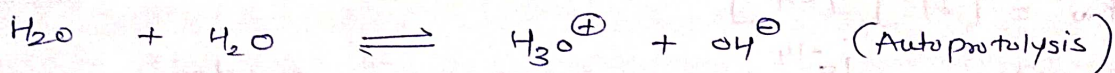


* Ionic Product of Water / Ionisation constant of water



$$K = \frac{[\text{H}^{\oplus}][\text{OH}^{\ominus}]}{[\text{H}_2\text{O}]^2}$$

$$K \cdot [\text{H}_2\text{O}]^2 = [\text{H}^{\oplus}][\text{OH}^{\ominus}]$$

$$K_w = [\text{H}^{\oplus}][\text{OH}^{\ominus}]$$

where, K_w = ionic product of water or autoprotolysis constant

K_w depends only on temperature ($K_w \propto \text{Temp.}$)

At 298 K, $K_w = 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$

Neutral :- $[\text{H}^{\oplus}] = [\text{OH}^{\ominus}] = 10^{-7} \text{ mol dm}^{-3}$

Acidic :- $[\text{H}^{\oplus}] > [\text{OH}^{\ominus}]$ } value of K_w always

Basic :- $[\text{H}^{\oplus}] < [\text{OH}^{\ominus}]$ } remains constant

* Find the conc. of $[\text{H}_3\text{O}^{\oplus}]$ and $[\text{OH}^{\ominus}]$ for solution of weak acid (HA) whose $K_a = 2 \times 10^{-8}$ and 8 moles of acid are present in 1 L of solution.



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

At initial : 8 moles

At equilibrium : $\frac{8 - 8\alpha}{1}$

$\frac{8\alpha}{1}$

$\frac{8\alpha}{1}$

$$K_a = \frac{(8\alpha) \times (8\alpha)}{8 - 8\alpha} = \frac{8\alpha^2}{(1 - \alpha)}$$

for weak acid, α is very small

$$K_a = \frac{8\alpha^2}{1} \Rightarrow \alpha = \sqrt{\frac{K_a}{8}} = \sqrt{\frac{2 \times 10^{-8}}{8}} = 0.5 \times 10^{-4}$$

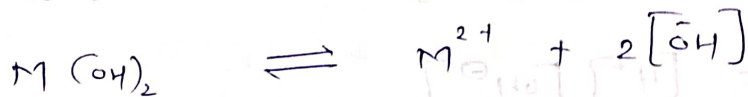
For conc. $[\text{H}_3\text{O}^{\oplus}] = \frac{8\alpha}{1 \text{ L}} = 8 \times 0.5 \times 10^{-4}$
 $= 4 \times 10^{-4} \text{ mol dm}^{-3}$

For conc. of $[OH^-]$,

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

$$[OH^-] = \frac{10^{-14}}{4 \times 10^{-4}} = 2.5 \times 10^{-11} \text{ mol dm}^{-3}$$

* If weak base $M(OH)_2$ has $K_b = 1.6 \times 10^{-9}$ at eqm
Find conc. of $[OH^-]$ and $[H_3O^+]$ in solution having
2M conc. of base.



At initial : 2

At equilibrium : $2 - 2\alpha$

0
 2α
 4α

$$K_b = \frac{[M^{2+}] [OH^-]^2}{[M(OH)_2]}$$

$$= \frac{(2\alpha) (4\alpha)^2}{(2 - 2\alpha)} = \frac{16\alpha^3}{1 - \alpha}$$

But α is very very small

$$K_b = \frac{16\alpha^3}{1}$$

$$\alpha = \sqrt[3]{\frac{K_b}{16}} = \sqrt[3]{\frac{1.6 \times 10^{-9}}{16}} = 10^{-3}$$

$$\text{For } [OH^-] = 4\alpha = 4 \times 10^{-3} \text{ mol dm}^{-3}$$

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

$$[H^+] = \frac{10^{-14}}{4 \times 10^{-3}} = 2.5 \times 10^{-12} \text{ mol dm}^{-3}$$

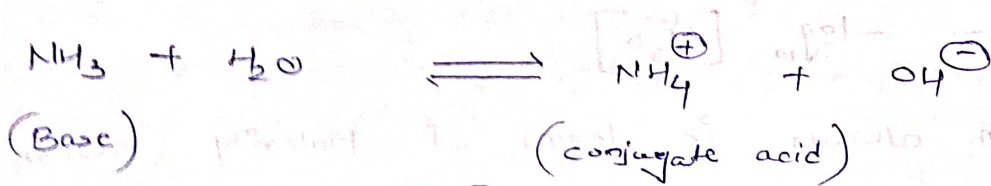
Limitations of Ostwald's dilution law :-

① Valid only for weak electrolyte

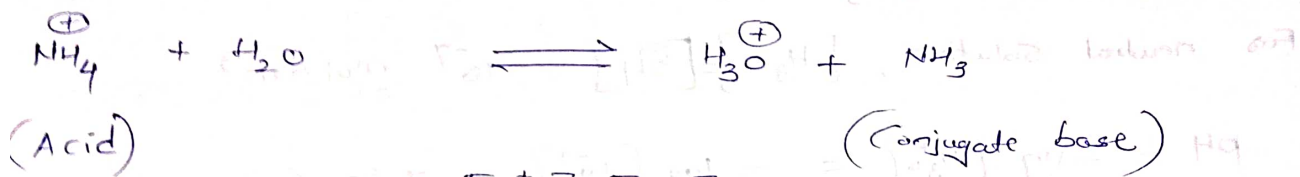
② $\alpha = \sqrt{\frac{K}{c}}$ valid only for monobasic acid and monacidic base

Relation between K_a , K_b and K_w for conjugate pair

Consider,



$$K_b = \frac{[\text{NH}_4^{\oplus}][\text{OH}^{\ominus}]}{[\text{NH}_3]}$$



$$K_a = \frac{[\text{H}_3\text{O}^{\oplus}][\text{NH}_3]}{[\text{NH}_4^{\oplus}]}$$

$$K_a \times K_b = [\text{H}_3\text{O}^{\oplus}][\text{OH}^{\ominus}]$$

$$\boxed{K_a \times K_b = K_w} \Rightarrow \text{Valid only for conjugate Acid Base pair}$$

↓ ↓
Acid conjugate base

$$K_a = \frac{K_w}{K_b} \Rightarrow K_a \propto \frac{1}{K_b} \quad (K_w \text{ is constant at given temp.})$$

Stronger the acid, weaker its conjugate base and vice versa

Which is more basic CN^{\ominus} or $\text{SO}_4^{2\ominus}$

CN^{\ominus} is conjugate base of HCN and $\text{SO}_4^{2\ominus}$ is conjugate base of HSO_4^{\ominus}

Here, $\text{HSO}_4^{\ominus} > \text{HCN}$ (Acidity)
 $\text{SO}_4^{2\ominus} < \text{CN}^{\ominus}$ (Basicity)

* pH of solution

$$pH = -\log_{10} [H_3O^+]$$

keep concentration always in terms of Molarity (mol dm⁻³)

Why pH of neutral solution is 7?

→ We know,

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

For neutral solution, $[H_3O^+] = [OH^-] = 10^{-7} \text{ mol dm}^{-3}$

$$pH = -\log_{10} [H_3O^+] = -\log_{10} [10^{-7}] = 7 \log_{10}(10) = 7$$

From this proof, we can easily prove that for acidic solution pH is less than 7 while for base it is greater than 7.

From the same proof, we can also prove that why the pH scale range between 0 to 14.

pH depends on temperature

⇒ At 63°C, $K_w = 10^{-13}$

For pure water, $[H_3O^+] = [OH^-]$

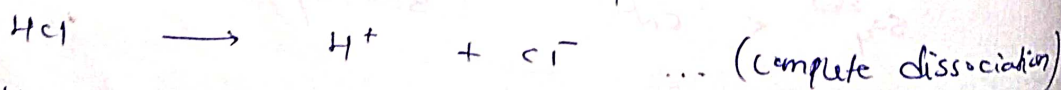
$$\Rightarrow [H_3O^+] = 10^{-6.5}$$

$$pH = -\log_{10} [H_3O^+] = -(-6.5) \log_{10}(10) = 6.5$$

Basically for pure water, pH = 7 (At room temperature) but with change in temperature, pH also changes.

pH calculation for strong Acid

① Calculate pH of 10^{-2} M HCl

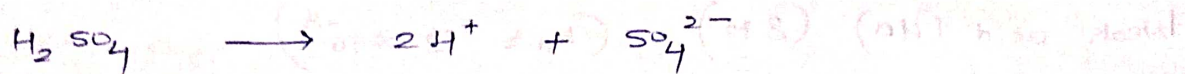


$$pH = -\log_{10} [H^+]$$

$$= -\log_{10} (10^{-2})$$

$$pH = 2$$

⇒ Calculate pH of 10^{-4} M H_2SO_4



$$10^{-4} \text{ M} \qquad 2 \times 10^{-4} \text{ M} \qquad 10^{-4} \text{ M}$$

$$pH = -\log_{10} [H^+] = -\log_{10} (2 \times 10^{-4})$$

$$= -\left[\log_{10} 2 - 4 \log_{10} 10 \right]$$

$$= -(0.30 - 4)$$

$$pH = 3.70$$

⇒ Calculate pH of 10^{-8} M HCl

$$pH = -\log_{10} [H^+] = -\log_{10} (10^{-8}) = 8 \log_{10} 10$$

$$pH = 8$$

But for acid $pH < 7$

here, Molarity of HCl is 10^{-8} M, Means HCl is very very dilute

⇒ $[H^+]$ of water also contribute in $[H^+]$ of ~~total~~ total solution

$$[H^+] \text{ of } HCl = 10^{-8} \text{ M}$$

$$[H^+] \text{ of } H_2O = 10^{-7} \text{ M (Approx.)}$$

$$\text{Total } [H^+] = [10^{-8} + 10^{-7}] = [10^{-8} (1 + 10)]$$

$$[H^+] = 10^{-8} (11)$$

Now,

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

$$= -\log_{10} [10^{-8} (11)]$$

$$= 8 \log_{10} 10 - \log_{10} 11$$

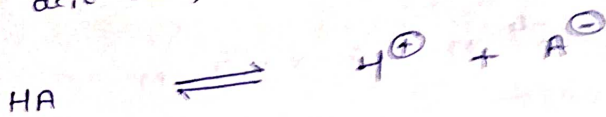
$$= 8 - 1.04$$

$$pH = 6.96$$

So, to avoid confusion, and for more accuracy, better to consider the $[H^+]$ of water also.

Find the pH of Weak Acid

① Weak acid (HA) (8M) ($K_a = 2 \times 10^{-8}$)



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

Initial : 8 M

At equilibrium : $8 - 8\alpha$

$$K_a = \frac{[\text{H}^+][\text{A}^{\ominus}]}{[\text{HA}]} = \frac{8\alpha^2}{1-\alpha}$$

But for weak acid, $\alpha \ll 1$

$$K_a = 8\alpha^2$$

$$\alpha = \sqrt{\frac{K_a}{8}} = \sqrt{\frac{2 \times 10^{-8}}{8}} = 0.5 \times 10^{-4}$$

$$[\text{H}^+] = 8\alpha = 8 \times 0.5 \times 10^{-4} = 4 \times 10^{-4} \text{ molar}$$

$$\text{pH} = -\log_{10} [\text{H}^+] = -\log_{10} (4 \times 10^{-4})$$

$$= -(0.602 - 4)$$

$$\text{pH} = 3.39$$

② Acetic acid of 0.002 M if it ionised to 2% calculate pH

→ Here $C = 0.002 \text{ M}$

$$\alpha = 2\% = 0.02$$



Initial : C

Equilibrium : $C - C\alpha$

$$[\text{H}^+] = C\alpha = 0.002 \times 0.02 = 4 \times 10^{-5} \text{ M}$$

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

$$= -\log (4 \times 10^{-5})$$

$$\text{pH} = 4.39$$

pOH calculation of strong base :-

1) Strong base 0.05 M Ba(OH)_2



$$5 \times 10^{-2}$$

$$2 \times 5 \times 10^{-2}$$

$$[\text{OH}^-] = 10 \times 10^{-2} = 10^{-1}$$

$$\text{pOH} = -\log [\text{OH}^-] = 1$$

2) 10^{-8} M NaOH

10^{-8} M , means very very dilute solutions

We have to consider OH^- ions from water also



$$[\text{OH}^-]_{(\text{NaOH})} = 10^{-8}$$

$$[\text{OH}^-]_{(\text{H}_2\text{O})} = 10^{-7}$$

$$[\text{OH}^-] = 10^{-8} + 10^{-7} = 10^{-8} (1 + 10) = 10^{-8} (11)$$

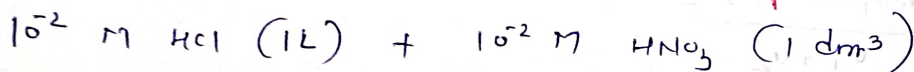
$$\text{pOH} = -\log [\text{OH}^-] = -\log (11 \times 10^{-8})$$

$$\text{pOH} = 6.95$$

pOH calculation of weak base :-

* Same concept like pH calculation of weak acid

pH calculation of mixture of strong acid :-



$$\Rightarrow n(\text{HCl}) = 10^{-2} \text{ moles} = 10^{-2} \text{ moles of H}^+$$

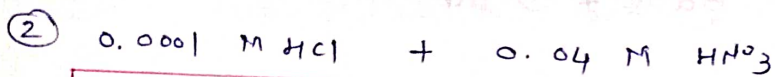
$$n(\text{HNO}_3) = 10^{-2} \text{ moles} = 10^{-2} \text{ moles of H}^+$$

$$n(\text{Total}) = 2 \times 10^{-2} \text{ moles of H}^+$$

$$\text{Total volume} = 2 \text{ dm}^3$$

$$[H^+] = \frac{n}{v} = \frac{2 \times 10^{-2}}{2} = 10^{-2}$$

$$pH = -\log [H^+] = -\log (10^{-2}) = 2$$



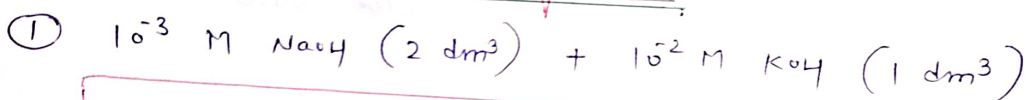
$$[H^+] = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2} \rightarrow \text{Valid only for strong acid which is monobasic}$$

$$= \frac{0.0001 + 0.04}{2}$$

$$[H^+] = 0.02$$

$$pH = -\log (0.02) = 1.69$$

pH calculation of strong base :-



$$[OH^-] = \frac{M_1 V_1 + M_2 V_2}{V_1 + V_2} \rightarrow \text{Valid only for strong base with monoacidic}$$

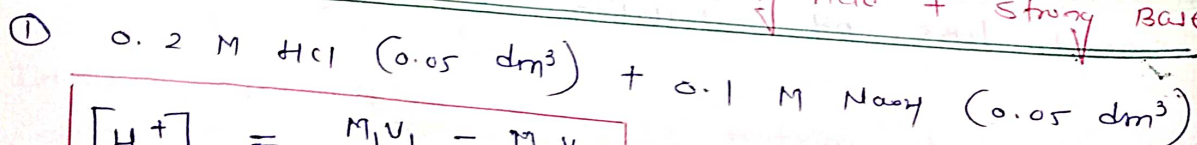
$$= \frac{2 \times 10^{-3} + 10^{-2}}{3}$$

$$[OH^-] = 4 \times 10^{-3}$$

$$pOH = -\log (4 \times 10^{-3}) = 2.40$$

$$pH = 11.6$$

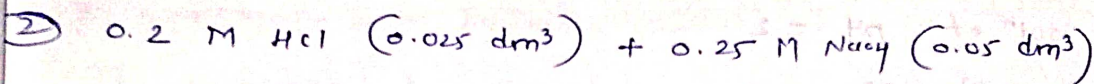
pH calculation of mix. of strong Acid + strong Base



$$[H^+] = \frac{M_1 V_1 - M_2 V_2}{V_1 + V_2}$$

$$[H^+] = \frac{10^{-2} - 0.5 \times 10^{-2}}{0.1} = \frac{0.5 \times 10^{-2}}{0.1} = 0.05$$

$$pH = -\log (0.05) = 1.30$$



$\Rightarrow 0.2 \times 0.025 = 0.005 \text{ moles of } \text{H}^+$

$0.25 \times 0.05 = 0.0125 \text{ moles of } \text{OH}^-$

$\Rightarrow \text{OH}^- \text{ moles} > \text{H}^+ \text{ moles}$

$\Rightarrow \text{OH}^-$ will dominate here

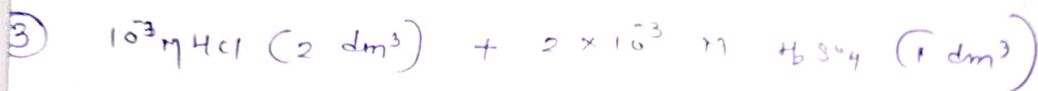
$$[\text{OH}^-] = \frac{M_2 V_2 - M_1 V_1}{V_1 + V_2}$$

$$= \frac{0.0125 - 0.005}{0.075}$$

$$[\text{OH}^-] = 10^{-1}$$

$$\text{pOH} = -\log(10^{-1}) = 1$$

$$\text{pH} = 13$$



Here, H_2SO_4 is dibasic acid

$$[\text{H}^+] = \frac{M_1 V_1 + 2 M_2 V_2}{V_1 + V_2}$$

$$= \frac{2 \times 10^3 + 4 \times 10^3}{3}$$

$$[\text{H}^+] = 2 \times 10^3$$

$$\text{pH} = -\log[2 \times 10^3] = 2.7$$

④ How many litres of water must be added to 1 L of an aqueous solution of HCl having $\text{pH} = 1$ to create an aqueous solution with $\text{pH} = 2$

$\rightarrow \text{pH}(\text{HCl}) = 1 \Rightarrow [\text{H}^+] = 10^{-1} \text{ M}$

Here $v(\text{HCl}) = 1$

$n = 10^{-1} \text{ moles of } \text{H}^+$

We required solⁿ = 10⁻² M

$$\Rightarrow [H^+] = 10^{-2} \text{ M}$$

Let 'x' L water is added to initial volume

$$\text{Total volume} = (x+1) \text{ L}$$

$n(\text{Req. sol}^n) = \text{Remains same} = 10^{-1} \text{ moles}$ (We have only water, so conc.ⁿ will change)

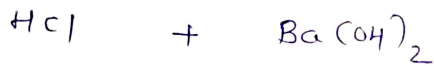
$$M = \frac{n(\text{Req. sol}^n)}{V}$$

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

$$x+1 = 10$$

$$x = 9 \text{ L}$$

⑤



$$pH = 3$$

$$2 \text{ L}$$

$$pOH = 3$$

$$0.5 \text{ L}$$

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

$$n = 2 \times 10^{-3} \text{ H}^+$$

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

$$n = 0.5 \times 10^{-3} \text{ OH}^-$$

$$\text{Total 'n'} = 2 \times 10^{-3} - 0.5 \times 10^{-3}$$

$$= 1.5 \times 10^{-3}$$

$$\text{Total 'V'} = 2 + 0.5 = 2.5 \text{ L}$$

$$\text{Total } [H^+] = \frac{1.5 \times 10^{-3}}{2.5}$$

$$[H^+] = 0.6 \times 10^{-3}$$

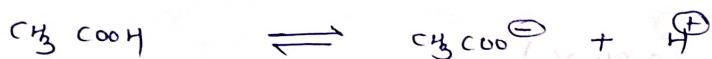
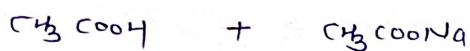
$$pH = -\log_{10} (0.6 \times 10^{-3})$$

$$= 3.22$$

∴ pH calculation of Acidic Buffer solution :-

$$pH = pK_a + \log_{10} \frac{[Salt]}{[Acid]}$$

Consider buffer solution of,



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

← coming from salt
← Here we keep initial conc.ⁿ because of common ion effect

$$* [H^+] = K_a \frac{[Acid]}{[Salt]}$$

$$-\log_{10} [H^+] = -\log_{10} K_a - \log_{10} [Acid] + \log_{10} [Salt]$$

$$pH = pK_a + \log_{10} \frac{[Salt]}{[Acid]}$$

Which is known as Henderson Hassel Balch equation

∴ Find pH of solution : $CH_3COOH (0.1 M) + CH_3COONa (0.2 M)$
 $K_a = 10^{-5}$

$$\rightarrow pH = pK_a + \log_{10} \frac{[Salt]}{[Acid]}$$

$$= -\log_{10} 10^{-5} + \log_{10} \left(\frac{0.2}{0.1} \right)$$

$$pH = 5.30$$

∴ What volume of 0.1 M $HCOONa$ should be added to 50 cm^3 of 0.05 M $HCOOH$ to produce buffer of $pH = 4$ ($pK_a = 3.7$)

→ 'V' consider of $HCOONa$

$$\text{Total volume} = V + 50$$

$$[Acid] = \frac{n}{T.V} = \frac{MV}{V+50} = \frac{50 \times 0.05}{V+50}$$

$$[\text{Salt}] = \frac{n}{T.V} = \frac{0.1 \times V}{V+50}$$

$$\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$4 = 3.7 + \log_{10} \frac{[0.1 \times V]}{0.05 \times 50}$$

$$0.3 = \log_{10} \frac{[0.1 \times V]}{0.05 \times 50}$$

=
=

③ pH of solution having 0.1 M CH_3COOH ($K_a = 10^{-4}$) and 0.02 M $\text{Ca}(\text{CH}_3\text{COO})_2$?

$$\rightarrow \text{pH} = \text{pK}_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log_{10} 10^{-4} + \log_{10} \frac{[2 \times 0.02]}{[0.1]}$$

$$= 4 +$$

=

④ pH of solution obtained by mixing 1L, 0.2 M HCOOH ($K_a = 10^{-4}$) and 1L, 0.1 M NaOH



Initial : 0.2 0.1 0 0

Used : 0.1 0.1 0.1 0.1

Final : 0.1 0 0.1 0.1

Yes, It will make buffer because at final it. in HCOOH and HCOONa both are present

$$\text{pH} = \text{pK}_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 4 + \log_{10} \left(\frac{0.1}{0.1} \right)$$

Mechanism of Acidic Buffer :-



a) on addition of Acid :-

i.e. Addition of H^+ which react with CH_3COO^- to form CH_3COOH



Conc.ⁿ of CH_3COOH increases and it tries to dissociate but due to common ion effect it not dissociate back

b) on addition of Base :-

Addition of OH^- react with H^+ to form H_2O . Now conc.ⁿ $[\text{H}^+]$ decreases which will be increased by dissociation of CH_3COOH to restore the $[\text{H}^+]$ conc.ⁿ in solution

* There is slight change in pH of buffer also due to addition of small amount of Acid/Base

$\overset{(12\text{ g})}{\text{CH}_3\text{COOH}}$ and 16.4 g CH_3COONa are dissolved in solution ($K_a = 10^{-5}$)

Calculate:

- ① pH of solution
- ② New pH if 3.65 g HCl is added
- ③ New pH if 7.3 g HCl is added
- ④ New pH if 4 g NaOH is added

$$\Rightarrow \overset{\textcircled{1}}{M_{\text{CH}_3\text{COONa}}} = \frac{16.4}{82} = 0.2 \text{ moles}$$

$$M_{\text{CH}_3\text{COOH}} = \frac{12}{60} = 0.2 \text{ moles}$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= -\log_{10} 10^{-5} + \log_{10} \left(\frac{0.2}{0.2} \right)$$

$$\text{pH} = 5$$

② 3.65 g HCl is added i.e. $\frac{3.65}{36.5} = 0.1\text{ mol}$ added

Now solution contain CH_3COOH , CH_3COONa , HCl
This HCl react with salt,



Initial: 0.2 0.1 0.2

Used: 0.1 0.1 0.1

Final: 0.1 0 0.3

Now, solution contain, $[\text{CH}_3\text{COONa}] = 0.1\text{ M}$ and

$$[\text{CH}_3\text{COOH}] = 0.3$$

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 5 - 0.47$$

$$\text{pH} = 4.53$$

Even on addition of strong Acid (HCl) with high conc (0.1 M) still there is small change in pH due to buffer

③ Addition of 7.3 g HCl i.e. $\frac{7.3}{36.5} = 0.2$ moles



Initial :	0.2	0.2	0.2
Used :	0.2	0.2	0.2
Final :	0	0	0.4

Now, solution does not remain buffer

It becomes purely weak acidic

$$\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{10^{-5}}{0.4}} = 5 \times 10^{-3}$$

$$[\text{H}^+] = C\alpha = 0.4 \times 5 \times 10^{-3} = 2 \times 10^{-2} \text{ M}$$

$$\text{pH} = -\log_{10} (2 \times 10^{-2}) = 2.70$$

Because of addition of large amount of strong acid (HCl), the pH of solution drastically changes and solution does not remain buffer.

④ Addition of 4 g of NaOH i.e. $\frac{4}{40} = 0.1$ mole

Now, this NaOH reacts with acid



Initial :	0.2	0.1	0.2
Used :	0.1	0.1	0.1
Final :	0.1	0	0.3

$$\text{pH} = \text{p}K_a + \log_{10} \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$= 5 + 0.47$$

$$\text{pH} = 5.47$$

* Buffer capacity :- Number of moles of H^+ or OH^- required to change the pH of buffer by unity

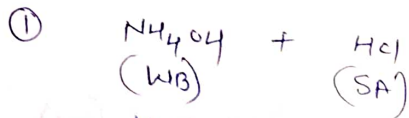
$$\phi = \frac{\text{No. of moles of } H^+ / OH^- \text{ added}}{\text{change in pH}}$$

② Basic Buffer :-

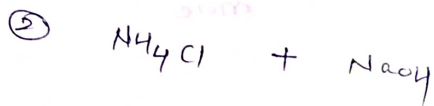
Weak Base + Salt (Weak base + Strong Acid)



* Show that following solutions are Buffer :-



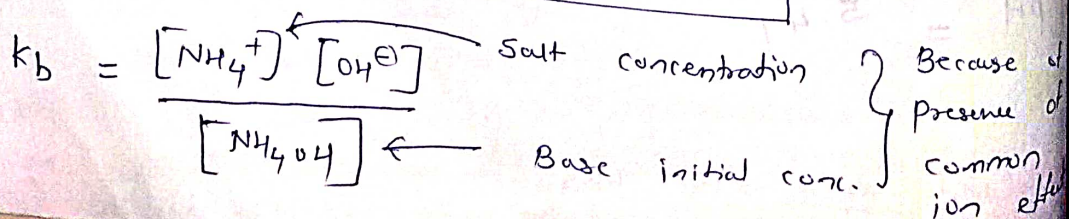
provided that NH_4OH concⁿ should be more than HCl



Forms Buffer (provided $[NH_4Cl] > [NaOH]$)

pH calculation of Basic buffer :-

$$pOH = pK_b + \log_{10} \frac{[Salt]}{[Base]}$$



$$K_b = \frac{[\text{Salt}] [\text{OH}^\ominus]}{[\text{Base}]}$$

$$[\text{OH}^\ominus] = \frac{K_b \times [\text{Base}]}{[\text{Salt}]}$$

$$-\log_{10} [\text{OH}^\ominus] = -\log_{10} K_b - \log_{10} [\text{Base}] + \log_{10} [\text{Salt}]$$

$$p^{\text{OH}} = pK_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

* Find pH of NH_4OH (0.02) + NH_4Cl (0.03 M) $K_b = 10^{-5}$

$$p^{\text{OH}} = pK_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

$$= 5 + \left(\frac{0.03}{0.02} \right)$$

$$= 5.47 - 0.3$$

$$p^{\text{OH}} = 5.17$$

$$\text{pH} = 14 - p^{\text{OH}} = 8.83$$

* Find pH of solution obtained by mixing 0.1 M NH_4OH ($K_b = 10^{-5}$) and 0.1 M $(\text{NH}_4)_2\text{SO}_4$ in 500 ml

$$p^{\text{OH}} = pK_b + \log_{10} \frac{[\text{Salt}]}{[\text{Base}]}$$

cations of base

$$= 5 + \log_{10} \left[\frac{2 \times 0.1}{500} \right]$$

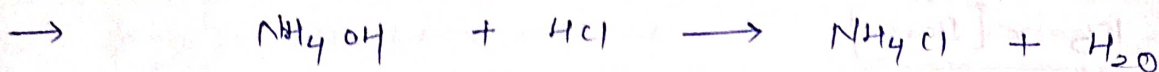
$$\left[\frac{0.1}{500} \right]$$

$$= 5 + 0.30$$

$$p^{\text{OH}} = 5.30$$

$$\text{pH} = 8.7$$

* Find pH of solution obtained by mixing (0.2 M, 500 ml) NH_4OH and (0.1 M, 200 ml) HCl ($K_b = 10^{-5}$)



Initial : 0.2 (500) 0.1 (200) 0 [1000]

mm mm

Used : 20 mm 20 mm 20 mm

Final : 80 mm 0 mm 20 mm

$$\text{pOH} = 5 + \log_{10} \left(\frac{20}{80} \right) = 4.4$$

$$\text{pH} = 9.6$$

Mechanism of Basic Buffer :-



Addition of Acid :-

When acid is added i.e. H^+ ions, they combine with OH^{\ominus} ions to form water. Now $[\text{OH}^{\ominus}]$ decreases and hence to attain equilibrium NH_4OH dissociate more to restore OH^{\ominus} ions

On Addition of Base :-

When Base is added i.e. OH^{\ominus} ions, they will combine with NH_4^{\oplus} and form NH_4OH . Now $[\text{NH}_4\text{OH}]$ increases it cannot dissociate because of common ion effect

* Solubility and Solubility Product *

Two types of salt ;

(A) Highly Soluble salt :-

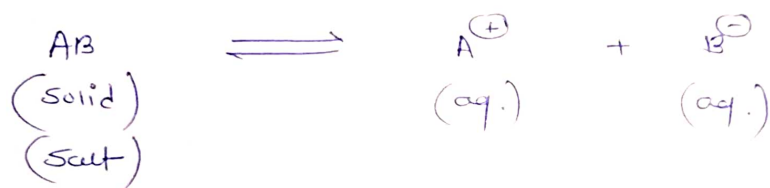
- 1) All nitrates are soluble
- 2) All salt of Na^+ , K^+ , NH_4^+ , Rb^+ , Cs^+ are soluble

(B) Sparingly Soluble salt :-

- 1) Inorganic chemistry - called insoluble salt
e.g. AgCl , AgBr , BaSO_4 , ZnS , AgI

For solubility and solubility product we only study sparingly soluble salt

Solubility Product (K_{sp}) :-



$$K = \frac{[\text{A}^{\oplus}][\text{B}^{\ominus}]}{[\text{AB}]}$$

Whenever any solid is in equilibrium with aq. solution then take concentration of solid as constant.

$$K[\text{AB}] = [\text{A}^{\oplus}][\text{B}^{\ominus}]$$

$$K_{sp} = [\text{A}^{\oplus}][\text{B}^{\ominus}]$$

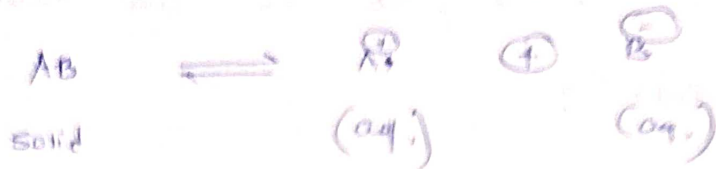
\Rightarrow Solubility product is the product of concentration of ions provided that the concentration taken will be of saturated solution

K_{sp} is depends on temperature and not depends on initial conc. of A^{\oplus} and B^{\ominus}

Solubility :- Amount of solute present in 100 g solvent in saturated state at given temperature.

II Relation between solubility and solubility product

a) For 1:1 electrolyte (AgCl, PbSO₄, BaSO₄)



Initial : s 0 0

Final : s s

$$K_{sp} = [A^{\oplus}] [B^{\ominus}] = s^2$$

$$K_{sp} = s^2$$

Solubility is 's' mol/l

b) For 1:2 or 2:1 electrolyte (Fe₂SO₄, Al₂SO₄)

eg. PbCl₂, Ag₂CO₃



$$K_{sp} = [A^{\oplus}] [B^{\ominus}]^2$$

$$= [s] [2s]^2$$

$$K_{sp} = 4s^3$$

c) For 1:3 electrolyte (AlCl₃)



$$K_{sp} = [A^{\oplus}] \times [3B^{\ominus}]^3$$

$$= (s) \cdot (3s)^3$$

$$K_{sp} = 27s^4$$

d) Give Solubility Product of A_2B_3

$$K_{sp} = (2s)^2 (3s)^3 = 108 s^5$$

* Arrange in order (of) Solubility ;

$$\left. \begin{array}{l} Mx = 4 \times 10^{-8} \\ Mx_2 = 3.2 \times 10^{-14} \\ M_3x = 2.7 \times 10^{-15} \end{array} \right\} K_{sp}$$

→ For Mx , $K_{sp} = s^2$

$$s = \sqrt{K_{sp}} = \sqrt{4 \times 10^{-8}} = 2 \times 10^{-4}$$

For Mx_2

$$s = \left(\frac{K_{sp}}{4} \right)^{\frac{1}{3}} = 2\sqrt{2} \times 10^{-5}$$

For M_3x

$$s = \left(\frac{K_{sp}}{27} \right)^{\frac{1}{4}} = 1 \times 10^{-4}$$

⇒ $Mx > M_3x > Mx_2$ (Solubility order)

* $PbCl_2$ at 298 K, Solubility is 0.279 g L^{-1}

Find K_{sp}



$$K_{sp} = (s)(2s)^2 = 4s^3$$

$$K_{sp} = 4s^3$$

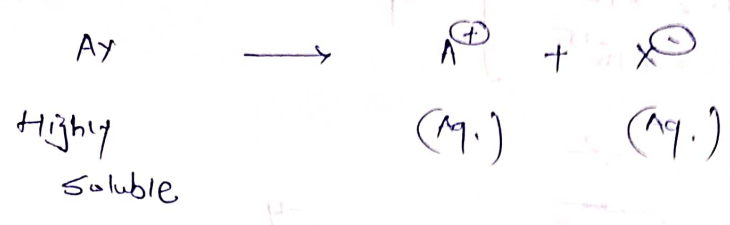
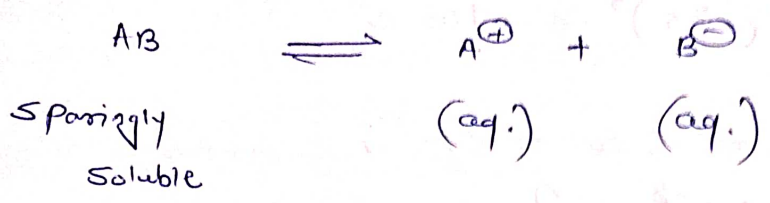
$$s = \frac{0.279 \text{ g}}{L}$$

$$\text{no. of moles} = \frac{\text{Wt}}{\text{M.wt}} = \frac{0.279}{279} = 10^{-3} \text{ moles}$$

$$\text{Now, } s = \frac{10^{-3} \text{ mol}}{L}$$

$$K_{sp} = 4s^3 = 4(10^{-3})^3 = 4 \times 10^{-9}$$

Common ion effect on solubility and solubility product



With increase in A^{\oplus} ions in solution, equilibrium disturb and reaction goes ~~from~~ backward. Because of solubility decreases because of common ion effect

* Find solubility of $BaSO_4$ ($K_{sp} = 10^{-4}$) in water, 0.2 M $Ba(NO_3)_2$ solution

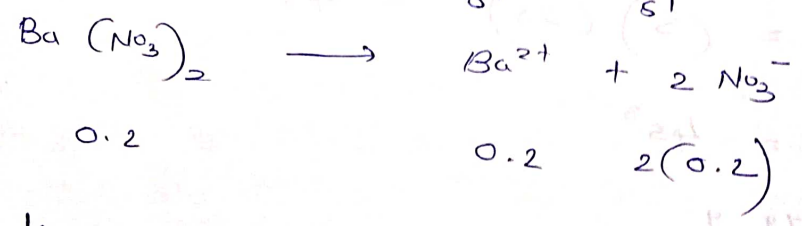
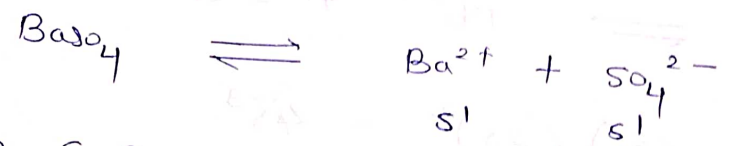
i) Water



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

$$s = \sqrt{K_{sp}} = \sqrt{10^{-4}} = 10^{-2} \text{ mol dm}^{-3}$$

ii) 0.2 M $Ba(NO_3)_2$



$$K_{sp} = [Ba^{2+}][SO_4^{2-}]$$

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

$$10^{-4} = (s' + 0.2)(s')$$

s' is negligible \because we compare it with solubility of $\text{Ba}(\text{NO}_3)_2$

$$10^{-4} = 0.2 s'$$

$$s' = 5 \times 10^{-4} \text{ mol dm}^{-3}$$

* In presence of common ion, solubility and K_{sp} decreases

* Ionic product and precipitation :-



$$K_{ip} = [\text{A}^{\oplus}][\text{B}^{\ominus}] \text{ At any concentration}$$

$$K_{sp} = [\text{A}^{\oplus}][\text{B}^{\ominus}] \text{ At saturated concentration}$$

i) $K_{ip} < K_{sp}$:- More salt can be dissolved

ii) $K_{ip} = K_{sp}$:- Saturated solution

iii) $K_{ip} > K_{sp}$:- Reaction backward \rightarrow Precipitation

* Solubility product *

→ Using Nernst equation



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

$$\Delta G = \Delta G^\circ + RT \ln g$$

$$-nFE_{cell} = -nFE_{cell}^\circ + RT \ln g$$

At equilibrium, $\Delta G = 0 \Rightarrow -nFE_{cell} = 0$

$$nFE_{cell}^\circ = RT \ln g$$

$$E_{cell}^\circ = \frac{2.303 RT}{nF} \log K_{eq}$$

$$E_{cell}^\circ = \frac{2.303 RT}{nF} \log_{10} K_{sp}$$

At 298 K

$$E_{cell}^\circ = \frac{0.0591}{n} \log_{10} K_{sp}$$

Q. The Solubility product of $\text{AgBr} (s)$ is 5×10^{-13} at 298 K. If the standard reduction potential of half cell $E^\circ_{\text{Ag} | \text{AgBr} | \text{Br}^-}$ is 0.07 V. The standard reduction potential $E^\circ_{\text{Ag}^+ | \text{Ag}}$ (in V) ?

→ $K_{sp} = 5 \times 10^{-13}$

$$E^\circ_{\text{Anode}} = 0.07 \text{ V}$$

$$E_{cell}^\circ = \frac{0.0591}{n} \log K_{sp} \dots (298 \text{ K})$$

$$= \frac{0.0591}{(1)} \log 5 \times 10^{-13}$$

$$E_{cell}^\circ = 0.72 \text{ V}$$

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

$$E_{\text{cathode}}^{\circ} = E_{\text{cell}}^{\circ} + E_{\text{anode}}^{\circ}$$

$$= 0.72 + 0.07$$

$$E_{\text{cathode}}^{\circ} = 0.79 \text{ V}$$