pH & Buffer

- **Ionic Product of Water** **(K_W):**

  Water is weak electrolyte.

  $H_2O \rightleftharpoons H^+ + OH^-$

  $K = \frac{[H^+][OH^-]}{[H_2O]}$ $[H_2O] \approx$ const as H_2O is weak electrolyte

  So K. $[H_2O]$ = new const = $[H^+][OH^-]$

  This new const is ionic product (K_W) of water.

  i.e $K_W = [H^+][OH^-]$

The product of $[H^+]$ & $[OH^-]$ is constant at a particular temperature and it is called ionic product of water.

$K_W = 10^{-14}$ at 25°C; K_W changes only with temp.

- To convert $[H^+]$ of fractional data i.e. 10^{-1} (M) to 10^{-14} (M) into the integral values, $\ominus$ve logarithmic operation is done on the fractional (dilute) molar concentration of H^+ ions.
- $\ominus$ve logarithm is designated as “p”. pH is an abbreviation for "power of hydrogen" where "p" is short form the German word for power, ***potenz*** and H is the element symbol for hydrogen.

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

- $[H^+]$ is molarity : $10^{-1}, 10^{-2}, 10^{-3}$ .... $10^{-7}, 10^{-8}$ .... 10^{-14} M

  pH = – log$[H^+]$ = 1, 2, 3, ...$\boxed{7,}$ 8 14

  ⟵ acidic ↓ Neutral basic ⟶

  This pH scale is only at 25°C

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

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

  $pK_w = pH + pOH = 14$ [$pK_w = -\log 10^{-14} = 14$]

  i.e pH = pOH = 7 for water

- **Is it possible to have (-)ve pH of any solution?**

Ans. pH scale is used to convert fractional dilute concentrations into integral values but if it is applied on integral concentration, then pH may be $\ominus$ve or zero also

pH of 2 (M) HCl $\Rightarrow -\log 2 = \ominus$ve

1 (M) HCl $\Rightarrow -\log 1 = 0$

- **pH of boiled water < 7 is it acidic ?**

i) pH < 7 acidic ; pH > 7 alkaline & pH = 7 neutral - this scale is only at 25°C temp. So for boiled water i.e at 100°C temp. This scale is changed i.e. < 7 or > 7 pH may be neutral.

ii) $H^+ + OH^- \rightarrow H_2O$ - This acid-base neutralization reaction is always **exothermic** so dissociation of water into H^+ & OH^- must be **endothermic** in nature.

$H_2O \rightleftharpoons H^+ + OH^-$ (endo)

So under hot / boiled condition forward rate i.e. ionization of H_2O increases, so $[H^+]$ increases i.e. pH decreases but at the same time $[OH^-]$ also increases in the same ratio so it remains neutral.

- **pH of ice > 7 - is it alkaline ?**

same type answer

- **Calculation of pH of dilute mono basic strong acid.**

Ex. 10^{-2}(N) HCl, 10^{-2} (N) HCl $\equiv 10^{-2}$ (M)

As HCl is strong acid, $[HCl] = [H^+] = [Cl^-]$

i.e. $[H^+] = 10^{-2}(M)$

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

- **Calculation of pH of dilute poly basic strong acid.**

Ex. 10^{-2}(N) H_2SO_4

$$10^{-2}(N)\ H_2SO_4 = \frac{10^{-2}}{\text{basicity}} = \frac{10^{-2}}{2}\ (M)\ H_2SO_4$$

$$[H^+] = \cancel{2} \times \frac{10^{-2}}{\cancel{2}} = 10^{-2}(M)$$

$\therefore$ pH = 2

- **Calculation of pH of dilute mono acidic strong alkali**

Ex 10^{-2}(N) NaOH

10^{-2}(N) NaOH $\equiv 10^{-2}$(M) NaOH

$[OH^-] = 10^{-2}(M)$

So, $pOH = -\log 10^{-2} = 2$

Again pH + pOH = 14

So, pH = 14 − pOH = 14 − 2 = 12

- **Calculation of pH of dilute weak acid**

Ex 10^{-2}(N) CH_3COOH (20% dissociated)

$HA \rightleftharpoons H^+ + A^-$ c = molar concentration

$c(1-\alpha) \quad c\alpha \quad c\alpha$ α = degree of dissociation.

$$[H^+] = c\alpha = 10^{-2} \times \frac{20}{100}$$

$$pH = -\log(10^{-2} \times 0.2) = 2 - \log 0.2$$

Ex 10^{-2}(N) CH_3COOH (pKa = 4.76)

$HA \rightleftharpoons H^+ + A^-$ c = concentration of acid

$c(1-\alpha) \quad c\alpha \quad c\alpha$ α = degree of ionization for 1 mole HA

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{c\alpha \cdot \cancel{c}\alpha}{\cancel{c}(1-\alpha)} = \frac{c\alpha^2}{1-\alpha} \approx c\alpha^2 \qquad \alpha << 1$$

$$\alpha = \sqrt{\frac{Ka}{c}} \quad \ldots \text{(i)} \qquad 1 - \alpha \approx 1$$

$$[H^+] = c\alpha = c\sqrt{\frac{Ka}{c}} = \sqrt{K_a.c}$$

$$pH = -\log\sqrt{K_a.c} = -\frac{1}{2}\log K_a - \frac{1}{2}\log c$$

$$\boxed{pH = \frac{1}{2}\,pKa - \frac{1}{2}\log c}$$

$$pH = \frac{1}{2} \times 4.76 - \frac{1}{2}\log 10^{-2}$$

$$= \left(\frac{4.76}{2} + \frac{2}{2}\right) = 1 + \frac{4.76}{2}$$

- **Calculation pH of very dilute acid / alkali**

Ex 10^{-8}(N) HCl

It is too dilute, so $[H^+]$ from water should not be neglected

$$[H^+]_t = [H^+]_a + [H^+]_w$$

$$= 10^{-8} + 10^{-7}$$

$$= 10^{-7}(10^{-1} + 1) = 1.1 \times 10^{-7}$$

$$pH = -\log(10^{-7} \times 1.1) = 7 - \log 1.1 \approx 6.96$$

Ex 10^{-8} (N) NaOH $\equiv 10^{-8}$(M) NaOH

It is too dilute, so $[H^+]$ from water should not be neglected

$$[OH^-]_t = [OH^-]_b + [OH^-]_w$$

$$= (10^{-8} + 10^{-7}) = 10^{-7}(1.1)$$

$$pOH = 7 - \log 1.1 = 6.96$$

$$\therefore \quad pH = 14 - 6.96 = 7.04$$

Mixing Problems:

Q. Calculate the pH value of a solution obtained by mixing 50 ml of 0.2 (N) HCl with 50 ml of 0.1 (N) NaOH.

Ans. 50 ml 0.2 (N) HCl ≡ (50 x 0.2) = 10 ml 1 (N) acid
50 ml 0.1 (N) NaOH (50 x 0.1) = 5 ml 1 (N) base
So after mixing 5 ml 1 (M) acid remains in excess.
Total volume = 50 + 50 = 100 ml
∴ New resulting solution: 100 ml S (N) ≡ 5 ml 1 (N) acid

$$\therefore S = \frac{\cancel{5} \times 1}{\cancel{100}_{20}} = \frac{1}{20} \text{ (N) acidic reaction}$$

$$\text{So, } pH = -\log\frac{1}{20} = -\log 0.05 = 1.30$$

Q. What will be the pH of a solution obtained by mixing 800 ml of 0.05 (N) NaOH and 200 ml of 0.1 (N) HCl.

Ans. 800 ml 0.05 (N) NaOH ≡ (800 x 0.05) = 40 ml 1 (N) base
200 ml 0.1 (N) HCl ≡ (200 x 0.1) = 20 ml 1 (N) acid

i.e after mixing (40 – 20) = 20 cc 1 (M) base is in excess.
But total volume = (800 + 200) = 1000 ml

$$\therefore \quad 1000 \times S_{final} = 20 \times 1 \text{ (N)}$$

$$S_f = \frac{2\cancel{0}}{100\cancel{0}} = \frac{1}{50} \text{ (N)} = 0.02 \text{ (N)}$$

So $pOH = -\log 0.02$ i.e $pH = 14 - pOH = (14 + \log 0.02) = 12.3$

Q. How many moles of $Ca(OH)_2$ must be dissolved to produce 250 ml. of an aqueous solution of pH = 10.65 ?

Ans. pH = 10.65 so pOH = 14 – 10.65 = 3.35

$[OH^-]_{solution} = 10^{-3.35} = 10^{-14} \times 100.65$

$= 10^{-4} \times 4.466$

$= 4.466 \times 10^{-4}$ (M)

One molecule of $Ca(OH)_2$ produces 2 OH^- ions

i.e.1000 C.C. solution needs 2.235×10^{-4} (M) $Ca(OH)_2$ to produce pH = 10.65

250 C.C. solution needs $\frac{2.235}{4} \times 10^{-4} = 5.58 \times 10^{-5}$ moles

Q. The pH of 0.1 (M) HCN is 5.2. Calculate its K_a

Ans. $pH = \frac{1}{2} pK_a - \frac{1}{2}\log c$ $\quad$ $2 \times pH = pK_a - \log c$

$5.2 = \frac{1}{2} pK_a - ½ \log 10^{-1}$

$5.2 \times 2 = pK_a + 1$

$pK_a = 10.4 - 1 = 9.4$; $\quad$ $-\log K_a = 9.4$

K_a = anti log (– 9.4) $\quad$ $\log K_a = -9.4$

$K_a = 3.98 \times 10^{-10}$

Q. What is the [H+] of 0.1 (N) CH_3COOH ? Calculate pH ? $\quad$ $K_a = 1.8 \times 10^{-5}$

Ans. $\alpha = \sqrt{\frac{Ka}{c}} = \sqrt{\frac{1.8 \times 10^{-5}}{0.1}}$

$[H^+] = c\alpha = \sqrt{K_a.c} = \sqrt{1.8 \times 10^{-5} \times 0.1}$

$= \sqrt{1.8 \times 10^{-6}}$

$= 1.34 \times 10^{-3}$ M

$pH = -\log (1.34 \times 10^{-3}) = 3 - \log 1.34$

$= 2.87$

Q. 10 C.C. 10^{-2} (N) HCl is titrated by 10^{-2} (N) NaOH. Calculate pH at the following stages :

i) Before adding alkali

ii) 2 C.C. alkali is added

iii) 5 C.C. alkali is added

iv) 9 C.C. alkali is added

v) 9.9 C.C. alkali is added

vi) 10.0 C.C. alkali is added

vii) 10.1 C.C. alkali is added

Draw a plot of pH vs. volume of alkali & extend the idea for all sorts of acid-base titration & comment on the choice of indicator.

Ans. **i) Before adding alkali:**

10^{-2} (N) HCl ≡ 10^{-2} (M) HCl ≡ 10^{-2} (M) $H^{\oplus}$ [strong acid]

$\therefore pH = -\log 10^{-2} = 2$

ii) 2 C.C. alkali is added:

2 c.c. 10^{-2} (N) NaOH consumes 2 c.c. 10^{-2} (N) HCl

Remaining acid = 8 c.c. 1^{-2} (N) HCl

As the salt so formed is NaCl (SA + SB) it cannot change the pH of the medium so pH is due to HCl only

$$[\text{Acid}] = \frac{8 \times 10^{-2}}{12 \longrightarrow \text{Total volume}}$$

$$\text{pH} = -\log(\text{H}^{+}) = -\log \frac{\overset{2}{\cancel{8}} \times 10^{-2}}{\underset{3}{\cancel{12}}}$$

$$= 2 - \log \frac{2}{3} = 2.176$$

iii) 5 C.C. NaOH is added:

$$\text{pH} = -\log \frac{5 \times 10^{-2}}{15} = 2.477$$

iv) 9 C.C. NaOH is added :

$$\text{pH} = -\log \frac{1 \times 10^{-2}}{19} = 3.278$$

v) 9.9 C.C. NaOH is added :

$$\text{pH} = -\log \frac{0.1 \times 10^{-2}}{19.9} = 4.298$$

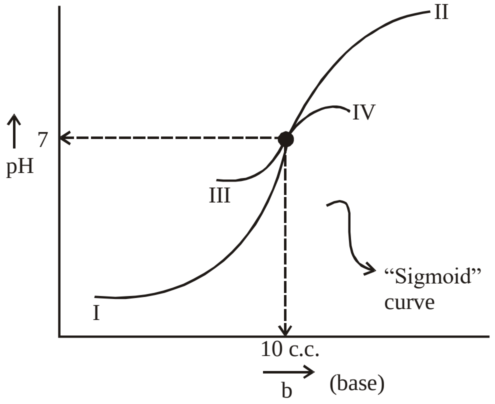
vi) 10 C.C. NaOH is added :

pH = 7 as total salt is NaCl which is salt of strong acid & strong base i.e. pH = 7

vii) 10.1 C.C. NaOH is added :

$$\text{pH} = 14 + \log \frac{0.1 \times 10^{-2}}{20.1} = 9.696$$

Plot



I – II → SA + SB
III – IV → WA + WB
I – IV → SA + WB
III – II → WA + SB

- That is for SA + SB pH group is maximum at the vicinity of end-pt.

Indicators are generally organic weak acids or base. Say, consider it is HIn. It ionizes as:

$$\text{HIn} \rightleftharpoons \text{H}^{+} + \text{In}^{-}$$

$K_{In} = [\text{H}^{+}]\,[\text{In}^{-}] / [\text{HIn}]$

$-\log K_{In} = -\log [\text{H+}] - \log [\text{In}^{-}] / [\text{HIn}]$

$pK_{In} = \text{pH} - \log [\text{In}^{-}] / [\text{HIn}]$

$\mathbf{pH = pK_{In} + \log [In^{-}] / [HIn]}$

Those indicators are accepted where the colour of molecular form and that of ionic form are different. There is a sensitivity factor for human eye to detect the change in colour over another. The concentration difference should be at least 10 times different to detect the change in colour.

If $[\text{In}^{-}] / [\text{HIn}] = 10$ → Colour of In^{-} is detected.

If $[\text{In}^{-}] / [\text{HIn}] = 1/10$ → Colour of HIn is detected.

So, to detect the visual change in colour by human eye the range of pH of an indicator will be

$pH = pK_{In} \pm \log 10$

$\mathbf{pH = pK_{In} \pm 1}$

If this range of pH resides within the range of pH at the vicinity of end point of titration, that indicator is chosen for that titration.

So, for SA-SB titration → any kind of indicator can be used because range of pH at the vicinity of end point is maximum.

For SA-WB titration → Indicator which ionizes in acid medium can be used like methyl orange.

For WA-SB titration → Indicator which ionizes in basic medium can be used like phenolphthalein

For WA-WB titration → No suitable Indicator is found.

Buffer Solution

Definition : A mixture of weak acid & its salt or weak base & its salt which can resist the change in pH by adding a little amount of acid or alkali is called acidic or alkaline buffer respectively.

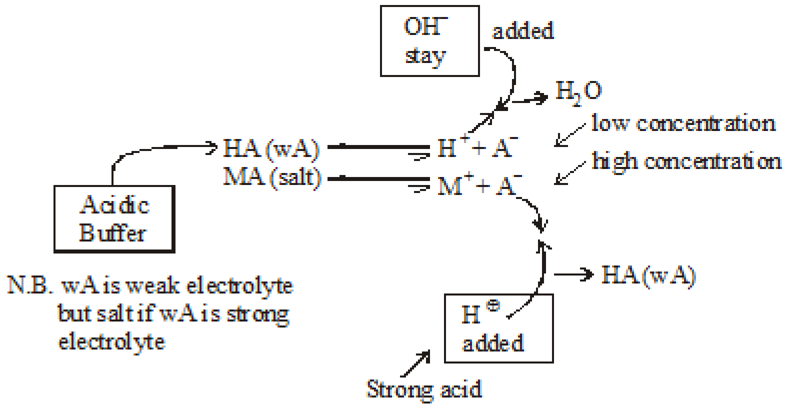
Ex. CH_3COOH (WA) + CH_3COONa ⟶ acidic buffer

NH_4OH (WB) + NH_4Cl ⟶ basic buffer

- **<u>Buffer action</u>:**

The mechanism by which a solution can resist the change in pH is called buffer action of that buffer.

Ex.



N.B. wA is weak electrolyte but salt if wA is strong electrolyte

I. After adding a few drop of S.A. it is internally converted into W.A. i.e. lowering of pH is not significant.

II. After adding a few drops of S.B it reacts with $H^{\oplus}$ from HA (WA) to form equivalent amount of H_2O (neutral). i.e. <u>to compensate the loss of $[H^+]$ molecular HA further ionizes i.e [HA] reduces</u> & again as H_2O is formed total volume also increases i.e. [MA] also decreases.

i.e $\frac{[MA]}{[HA]}$ <u>ratio remains almost unaltered</u>.

i.e $pH = pK_a + \log \frac{[Salt]}{[Acid]}$ equation tells us pH remains almost const.

⇒ the above two explanations tells us <u>acidic buffer</u> is a best buffer towards alkali and acidic buffer exhibits bad bufferial action towards acid.

- **Buffer Capacity:**

Definition: The amount of base (b) added to create unit change of pH is called buffer capacity (β) of that buffer.

$$\text{So, } \beta = \frac{db}{d(pH)}$$

Say, $d(pH) = 1$; $\beta = db$

Say, a cc S(N) weak acid is added with b c.c. S(N) strong base & a > b.

$$[\text{Salt}] = \frac{b \times s}{(a+b)};\ [\text{Acid}] = \frac{(a-b)\,s}{(a+b)}$$

By Henderson equation

$$pH = pK_a + \log\frac{[\text{Salt}]}{[\text{Acid}]} = pKa + \log\frac{b \times \cancel{s}\,\cancel{(a+b)}}{\cancel{(a+b)}\,(a-b)\,\cancel{s}}$$

$$pH = pK_a + \log\frac{b}{(a-b)}$$

$$pH = pK_a + 2.303 \ln\frac{b}{(a-b)} \qquad \ln = \log_e$$

$$\frac{d(pH)}{db} = 2.303\,\frac{\cancel{(a-b)}}{b}\left[\frac{\cancel{(a-b)}\,.\,1 + \cancel{b}}{(a-b)^{\cancel{2}}}\right]$$

$$\frac{d(pH)}{db} = 2.303\,\frac{a}{b(a-b)}$$

$$\boxed{\beta = \frac{db}{d(pH)}\ \frac{1}{2.303}\ \frac{b(a-b)}{a}}$$

$$\frac{d\beta}{db} = \frac{1}{2.303}\ .\ [\,b \times -1 + (a-b)\,.1]$$

$$\frac{d\beta}{db} = \frac{1}{2.303} = \frac{(a-2b)}{a}$$

$$\text{If } b = \frac{a}{2},\ \frac{d\beta}{db} = 0$$

$$\frac{d^2\beta}{db^2} = (-)\text{ ve i.e. } b = \frac{a}{2} \text{ it is the condition of maxima.}$$

Conclusion : β is maximum at $b = \frac{a}{2}$. i.e for any buffer, buffer capacity (β) is maximum at half neutralization point.

$$\text{So, } \beta_{max} = \frac{1}{2.303} \times \frac{a^2}{4.a} = \frac{1}{2.303}\ \frac{a}{4}$$

$$\boxed{\beta_{max} = \frac{1}{2.303}\ \frac{a}{4}}$$

Q1. 100 cc $\left(\frac{N}{10}\right)$ CH_3COOH + 50 cc $\left(\frac{N}{10}\right)$ NaOH ⇒ pH ? & comment on its Buffer capacity.

$$pH = 4.76 + \log\frac{\cancel{\dfrac{50 \times \frac{1}{10}}{150}}}{\cancel{\dfrac{50 \times \frac{1}{10}}{150}}}$$

$\boxed{pH = 4.76}$ max β