

Chapter 25

# Theory of Electrolytic Dissociation

Cont.

1

## Solubility of sparingly soluble salts

- Water-insoluble substances as  $\text{AgCl}$  or  $\text{PbSO}_4$  still possess a definite solubility which can be determined from conductance measurements.



- Since a very small amount of solute is present it must be completely dissociated into ions even in a saturated solution so that the equivalent conductance ( $\Lambda = \kappa \times V_{cc}$ ) equals to equivalent conductance at infinite dilution ( $\Lambda_{\infty} = \lambda_{\infty}^+ + \lambda_{\infty}^-$ ).

$$\kappa \times V_{cc} = \Lambda_{\infty} = \lambda_{\infty}^+ + \lambda_{\infty}^- \text{ or } \lambda_c + \lambda_a$$

2

**Problem**

↓ The specific conductance of saturated solution of silver chloride at 18°C is  $1.24 \times 10^{-6}$  mhos  $\text{cm}^{-1}$  after subtracting that of water. The ionic conductivities at infinite dilution of  $\text{Ag}^+$  and  $\text{Cl}^-$  ions at this temperature are 53.8 and 65.3, respectively. Calculate the solubility of silver chloride in grams per litre?

**Solution**

$$\Lambda_{\infty}(\text{AgCl}) = \lambda_c(\text{Ag}^+) + \lambda_a(\text{Cl}^-)$$

$$= 53.8 + 65.3 = 119.1 \text{ S cm}^2 \text{ eqvt}^{-1}$$

$$\kappa = 1.24 \times 10^{-6} \text{ S cm}^{-1}$$

$$\kappa \times V_{cc} = \Lambda_{\infty}$$

$$V_{cc} = \frac{\Lambda_{\infty}}{\kappa} = \frac{119.1 \text{ S cm}^2 \text{ eqvt}^{-1}}{1.24 \times 10^{-6} \text{ S cm}^{-1}}$$

$$= 96 \times 10^6 \text{ cm}^3 \text{ eqvt}^{-1}$$

3

$$96 \times 10^6 \text{ cm}^3 \text{ eqvt}^{-1}$$

means



$96 \times 10^6 \text{ cm}^3$  solution contains 1 geqvt

$10^3 \text{ cm}^3 = 1\text{L}$  solution contains X geqvt

$$X = \frac{1 \text{ g eqvt}^{-1} \times 10^3 \text{ cm}^3}{96 \times 10^6 \text{ cm}^3} = 1.04 \times 10^{-5} \text{ geqvt}$$

**It means**

The no. of geqvt of AgCl in 1 L =

$$N = 1.04 \times 10^{-5} \text{ g eqvt L}^{-1}$$

$$\text{Eq. mass of AgCl} = 108 + 35.5 = 143.5 \text{ g /geqvt}$$

$$S = 1.04 \times 10^{-5} \frac{\text{geqvt}}{\text{L}} \times \frac{143.5 \text{ g}}{\text{geqvt}} = 1.49 \times 10^{-3} \text{ g L}^{-1}$$

4

### Degree of Dissociation, $\alpha$ Conductance Ratio

$$\alpha = \frac{\Lambda_V}{\Lambda_\infty} = \frac{\Lambda}{\lambda_c + \lambda_a}$$

$\Lambda_V$  (simply  $\Lambda$ ): Electrolyte's equivalent conductance at a dilution  $V$

**Problem**

✦ The conductance at infinite dilution of silver ion at  $18^\circ$  is 55.7 and of the nitrate ion 60.8. If the specific conductance of  $\text{AgNO}_3$  in a decinormal solution at  $18^\circ$  is  $0.00947 \text{ S cm}^{-1}$ , what will be the percentage of dissociation of the salt at this concentration?

**Solution**

$$\Lambda = \kappa \times V_{cc} = 9.47 \times 10^{-3} \frac{\text{S}}{\text{cm}} \times \frac{10000 \text{ cm}^3}{\text{eqvt}} = 94.7 \text{ S cm}^2 \text{ eqvt}^{-1}$$

5

$$\begin{aligned} \Lambda_\infty(\text{AgNO}_3) &= \lambda_c(\text{Ag}^+) + \lambda_a(\text{NO}_3^-) \\ &= 55.7 + 60.8 = 116.5 \text{ S cm}^2 \text{ eqvt}^{-1} \end{aligned}$$

$$\alpha = \frac{\Lambda}{\Lambda_\infty} = \frac{94.7 \text{ S cm}^2 \text{ eqvt}^{-1}}{116.5 \text{ S cm}^2 \text{ eqvt}^{-1}} = 0.8128$$

✦ Hence the salt is 81.28% dissociated

6

## Ionic product for Water

✚ The observed specific conductance of the purest water at 25°C is  $5.54 \times 10^{-8} \text{ S cm}^{-1}$ .

✚ The conductance of 1L of water containing 1 geqvt of it would be :

$$\begin{aligned}\Lambda &= \kappa \times V_{cc} = 5.54 \times 10^{-8} \frac{\text{S}}{\text{cm}} \times \frac{1000 \text{ cm}^3}{\text{eqvt}} \\ &= 5.54 \times 10^{-5} \text{ S cm}^2 \text{ eqvt}^{-1}\end{aligned}$$

✚ At the same temperature

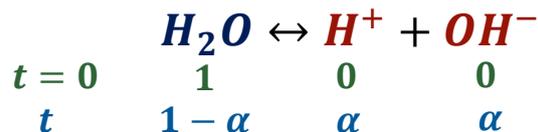
$$\lambda_c(\text{H}^+) = 349.8 \text{ S cm}^2 \text{ eqvt}^{-1}$$

$$\lambda_a(\text{OH}^-) = 198.5 \text{ S cm}^2 \text{ eqvt}^{-1}$$

$$\Lambda_{\infty}(\text{H}_2\text{O}) = \lambda_c(\text{H}^+) + \lambda_a(\text{OH}^-) = 548.3 \text{ S cm}^2 \text{ eqvt}^{-1}$$

7

## Considering this equilibrium



✚ One may realize that the ionic  $[\text{H}^+]$  and  $[\text{OH}^-]$  concentrations are proportional to conductance.

$$\begin{aligned}[\text{H}^+] &= [\text{OH}^-] = \alpha = \frac{\Lambda}{\Lambda_{\infty}} \\ &= \frac{5.54 \times 10^{-5} \text{ S cm}^2 \text{ eqvt}^{-1}}{548.3 \text{ S cm}^2 \text{ eqvt}^{-1}} = 1.01 \times 10^{-7}\end{aligned}$$

$$\begin{aligned}K_w &= [\text{H}^+] \times [\text{OH}^-] = \alpha^2 \\ &= (1.01 \times 10^{-7})^2 = 1.02 \times 10^{-14}\end{aligned}$$

8

## CONDUCTOMETRIC TITRATIONS

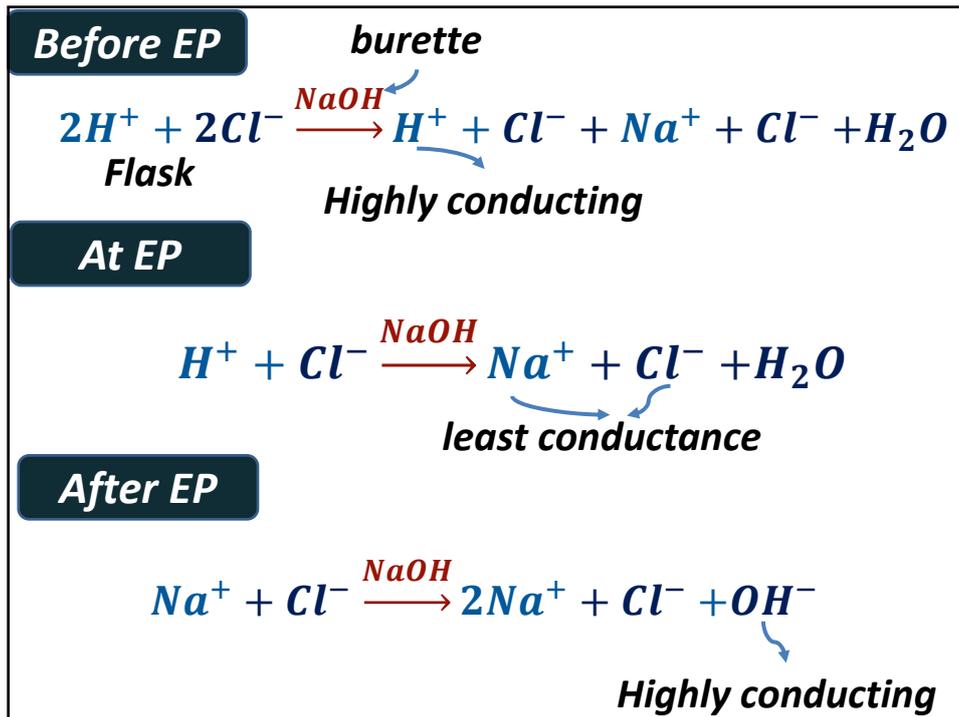
- ✚ Conductance measurements determines the **end-point** of **acid-alkali**, some **displacement** or **precipitation** reactions.
- ✚ The conductance of a solution at a constant temperature depends upon the **number of solution's ions** and their **mobility**.
- ✚ Two linear curves are obtained before and after the **end-point** (point of intersection).
- ✚ Several phenomena like **hydrolysis** of reactants or products or **partial solubility** of a precipitated product give rise to a **curvature** in the curves

9

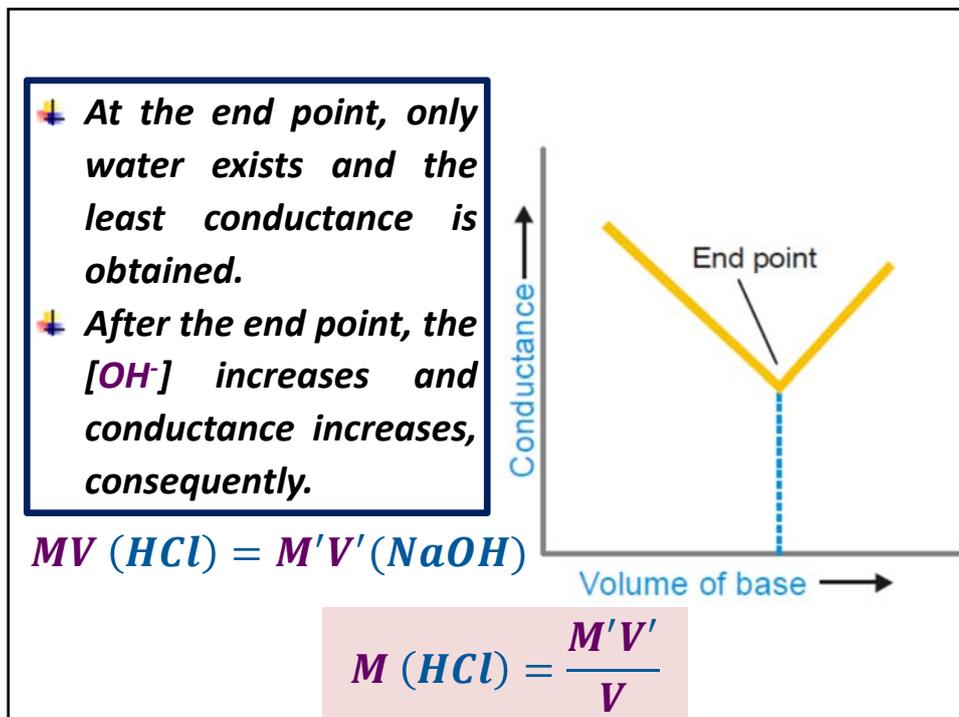
## A Strong acid against a Strong base

- ✚ Titrate **20 mL HCl** unknown solution (in a thermostatic conductance cell) against **0.1 M NaOH** (**1 mL** each addition from a burette)
- ✚ Mix perfectly after each addition and measure the conductance of the solution.
- ✚ Plot the conductance of the solution against the volume of the alkali added.
- ✚ Before adding **NaOH**, the conductance of the solution is due to presence of **H<sup>+</sup>** (having the **ever greatest mobility**) and **Cl<sup>-</sup>** ions.
- ✚ By adding **NaOH**, **[H<sup>+</sup>]** and conductance decrease.

10



11



12

### Important

- ✚ In order to get accurate results, the volume change (dilution: influence ions association for strong electrolytes or degree of dissociation for weak electrolytes) during titration should be as little as possible.
- ✚ The titrant (burette) should, therefore, be about 10 times as strong as the acid solution in the conductance cell or, otherwise, a correction is required.

$$\text{Actual conductance} = \frac{v(\text{added NaOH}) + V(\text{HCl})}{V(\text{HCl})} \times \text{observed conductance}$$

13

### A Weak acid against a Strong base

- ✚ If acetic acid is titrated against NaOH, the initial conductance of CH<sub>3</sub>COOH is low because of CH<sub>3</sub>COOH poor dissociation (CH<sub>3</sub>COOH ↔ H<sup>+</sup> + CH<sub>3</sub>COO<sup>-</sup>).
- ✚ On adding NaOH, highly ionized CH<sub>3</sub>COONa is formed.



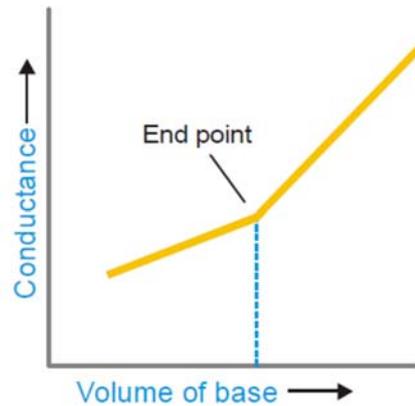
- ✚ The CH<sub>3</sub>COO<sup>-</sup> ions at first tend to suppress the ionization of CH<sub>3</sub>COOH (Common Ion Effect) but after a while the conductance begins to increase because the conducting power of highly ionized salt exceeds that of the weak acid.

14

✚ Immediately after the end point,



✚ Further addition of **NaOH** releases the fast moving  $\text{OH}^-$  ions. Thus, the conductance increases sharply.



15

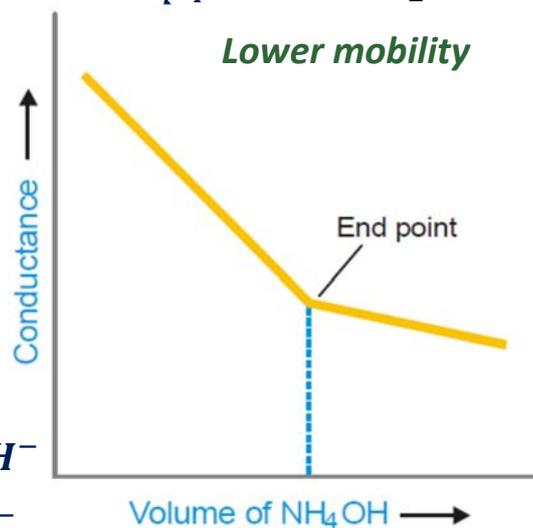
### A strong acid against a weak base



Higher mobility

Lower mobility

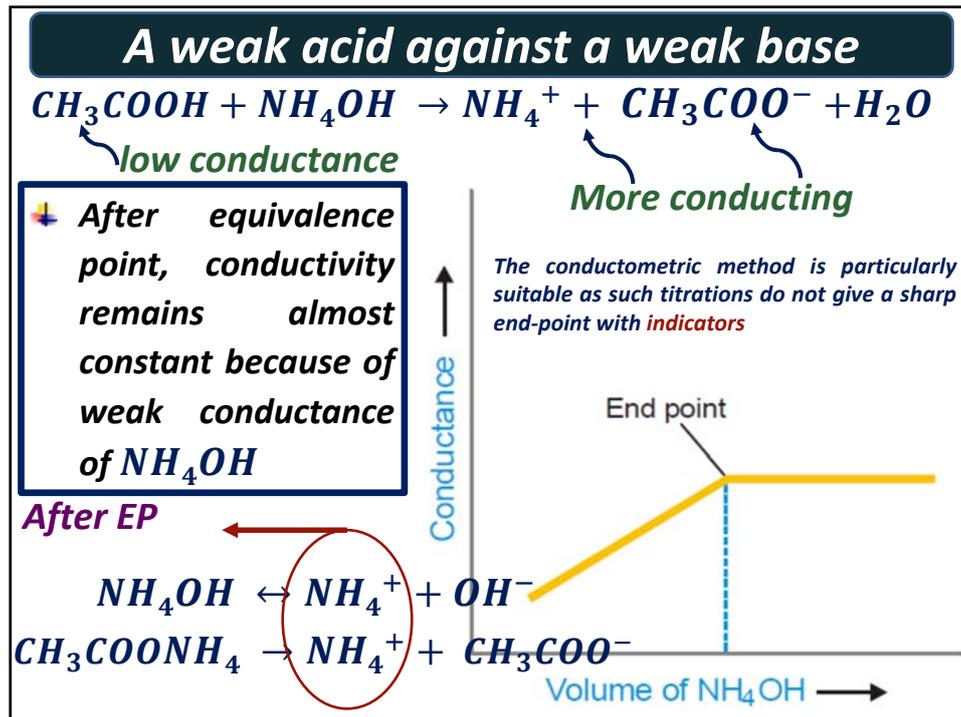
✚ the conductance of the solution will first decrease due to the fixing up of the fast moving  $\text{H}^+$



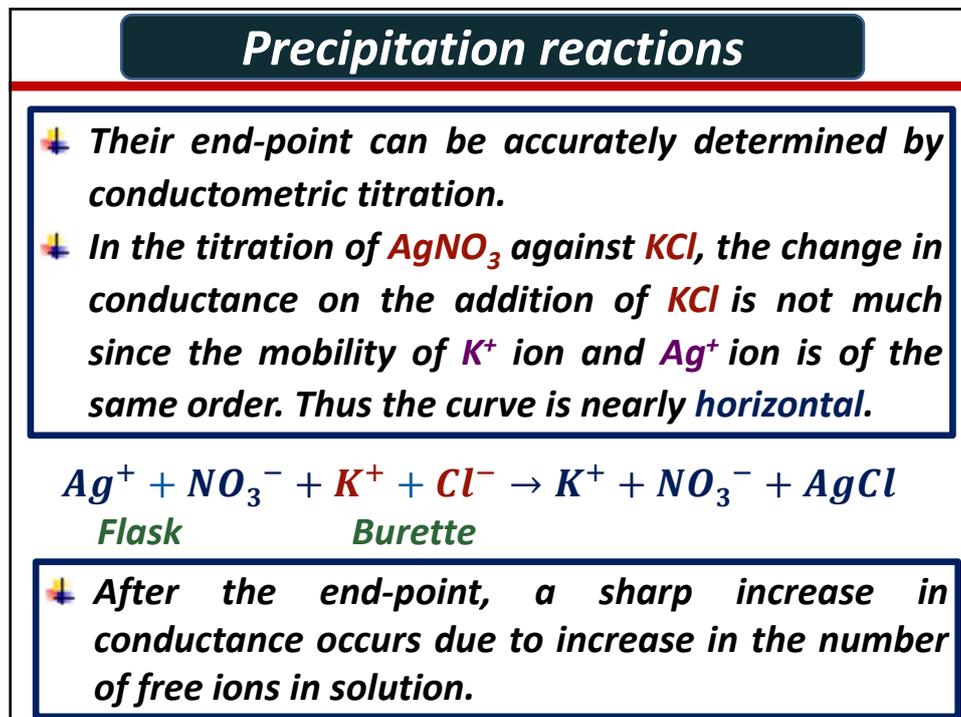
After EP



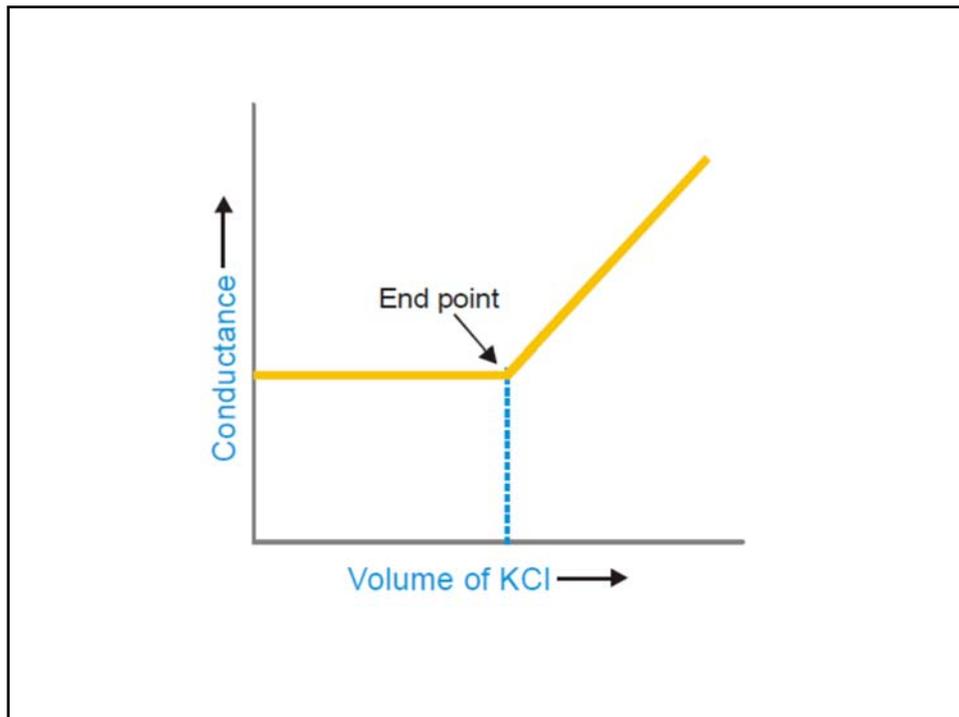
16



17



18



19

### Advantage of Conductometric Titrations

- ✚ *Colored solutions* where no indicator is found to work satisfactorily can be successfully titrated.
- ✚ *Titration of weak acids* against weak bases are **feasible** which do not give a sharp change of color with indicators in ordinary volumetric analysis.
- ✚ *More accurate results* are obtained because the end - point is determined **graphically**.

### Precaution

- ✚ *It is necessary to keep the temperature constant* throughout the experiment.
- ✚ *In acid-alkali titrations, the titrant should be about 10 times stronger* than the solution to be titrated so that the volume change is as little as possible.

20

<b><i>Conductometric Titrations</i></b>	<b><i>Volumetric Titrations</i></b>
<b><i>Conductance measurements are done to check EP</i></b>	<b><i>Volume measurements are done to check EP</i></b>
<b><i>Colored solutions can be titrated.</i></b>	<b><i>Titrations of colored solutions are difficult as suitable indicators are not available.</i></b>
<b><i>Accurate</i></b>	<b><i>Not so accurate.</i></b>
<b><i>EP is determined graphically.</i></b>	<b><i>EP is determined by change in color of indicator.</i></b>
<b><i>In case of polybasic acids conductometric titrations can be used.</i></b>	<b><i>In case of polybasic acids volumetric titrations do not give correct EP</i></b>

21