

ELECTROCHEMISTRY

Some common terms:

Electrolysis. Is the decomposition of molten or aqueous compounds when electricity is passed through them.

Electrolyte: Is a substance which in **molten** or **aqueous** state conducts electricity.

Electrolytes are divided into;

- True electrolytes:** conduct electricity both in molten and aqueous state (form) e.g. NaCl, KNO₃, etc.
- Potential electrolytes:** conduct electricity only in aqueous solution e.g. HCl
- Weak electrolytes:** least poorly conduct electricity due to partial ionization or dissociation in aqueous solution, providing a small number of aqueous ions. E.g. ethanoic acid, Benzoic acid, ammonia solution, carbonic acid, phenols.
- Strong electrolytes:** readily conduct electricity due to almost complete ionization or dissociation in aqueous solution, providing discrete ions. E.g. NaCl, KNO₃, Ca(OH)₂, etc

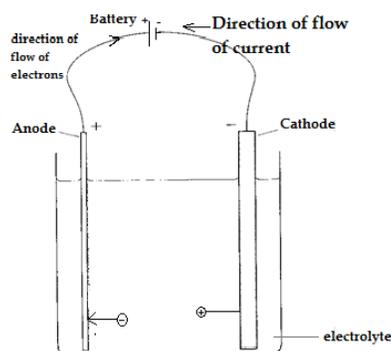
Electrode:

- Cathode: Electrodes towards which cations move during electrolysis
- Anode: electrodes towards which anions move during electrolysis

Electrolytic cell:

- Is a chemical setup in which electrolysis occurs.
- Electric current causes chemical change/ decomposition of the compound.

Typical electrolytic cell



During electrolysis;

- ❖ Electrolyte dissociates/ionizes into cations and anions
- ❖ Anions are attracted to the anode; losing electron(s) to the anode; forming a neutral atom or molecule. i.e (**oxidation occurs at the anode**)
- ❖ Cations are attracted to the cathode; combine with negative electrons from the battery; forming a neutral atom/ molecule. (**reduction occurs at the cathode**)

FACTORS AFFECTING SELECTIVE DISCHARGE AT THE ELECTRODE

Position of the electrochemical series/reactivity series

Ions lower down in the electrochemical series/ion with lower electrode potential are discharged in preference to those high up or with higher electrode potential.

K^+ , Na^{2+} , Ca^{2+} , Mg^{2+} , Al^{3+} , Zn^{2+} , Fe^{2+} , Sn^{2+} , Pb^{2+} , H_3O^+ , Cu^{2+} , Ag^+ , Au^+

Ease of discharge increases →

$\bar{O}H$, I^- , Br^- , Cl^- , NO_3^- , SO_4^{2-} , F^-

← Ease of discharge increases

Concentration

Increase in concentration of an ion increases its chances of being discharged. E.g. in the electrolysis of brine (concentrated solution of NaCl) using inert electrodes;

- Ions present are Na^+ and Cl^- , H^+ and $\bar{O}H$ (from decomposition of water)
- Cl^- is discharged at the anode in preference of $\bar{O}H$ because of their higher concentration
- Na^+ is discharged preferentially to hydrogen ions because of high concentration

Nature / type of the electrode

Type of electrode affects the ion discharged, hence affecting the product. Consider electrolysis of $CuSO_4$ using,

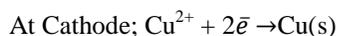
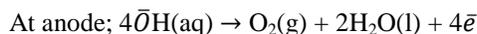
(a). Copper electrode;

- Copper anode dissolves to form Cu^{2+} (**energy required to remove electrodes from copper is less than energy required to discharge either $\bar{O}H$ or SO_4^{2-} ions**)

Anode: $Cu(s) \rightarrow Cu^{2+}(s) + 2\bar{e}$

- **At cathode;** $\text{Cu}^{2+} + 2\bar{e} \rightarrow \text{Cu(s)}$ (Cu(s) is preferentially discharged to hydrogen; because its lower than the hydrogen ions in the electrochemical series)

(b). Graphite electrode;



FARADAY'S LAWS OF ELECTROLYSIS:

- ❖ **Mass of any substance liberated at the electrodes is directly proportional to the amount of electric charge passing through the circuit.**

If **m** is the mass of substance liberated, **I** is the current passed and **t** is time in seconds.

$m \propto Q$, where **Q** is the electric charge passing through the circuit.

$m \propto It$

$m = EIt$. Where **E** is the electrochemical equivalent/ proportionality constant of the substance.

If $I = 1\text{A}$, $t = 1\text{s}$; then $m = E$;

NB; Therefore **E**, (**electrochemical equivalent**) is the **mass of the ion deposited by passage of one ampere current for one second**;

- ❖ **Quantity of electricity required to liberate 1 mole of a substance is proportional to the charge number of its ions.**

NB: -Faraday's constant (96500 coulombs) is the quantity of charge required to liberate one mole of a univalent ion; /Quantity of electricity carried by one mole of electrons;

- Coulomb is the quantity of electricity transported by a current of one ampere in one second.

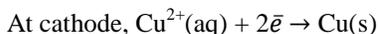
Examples

1. Calculate the mass of Copper deposited when a current of 4A was passed through a solution of $\text{CuSO}_4\text{(aq)}$ for 30 minutes (Cu = 64, IF = 96500C)

Solution

From $Q = It$

$$Q = 4 \times 30 \times 60 = \mathbf{7200C}$$



(96500×2)C is liberated by 64g of Cu

7200C is liberated by $\left(\frac{64 \times 7200}{96500 \times 2}\right)$ g of Cu

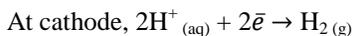
$$\equiv \mathbf{2.388g}$$

2. A current of 3A was passed for 20 minutes through a cell containing H_2SO_4 and the hydrogen produced at the cathode was collected. Calculate the volume of H_2 that was collected at 25°C at 120kPa.

Solution

From $Q = It$

$$Q = 3 \times 20 \times 60 = \mathbf{3600C}$$



(2 × 96500) is liberated by 1 mole of H_2

36000 is liberated by x moles of H_2

$$X = \frac{3600}{(96500 \times 2)}$$

$$X = \mathbf{0.0187\text{moles}}$$

From $PV = nRT$

$$V = \frac{nRT}{P}$$

$$V = \left(\frac{0.0187 \times 8.314 \times 298}{120000}\right)$$

$$\mathbf{V = 3.86 \times 10^{-4}\text{m}^3}$$

Activity

1. What mass of metallic silver will be deposited when a current of 0.53A is passed through AgNO_3 solution for 35minutes?
2. A Copper spoon was electroplated using Ag. Calculate the mass of silver deposited on the spoon if a current of 0.03A was passed for 2hrs. (IF = 96500C, RAM of Ag = 108)

3. Find how long it will take to deposit 1g of Chromium when a current of 0.120A flows through a solution of chromium(III) sulphate solution.
4. During the extraction of aluminium, a current of 0.2ampere was passed for one hour through aluminium sulphate solution.
- (a) Write an equation for the reaction that took place at each electrode. (3marks)
- (b) Calculate the mass of aluminium produced. (3marks) **UNEB 2004**

Paper 1 no 6.

5. A current of 0.1 A is passed through a solution of nickel ions for 16minutes and 5seconds. 0.0294g of nickel was deposited on the cathode, determine the charge on the nickel ion in this solution.(Ni=58.7, faradays constant = 96500Cmol⁻¹) **JJEB2016 p2 2f**

INDUSTRIAL APPLICATIONS OF ELECTROLYSIS

- ❖ Extraction of metals eg Aluminum from the electrolysis of molten aluminum (III) oxide.
- ❖ Purification of copper and gold
- ❖ Anodic oxidation of aluminum; electrolysis of dilute sulphuric acid is used to deposit a tough oxide film on aluminum.
- ❖ Electroplating of metals e.g. plating with silver, gold, Chromium and Nickel.
- ❖ Manufacture of NaOH by electrolysis of concentrated sodium chloride solution.
- ❖ Manufacture of Chlorine by electrolysis of brine.

ELECTROLYTIC CONDUCTION

- Resistance (R) offered by solution to the flow of current of constant temperature is;
 - i. Directly proportional to the distance, l between the electrodes. $R \propto l$
 - ii. Inversely proportional to the cross sectional area, A of the solution between the electrodes

$$R \propto \frac{l}{A}$$

Where ρ = resistivity
 l = distance between the electrodes
 A = Cross section area
 $\frac{l}{A}$ = cell constant

$$R = \rho \frac{l}{A}$$

Therefore **R = resistivity × cell constant**

CONDUCTANCE, RESISTIVITY AND ELECTROLYTIC CONDUCTIVITY

CONDUCTANCE (L); Is the resistance offered to the flow of current by a solution./ reciprocal of resistance.

$$L = \frac{1}{R}$$

Unit is *Siemens* (S)/ Ω^{-1}

RESISTIVITY (SPECIFIC RESISTANCE). Is the resistance of a solution kept between electrodes one metre apart and cross sectional area 1m² between electrodes.

$$\rho = \frac{RA}{l} \quad \text{From } R = \rho \frac{l}{A}, \text{ if } l \text{ is } 1\text{m, } A \text{ is } 1\text{m}^2, \text{ then } R = \rho$$

unit is **Ωm**

ELECTROLYTIC CONDUCTIVITY/ SPECIFIC CONDUCTANCE (Kappa, K). Is the conductance /conductivity of a solution placed between electrodes of unit cross sectional area and unit distance apart.

Is the reciprocal of resistivity (*earns a candidate ½ mk only if used*).

$$\text{From } \rho = \frac{RA}{l} \\ \Rightarrow \kappa = \frac{1}{\rho} = \frac{l}{RA}$$

Unit is $\Omega^{-1}\text{m}^{-1} = \text{Sm}^{-1}$

FACTORS AFFECTING ELECTROLYTIC CONDUCTIVITY OF A SOLUTION

-Concentration of solution/ electrolyte

For weak electrolytes;

- Increase in concentration increases slowly the electrolytic conductivity; because of increase in number of ions conducting per unit volume. Further increase in concentration decreases electrolytic conductivity; because degree of ionization of the electrolyte reduces; decreasing the number of ions per unit volume and thus decreasing electrolytic conductivity.

For strong electrolytes;

- Increase in concentration increase electrolytic conductivity; because increased number of conducting ions per unit volume. Further increase in concentration decreases electrolytic conductivity; because ions of opposite

charges come close together; exerting a dragging effect on one another/ionic interference increases ; lowering the speed of the ions/ mobility of ions.

-Temperature;

For strong electrolytes

- Increase in temperature increase the electrolytic conductivity; because increase temperature decreases the viscosity of water; allowing free movement of ions;/ mobility of the ions is increased. Low temperature lowers ionic mobility hence electrolytic conductivity.

For weak electrolytes which;

- (i) ionize with loss of heat;
 - Increase in temperature decreases the degree of ionisation,; number of conducting ions in a unit volume is reduced ;decreasing the electrolytic conductivity;
- (ii) ionize with absorption of heat;
 - Increase in temperature increases the degree of ionisation, more conducting ions are produced; increasing the conductivity.

NB. (Give how temperature affects electrolytic conductivity of a strong electrolyte if examiner is not specific of the type electrolyte)

MOLAR CONDUCTIVITY (Λ_c)

Is the conductance of one mole of an electrolyte in a given volume of solution enclosed between two electrodes of cross sectional area $1m^2$ and $1m$ apart/ Is the electrolytic conductivity multiplied by the volume of solution that contains one mole of the electrolyte.

$\Lambda_c = \kappa \cdot V$ where κ is electrolytic conductivity.

But $V \propto \frac{1}{C}$

$$\Lambda_c = \frac{\kappa}{C}$$

$$\text{Units } \frac{Sm^{-1}}{mol\ m^{-3}} = Smol^{-1}m^2$$

If unit of $\kappa = Scm^{-1}$, Concentration = $mol\ dm^{-3}$

From $\Lambda_c = \frac{\kappa}{C}$

$$\Lambda_c = \frac{1000\kappa}{C}$$

Examples

1. An electrolyte in a solution containing $5\ mol\ dm^{-3}$ has a resistance of $50.7\ \Omega$ in a conducting cell with a cell constant of $3.5\ m^{-1}$. Calculate;
 - i. Electrolytic conductivity, κ at that temperature and concentration
 - ii. Molar conductivity, Λ_c of the electrolyte

Solution

$$i. \text{ From } \kappa = \frac{1}{\rho} = \frac{l}{RA} = \frac{l}{A \cdot R} = 3.5 \times \frac{1}{50.7} = \underline{0.069\ \Omega^{-1}m^{-1}}$$

$$ii. \Lambda_c = \frac{\kappa}{C} \\ \Lambda_c = \frac{0.069}{5} = \underline{0.0138\ Sm^2mol^{-1}}$$

2. Using the same conductivity cell, resistance of $0.1M$ potassium chloride solution and $0.1M$ Bromoethanoic acid solution were found to be $24.96\ \Omega$ and $66.5\ \Omega$ respectively at $25^\circ C$ when determined using the same conductivity cell (conductivity of KCl at $25^\circ C = 0.01164\ \Omega^{-1}cm^{-1}$ and molar conductivity of Bromoethanoic acid at infinite dilution is $389\ \Omega^{-1}cm^2mol^{-1}$)

- i. Calculate the cell constant
- ii. Calculate the molar conductivity of the $0.1M$ Bromoethanoic acid **UNEB 2004 p2, no 2(b)**

Solution

(i). Using Potassium Chloride

$$R_{cell} = \rho \left(\frac{l}{A} \right)$$

$$\text{But } K = \frac{1}{\rho} \Rightarrow \rho = \frac{1}{K}$$

$$\frac{l}{A} (\text{cell constant}) = R_{cell} \div \frac{1}{K} = R_{cell} \times K$$

$$\frac{l}{A} = (24.96 \times 0.01164) = \underline{0.2905\ cm^{-1}}$$

$$ii. \Lambda_{0.1M} = \frac{K}{C}$$

$$\text{From } R = \rho \left(\frac{l}{A} \right)$$

$$\rho = \frac{RA}{l}$$

$$K_{BrCH_2COOH} = \frac{l}{\rho} = \frac{l}{A} \cdot \frac{1}{R} = 0.2905 \times \frac{1}{66.5} = 4.368 \times 10^{-3}\ \Omega^{-1}cm^{-1}$$

$$\Lambda_{0.1M} = \frac{4.368 \times 10^{-3}}{0.1} = 0.04368\ \Omega^{-1}cm^{-1}mol^{-1}dm^3 = (0.04368 \times 1000)\ \Omega^{-1}cm^{-1}mol^{-1}cm^3$$

$$\underline{\Lambda_{0.1} = 43.68\ \Omega^{-1}cm^2\ mol^{-1}}$$

Activitiy

1. Calculate the molar conductivity of;

(i). 0.1M KCl solution whose electrolytic conductivity is $1.29 \Omega^{-1}\text{m}^{-1}$

(ii) 0.01M CH_3COOH whose electrolytic conductivity is $0.163\Omega^{-1}\text{m}^{-1}$

2. **UNEB 2014 P1 NO.3(b).**

3. The resistance of 0.01M methanoic acid and 0.01M potassium chloride solutions are 95.2Ω and 25.0Ω respectively. The electrolytic conductivity of potassium chloride is $1.164 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$. Calculate the molar conductivity of 0.01M methanoic acid. **(Wakisha 2013 p1, no 12b, modified)**

4. A conductivity cell of filled with 0.2M aqueous potassium sulphate solution gave a resistance at 25°C of 564Ω . Calculate the cell constant given that the molar conductivity of this solution is $139.20 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

FACTORS AFFECTING MOLAR CONDUCTIVITY

-Ionic charge

Molar conductivity increases with increase in ionic charge; ions with bigger charges transfer more charges than those that have smaller charges. E.g. the conductivity of Na^+ is less than that of Mg^{2+} which is in turn less than that of Al^{3+} .

-Ionic radius

Molar conductivity decreases with decrease in the ionic radius

Ions with very small radius have high charge density, shell of water molecules are strongly attracted/ are highly hydrated ; lowering the mobility of ions, therefore lowering their conductivities.

Ions with large radius are less hydrated; thus have high mobility; giving it high conductivity.

-Temperature.

Increase in temperature increase conductivity; because increased temperature decreases the viscosity of water; allowing free movement of ions;/ mobility of the ions is increased. Low temperature lowers ionic mobility hence conductivity decreases.

-Viscosity of solution

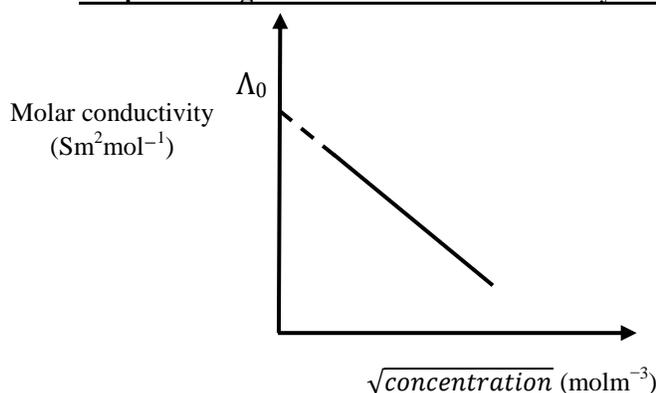
The viscous a solution is, the lower the ionic mobility, hence conductivity is low. Less viscous solutions have their ions moving at higher velocity; solution conducts more.

-Concentration

Molar conductivity decreases with increase in concentration for both weak and strong electrolytes.

a) **For strong electrolytes:**

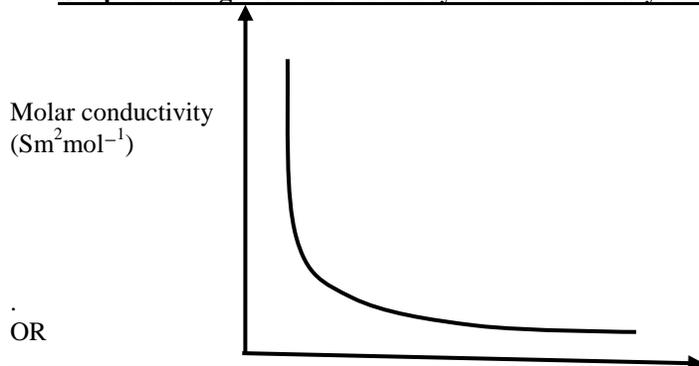
Graph showing variation of molar conductivity of strong electrolyte with concentration



- At low concentration, conductivity is high; because ions are far apart; and their mobility is high.
- Increase in concentration of ions conductivity decreases; because ions get close to each other; and ionic interference/ dragging effect increases ; leading to a decrease in mobility of ions

b) **For weak electrolytes;**

Graph showing molar conductivity of weak electrolyte against concentration

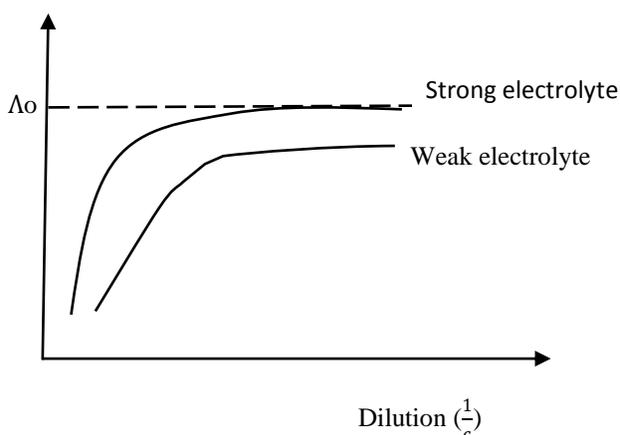


- Molecules are only partly dissociated; increase in concentration decreases the degree of ionisation; decreasing the number of conducting ions per unit volume; thus decreasing conductivity

OR

Variation of molar conductivity with dilution ($\frac{1}{c}$) of strong electrolyte weak electrolyte

Molar conductivity ($\text{Sm}^2\text{mol}^{-1}$)



- For strong electrolyte, molar conductivity increases with increasing dilution/ decreasing concentration until at infinite dilution where it becomes fairly constant.
- Because with increase in dilution, separation between ions of opposite charges increases / ions of opposite charges are far apart; decreasing the drag effect/ interionic interference between ions; mobility of the ions increases thus increasing molar conductivity.
- At infinite dilution, separation between ions is exceedingly great; ions of opposite charges move independently without exerting any drag on each other hence higher molar conductivity

For weak electrolytes;

- Molar conductivity is lower than the strong electrolyte at same dilution because are only partly dissociated to produce few ions
- Increase in dilution increases the degree of ionisation, increasing the number of conducting ions per unit volume; and so increasing the molar conductivity.

Activity.

- (a). Draw sketch graphs to show how molar conductivities of the following compounds vary with concentration. (2marks)

- Copper(II) Sulphate solution
- Hydrochloric acid

- Explain the shape of the graphs you have sketched in (a) above. (6marks)

- The table below shows how the molar conductivity of lithium chloride in water at 25°C varies with dilution, $1/C$, where C is the concentration.

Dilution ($\text{mol}^{-1}\text{dm}^3$)	2000	1000	500	200	100	20
Molar conductivity, Λ_c ($\text{Scm}^2\text{mol}^{-1}$)	113.2	112.5	111.5	109.4	107.3	100.1

- Plot a graph of molar conductivity of lithium chloride against dilution, $1/C$, at 25°C. (4marks)
- explain the shape of the graph (2marks)
- Using the graph, estimate the molar conductivity of lithium chloride at infinite dilution at 25°C (1mark)

UNEB 2016 P2, No (1b,c)

2. UNEB 2013 P1 No 10b; 2006 P1no 11a,b; 2005 P2No 4 c,d; 2004 P2 No 4a;

KOHLRAUSCH'S LAW OF INDEPENDENT MIGRATION OF IONS

States, "Molar conductivity of an electrolyte at infinite dilution is equal to the sum of molar conductivities of its ions"

- Used to determine molar conductivity at infinite dilution for weak electrolyte whose molar conductivity can not be determined experimentally or directly.

Examples

- The molar conductivities of AgNO_3 , KNO_3 and KCl are 1340, 143.2, and $140.8\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively at infinite dilution at 25°C. Calculate the molar conductivity of AgCl at infinite dilution. (UNEB 2007 P1 17bi)

Solution

$$\Lambda_s \text{AgCl} = \Lambda_s \text{AgNO}_3 + \Lambda_s \text{KCl} - \Lambda_s \text{KNO}_3$$

$$= 134.0 + 140.8 - 143.2$$

$$\Lambda_s \text{AgCl} = 131.6 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

- The molar conductivity of HNO_3 , KNO_3 and KF are 421, 145 and $129\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively at infinite dilution, calculate the molar conductivity of HF acid at infinite dilution. (UNEB 2006 (11Ci))

Solution

$$\Lambda_0 \text{HF} = \Lambda_0 \text{HNO}_3 + \Lambda_0 \text{KF} - \Lambda_0 \text{KNO}_3$$

$$= 421 + 129 - 145$$

$$= 405 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

ACTIVITY.

- UNEB 2016 P2 NO1(a); 2004 P1 no 12b(i); 1998 P1no13(a-c); 1996 P1 No 15c;

2. The molar conductivities of hydrochloric acid, sodium chloride and sodium ethanoate at infinite dilution are 426.2, 126.5, and 91.0 $\Omega^{-1}\text{cm}^2 \text{mol}^{-1}$ respectively. If the electrolytic conductivity of 0.01M ethanoic acid is 0.000143 $\Omega^{-1}\text{cm}^{-1}$. Calculate the;

- (i) molar conductivity of ethanoic acid at infinite dilution
 (ii) percentage of ethanoic acid that exists as ions in a 0.01M solution

UTEC 2015 P1 no 17b(i, ii).

APPLICATIONS OF CONDUCTIVITY MEASUREMENTS

- ❖ *Determination of molar conductivity of weak electrolytes at infinite dilution using Kohlrausch's law.*
- ❖ *Determination of solubility and thus solubility product (Ksp) of a sparingly soluble salt*

Conductivity of a solute;

$$K_{\text{solute}} = K_{\text{solution}} - K_{\text{solvent}}$$

Also;
$$\lambda = \frac{K_{\text{solute}}}{C}$$

Where C = concentration / solubility in mol dm^{-3}

Example:

1. A saturated solution of AgCl has a conductivity of $1.887 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$ at 25°C. The electrolytic conductivity of water is $5.5 \times 10^{-8} \Omega^{-1}\text{cm}^{-1}$. Molar conductivity of AgNO_3 , KCl, KNO_3 are 133.4, 149.9, 145 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively. Calculate the solubility product of AgCl.

Solution

$$K_{\text{solute}} = K_{\text{solution}} - K_{\text{solvent}}$$

$$K_{\text{solute}} = 1.887 \times 10^{-6} - 5.5 \times 10^{-8} = 1.832 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$$

$$\text{From } \lambda = \frac{K_{\text{solute}}}{C}$$

$$\lambda_{\text{AgCl}} = \lambda_{\text{KCl}} + \lambda_{\text{AgNO}_3} - \lambda_{\text{KNO}_3}$$

$$\lambda_{\text{AgCl}} = (149.9 + 133.4) - 145 = 138.3 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

$$\lambda_{\text{AgCl}} = \frac{K_{\text{AgCl}}}{C}$$

$$C = \frac{K_{\text{AgCl}}}{\lambda_{\text{AgCl}}} = \frac{1.832 \times 10^{-6}}{138.3} = 1.325 \times 10^{-8} \text{ mol cm}^{-3}$$

$$\text{But } \text{AgCl}_{(s)} + \text{(aq)} \rightleftharpoons \text{Ag}^+_{\text{(aq)}} + \text{Cl}^-_{\text{(aq)}}$$

$$K_{\text{sp}} = [\text{Ag}^+][\text{Cl}^-]$$

$$\text{But } 1.325 \times 10^{-8} \text{ mol cm}^{-3} = 1.325 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\Rightarrow K_{\text{sp}} = (1.325 \times 10^{-5})(1.325 \times 10^{-5})$$

$$= \mathbf{1.76 \times 10^{-10} \text{ mol}^2\text{dm}^{-6}}$$

Activity

1. The electrolytic conductivity of a saturated of a solution of AgCl at 291K after deducting the electrolytic conductivity of water is $1.22 \times 10^{-4} \text{ Sm}^{-1}$. The molar conductivity of the Ag^+ and Cl^- at infinite dilution at 291K are 0.540×10^{-2} and $0.652 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$ respectively. Calculate the solubility of AgCl at 291K in gmol^{-1} (Ag = 108, Cl = 35.5)

2. UNEB 2007 (17b,c),

- ❖ *Determining dissociation/ionization constants for weak electrolytes.*

- Degree of dissociation/ ionization = $\frac{\lambda_c}{\lambda_0}$ where λ_c = molar conductivity at given concentration
 λ_0 = Molar conductivity of infinite dilution

But From $K_a = C\alpha^2$
 \Rightarrow

$$K_a = C \left(\frac{\lambda_c}{\lambda_0} \right)^2$$

Example

Calculate the dissociation constant of 0.1M Hydrogen fluoride solution whose molar conductivity at infinite dilution is $405 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ (Electrolytic conductivity of HF(aq) is $3.15 \times 10^{-5} \Omega^{-1}\text{cm}^{-1}$)

Solution

$$\kappa = 3.15 \times 10^{-5} \Omega^{-1}\text{cm}^{-1} \quad K_a = C\alpha^2$$

$$\text{But; } \alpha = \frac{\lambda_c}{\lambda_0}$$

$$\lambda_c = \frac{\kappa}{C} = \frac{3.15 \times 10^{-5}}{0.1}$$

$$\lambda_c = 3.15 \times 10^{-4} \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

$$\lambda_c = (3.15 \times 10^{-4} \times 1000) \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

$$\lambda_c = 3.15 \times 10^{-1} \Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

$$\alpha = \frac{3.15 \times 10^{-1}}{405}$$

$$\alpha = 7.78 \times 10^{-4}$$

$$K_a = (7.78 \times 10^{-4})^2 \times 0.1$$

$$K_a = 6.05 \times 10^{-8} \text{ mol dm}^{-3}$$

Activity . 2006 P1 no 11c,d, 2001 P2 No 7c,

❖ **Determining of the formula of complexes**

Example .

The table below shows the variation of conductivity with volume of ammonia when two inert electrodes connected to a conductivity meter were immersed in 50cm³ of 0.025M zinc nitrate solution and 2cm³ portions of 0.5M ammonia , added at intervals.

Volume of ammonia solution(cm³)	0	2	4	6	8	10	12	14
Conductivity of resultant solution(Ω⁻¹cm⁻¹)	1.2	1.16	1.12	1.08	1.05	1.045	1.06	1.10

- (i) Draw a graph of conductivity of solution versus volume of ammonia (3marks)
 (ii) Determine the volume of ammonia solution that gave the lowest conductivity (1 mark)
 (iii) Determine the formula of the species present in the solution in above. (4marks)

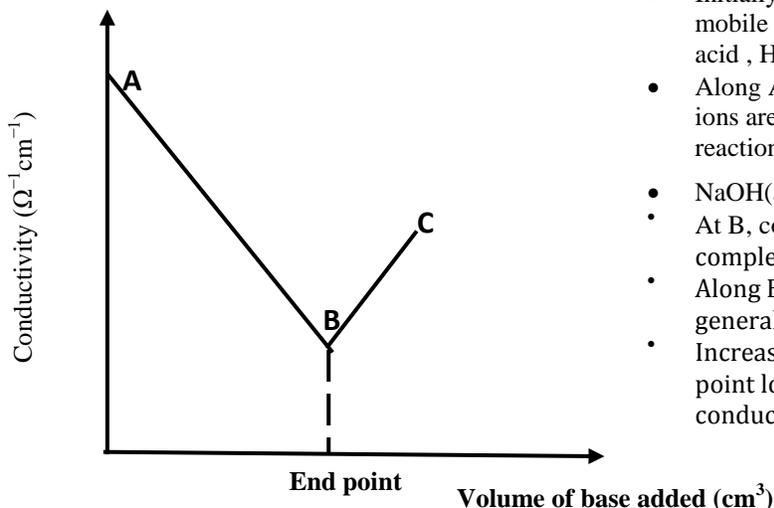
UNEB 2005 P2 No 4e

Approach. (ii) from plotted graph, volume is **9.2cm³**

(iii) first obtain moles of Zinc nitrate solution; get moles of ammonia reacted using the minimum volume obtained above, then use these moles to get the simplest mole ratio, from which formula of the complex obtained as **Zn(NH₃)₄**.

❖ **Volumetric analysis to estimate end points of reactions/ conductimetric titrations**

a) **Strong acid versus strong base (HCl Vs NaOH)**



- Initially, conductivity is high; there are high concentration of mobile and highly conducting hydrogen ions from strong acid , HCl.
- Along AB; conductivity decreases; highly mobile hydrogen ions are being replaced by the less mobile Na⁺ due to the reaction;
- NaOH(aq) + HCl(aq) → NaCl(aq) + H₂O(l)
- At B, conductivity is due to Na⁺ and Cl⁻ formed after complete neutralization of the acid (at the end point).
- Along BC; conductivity increases; excess OH⁻ ions and the general increase in the number of conducting ions
- Increase in conductivity to excess. OH⁻ ions ends at a point lower than A; because they are not as highly conducting and mobile as the H⁺ ions.

Activity

1. UNEB 2003 (2) p2, no 2a

2. Small volumes of approximately 1M sodium hydroxide solution were added to 50cm³ of 0.1M hydrochloric acid. The conductivity was measured and the following results obtained.

Volume of sodium hydroxide(cm³)	1	3	5	7	9	11
Conductivity(Ω⁻¹m⁻¹)	3.35	2.27	1.17	0.76	1.62	2.47

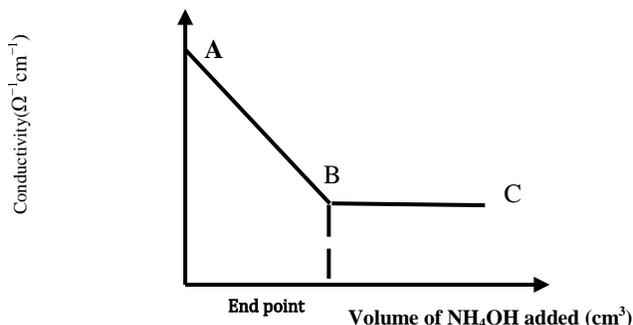
- (a). Plot a graph of conductivity against volume of sodium hydroxide
 (b). Determine the volume of sodium hydroxide that reacted completely with 50cm³ of hydrochloric acid
 (c). calculate the molarity of sodium hydroxide
 (d). Account for the shape of the graph

3. The limiting molar ionic conductivities of hydrogen ions, sodium ions, hydroxide ions and chloride ions are 350, 50, 200, and 76 Ω⁻¹cm² mol⁻¹ respectively. 0.01M hydrochloric acid was titrated with 1.0M sodium hydroxide solution. The conductivity of the resultant solution was measured during the titration. Assuming water doesnot conduct; calculate the conductivity of the solution;

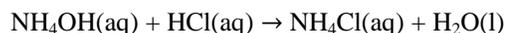
- (a) before the titration was started
 (b) when the acid was exactly neutralised
 (c) when twice as much sodium hydroxide had been added
 (d) (i) sketch a graph to show how the conductivity of the solution varies as sodium hydroxide is added
 (ii) Explain the shape of the graph in d(i) above

UTEC 2016 P2 no (b,c)

b) **Strong Acid Versus weak base e.g (hydrochloric acid Vs ammonium hydroxide)**

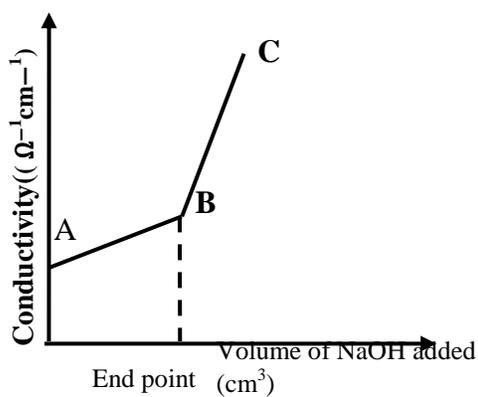


- Initially at A, conductivity is high due to highly conducting H^+ ions from the strong acid, HCl
- Along AB, conductivity decreases; fast moving hydrogen ions are replaced by slow moving ammonium ions due to the reaction;

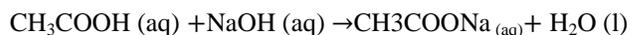


- At B, Conductivity is due to ammonium ions, NH_4^+ and Cl^- ions after complete neutralization.
- Along BC, conductivity remains constant; ionization of excess ammonia solution is suppressed by the ammonium ions from ammonia chloride, conductivity of excess hydroxyl ions $\bar{O}H$ is negligible.

c.) **Weak acid versus strong base (CH₃COOH Vs NaOH)**

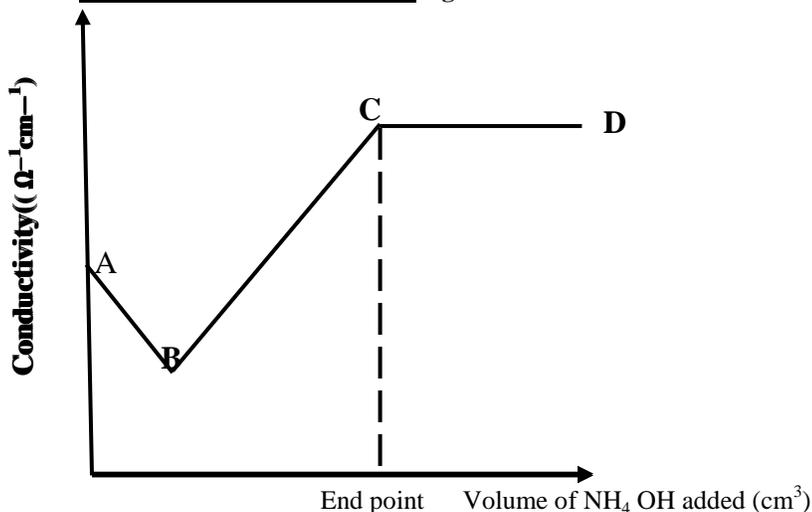


- Initially at A, conductivity is low, ethanoic acid is a weak acid, partially ionizes producing few conducting hydrogen ions.
- Along AB, conductivity slowly increases; number of conducting ions increase; produced by dissociation of Sodium ethanoate; strong electrolyte;



- At B, conductivity is due to ethanoate and sodium ions after complete neutralization.
- Along BC, Conductivity rapidly increases due to addition of excess $\bar{O}H$ ions which are highly conducting compared to ethanoate ions

d) **Weak acid versus weak base e.g ethanoic acid and ammonium hydroxide)**



- Initially at A, Conductivity is low; ethanoic acid is a weak acid, partially ionizes producing few conducting hydrogen ions.
- Along AB, conductivity slightly decreases, ionization of ethanoic acid is suppressed by ethanoate from ammonium ethanoate formed.
- Along BC, Conductivity increases, number of conducting ions increases produced by dissociation of ammonium ethanoate.
- Along CD, conductivity remains constant; ionization of excess NH_4OH is suppressed by ammonium ethanoate.

Activity .Describe an experiment to determine end point by conductivity measurements.