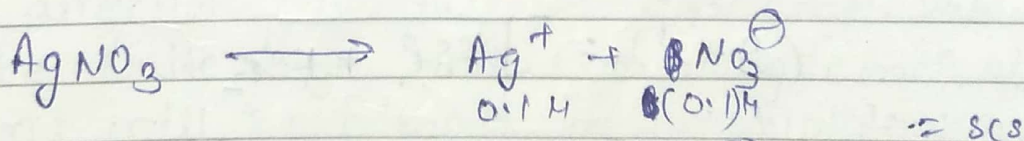


$$4 \times 10^{-9} = s(s + 0.1)^2$$

$$s = 4 \times 10^{-7} \text{ mol/litre}$$

$$\frac{4 \times 10^{-7} \times 463}{1000} \text{ gm/ml}$$

Q. Solubility of $AgCl$ in pure H_2O is 4.3×10^{-6} gm/ml then calculate solubility of $AgCl$ in $0.1M$ $AgNO_3$ solution. Mwt of $AgCl = 143$



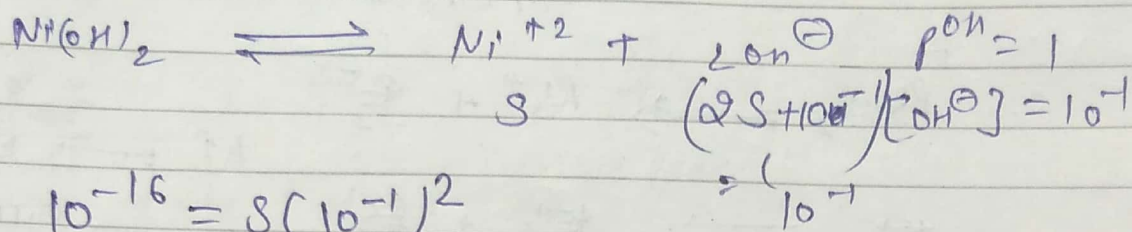
$$10^{-10} = (s' + 0.1)(s')$$

$$s' = 10^{-9} \text{ mol/litre}$$

$$S = \frac{1.43 \times 10^{-6}}{143} \times 1000 \text{ mol/litre}$$

$$\begin{array}{l}
 K_{sp} = s^2 \\
 K_{sp} = 10^{-10}
 \end{array}$$

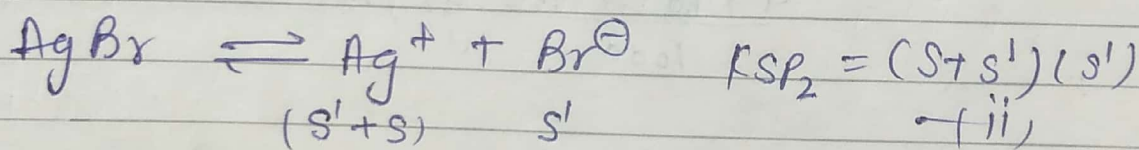
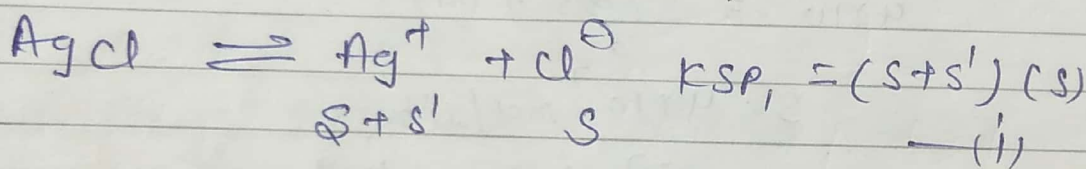
Ques: Calculate solubility of $\text{Ni}(\text{OH})_2$ in $\text{pH} = 13$ buffer solution $K_{sp}(\text{Ni}(\text{OH})_2) = 10^{-16}$.



$$10^{-16} = s(10^{-1})^2$$

$$s = 10^{-14} \text{ mol/litre}$$

(ii) Simultaneous solubility:



(i) + (ii)

$$(s + s')(s + s') = K_{sp1} + K_{sp2}$$

$$(s + s') = \sqrt{K_{sp1} + K_{sp2}}$$

$$s = \frac{K_{sp1}}{s + s'}$$

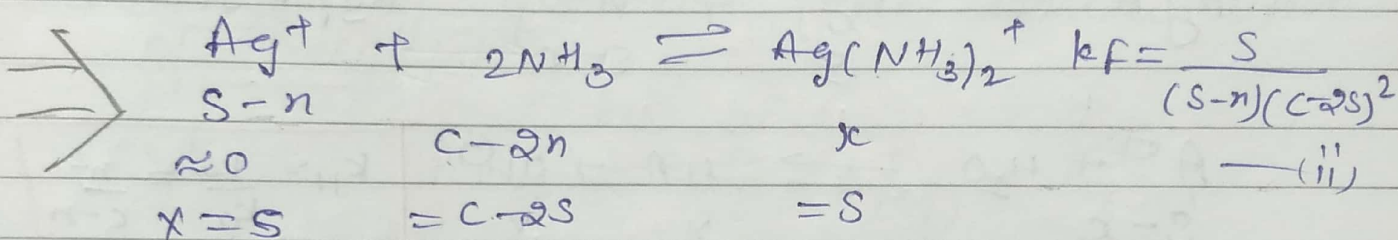
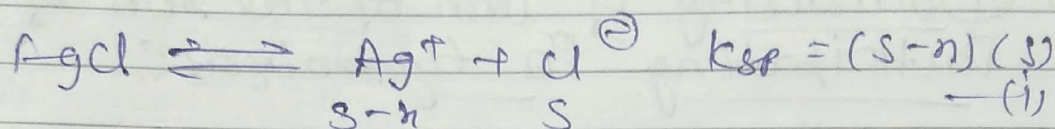
↑ Solubility of AgCl

$$s' = \frac{K_{sp2}}{s + s'}$$

↑ Solubility of AgBr.

In simultaneous solubility solubility of individual salt will decrease due to common ion effect

(iii) Solubility in ^{Complex} Ion formation R_{x^n}



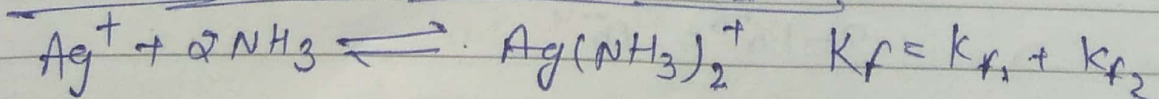
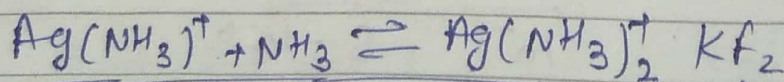
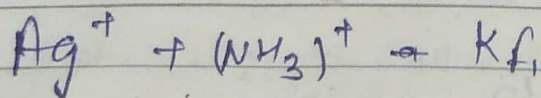
(i) x (ii)

$$K_{sp} \cdot K_f = \frac{s^2}{(c-2s)^2}$$

$$\frac{s}{c-2s} = \sqrt{K_{sp} \cdot K_f}$$

* Complex ion formation R_{x^n} will almost go in forward direction because its eqb const. value (K_f) will be quite high and remaining concⁿ of L.R (Ag^+) will be almost zero equal to zero

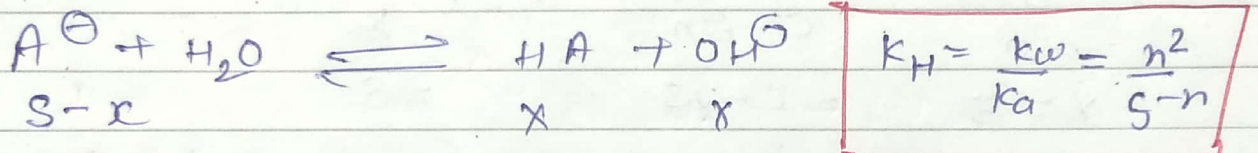
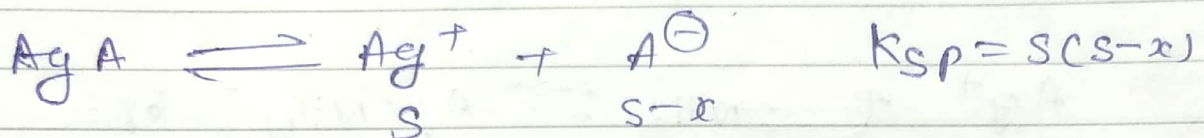
If K_f of individual ^{Ag} step given then value of overall K_f



★ ★

Important Note: In presence of Ammonia Solubility of Ag AgCl will increase as compared to its normal value.

(iv) Solubility if one of the ion of Salt participating in hydrolysis:



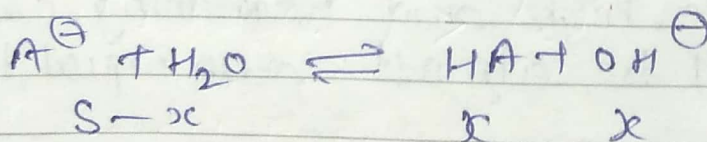
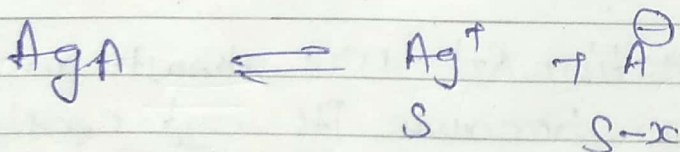
Ques: pH of saturation solution of Ag_nA is 8 then Calculate K_{sp} of Ag_nA. Suppose hydrolysis of A⁻ occur in its solⁿ?

$$K_a(\text{HA}) = 10^{-6}$$

$$\text{pH} = 8$$

$$\text{pOH} = 6$$

$$[\text{OH}^-] = 10^{-6}$$



$$\text{pH} = 8$$

$$\text{pOH} = 6$$

$$x = [\text{OH}^-] = 10^{-6}$$

$$\frac{10^{-14}}{10^{-6}} = \frac{10^{-12}}{\text{S} - 10^{-6}}$$

$$\text{S} - 10^{-6} = 10^{-4}$$



$$s = 10^{-4} + 10^{-6}$$

$$s \approx 10^{-4}$$

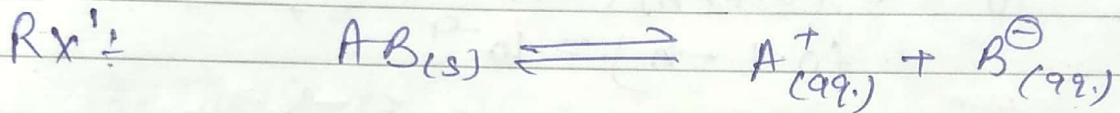
Important

$$K_{SP} = s(s-n)$$

$$K_{SP} = 10^{-4} (10^{-4} - 10^{-6})$$

$$K_{SP} = 10^{-8}$$

* Solubility quotient (Q_{SP}) and condition of precipitation:



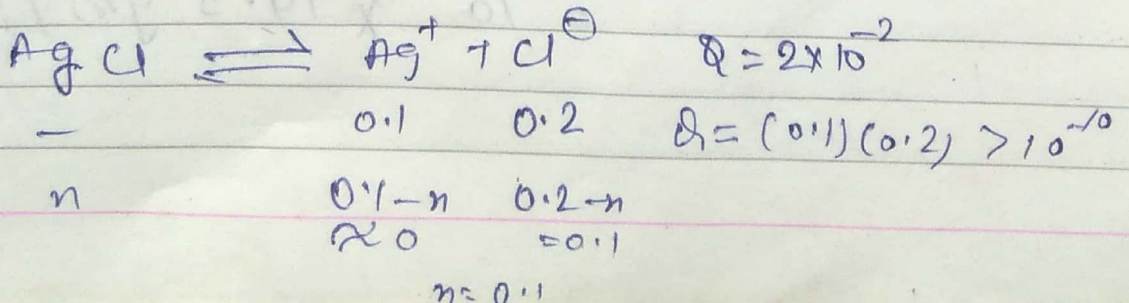
$$Q_{SP} = \frac{[A^+][B^-]}{1}$$

$Q_{SP} < K_{SP}$ [Unsaturated solution. eq^s will move in forward direction and some more amount of AB solid can be mixed in solⁿ]

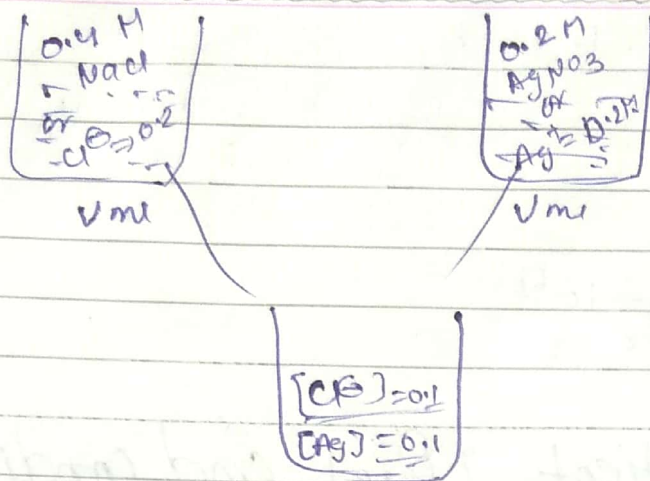
$Q_{SP} = K_{SP}$ [Saturated solution no more amount of AB solid can be mixed in solⁿ]

$Q_{SP} > K_{SP}$ [Supersaturated solution eq^s will move in backward direction and precipitation of AB solid will form.]

Ques: 0.4M NaCl solⁿ is mixed with 0.2M AgNO₃ solⁿ of equal volume. Then precipitation of AgCl will form or not and also calculate Remaining concn of Ag⁺ ion in resultant solⁿ. K_{SP} of AgCl = 10^{-10}



How Que! S-1: 43 to 53
 0-2 Complete.
 11 to 23

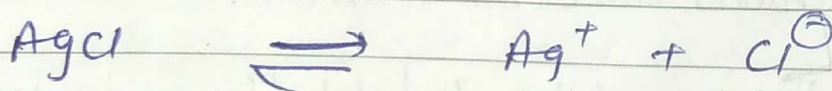
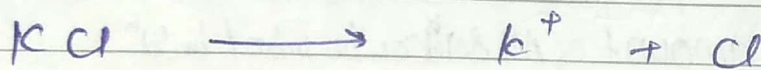


$$10^{-10} = (0.1 - x)(0.1)$$

$$(0.1 - x) = 10^{-9}$$

Que! Calculate minimum amount of KCl (in gram) that must be added in 100 ml 0.1 M AgNO₃ solution
 Just start precipitation of AgCl $K_{sp}(AgCl) = 10^{-10}$

Ans



$$[Ag^+][Cl^-] > K_{sp}$$

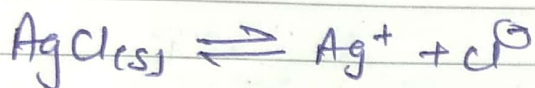
$$0.1 [Cl^-] > 10^{-10}$$

$$[Cl^-] > 10^{-9} \text{ mol/litre}$$

$$[KCl] > 10^{-9} \text{ mol/litre}$$

$$= 10^{-10} \times 74.5 \text{ gm} / 100 \text{ ml}$$

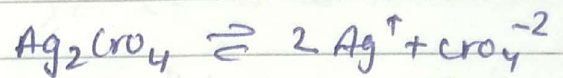
Q. In a solution $10^{-3} M$ NaCl and $10^{-2} M$ K_2CrO_4 are present. In this solution $AgNO_3$ is added slowly then which will form ppt first AgCl or Ag_2CrO_4 . $K_{sp}(AgCl) = 10^{-10}$
 $K_{sp}(Ag_2CrO_4) = 10^{-12}$



$$[Ag^+][Cl^-] > 10^{-10}$$

$\hookrightarrow 10^{-3}$

$$[Ag^+] > 10^{-7} M$$



$$[Ag^+]^2 [CrO_4^{2-}] > 10^{-12}$$

$$[Ag^+]^2 \times 10^{-2} > 10^{-12}$$

$$[Ag^+] > 10^{-5} M$$

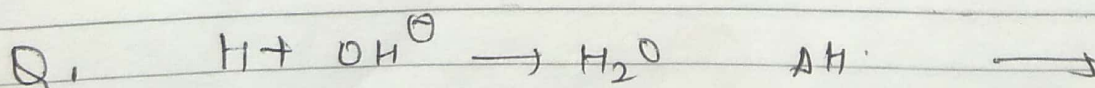
AgCl will form ppt first because required Ag^+ will be less for precipitation of AgCl

(ii) Calculate remaining concn of Cl^- ion in solution when Ag_2CrO_4 will precipitated along with AgCl.

$$[Cl^-] = 10^{-5} M$$

$$\% = \frac{10^{-5}}{10^{-3}} \times 100 = 1\%$$

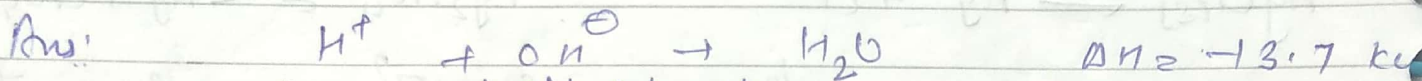
* Heat generate in acid-base titration.



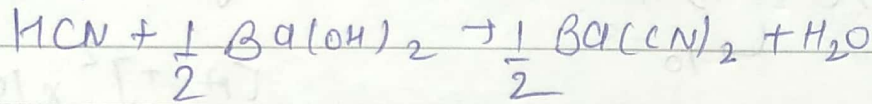
How $\Delta J(A) = 1$ to 7



- (i) Calculate ΔH neutralisation of Rx^n b/w $HCN(aq)$ & $Ba(OH)_2$ if ΔH° diss of HCN is 6.7 kcal/mol
(ii) also calculate heat produced in Rxn if 0.1 M , 100 ml HCN react with 0.1 M , 100 ml $Ba(OH)_2$?



↳ neutralisation Rxn



$10 \text{ mm} \quad 10 \text{ mm} \quad \Delta H_{\text{meat}} = -13.7 + \Delta H_{\text{diss}}(HCN)$
 $= 10^{-2} \text{ mol} \quad 10^{-2} \text{ mol} \quad = -7 \text{ kcal}$

Release heat = $7 \times 10^{-7} \text{ kcal}$
 $= -70 \text{ Cal}$