

# IONIC EQUILIBRIUM (ELEMENTARY)

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### JEE(Advanced) Syllabus

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Solubility product, common ion effect, pH and buffer solutions; Acids and bases (Bronsted and Lewis concepts); Hydrolysis of salts.

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### JEE(Main) Syllabus

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Ionic equilibrium: Weak and strong electrolytes, ionization of electrolytes, various concepts of acids and bases (Arrhenius, Bronsted – Lowry and Lewis) and their ionization, acid – base equilibria (including multistage ionization) and ionization constants, ionization of water, pH scale, common ion effect, hydrolysis of salts and pH of their solutions, solubility of sparingly soluble salts and solubility products, buffer solutions.



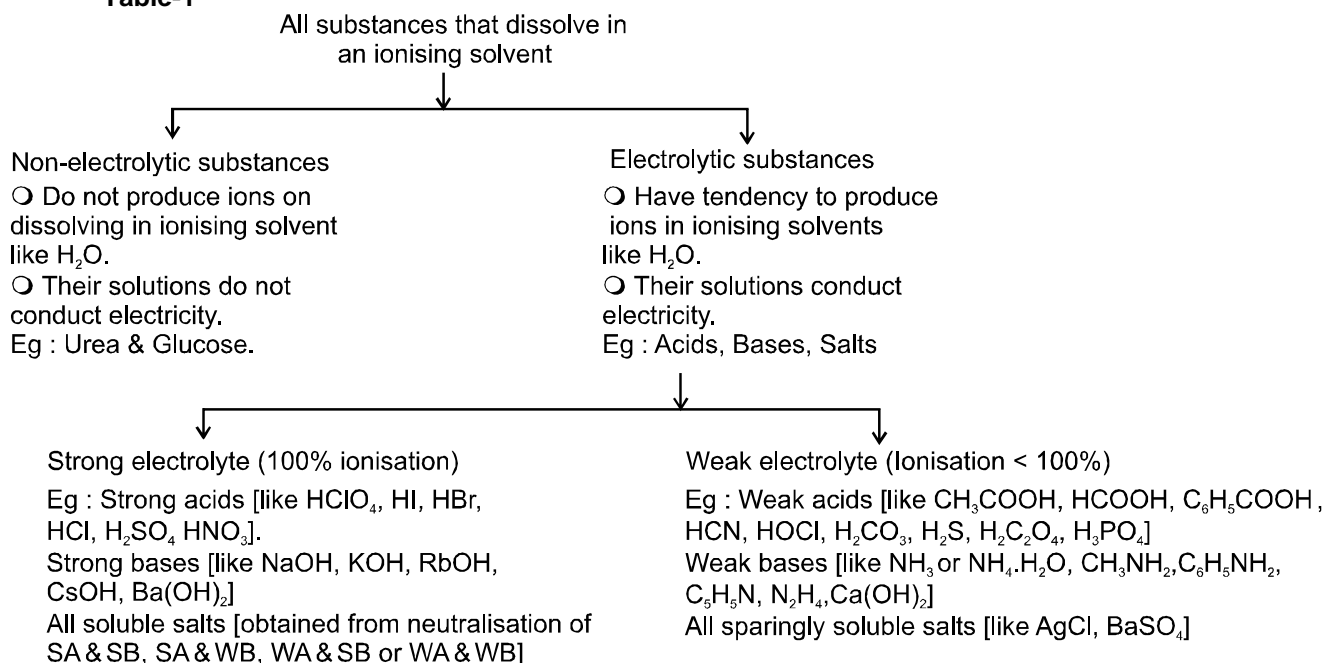
# Ionic Equilibrium (Elementary)

## Ionic Equilibrium-I

### Introduction :

Here we deal with the equilibria of species which are ionic in nature. Generally the concentration of  $H^+$  and  $OH^-$  ions is of importance. Also the concentration of ions forming precipitates is focused upon. As like dissolves like, the solvent for production of these ions should be polar. It is generally water.

**Table-1**



**SA : Strong Acid ; SB : Strong Base ; WA : Weak Acid ; WB : Weak Base**

### (A) Acid-Base concepts Arrhenius Concept

**D1 : Arrhenius Acid :** Substance which gives  $H^+$  ion from its own molecule on dissolving in an ionising solvent .

Eg :  $HCl$ ,  $H_2SO_4$ ,  $CH_3COOH$  etc.

**Table-2**

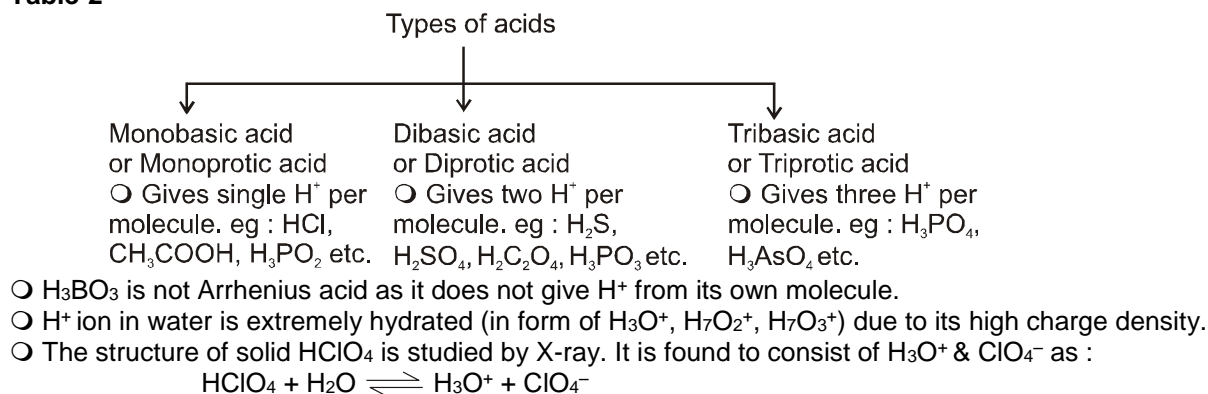
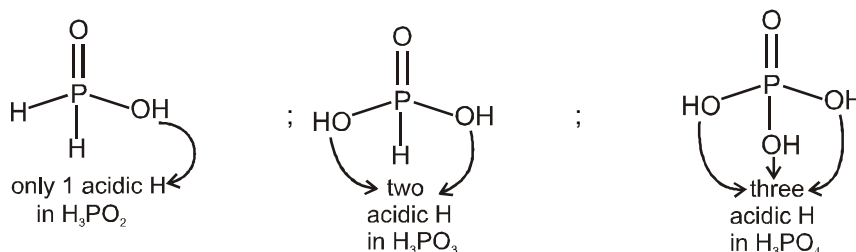




Figure-1



**D2 : Arrhenius Base :** Substance which gives  $\text{OH}^-$  ion from its own molecule on dissolving in an ionising solvent.

Eg :  $\text{NaOH}$ ,  $\text{Ba(OH)}_2$ ,  $\text{NH}_4\text{OH}$  etc.

Table-3

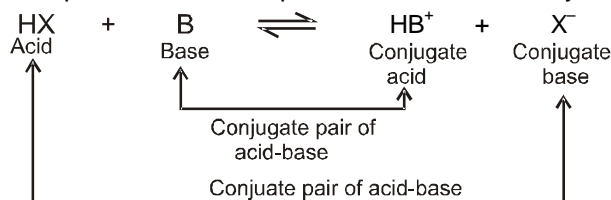
Types of bases		
<b>Mono acidic base</b> ○ Gives single $\text{OH}^-$ per molecule. eg : $\text{NaOH}$ , $\text{KOH}$ $\text{NH}_3 \cdot \text{H}_2\text{O}$	<b>Diacidic base</b> ○ Gives two $\text{OH}^-$ per molecule. eg : $\text{Ba(OH)}_2$ , $\text{Sr(OH)}_2$	<b>Triacidic base</b> ○ Gives three $\text{OH}^-$ per molecule. eg : $\text{Al(OH)}_3$ , $\text{Cr(OH)}_3$

○  $\text{OH}^-$  ion also exists in hydrated form of  $\text{H}_3\text{O}_2^-$ ,  $\text{H}_2\text{O}_4^-$ ,  $\text{H}_5\text{O}_3^-$ .  
 ○ First group elements of modern periodic table (except Li) form strong bases.  
 ○ Insoluble hydroxides - like  $\text{Fe(OH)}_3$ ,  $\text{Mg(OH)}_2$ ,  $\text{Cr(OH)}_3$ .

### Bronsted-Lowry concept (Conjugate acid-base concept / Protonic concept)

**D3 : Bronsted Lowry Acid :** Species which donate  $\text{H}^+$  are Bronsted Lowry acids ( $\text{H}^+$  donor).

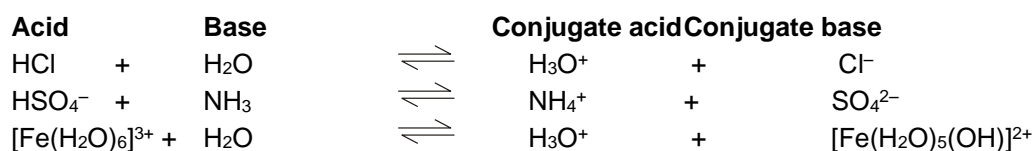
**D4 : Bronsted Lowry Base :** Species which accept  $\text{H}^+$  are Bronsted Lowry bases ( $\text{H}^+$  acceptor).



**Conjugated acid-base pairs :** In a typical acid-base reaction,

**Forward reaction :** Here  $\text{HX}$ , being a proton donor is an acid. Here  $\text{HB}$ , being a proton acceptor is a base.

**Backward reaction :** Here  $\text{HB}^+$ , being a proton donor is an acid. Here  $\text{X}^-$ , being a proton acceptor is a base.



○ Conjugate acid-base pair differ by only one proton ( $\text{H}^+$ ).

○ Strong acid will have weak conjugate base. This can be explained as the strong electrolyte will move the equilibrium where it is in dissociated form.

○ Weak acid/base will also have weak conjugate base/acid, because weak electrolyte has tendency to be in undissociated form.

○ Reaction will always proceed in a direction from stronger acid to weaker acid or from stronger base to weak base.



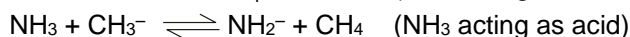
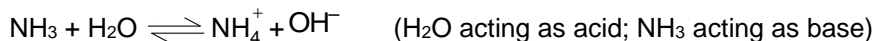
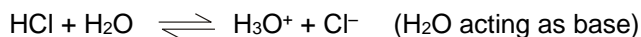
Table-4 Some Acid-Base Conjugate Pairs

Acid	Conjugate base = Acid - H <sup>+</sup>	Base	Conjugate acid = Base + H <sup>+</sup>
HClO <sub>4</sub>	ClO <sub>4</sub> <sup>-</sup>	H <sub>2</sub> O	H <sub>3</sub> O <sup>+</sup>
HI	I <sup>-</sup>	C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> OH <sub>2</sub> <sup>+</sup>
HBr	Br <sup>-</sup>	NH <sub>3</sub> or NH <sub>3</sub> .H <sub>2</sub> O	NH <sub>4</sub> <sup>+</sup>
H <sub>2</sub> SO <sub>4</sub>	HSO <sub>4</sub> <sup>-</sup>	R-NH <sub>2</sub>	R-NH <sub>3</sub> <sup>+</sup>
HCl	Cl <sup>-</sup>	CN <sup>-</sup>	HCN
HNO <sub>3</sub>	NO <sub>3</sub> <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>	C <sub>6</sub> H <sub>5</sub> OH
H <sub>3</sub> O <sup>+</sup>	H <sub>2</sub> O	NH <sub>2</sub> <sup>-</sup>	NH <sub>3</sub>
HSO <sub>4</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	CH <sub>3</sub> <sup>-</sup>	CH <sub>4</sub>
HNO <sub>2</sub>	NO <sub>2</sub> <sup>-</sup>		
H <sub>3</sub> PO <sub>4</sub>	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>		
CH <sub>3</sub> COOH	CH <sub>3</sub> COO <sup>-</sup>		
H <sub>2</sub> CO <sub>3</sub>	HCO <sub>3</sub> <sup>-</sup>		
H <sub>2</sub> S	HS <sup>-</sup>		
NH <sub>4</sub> <sup>+</sup>	NH <sub>3</sub>		
HCN	CN <sup>-</sup>		
C <sub>6</sub> H <sub>5</sub> OH	C <sub>6</sub> H <sub>5</sub> O <sup>-</sup>		
H <sub>2</sub> O	OH <sup>-</sup>		
C <sub>2</sub> H <sub>5</sub> OH	C <sub>2</sub> H <sub>5</sub> O <sup>-</sup>		
NH <sub>3</sub>	NH <sub>2</sub> <sup>-</sup>		
CH <sub>4</sub>	CH <sub>3</sub> <sup>-</sup>		

**Note :** In polyprotic acids, the tendency of release of subsequent H<sup>+</sup> decreases.

Eg : Order of acidic strength: H<sub>3</sub>PO<sub>4</sub> > H<sub>2</sub>PO<sub>4</sub><sup>-</sup> > HPO<sub>4</sub><sup>2-</sup>.

**D5 : Amphiprotic/Amphoteric Species :** Species which can act as an acid as well as a base. Eg : H<sub>2</sub>O, NH<sub>3</sub>.



### Lewis Concept (Electronic Concept)

**D6 : Lewis Acid :** An Lewis acid is a species which can accept an electron pair with the formation of coordinate bond.

**Acid** ← Electron pair donor ⇒ **Acid** : Electron pair acceptor.

eg : Electron deficient molecules : BF<sub>3</sub>, AlCl<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, BeCl<sub>2</sub>

**Cations :** H<sup>+</sup>, Fe<sup>3+</sup>, Na<sup>+</sup>

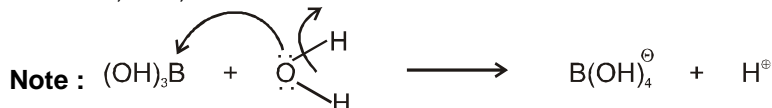
**Molecules with vacant orbitals :** SiCl<sub>4</sub>, SO<sub>2</sub>.

**D7 : Lewis Base :** A Lewis base is a species which has a lone pair of electrons available for donation.

**Base** → Electron pair acceptor ⇒ **Base** : Electron pair donor

eg : Molecules with donatable lone pairs :  $\ddot{\text{N}}\text{H}_3$ ,  $\text{H}_2\ddot{\text{O}}$ ,  $\text{CH}_3\ddot{\text{O}}\text{H}$

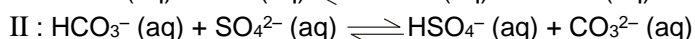
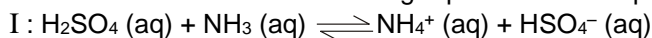
**Ions :** X<sup>-</sup>, CN<sup>-</sup>, OH<sup>-</sup>.



Here, Boric acid [i.e. B(OH)<sub>3</sub>] accepts a lone pair. So, it is a Lewis acid.

## Solved Examples

**Ex-1.** In which direction will the following equilibria I and II proceed ?



(A) I forward & II backward

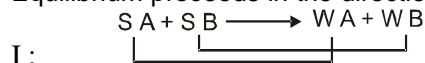
(B) I backward & II forward

(C) Both forward

(D) Both backward

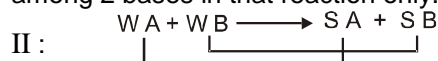


**Sol.** Equilibrium proceeds in the direction from strong (Acid/Base) to weak (Acid/Base).



I :

Here, acidic strength is compared among the 2 acids in the reaction & basic strength is compared among 2 bases in that reaction only.



II :

**Ans. (A)**

**Ex-2.** For the given reaction, identify the true (T) & false (F) statements.



S<sub>1</sub> : HI is bronsted base.

S<sub>2</sub> : HI is bronsted acid.

S<sub>3</sub> : HI is arrhenius acid.

S<sub>4</sub> : HI is lewis acid.

S<sub>5</sub> : HI is arrhenius base.

S<sub>6</sub> : HI is lewis base.

(A) T F F F T T

(B) F T T T F F

(C) F T T F F F

(D) T F F F T F

**Sol.** HI has donated H<sup>+</sup> in the above reaction. So it acts as an Arrhenius acid as well as a Bronsted acid.

**Ans. (C)**

**Ex-3.** In the above question, identify the true (T) & false (F) statements if HI is replaced with C<sub>2</sub>H<sub>5</sub>NH<sub>2</sub> in each statement.

(A) T F F F T T

(B) T F F F F T

(C) F F T T F F

(D) F T T T F F

**Sol.** Lewis base donates a lone pair to an electron deficient species. Arrhenius base releases OH<sup>-</sup>. Bronsted base accepts H<sup>+</sup> from a species.

**Ans. (B)**

**Ex-4.** Ammonium ion is :

(A) Lewis acid

(B) Lewis base

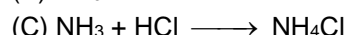
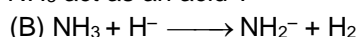
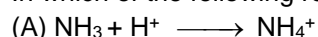
(C) Bronsted acid

(D) Bronsted base

**Sol.**  $NH_4^+ \longrightarrow NH_3 + H^+ \Rightarrow$  Bronsted Acid

**Ans. (C)**

**Ex-5.** In which of the following reactions, does NH<sub>3</sub> act as an acid ?



**Sol.** In the reaction, NH<sub>3</sub> changes to NH<sub>2</sub><sup>-</sup>. So, NH<sub>3</sub> has donated a proton (H<sup>+</sup>) and hence acts as an acid.

**Ans. (B)**

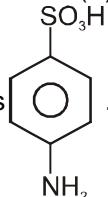
**Ex-6.** Sulphanilic acid is a/an :

(A) Arrhenius acid

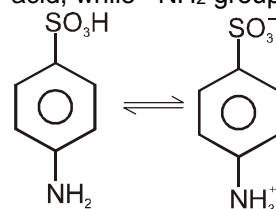
(B) Lewis base

(C) Neither (A) or (B)

(D) Both (A) & (B)

**Sol.** Sulphanilic acid is . Its -SO<sub>3</sub>H group is capable of donating H<sup>+</sup>, and hence it acts as arrhenius

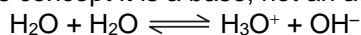
acid, while -NH<sub>2</sub> group's nitrogen has lone pair of electron which can be donated as :



**Ans. (D)**

**(B) Properties of Water, pH scale, autoprotolysis****Properties of water :****Amphoteric Acid / Base Nature :**

Water acts as an acid as well as base according to Arrhenius & Bronsted - Lowry theory, but according to Lewis concept it is a base, not an acid.



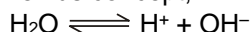
In pure water,  $[\text{H}^+] = [\text{OH}^-]$ , so it is always neutral

**○ Molar concentration / Molarity of water :**

$$\begin{aligned}\text{Molarity} &= \text{No. of moles} / \text{litre} = \frac{1000/18}{1} = 55.55 \text{ moles / litre} \\ &= 55.55 \text{ M (taking density} = 1 \text{ g / cc)}\end{aligned}$$

**Ionic product of water :**

According to arrhenius concept,



Ionic product of water is defined as :

**F1 :  $K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$  at 25°C (experimental data)**

∴ at 25°C pure water contains  $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$

Dissociation of water is endothermic, so on increasing temperature,  $K_{eq}$  increases. So,  $K_w$  increases with increase in temperature & decreases with decrease in temperature.

For eg. at 25°C,  $K_w = 1 \times 10^{-14}$  ; at 40°C,  $K_w = 2.916 \times 10^{-14}$  ; at 90°C,  $K_w = 10^{-13}$

Ionic product of water is always a constant whatever may be dissolved in water. As it is an equilibrium constant, it will depend only on temperature.

**Der1 : Degree of dissociation of water :**

$$\begin{aligned}\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \Rightarrow \alpha &= \frac{\text{no. of moles dissociated}}{\text{no. of moles initially taken}} = \frac{10^{-7}}{55.55} \\ \alpha &= 1.8 \times 10^{-9} \text{ or } 1.8 \times 10^{-7} \% \text{ (at 25°C)}\end{aligned}$$

**Der2 : Absolute dissociation constant of water :**

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \Rightarrow K_a = K_b = \frac{[\text{H}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

So,  $\text{p}K_a \text{ of } \text{H}_2\text{O} = \text{p}K_b \text{ of } \text{H}_2\text{O} = -\log(1.8 \times 10^{-16}) = 15.74 \text{ (at 25°C)}$

**pH Scale :**

○ Acidic strength means the tendency of an acid to give  $\text{H}_3\text{O}^+$  or  $\text{H}^+$  ions in water.  
So greater the tendency to give  $\text{H}^+$ , more will be the acidic strength of the substance.

○ Basic strength means the tendency of a base to give  $\text{OH}^-$  ions in water.  
So greater the tendency to give  $\text{OH}^-$  ions, more will be basic strength of the substance.

**D8 :** The concentration of  $\text{H}^+$  ions is written in a simplified form introduced by Sorenson known as pH scale.  
pH is

defined as negative logarithm of activity of  $\text{H}^+$  ions.

∴  $\text{pH} = -\log a_{\text{H}^+}$  (where  $a_{\text{H}^+}$  is the activity of  $\text{H}^+$  ions)

○ Activity of  $\text{H}^+$  ions is the concentration of free  $\text{H}^+$  ions or  $\text{H}_3\text{O}^+$  ions in a dilute solution.

○ The pH scale was marked from 0 to 14 with central point at 7 at 25°C taking water as solvent.

**F2 :  $\text{pH} = -\log [\text{H}^+]$  or  $\text{pH} = \log \frac{1}{[\text{H}^+]}$  or  $\text{pH} = -\log [\text{H}_3\text{O}^+]$** **F3 :  $\text{pOH} = -\log [\text{OH}^-]$  or  $\text{pOH} = \log \frac{1}{[\text{OH}^-]}$** 



**Der3 :** From,  $K_w = [H^+][OH^-] = 10^{-14}$  (at 25°C)

Taking negative log both sides,

$$-\log [H^+] - \log [OH^-] = -\log (10^{-14}) = -\log K_w = 14$$

$$\Rightarrow \mathbf{pH + pOH = pK_w = 14 \text{ (for an aqueous solution at 25°C)}}$$

- If the temperature and the solvent are changed, the pH range of the scale will also change.

For example :

0 – 14 at 25°C

Neutral point pH = 7

0 – 13 at 80°C ( $K_w = 10^{-13}$ )

Neutral point pH = 6.5

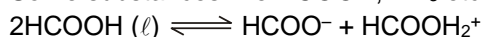
- pH can also be negative or greater than 14.

- Now,  $pH = -\log [H^+] = 7$  and  $pOH = -\log [OH^-] = 7$ , for water at 25°C (experimental)

$$\left. \begin{array}{ll} pH = 7 = pOH & \Rightarrow \text{neutral} \\ pH < 7 \text{ or } pOH > 7 & \Rightarrow \text{acidic} \\ pH > 7 \text{ or } pOH < 7 & \Rightarrow \text{basic} \end{array} \right\} \text{at } 25^\circ \text{C only}$$

### Autoprotolysis :

**D9 :** Some substances like HCOOH,  $NH_3$  etc are observed to be self ionised in pure liquid state as follows :

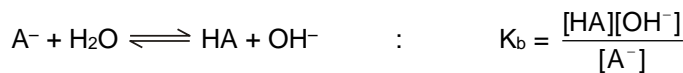
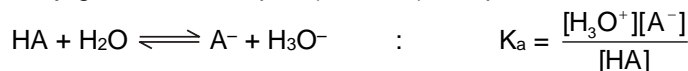


This phenomena is called Self-Ionisation or Autoprotolysis and equilibrium constant corresponding to above is called Autoprotolysis constant defined as follows :

$$K_{eq} = [HCOO^-][HCOOH_2^+]$$

### (C) Relation between $K_a$ and $K_b$ for conjugate acid-base pair

**Der4 :** For any conjugate acid-base pair ( $HA$  &  $A^-$ ) in aqueous solution :

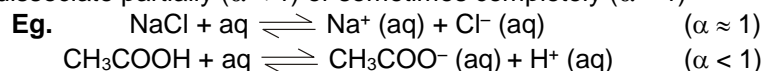


$$\text{Now, } K_a \times K_b = K_w \Rightarrow \mathbf{pK_a + pK_b = pK_w = 14 \text{ (at } 25^\circ\text{C)}}$$

$$\text{Eg. } pK_a(CH_3COOH) + pK_b(CH_3COO^-) = pK_w = 14 ; pK_a(NH_4^+) + pK_b(NH_3) = pK_w = 14.$$

### Degree of dissociation ( $\alpha$ )

- When an electrolyte is dissolved in a solvent ( $H_2O$ ), it spontaneously dissociates into ions.  
○ It may dissociate partially ( $\alpha < 1$ ) or sometimes completely ( $\alpha \approx 1$ )



**D10 :** The degree of dissociation of an electrolyte ( $\alpha$ ) is the fraction of one mole of the electrolyte that has dissociated under the given conditions.

$$\mathbf{F4 :} \quad \alpha = \frac{\text{No. of moles dissociated}}{\text{No. of moles taken initially}}$$

The value of  $\alpha$  depends on :

- Nature of electrolyte:** Strong electrolytes dissociate completely ( $\alpha = 1$ ) whereas weak electrolytes dissociate partially. ( $\alpha < 1$ )
- Nature of solvent:** A solvent having high value of dielectric constant will favour dissociation. (Generally polar solvents)
- Dilution:** For weak electrolytes, degree of dissociation will increase with dilution (**Ostwald's dilution law**)
- Temperature:** On increasing temperature, generally degree of dissociation increases. (For endothermic dissociations)



- (e) **Presence of other solute:** When a substance is present in a solution, it may effect the dissociation of another substance. Generally, presence of common ion suppresses degree of dissociation of weak electrolyte. **(Common ion effect)**

**(D) pH Calculation : Strong acid Solutions, strong base solutions, solutions containing mixture of two or more strong acids, solutions containing mixture of two or more strong bases, solutions containing mixture of strong acid and strong base**

**(a) Strong acid solution :**

- (i) If  $[H^+]_{\text{from strong acid}}$  is greater than  $10^{-6}$  M  
In this case,  $H^+$  ions coming from water can be neglected.

**F5 :** So,  $[H^+] = \text{Molarity of strong acid solution} \times \text{number of } H^+ \text{ ions per acid molecule.}$

- (ii) If  $[H^+]_{\text{from strong acid}}$  is less than  $10^{-6}$  M  
In this case,  $H^+$  ions coming from water cannot be neglected.

**F6 :** So,  $[H^+] = [H^+]_{\text{from strong acid}} + [H^+]_{\text{coming from water in presence of this strong acid.}}$

### Solved Examples

**Ex-7.** Find the pH of :

- (a)  $10^{-3}$  M  $HNO_3$  solution  
(b)  $10^{-4}$  M  $H_2SO_4$  solution (Take  $\log 2 = 0.3$ )

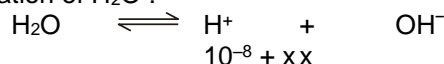
**Sol.** (a)  $pH = -\log[H^+]_{HNO_3} = -\log(10^{-3}) = 3$

(b)  $pH = -\log[H^+]_{H_2SO_4} = -\log(2 \times 10^{-4}) = 4 - \log 2 = 3.7$

In both solutions,  $[H^+]_{\text{from strong acid}} > 10^{-6}$  M. So  $H^+$  from water has not been considered.

**Ex-8.** Calculate pH of  $10^{-8}$  M  $HCl$  solution at  $25^\circ C$ . (Take  $\log 1.05 = 0.02$ )

**Sol.** Here,  $[H^+]_{HCl} = 10^{-8}$  M ( $< 10^{-6}$  M). So  $[H^+]_{\text{from water}}$  has to be considered. But,  $[H^+]_{\text{from } H_2O} \neq 10^{-7}$  M because of common ion effect exerted on it by  $H^+$  ions of  $HCl$ . So, considering dissociation of  $H_2O$  :



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

$$10^{-14} = x(x + 10^{-8})$$

$$\Rightarrow x^2 + x \times 10^{-8} - 10^{-14} = 0$$

$$x = \frac{-10^{-8} \pm \sqrt{10^{-16} + 4 \times 10^{-14}}}{2} = \frac{-10^{-8} + 10^{-7} \sqrt{4 + \frac{1}{100}}}{2} = \frac{(\sqrt{401} - 1)10^{-8}}{2} = 0.95 \times 10^{-7}$$

$$[H^+] = 10.5 \times 10^{-8} = 1.05 \times 10^{-7} \text{ M}$$

$$pH = 7 - \log 1.05 \approx 6.98$$

**Note :** For  $10^{-9}$  M  $HCl$   $pH \approx 7$ , For  $10^{-12}$  M  $HCl$   $pH \approx 7$

**(b) Strong base solution :**

- (i) If  $[OH^-]_{\text{from strong base}}$  is greater than  $10^{-6}$  M  
In this case,  $OH^-$  ions coming from water can be neglected.

**F7 :** So,  $[OH^-] = \text{Molarity of strong base solution} \times \text{number of } OH^- \text{ ions per base molecule.}$

- (ii) If  $[OH^-]_{\text{from strong base}}$  is less than  $10^{-6}$  M  
In this case  $OH^-$  ions coming from water cannot be neglected.

**F8 :** So,  $[OH^-] = [OH^-]_{\text{from strong base}} + [OH^-]_{\text{coming from water in presence of this strong base.}}$

### Solved Examples

**Example-9.** What will be the pH of  $5 \times 10^{-6}$  M  $Ba(OH)_2$  solution at  $25^\circ C$  ?

**Solution.**  $[OH^-]_{\text{from strong base}} = 2(5 \times 10^{-6}) = 10^{-5}$  M

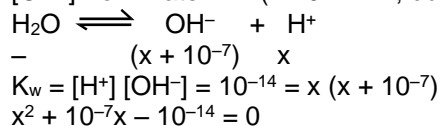
$$\therefore pH = 14 - p(OH) = 14 - (-\log [OH^-]) = 14 - (-\log 10^{-5}) = 14 - 5 = 9$$





**Example-10.** Calculate pH of  $10^{-7}$  M of NaOH solution at  $25^{\circ}\text{C}$ . (Take  $\log 0.618 = 0.21$ )

**Solution.**  $[\text{OH}^-]$  from NaOH =  $10^{-7}$  M ( $< 10^{-6}$  M)  
 $[\text{OH}^-]$  from water =  $x$  ( $< 10^{-7}$  M ; due to common ion effect)



$$\Rightarrow x = \frac{\sqrt{5}-1}{2} \times 10^{-7} = 0.618 \times 10^{-7} \text{ M} = [\text{H}^+] \quad (\sqrt{5} = 2.236)$$

$$\therefore \text{pH} = 7.21$$

### pH OF ACIDS/BASES MIXTURES :

#### (A) Mixture of two strong acids :

If  $V_1$  volume of a strong acid solution with  $\text{H}^+$  concentration  $[\text{H}^+]_1$  is mixed with  $V_2$  volume of another strong acid solution with  $\text{H}^+$  concentration  $[\text{H}^+]_2$ , then

moles of  $\text{H}^+$  ions from I-solution =  $M_1 V_1$

moles of  $\text{H}^+$  ions from II-solution =  $M_2 V_2$

If final  $\text{H}^+$  ion concentration is  $[\text{H}^+]_f$  and final volume is  $V_f (= V_1 + V_2)$ , then :

$$[\text{H}^+]_f V_f = [\text{H}^+]_1 V_1 + [\text{H}^+]_2 V_2$$

[Dissociation equilibrium of none of these acids will be disturbed as both are strong acids]

$$\text{F9 : } \therefore [\text{H}^+]_f = \frac{[\text{H}^+]_1 V_1 + [\text{H}^+]_2 V_2}{V_1 + V_2}$$

#### (B) Mixture of two strong bases :

Similar to above calculation,

$$\text{F10 : } [\text{OH}^-]_f = \frac{[\text{OH}^-]_1 V_1 + [\text{OH}^-]_2 V_2}{V_1 + V_2} \quad \& \quad [\text{H}^+]_f = \frac{10^{-14}}{[\text{OH}^-]_f}$$

### Solved Examples

**Ex-11.** Calculate pH of mixture of (400 mL,  $\frac{1}{200}$  M  $\text{H}_2\text{SO}_4$ ) + (400 mL,  $\frac{1}{100}$  M HCl) + (200 mL of water).

Take  $\log 2 = 0.3$

**Sol.**  $[\text{H}^+]_1 V_1 = \frac{1}{100} \times \frac{400}{1000} = \frac{4}{1000}$ ,  $[\text{H}^+]_2 V_2 = \frac{4}{1000}$ ,  $\text{H}^+$  ions from water can be neglected

$$[\text{H}^+]_1 V_1 + [\text{H}^+]_2 V_2 = 8 \times 10^{-3} \text{ and } V_f = 0.4 + 0.4 + 0.2 = 1 \text{ L}$$

$$\Rightarrow [\text{H}^+]_f = \frac{8 \times 10^{-3}}{1} = 8 \times 10^{-3} \text{ M} \quad \therefore \text{pH} = 3 - \log 8 = 2.1.$$

**Ex-12.** 500 mL of  $10^{-5}$  M NaOH is mixed with 500 mL of  $2.5 \times 10^{-5}$  M of  $\text{Ba}(\text{OH})_2$ . To the resulting solution, 99 L water is added. Calculate pH of final solution. Take  $\log 0.303 = -0.52$ .

$$\text{Sol. } [\text{OH}^-]_f = \frac{(500 \times 10^{-5}) + (500 \times 2 \times 2.5 \times 10^{-5})}{1000} = 3 \times 10^{-5} \text{ M}$$

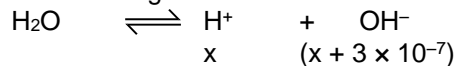
$$V_i = 1 \text{ L} \& \quad V_f = 100 \text{ L}$$

no. of moles of  $[\text{OH}^-]$  in resulting solution = no. of moles of  $[\text{OH}^-]$  in final

$$3 \times 10^{-5} = [\text{OH}^-]_f \times 100$$

$$\therefore [\text{OH}^-]_f = 3 \times 10^{-7} \text{ M} (< 10^{-6} \text{ M})$$

So,  $\text{OH}^-$  ions coming from  $\text{H}_2\text{O}$  should also be considered.



$$K_w = x(x + 3 \times 10^{-7}) = 10^{-14}$$

$$\therefore x = \left( \frac{\sqrt{13}-3}{2} \right) \times 10^{-7} \text{ M} = [\text{H}^+]$$

$$\text{So, } \text{pH} = 7 - \log 0.303 = 7.52.$$

**(C) Mixture of a strong acid and a strong base :**

- Acid Base neutralisation reaction will take place.
- The solution will be acidic or basic, depending on which component has been taken in excess.

**Der5:** If  $V_1$  volume of a strong acid solution with  $H^+$  concentration  $[H^+]$  is mixed with  $V_2$  volume of a strong base solution with  $OH^-$  concentration  $[OH^-]$ , then

Number of moles  $H^+$  ions from I-solution =  $[H^+]_1 V_1$

Number of moles  $OH^-$  ions from II-solution =  $[OH^-]_2 V_2$

**F11 :**

If  $[H^+]V_1 > [OH^-]V_2$

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

final solution will  
be acidic in nature

If  $[OH^-]V_2 > [H^+]V_1$

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

final solution will  
be basic in nature

$$\text{Further, } [H^+]_f = \frac{10^{-14}}{[OH^-]_f} \text{ (at } 25^\circ\text{C)}$$

## Solved Examples

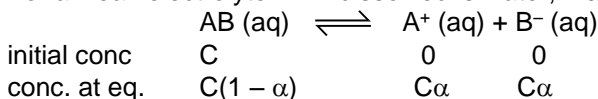
**Ex-13.** Calculate pH of mixture of (400 mL,  $\frac{1}{200}$  M  $Ba(OH)_2$ ) + (400 mL,  $\frac{1}{50}$  M  $HCl$ ) + (200 mL of Water)

**Sol.**  $[H^+]_f = \frac{\left(0.4 \times \frac{1}{50}\right) - \left(0.4 \times \frac{1}{200} \times 2\right)}{0.4 + 0.4 + 0.2} = 4 \times 10^{-3} \text{ M.}$  So,  $pH = 3 - 2\log 2 = 2.4.$

## (E) Ostwald's Dilution Law, pH calculation: Solutions of weak monoprotic acid, solutions of weak monoacidic base

### Ostwald's Dilution Law

**Der6 :** For a weak electrolyte  $A^+B^-$  dissolved in water, if  $\alpha$  is the degree of dissociation then :



Then,

**F12 :**  $K_{eq} = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \cdot C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{(1 - \alpha)}$  = dissociation constant of the weak electrolyte

( $K_{eq} = K_a$  for weak acid;  $K_b$  for weak base)

**F13 :** If  $\alpha$  is negligible in comparison to unity, then  $1 - \alpha \approx 1$ . So  $K_{eq} = \alpha^2 C \Rightarrow \alpha = \sqrt{\frac{K_{eq}}{C}}$

$$\alpha \propto \frac{1}{\sqrt{\text{concentration}}}$$

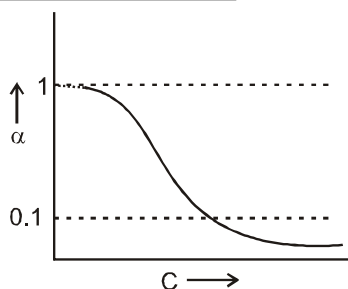
- As concentration increases  $\Rightarrow \alpha$  decreases

**F14 :**  $[A^+] = [B^-] = C\alpha = \sqrt{CK_{eq}}$ . Upon dilution,  $C \downarrow$  &  $K_{eq}$  remains same, so  $[ions] \downarrow$  and moles of ions  $\uparrow$

- At infinite dilution  $\alpha$  reaches its maximum value, unity (1). Here, weak electrolyte also starts behaving like a strong electrolyte.



Figure-2

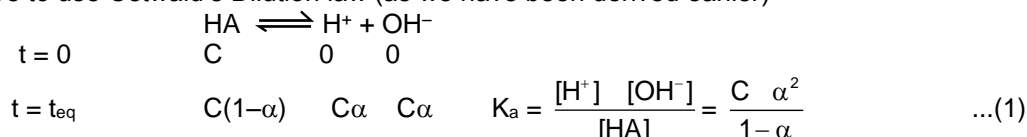


### pH calculation : Solutions of weak monoprotic acid, solutions of weak monoacidic base

#### Weak Acid (monoprotic) solution :

- Weak acid does not dissociate 100% therefore we have to calculate the percentage dissociation using  $K_a$  (dissociation constant of the acid).

**Der7 :** We have to use Ostwald's Dilution law (as we have been derived earlier)



Assume  $\alpha \ll 1 \Rightarrow (1-\alpha) \approx 1 \Rightarrow K_a \approx C\alpha^2 \Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$  (valid if  $\alpha < 0.1$  or 10%)

**F15 :**  $[\text{H}^+] = C\alpha = C\sqrt{\frac{K_a}{C}} = \sqrt{K_a \times C} \Rightarrow \text{So, pH} = \frac{1}{2}(\text{p}K_a - \log C)$  (valid if  $\alpha < 0.1$  or 10%)  
on dilution  $\Rightarrow C \downarrow \Rightarrow \alpha \uparrow$  and  $[\text{H}^+] \downarrow \Rightarrow \text{pH} \uparrow$

**Note :** If  $\alpha$  obtained from  $\sqrt{\frac{K_a}{C}}$  is greater than 0.1, solve quadratic equation (1) and get accurate  $\alpha$ .  
Then,  $[\text{H}^+] = C\alpha$  & now pH calculation can be done.

### Solved Examples

**Ex-14.** Calculate pH of (a)  $10^{-1}$  M  $\text{CH}_3\text{COOH}$  (b)  $10^{-3}$  M  $\text{CH}_3\text{COOH}$  (c)  $10^{-6}$  M  $\text{CH}_3\text{COOH}$   
Take  $K_a = 2 \times 10^{-5}$ , at  $25^\circ\text{C}$ .

**Sol.** (a)  $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-1}}} = \sqrt{2 \times 10^{-4}}$  ( $\alpha \ll 0.1$ )

So,  $[\text{H}^+] = 10^{-1} \times \sqrt{2} \times 10^{-2} \Rightarrow \text{pH} = 3 - \frac{1}{2} \log 2 = 2.85$  **Ans.**

(b)  $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{2 \times 10^{-5}}{10^{-3}}} = \sqrt{2 \times 10^{-2}}$  ( $\alpha > 0.1$ )

So, we have to do the exact calculations

$$K_a = \frac{C\alpha^2}{1-\alpha} \Rightarrow 2 \times 10^{-5} = \frac{10^{-3} \times \alpha^2}{1-\alpha} \Rightarrow \alpha = 13.14\%$$

$$[\text{H}^+] = 10^{-3} \times 0.1314 = 1.314 \times 10^{-4} \Rightarrow \text{pH} = 4 - \log(1.314) = 3.8$$
 **Ans.**

(c) If approximation is used, then  $\alpha = \sqrt{\frac{2 \times 10^{-5}}{10^{-6}}} = \sqrt{20}$  ( $> 1$ ; not possible)

So, we have to do the exact calculations,  $2 \times 10^{-5} = 10^{-6} \frac{\alpha^2}{1-\alpha} \Rightarrow \alpha = 0.95$  or 95%

$$[\text{H}^+] = 0.95 \times 10^{-6} = 9.5 \times 10^{-7} \Rightarrow \text{pH} = 7 - \log(9.5) = 6.022$$
 **Ans.**

- At very low concentration (at infinite dilution), weak electrolyte will be almost 100% dissociated, so it will behave as strong electrolyte

$$\text{pH of } 10^{-6} \text{ M HCl} \approx \text{pH of } 10^{-6} \text{ M CH}_3\text{COOH} \approx 6)$$

**Weak base (monoacidic) solution :**

Proceed similarly as done for weak monoprotic acid.

$$\text{F16 : } \therefore \text{pOH} = \frac{1}{2} (\text{pK}_b - \log C) \quad (\text{if } \alpha < 0.1 \text{ or } 10\%)$$

& then  $\text{pH} = 14 - \text{pOH}$ .

**Isohydric solutions:**

**D11 :** If the concentration of the common ions in the solution of two electrolytes, for example  $\text{H}^+$  ion concentration in two acid solutions  $\text{HA}_1$  and  $\text{HA}_2$  or  $\text{OH}^-$  ion concentration in two base solutions  $\text{B}_1\text{OH}$  and  $\text{B}_2\text{OH}$  is same, then on mixing them, there is no change in the degree of dissociation of either of the electrolytes (common ion effect is not exerted by one on other). Such solutions are called isohydric solutions.

Consider two isohydric solutions of weak acids  $\text{HA}_1$  and  $\text{HA}_2$ . Let  $C_1$  and  $C_2$  be their concentration and  $\alpha_1$  and  $\alpha_2$  be their degree of dissociation. Then,

$$\text{F17 : } C_1\alpha_1 = C_2\alpha_2 \text{ (on equating the } \text{H}^+ \text{ concentrations from both acids).}$$

**Relative strength of acids and bases :**

In practice,  $K_a$  is used to define the strength only of those acids that are weaker than  $\text{H}_3\text{O}^+$  and  $K_b$  is used to define the strength of only those bases that are weaker than  $\text{OH}^-$ . For two weak acids  $\text{HA}_1$  and  $\text{HA}_2$  of ionisation constant  $K_{a1}$  and  $K_{a2}$  respectively at the same concentration  $C$ , we have :

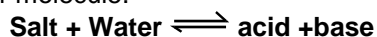
$$\text{F18 : } \frac{\text{Acid strength of } \text{HA}_1}{\text{Acid strength of } \text{HA}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}$$

Similarly, relative strengths of any two weak bases at the same concentration are given by the ratio of the square-roots of their dissociation constants i.e.,

$$\text{F19 : } \frac{\text{Basic strength of } \text{BOH}_1}{\text{Basic strength of } \text{BOH}_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$

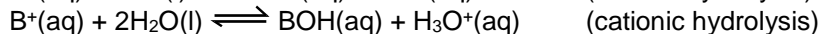
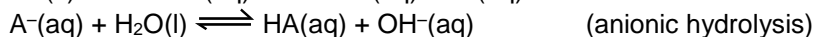
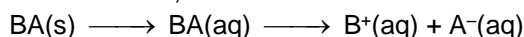
**(F) Salt Hydrolysis, pH calculation : solutions of salt of monoprotic acid and monoacidic base****Salt Hydrolysis**

**D12 : Hydrolysis :** The reaction of an ion with water in which either  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  is produced, by dissociation of water molecule.

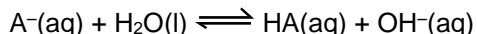


When acids and bases are mixed so that none of the two is left, then we will have salt solution in water and we have to calculate pH of salt solution.

When a salt is added to water, the solid salt first dissolves and breaks into ions completely (unless otherwise specified). The ions of the salt may or may not react with water. The cations on reaction with water will produce  $\text{H}_3\text{O}^+$  ions and the anions on reaction with water will produce  $\text{OH}^-$  ions. Depending on the extent of hydrolysis and on the amounts of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  ions, the solution can be acidic, basic or neutral. If salt is  $\text{BA}$ , then :

**ANIONIC HYDROLYSIS**

Anions can function as a base on reaction with water and hydrolyse as follows :



The extent of hydrolysis of a given anion depends on its basic strength.

**(a) Complete hydrolysis**

The anions, which are stronger base than  $\text{OH}^-$  and have conjugate acids weaker than  $\text{H}_2\text{O}$ , will show complete hydrolysis in aqueous medium.



**(b) Hydrolysis to a limited extent**

The anions, which are weaker base than  $\text{OH}^-$  and have conjugate acids stronger than  $\text{H}_2\text{O}$  but weaker acid than  $\text{H}_3\text{O}^+$ , will hydrolyse to a limited extent in aqueous medium.

For example :  $\text{CN}^- + \text{H}_2\text{O} \rightleftharpoons \text{HCN} + \text{OH}^-$

Other examples are  $\text{CH}_3\text{COO}^-$ ,  $\text{NO}_2^-$ ,  $\text{S}^{2-}$  etc.

**(c) No hydrolysis**

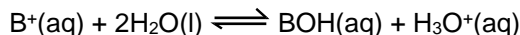
The anions, which are weaker base than  $\text{OH}^-$  and have conjugate acids stronger than both  $\text{H}_2\text{O}$  and  $\text{H}_3\text{O}^+$ , do not hydrolyse at all.

For example :  $\text{Cl}^- + \text{H}_2\text{O} \nrightarrow \text{HCl} + \text{OH}^-$

Other examples include  $\text{HSO}_4^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$  etc.

**CATIONIC HYDROLYSIS**

Cations can function as acid on reaction with water and hydrolyse as follows :



The extent of hydrolysis of a given cation depends on its acidic strength.

**(a) Complete hydrolysis**

The cations, which are stronger acids than  $\text{H}_3\text{O}^+$  and their conjugate bases are very much weaker than  $\text{H}_2\text{O}$  will show complete hydrolysis.

For example :  $\text{PH}_4^+ + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{PH}_3$

**(b) Hydrolysis to a limited extent**

The cations, which are weaker acid than  $\text{H}_3\text{O}^+$  ion and their conjugate bases are stronger than  $\text{H}_2\text{O}$  but weaker than  $\text{OH}^-$ , show hydrolysis to a limited extent.

For example :  $\text{NH}_4^+ + 2\text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}_3\text{O}^+$

Other examples are  $\text{C}_6\text{H}_5\text{NH}_3^+$ ,  $\text{CH}_3\text{NH}_3^+$  etc.

**(c) No hydrolysis**

The cations, which are weaker acid than  $\text{H}_3\text{O}^+$  and their conjugate bases are stronger than both  $\text{H}_2\text{O}$  and  $\text{OH}^-$ , do not hydrolyze at all. Examples are alkali and alkaline earth metal ions.

For example :  $\text{Na}^+ + 2\text{H}_2\text{O} \nrightarrow \text{NaOH} + \text{H}_3\text{O}^+$

**pH calculation : Solutions of salt of monoprotic acid and monoacidic base.**

There are four types of salts :

(A) Salt of strong acid and strong base

(B) Salt of strong acid and weak base

(C) Salt of weak acid and strong base

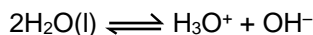
(D) Salt of weak acid and weak base

Salts of first type does not undergo hydrolysis and rest three types undergo hydrolysis.

Currently considering only monoprotic acids & monoacidic bases,

**(A) Salt of strong acid and strong base**

Neither of the ions will undergo hydrolysis, so the solution involves only the equilibrium of ionization of water.



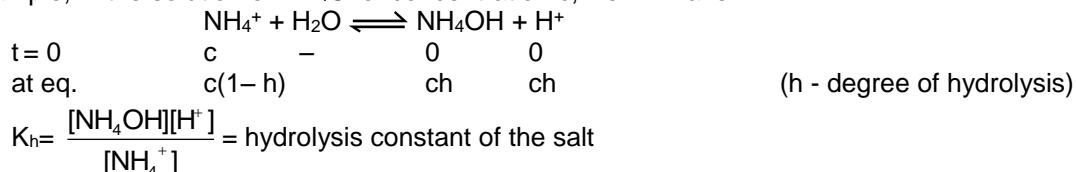
Thus, the pH of solution will be 7 (neutral solution at  $25^\circ\text{C}$ ).

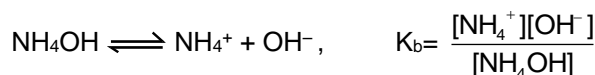
**(B) Salt of strong acid and weak base**

Examples can be  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$ ,  $\text{C}_6\text{H}_5\text{NH}_3^+\text{Cl}^-$

Only the cation will undergo hydrolysis and the solution will be acidic in nature. Cation is considered responsible for the acidic nature of solution.

**Der8 :** For example, in the solution of  $\text{NH}_4\text{Cl}$  of concentration  $c$ , we will have :





From above equations, we can get :

$$K_h \times K_b = K_w$$

$$K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)} \quad \dots(2)$$

**F20 :** Generally,  $h \ll 1 \therefore 1-h \approx 1$ . So we get  $\Rightarrow h = \sqrt{\frac{K_h}{c}}$

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

$$\Rightarrow \text{pH} = -\log [\text{H}^+] = -\frac{1}{2} [\log K_w - \log K_b + \log c]$$

**F21 :**  $\Rightarrow \text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log c]$  (valid if  $h < 0.1$  or 10%)

**Note :** (1)  $c$  is the concentration of ion undergoing hydrolysis, not the concentration of salt.

(2) If  $h$  obtained from  $\sqrt{\frac{K_h}{c}}$  is greater than 0.1, solve quadratic equation (2) and get accurate  $h$ . Then,  $[\text{H}^+] = ch$  & now pH calculation can be done.

## Solved Examples

**Ex-15.** Calculate degree of hydrolysis,  $K_h$  and pH of 1 M urea hydrochloride solution in water,  $K_b$  (Urea) =  $1.5 \times 10^{-14}$  at  $25^\circ\text{C}$ . Consider urea as a monoacidic base. Take  $\log 0.55 = -0.26$ .

**Sol.**  $\text{NH}_2\text{CONH}_3\text{Cl}$  is a salt of SA + WB

$$K_h = \frac{K_w}{K_b} = \frac{10^{-14}}{1.5 \times 10^{-14}} = 6.667 \times 10^{-1}$$

$$\text{Now } h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14}}{1.5 \times 10^{-14} \times 1}}$$

or  $h = 0.816 (> 0.1)$  So we use actual relation

$$K_h = \frac{Ch^2}{1-h} = \frac{1}{1.5}$$

$$1.5h^2 + h - 1 = 0$$

$$[\text{H}^+] = ch = 0.55 \text{ M}$$

$$\therefore \text{pH} = 0.26.$$

**Ex-16.** Equal volume of 0.2 M  $\text{NH}_4\text{OH}$  (or ammonia) and 0.1 M  $\text{H}_2\text{SO}_4$  are mixed. Calculate pH of final solution. Given :  $K_b$  of  $\text{NH}_3 = 1.8 \times 10^{-5}$  at  $25^\circ\text{C}$ .

**Sol.**  $C = [\text{NH}_4^+] = 0.1 \text{ M}$  ( $\because$  volume got doubled, so concentration must have been halved)

$$h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-14}}{1.8 \times 10^{-5} \times 0.1}} \quad (< 0.1)$$

$$\therefore \text{pH} = \frac{1}{2} \{14 - 4.74 + 1\} = \frac{10.26}{2} = 5.13$$

### (C) Salt of weak acid and strong base

The examples can be  $\text{CH}_3\text{COONa}$ ,  $\text{KCN}$  etc.

**Der9 :** Proceeding similar to above analysis of salt of weak base & strong acid, we will get :

$$K_h \times K_a = K_w \quad \& \quad K_h = \frac{ch \cdot ch}{c(1-h)} = \frac{ch^2}{(1-h)}$$



**F22 :** So,  $h = \sqrt{\frac{K_h}{c}}$

$$[\text{OH}^-] = ch = \sqrt{K_h \times c} = \sqrt{\frac{K_w}{K_a} \times c}$$

$$\therefore [\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \sqrt{\frac{K_w \times K_a}{c}}$$

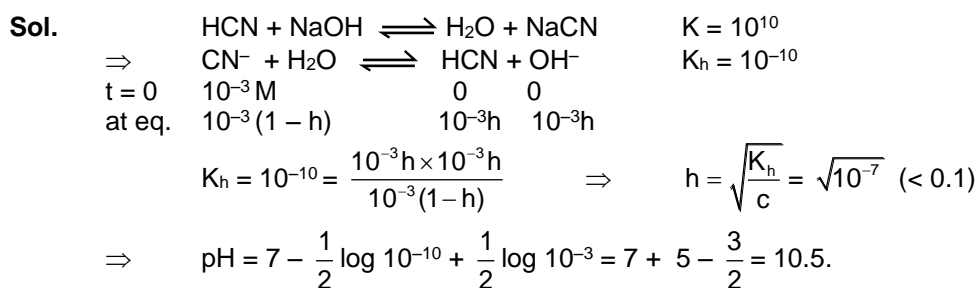
$$\text{pH} = -\log [\text{H}^+] = -\frac{1}{2} [\log K_w + \log K_a - \log c]$$

**F23 :**  $\therefore \text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]$  (valid if  $h < 0.1$  or 10%)

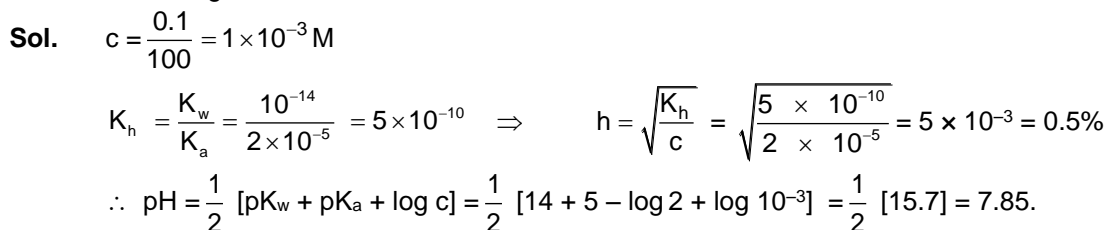
○ Solution will be basic in nature due to hydrolysis of anion.

### Solved Examples

**Ex-17.** If the equilibrium constant for reaction of HCN with NaOH is  $10^{10}$ , then calculate pH of  $10^{-3}$  M NaCN solution at  $25^\circ\text{C}$ .



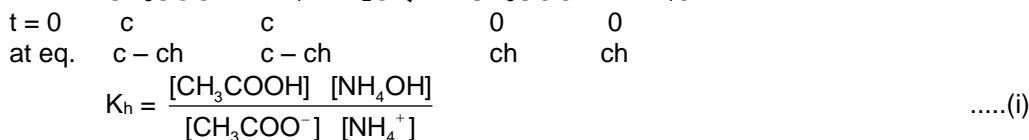
**Ex-18.** Calculate degree of hydrolysis( $h$ ) and pH of solution obtained by dissolving 0.1 mole of  $\text{CH}_3\text{COONa}$  in water to get 100 L of solution. Take  $K_a$  of acetic acid =  $2 \times 10^{-5}$  at  $25^\circ\text{C}$ .



#### (D) Salt of weak acid and weak base

Examples can be  $\text{CH}_3\text{COONH}_4$ ,  $\text{NH}_4\text{CN}$  etc.

**Der10 :**  $\text{CH}_3\text{COO}^- + \text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$



So,  $K_h \times K_a \times K_b = K_w$ ,

$$\Rightarrow K_h = \frac{ch \cdot ch}{c(1-h) \cdot c(1-h)} = \left( \frac{h}{1-h} \right)^2$$



F24 :  $\Rightarrow \left( \frac{h}{1-h} \right) = \sqrt{K_h}$

From (ii) equation,

$$[H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]} = K_a \frac{ch}{c(1-h)} = K_a \times \frac{h}{1-h} = K_a \times \sqrt{K_h} = K_a \times \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{K_w \times K_a}{K_b}}$$

F25 :  $pH = -\log [H^+] = \frac{1}{2} [pK_w + pK_a - pK_b]$

- This formula is always valid for any  $K_a$  and  $K_b$  at any temperature, for any  $h$ .
- pH is independent of concentration of salt solution.
- Even if  $K_a$  of weak acid  $\neq K_b$  of weak base, degree of hydrolysis of cations & anions are very close to each other when they are getting hydrolysed in presence of each other. So, for numerical analysis, they are taken same.

## Solved Examples

**Ex-19.** Calculate pH and degree of hydrolysis of  $10^{-2}$  M  $NH_4CN$  solution.

Given that  $K_a$  of  $HCN = 5 \times 10^{-10}$  and  $K_b$  of  $(aq.NH_3) = 2 \times 10^{-5}$  at  $25^\circ C$ .

**Sol.**  $pH = \frac{1}{2} [14 + pK_a - pK_b] = \frac{1}{2} [14 + 10 - \log 5 - 5 + \log 2] = \frac{1}{2} [18.6] = 9.3$

$$\frac{h}{1-h} = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a \times K_b}} = \sqrt{\frac{10^{-14}}{5 \times 10^{-10} \times 2 \times 10^{-5}}} = 1$$

$\Rightarrow 2h = 1$

$\Rightarrow h = \frac{1}{2} = 0.5$

Table-5

Types of salt	Expression for $K_h$	Expression for $h$	Expression for pH
(i) Salt of weak acid and strong base	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\left( \frac{K_h}{C} \right)}$ ( $h < 0.1$ )	$pH = \frac{1}{2} [pK_w + pK_a + \log C]$
(ii) Salt of strong acid and weak base	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\left( \frac{K_h}{C} \right)}$ ( $h < 0.1$ )	$pH = \frac{1}{2} [pK_w - pK_b - \log C]$
(iii) Salt of weak acid and weak base	$K_h = \frac{K_w}{K_a K_b}$	$\frac{h}{1-h} = \sqrt{K_h}$	$pH = \frac{1}{2} [pK_w + pK_a - pK_b]$

## Ionic Equilibrium-II

### (A) Buffer Solution: Definition and identification

**D13 :** Buffer solutions are those solutions which resist a change in pH upon addition of small amount of small amount of acid or base.

This does not mean that the pH will not change, all it means is that the pH change would be less than the change that would have occurred had it not been a buffer.



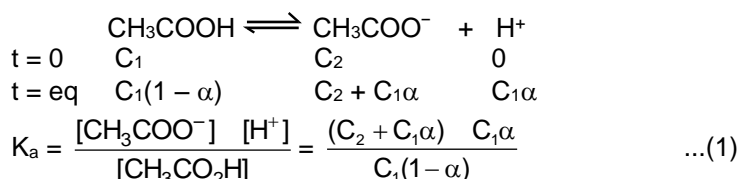


There are various types of buffers :

- (i) **Buffer of a weak acid and its salt with a strong base** : Can be prepared by  
 (a) Mixing weak acid solution and solution of its salt with a strong base.  
 (b) Mixing weak acid solution and lesser amount of strong base solution than that required for neutralization.  
 (c) Mixing salt solution of a weak acid and strong base with lesser amount of strong acid solution than that required for complete reaction.  
 Eg. A solution containing  $\text{CH}_3\text{COOH}$  &  $\text{CH}_3\text{COONa}$ .
- (ii) **Buffer of a weak base and its salt with a strong acid** : Can be prepared by  
 (a) Mixing weak base solution and solution of its salt with a strong acid.  
 (b) Mixing weak base solution and lesser amount of strong acid solution than that required for neutralization  
 (c) Mixing salt solution of a weak base and strong acid with lesser amount of strong base solution than that required for complete reaction.  
 Eg. A solution containing  $\text{NH}_4\text{OH}$  &  $\text{NH}_4\text{Cl}$ .
- (iii) **Solution of salt of a weak acid and a weak base** :  
 Eg. A solution of  $\text{CH}_3\text{COONH}_4$ .

## (B) pH calculation: Buffer solutions generated from monobasic acid / monoacidic base

**Der11:** To calculate the pH of a buffer solution consisting of a weak acid ( $\text{CH}_3\text{COOH}$ ;  $C_1$  concentration) and its salt with a strong base ( $\text{CH}_3\text{COONa}$ ;  $C_2$  concentration of anion), we have :



Expecting  $\alpha \ll 1$  (due to common ion effect exerted by  $\text{CH}_3\text{COO}^-$  on dissociation of  $\text{CH}_3\text{COOH}$ ),

$$\alpha = \frac{K_a}{C_2} \quad \dots(2)$$

$$\therefore [\text{H}^+] = C_1\alpha = K_a \times \frac{C_1}{C_2}$$

Taking log of both sides,  $\log [\text{H}^+] = \log K_a + \log \frac{[\text{Acid}]}{[\text{Anion of Salt}]}$

**F26 :**  $\therefore \text{pH} = \text{pK}_a + \log \frac{[\text{Anion of Salt}]}{[\text{Acid}]}$

This is known as the **Henderson's equation of a buffer**.

**NOTE :** If  $\alpha$  from (2) comes greater than 0.1, calculate exact  $\alpha$  by solving quadratic (1) & then  $[\text{H}^+] = C_1\alpha$ .

For a buffer made up of weak base and its salt with a strong acid, the Henderson's equation looks like this:

**F27 :**  $\text{pOH} = \text{pK}_b + \log \frac{[\text{Cation of Salt}]}{[\text{Base}]}$

## Solved Examples

**Ex-20.** Calculate the amount of  $(\text{NH}_4)_2\text{SO}_4$  in grams which must be added to 500 ml of 0.2 M  $\text{NH}_3$  to give a solution of pH = 9.3. Given  $\text{pK}_b$  for  $\text{NH}_3 = 4.7$

**Sol.** This is a buffer solution made up of weak base and its salt with a strong acid. On checking  $\alpha$  (refer derivation), it comes less than 0.1 (can be considered negligible).

$$\therefore \text{pOH} = \text{pK}_b + \log \frac{[\text{Conjugate acid}]}{[\text{Base}]} \quad (\text{Cation of salt here is same as conjugate acid})$$





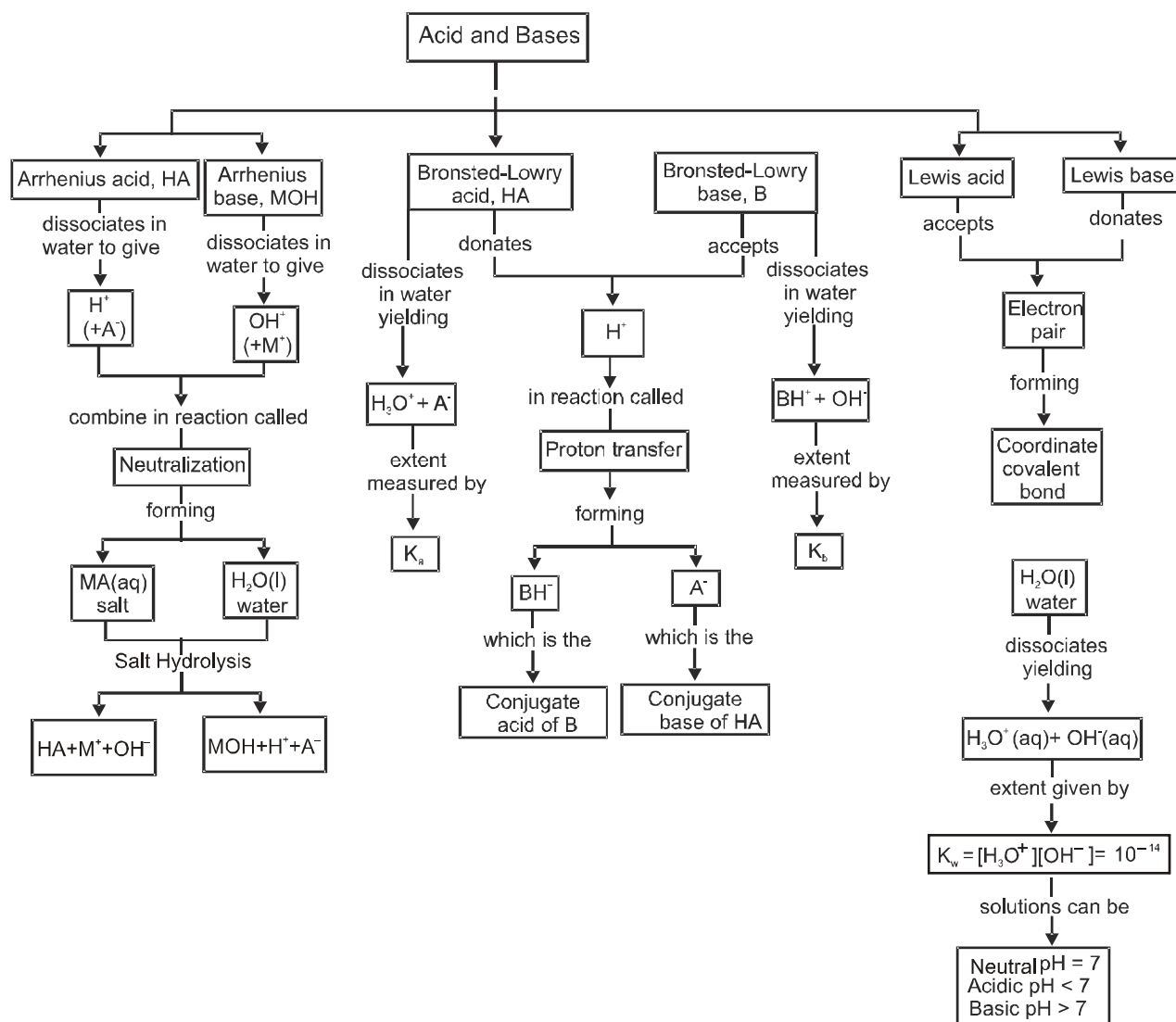
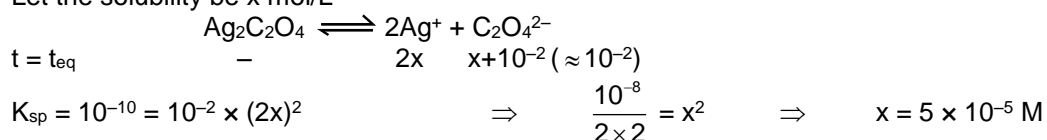
### Common Ion effect on solubility

- Because of the presence of common ion in solution, the solubility of the sparingly soluble salt generally decreases.
- Neglect the concentration of common ion coming from sparingly soluble salt with respect to that coming from completely soluble salt.

### Solved Examples

**Ex-24.** Calculate solubility of silver oxalate in  $10^{-2}$  M potassium oxalate solution. Given that  $K_{sp}$  of silver oxalate =  $10^{-10}$ .

**Sol.** Let the solubility be  $x$  mol/L





## Check List

Definitions (D)			
D1	Arrhenius Acid	F14	Concentrations of ions produced by weak electrolyte (with $\alpha < 0.1$ )
D2	Arrhenius Base	F15	$[H^+]$ & pH of a weak monoprotic acid solution
D3	Brønsted–Lowry Acid	F16	pOH of a weak monoacidic base solution
D4	Brønsted–Lowry Base	F17	Condition for two solution to be isohydric
D5	Amphiprotic species	F18	Relative strength of two weak acids
D6	Lewis Acid	F19	Relative strength of two weak bases
D7	Lewis Base	F20	Degree of hydrolysis (h) of a salt of WB & SA ( $< 0.1$ )
D8	pH & pOH scale	F21	pH of a solution of a salt of WB & SA ( $h < 0.1$ )
D9	Autoprotolysis	F22	Degree of hydrolysis (h) of a salt of WA & SB ( $< 0.1$ )
D10	Degree of dissociation ( $\alpha$ )	F23	pH of a solution of a salt of WA & SB ( $h < 0.1$ )
D11	Isohydric Solutions	F24	Degree of hydrolysis (h) of a salt of WA & WB
D12	Hydrolysis	F25	pH of a solution of a salt of WA & WB
D13	Buffer solution	F26	pH of a buffer solution of WA & its conjugate base
Formulae (F)		F27	pH of a buffer solution of WB & its conjugate acid
F1	Ionic Product of Water ( $K_w$ )	F28	Relation between solubility(s) & solubility product ( $K_{sp}$ ) for sparingly soluble salts
F2	pH	Derivation (Der)	
F3	pOH	Der1	
F4	$\alpha$	Der2	Absolute dissociation constant of water ( $K_a$ or $K_b$ )
F5	$[H^+]$ in strong acid solution ( $H^+$ from $H_2O$ negligible)	Der3	Relation between pH & pOH for an aqueous solution
F6	$[H^+]$ in strong acid solution ( $H^+$ from $H_2O$ significant)	Der4	Relation between $pK_a$ & $pK_b$ for a conjugate acid base pair
F7	$[OH^-]$ in strong base solution ( $OH^-$ from $H_2O$ negligible)	Der5	$[H^+]/[OH^-]$ in a solution containing mixture of SA & SB
F8	$[OH^-]$ in strong base solution ( $OH^-$ from $H_2O$ significant)	Der6	Ostwald's Dilution Law
F9	$[H^+]$ in a solution containing mixture of two strong acids	Der7	Equilibrium of a weak monoprotic acid
F10	$[OH^-]$ in a solution containing mixture of two strong bases	Der8	Hydrolysis of cation in a salt solution of WB & SA
F11	$[H^+]/[OH^-]$ in a solution containing mixture of a strong acid & a strong base	Der9	Hydrolysis of anion in a salt solution of WA & SB
F12	$K_{eq}$ for a weak electrolyte (in terms of C & $\alpha$ )	Der10	Hydrolysis of cation & anion in a salt solution of WA & WB
F13	$\alpha$ for weak electrolyte (if $< 0.1$ )	Der11	pH calculation of a buffer solution consisting of a weak acid & its salt with SB

### MISCELLANEOUS SOLVED PROBLEMS (MSPs)

- Which of the following is the strongest base?  
(A)  $C_2H_5^-$  (B)  $C_2H_5COO^-$  (C)  $C_2H_5O^-$  (D)  $OH^-$   
**Ans.** (A)  
**Sol.** Acidic strength,  $C_2H_6 < C_2H_5OH < H_2O < C_2H_5COOH$   
Weakest acid will have strongest conjugate base.
- A solution of HCl has a pH = 5. If one mL of it is diluted to 1 litre, what will be pH of resulting solution.  
**Sol.**  $[HCl]_i = 10^{-5} \text{ M}$  since pH = 5  
Since volume of original solution has been made 1000 times, so concentration of solution will decrease by 1000 times.  
 $\therefore [HCl]_f = 10^{-8} \text{ M}$ . So  $H^+$  from water should also be considered (as done in solved example-8)  
Then, pH of resulting solution = **6.96**
- Calculate the pH of 0.001 M HOCl having 25% dissociation. Also calculate dissociation constant of the acid. Take  $\log 2 = 0.3$   
**Sol.**  $HOCl \rightleftharpoons H^+ + OCl^-$   

t=0	a	0	0
t=eq	$a - a\alpha$	$a\alpha$	$a\alpha$

So,  $[H^+] = a\alpha = 10^{-3} \times \frac{25}{100} = 2.5 \times 10^{-4}$   
So, pH = **3.6**  
Now,  $K_a = \frac{(a\alpha)(a\alpha)}{a(1-\alpha)} = \frac{a\alpha^2}{1-\alpha} = \frac{1}{12} \times 10^{-3}$
- The solubility product of  $SrF_2$  in water is  $8 \times 10^{-10}$ . Calculate its solubility in 0.1 M NaF aqueous solution.  
**Sol.**  $K_{sp} = [Sr^{2+}][F^-]^2$   
 $8 \times 10^{-10} = s[2s + 0.1]^2 = s[0.1]^2$  (neglecting the  $F^-$  coming from sparingly soluble salt  $SrF_2$ )  
 $\therefore s = \frac{8 \times 10^{-10}}{(0.1)^2} = 8 \times 10^{-8} \text{ M}$



# IONIC EQUILIBRIUM-I

## Exercise-1

Marked questions are recommended for Revision.

### PART - I : SUBJECTIVE QUESTIONS

#### Section (A) : Acid-Base Concepts

##### Commit to memory :

Polyprotic Arrhenius acid : 2 or more replaceable H per acid molecule.  
 Polyprotic Arrhenius base : 2 or more replaceable OH per base molecule.  
 Acid – 1 H<sup>+</sup> = its Conjugate Base  
 Base + 1 H<sup>+</sup> = its Conjugate Acid  
 Amphiprotic species : H<sup>+</sup> donor as well as acceptor.  
 Lewis acid : Lone pair acceptor  
 Lewis base : Lone pair donor

- A-1.** (a) Select Polyprotic Arrhenius acids from the following : H<sub>3</sub>PO<sub>2</sub>, H<sub>3</sub>PO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, HCOOH, (COOH)<sub>2</sub>.  
 (b) Write conjugate acids of SO<sub>4</sub><sup>2-</sup>, RNH<sub>2</sub>, NH<sub>2</sub><sup>-</sup>, C<sub>2</sub>H<sub>5</sub>OC<sub>2</sub>H<sub>5</sub>, F<sup>-</sup>  
 (c) Write conjugate base of HNO<sub>2</sub>, OH<sup>-</sup>, H<sub>2</sub>CO<sub>3</sub>, HClO<sub>4</sub>.  
 (d) Write conjugate acid and conjugate base of following amphoteric species :  
 HS<sup>-</sup>, NH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>OH, H<sub>2</sub>O  
 (e) Classify the following into Lewis acid & Lewis base : H<sup>+</sup>, FeCl<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>N, F<sup>-</sup>,  $\ddot{\text{C}}\text{H}_2$
- A-2.** Classify the following into acid, base and amphiprotic species on the basis of protonic concept :  
 (i) H<sub>2</sub>PO<sub>2</sub><sup>-</sup> (ii) H<sub>2</sub>PO<sub>3</sub><sup>-</sup> (iii) H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (iv) HPO<sub>3</sub><sup>2-</sup>  
 (v) HPO<sub>4</sub><sup>2-</sup> (vi) NH<sub>4</sub><sup>+</sup> (vii) CH<sub>3</sub>COOH<sub>2</sub><sup>+</sup>
- A-3.** Comment upon H<sub>2</sub>O as an Arrhenius acid/base, Bronsted–Lowry acid/base and Lewis acid/base.

#### Section (B) : Properties of water, pH scale, Autoprotolysis

##### Commit to memory :

$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$  at 25°C  
 $[\text{H}^+] = [\text{OH}^-]$  (in water / a neutral solution)  
 $\text{pH} = -\log [\text{H}^+]$  ;  $\text{pOH} = -\log [\text{OH}^-]$   
 For H<sub>2</sub>O, pH & pOH ↓ with ↑ in temperature  
 $\text{pH} + \text{pOH} = \text{p}K_w = 14$  (for an aqueous solution at 25°C)  
 $K_{\text{self ionisation of HA}} = [\text{A}^-][\text{H}_2\text{A}^+]$

- B-1.** At –50°C, liquid NH<sub>3</sub> has ionic product is 10<sup>-30</sup>. How many amide (NH<sub>2</sub><sup>-</sup>) ions are present per mm<sup>3</sup> in pure liquid NH<sub>3</sub> ? (Take N<sub>A</sub> = 6 × 10<sup>23</sup>)

#### Section (C) : Relation between K<sub>a</sub> and K<sub>b</sub> for conjugate acid - base pair

##### Commit to memory :

$K_a(\text{acid}) \times K_b(\text{conjugate base}) = K_w$   
 $\text{p}K_a(\text{acid}) + \text{p}K_b(\text{conjugate base}) = \text{p}K_w = 14$  (at 25°C)

- C-1.** What is ionisation constant of HOCl, if K<sub>b</sub> of OCl<sup>-</sup> = 4 × 10<sup>-10</sup> ? Also find its pK<sub>a</sub>.
- C-2.** K<sub>a1</sub>, K<sub>a2</sub> and K<sub>a3</sub> values for H<sub>3</sub>PO<sub>4</sub> are 10<sup>-3</sup>, 10<sup>-8</sup> and 10<sup>-12</sup> respectively. If K<sub>w</sub> (H<sub>2</sub>O) = 10<sup>-14</sup>, then :  
 (i) What is dissociation constant of HPO<sub>4</sub><sup>2-</sup> ?  
 (ii) What is K<sub>b</sub> of HPO<sub>4</sub><sup>2-</sup> ?  
 (iii) What is K<sub>b</sub> of H<sub>2</sub>PO<sub>4</sub><sup>-</sup> ?  
 (iv) What is order of K<sub>b</sub> of PO<sub>4</sub><sup>3-</sup> (K<sub>b3</sub>), HPO<sub>4</sub><sup>2-</sup> (K<sub>b2</sub>) and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> (K<sub>b1</sub>) ?



### Section (D) : pH calculation : Strong acid solutions, Strong base solutions, Solutions containing mixture of two or more strong acids, Solutions containing mixture of two or more strong bases, Solutions containing mixture of strong acid and strong base

#### Commit to memory :

Strong acid solution:  $[H^+] = \text{Molarity of strong acid solution} \times \text{number of } H^+ \text{ ions per acid molecule.}$

Strong base solution:  $[OH^-] = \text{Molarity of strong base solution} \times \text{number of } OH^- \text{ ions per base molecule.}$

Mixture of two strong acids :  $[H^+]_f = \frac{[H^+]_1 V_1 + [H^+]_2 V_2}{V_1 + V_2}$

Mixture of two strong bases :  $[OH^-]_f = \frac{[OH^-]_1 V_1 + [OH^-]_2 V_2}{V_1 + V_2}$

Mixture of a strong acid and a strong base :

If  $[H^+]V_1 > [OH^-]V_2$   
 $[H^+] = \frac{[H^+]V_1 - [OH^-]V_2}{V_1 + V_2}$

final solution will be acidic in nature

If  $[OH^-]V_2 > [H^+]V_1$   
 $[OH^-] = \frac{[OH^-]V_2 - [H^+]V_1}{V_1 + V_2}$

final solution will be basic in nature

Further,  $[H^+]_f = \frac{10^{-14}}{[OH^-]_f}$  (at 25°C)

**D-1.** Calculate pH of following solutions :

(i) 0.001 M  $HNO_3$ ,

(ii) 0.005 M  $H_2SO_4$ ,

(iii) 0.01 M KOH

(iv)  $10^{-8}$  M NaOH,

(v) 0.0008 M  $Ba(OH)_2$ .

**D-2.** Calculate the pH of the following solutions :

(i) 2.21 g of T/OH dissolved in water to give 2 litre of solution. (Assume T/OH to be a strong base)

(ii) 0.49% w/v  $H_2SO_4$  solution

(iii)  $\frac{M}{1000}$   $Sr(OH)_2$  solution is diluted to quadruple volume.

(iv) 1 mL of 12 M HCl is diluted with water to obtain 1 litre of solution.

**D-3.** Calculate the pH of solution obtained by mixing 10 mL of 0.2 M HCl and 40 mL of 0.1 M  $H_2SO_4$ .

**D-4.** Calculate the pH of the resulting solution formed by mixing the following solutions :

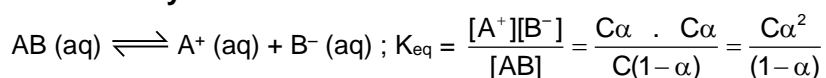
(a) 20 mL of 0.2 M  $Ba(OH)_2$  + 30 mL of 0.1 M HCl

(b) 2 mL of 0.1 M HCl + 10 mL of 0.01 M  $Sr(OH)_2$

(c) 10 mL of 0.1 M  $H_2SO_4$  + 10 mL of 0.1 M KOH.

### Section (E) : Ostwald dilution law, pH calculation : Solutions of weak monoprotic acid, Solutions of weak monoacidic base

#### Commit to memory :



$$\alpha = \sqrt{\frac{K_{eq}}{C}}; [A^+] = [B^-] = C\alpha = \sqrt{CK_{eq}} \quad (\text{both valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$\text{Weak Acid (monoprotic) solution : } \alpha = \sqrt{\frac{K_a}{C}}; pH = \frac{1}{2}(pK_a - \log C) \quad (\text{both valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$\text{Weak base (monoacidic) solution : } \alpha = \sqrt{\frac{K_b}{C}}; pOH = \frac{1}{2}(pK_b - \log C) \quad (\text{both valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$\frac{\text{Acid strength of } HA_1}{\text{Acid strength of } HA_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a1}}{K_{a2}}}; \frac{\text{Basic strength of } BOH_1}{\text{Basic strength of } BOH_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b1}}{K_{b2}}}$$



- E-1.** Acetic acid gets 1.3% ionised in its decimolar solution. What is the ionisation constant of acetic acid?
- E-2.** Prove that degree of dissociation of a weak monoprotic acid is given by :
- $$\alpha = \frac{1}{1 + 10^{(pK_a - pH)}}$$
- where  $K_a$  is its dissociation constant.
- E-3.** Calculate the pH of a 500 mL solution of 1 M BOH. ( $K_b = 2.5 \times 10^{-5}$ )
- E-4.** Whose pH increases by greater value on dilution from initial pH = 2 ?  
(a)  $\text{CH}_3\text{COOH}$  solution (b) HCl solution.

### Section (F) : Salt hydrolysis, pH calculation : Solutions of salt of monoprotic acid and monoacidic base

#### Commit to memory :

Salt of strong acid and weak base :  $K_h \times K_b = K_w$ ;  $h = \sqrt{\frac{K_h}{c}}$ ;  $\text{pH} = \frac{1}{2} [\text{p}K_w - \text{p}K_b - \log c]$  (valid if  $h < 0.1$  or 10%)

Salt of strong base and weak acid :  $K_h \times K_a = K_w$ ;  $h = \sqrt{\frac{K_h}{c}}$ ;  $\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a + \log c]$  (valid if  $h < 0.1$  or 10%)

Salt of weak acid and weak base :  $K_h \times K_a \times K_b = K_w$ ;  $\left(\frac{h}{1-h}\right) = \sqrt{K_h}$ ;  $\text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_a - \text{p}K_b]$

- F-1.** Which of the following ions or compounds in a solution tend to produce an acidic, a basic or a neutral solution ?  
(a)  $\text{C}_2\text{H}_5\text{O}^-$  (b)  $\text{Cu}^{+2}$  (c)  $\text{SO}_3^{2-}$  (d)  $\text{F}^-$  (e)  $\text{NH}_4^+$  (f)  $\text{CH}_3\text{COONa}$   
(g)  $\text{KNO}_3$  (h)  $\text{NaOCl}$  (i)  $\text{Na}_2\text{CO}_3$  (j)  $\text{ZnCl}_2$
- F-2.** Calculate pH of 0.2 M aqueous solution of sodium butyrate. Given :  $K_a$  of butyric acid =  $2 \times 10^{-5}$ .
- F-3.** A 0.25 M solution of pyridinium chloride  $\text{C}_5\text{H}_5\text{NH}^+\text{Cl}^-$  was found to have a pH of 2.75. What is  $K_b$  for pyridine,  $\text{C}_5\text{H}_5\text{N}$  ?
- F-4.** Calculate the percentage hydrolysis & the pH of 0.02 M  $\text{CH}_3\text{COONH}_4$ .  $K_b(\text{NH}_3) = 1.6 \times 10^{-5}$ ,  $K_a(\text{CH}_3\text{COOH}) = 1.6 \times 10^{-5}$ .

## PART - II : ONLY ONE OPTION CORRECT TYPE

### Section (A) : Acid-Base Concepts

#### Commit to memory :

Polyprotic Arrhenius acid : 2 or more replaceable H per acid molecule.

Polyprotic Arrhenius base : 2 or more replaceable OH per base molecule.

Acid -  $1 \text{ H}^+$  = its Conjugate Base

Base +  $1 \text{ H}^+$  = its Conjugate Acid

Amphiprotic species :  $\text{H}^+$  donor as well as acceptor.

Lewis acid : Lone pair acceptor

Lewis base : Lone pair donor

- A-1.** An acid with molecular formula  $\text{C}_7\text{H}_6\text{O}_3$  forms three types of sodium salts. i.e.  $\text{C}_7\text{H}_5\text{O}_3\text{Na}$ ,  $\text{C}_7\text{H}_4\text{O}_3\text{Na}_2$  and  $\text{C}_7\text{H}_3\text{O}_3\text{Na}_3$ . The basicity of the acid is :  
(A) One (B) Two (C) Three (D) Six
- A-2.** Select the incorrect option :  
(A)  $\text{H}_3\text{PO}_4$  is a tribasic acid. (B)  $\text{H}_3\text{BO}_3$  is not an Arrhenius acid.  
(C)  $\text{Sr}(\text{OH})_2$  is a strong diacidic base. (D)  $\text{NH}_3 \cdot \text{H}_2\text{O}$  is a strong monoacidic base.







- A-3.** In the reaction  $\text{HC}_2\text{O}_4^- (\text{aq}) + \text{PO}_4^{3-} (\text{aq}) \rightleftharpoons \text{HPO}_4^{2-} (\text{aq}) + \text{C}_2\text{O}_4^{2-} (\text{aq})$ , which are the two Bronsted bases ?  
 (A)  $\text{HC}_2\text{O}_4^-$  and  $\text{PO}_4^{3-}$  (B)  $\text{HPO}_4^{2-}$  and  $\text{C}_2\text{O}_4^{2-}$   
 (C)  $\text{HC}_2\text{O}_4^-$  and  $\text{HPO}_4^{2-}$  (D)  $\text{PO}_4^{3-}$  and  $\text{C}_2\text{O}_4^{2-}$
- A-4.** The following equilibrium is established when  $\text{HClO}_4$  is dissolved in weak acid  $\text{HF}$  solvent :  
 $\text{HF} + \text{HClO}_4 \rightleftharpoons \text{ClO}_4^- + \text{H}_2\text{F}^+$   
 Which of the following is correct set of conjugate acid base pair ?  
 (A)  $\text{HF}$  and  $\text{HClO}_4$  (B)  $\text{HF}$  and  $\text{ClO}_4^-$  (C)  $\text{HF}$  and  $\text{H}_2\text{F}^+$  (D)  $\text{HClO}_4$  &  $\text{H}_2\text{F}^+$
- A-5.** Which of the following correctly explains the nature of boric acid in aqueous medium ?  
 (A)  $\text{H}_3\text{BO}_3 \xrightarrow{\text{H}_2\text{O}} \text{H}_3\text{O}^+ + \text{H}_2\text{BO}_3^-$  (B)  $\text{H}_3\text{BO}_3 \xrightarrow{2\text{H}_2\text{O}} 2\text{H}_3\text{O}^+ + \text{HBO}_3^{2-}$   
 (C)  $\text{H}_3\text{BO}_3 \xrightarrow{3\text{H}_2\text{O}} 3\text{H}_3\text{O}^+ + \text{BO}_3^{3-}$  (D)  $\text{H}_3\text{BO}_3 \xrightarrow{\text{H}_2\text{O}} \text{B}(\text{OH})_4^- + \text{H}^+$

## Section (B) : Properties of water, pH scale, Autoprotolysis

### Commit to memory :

$K_w = [\text{H}^+][\text{OH}^-] = 10^{-14}$  at  $25^\circ\text{C}$   
 $[\text{H}^+] = [\text{OH}^-]$  (in water / a neutral solution)  
 $\text{pH} = -\log [\text{H}^+]$  ;  $\text{pOH} = -\log [\text{OH}^-]$   
 For  $\text{H}_2\text{O}$ ,  $\text{pH}$  &  $\text{pOH} \downarrow$  with  $\uparrow$  in temperature  
 $\text{pH} + \text{pOH} = \text{p}K_w = 14$  (for an aqueous solution at  $25^\circ\text{C}$ )  
 $K_{\text{self ionisation of HA}} = [\text{A}^-][\text{H}_2\text{A}^+]$

- B-1.** Which of the following expression is not true ?  
 (A)  $[\text{H}^+] = [\text{OH}^-] = \sqrt{K_w}$  for a neutral solution at all temperatures.  
 (B)  $[\text{H}^+] > \sqrt{K_w}$  &  $[\text{OH}^-] < \sqrt{K_w}$  for an acidic solution.  
 (C)  $[\text{H}^+] < \sqrt{K_w}$  &  $[\text{OH}^-] > \sqrt{K_w}$  for an alkaline solution.  
 (D)  $[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ M}$  for a neutral solution at all temperatures .
- B-2.**  $\text{pOH}$  of  $\text{H}_2\text{O}$  is 7 at 298 K. If water is heated to 350 K, which of the following statement should be true ?  
 (A)  $\text{pOH}$  will decrease. (B)  $\text{pH}$  will increase.  
 (C)  $\text{pOH}$  will remain 7. (D) Both (A) and (B).
- B-3.**  $K_w$  of  $\text{H}_2\text{O}$  at 373 K is  $1 \times 10^{-12}$ . Identify, which of the following is incorrect :  
 (A)  $\text{pH} + \text{pOH} = 12$ , for every aqueous solutions.  
 (B)  $\text{pH}$  of  $\text{H}_2\text{O}$  is 6.  
 (C)  $\alpha_{\text{H}_2\text{O}}$  has increased from its value at 298 K.  
 (D)  $\text{H}_2\text{O}$  is acidic.
- B-4.** In pure  $\text{HCOOH}$  liquid, concentration of  $\text{HCOO}^- = 10^{-3} \text{ M}$  at  $27^\circ\text{C}$ . What is the self ionisation constant at  $27^\circ\text{C}$  ( $K = [\text{HCOOH}_2^+][\text{HCOO}^-]$ ) ?  
 (A)  $10^{-3}$  (B)  $10^3$  (C)  $10^6$  (D)  $10^{-6}$

## Section (C) : Relation between $K_a$ and $K_b$ for conjugate acid-base pair

### Commit to memory :

$K_a (\text{acid}) \times K_b (\text{conjugate base}) = K_w$   
 $\text{p}K_a (\text{acid}) + \text{p}K_b (\text{conjugate base}) = \text{p}K_w = 14$  (at  $25^\circ\text{C}$ )

- C-1.** Given :  $\text{HF} + \text{H}_2\text{O} \xrightleftharpoons{K_a} \text{H}_3\text{O}^+ + \text{F}^-$   
 $\text{F}^- + \text{H}_2\text{O} \xrightleftharpoons{K_b} \text{HF} + \text{OH}^-$   
 Which relation is correct.  
 (A)  $K_b = \frac{1}{K_a}$  (B)  $K_a \cdot K_b = K_w$  (C)  $K_a \cdot K_b \cdot K_w = 1$  (D)  $\frac{K_a}{K_b} = K_w$





- C-2.** Which of the following is incorrect ?  
 (A)  $K_a$  (weak acid).  $K_b$  (conjugate weak base) =  $K_w$   
 (B)  $K_a$  (strong acid).  $K_b$  (conjugate weak base) =  $K_w$   
 (C)  $K_a$  (weak acid).  $K_b$  (weak base) =  $K_w$   
 (D)  $K_a$  (weak acid).  $K_b$  (conjugate strong base) =  $K_w$

**Section (D) : pH calculation : Strong acid solutions, Strong base solutions, Solutions containing mixture of two or more strong acids, Solutions containing mixture of two or more strong bases, Solutions containing mixture of strong acid and strong base**

**Commit to memory :**

Strong acid solution :  $[H^+] = \text{Molarity of strong acid solution} \times \text{number of } H^+ \text{ ions per acid molecule.}$

Strong base solution :  $[OH^-] = \text{Molarity of strong base solution} \times \text{number of } OH^- \text{ ions per base molecule.}$

Mixture of two strong acids :  $[H^+]_f = \frac{[H^+]_1 V_1 + [H^+]_2 V_2}{V_1 + V_2}$

Mixture of two strong bases :  $[OH^-]_f = \frac{[OH^-]_1 V_1 + [OH^-]_2 V_2}{V_1 + V_2}$

Mixture of a strong acid and a strong base :

If  $[H^+]V_1 > [OH^-]V_2$

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

final solution will be acidic in nature

If  $[OH^-]V_2 > [H^+]V_1$

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

final solution will be basic in nature

Further,  $[H^+]_f = \frac{10^{-14}}{[OH^-]_f}$  (at 25°C)

- D-1.** The  $[OH^-]$  in 100 mL of 0.016 M HCl (aq) is :  
 (A)  $6.25 \times 10^{-12}$  M (B)  $3 \times 10^{-10}$  M (C)  $6.25 \times 10^{-13}$  M (D)  $1.6 \times 10^{-3}$  M
- D-2.** How many moles of NaOH must be removed from one litre of its aqueous solution to change its pH from 12 to 11 ?  
 (A) 0.009 (B) 0.01 (C) 0.09 (D) 0.1
- D-3.** Which statement/relationship is correct ?  
 (A) pH of aqueous solutions of 0.1 M  $HNO_3$ , 0.1M HCl, 0.1M HI at 25°C is not equal.  
 (B) For a dilute solution,  $pH = -\log \frac{1}{[H^+]}$   
 (C) At 25°C, the pH of pure water is 7.  
 (D) The value of  $pK_w$  at 25°C is 7.
- D-4.** Upon mixing equal volume of two solutions of strong acids having pH values 2 & 4, resulting solution will have pH :  
 (A) equal to 3 (B) closer to 2 than 4  
 (C) closer to 4 than 2 (D) closer to 3 than 2
- D-5.** On adding 0.04 g solid NaOH to a 100 mL,  $\frac{M}{200}$   $Ba(OH)_2$  solution, determine change in pH :  
 (A) 0 (B) +0.3 (C) -0.3 (D) +0.7
- D-6.** Upon mixing equal volume of a strong acid solution (HA) and a strong base (BOH) solution, pH of resulting solution :  
 (A) may be less than 7 (B) may be greater than 7  
 (C) will be equal to 7 (D) Both (A) & (B)

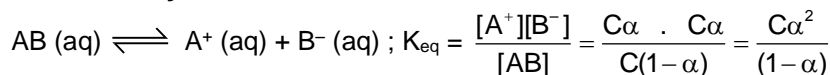


**D-7.** Which of the following solutions will have pH close to 1 ?

- (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  
 (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.

### Section (E) : Ostwald dilution law, pH calculation : Solutions of weak monoprotic acid, Solutions of weak monoacidic base

**Commit to memory :**



$$\alpha = \sqrt{\frac{K_{eq}}{C}}; [A^+] = [B^-] = C\alpha = \sqrt{CK_{eq}} \text{ (both valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$\text{Weak Acid (monoprotic) solution : } \alpha = \sqrt{\frac{K_a}{C}}; pH = \frac{1}{2} (pK_a - \log C) \text{ (both valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$\text{Weak base (monoacidic) solution : } \alpha = \sqrt{\frac{K_b}{C}}; pOH = \frac{1}{2} (pK_b - \log C) \text{ (both valid if } \alpha < 0.1 \text{ or } 10\%)$$

$$\frac{\text{Acid strength of } HA_1}{\text{Acid strength of } HA_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}; \frac{\text{Basic strength of } BOH_1}{\text{Basic strength of } BOH_2} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$$

**E-1.** Which of the following has the maximum degree of ionisation ?

- (A) 1 M NH<sub>3</sub> (B) 0.001 M NH<sub>3</sub> (C) 0.1 M NH<sub>3</sub> (D) 0.0001 M NH<sub>3</sub>.

**E-2.** K<sub>a</sub> for formic acid and acetic acid are 1.8 × 10<sup>-4</sup> and 1.8 × 10<sup>-5</sup> respectively. The relative strength of acids is :

- (A) 10 : 1 (B) 1 : 10 (C) 1 : √10 (D) √10 : 1

**E-3.** K<sub>a</sub> for a monobasic acid, whose 0.1 M solution has pH of 4.5, is :

- (A) 10<sup>-10</sup> (B) 10<sup>-8</sup> (C) √10 × 10<sup>-4</sup> (D) √10 × 10<sup>-6</sup>

### Section (F) : Salt hydrolysis, pH calculation : Solutions of salt of monoprotic acid and monoacidic base.

**Commit to memory :**

$$\text{Salt of strong acid and weak base : } K_h \times K_b = K_w; h = \sqrt{\frac{K_h}{c}}; pH = \frac{1}{2} [pK_w - pK_b - \log c] \text{ (valid if } h < 0.1 \text{ or } 10\%)$$

$$\text{Salt of strong base and weak acid : } K_h \times K_a = K_w; h = \sqrt{\frac{K_h}{c}}; pH = \frac{1}{2} [pK_w + pK_a + \log c] \text{ (valid if } h < 0.1 \text{ or } 10\%)$$

$$\text{Salt of weak acid and weak base : } K_h \times K_a \times K_b = K_w; \left( \frac{h}{1-h} \right) = \sqrt{K_h}; pH = \frac{1}{2} [pK_w + pK_a - pK_b]$$

**F-1.** Aqueous solution of NH<sub>4</sub>Cl is \_\_\_\_ in nature due to behaviour of \_\_\_\_ ion in solution :

- (A) acidic ; NH<sub>4</sub><sup>+</sup> (B) alkaline ; NH<sub>4</sub><sup>+</sup> (C) acidic ; Cl<sup>-</sup> (D) alkaline ; Cl<sup>-</sup>

**F-2.** The chloride salt of a certain weak monoacidic organic base is hydrolysed to an extent of 3% in its 0.1M solution at 25°C. Given that the ionic product of water is 10<sup>-14</sup> at this temperature, what is the dissociation constant of the base?

- (A) ≈ 1 × 10<sup>-10</sup> (B) ≈ 1 × 10<sup>-9</sup> (C) 3.33 × 10<sup>-9</sup> (D) 3.33 × 10<sup>-10</sup>

**F-3.** The pH of 0.1 M solution of the following salts increases in the order :

- (A) NaCl < NH<sub>4</sub>Cl < NaCN < HCl (B) HCl < NH<sub>4</sub>Cl < NaCl < NaCN  
 (C) NaCN < NH<sub>4</sub>Cl < NaCl < HCl (D) HCl < NaCl < NaCN < NH<sub>4</sub>Cl



- F-4.** The degree of hydrolysis of a salt of weak monobasic acid and weak monoacidic base in its 0.1 M solution is found to be 50%. If the molarity of the solution is 0.2 M, the percentage hydrolysis of the salt should be :  
 (A) 100 % (B) 50 % (C) 25 % (D) None of these

### PART - III : MATCH THE COLUMN

1. Match the Column.

	Column-I		Column-II
(A)	HCl	(p)	Lewis acid
(B)	KOH	(q)	Arrhenius acid
(C)	NH <sub>3</sub>	(r)	Lewis base
(D)	BF <sub>3</sub>	(s)	Arrhenius base

## Exercise-2

Marked questions are recommended for Revision.

### PART - I : ONLY ONE OPTION CORRECT TYPE

- The self ionisation constant for pure formic acid,  $K = [\text{HCOOH}_2^+][\text{HCOO}^-]$  has been estimated as  $10^{-6}$  at room temperature. The density of formic acid is  $1.15 \text{ g/cm}^3$ . What percentage of formic acid molecules in pure formic acid are converted to formate ion ?  
 (A) 0.002% (B) 0.004% (C) 0.006% (D) 0.008%
- $\text{pK}_a$  for an acid HA is 6. The value of K for the reaction  $\text{A}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HA} + \text{H}_2\text{O}$  is :  
 (A)  $1 \times 10^{-6}$  (B)  $1 \times 10^8$  (C)  $1 \times 10^{-8}$  (D)  $1 \times 10^6$
- $10^{-6} \text{ M HCl}$  is diluted to 100 times. Its pH is :  
 (A) 6 (B) 8 (C) 6.98 (D) 7.02
- Which of the following solutions has a pH exactly equal to 8 ?  
 (A)  $10^{-8} \text{ M HCl}$  solution (B) Solution containing  $10^{-8} \text{ M H}^+$   
 (C)  $2 \times 10^{-6} \text{ M Ba(OH)}_2$  solution (D)  $10^{-8} \text{ M NaOH}$  solution
- 10 mL of a strong acid solution of pH = 2 are mixed with 990 mL of another strong acid solution of pH = 4. The pH of the resulting solution will be :  
 (A) 3 (B) 3.3 (C) 3.7  
 (D) Molecular formula of both strong acids should be known to answer above question.
- % dissociation of a 0.024 M solution of a weak acid HA ( $K_a = 2 \times 10^{-3}$ ) is :  
 (A) 0.25% (B)  $\approx 29\%$  (C) 25% (D)  $\approx 0.29\%$
- For a weak base BOH,  $K_b = 10^{-4}$ . Calculate pH of  $10^{-4} \text{ M BOH}$  solution. (Take  $\log 6.2 = 0.79$ )  
 (A) 10 (B) 9.79 (C) 8 (D) None of these
- Four separate solutions of sodium salts NaW, NaX, NaY and NaZ have pH 7, 9, 10 and 11 respectively, when each solution has concentration 0.1 M. Then the strongest acid is :  
 (A) HW (B) HX (C) HY (D) HZ

### PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

- If an acid-base reaction  $\text{HA(aq)} + \text{B}^- (\text{aq}) \rightleftharpoons \text{HB(aq)} + \text{A}^- (\text{aq})$  has  $K_{\text{eq}} = 10^{-4}$ , how many of the following statements are true ?  
 (i) HB is stronger acid than HA (ii) HA is stronger acid than HB  
 (iii) HA and HB have the same acidic strength (iv)  $\text{B}^-$  is stronger base than  $\text{A}^-$   
 (v)  $\text{A}^-$  is stronger base than  $\text{B}^-$  (vi)  $\text{B}^-$  and HB are conjugate acid-base pair  
 (vii)  $\text{A}^-$  is the conjugate base of acid HA. (viii) HA can be  $\text{HSO}_4^-$  and HB can be  $\text{HCOOH}$ .  
 (ix)  $\text{A}^-$  can be  $\text{F}^-$  and  $\text{B}^-$  can be  $\text{CN}^-$ .



2. What is pOH of an aqueous solution with  $[H^+] = 10^{-2} \text{ M}$  and  $K_w = 2 \times 10^{-12}$  ? Report your answer after dividing by 2 and round it off to the nearest whole number.
3. Percentage ionisation of water as follows at certain temperature is  $3.6 \times 10^{-7} \%$ . Calculate  $K_w$  and pH of water at this temperature.  $2H_2O \rightleftharpoons H_3O^+ + OH^-$
4. 0.1 mole HCl is dissolved in distilled water of volume V. Then, at  $\lim_{V \rightarrow \infty}$ ,  $(pH)_{\text{solution}}$  is equal to .....
5. Determine  $pK_a(H_2O) + pK_a(H_3O^+)$ .
6. What volume (in L) of water must be added to 1 L of 0.1 M solution of B (weak organic monoacidic base; ionisation constant =  $10^{-5}$ ) to triple the % ionisation of base ?
7. If  $pH_{x\%}$  is the pH of a 1 M weak monoprotic acid which is x % ionised, then find the value of  $\left[ \frac{pH_{50\%}}{pH_{10\%}} \right] \times 100$ .
8. If the equilibrium constant for the reaction of weak acid HA with a strong base is  $10^9$ , then determine pH of 0.1 M NaA solution.
9. What is the concentration of  $CH_3COOH(aq)$  in a solution prepared by dissolving 0.01 mole of  $NH_4^+CH_3COO^-$  in 1 L  $H_2O$  ? Report your answer after multiplying by  $9 \times 10^5$ .  
 $[K_a(CH_3COOH) = 1.8 \times 10^{-5}; K_b(NH_3 \cdot H_2O) = 1.8 \times 10^{-5}]$

### PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. Which statement(s) is/are correct ?  
 (A) All Bronsted bases are also Lewis bases.  
 (B) All Bronsted acids are not Lewis acids.  
 (C) Most cations are acids and most anions are bases.  
 (D) All Bronsted bases are also Arrhenius bases.
2. Select the incorrect statement(s) :  
 (A)  $NH_4^+(aq)$  is a strong acid. (B)  $CH_3COO^-(aq)$  is a weak base.  
 (C)  $H^-$  is a weak base. (D)  $HS^-$  is a weak acid as well as a weak base.
3. For pure water :  
 (A)  $pK_w$  increases with decrease in temperature.  
 (B) Absolute dissociation constant decreases with decrease in temperature.  
 (C)  $\alpha_{H_2O}$  increases with decrease in temperature.  
 (D) Both pH and pOH decrease with rise in temperature.
4. One litre of a strong acid solution contains  $10^{-5}$  moles of  $H^+$  ions. Then :  
 (A)  $pOH = 9$ .  
 (B) Percentage ionisation of water in solution is  $1.8 \times 10^{-9} \%$ .  
 (C) Number of  $OH^-$  ions per mL of solution =  $6.022 \times 10^{15}$ .  
 (D)  $[H^+]_{\text{from } H_2O} = 10^{-9} \text{ M}$
5. Equal volumes of 0.2 M HCl and 0.2 M  $Sr(OH)_2$  are mixed. Which of the following statement is/are correct ?  
 (A)  $[Sr^{2+}] = 0.1 \text{ M}$  (B)  $[Cl^-] = 0.1 \text{ M}$   
 (C) pH of resulting solution = 13 (D) Solution is neutral.
6. If 0.1 M  $CH_3COOH$  ( $K_a = 1.8 \times 10^{-5}$ ) is diluted at  $25^\circ\text{C}$ , then which of the following will be correct ?  
 (A)  $[H^+]$  will increase. (B) pH will increase.  
 (C) number of  $H^+$  ions will increase. (D)  $K_a$  will increase.



7. Degree of hydrolysis for a salt of strong acid and weak base :  
 (A) is independent of dilution  
 (B) increases with dilution  
 (C) increases with decrease in  $K_b$  of the bases  
 (D) decreases with decrease in temperature.
8. Equal volumes of following solutions are mixed, in which case the pH of resulting solution will be average value of pH of two solutions.  
 (A) Aqueous HCl of pH = 2, aqueous NaOH of pH = 12  
 (B) Aqueous HCl of pH = 2, aqueous HCl of pH = 4  
 (C) Aqueous NaOH of pH = 12, aqueous NaOH of pH = 10  
 (D) Aqueous  $\text{CH}_3\text{COOH}$  of pH = 5, aqueous  $\text{NH}_3$  of pH = 9. [ $K_a(\text{CH}_3\text{COOH}) = K_b(\text{NH}_3)$ ]

## PART - IV : COMPREHENSION

Read the following passages carefully and answer the questions.

### Comprehension # 1

pH calculation upon dilution of a strong acid solution is generally done by equating  $n_{\text{H}^+}$  in original solution & diluted solution. However, if strong acid solution is very dilute, then  $\text{H}^+$  from water are also to be considered.

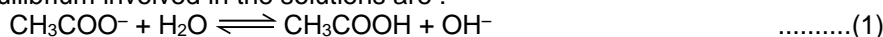
Take  $\log 3.7 = 0.568$  and answer the following questions.

1. A 1 litre solution of pH = 4 (solution of a strong acid) is added to the 7/3 litre of water. What is the pH of resulting solution ?  
 (A) 4.52 (B) 4.365 (C) 4.4 (D) 4.432
2. A 1 litre solution of pH = 6 (solution of a strong acid) is added to the 7/3 litre of water. What is the pH of resulting solution ? Neglect the common ion effect on  $\text{H}_2\text{O}$ .  
 (A) 6.4 (B) 6.52 (C) 6.365 (D) 6.432

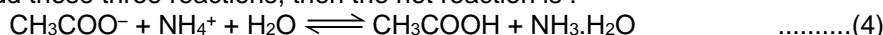
### Comprehension # 2

Consider a solution of  $\text{CH}_3\text{COONH}_4$  which is a salt of weak acid & weak base.

The equilibrium involved in the solutions are :



If we add these three reactions, then the net reaction is :



Both  $\text{CH}_3\text{COO}^-$  and  $\text{NH}_4^+$  get hydrolysed independently and their hydrolysis depends on :

- (i) their initial concentration
- (ii) the value of  $K_h$  which is  $\frac{K_w}{K_a}$  for  $\text{CH}_3\text{COO}^-$  and  $\frac{K_w}{K_b}$  for  $\text{NH}_4^+$ .

Since both of the ions were produced from the same salt, their initial concentrations are same.

Therefore unless & until the value of  $\frac{K_w}{K_a}$  and  $\frac{K_w}{K_b}$  or  $K_a$  and  $K_b$  is same, the degree of hydrolysis of ion

can't be same.

To explain why we assume that degree of hydrolysis of cation and anion is same, we need to now look at the third reaction i.e., combination of  $\text{H}^+$  and  $\text{OH}^-$  ions. It is obvious that this reaction happens only because one reaction produced  $\text{H}^+$  ion and the other produced  $\text{OH}^-$  ions. We can also note that this reaction causes both the hydrolysis reaction to occur more since their product ions are being consumed. Keep this thing in mind that the equilibrium which has smaller value of equilibrium constant is affected more by the common ion effect. For the same reason, if for any reason a reaction is made to occur to a greater extent by the consumption of any one of the product ion, the reaction with the smaller value of equilibrium constant tends to get affected more.



Therefore we conclude that firstly the hydrolysis of both the ions occurs more in the presence of each other (due to consumption of the product ions) than in each other's absence. Secondly, the hydrolysis of the ion which occurs to a lesser extent (due to smaller value of  $K_h$ ) is affected more than the one whose  $K_h$  is greater. Hence, we can see that the degree of hydrolysis of both the ions would be close to each other when they are getting hydrolysed in the presence of each other.

Now answer the following questions :

3. In the hydrolysis of salt of weak acid & weak base :  
 (A) degree of hydrolysis of cation and anion is different  
 (B) degree of hydrolysis of cation and anion is same  
 (C) degree of hydrolysis of cation and anion is different and they can never be assumed same.  
 (D) degree of hydrolysis of cation and anion is different but they are very close to each other when they are getting hydrolysed in the presence of each other.
4. For 0.1 M  $\text{CH}_3\text{COONH}_4$  salt solution given,  $K_a(\text{CH}_3\text{COOH}) = K_b(\text{NH}_3 \cdot \text{H}_2\text{O}) = 2 \times 10^{-5}$ .  
 In this case, degree of hydrolysis of cation and anion are :  
 (A) exactly same  
 (B) slightly different  
 (C) can't say  
 (D) different but can be taken approximately same

## Exercise-3

### JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

#### JEE(MAIN) OFFLINE PROBLEMS

- The conjugate base of  $\text{H}_2\text{PO}_4^-$  is : [AIEEE-2005, 3/225]  
 (1)  $\text{PO}_4^{3-}$  (2)  $\text{P}_2\text{O}_5$  (3)  $\text{H}_3\text{PO}_4$  (4)  $\text{HPO}_4^{2-}$
- What is the conjugate base of  $\text{OH}^-$  ? [AIEEE-2005, 3/225]  
 (1)  $\text{O}_2$  (2)  $\text{H}_2\text{O}$  (3)  $\text{O}^-$  (4)  $\text{O}^{2-}$
- Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be : [AIEEE-2005, 3/225]  
 (1)  $3.98 \times 10^8$  (2)  $3.88 \times 10^6$  (3)  $3.68 \times 10^{-6}$  (4)  $3.98 \times 10^{-6}$
- The first and second dissociation constants of an acid  $\text{H}_2\text{A}$  are  $1.0 \times 10^{-5}$  and  $5.0 \times 10^{-10}$  respectively. The overall dissociation constant of the acid will be : [AIEEE-2007, 3/120]  
 (1)  $5.0 \times 10^{-15}$  (2)  $0.2 \times 10^5$  (3)  $5.0 \times 10^{-5}$  (4)  $5.0 \times 10^{15}$
- The  $\text{p}K_a$  of a weak acid, HA, is 4.80. The  $\text{p}K_b$  of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be : [AIEEE-2008, 3/105]  
 (1) 4.79 (2) 7.01 (3) 9.22 (4) 9.58
- Three reactions involving  $\text{H}_2\text{PO}_4^-$  are given below : [AIEEE-2010, 4/144]  
 (i)  $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$   
 (ii)  $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{HPO}_4^{2-} + \text{H}_3\text{O}^+$   
 (iii)  $\text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{H}_3\text{PO}_4 + \text{O}^{2-}$   
 In which of the above, does  $\text{H}_2\text{PO}_4^-$  act as an acid ?  
 (1) (ii) only (2) (i) and (ii) (3) (iii) only (4) (i) only
- The pH of a 0.1 molar solution of the acid HQ is 3. The value of the ionization constant,  $K_a$  of the acid is: [AIEEE-2012, 4/120]  
 (1)  $3 \times 10^{-1}$  (2)  $1 \times 10^{-3}$  (3)  $1 \times 10^{-5}$  (4)  $1 \times 10^{-7}$
- How many litres of water must be added to 1 litre an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2 ? [JEE(Main) 2013, 4/120]  
 (1) 0.1 L (2) 0.9 L (3) 2.0 L (4) 9.0 L



9.  $pK_a$  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 : **[JEE(Main) 2017, 4/120]**  
 (1) 6.9 (2) 7.0 (3) 1.0 (4) 7.2
10. Which of the following salts is the most basic in aqueous solution? **[JEE(Main) 2018, 4/120]**  
 (1)  $FeCl_3$  (2)  $Pb(CH_3COO)_2$  (3)  $Al(CN)_3$  (4)  $CH_3COOK$

### JEE(MAIN) ONLINE PROBLEMS

1. Assuming that the degree of hydrolysis is small, the pH of 0.1 M solution of sodium acetate ( $K_a = 1.0 \times 10^{-5}$ ) will be : **[JEE(Main) 2014 Online (11-04-14), 4/120]**  
 (1) 5.0 (2) 6.0 (3) 8.0 (4) 9.0
2. The conjugate base of hydrazoic acid is : **[JEE(Main) 2014 Online (12-04-14), 4/120]**  
 (1)  $N^{-3}$  (2)  $N_3^{-}$  (3)  $N_2^{-}$  (4)  $HN_3^{-}$
3. What quantity (in mL) of a 45% acid solution of a mono-protic strong acid must be mixed with a 20% solution of the same acid to produce 800 mL of a 29.875% acid solution ? **[JEE(Main) 2017 Online (09-04-17), 4/120]**  
 (1) 330 (2) 316 (3) 320 (4) 325
4. Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of the them will be equal to 1? **[JEE(Main) 2018 Online (15-04-18), 4/120]**
- (1)  $100 \text{ mL } \frac{M}{10} \text{ HCl} + 100 \text{ mL } \frac{M}{10} \text{ NaOH}$  (2)  $75 \text{ mL } \frac{M}{5} \text{ HCl} + 25 \text{ mL } \frac{M}{5} \text{ NaOH}$   
 (3)  $60 \text{ mL } \frac{M}{10} \text{ HCl} + 40 \text{ mL } \frac{M}{10} \text{ NaOH}$  (4)  $55 \text{ mL } \frac{M}{10} \text{ HCl} + 45 \text{ mL } \frac{M}{10} \text{ NaOH}$







# Answers

## EXERCISE - 1

### PART - I

- A-1.** (a)  $\text{H}_3\text{PO}_3$ ,  $(\text{COOH})_2$   
 (b)  $\text{HSO}_4^-$ ,  $\text{RNH}_3^+$ ,  $\text{NH}_3$ ,  $(\text{C}_2\text{H}_5)_2\text{OH}^+$ ,  $\text{HF}$   
 (c)  $\text{NO}_2^-$ ,  $\text{O}^{2-}$ ,  $\text{HCO}_3^-$ ,  $\text{ClO}_4^-$   
 (d) Conjugate acids:  $\text{H}_2\text{S}$ ,  $\text{NH}_4^+$ ,  $\text{C}_2\text{H}_5\text{OH}_2^+$ ,  $\text{H}_3\text{O}^+$   
 Conjugate base:  $\text{S}^{2-}$ ,  $\text{NH}_2^-$ ,  $\text{C}_2\text{H}_5\text{O}^-$ ,  $\text{OH}^-$   
 (e) Lewis acid:  $\text{H}^+$ ,  $\text{FeCl}_3$ ,  $\text{CH}_2$   
 Lewis base:  $(\text{CH}_3)_3\text{N}$ ,  $\text{F}^-$
- A-2.** Acidic – (vi), (vii) ; Basic – (i), (iv) ; Amphiprotic – (ii), (iii), (v)
- A-3.**  $\text{H}_2\text{O}$  – Arrhenius acid, Arrhenius base, Bronsted–Lowry acid, Bronsted–Lowry base, Lewis base but not Lewis acid.
- B-1.** 600 ions /  $\text{mm}^3$  **C-1.**  $2.5 \times 10^{-5}$  ; 4.6
- C-2.** (i)  $10^{-12}$  (ii)  $10^{-6}$  (iii)  $10^{-11}$  (iv)  $K_{b_1} < K_{b_2} < K_{b_3}$
- D-1.** (i) 3, (ii) 2, (iii) 12, (iv) 7.02, (v) 11.2
- D-2.** (i) 11.7, (ii) 1, (iii) 10.7, (iv) 1.92 **D-3.** 0.7 **D-4.** (a) 13 ; (b) 7 ; (c) 1.3.
- E-1.**  $1.69 \times 10^{-5}$  **E-2.** Refer class notes / sheet theory.
- E-3.** 11.7 **E-4.**  $\text{HCl}$
- F-1.** (a) Basic (b) acidic (c) basic (d) basic (e) acidic (f) basic  
 (g) neutral (h) basic (i) basic (j) acidic
- F-2.** 9 **F-3.**  $K_b = 8 \times 10^{-10}$  **F-4.** 0.625%, pH = 7

### PART - II

- A-1.** (C) **A-2.** (D) **A-3.** (D) **A-4.** (C) **A-5.** (D)  
**B-1.** (D) **B-2.** (A) **B-3.** (D) **B-4.** (D) **C-1.** (B)  
**C-2.** (C) **D-1.** (C) **D-2.** (A) **D-3.** (C) **D-4.** (B)  
**D-5.** (B) **D-6.** (D) **D-7.** (D) **E-1.** (D) **E-2.** (D)  
**E-3.** (B) **F-1.** (A) **F-2.** (A) **F-3.** (B) **F-4.** (B)

### PART - III

1. (A)  $\rightarrow$  r; (B)  $\rightarrow$  s; (C)  $\rightarrow$  r; (D)  $\rightarrow$  p

## EXERCISE – 2

### PART - I

1. (B) 2. (D) 3. (C) 4. (B) 5. (C)  
 6. (C) 7. (B) 8. (A)





### PART - II

- |                      |                            |   |
|----------------------|----------------------------|---|
| 1. 4 (i, v, vi, vii) | 2. 5 (Actual answer = 9.7) | 3. $K_w = 4 \times 10^{-14}$ , pH = 6.7 |
| 4. 7                 | 5. 14                      | 6. 8                                    |
| 8. 9                 | 9. 50                      | 7. 30                                   |

### PART - III

- |          |          |          |          |          |
|----------|----------|----------|----------|----------|
| 1. (ABC) | 2. (AC)  | 3. (ABD) | 4. (ABD) | 5. (ABC) |
| 6. (BC)  | 7. (BCD) | 8. (AD)  |          |          |

### PART - IV

- |        |        |        |        |
|--------|--------|--------|--------|
| 1. (A) | 2. (D) | 3. (D) | 4. (A) |
|--------|--------|--------|--------|

## EXERCISE – 3

### JEE(MAIN) OFFLINE PROBLEMS

- |        |        |        |        |         |
|--------|--------|--------|--------|---------|
| 1. (4) | 2. (4) | 3. (4) | 4. (1) | 5. (2)  |
| 6. (1) | 7. (3) | 8. (4) | 9. (1) | 10. (4) |

### JEE(MAIN) ONLINE PROBLEMS

- |        |        |        |        |
|--------|--------|--------|--------|
| 1. (4) | 2. (2) | 3. (2) | 4. (2) |
|--------|--------|--------|--------|





## IONIC EQUILIBRIUM-II

### Exercise-1

**Note :** Take water as solvent and temperature as 25°C, if not specified.

Take  $\log 2 = 0.3$ ,  $\log 3 = 0.48$ ,  $\log 5 = 0.7$ ,  $\log 7 = 0.845$ , if not specified.

✎ Marked questions are recommended for Revision.

### PART - I : SUBJECTIVE QUESTIONS

#### Section (A) : Buffer Solutions : Definition and Identification

##### Commit to memory :

**Buffer Solutions :** Solution containing weak acid and its conjugate base, solution containing weak base and its conjugate acid, solution containing salt of weak acid and weak base.

##### Preparation :

- (i) Solution of weak acid (or weak base) + Solution of its conjugate base (or its conjugate acid)
- (ii) Solution of weak acid (or weak base) + Solution of strong base (or strong acid) ( $n_1 > n_2$ )
- (iii) Solution of salt of weak acid and strong base (or salt of weak base and strong acid) + Solution of strong acid (or strong base) ( $n_1 > n_2$ )

**A-1. ✎**  $V_1$  mL of a  $\text{CH}_3\text{COONa}$  solution (of molarity  $M_1$ ) and  $V_2$  mL of a  $\text{HCl}$  solution (of molarity  $M_2$ ) are available. Can the two be mixed to obtain a buffer solution? If yes, what should be the mathematical condition relating  $M_1$ ,  $M_2$ ,  $V_1$  &  $V_2$  for this?

**A-2. ✎** Select pair(s) of solutions from below which could be mixed to produce a buffer solution :  
 $\text{NH}_4\text{OH}$  solution ( $S_1$ ),  $(\text{NH}_4)_2\text{SO}_4$  solution ( $S_2$ ),  $\text{HCl}$  solution ( $S_3$ ),  $\text{KOH}$  solution ( $S_4$ ).

#### Section (B) : pH Calculation : Buffer solutions generated from Monobasic acid / Monoacidic base

##### Commit to memory :

pH Calculation : Buffer solutions generated from Monobasic acid / Monoacidic base :

- (i) pH of a buffer solution consisting of a weak acid ( $\text{HA}$  ;  $C_1$  concentration) and its salt with a strong base ( $\text{NaA}$  ;  $C_2$  concentration of anion) :  $\text{pH} = \text{pK}_a + \log \frac{[\text{Anion of Salt}]}{[\text{Acid}]}$
- (ii) pH of a buffer solution consisting of a weak base ( $\text{B}$  ;  $C_1$  concentration) and its salt with a strong acid ( $\text{BH}^+\text{Cl}^-$  ;  $C_2$  concentration of cation) :  $\text{pOH} = \text{pK}_b + \log \frac{[\text{Cation of Salt}]}{[\text{Base}]}$

**B-1.** Calculate pH of following solutions :

- (a) (4 g  $\text{CH}_3\text{COOH}$  + 4.1 g  $\text{CH}_3\text{COONa}$ ) in 100 mL aqueous solution ;  $K_a$  for  $\text{CH}_3\text{COOH} = 1.8 \times 10^{-5}$
- (b) 5 mL of 0.1 M  $\text{BOH}$  + 25 mL of 0.1 M  $\text{BCl}$  ;  $K_b$  for  $\text{BOH} = 1.8 \times 10^{-5}$

**B-2. ✎** 50 mL of 0.2 M solution of an acid  $\text{HA}$  ( $K_a = 10^{-5}$ ) & 50 mL of a  $\text{NaA}$  solution are given. What should be the concentration of  $\text{NaA}$  solution to make a buffer solution with  $\text{pH} = 4$  upon mixing the two?

**B-3.** Calculate the pH of 0.5 L of a 0.2 M  $\text{NH}_4\text{Cl}$  – 0.2 M  $\text{NH}_3$  buffer before and after addition of (a) 0.05 mole of  $\text{NaOH}$  and (b) 0.05 mole of  $\text{HCl}$ . Assume that the volume remains constant.  
 [Given :  $\text{pK}_b$  of  $\text{NH}_3 = 4.74$ ]



## PART - II : ONLY ONE OPTION CORRECT TYPE

### Section (A) : Buffer Solutions : Definition and Identification

#### Commit to memory :

**Buffer Solutions** : Solution containing weak acid and its conjugate base, solution containing weak base and its conjugate acid, solution containing salt of weak acid and weak base.

#### Preparation :

- (i) Solution of weak acid (or weak base) + Solution of its conjugate base (or its conjugate acid)
- (ii) Solution of weak acid (or weak base) + Solution of strong base (or strong acid) ( $n_1 > n_2$ )
- (iii) Solution of salt of weak acid and strong base (or salt of weak base and strong acid) + Solution of strong acid (or strong base) ( $n_1 > n_2$ )

- A-1.** A solution is 0.1 M in  $\text{CH}_3\text{COOH}$  and 0.1 M in  $\text{CH}_3\text{COONa}$ . Which of the following will change its pH significantly?  
 (A) Addition of small amount of water (B) Addition of small amount of HCl  
 (C) Addition of small amount of NaOH (D) None will change the pH significantly.
- A-2.** Which of the following may be added to one litre of water to act a buffer ?  
 (A) One mole of  $\text{CH}_3\text{COOH}$  and one mole of HCl  
 (B) One mole of  $\text{NH}_4\text{OH}$  and one mole of NaOH  
 (C) One mole of  $\text{NH}_4\text{Cl}$  and one mole of HCl  
 (D) One mole of  $\text{CH}_3\text{COOH}$  and 0.5 mole of NaOH
- A-3.** In which of the following respective volume ratios should 0.1 M  $\text{NH}_4\text{OH}$  solution & 0.1 M HCl solution be mixed, so that the resulting solution behaves like a buffer solution ?  
 (A) 1 : 1 (B) 2 : 1  
 (C) 1 : 2 (D) No such volume ratio is possible

### Section (B) : pH Calculation : Buffer solutions generated from Monobasic acid / Monoacidic base

#### Commit to memory :

pH Calculation : Buffer solutions generated from Monobasic acid / Monoacidic base :

- (i) pH of a buffer solution consisting of a weak acid ( $\text{HA}$  ;  $C_1$  concentration) and its salt with a strong base ( $\text{NaA}$  ;  $C_2$  concentration of anion) :  $\text{pH} = \text{pK}_a + \log \frac{[\text{Anion of Salt}]}{[\text{Acid}]}$
- (ii) pH of a buffer solution consisting of a weak base ( $\text{B}$  ;  $C_1$  concentration) and its salt with a strong acid ( $\text{BH}^+\text{Cl}^-$  ;  $C_2$  concentration of cation) :  $\text{pOH} = \text{pK}_b + \log \frac{[\text{Cation of Salt}]}{[\text{Base}]}$

- B-1.** Fear or excitement generally cause one to breathe rapidly and it results in the decrease of concentration of  $\text{CO}_2$  in blood. In what way, it will change pH of blood ?  
 (A) pH will significantly increase (B) pH will significantly decrease  
 (C) No significant change in pH (D) pH will be 7
- B-2.** pH of a mixture containing 0.1 M  $\text{X}^-$  and 0.2 M  $\text{HX}$  is : [ $\text{pK}_b(\text{X}^-) = 4$ ]  
 (A)  $4 + \log 2$  (B)  $4 - \log 2$  (C)  $10 + \log 2$  (D)  $10 - \log 2$
- B-3.**  $K_a$  for HCN is  $5 \times 10^{-10}$ . For maintaining a constant pH of 9, the volume of 5 M KCN solution required to be added to 10 mL of 2 M HCN solution is :  
 (A) 4 mL (B) 8 mL (C) 2 mL (D) 10 mL
- B-4.** A buffer solution made up of BOH and BCl of total molarity 0.29 M has pH = 9.6 and  $K_b = 1.8 \times 10^{-5}$ . Concentration of salt and base respectively is :  
 (A) 0.09 M and 0.2 M (B) 0.2 M and 0.09 M  
 (C) 0.1 M and 0.19 M (D) 0.19 M and 0.1 M



### PART - III : MATCH THE COLUMN

1. At the equivalence point of titration of (equivalence point = the point at which reaction is just complete) :
- |                                      |  |
|--------------------------------------|--|
| (A) a strong acid with a strong base | (p) $\text{pH} < 7$                                |
| (B) a weak acid with a strong base   | (q) $\text{pH} > 7$                                |
| (C) a weak base with a strong acid   | (r) $\text{pH} = 7$                                |
| (D) a weak acid with a weak base     | (s) $\text{pH}$ may be less than or greater than 7 |

## Exercise-2

Marked questions are recommended for Revision.

### PART - I : ONLY ONE OPTION CORRECT TYPE

1. To prepare a buffer of pH 8.26 amount of  $(\text{NH}_4)_2\text{SO}_4$  to be added to 500 mL of 0.01 M  $\text{NH}_4\text{OH}$  solution is : [ $\text{pK}_a(\text{NH}_4^+) = 9.26$ ]
- |               |                |
|---------------|----------------|
| (A) 0.05 mole | (B) 0.025 mole |
| (C) 0.10 mole | (D) 0.005 mole |
2. A weak acid (HA) after treatment with 12 mL of 0.1 M strong base (BOH) solution has a pH of 5. At the end point, the volume of same base solution required is 27 mL.  $K_a$  of acid is :
- |                          |                        |                          |                        |
|--------------------------|------------------------|--------------------------|------------------------|
| (A) $1.8 \times 10^{-5}$ | (B) $8 \times 10^{-6}$ | (C) $1.8 \times 10^{-6}$ | (D) $8 \times 10^{-5}$ |
|--------------------------|------------------------|--------------------------|------------------------|

### PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. How many of the following statement(s) is/are correct for making a buffer solution ?
- It can be formed by mixing equal concentrations of HCl and  $\text{CH}_3\text{COONa}$
  - It can be formed by mixing equal concentrations of  $\text{HNO}_3$  and  $\text{NH}_3$
  - It can be formed by mixing equal concentrations of  $\text{HCOOH}$  and Aniline.
  - It can be formed by mixing equal volumes of  $\text{NH}_4\text{OH}$  and  $\text{HClO}_4$ .
  - It can be formed by mixing equal volumes of HCN and KOH.
  - There is no change in the pH of a buffer solution on adding small amount of a strong acid/base.
  - The concentrations of acid and base being mixed must be different to form a buffer.
  - The volumes of acid and base being mixed must be different to form a buffer.
  - The concentrations and volumes of acid and base being mixed must be different to form a buffer.
2. 1 M benzoic acid ( $\text{pK}_a = 4.2$ ) and 1M  $\text{C}_6\text{H}_5\text{COONa}$  solutions are given separately. What is the volume of benzoic acid required to prepare a 93 mL buffer solution of  $\text{pH} = 4.5$  ?

### PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. A buffer solution can be prepared from a mixture of : [JEE-1999, 3/80]
- Sodium acetate and acetic acid in water
  - Sodium acetate and hydrochloric acid in water
  - Ammonia and ammonium chloride in water
  - Ammonia and sodium hydroxide in water

## Exercise-3

### JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

#### JEE(MAIN) OFFLINE PROBLEMS

1. The  $\text{pK}_a$  of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA, in which 50% of the acid is ionized, is : [AIEEE-2007, 3/120]
- |         |         |         |         |
|---------|---------|---------|---------|
| (1) 9.5 | (2) 7.0 | (3) 4.5 | (4) 2.5 |
|---------|---------|---------|---------|

**JEE(MAIN) ONLINE PROBLEMS**

1. In some solutions, the concentration of  $\text{H}_3\text{O}^+$  remains constant even when small amounts of strong acid or strong base are added to them. These solutions are known as :  
[JEE(Main) 2014 Online (11-04-14), 4/120]  
(1) Ideal solutions      (2) Colloideal solutins      (3) true solutions      (4) Buffer solutions
2. Addition of sodium hydroxide solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is  $10^{-5}$ , the ratio of salt to acid concentration in the buffer solution will be :  
[JEE(Main) 2017 Online (08-04-17), 4/120]  
(1) 10 : 1      (2) 4 : 5      (3) 1 : 10      (4) 5 : 4
3. 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M HCl . If  $\text{pK}_b$  of ammonia solution is 4.75, the pH of the mixture will be :  
[JEE(Main) 2017 Online (09-04-17), 4/120]  
(1) 4.75      (2) 3.75      (3) 9.25      (4) 8.25
4. 20 mL of 0.1 M  $\text{H}_2\text{SO}_4$  solution is added to 30 mL of 0.2 M  $\text{NH}_4\text{OH}$  solution. The pH of the resultant mixture is : ( $\text{pK}_b$  of  $\text{NH}_4\text{OH} = 4.7$ )  
[JEE(Main) 2019 Online (09-01-19), 4/120]  
(1) 9.0      (2) 5.2      (3) 9.4      (4) 5.0



# Answers

## EXERCISE – 1

### PART – I

**A-1.** Yes,  $M_1 V_1 > M_2 V_2$ .

**A-2.**  $S_1 \text{ \& } S_2$ ;  $S_1 \text{ \& } S_3$ ;  $S_2 \text{ \& } S_4$ .

**B-1.** (a) 4.62 (b) 8.56

**B-2.** 0.02 M

**B-3.** pH = 9.26 ; (a) pH = 9.74 ; (b) 8.78

### PART - II

**A-1.** (D)

**A-2.** (D)

**A-3.** (B)

**B-1.** (C)

**B-2.** (D)

**B-3.** (C)

**B-4.** (A)

### PART - III

1. (A)  $\rightarrow$  R; (B)  $\rightarrow$  Q; (C)  $\rightarrow$  P; (D)  $\rightarrow$  S

## EXERCISE – 2

### PART - I

1. (B)

2. (B)

### PART - II

1. 5 [(i) to (v)]

2. 31

### PART - III

1. (A) (B)(C)

## EXERCISE – 3

### JEE(MAIN) OFFLINE PROBLEMS

1. (1)

### JEE(MAIN) ONLINE PROBLEMS

1. (4)

2. (1)

3. (3)

4. (1)



## IONIC EQUILIBRIUM-III

### Exercise-1

✎ Marked questions are recommended for Revision.

### PART - I : SUBJECTIVE QUESTIONS

#### Section (A) : Solubility, Solubility product and Simple solubility calculations

##### Commit to memory :

Solubility ( $s$  ; in mol/L) of a sparingly soluble salt  $A_xB_y$  :  $K_{sp} = x^x \cdot y^y \cdot (s)^{x+y}$

- A-1.** If the solubility product of a salt  $MX$  is  $3 \times 10^{-10}$  at  $0^\circ\text{C}$ , determine its solubility.
- A-2.** A saturated solution of  $PbCl_2$  contains  $2 \times 10^{-3}$  mol of  $PbCl_2$  per litre. What is the  $K_{sp}$  of  $PbCl_2$  ?
- A-3.**  $K_{sp}$  at  $25^\circ\text{C}$  of  $AgCl$ ,  $AgBr$  and  $AgI$  are respectively  $3 \times 10^{-10}$ ,  $7.7 \times 10^{-13}$ ,  $1.5 \times 10^{-16}$ . Write decreasing order of solubility of these salts.
- A-4.** ✎ Write solubility product expression for  $Hg_2SO_4$ .

#### Section (B) : Condition for precipitation, Common ion effect on solubility

##### Commit to memory :

Condition for precipitation of  $A_xB_y$  : Ionic product or  $K_{IP} > K_{sp}$  ;  $[A^{y+}]^x [B^{x-}]^y > K_{sp}$  of  $A_xB_y$

Common ion effect on solubility : Solubility ( $s'$ ) of  $A_xB_y$  (sparingly soluble ;  $K_{sp}$ ) in a solution of ' $c$ ' M  $A_pD_q/E_rB_p$  (both readily soluble) :  $(pc)^x(ys')^y = K_{sp}$  ;  $s' = \dots$

- B-1.** ✎ Determine solubility of  $PbI_2$  in a 0.1 M solution of  $NaI$ . ( $K_{sp}$  of  $PbI_2 = 8 \times 10^{-9}$ )
- B-2.** ✎ Determine solubility of  $PbI_2$  in a 0.1 M solution of  $Pb(NO_3)_2$ . ( $K_{sp}$  of  $PbI_2 = 8 \times 10^{-9}$ )
- B-3.** At  $25^\circ\text{C}$ , the solubility of  $Ag_2CO_3$  ( $K_{sp} = 4.3 \times 10^{-13}$ ) would be in what order in the following solutions ?  
 (a) 0.01 M  $AgNO_3$       (b) 0.04 M  $K_2CO_3$       (c) pure water      (d) in a buffer ( $pH = 4$ )

### PART - II : ONLY ONE OPTION CORRECT TYPE

#### Section (A) : Solubility, Solubility product and Simple solubility calculations

##### Commit to memory :

Solubility ( $s$  ; in mol/L) of a sparingly soluble salt  $A_xB_y$  :  $K_{sp} = x^x \cdot y^y \cdot (s)^{x+y}$

- A-1.** ✎  $M(OH)_x$  (producing  $M^{x+}$  and  $OH^-$  ions) has  $K_{sp} 4 \times 10^{-12}$  and solubility  $10^{-4}$  M. The value of  $x$  is :  
 (A) 1      (B) 2      (C) 3      (D) 4
- A-2.** If the solubility of Lithium sodium hexafluoroaluminate,  $Li_3Na_3[AlF_6]_2$  is ' $s$ ' mol  $L^{-1}$ , its solubility product is: (Assume no ionisation of  $[AlF_6]^{3-}$ )  
 (A)  $18 s^3$       (B)  $186624 s^8$       (C)  $1458 s^8$       (D)  $2916 s^8$
- A-3.** Which of the following is most soluble in water ? Assume no reaction of cation/anion.  
 (A)  $MnS$  ( $K_{sp} = 2.5 \times 10^{-13}$ )      (B)  $ZnS$  ( $K_{sp} = 1.6 \times 10^{-24}$ )  
 (C)  $Bi_2S_3$  ( $K_{sp} = 1.6 \times 10^{-72}$ )      (D)  $Ag_2S$  ( $K_{sp} = 10^{-51}$ )
- A-4.** When different types of salts have nearly same solubility product constants  $K_{sp}$ , but less than one, the most soluble salt is that :  
 (A) Which produces maximum number of ions per formula unit  
 (B) Which produces minimum number of ions per formula unit  
 (C) Which produces ions with maximum charge  
 (D) Which produces ions with minimum charge



- A-5.** In a saturated solution of  $\text{Ag}_2\text{SO}_4$ , silver ion concentration is  $3 \times 10^{-2} \text{ M}$ . Its solubility product is : Assume no reaction of cation/anion.  
 (A)  $1.35 \times 10^{-5}$  (B)  $1.08 \times 10^{-4}$  (C)  $2.7 \times 10^{-5}$  (D)  $4.5 \times 10^{-4}$
- A-6.** The minimum volume of the water needed to dissolve 1 g of  $\text{BaSO}_4$  ( $K_{\text{sp}} = 10^{-10}$ ) is about: Assume no reaction of cation/anion. [Mol. mass ( $\text{BaSO}_4$ ) = 233 u]  
 (A)  $10^5$  litres (B) 430 litres (C) 43 litres (D) 4300 litres

### Section (B) : Condition for precipitation, Common ion effect on solubility

#### Commit to memory :

Condition for precipitation of  $\text{A}_x\text{B}_y$  : Ionic product or  $K_{\text{IP}} > K_{\text{sp}}$  ;  $[\text{A}^{y+}]^x [\text{B}^{x-}]^y > K_{\text{sp}}$  of  $\text{A}_x\text{B}_y$   
 Common ion effect on solubility : Solubility ( $s'$ ) of  $\text{A}_x\text{B}_y$  (sparingly soluble ;  $K_{\text{sp}}$ ) in a solution of 'c' M  $\text{A}_p\text{D}_q/\text{E}_r\text{B}_p$  (both readily soluble) :  $(pc)^x(ys')^y = K_{\text{sp}}$  ;  $s' = \dots$

- B-1.** The solubility product of  $\text{BaCrO}_4$  is  $2.4 \times 10^{-10} \text{ M}^2$ . The maximum concentration of  $\text{Ba}(\text{NO}_3)_2$  possible without precipitation in a  $6 \times 10^{-4} \text{ M}$   $\text{K}_2\text{CrO}_4$  solution is :  
 (A)  $4 \times 10^{-7} \text{ M}$  (B)  $1.44 \times 10^{-13} \text{ M}$  (C)  $2 \times 10^{-7} \text{ M}$  (D)  $2.5 \times 10^6 \text{ M}$
- B-2.** The solubility product of  $\text{AgCl}$  is  $1.8 \times 10^{-10}$ . Precipitation of  $\text{AgCl}$  will occur only when equal volumes of solutions of :  
 (A)  $2 \times 10^{-5} \text{ M}$   $\text{Ag}^+$  and  $2 \times 10^{-5} \text{ M}$   $\text{Cl}^-$  are mixed.  
 (B)  $10^{-7} \text{ M}$   $\text{Ag}^+$  and  $10^{-7} \text{ M}$   $\text{Cl}^-$  are mixed.  
 (C)  $10^{-5} \text{ M}$   $\text{Ag}^+$  and  $10^{-5} \text{ M}$   $\text{Cl}^-$  are mixed.  
 (D)  $10^{-4} \text{ M}$   $\text{Ag}^+$  and  $10^{-4} \text{ M}$   $\text{Cl}^-$  are mixed
- B-3.** The solubility of  $\text{CaF}_2$  ( $K_{\text{sp}} = 5.3 \times 10^{-9}$ ) in 0.1 M solution of  $\text{NaF}$  would be : Assume no reaction of cation/anion.  
 (A)  $5.3 \times 10^{-10} \text{ M}$  (B)  $5.3 \times 10^{-8} \text{ M}$  (C)  $5.3 \times 10^{-7} \text{ M}$  (D)  $5.3 \times 10^{-11} \text{ M}$
- B-4.** Let the solubilities of  $\text{AgCl}$  in pure water, 0.01 M  $\text{CaCl}_2$ , 0.01 M  $\text{NaCl}$  & 0.05 M  $\text{AgNO}_3$  be  $s_1$ ,  $s_2$ ,  $s_3$  &  $s_4$  respectively. What is the correct order of these quantities ? Neglect any complexation.  
 (A)  $s_1 > s_4 > s_3 > s_2$  (B)  $s_1 > s_2 = s_3 > s_4$  (C)  $s_1 > s_3 > s_2 > s_4$  (D)  $s_4 > s_2 > s_3 > s_1$
- B-5.** Solubility of  $\text{BaF}_2$  in a solution of  $\text{Ba}(\text{NO}_3)_2$  will be represented by which concentration term ? Assume no reaction of cation/anion.  
 (A)  $[\text{Ba}^{2+}]$  (B)  $[\text{F}^-]$  (C)  $[\text{F}^-]/2$  (D)  $2[]$

### PART - III : MATCH THE COLUMN

1. Match the correct  $K_{\text{sp}}$  expression in terms of solubility ( $s$ ) for given salts :  
 (Don't assume hydrolysis of any ion)

	Column-I		Column-II
(A)	$\text{Ca}_3(\text{PO}_4)_2$	(p)	$4s^3$
(B)	$\text{Hg}_2\text{I}_2$	(q)	$27s^4$
(C)	$\text{Cr}(\text{OH})_3$	(r)	$108s^5$
(D)	$\text{CaF}_2$	(s)	$16s^4$

## Exercise-2

Marked questions are recommended for Revision.

### PART - I : ONLY ONE OPTION CORRECT TYPE

1. Slaked lime,  $\text{Ca}(\text{OH})_2$  is used extensively in sewage treatment. What can be the maximum pH of  $\text{Ca}(\text{OH})_2$  (aq) ? (Take  $\log 11 = 1.04$ )  
 $\text{Ca}(\text{OH})_2(s) \rightleftharpoons \text{Ca}^{2+}(aq) + 2\text{OH}^-(aq)$  ;  $K_{\text{sp}} = 5.324 \times 10^{-6}$   
 (A) 12.04 (B) 12.34 (C) 10.68 (D) 14



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2. The solubility of  $\text{Ag}_2\text{CO}_3$  in water is  $1.26 \times 10^{-4}$  mole/litre. What is its solubility in  $0.02 \text{ M Na}_2\text{CO}_3$  solution? Assume no hydrolysis of  $\text{CO}_3^{2-}$  ion. (Take  $\sqrt[3]{2} = 1.26$ )  
 (A)  $5 \times 10^{-6} \text{ M}$  (B)  $\sqrt{50} \times 10^{-6} \text{ M}$  (C)  $10^{-5} \text{ M}$  (D)  $2 \times 10^{-5} \text{ M}$

## PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. How many of the following relations are correct for the solubility product ( $K_{\text{sp}}$ ) & solubility ( $s$  g/litre) of sparingly soluble salt  $\text{A}_3\text{B}_2$  (producing  $\text{A}^{2+}$  &  $\text{B}^{3-}$  ions; mol. wt.  $M$ ) in water? (Assume no hydrolysis of any ion).
1.  $K_{\text{sp}} = 108s^5$
  2.  $K_{\text{sp}} = \left[\frac{3s}{M}\right]^3 \left[\frac{2s}{M}\right]^2$
  3.  $K_{\text{sp}} = (3[\text{A}^{2+}])^3 (2[\text{B}^{3-}])^2$
  4.  $[\text{B}^{3-}] = \frac{2s}{M}$
  5.  $\frac{[\text{B}^{3-}]}{K_{\text{sp}}} = \frac{1}{54} \frac{M^4}{s^4}$
  6.  $[\text{A}^{2+}] = \left(\frac{K_{\text{sp}}}{[\text{B}^{3-}]^3}\right)^{1/2}$
  7.  $[\text{A}^{2+}]^3 M^5 = \frac{108s^5}{[\text{B}^{3-}]^2}$
  8.  $\frac{K_{\text{sp}}}{[\text{A}^{2+}]} = 36s^4$
  9.  $K_{\text{sp}} = [\text{A}^{2+}]^2 [\text{B}^{3-}]^3$
2.  $8 \times 10^{-6} \text{ M AgNO}_3$  solution is gradually added in  $1 \text{ L}$  of  $10^{-4} \text{ M KCl}$  solution. Upto what volume of  $\text{AgNO}_3$  solution being added (in  $\text{L}$ ), precipitation of  $\text{AgCl}$  will not take place? ( $K_{\text{sp}}$  of  $\text{AgCl} = 2 \times 10^{-10}$ )

## PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. The solubility of a sparingly soluble salt  $\text{A}_x\text{B}_y$  in water is  $1.4 \times 10^{-4} \text{ M}$ . The solubility product is  $1.1 \times 10^{-11}$ . The possibilities are :  
 (A)  $x = 1, y = 2$  (B)  $x = 2, y = 1$  (C)  $x = 1, y = 3$  (D)  $x = 3, y = 1$

## Exercise-3

### JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

1. The solubility of  $\text{Mg}(\text{OH})_2$  is  $s$  moles/litre. The solubility product under the same condition is :  
 (1)  $4s^3$  (2)  $3s^4$  (3)  $4s^2$  (4)  $s^3$  [AIEEE-2002, 3/225]
2. The solubility in water of a sparingly soluble salt  $\text{AB}_2$  is  $1.0 \times 10^{-5} \text{ mol L}^{-1}$ . Its solubility product will be :  
 (1)  $4 \times 10^{-15}$  (2)  $4 \times 10^{-10}$  (3)  $1 \times 10^{-15}$  (4)  $1 \times 10^{-10}$  [AIEEE-2003, 3/225]
3. The molar solubility (in  $\text{mol L}^{-1}$ ) of a sparingly soluble salt  $\text{MX}_4$  is  $s$ . The corresponding solubility product is  $K_{\text{sp}}$ .  $s$  is given in terms of  $K_{\text{sp}}$  by the relation :  
 (1)  $s = (K_{\text{sp}}/128)^{1/4}$  (2)  $s = (128K_{\text{sp}})^{1/4}$  (3)  $s = (256K_{\text{sp}})^{1/5}$  (4)  $s = (K_{\text{sp}}/256)^{1/5}$  [AIEEE-2004, 3/225]
4. The solubility product of a salt having general formula  $\text{MX}_2$ , in water is :  $4 \times 10^{-12}$ . The concentration of  $\text{M}^{2+}$  ions in the saturated aqueous solution of the salt is :  
 (1)  $2.0 \times 10^{-6} \text{ M}$  (2)  $1.0 \times 10^{-4} \text{ M}$  (3)  $1.6 \times 10^{-4} \text{ M}$  (4)  $4.0 \times 10^{-10} \text{ M}$  [AIEEE-2005, 3/225]
5. In a saturated solution of the sparingly soluble strong electrolyte  $\text{AgIO}_3$  (Molecular mass = 283), the equilibrium which sets in is :  
 $\text{AgIO}_3(\text{s}) \rightleftharpoons \text{Ag}^+(\text{aq}) + \text{IO}_3^-(\text{aq})$   
 If the solubility product constant  $K_{\text{sp}}$  of  $\text{AgIO}_3$  at a given temperature is  $1.0 \times 10^{-8}$ , what is the mass of  $\text{AgIO}_3$  contained in  $100 \text{ mL}$  of its saturated solution?  
 (1)  $1.0 \times 10^{-7} \text{ g}$  (2)  $1.0 \times 10^{-4} \text{ g}$  (3)  $28.3 \times 10^{-2} \text{ g}$  (4)  $2.83 \times 10^{-3} \text{ g}$  [AIEEE-2007, 3/120]
6. Solid  $\text{Ba}(\text{NO}_3)_2$  is gradually dissolved in  $1.0 \times 10^{-4} \text{ M Na}_2\text{CO}_3$  solution. At what concentration of  $\text{Ba}^{2+}$  will a precipitate begin to form? ( $K_{\text{sp}}$  for  $\text{BaCO}_3 = 5.1 \times 10^{-9}$ )  
 (1)  $5.1 \times 10^{-5} \text{ M}$  (2)  $8.1 \times 10^{-8} \text{ M}$  (3)  $8.1 \times 10^{-7} \text{ M}$  (4)  $4.1 \times 10^{-5} \text{ M}$  [AIEEE-2009, 4/144]



7. Solubility product of silver bromide is  $5.0 \times 10^{-13}$ . The quantity of potassium bromide (molar mass taken as  $120 \text{ g mol}^{-1}$ ) to be added to 1 litre of 0.05 M solution of silver nitrate to start the precipitation of AgBr is : **[AIEEE-2010, 4/144]**  
 (1)  $1.2 \times 10^{-10} \text{ g}$  (2)  $1.2 \times 10^{-9} \text{ g}$  (3)  $6.2 \times 10^{-5} \text{ g}$  (4)  $5.0 \times 10^{-8} \text{ g}$
8. At  $25^\circ\text{C}$ , the solubility product of  $\text{Mg}(\text{OH})_2$  is  $1.0 \times 10^{-11}$ . At what pH, will  $\text{Mg}^{2+}$  ions start precipitating in the form of  $\text{Mg}(\text{OH})_2$  from a solution of 0.001 M  $\text{Mg}^{2+}$  ions ? **[AIEEE-2010, 4/144]**  
 (1) 9 (2) 10 (3) 11 (4) 8
9. An aqueous solution contains an unknown concentration of  $\text{Ba}^{2+}$ . When 50 mL of a 1M solution of  $\text{Na}_2\text{SO}_4$  is added,  $\text{BaSO}_4$  just begins to precipitate. The final volume is 500 mL. The solubility product of  $\text{BaSO}_4$  is  $1 \times 10^{-10}$ . What is the original concentration of  $\text{Ba}^{2+}$ . **[JEE(Main) 2018, 4/120]**  
 (1)  $1.1 \times 10^{-9} \text{ M}$  (2)  $1.0 \times 10^{-10} \text{ M}$  (3)  $5 \times 10^{-9} \text{ M}$  (4)  $2 \times 10^{-9} \text{ M}$

### JEE(Main) ONLINE PROBLEMS

1. Zirconium phosphate  $[\text{Zr}_3(\text{PO}_4)_4]$  dissociates into three zirconium cations of charge +4 and four phosphate anions of charge -3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by  $K_{\text{sp}}$  then which of the following relationship between S and  $K_{\text{sp}}$  is correct ? **[JEE(Main) 2014 Online (19-04-14), 4/120]**  
 (1)  $S = \{K_{\text{sp}} / (6912)^{1/7}\}$  (2)  $S = \{K_{\text{sp}} / 144\}^{1/7}$  (3)  $S = (K_{\text{sp}} / 6912)^{1/7}$  (4)  $S = \{K_{\text{sp}} / 6912\}^7$
2. The minimum volume of water required to dissolve 0.1 g lead(II) chloride to get a saturated solution ( $K_{\text{sp}}$  of  $\text{PbCl}_2 = 3.2 \times 10^{-8}$ ; atomic mass of Pb = 207 u) is : **[JEE(Main) 2018 Online (15-04-18), 4/120]**  
 (1) 1.798 L (2) 0.36 L (3) 17.98 L (4) 0.18 L
3. A mixture of 100 m mol of  $\text{Ca}(\text{OH})_2$  and 2 g of sodium sulphate was dissolved in water and the volume was made up to 100 mL. The mass of calcium sulphate formed and the concentration of  $\text{OH}^-$  in resulting solution, respectively, are : (Molar mass of  $\text{Ca}(\text{OH})_2$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{CaSO}_4$  are 74, 143 and 136  $\text{g mol}^{-1}$ , respectively;  $K_{\text{sp}}$  of  $\text{Ca}(\text{OH})_2$  is  $5.5 \times 10^{-6}$ ) **[JEE(Main) 2019 Online (10-01-19), 4/120]**  
 (1) 13.6 g,  $0.14 \text{ mol L}^{-1}$  (2) 13.6 g,  $0.28 \text{ mol L}^{-1}$   
 (3) 1.9 g,  $0.28 \text{ mol L}^{-1}$  (4) 1.9 g,  $0.14 \text{ mol L}^{-1}$
4. If  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CO}_3$  is  $8 \times 10^{-12}$ , the molar solubility of  $\text{Ag}_2\text{CO}_3$  in 0.1 M  $\text{AgNO}_3$  is : **[JEE(Main) 2019 Online (12-01-19), 4/120]**  
 (1)  $8 \times 10^{-10} \text{ M}$  (2)  $8 \times 10^{-12} \text{ M}$  (3)  $8 \times 10^{-13} \text{ M}$  (4)  $8 \times 10^{-11} \text{ M}$



# Answers

## EXERCISE - 1

### PART - I

A-1.  $1.73 \times 10^{-5} \text{ mol/L}$ A-2.  $3.2 \times 10^{-8}$ A-3.  $\text{AgCl} > \text{AgBr} > \text{AgI}$ A-4.  $[\text{Hg}_2^{2+}][\text{SO}_4^{2-}]$ B-1.  $8 \times 10^{-7} \text{ M}$ B-2.  $1.414 \times 10^{-4} \text{ M}$ 

B-3. (d) &gt; (c) &gt; (b) &gt; (a)

### PART - II

A-1. (B)

A-2. (D)

A-3. (A)

A-4. (A)

A-5. (A)

A-6. (B)

B-1. (A)

B-2. (D)

B-3. (C)

B-4. (C)

B-5. (C)

### PART - III

1.  $(A \rightarrow r) ; (B \rightarrow p) ; (C \rightarrow q) ; (D \rightarrow p)$ 

## EXERCISE - 2

### PART - I

1. (B)

2. (C)

### PART - II

1. 4 (2, 4, 5 and 7)

2. 1

### PART - III

1. (A) B

## EXERCISE - 3

### JEE(MAIN) OFFLINE PROBLEMS

1. (1)

2. (1)

3. (4)

4. (2)

5. (4)

6. (1)

7. (2)

8. (2)

9. (1)

### JEE(MAIN) ONLINE PROBLEMS

1. (3)

2. (4)

3. (3)

4. (1)