* Ionic Product of Water / Ionisation constant of water

$$H_2O + H_2O \rightleftharpoons H_3O^{\oplus} + OH^{\ominus}$$ (Autoprotolysis)

$$K = \frac{[H^{\oplus}][OH^-]}{[H_2O]^2}$$

$$K \cdot [H_2O]^2 = [H^+][OH^{\ominus}]$$

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

where, K_w = ionic product of water or autoprotolysis constant

K_w is depends only on temperature ($K_w \propto$ Temp.)

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

Neutral :- $[H^+] = [\overset{\ominus}{O}H] = 10^{-7}$ mol dm^{-3}

Acidic :- $[H^+] > [\overset{\ominus}{O}H]$

Basic :- $[H^+] < [\overset{\ominus}{O}H]$

} Value of K_w always remains constant

* Find the conc.^{n} of $[H_3O^+]$ and $[\overset{\ominus}{O}H]$ 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.

$$HA \rightleftharpoons H^{\oplus} + \overset{\ominus}{A}$$

$$\boxed{\alpha = \sqrt{\frac{K_a}{c}}}$$

		HA	$H^{\oplus}$	$\overset{\ominus}{A}$
At initial	:	8 moles	0	0
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. $[\overset{\oplus}{H_3O}] = \frac{8\alpha}{1\ L} = 8 \times 0.5 \times 10^{-4}$

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

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 $K_b = 1.6 \times 10^{-8}$ at 298 K. Find conc.^{n} of $[\bar{O}H]$ and $[\overset{\oplus}{H_3O}]$ in solution having 2M conc.^{n} of base.

$$M(OH)_2 \rightleftharpoons M^{2+} + 2[\bar{O}H]$$

At initial : 2 $\quad 0 \quad 0$

At equilibrium : $2 - 2\alpha$ $\quad 2\alpha \quad 4\alpha$

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

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

But α is very very small

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

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

For $[\overset{\ominus}{O}H] = 4\alpha = 4 \times 10^{-3}$ 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 monoacidic base.

Relation between Ka , Kb and Kw for conjugate pair

Consider,

$$NH_3 + H_2O \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$$

(Base) (conjugate acid)

$$K_b = \frac{[NH_4^{\oplus}][OH^{\ominus}]}{[NH_3]}$$

$$NH_4^{\oplus} + H_2O \rightleftharpoons H_3O^{\oplus} + NH_3$$

(Acid) (Conjugate base)

$$K_a = \frac{[H_3O^+][NH_3]}{[NH_4^{\oplus}]}$$

$$K_a \times K_b = [H_3O^{\oplus}][OH^{\ominus}]$$

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

K_a ↓ Acid

K_b ↓ conjugate base

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

Stronger the acid, weaker its conjugate base and vise versa

Which is more Basic $CN^{\ominus}$ or $SO_4^{2\ominus}$

$CN^{\ominus}$ is conjugate base of HCN and $SO_4^{2\ominus}$ is conjugate base of $HSO_4^{\ominus}$

Here, $HSO_4^{\ominus} > HCN$ (Acidity)

$SO_4^{2\ominus} < CN^{\ominus}$ (Basicity)

* pH of Solution :-

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

Keep concentration always in terms of Molarity (mold

Why pH of neutral solution is 7 ?

→ We know,

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

For neutral solution, $[H_3O^{+}]=[OH^{-}] = 10^{-7}$ 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 so
pH is less than 7 while for base it is greater tha
From the same proof, we can also prove that, why the
pH scale range between 0 to 14

$\boxed{\text{pH depends on temperature}}$

⇒ At 63 °C, $K_w = 10^{-13}$

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

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

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

Basically for pure water, pH = 7 (At room temperatu
but with change in temperature, pH also chan

pH calculation for strong Acid :-

① Calculate pH of 10^{-2} M HCl

$$HCl \longrightarrow H^{+} + Cl^{-}$$ ... (complete dissociation)

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

) Calculate pH of 10^{-4} M H_2SO_4

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

10^{-4} M $\quad 2 \times 10^{-4}$ M $\quad 2 \times 10^{-4}$ M

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

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

$$= -(0.30 - 4)$$

$$pH = 3.70$$

) Calculate pH of 10^{-8} M HCl

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

$$pH = 8$$

But for acid pH < 7

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

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

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

$[H^+]$ of H_2O $= 10^{-7}$ 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) (8 M) $(K_a = 2 \times 10^{-8})$

$$\boxed{\alpha = \sqrt{\frac{K_a}{c}}}$$

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

Initial : 8 M 0 0

At equilibrium : $8 - 8\alpha$ 8α 8α

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

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

$$K_a = 8\alpha^2$$

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

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

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

$$= -(0.602 - 4)$$

$$pH = 3.39$$

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

→ Here $c = 0.002$ M

$\alpha = 2\% = 0.02$

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$$

Initial : c 0 0

Equilibrium : $c - c\alpha$ $c\alpha$ $c\alpha$

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

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

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

$$pH = 4.39$$

pOH calculation of strong Base :-

1) Strong base 0.05 M $Ba(OH)_2$

$$Ba(OH)_2 \longrightarrow Ba^{2+} + 2\,OH^{\ominus}$$

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

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

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

2) 10^{-8} M NaOH

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

We have to consider $OH^{\ominus}$ ions from water also

$$NaOH \longrightarrow Na^+ + OH^{\ominus}$$

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

$$[OH^-]\ (H_2O) = 10^{-7}$$

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

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

$$pOH = 6.95$$

pOH calculation of weak base :

→ Same concept like pH calculation of weak acid

pH calculation of mixture of strong acid :-

10^{-2} M HCl (1L) + 10^{-2} M HNO_3 (1 dm^3)

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

$n(HNO_3) = 10^{-2}$ moles $= 10^{-2}$ moles of H^+

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

Total volume $= 2\ dm^3$

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

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

② 0.0001 M HCl + 0.04 M HNO_3

$$\boxed{[H^+] = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}}$$ → 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 :-

① 10^{-3} M NaOH (2 dm^3) + 10^{-2} M KOH (1 dm^3)

$$\boxed{[OH^-] = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}}$$ → 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 :

① 0.2 M HCl (0.05 dm^3) + 0.1 M NaOH (0.05 dm^3)

$$\boxed{[H^+] = \frac{M_1V_1 - M_2V_2}{V_1 + V_2}}$$

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

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

② 0.2 M HCl (0.025 dm³) + 0.25 M NaOH (0.05 dm³)

$\Rightarrow$ 0.2 × 0.025 = 0.005 moles of $H^{\oplus}$

0.25 × 0.05 = 0.0125 moles of $OH^{\ominus}$

$\Rightarrow$ $OH^{\ominus}$ moles > $H^{\oplus}$ moles

$\Rightarrow$ $OH^{\ominus}$ will dominate here

$$\boxed{[OH^{\ominus}] = \frac{M_2V_2 - M_1V_1}{V_1 + V_2}}$$

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

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

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

$$pH = 13$$

③ 10^{-3} M HCl (2 dm³) + 2×10^{-3} M H_2SO_4 (1 dm³)

Here, H_2SO_4 is dibasic acid

$$\boxed{[H^+] = \frac{M_1V_1 + 2M_2V_2}{V_1 + V_2}}$$

→ only if both are Acid / Base

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

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

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

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

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

Here v (HCl) = 1

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

the required sol

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

Let 'x' L water is added to initial volume

Total volume = $(x+1)$ L

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

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

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

$$x+1 = 10$$

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

⑤ HCl + $Ba(OH)_2$

pH = 3 pOH = 3

2 L 0.5 L

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

$n = 2 \times 10^{-3}\ H^+$ $n = 0.5 \times 10^{-3}\ OH^{\ominus}$

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

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

Total 'V' = 2 + 0.5 = 2.5 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 .

CH_3COOH + CH_3COONa

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$$

$$CH_3COONa \longrightarrow CH_3COO^{\ominus} + Na^{\oplus}$$

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

coming from salt

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

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

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

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

Which is known as Hendersson Hassel Balch equation

) Find pH of solution : CH_3COOH (0.1 M) + CH_3COONa (0.2 M)

$K_a = 10^{-5}$

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

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

$$pH = 5.30$$

) What volume of 0.1 M HCOONa should be added to 50 cm³ of 0.05 M HCOOH to produce buffer of pH = 4 ($pK_a = 3.7$)

→ 'V' consider of HCOONa

Total volume = V + 50

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

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

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

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

$$0.3 = \cancel{\log_{10}} \cancel{+} \log_{10} (0.04\ V)$$

$$=$$

$$=$$

③ pH of solution having 0.1 M CH_3COOH ($K_a = 10^{-4}$) and 0.02 M $Ca(CH_3COO)_2$?

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

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

$$= 4 +$$

$$=$$

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

$$HCOOH + NaOH \longrightarrow HCOONa + H_2O$$

		$HCOOH$	$NaOH$	$HCOONa$	H_2O
Initial	:	0.2	0.1	0	0
Used	:	0.1	0.1	0.1	
Final	:	0.1	0	0.1	

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

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

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

Mechanism of Acidic Buffer :-

$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$

$CH_3COONa \longrightarrow CH_3COO^{\ominus} + Na^{\oplus}$

a) On addition of Acid :-

i.e. Addition of H^+ which react with $CH_3COO^{\ominus}$ to form CH_3COOH

$CH_3COO^{\ominus} + H^{\oplus} \longrightarrow CH_3COOH$

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

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

(12 g) CH_3COOH 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

①

$\Rightarrow M_{CH_3COONa} = \frac{16.4}{82} = 0.2$ moles

$M_{CH_3COOH} = \frac{12}{60} = 0.2$ moles

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

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

$$pH = 5$$

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

Now Solution contain CH_3COOH, CH_3COONa, HCl

This HCl ~~react~~ with Salt,

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

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

Now, Solution contain, $[CH_3COONa] = 0.1$ M and $[CH_3COOH] = 0.3$

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

$$= 5 - 0.47$$

$$pH = 4.53$$

Even on addition of strong Acid (HCl) with high co
(0.1 M) Still there is small change in pH due to buff

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

	CH_3COONa	+	HCl	$\longrightarrow$	CH_3COOH	+	$NaCl$
Initial :	0.2		0.2		0.2		
Used :	0.2		0.2		0.2		
Final :	0		0		0.4		

Now, solution does not remains buffer
It becomes purely weak acidic

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

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

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

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

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

Now, this NaOH react with acid

	CH_3COOH	+	$NaOH$	$\longrightarrow$	CH_3COONa	+	H_2O
Initial :	0.2		0.1		0.2		
Used :	0.1		0.1		0.1		
Final :	0.1		0		0.3		

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

$$= 5 + 0.47$$

$$pH = 5.47$$

* Buffer capacity :– Number of moles of $H^{\oplus}$ or $OH^{\ominus}$ required to change the pH of buffer by unity

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

② Basic Buffer :–

Weak Base + Salt (Weak base + Strong Acid)

a) NH_4OH + NH_4Cl

b) NH_4OH + $(NH_4)_2SO_4$

* Show that following solutions are Buffer :–

① NH_4OH (WB) + HCl (SA)

NH_4OH (WB) + HCl → NH_4Cl ~~(Salt)~~ Salt + H_2O

Provided that NH_4OH concⁿ should be more than H

② NH_4Cl + NaOH

NH_4Cl (Salt) + NaOH → NH_4OH (Weak Base) + NaCl

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

pOH calculation of Basic buffer :–

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

$$K_b = \frac{[NH_4^+][OH^{\ominus}]}{[NH_4OH]}$$

← Salt concentration

← Base initial conc.

} Because of Presence of common ion eff

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

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

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

$$\boxed{pOH = pk_b + \log_{10}\frac{[\text{Salt}]}{[\text{Base}]}}$$

* Find pH of NH_4OH (0.02) + NH_4Cl (0.03 M)

$k_b = 10^{-5}$

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

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

$$= 5.47 - 0.3$$

$$pOH = 5.17$$

$$pH = 14 - pOH = 8.83$$

* Find pH of solution obtained by mixing 0.1 M NH_4OH ($K_b = 10^{-5}$) and 0.1 M $(NH_4)_2SO_4$ in 500 ml

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

Cations of base

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

$$= 5 + 0.30$$

$$pOH = 5.30$$

$$pH = 8.7$$

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

→	NH_4OH	+ HCl →	NH_4Cl + H_2O
Initial :	0.2(500) mm	0.1(200) mm	0
Used :	20 mm	20 mm	20 mm
Final :	80 mm	0	20 mm

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

$pH = 9.6$

Mechanism of Basic Buffer :-

$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$

$NH_4Cl \longrightarrow NH_4^{\oplus} + Cl^{\ominus}$

Addition of Acid :-

When acid is added i.e. H^+ ions, they combine wi $OH^{\ominus}$ ions to form water. Now $[OH^{\ominus}]$ 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 con with $NH_4^{\oplus}$ and form NH_4OH. Now $[NH_4OH]$ increases it cannot dissociate because of common ion eff

* Solubility and Solubility Product *

Two types of salt ;

Ⓐ Highly soluble salt :-

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

Ⓑ 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}) :-

$$\underset{\substack{(solid)\\(salt)}}{AB} \rightleftharpoons \underset{(aq.)}{A^{\oplus}} + \underset{(aq.)}{B^{\ominus}}$$

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

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

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

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

⇒ 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.ⁿ of $A^{\oplus}$ and $B^{\ominus}$

Solubility :— Amount of solute present in 100 g sol in Saturated state at given temperature.

Relation between solubility and solubility product :

a) For 1 : 1 electrolyte (AgCl , $PbSO_4$, $BaSO_4$)

$$\underset{\text{solid}}{AB} \rightleftharpoons \underset{(aq.)}{A^{\oplus}} \; + \; \underset{(aq.)}{B^{\ominus}}$$

Solubility is 's' mol/dm³

Initial : s 0 0

Final : s s

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

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

b) For 1 : 2 or 2 : 1 electrolyte (AB_2 , A_2B)

e.g. $PbCl_2$, Ag_2CrO_4

$$\underset{\text{Solid}}{AB_2} \rightleftharpoons \underset{(aq)}{A^{(+)}} + \underset{(aq)}{2B^{\ominus}}$$

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

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

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

c) For 1 : 3 electrolyte ($AlCl_3$)

$$AB_3 \rightleftharpoons A^{\oplus} + 3B^{\ominus}$$

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

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

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

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}

$$PbCl_2 \rightleftharpoons Pb^{2+} + 2Cl^{\ominus}$$

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

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

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

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

Now, $s = \cancel{0.279}\ \frac{10^{-3}\ mol}{L}$

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

Common ion effect on solubility and solubility Product

$$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$$

Sparingly soluble (aq.) (aq.)

$$AY \longrightarrow A^{\oplus} + X^{\ominus}$$

Highly soluble (Aq.) (Aq.)

With increase in $A^{\oplus}$ ions in solution, equilibrium disturb and reactions goes ~~forw~~ 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

$$BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$$

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

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

ii) 0.2 M $Ba(NO_3)_2$

$$BaSO_4 \rightleftharpoons \underset{s'}{Ba^{2+}} + \underset{s'}{SO_4^{2-}}$$

$$\underset{0.2}{Ba(NO_3)_2} \longrightarrow \underset{0.2}{Ba^{2+}} + \underset{2(0.2)}{2NO_3^-}$$

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

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

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

s' is negligible as we compare it with solubility of $Ba(NO_3)_2$

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

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

* In presence of common ion, solubility and Ksp decreases

* Ionic product and Precipitation :-

$$AB \rightleftharpoons A^{\oplus} + B^{\ominus}$$

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

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

* Solubility product *

→ Using Nerst equation

$$AgBr \rightleftharpoons Ag^+ + Br^{\ominus}$$

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

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

$$-nFE_{cell} = -nFE^\circ_{cell} + RT \ln q$$

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

$$nFE^\circ_{cell} = RT \ln q$$

$$E^\circ_{cell} = \frac{2.303\,RT}{nF} \log K_{eq}$$

$$\boxed{E^\circ_{cell} = \frac{2.303\,RT}{nF} \log_{10} K_{sp}}$$

At 298 K

$$E^\circ_{cell} = \frac{0.0591}{n} \log_{10} K_{sp}$$

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

→ $K_{sp} = 5 \times 10^{-13}$

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

$$E^\circ_{cell} = \frac{0.0591}{n} \log K_{sp} \quad \ldots (298\ K)$$

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

$$E^\circ_{cell} = 0.72\ V$$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{Anode}$$

$$E^\circ_{cathode} = E^\circ_{cell} + E^\circ_{Anode}$$

$$= 0.72 + 0.07$$

$$E^\circ_{cathode} = 0.79\ V$$