Ministry of Higher Education
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Lecture (3)

- Volumetric analysis.
- Definition of some terms.
- Neutralization Titrations.

Volumetric analysis:-

Volumetric(titrimetric) methods involve measuring the volume of a solution of known concentration that is needed to react essentially completely with the analyte.

Titimetric methods are classified into four groups based on the type of reaction involved:

- ✓ **Neutralization or acid-base titrations** (reaction between base and acid).
- ✓ **Complex formation titrations** (Ions or compounds combination to form stable-soluble slightly dissociated ions or compounds).
- ✓ **Precipitation titrations** (form a simple precipitate).
- ✓ **Oxidation–reduction titrations** (include all reactions involving change in oxidation number or transfer of electrons among the reaction substances).

Definition of some terms

- **Titration:** is a process in which a standard reagent is added to a solution of an analyte until the reaction between them is completed.

- **Standard solution:-** is a reagent of known concentration that is used to carry out a titrimetric analysis.

- The reagent of known concentration is called the "**titrant**" and the substance being titrated is termed the **"titrand".**

- **A primary standard:-** is an ultrapure compound that serves as the reference material for a titrimetric method of analysis, Example of primary standards for titration of acids are: sodium carbonate: $\mathbf{Na_2CO_3}$, Example of primary standards for titration of bases are: potassium hydrogen iodate: $\mathbf{KH(IO_3)_2}$

- **A secondary standard:** Is a standard that is prepared in the laboratory for a specific analysis. It is usually standardized against a primary standard.

Example of a secondary standard is the base **NaOH**. Commercially available NaOH contains impurities of NaCl, Na_2CO_3, and Na_2SO_4, and readily absorbs H_2O from the atmosphere.

- **Equivalence point:** Is the point where the volume of added titrant at which the number of moles of titrant is equal to the number of moles of analyte.
- **End point:** Is the point where the indicator changes color.

For example, suddenly change in a physical property of the solution or change the color.

- **Indicator:** Is a substance that undergoes a color change when a reaction approaches completion

- **Titration error:** The difference between the end point and the equivalence point (it must be very small).

Requirements for a primary standard

1. High purity.
2. Stability toward air.
3. Absence of hydrate water.
4. Ready availability at modest cost.
5. Reasonable solubility in the titration medium.
6. Reasonable large molar mass so that the relative error associated with weighing the standard is minimized.

Neutralization Titrations:-

- The standard solution employed in neutralization titrations are strong acids or strong bases because these substances react more completely with the analyte than do their weaker counterparts and thus yield sharper end points.
- Weak acids and bases never used as standard reagents because they react incompletely with analytes.

Notes:

Acids are species that are capable of donating protons to other species.

Bases are species that are capable of accepting protons from donor species.

- ✓ **Strong acids:** HNO_3, $HCLO_4$, H_2SO_4, HCl, HI, HBr, $HClO_3$, $HBrO_3$.
- ✓ **Weak acids:** H_2CO_3, H_3BO_3, H_3PO_4, H_2S, H_2SO_3 and most organic acid such as CH_3COOH, CH_3CH_2COOH, C_6H_5COOH.
- ✓ **Strong bases:** NaOH, KOH, $Ba(OH)_2$.
- ✓ **Weak bases:** NH_4OH, Na_2CO_3 and most organic bases.

❖ Volumetric Calculations for Acid-Base Titrations

a A + b B → product ; $R = \frac{b}{a}$

titrant titrand

At equivalent point:

no. mmol of titrant (A)=no. mmol of titrand (B)

$$R \times M_A \times V_A = M_B \times V_B \quad ; \quad M = \frac{wt}{M.wt} \times \frac{1000}{V(mL)}$$

❖

$$R \times M_A \times V_A = \frac{wt_B}{M.wt_B} \times 1000 \Longrightarrow wt_B = \frac{M.wt_B \times M_A \times V_A \times R}{1000}$$

no. meq of titrant (A)=no. meq of titrand (B)

$$N_A \times V_A = N_B \times V_B$$

$$N = \frac{wt}{eq.wt} \times \frac{1000}{V(mL)}$$

$$N_A \times V_A = \frac{wt_B}{eq.wt_B} \times 1000 \Longrightarrow wt_B = \frac{eq.wt_B \times N_A \times V_A}{1000}$$

$$\%\ (w/w)_B = \frac{wt_B}{\text{weight of sample}} \times 100$$

Note:

$$\text{no. mol} = M \times V \rightarrow V = \text{volume (L)}$$

$$= \text{mol } L^{-1} \times L = \text{mol}$$

$$\text{no. mmol} = M \times V \rightarrow V = \text{volume (mL)}$$

$$= \frac{mol}{L} \times \frac{1000\ mmol\ \ mol^{-1}}{1000\ ml\ L^{-1}} \times mL = mmol$$

Example 1:-

A solution of $Ba(OH)_2$ was standardized by titration against HCl (0.128 N). Exactly 31.76 mL of the base were required to neutralize 46.25 mL of the acid. What is the normality of the $Ba(OH)_2$ solution?

Solution:

no. meq of HCl =no. meq of $Ba(OH)_2$

$N_{HCl} \times V_{HCl} = N_{Ba(OH)2} \times V_{Ba(OH)2}$

$0.128 \times 46.25 = N_{Ba(OH)2} \times 31.76 \quad \rightarrow N_{Ba(OH)2} = 0.1864 \text{ eq } L^{-1}$

Example 2:-

What volume of H_2SO_4(5N) is required to neutralize a solution containing 2.5g of NaOH? M.wt $_{NaOH}$=40 g mol^{-1}

Solution:

$$N_{H2SO4} \times V_{H2SO4} = N_{NaOH} \times V_{NaOH}$$

$$N_{H2SO4} \times V_{H2SO4} = \frac{wt_{NaOH}}{eq.wt_{NaOH}} \times \frac{1000}{\cancel{V_{NaOH}}} \times \cancel{V_{NaOH}}$$

$$wt_{NaOH} = \frac{eq.wt_{NaOH} \times N_{H2SO4} \times V_{H2SO4}}{1000} \quad ; eq.wt_{NaOH} = \frac{40}{1} = 40 \text{ g eq}^{-1}$$

$$2.5 = \frac{40 \times 5 \times V_{H2SO4}}{1000} \quad \rightarrow \quad V_{H2SO4} = 12.5 \text{ mL.}$$

❖ Calculating the pH of strong acids and base solutions

Note:

$pH=-\log[H_3O^+]$, $pOH=-\log[OH^-]$, $pK_w=-\log[K_w]$

Ion-product constant of water $(K_w)=1\times10^{-14}$, $pK_w=14$

$pH + pOH= pK_w$, $pH=14-pOH$, $pOH=14-pH$

Example 3:-

Calculate the pH and pOH of 0.05M solution of HCl?

Solution:

$[H_3O^+]=0.05$, $pH= -\log[H_3O^+]$ $\rightarrow pH= -\log[0.05]=1.3$

$pOH=14-1.3=12.7$

Example 4:-

Calculate the pH and pOH of 3.2×10^{-4}M solution of $Ba(OH)_2$?

Solution:

$$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$$

$$[OH^-]=2\times3.2\times10^{-4} = 6.4\times10^{-4}\ M$$

$$pOH = -\log[6.4\times10^{-4}] \rightarrow pOH = 3.19$$

$$pH = 14 - 3.19 = 10.81$$

❖ Calculating the pH of weak acids and base solutions

1-Weak acid

$[H_3O^+]=\sqrt{K_a \times C_a}$, C_a=concentration of acid $\Longrightarrow$ $pH = \frac{1}{2}(pK_a - \log C_a)$

2-Weak base

$[OH^-]=\sqrt{K_b \times C_b}$, C_b=concentration of base $\Rightarrow$ $pOH = \frac{1}{2}(pK_b - \log C_b)$

pH=14-pOH

Example 5:-

Calculate the pH of 0.075 M solution of NH_3, $K_b=1.86\times10^{-5}$.

Solution:

$[OH^-]=\sqrt{K_b \times C_b}$ $\Rightarrow$ $= \sqrt{1.86 \times 10^{-5} \times 0.075}$

$[OH^-]=1.18\times10^{-3}$ M $\Rightarrow$ $pOH=-\log 1.18\times10^{-3}=2.93$ $\Rightarrow$ $pH=14-2.93=11.07$

Example 6:-

Calculate the ionization constant of acetic acid (0.06 M) at a specific temperature, if 1.7% of the acid solution is ionized.

Solution:

$$CH_3COOH \rightleftharpoons CH_3COO^- + H_3O^+$$

$$0.06 \qquad 0 \qquad 0$$

$$0.06-(\frac{1.7}{100}\times 0.06) \qquad (\frac{1.7}{100}\times 0.06) \qquad (\frac{1.7}{100}\times 0.06)$$

$$[CH_3COO^-]=[H_3O^+]=\frac{1.7}{100}\times 0.06 = 0.00102\ M$$

$$[CH_3COOH]= 0.06-(\frac{1.7}{100}\times 0.06)$$

$$[CH_3COOH]=0.06-0.00102=0.059M \quad \text{(remained)}$$

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = \frac{(0.00102)^2}{0.059} = 1.76\times 10^{-5}$$

❖ Titration of strong acid with strong base

In this titration, the titrant and analyte ionize completely since strong acid and strong base dissociate completely. For the reaction between HCl and NaOH, the reaction is as follows:

$$NaOH + HCl \leftrightarrow NaCl + H_2O$$

Example 7:-

Let us consider the titration of 50 ml of (0.1 M) HCl with 0.1 M NaOH solution: Calculate : pH after adding: 0,10,50,50.01ml of NaOH.

Solution:

1- To calculate pH after addition of 0 ml NaOH

pH = - log H+

pH= - log 0.1

= 1

2- To calculate pH after addition of 10 ml NaOH:

$$[H+]= \frac{\text{Initial no. mmol HCl} - \text{no.mmol NaOH added}}{\text{Total volume of solution}}$$

$$[HCl] \text{ remaining} = \frac{(50\times0.1)-(10\times0.1)}{\text{Vacis}+\text{Vbase}}$$

$$[HCl]= = \frac{4}{50+10}$$

$$pH= - \log (4/60)$$

$$= 1.18 \longleftarrow \text{acidic}$$

3- To calculate pH after addition of 50 ml of base:

Initial mmol H^+ = 50 mL× 0.1 mmol/mL =5 mmol

mmol OH^- added= 50 mL× 0.1 mmol/mL =5 mmol

	HCl	+ NaOH	↔ NaCl	+ H_2O
Initial (mmol)	5	5	0	0
Equilibrium (mmol)	0	0	5	5

At the equivalent point, neither HCl nor NaOH is in excess, so the concentrations of hydronium and hydroxide ions must be equal.

$[H^+] = [OH^-]$; $K_w = [H_3O^+] \times [OH^-]$ $\Longrightarrow$ $K_w = [H_3O^+]^2$

$[H^+] = \sqrt{K_w} = \sqrt{1 \times 10^{-14}} = 1 \times 10^{-7}$

pH= -log[H^+]= -log $1 \times 10^{-7} = 7$

4- To calculate pH after addition of 50.01 ml of NaOH:

The addition of 50.01 ml of NaOH produces a slight excess of base in the solution, we can obtain the pH from its concentration:

$$[OH^-] = \frac{\text{no. mmol NaOH added} - \text{Initial no. mmol HCl}}{\text{Total volume of solution}}$$

$$[OH\text{-}] = \frac{(55\times0.1)-(50\times0.1)}{50+55}$$

$$[OH^-] = \frac{0.5\text{ mmol}}{(55+50)\text{mL}} = 4.8\times10^{-3}\text{ M}$$

$$pOH = -\log[OH^-] = -\log 0.0333 = 2.32$$

$pH + pOH = pK_w$ $\qquad$ $pH = 14 - 2.32 = 11.68$

Thank you