

# IONIC EQUILIBRIUM

## OSTWALD DILUTION LAW :

- Dissociation constant of weak acid ( $K_a$ ),

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[C\alpha][C\alpha]}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha}$$

If  $\alpha \ll 1$ , then  $1 - \alpha \cong 1$  or  $K_a = C\alpha^2$  or  $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{K_a \times V}$

- Similarly for a weak base,  $\alpha = \sqrt{\frac{K_b}{C}}$ . Higher the value of  $K_a / K_b$ , strong is the acid / base.

## Acidity and pH scale :

- ∴  $pH = -\log a_{H^+}$  (where  $a_{H^+}$  is the activity of  $H^+$  ions = molar concentration for dilute solution).

**[Note : pH can also be negative or > 14]**

$$\begin{aligned} pH &= -\log [H^+] ; & [H^+] &= 10^{-pH} \\ pOH &= -\log [OH^-] ; & [OH^-] &= 10^{-pOH} \\ pKa &= -\log Ka ; & Ka &= 10^{-pKa} \\ pKb &= -\log Kb ; & Kb &= 10^{-pKb} \end{aligned}$$

## PROPERTIES OF WATER :

1. In pure water  $[H^+] = [OH^-]$  so it is Neutral.
2. Molar concentration / Molarity of water = 55.56 M.
3. Ionic product of water ( $K_w$ ) :

$K_w = [H^+][OH^-] = 10^{-14}$  at 25° (experimentally)

$$\begin{aligned} pH = 7 = pOH &\Rightarrow \text{neutral} \\ pH < 7 \text{ or } pOH > 7 &\Rightarrow \text{acidic} \\ pH > 7 \text{ or } pOH < 7 &\Rightarrow \text{Basic} \end{aligned}$$

4. Degree of dissociation of water :

$$\alpha = \frac{\text{no. of moles dissociated}}{\text{Total No. of moles initially taken}} = \frac{10^{-7}}{55.55} = 18 \times 10^{-10} \text{ or } 1.8 \times 10^{-7}\%$$

5. Absolute dissociation constant of water :

$$K_a = K_b = \frac{[H^+][OH^-]}{[H_2O]} = \frac{10^{-7} \times 10^{-7}}{55.55} = 1.8 \times 10^{-16}$$

$$pK_a = pK_b = -\log (1.8 \times 10^{-16}) = 16 - \log 1.8 = 15.74$$

$$K_a \times K_b = [H^+] [OH^-] = K_w$$

⇒ **Note: for a conjugate acid- base pairs**

$$pK_a + pK_b = pK_w = 14 \quad \text{at } 25^\circ\text{C.}$$

$$pK_a \text{ of } H_3O^+ \text{ ions} = -1.74$$

$$pK_b \text{ of } OH^- \text{ ions} = -1.74.$$

## ○ pH Calculations of Different Types of Solutions:

### (a) Strong acid solution :

(i) If concentration is greater than  $10^{-6}$  M

In this case  $H^+$  ions coming from water can be neglected,

(ii) If concentration is less than  $10^{-6}$  M

In this case  $H^+$  ions coming from water cannot be neglected

### (b) Strong base solution :

Using similar method as in part (a) calculate first  $[OH^-]$  and then use  $[H^+] \times [OH^-] = 10^{-14}$

### (c) pH of mixture of two strong acids :

Number of  $H^+$  ions from I-solution =  $N_1V_1$

Number of  $H^+$  ions from II-solution =  $N_2V_2$

$$[H^+] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

### (d) pH of mixture of two strong bases :

$$[OH^-] = N = \frac{N_1V_1 + N_2V_2}{V_1 + V_2}$$

### (e) pH of mixture of a strong acid and a strong base :

If  $N_1V_1 > N_2V_2$ , then solution will be acidic in nature and

$$[H^+] = N = \frac{N_1V_1 - N_2V_2}{V_1 + V_2}$$

If  $N_2V_2 > N_1V_1$ , then solution will be basic in nature and

$$[OH^-] = N = \frac{N_2V_2 - N_1V_1}{V_1 + V_2}$$

### (f) pH of a weak acid(monoprotic) solution :

$$K_a = \frac{[H^+] [OH^-]}{[HA]} = \frac{C\alpha^2}{1-\alpha}$$

$$\text{if } \alpha \ll 1 \Rightarrow (1 - \alpha) \approx 1 \quad \Rightarrow \quad K_a \approx C\alpha^2$$

$$\Rightarrow \alpha = \sqrt{\frac{K_a}{C}} \quad (\text{is valid if } \alpha < 0.1 \text{ or } 10\%)$$

On increasing the dilution  
 $\Rightarrow C \downarrow \Rightarrow \alpha \uparrow$  and  $[H^+] \downarrow \Rightarrow \text{pH} \uparrow$

### RELATIVE STRENGTH OF TWO ACIDS :

$$\frac{[H^+] \text{ furnished by I acid}}{[H^+] \text{ furnished by II acid}} = \frac{c_1 \alpha_1}{c_2 \alpha_2} = \sqrt{\frac{k_{a_1} c_1}{k_{a_2} c_2}}$$

### ○ SALT HYDROLYSIS :

Salt of	Type of hydrolysis	$k_h$	h	pH
(a) weak acid & strong base	anionic	$\frac{k_w}{k_a}$	$\sqrt{\frac{k_w}{k_a c}}$	$7 + \frac{1}{2} \text{p}k_a + \frac{1}{2} \log c$
(b) strong acid & weak base	cationic	$\frac{k_w}{k_b}$	$\sqrt{\frac{k_w}{k_b c}}$	$7 - \frac{1}{2} \text{p}k_b - \frac{1}{2} \log c$
(c) weak acid & weak base	both	$\frac{k_w}{k_a k_b}$	$\sqrt{\frac{k_w}{k_a k_b}}$	$7 + \frac{1}{2} \text{p}k_a - \frac{1}{2} \text{p}k_b$
(d) Strong acid & strong base	-----do not hydrolysed-----			pH = 7

### Hydrolysis of polyvalent anions or cations

For  $[\text{Na}_3\text{PO}_4] = C$ .

$$K_{a_1} \times K_{h_3} = K_w$$

$$K_{a_1} \times K_{h_2} = K_w$$

$$K_{a_3} \times K_{h_1} = K_w$$

Generally pH is calculated only using the first step Hydrolysis

$$K_{h_1} = \frac{Ch^2}{1-h} \approx Ch^2$$

$$h = \sqrt{\frac{K_{h_1}}{C}} \Rightarrow [\text{OH}^-] = ch = \sqrt{K_{h_1} \times C} \Rightarrow [\text{H}^+] = \sqrt{\frac{K_w \times K_{a_3}}{C}}$$

$$\text{So } \text{pH} = \frac{1}{2} [\text{p}K_w + \text{p}K_{a_3} + \log C]$$

## **BUFFER SOLUTION :**

**(a) Acidic Buffer :** e.g.  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COONa}$ . (weak acid and salt of its conjugate base).

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \text{[Henderson's equation]}$$

**(b) Basic Buffer :** e.g.  $\text{NH}_4\text{OH}$  +  $\text{NH}_4\text{Cl}$ . (weak base and salt of its conjugate acid).

$$\text{pOH} = \text{pK}_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$$

## **SOLUBILITY PRODUCT :**

$$K_{\text{sp}} = (\text{xs})^x (\text{ys})^y = \text{x}^x \cdot \text{y}^y \cdot (\text{s})^{x+y}$$

## **CONDITION FOR PRECIPITATION :**

If ionic product  $K_{\text{I.P.}} > K_{\text{SP}}$  precipitation occurs,

if  $K_{\text{I.P.}} = K_{\text{SP}}$  saturated solution (precipitation just begins or is just prevented).