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NAAC ACCREDITED ‘A’ GRADE

Topic: Ionic Equilibrium

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⇒ Relative strength of acids & bases:

→ Consider an acid HA which ionizes in aqueous medium as

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

The equilibrium constant

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$$

Since, $[H_2O]$ is practically a constant, its product with K gives a new constant.

$$K \times [H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$$

$$\Rightarrow K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

→ K_a is called the dissociation constant of an acid. Higher value of K_a means higher values for $[H_3O^+]$ and $[A^-]$ i.e. the acid dissociates to a greater extent or is a strong acid.

∴ Higher K_a means stronger acid.

$$pK_a = -\log K_a$$

Thus, higher pK_a means weaker acid.

→ For a base B, its aqueous dissociation can be written as

$$B + H_2O \rightleftharpoons BH^+ + OH^-$$

$$\therefore K = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

$$\therefore K \times [H_2O] = \text{constant} = K_b = \frac{[BH^+][OH^-]}{[B]}$$

Higher K_b means stronger base.
Higher pK_b means weaker base.

⇒ Buffer solutions:

→

Certain solutions posess the ability to resist an appreciable change in its pH i.e. $[H^+]$ when an acid or a base is added to it. this resistance of a solution is known as buffer action and these solutions of reserved acidity and ~~alkalit altt~~ alkalinity are known as buffer solutions.

→ Buffers consists of a weak acid or base with their corresponding salt.

e.g. NaOAc and AcOH
NH_4Cl and NH_4OH

→ pH of an acidic buffer:

Let a weak acid HA and its metal salt MA constitute an acidic buffer

Let, $[HA] = C_a$ and
$[MA] = C_s = [M^+] = [A^-]$

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

$$\Rightarrow K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

or, K_a simply represents $\frac{[H^+][A^-]}{[HA]}$

All the $[H^+]$ comes from the acid.
Now, total concentration of HA at equilibrium
= initial concentration of HA
− amount dissociated

ie. $[HA] = C_a - [H^+]$ .. ①

[We neglect any H^+ contribution by H_2O]

At the same time, the salt MA undergoes hydrolysis
as $MA \rightleftharpoons M^+ + A^-$.

∴ charge balance : total ⊕ = total ⊖

$$[A^-] = [H^+] + [A^-]$$

$$\Rightarrow [A^-] = [H^+] + C_s \quad \ldots ②$$

[Here we neglected the contribution of OH^- from H_2O]

$$\therefore K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+]\{C_s + [H^+]\}}{\{C_a - [H^+]\}}$$

$$\therefore [H^+] = K_a \times \left\{\frac{C_a - [H^+]}{C_s + [H^+]}\right\} \quad \dots ③$$

Compared to C_a and C_s, the $[H^+]$ is neglected since an acidic buffer dissociates to a very small extent due to common ion effect from $[A^-]$. $[A^-]$ is almost wholly contributed by the salt MA.

$$\therefore [H^+] = K_a \times \frac{C_a}{C_s}$$ [neglecting proton contribution by acid dissociation]

$$\therefore -\log [H^+] = -\log K_a - \log \frac{C_a}{C_s}$$

or, $$pH = pK_a + \log \frac{C_s}{C_a}$$

$$\Rightarrow \boxed{pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]}}$$

This is the Henderson-Hasselbalch equation depicting the pH of an acidic buffer.

→ For a basic buffer, the Henderson equation becomes

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

Also, $\boxed{pH + pOH = 14}$

→ Thus the pH of an acidic buffer depends on the ratio of concentrations of its salt and acid, and not on their individual concentrations.

Thus, on dilution the pH remains unchanged as the ratio of $[salt]/[acid]$ remains unchanged.

⇒ Buffer index:

Buffer capacity or buffer index indicates the change in the concentration of a buffer acid or base required to change its pH value by 1, ~~kep~~ keeping $(C_s + C_a)$ or $(C_s + C_b)$ constant.

i.e. $-\dfrac{\partial C_{HA}}{\partial (pH)}$ or $\dfrac{\partial C_B}{\partial (pH)}$

We know,

$$pH = pKa + \log\frac{[salt]}{[acid]}$$

Let, total amount of acid + salt = x.

and total amount of salt = s.

$$\therefore pH = pKa + \log\left(\frac{s}{x-s}\right)$$

$$= pKa + \frac{1}{2.303}\ln\left(\frac{s}{x-s}\right)$$

Differentiating w.r.t. s,

$$\frac{\partial pH}{\partial s} = \frac{1}{2.303}\left[\frac{1}{s} + \frac{1}{x-s}\right]$$

$$\Rightarrow \frac{\partial pH}{\partial s} = \frac{1}{2.303} \times \left\{\frac{x}{s(x-s)}\right\}$$

$$\Rightarrow \frac{\partial s}{\partial pH} = \frac{2.303\ s(x-s)}{x}$$

If 'a' is the amount of acid in solution, then,

total amount of acid + salt = x

$$\Rightarrow a + s = x.$$

$$\Rightarrow a = x - s.$$

$$\therefore \boxed{\frac{\partial s}{\partial pH} = 2.303\left[\frac{sa}{a+s}\right]}$$

⇒ Buffer index has a maximum value when $\frac{[\text{salt}]}{[\text{acid}]} = 1$.

i.e. $\log \frac{[\text{salt}]}{[\text{acid}]} = \log 1 = 0$.

$$\therefore \boxed{pH = pK_a}$$

Thus, for an acidic buffer, the solutions can be prepared at pH lying between ~~pH~~ $(pK_a - 1)$ to $(pK_a + 1)$ for maximum buffer effectiveness.

[When buffer index is maximum, $\frac{\partial s}{\partial pH}$ differential wrt ∂s is zero.

i.e. at maxima,

$$\frac{\partial}{\partial s}\left(\frac{\partial s}{\partial pH}\right) = 0$$

$$\Rightarrow \frac{\partial}{\partial s}\left[2.303 \times \frac{s(x-s)}{x}\right] = 0.$$

$$\Rightarrow \frac{\partial}{\partial s}\left[\frac{s(x-s)}{x}\right] = 0$$

$$\Rightarrow \frac{\partial}{\partial s}(sx - s^2) = 0$$

$$\Rightarrow x - 2s = 0$$

$$\Rightarrow x = 2s$$

$$\Rightarrow s = \frac{x}{2}.$$]

Putting $s = \frac{x}{2}$, we get

$$\frac{[\text{salt}]}{[\text{acid}]} = \frac{s}{x-s} = \frac{x/2}{x - x/2} = 1.$$

i.e. buffer capacity is maximum at this point.

e.g. AcOH has a pK_a of 4.75 at 25°C. Thus mixtures of acetic acid and sodium acetate can be used for preparing buffers in the pH range 3.75 - 5.75, where buffer capacity will be maximum.

e.g. Glycine and glycine hydrochloride has a pH range of 1.0 - 3.7.