## Substance

- Electrolytes
  (dissociate into ions)
  - Complete diss
    Strong electrolytes
    $\boxed{\alpha = 1}$
  - Partial disso.
    weak electro
    $\boxed{0 < \alpha < 1}$
- Non Electrolytes
  (do not disso. Into ions)
  $\boxed{\alpha = 0}$
  Urea glucose fructose etc.

## Strong Electrolytes

SA

$H_2SO_4$, $HClO_4$, $HClO_3$

$HNO_3$, $HCl$, $HBr$, $HI$

All type of salts

SB

All alkali metal hydroxides and $Ba(OH)_2$

# Weak Electrolytes

WA

$H_2SO_3$, $HClO_2$, $HClO$

$HNO_2$, All oxy acids of P, All organic carboxylic acid, HCN $H_3BO_3$, $H_2CO_3$, HF etc

WB

All alkaline earth metal hydroxides Except $Ba(OH)_2$, $Al(OH)_3$, All organic bases, $NH_3$, d block metal hydroxides

# Arrhenius Acid Base theory

AA

Donate $H^+$ ion in aq Sol$^n$

$HX$, $H_2SO_4$, $H_3PO_4$

$HClO_4$, $HCN$ etc.

AB

$\bar{O}H$ donor in aq Sol$^n$

$MOH$, $M(OH)_2$, $M(OH)_3$

## Bronsted Acid Base theory

BA

$H^+$ donor

$HX \rightarrow H^+ + X^-$

* All AA are BA

BB

$H^+$ acceptor

$X^- \xrightarrow{H^+} HX$

$HCO_3^- \xrightarrow{H^+} H_2CO_3$

$H_2PO_4^- \xrightarrow{H^+} H_3PO_4$

$HO^- \xrightarrow{H^+} H_2O$

## Lewis Acid Base theory

**L. A**

L. P acceptor

$H^+$, $CO_2$, $SF_4$, $PF_5$, $BCl_3$, $AlCl_3$
$FeCl_3$ etc.

**L. B**

L. P donor

$X^-$, $^-OH$, $NH_3$, $H_2O$ etc.

## Conjugate Acid Base theory

$Base + H^+ \rightarrow Conjugate\ Acid$

| | |
|---|---|
| WB | SCA |
| SB | WCA |

$NO_3^- + H^+ \rightarrow HNO_3$

| | |
|---|---|
| WB | SCA |

$HCO_3^- + H^+ \rightarrow H_2CO_3$

| | |
|---|---|
| SB | WCA |

$Acid \rightarrow H^+ + Conjugate\ Base$

| | |
|---|---|
| SA | WCB |
| WA | SCB |

$HNO_3 \rightarrow H^+ + NO_3^-$

| | |
|---|---|
| SA | WCB |

$HF \rightarrow H^+ + F^-$

| | |
|---|---|
| WA | SCB |

## Amphiprotic species

$H^+$ donor as well as acceptor

Bronsted acid as well as bronsted base

$$HCO_3^- \xrightarrow{+H^+} H_2CO_3$$

$$HCO_3^- \xrightarrow{-H^+} CO_3^{2-}$$

**pH Calculation**

**Case 1** $\underbrace{\text{Strong acid}}$ / $\underbrace{\text{Base}}$ Strong

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

$pOH = -\log[\bar{O}H]$

$pH + pOH = 14$ at $25^\circ C$

$pH + pOH = 12$ at $90^\circ C$

$T \uparrow \; K_w \uparrow$

(1) $pH$ of $10^{-8}$ M HCl $\quad \underbrace{[H^+] < 10^{-6} M}$

$$[H^+]_{net} = [H^+]_{\substack{from\\acid}} + [H^+]_{from\ H_2O}$$

$$[H^+]_{net} = 10^{-8} + 10^{-7}$$

$$pH = -\log[H^+]_{new} = 6.9$$

(2) $[H^+] \geq 10^{-6}$ M

find $p^H$ of $10^{-4}$ M HCl

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

$p^H = -\log 10^{-4}$

$p^H = 4$

**Case 2** pH of mix of two SA & SB

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

2) & for conju acid base pair $pK_a + pK_b = 14$

① Two SA

$$[H^+]_{mix} = \frac{M_1 V_1 nf_1 + M_2 V_2 nf_2}{V_1 + V_2}$$

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

② Two strong Bases

$$[\bar{O}H]_{mix} = \frac{M_1 V_1 nf_1 + M_2 V_2 nf_2}{V_1 + V_2}$$

$$p^{OH} = -\log[\bar{O}H]$$

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

(3) One SA + one S.B

$$[H^+] / [^-OH] = \frac{|M_1 V_1 nf_1 - M_2 V_2 nf_2|}{V_1 + V_2}$$

Q. Find pH

50 mL of $\frac{M}{5}$ HCl + 50 mL of $\frac{M}{10}$ $H_2SO_4$

A A

$$[H^+]_{mix} = \frac{\frac{1}{\cancel{5}} \times \cancel{50}^{10} \times 1 + \frac{1}{1\cancel{0}} \times 5\cancel{0} \times 2}{100}$$

$$= \frac{10 + 10}{100}$$

$$= \frac{20}{100}$$

$$= \frac{1}{5}$$

$$pH = -\log \frac{1}{5}$$

$$pH = +\log 5$$

$$pH = 0.7$$

Q. Find pH

SB ✓ SA

75 mL of $\frac{M}{2}$ Ba(OH)2 + 25 mL of $\frac{M}{1}$ HCl

$$[H^+] / [\bar{O}H] = \frac{\left|\frac{1}{\cancel{2}} \times 75 \times \cancel{2} - 1 \times 25 \times 1\right|}{100}$$

$$[\bar{O}H] = \frac{|75 - 25|}{100}$$

$$[\bar{O}H] = \frac{1}{2}$$

$$p^{OH} = -\log \frac{1}{2}$$

$$p^{OH} = +\log 2$$

$$p^{OH} = 0.3$$

$$p^{H} = 14 - 0.3$$

$$= 13.7$$

## Case 3 pH of weak mono basic acid or weak mono acidic base

$\underbrace{\text{weak mono basic acid}}_{}$ (HA) or $\underbrace{\text{weak mono acidic base}}_{}$ (BOH)

Ostwald dilution Law

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

$$D.O.D = \frac{\cancel{C}\alpha}{\cancel{C}} = \alpha$$

$$\begin{array}{cccc} C & & 0 & 0 \\ HA & \rightleftharpoons & H^+ & + A^- \quad K_a \\ C - C\alpha & & C\alpha & C\alpha \end{array}$$

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

$$\boxed{1 >>> \alpha}$$

$$1 - \alpha \simeq 1$$

$$\boxed{\begin{array}{ll} K_a = C\alpha^2 & [H^+] = C\alpha \\ \alpha = \sqrt{\frac{K_a}{C}} & [H^+] = \sqrt{K_a C} \end{array}}$$

$$pH = \frac{1}{2}\left[pK_a - \log C\right]$$

Q. Calculate pH of $\underbrace{0.1\ M}$ $CH_3COOH$ $\underbrace{(K_a = 10^{-5})}$

$pK_a = -\log K_a$

$= -\log 10^{-5}$

$= 5$

$pH = \frac{1}{2}[5 - \log 10^{-1}]$

$pH = \frac{1}{2}[5 + 1]$

$pH = 3$

**Case 4** pH of $\underbrace{\text{weak poly basic acid}}$ or $\underbrace{\text{Weak poly acidic base}}$

$Mg(OH)_2$ etc
$Al(OH)_3$

$H_2S$, $H_3PO_4$, $H_3PO_3$ etc

| | | |
|---|---|---|
| $K_{a_1}$ | $K_{a_1}$ | $K_{a_1}$ |
| $K_{a_2}$ | $K_{a_2}$ | $K_{a_2}$ |
| | $K_{a_3}$ | |

$$\boxed{pH = \frac{1}{2}[pK_{a_1} - \log c]}$$

Q. Find pH of 0.1 M $H_3PO_4$ $Ka_1 = 10^{-3}$ ✓ $pKa_1 = -\log 10^{-3} = 3$

$Ka_2 = 10^{-8}$ ✗

$Ka_3 = 10^{-13}$ ✗

$$pH = \frac{1}{2}\left[pKa_1 - \log c\right]$$

$$= \frac{1}{2}\left[3 - \log 10^{-1}\right]$$

$$= \frac{1}{2}\left[3 + 1\right]$$

$$pH = 2$$

**Case 5** pH of mix of $\underbrace{\text{two weak acids}}$ or $\underbrace{\text{two weak bases}}$

$\boxed{WA_1 + WA_2}$ or $\boxed{WB_1 + WB_2}$

$$\boxed{[H^+] = \sqrt{Ka_1 C_1 + Ka_2 C_2}}$$

$C_1$ & $C_2$ conc$^n$ after mixing

Q. Find pH of Sol$^n$ obtained by mixing equal volumes of 0.02 HOCl ($K_a = 2 \times 10^{-4}$) and 0.2 $CH_3COOH$ ($K_a = 2 \times 10^{-5}$)

$[H^+] = A \times 10^{-B}$

$pH = B - \log A$

$$[H^+] = \sqrt{K_{a_1} C_1 + K_{a_2} C_2}$$

$$C_1 = \frac{0.02}{2} = 0.01$$

$$C_2 = \frac{0.2}{2} = 0.1$$

$$[H^+] = \sqrt{2 \times 10^{-4} \times 10^{-2} + 2 \times 10^{-5} \times 10^{-1}}$$

$$= \sqrt{2 \times 10^{-6} + 2 \times 10^{-6}}$$

$$= \sqrt{4 \times 10^{-6}}$$

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

$$pH = 3 - \log 2 = 3 - 0.3 = 2.7$$

**Case 6** pH of mix of $\boxed{\text{WA and SA}}$ or $\boxed{\text{WB and SB}}$

$$\boxed{[H^+] = \frac{-c_2 \pm \sqrt{c_2^2 + 4K_{a_1}c_1}}{2}}$$

$c_2$ = concⁿ of SA

$c_1$ = concⁿ of WA

Q. Find pH of mix of $10^{-4}$ M HCl + $10^{-2}$ M $CH_3COOH$ ($K_a = 2 \times 10^{-5}$)

$$\underbrace{10^{-4}\text{ M HCl}}_{SA} + \underbrace{10^{-2}\text{ M } CH_3COOH}_{WA}$$

$c_2 = 10^{-4}$ $\qquad$ $c_1 = 10^{-2}$

$$[H^+] = \frac{-10^{-4} \pm \sqrt{(10^{-4})^2 + 4 \times 2 \times 10^{-5} \times 10^{-2}}}{2}$$

$$= \frac{-10^{-4} + \sqrt{10^{-8} + 8 \times 10^{-7}}}{2}$$

$$= \frac{-10^{-4} + \sqrt{10^{-8} + 80 \times 10^{-8}}}{2} = \frac{-10^{-4} + \sqrt{81 \times 10^{-8}}}{2}$$

$$[H^+] = \frac{-10^{-4} + 9\times10^{-4}}{2}$$

$$= \frac{8\times10^{-4}}{2}$$

$$[H^+] = 4\times10^{-4}$$

$$pH = 4 - \log 4$$

$$= 4 - 0.6$$

$$pH = 3.4$$

## Case 7 pH of Amphiprotic Species

$\underbrace{\text{Amphiprotic}}_{[H^+] \text{ donor \& acceptor}}$

$Ka_1 \checkmark \quad Ka_2 \checkmark$

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

**Q** Find pH of NaHA given $K_{a1} = 10^{-3}$ $pK_{a_1} = 3$

$K_{a2} = 10^{-8}$ $pK_{a_2} = 8$

$HA^{\ominus}$

$$pH = \frac{3+8}{2} = \frac{11}{2} = 5.5$$

## Some Important points

1. Isohydric $Sol^n$

$Sol^n$ having same $[H^+]$

2. Relative strength of acids

$$RS = \frac{[H^+]_1}{[H+]_2} = \frac{\sqrt{Ka_1 C_1}}{\sqrt{Ka_2 C_2}}$$

# Salt hydrolysis

WA + SB ($CH_3COONa$)

1) $K_H = \frac{K_w}{K_a}$

2) $\alpha = \sqrt{\frac{K_H}{c}}$

3) $p^H = 7 + \frac{1}{2}[pK_a + \log c]$

4) $p^H > 7$, Nature of $sol^n$ Basic

SA + WB ($NH_4Cl$)

1) $K_H = \frac{K_w}{K_b}$

2) $\alpha = \sqrt{\frac{K_H}{c}}$

3) $p^H = 7 - \frac{1}{2}[pK_b + \log c]$

4) $p^H < 7$, Nature of $sol^n$ acidic

WA + WB ($CH_3COONH_4$)

1) $K_H = \frac{K_w}{K_a K_b}$

2) $\alpha = \sqrt{K_H}$

3) $p^H = 7 + \frac{1}{2}[pK_a - pK_b]$

a) $K_a > K_b$ ; $pK_a < pK_b$ ; $p^H < 7$

b) $K_a < K_b$ ; $pK_a > pK_b$ ; $p^H > 7$

c) $K_a = K_b$ , $pK_a = pK_b$ ; $p^H = 7$

(WA+SB)

weak part $\quad$ strong part

$CH_3COONa \longrightarrow CH_3COO^- + Na^+$

c molar $\quad$ c

Hydrolysis const

① $CH_3COO^{\ominus} + H_2O \rightleftharpoons CH_3COOH + {}^-OH$ $\quad K_H$

c $\quad\quad\quad\quad\quad\quad$ 0 $\quad\quad$ 0

$c - c\alpha$ (Excess) $\quad c\alpha \quad c\alpha$

$K_H = c\alpha^2$

$\alpha = \sqrt{\frac{K_H}{c}}$

② $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ $\quad K_a$

③ $H_2O \rightleftharpoons H^+ + {}^-OH$ $\quad K_w = 10^{-14}$

$$K_H = \frac{K_w}{K_a}$$

Q. Which salts will have highest pH?

SA+SB

(A) KCl $pH = 7$

WA+SB $pH > 7$

(B) $Na_2CO_3$

(C) $CuSO_4$

SA+WB

$pH < 7$

(D) NOT

Q. PKb for $CN^-$ is 4.7 The pH of 0.5 M aq NaCN Sol$^n$ is

WA+SB

$$pH = 7 + \frac{1}{2}[pKa + \log c]$$

$$pKb = 4.7$$

$$pKa = 14 - 4.7 = 9.3$$

$$pH = 7 + \frac{1}{2}[9.3 + \log(5 \times 10^{-1})]$$

$$= 7 + \frac{1}{2}[9.3 + \log 5 + \log 10^{-1}]$$

$$= 7 + \frac{1}{2}[9.3 + 0.7 - 1]$$

$$= 7 + \frac{1}{2} \times 9 = 11.5$$

Q. Kb for $NH_4OH$ is $\underbrace{2 \times 10^{-5}}$ Find $k_H$ of $\underbrace{NH_4Cl}_{SA+WB}$

$$K_H = \frac{K_w}{K_b} = \frac{10^{-14}}{2 \times 10^{-5}} = \frac{10^{-9}}{2}$$

Q. [Incorrect match] pH < 7

SA + WB

(A) $FeCl_3$ in $H_2O$ – Basic

(B) $NH_4Cl$ in $H_2O$ – Acidic

SA + WB pH < 7

(C) $CH_3COONH_4$ in $H_2O$ – Neutral

WA + WB

$CH_3COOH$ $K_a = 2 \times 10^{-5}$

$NH_4OH$ $K_b = 2 \times 10^{-5}$

(D) $Na_2CO_3$ in $H_2O$ – Basic

WA + SB

pH > 7

# Buffer Solution

Acidic Buffer

$\underbrace{WA}$ + $\underbrace{\text{Salt of } WA + SB}$

Basic Buffer

$\underbrace{WB}$ + $\underbrace{\text{Salt of } WB + SA}$

Examples of B.S

Acidic

1. $HCN + NaCN$
2. $H_3BO_3 + Na_2B_4O_7$
3. $H_2CO_3 + NaHCO_3$
4. $H_3PO_4 + NaH_2PO_4$
5. $CH_3COOH + CH_3COONa$
6. $HNO_2 + NaNO_2$

Examples of B.S

Basic

1. $CH_3NH_2 + CHNH_3^+Cl^-$
2. $NH_4OH + NH_4Cl$
3. $PhNH_2 + PhNH_3^+Cl^-$
2. $C_5H_5N + C_5H_5NH^+ Cl^-$

$CH_3COONH_4$

Salt Buffer –Salt of WA+WB

# Acidic Buffer can be prepared by

1. WA + Salt of WA+SB

$CH_3COOH$ $CH_3COONa$ $n_{WA} > n_{SB}$

2. WA + SB

Salt of WA+SB

$$\begin{array}{lcccc} & 10 & 5 & 0 & 0 \\ & \boxed{CH_3COOH} + NaOH & \rightleftharpoons & \boxed{CH_3COONa} + H_2O \\ WA & \frac{10}{1} & \frac{5}{1} & & \\ & (10-5)\times 1 & 0 & 5\times 1 & 5\times 1 \end{array}$$

3. Salt of WA+SB with SA

$(n_{WA+SB} > n_{SA})$

$$\begin{array}{cccc} 10 & 5 & 0 & 0 \\ \boxed{CH_3COONa} + HCl & \rightleftharpoons & \boxed{CH_3COOH} + NaCl \\ \frac{10}{1} & \frac{5}{1} & & \\ (10-5)\times 1 & 0 & 5\times 1 & 5\times 1 \end{array}$$

Acidic Buffer

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

Basic Buffer

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

$$pH = 14 - pOH$$

# Buffer Range

$$\frac{1}{10} \leq \frac{\overset{\text{[Salt]}}{\text{[conju base]}}}{\text{[Acid]}} \leq 10$$

$$[P^k a - 1 \leq pH \leq P^k a + 1]$$

# Buffer Capacity

$$\text{Buffer Capacity} = \frac{\text{No of moles of Strong acid or Strong base added per L of sol}^n}{\text{Change in pH of buffer}}$$

Q. when 2 moles of HCl is added to 1 L of an acidic buffer $sol^n$ its pH changes from 3.9 to 3.4 find its buffer capacity

$$B.C = \frac{(2/1)}{3.9 - 3.4} = \frac{2}{0.5} = 4$$

Calculation of pH of buffer $Sol_n$

2 M $CH_3COOH$ mixed with 1 M $CH_3COONa$ will have an approx pH of ? ($Ka = 10^{-5}$)

$pKa = 5$

$$pH = 5 + \log \frac{1}{2}$$

$$= 5 - \log 2$$

$$= 5 - 0.3$$

$$= 4.7$$

Q. $\underbrace{0.05\text{ M NH4OH Sol}^{n}}$ is dissolved in $\underbrace{0.001\text{ M }NH_4Cl\text{ Sol}^{n}}$ find pH (Kb = $10^{-5}$)

$pK_b = 5$

$$pOH = 5 + \log\left(\frac{10^{-3}}{5\times10^{-2}}\right)$$

$$= 5 + \log\left(\frac{1}{50}\right)$$

$$= 5 - \log 50$$

$$= 5 - 1.7$$

$$= 3.3$$

$pOH = 3.3$

$pH = 14 - 3.3$

$= 10.7$

Q. $CH_3COOH$ was titrated with NaOH when $\underbrace{\text{75\% of titration is over}}$ then find pH? $(Ka = 10^{-5})$ $pKa = 5$

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

25%     75%

$$pH = 5 + \log\left(\frac{75}{25}\right)$$

$$= 5 + \log 3$$

# Caculation of pH when WA + SB mixing

$k_a(CH_3COOH) = 10^{-5}$ $pK_a = 5$

Case (1) 75 mL of 0.1 M CH3COOH + 25 mL of 0.1 M NaOH

$$\begin{array}{cccc} 7.5 & 2.5 & 0 & 0 \\ CH_3COOH + & NaOH & \rightleftharpoons CH_3COONa + & H_2O \\ \frac{7.5}{1} & \frac{2.5}{1} & & \\ 1\times(7.5-2.5) & 0 & 2.5\times 1 & 2.5\times 1 \\ (5) & & & \end{array}$$

$$pH = pK_a + \log\frac{[S]}{[A]} = 5 + \log\left(\frac{2.5}{5}\right) = 5 + \log\frac{1}{2} = 4.7$$

Case (2) 25 mL of 0.1 M CH3COOH + 25 mL of 0.1 M NaOH

$$\overset{2.5}{CH_3COOH} + \overset{2.5}{NaOH} \rightleftharpoons \underbrace{\overset{0}{CH_3COONa}} + \overset{0}{H_2O}$$

$$\frac{2.5}{1} \qquad \frac{2.5}{1}$$

$$0 \qquad 0 \qquad\qquad 2.5\times1 \qquad 2.5\times1$$

$$p^H = 7+\frac{1}{2}[pK_a + \log c]$$

$$= 7+\frac{1}{2}[5 + \log\frac{1}{20}]$$

$$= 7+\frac{1}{2}[5 - 1.3]$$

$$C = \frac{2.5}{50}$$

$$= \frac{25}{500}$$

$$= \frac{1}{20}$$

Case (3) 25 mL of 0.1 M CH3COOH + 75 mL of 0.1 M NaOH

$$\overset{2.5}{CH_3COOH} + \overset{7.5}{NaOH} \rightleftharpoons \overset{0}{CH_3COONa} + \overset{0}{H_2O}$$

$$\frac{2.5}{1} \qquad \frac{7.5}{1} \qquad \text{(Discarded)}$$

$$0 \qquad \underbrace{(7.5-2.5)\times 1} \qquad \underbrace{2.5\times 1} \qquad 2.5\times 1$$

$$n_{\bar{O}H} = 5$$

$$[\bar{O}H] = \frac{5}{100} = \frac{1}{20}$$

$$pOH = -\log\frac{1}{20} = \log 20 = 1.3$$

$$pH = 14 - 1.3$$

Q. $pH - Pk_a = 1$ will be applicable to an acidic buffer when

(A) [Acid] = [Conju base]

(B) [Acid] × 10 = [Conju base]

(C) [Acid] = [Conju base] × 10

(D) N.O.T

$$\log \frac{[S]}{[A]} = 1$$

$$\frac{[S]}{[A]} = 10$$

# Solubility and solubility product

$\left(\frac{mol}{L}\right)$

Solubility : max no of moles of solute dissolved in a solvent to obtain 1L soln

$$\left( S\left(\frac{mol}{L}\right) = \frac{S\,(gm/L)}{M.W} \right)$$

Relation b/w $K_{sp}$ and S

$$\underset{-}{\overset{S}{A_xB_{y(s)}}} \rightleftharpoons \underset{xS}{\overset{0}{x A^{y+}_{(aq)}}} + \underset{yS}{\overset{0}{y B^{x-}_{(aq)}}} \quad K_{sp}$$

$$K_{sp} = (xS)^x (yS)^y$$

$$\boxed{K_{sp} = x^x y^y S^{x+y}}$$

| Compound | X | Y | Relation b/W S and $k_{sp}$ |
|---|---|---|---|
| $AgCl$ | 1 | 1 | $1^1 \cdot 1^1 \cdot S^{1+1} = S^2$ |
| $MgCl_2$ | 1 | 2 | $1^1 \cdot 2^2 \cdot S^{1+2} = 4S^3$ |
| $AlCl_3$ | 1 | 3 | $1^1 \cdot 3^3 \cdot S^{1+3} = 27S^4$ |
| * $Hg_2Cl_2$ | $\cancel{2}$ 1 | 2 | $1^1 \cdot 2^2 \cdot S^{1+2} = 4S^3$ |

$\overset{+}{Hg}-\overset{+}{Hg}$

Q. if solubility of $\underbrace{Ag_2\,SO_4}$ is $10^{-2}\,\frac{\text{mol}}{\text{L}}$ then find its $k_{sp}$ ?

$x=2,\ y=1$

$$K_{sp} = 2^2 \cdot 1^1 \cdot s^{2+1}$$

$$= 4s^3$$

$$= 4 \times (10^{-2})^3$$

$$= 4 \times 10^{-6}$$

Q. if solubility of AgCl is $10^{-10}$ then find its solubility in gm/L ?

product

$$1^1 \cdot 1^1 s^{1+1} = K_{sp}$$

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

$$s = 10^{-5} \frac{mol}{L}$$

$$s\,(gm/L) = 10^{-5} \times 143.5$$

# Solubility in common ion effect

Solubility decreases by adding common ion

AgCl is mixed with NaCl

$$\underset{s-c}{AgCl} \rightleftharpoons \underset{s}{\overset{0}{Ag^+}} + \underset{s+c}{\overset{0}{Cl^-}}$$

$$NaCl \longrightarrow \underset{c}{\overset{0}{Na^+}} + \underset{c}{\overset{0}{Cl^-}}$$

Q. Find solubility of AgCl ($K_{sp}$ = $10^{-10}$)

(a) In $H_2O$

$$\underset{-}{\overset{s}{AgCl}} \rightleftharpoons \underset{s}{\overset{0}{Ag^+}} + \underset{s}{\overset{0}{Cl^-}} \quad K_{sp}$$

$K_{sp} = s \times s$

$s = 10^{-5}$

(b) In 0.1 M $AgNO_3$

$$\underset{-}{\overset{s}{AgCl}} \rightleftharpoons \underset{0.1+s}{\overset{0}{Ag^+}} + \underset{s}{\overset{0}{Cl^-}} \quad K_{sp}$$

$$\overset{0.1}{AgNO_3} \rightarrow \underset{0.1M}{Ag^+} + \underset{0.1M}{NO_3^-}$$

$K_{sp} = (0.1 + \cancel{s}) \times s$

$s = \dfrac{10^{-10}}{0.1} = 10^{-9}$

(c) In 0.1 M $CaCl_2$

$$\underset{-}{\overset{s}{AgCl}} \rightleftharpoons \underset{s}{\overset{0}{Ag^+}} + \underset{s+0.2}{\overset{0}{Cl^-}} \quad K_{sp}$$

$$\overset{0.1}{CaCl_2} \rightarrow \underset{0.1}{Ca^{2+}} + \underset{2\times0.1}{2Cl^-}$$

$K_{sp} = s \times (\cancel{s} + 0.2)$

$s = \dfrac{10^{-10}}{0.2}$

# Ionic Product of salt

$$A_x B_y \rightleftharpoons x A^{y+} + y B^{x-}$$

$$K_{IP} = [A^{y+}]^x [B^{x-}]^y$$

Case ① $K_{sp} = K_{IP}$ saturated sol$^n$

Case ② $K_{sp} > K_{IP}$ Unsaturated sol$^n$

Case ③ $K_{IP} > K_{sp}$ ppt occurs.

Q. The ppt of $CaF_2$($K_{sp}$= $1.7 \times 10^{-10}$) is obtained when following are mixed in equal volume

| | $[Ca^{2+}]$ | $[F^-]$ |
|---|---|---|
| (A) | $10^{-3}$ M | $10^{-5}$ M |
| (B) | $10^{-5}$ M | $10^{-3}$ M |
| (C) | $10^{-2}$ M | $10^{-3}$ M |
| (D) | $10^{-4}$ M | $10^{-4}$ M |

$CaF_2 \rightleftharpoons Ca^{2+} + 2F^-$

$K_{IP} = [Ca^{2+}][F^-]^2$

(A) $K_{IP} = \frac{10^{-3}}{2}\left(\frac{10^{-5}}{2}\right)^2 < K_{sp}$

(B) $K_{IP} = \frac{10^{-5}}{2} \times \left(\frac{10^{-3}}{2}\right)^2$

$\frac{10^{-11}}{8}$

(C)

$K_{IP} = 10^{-2} \times \left(\frac{10^{-3}}{2}\right)^2 > K_{sp}$

## Some Important points

1. Types of salts

(a) Normal Salt

$NaCl$, $Na_2SO_4$, $Na_3\ PO_4$ etc

(b) Acid salts

$NaHCO_3$ , $NaHSO_4$

c) Basic salts

zn (OH)Cl, Mg(OH)Cl & etc

(d) Double salts

$K_2SO_4$. Al2($SO_4$)3. 24$H_2O$ potash alum

(e) Complex salts

$[Ag\ (NH_3)_2]\ Cl$, $[Cu\ (NH_3)_4]\ SO_4$ etc

(f) mixed salts

NaKS , Na k Rb $PO_4$ etc.

# pyQs

**Q.** The molar solubility of Cd $(OH)_2$ is $1.84 \times 10^{-5}$ M in water. The expected solubility of $Cd(OH)_2$ in a buffer solution of pH = 12 is $pOH = 2$ $[\bar{O}H] = 10^{-2}$ (2019 Main, 12 April II)

a. $1.84 \times 10^{-9}$ M

b. $\frac{2.49}{1.84} \times 10^{-9}$ M

c. $6.23 \times 10^{-11}$ M

d. $2.49 \times 10^{-10}$ M

**Solution:**

$$\underset{s}{Cd(OH)_2} \rightleftharpoons \underset{s}{\overset{0}{Cd^{2+}}} + \underset{2s+10^{-2}}{\overset{0}{2\bar{O}H}} \quad Ksp = 4 \times (1.84 \times 10^{-5})^3$$

$$Ksp = s^1 \times (10^{-2})^2$$

$$s = \frac{Ksp}{10^{-4}}$$

**Q.** What is the molar solubility of $Al(OH)_3$ in 0.2 M NaOH solution? Given that, solubility product of $Al(OH)_3 = 2.4 \times 10^{-24}$

(2019 Main, 12 April II)

a. $3 \times 10^{-19}$

b. $12 \times 10^{-21}$

c. $3 \times 10^{-22}$

d. $12 \times 10^{-23}$

Solution:

$$\underset{-}{\overset{s}{Al(OH)_3}} \rightleftharpoons \underset{s}{\overset{0}{Al^{3+}}} + \underset{3\cancel{s}+0.2}{\overset{0}{3\overline{O}H}} \quad K_{sp}$$

$$s \times (0.2)^3 = 2.4 \times 10^{-24}$$

**Q.** $(SA+WB)$

The pH of a 0.02 M $NH_4Cl$ solution will be [Given $K_b(NH_4OH) = 10^{-5}$ and $\log 2 = 0.301$] **(2019 Main, 10 April II)**

(a) 4.65 (b) 2.65 (c) 5.35 (d) 4.35

Solution:

$$pH = 7 - \frac{1}{2}[pK_b + \log C]$$

$$= 7 - \frac{1}{2}[5 + \log(2 \times 10^{-2})]$$

**Q.** Consider the following statements.

I. The pH of a mixture containing 400 mL of 0.1 M $H_2SO_4$ and 400 mL of 0.1 M NaOH will be approximately 1.3.

II. Ionic product of water is temperature dependent.

III. A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.

IV. The Le-Chatelier's principle is not applicable to common-ion effect.

The correct statements are **(2019 Main, 10 April I)**

(a) I, II and IV
(b) II and III
(c) I and II
(d) I, II and III

Solution:

$$[H^+] \checkmark / [OH^-] \times = \frac{|0.1 \times 400 \times 2 - 0.1 \times 400 \times 1|}{800}$$

$$[H^+] = \frac{|80 - 40|}{800}$$

$$= \frac{40}{800}$$

$$= \frac{1}{20}$$

$$pH = -\log \frac{1}{20}$$

$$= 1.3$$

$$k_a = \frac{c\alpha^2}{1-\alpha}$$

$$k_a = \frac{c\alpha \times \alpha}{1-\alpha}$$

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

$$\frac{\alpha}{1-\alpha} = 1 \qquad \alpha = \frac{1}{2} \qquad 50\%$$

$$\alpha = 1-\alpha$$

**Q.** If solubility product of $\underbrace{Zr_3(PO_4)_4}$ is denoted by $K_{sp}$ and its molar solubility is denoted by $S$, then which of the following relation between $S$ and $K_{sp}$ is correct? **(2019 Main, 8 April I)**

$3^3 \times 4^4 \times S^{3+4} = Ksp$

(a) $S = \left(\frac{K_{sp}}{144}\right)^{1/6}$

✓ (b) $S = \left(\frac{K_{sp}}{6912}\right)^{1/7}$

(c) $S = \left(\frac{K_{sp}}{929}\right)^{1/9}$

(d) $S = \left(\frac{K_{sp}}{216}\right)^{1/7}$

Solution:

**Q.** If $K_{sp}$ of $Ag_2CO_3$ is $8 \times 10^{-12}$, the molar solubility of $Ag_2CO_3$ in $\underbrace{0.1 \text{ M } AgNO_3}$ is (2019 Main, 12 Jan II)

(a) $8 \times 10^{-12}$ M (b) $8 \times 10^{-13}$ M

(c) $8 \times 10^{-10}$ M (d) $8 \times 10^{-11}$ M

Solution:

$$\overset{s}{Ag_2CO_3} \rightleftharpoons \overset{0}{2Ag^+} + \overset{0}{CO_3^{2-}} \quad K_{sp} = 8 \times 10^{-12}$$

$$\cancel{2s} + 0.1 \quad s$$

$$0$$

$$K_{sp} = (0.1)^2 \times s \qquad s = 8 \times 10^{-10}$$

**Q.** 20 mL of 0.1 M $\overset{SA}{H_2SO_4}$ solution is added to 30 mL of 0.2 M $\overset{WB}{NH_4OH}$ solution. The pH of the resultant mixture is [$pK_b$ of $NH_4OH = 4.7$] **(2019 Main, 9 Jan I)**

(a) 9.3 (b) 5.0 (c) 9.0 (d) 5.2

**Solution:**

$$\overset{2}{H_2SO_4} + 2\,\overset{6}{\boxed{NH_4OH}} \rightleftharpoons \boxed{(NH_4)_2SO_4} + 2H_2O$$

WB SA+WB

$\frac{2}{1}$ $\frac{6}{2}$

2 3

0 $(3-2)\times 2$ 2 $2\times 2$

2 2

$$p^{OH} = pK_b + \log \frac{[S]}{[B]}$$

$$= 4.7 + \log 1$$

$$= 4.7$$

$$p^{H} = 14 - 4.7$$

$$= 9.3$$

**Q.** Which of the following are Lewis acids? (2018 Main)

(a) $PH_3$ and $BCl_3$

(b) $AlCl_3$ and $SiCl_4$

(c) $PH_3$ and $SiCl_4$

(d) $BCl_3$ and $AlCl_3$

Solution:

**Q.** Which of the following salts is the most basic in aqueous solution? (2018 Main)

WA+WB

(a) $Al(CN)_3$

WA+SB $p^H > 7$

(b) $CH_3COOK$

(c) $FeCl_3$

SA+WB

(d) $Pb(CH_3COO)_2$

WA+WB

**Solution:**

**Q.** $pK_a$ of a weak acid ($HA$) and $pK_b$ of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt ($AB$) solution is

(2017 Main)

(a) 7.2 (b) 6.9 (c) 7.0 (d) 1.0

**Solution:**

$$pH = 7 + \frac{1}{2}[pK_a - pK_b]$$

$$= 7 + \frac{1}{2}[3.2 - 3.4]$$

$$= 7 + \frac{1}{2}[-0.2]$$

$$= 6.9$$

**Q.** How many litres of water must be added to 1 L of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2? **(2013 Main)**

(a) 0.1 L (b) 0.9 L (c) 2.0 L (d) 9.0 L

**Solution:**

$[H^+]_1 = 10^{-1}$ $V_1 = 1\ L$

$[H^+]_2 = 10^{-2}$ $V_2 = ?$

$M_1 V_1 = M_2 V_2$

$10^{-1} \times 1 = 10^{-2} \times V_2$

$V_2 = 10\ L$

$1\ L + 9\ L = 10\ L$

**Q.** Solubility product constant ($K_{sp}$) of salts of types $MX$, $MX_2$ and $M_3X$ at temperature '$T$' are $4.0 \times 10^{-8}$, $3.2 \times 10^{-14}$ and $2.7 \times 10^{-15}$, respectively. Solubilities ($mol\ dm^{-3}$) of the salts at temperature '$T$' are in the order **(2008, 3M)**

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$

(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

**Solution:**

$S_1^2 = Ksp_1$ $4S_2^3 = Ksp_2$ $27S_3^4 = Ksp_3$

$S_1 = 2 \times 10^{-4}$ $4S_2^3 = 3.2 \times 10^{-14}$ $27S_3^4 = 2.7 \times 10^{-15}$

$S_2 = 2 \times 10^{-5}$ $S_3 = 10^{-4}$

**Q.** $CH_3NH_2$ (0.1 mole, $K_b = 5\times10^{-4}$) is added to 0.08 mole of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is (2005, 1M)

(a) $1.6\times10^{-11}$
(b) $8\times10^{-11}$
(c) $5\times10^{-5}$
(d) $8\times10^{-2}$

$pK_b = 4 - \log 5$
$= 3.3$

**Solution:**

WB

$$\begin{array}{cccc} 0.1 & 0.08 & & 0 \\ CH_3NH_2 & + \; HCl & \rightleftharpoons & CH_3\overset{+}{N}H_3Cl^- \\ \frac{0.1}{1} & \frac{0.08}{1} & & \\ (0.1-0.08) & 0 & & (0.08) \end{array}$$

Salt of SA + WB

$$pOH = pK_b + \log \frac{[S]}{[B]}$$

$$= 3.3 + \log\left(\frac{0.08}{0.02}\right)$$

$$= 3.3 + 0.6$$

$$pOH = 3.9$$

$$pH = 14 - 3.9$$

$$pH = 10.1$$

**Q.** HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1M) on reacting with caustic soda. The degree of hydrolysis of NaX is

WA + SB

(2004, 1M)

(a) 0.01%
(b) 0.0001%
(c) 0.1%
(d) 0.5%

**Solution:**

$$\alpha = \sqrt{\frac{K_H}{C}} = \sqrt{\frac{10^{-14}}{10^{-5} \times 0.1}} = 10^{-4} = 0.01\,\%$$

**Q.** A solution which is $10^{-3}$ M each in $Mn^{2+}$, $Fe^{2+}$, $Zn^{2+}$ and $Hg^{2+}$ is treated with $10^{-16}$ M sulphide ion. If $K_{sp}$ of MnS, FeS, ZnS and HgS are $10^{-15}$, $10^{-23}$, $10^{-20}$ and $10^{-54}$ respectively, which one will precipitate first? **(2003, 1M)**

(a) FeS (b) MgS (c) HgS (d) ZnS

Solution:

**Q.** For a sparingly soluble salt $A_pB_q$, the relationship of its solubility product ($L_s$) with its solubility ($S$) is **(2001, 1M)**

(a) $L_s = S^{p+q} \cdot p^p \cdot q^q$

(b) $L_s = S^{p+q} \cdot p^q \cdot q^p$

(c) $L_s = S^{pq} \cdot p^p \cdot q^q$

(d) $L_s = S^{pq} \cdot (p.q)^{(p+q)}$

Solution:

**Q.** The pH of 0.1 M solution of the following salts increases in the order (1999, 2M)

(a) $NaCl < NH_4Cl < NaCN < HCl$

(b) $HCl < NH_4Cl < NaCl < NaCN$

(c) $NaCN < NH_4Cl < NaCl < HCl$

(d) $HCl < NaCl < NaCN < NH_4Cl$

Solution:

HCl SA pH < 7

$NH_4Cl$ SA+WB pH < 7

NaCl pH = 7

NaCN pH > 7
WA+SB

**Q.** Which of the following solutions will have pH close to 1.0 ?

(1992, 1M)

$\frac{1}{10}\times 100\times 1-\frac{1}{10}\times 100\times 1$

$pH=7$

(a) 100 mL of (M/10) HCl + 100 mL of (M/10) NaOH

(b) 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH $\quad \frac{1}{100}$

(c) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH

(d) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH

**Solution:** (A)

$$[H^+]/[OH^-]=\frac{|M_1V_1nf_1-M_2V_2nf_2|}{V_1+V_2}$$

$$[H^+]=\frac{\left|\frac{1}{5}\times 75\times 1-\frac{1}{5}\times 25\times 1\right|}{100}=10^{-1}$$

**Q.** Which of the following is the strongest acid? **(1989, 1M)**

(a) $ClO_3(OH)$ (b) $ClO_2(OH)$

(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

Solution:

Q. When equal volumes of the following solutions are mixed, precipitation of AgCl $(K_{sp} = 1.8 \times 10^{-10})$ will occur only with

(1988, 1M)

(a) $10^{-4}$ M $(Ag^{+})$ and $10^{-4}$ M $(Cl^{-})$

(b) $10^{-5}$ M $(Ag^{+})$ and $10^{-5}$ M $(Cl^{-})$

(c) $10^{-6}$ M $(Ag^{+})$ and $10^{-6}$ M $(Cl^{-})$

(d) $10^{-10}$ M $(Ag^{+})$ and $10^{-10}$ M $(Cl^{-})$

A

$K_{IP} = [Ag^{+}][Cl^{-}]$

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

Solution:

**Q.** The conjugate acid of $NH_2^-$ is $\xrightarrow{H^+}$ (1985, 1M)

(a) $NH_3$ (b) $NH_2OH$ (c) $NH_4^+$ (d) $N_2H_4$

Solution:

**Q.** A certain weak acid has a dissociation constant of $1.0 \times 10^{-4}$. The equilibrium constant for its reaction with a strong base is

(1984, 1M)

(a) $1.0 \times 10^{-4}$

(b) $1.0 \times 10^{-10}$

(c) $1.0 \times 10^{10}$

(d) $1.0 \times 10^{14}$

$K_a = 10^{-4}$

① $HA + \bar{O}H \rightleftharpoons H_2O + A^-$ $K_1$

② $HA \rightleftharpoons H^+ + A^-$ $K_2 = 10^{-4}$

③ $H_2O \rightleftharpoons H^+ + \bar{O}H$ $K_3 = 10^{-14}$

Solution: $K_1 = \dfrac{10^{-4}}{10^{-14}}$

**Q.** A certain buffer solution contains equal concentration of $X^-$ and H$X$. The $K_b$ for $X^-$ is $10^{-10}$. The pH of the buffer is

$K_a \times K_b = 10^{-14}$

Acidic buffer

(1984, 1M)

(a) 4 (b) 7

(c) 10 (d) 14

**Solution:**

$$K_a(HX) = \frac{10^{-14}}{10^{-10}} = 10^{-4}$$

$$pK_a = 4$$

$$pH = pK_a + \log\frac{[S]}{[A]}$$

$$= 4 + 0$$

**Q.** An acidic buffer solution can be prepared by mixing the solution of (1981, 1M)

$CH_3COO^-Na^+$ $CH_3COOH$

(a) acetate and acetic acid

Basic Buffer

(b) ammonium chloride and ammonium hydroxide $NH_4OH + NH_4Cl$

(c) sulphuric acid and sodium sulphate

(d) sodium chloride and sodium hydroxide

Solution:

**Q.** Of the given anions, the strongest base is (1981, 1M)

(a) $ClO^-$ (b) $ClO_2^-$

(c) $ClO_3^-$ (d) $ClO_4^-$

Solution:

$$\underset{WA}{HClO} \longrightarrow H^+ + \underset{SCB}{ClO^-}$$

**Q.** At 90°C, pure water has $[H_3O^+]$ as $10^{-6}$ mol $L^{-1}$. What is the value of $K_w$ at 90°C ? (1981, 1M)

(a) $10^{-6}$ (b) $10^{-12}$ (c) $10^{-14}$ (d) $10^{-8}$

**Solution:**

$K_w = [H^+][\bar{O}H] = 10^{-6} \times 10^{-6}$

$= 10^{-12}$

**Q.** The pH of $10^{-8}$ M solution of HCl in water is **(1981, 1M)**

(a) 8

(b) $-8$

(c) between 7 and 8

(d) between 6 and 7

Solution: