

## CHM 203: Electrochemistry

### Introduction

Electrochemistry is the study of electrolyte solutions and the phenomena occurring at the electrodes immersed in them.

Electrolytes are (ionic solutions) media in which ions exist. Ions are the reservoir of charges for electrode processes, therefore, thermodynamic considerations of the behavior of ions in aqueous solution is of great importance in electrochemistry.

Electrolytic conduction is the conduction of electrolyte (solid or solution). Two examples of cells are presented in Fig. 1 below:

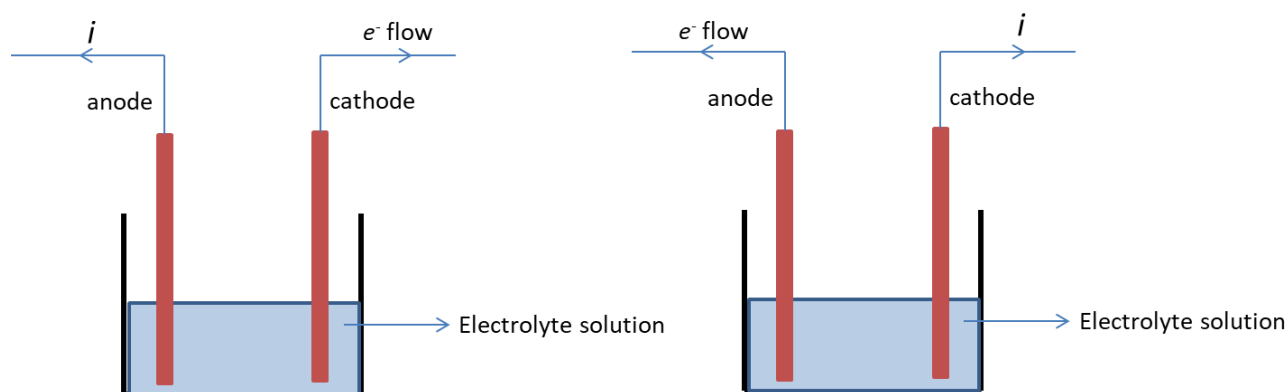


Fig. 1: The two types of cells: electrolytic and galvanic cells

It is known for a long time that metallic conductor such as copper wires obey the Ohm's law:

$$E = iR \quad (1)$$

i.e. the current  $i$  is directly proportional to the emf  $E$  which produces it.  $R$  is the proportionality constant called the resistance. The unit of  $i$  is amperes (A), the unit of resistance is ohm ( $\Omega$ ) and the unit of emf is volt (V). It has been shown that electrolyte solutions also obey the Ohm's law. The ability of a solution to conduct electricity is known as *conductance*. The conductance  $L$  is defined as:

$$L = \frac{1}{R} = \frac{i}{E} \quad (2)$$

The unit of  $L$  is  $\Omega^{-1}$  (per ohm). The conductance of a solution depends upon:

- i.) the nature of the electrolyte

- ii.) the size of the electrodes and
- iii.) the distance between the electrodes

The resistance of the electrolyte between the two electrodes is directly proportional to the length of the electrolyte, and inversely proportional to its cross-sectional area. This implies that the electrolyte can be viewed as a 3-dimensional conducting object,

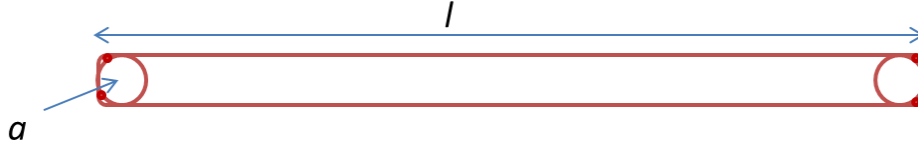


Fig. 2: Electrolyte solution imagined as a three-dimensional conducting object

$$R = \left(\frac{l}{a}\right) \rho \quad (3)$$

where  $l$  is the distance between the two electrodes,  $a$  is the cross-sectional area of the electrolyte (the container) and  $\rho$  is the proportionality constant called resistivity. The resistivity is measured in ohm-meter ( $\Omega \cdot m$ ). We may therefore define resistivity as the resistance between the electrodes of  $1 \text{ cm}^2$  area which are  $1 \text{ cm}$  distance apart.

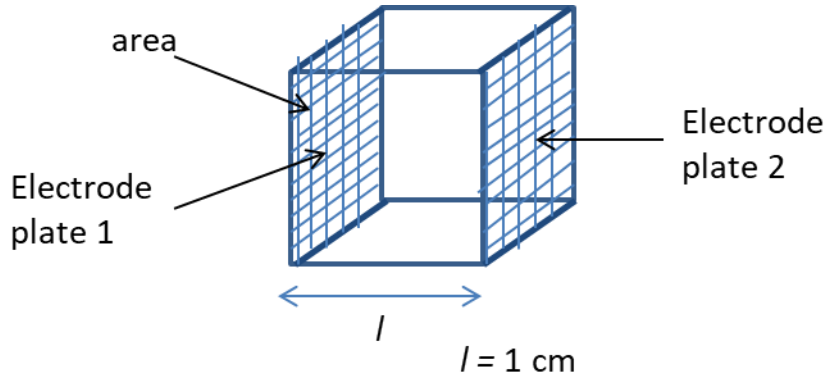


Figure 3: Resistance (resistivity) of a cube of solution

The reciprocal of resistivity is called conductivity  $\kappa$ .

$$\kappa = \frac{1}{\rho} = \frac{1}{R} \left(\frac{l}{a}\right) \quad (4)$$

$$\text{also, } L = \kappa \left(\frac{a}{l}\right) = \frac{1}{R} \quad (5)$$

$\frac{l}{a} = \kappa R$  is called the cell constant. It depends on the geometry of the cell.  $\kappa$  depends on the nature of the electrolyte. The cell constant  $l/a$  is usually evaluated by measuring resistance of an electrolyte whose conductivity ( $\kappa$ ) is known. KCl is usually used as a standard electrolyte solution. Once the cell constant is known, the cell is then filled with a solution whose conductivity  $\kappa$  is not known, and using equation 5, the  $\kappa$  value can be determined.

### Concentration dependent conductivity

The concentration dependent conductivity is called the molar conductivity and given the symbol  $\Lambda$  (lamda). It is defined as the electrolytic conductivity  $\kappa$  divided by concentration  $c$ :

$$\Lambda = \frac{\kappa}{c} \quad (6)$$

The molar conductivity was formerly known as the equivalent conductivity. It is important because it gives information about the conductivity of the ions produced in solution by 1 mol of a substance. In all cases, the molar conductivity diminishes as the concentration is raised, and two patterns of behavior can be distinguished.

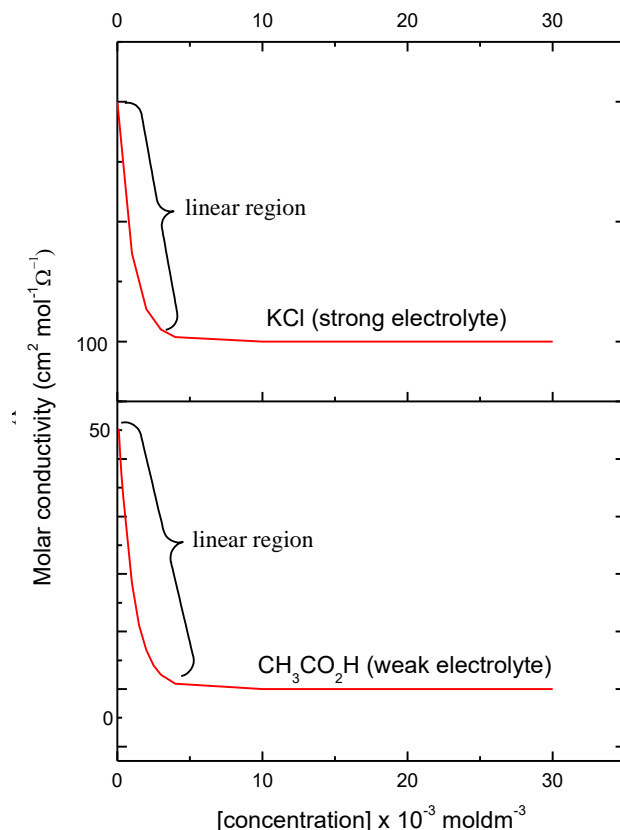


Fig. 4: The dependence of molar conductivity on concentration

In reality, the relationship between molar conductivity and concentration may be expressed as equation 7;

$$\Lambda = \Lambda^{\circ} - bc \quad (7)$$

The intercept in Fig. 4 is equivalent to  $\Lambda^{\circ}$  (molar conductivity at infinite dilution),  $b$  is an experimental constant and  $c$  is the concentration. Meanwhile, the ideal behavior should be a straight line with a -ve slope as against what is presented in Fig. 4, which shows the real behavior (an exponential decrease) in each case (strong and weak electrolytes). It can be seen from Fig. 4 that strong electrolytes' molar conductivity falls relatively slowly as the concentration is raised when compared to the weak electrolyte. This is because the weak electrolyte ( $\text{CH}_3\text{CO}_2\text{H}$ ) produce fewer ions, therefore exhibit a much more pronounced fall of  $\Lambda$  with increasing concentration (Fig. 4).

The relationship between the degree of dissociation and molar conductivity is given as:

$$\alpha = \frac{\Lambda}{\Lambda^{\circ}} \quad (8)$$

where  $\alpha$  is the degree of dissociation.

### **Ostwalds dilution law**

Consider an electrolyte AB that exists in solution partly as the undissociated species AB and partly as the ions  $\text{A}^+$  and  $\text{B}^-$  :



The equilibrium constant on the assumption of ideality is:

$$K_c = \frac{[\text{A}^+][\text{B}^-]}{[\text{AB}]} \quad (9)$$

suppose that an amount  $n$  of the electrolyte is present in a volume  $V$  and that the fraction dissociated is  $\alpha$ ; the fraction not dissociated is  $1 - \alpha$ . The amount of the three species present at equilibrium, and the corresponding concentrations, are therefore:



Amount present @ equil.       $n(1 - \alpha)$        $n\alpha$        $n\alpha$

conc. @ equil.                       $\frac{n(1-\alpha)}{V}$        $\frac{n\alpha}{V}$        $\frac{n\alpha}{V}$

The equilibrium constant is:

$$K_c = \frac{\left(\frac{n\alpha}{V}\right)^2}{\frac{n(1-\alpha)}{V}} = \frac{n\alpha^2}{V(1-\alpha)} \quad (10)$$

Thus, for a given amount of substance, the degree of dissociation  $\alpha$  must vary with the volume as follows;

$$\frac{\alpha^2}{1-\alpha} = \text{constant} \times V \quad (11)$$

or we write

$$\frac{c\alpha^2}{1-\alpha} = K_c \quad \text{since } \frac{n}{V} = c \quad (12)$$

Thus, the larger the volume  $V$ , the lower the concentration  $c$  and the larger the degree of dissociation. If 1 mol of electrolyte is diluted, the degree of dissociation increases and the amounts of the ionized species increase as  $V$  becomes very large (i.e. with  $c \rightarrow 0$ ). At this point, the degree of dissociation approaches unity, i.e.  $\Lambda \rightarrow \Lambda^0$ . The experimental value of  $\Lambda^0$  corresponds to complete dissociation of AB. The dilution law can thus be expressed as:

$$K = \frac{c\Lambda^2}{\Lambda^0(\Lambda^0-\Lambda)} \quad \text{by putting } \frac{\Lambda}{\Lambda^0} = \alpha \quad (13)$$

**Note that equation 13 is true only for weak electrolytes.**

### **Independent migration of ions**

In principle, the plots of  $\Lambda$  versus concentration (Fig. 4) can be extrapolated back to zero concentration to give the  $\Lambda^0$  value. In practice, this extrapolation can only satisfactorily be made with strong electrolytes. With weak electrolytes, there's a strong dependence of  $\Lambda$  on  $c$  at low concentration and therefore the extrapolations do not lead to reliable  $\Lambda^0$  values.

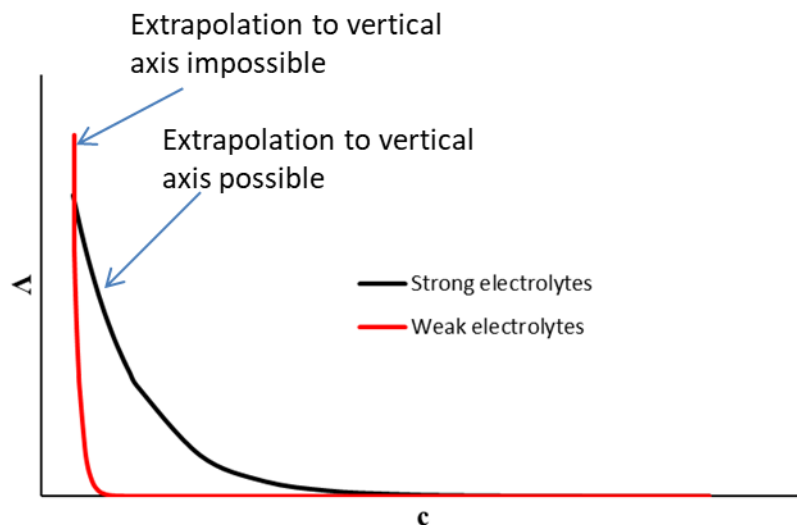


Fig. 5: Profile of molar conductivity of strong and weak electrolytes versus their concentration

Table 1: Molar conductivity at infinite dilution for various sodium and potassium salts in aqueous solution at 25°C

| Electrolyte                        | $\Lambda^o$                                 | Electrolyte                         | $\Lambda^o$                                 | Difference |
|------------------------------------|---|-------------------------------------|---|------------|
|                                    | $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ |                                     | $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ |            |
| KCl                                | 149.9                                       | NaCl                                | 126.5                                       | 23.4       |
| KI                                 | 150.3                                       | NaI                                 | 126.9                                       | 23.4       |
| $\frac{1}{2}\text{K}_2\text{SO}_4$ | 153.5                                       | $\frac{1}{2}\text{Na}_2\text{SO}_4$ | 130.1                                       | 23.4       |

The above table shows that the difference between the molar conductivities of potassium and a sodium salt of the same anion is independent of the nature of the ion. Similar results were obtained for a variety of pairs of salts with common cations or anions, in both aqueous and non-aqueous solvents. It was explained in terms of *Kohlrausch's law of independent migration of ions* given below:

$$\Lambda^o = \lambda_+^o + \lambda_-^o \quad (14)$$

where  $\lambda_+^o$  = conductivity of cation at infinite dilution, and  $\lambda_-^o$  = conductivity of anion at infinite dilution.

The law assumes that each ion makes its own independent contribution to the molar conductivity at infinite dilution, irrespective of the nature of the other ion with which it is associated.

E.g., for KCl

$$\Lambda^o(\text{KCl}) = \lambda_{\text{K}^+}^o + \lambda_{\text{Cl}^-}^o = 149.9 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ (see table 1)}$$

For NaCl

$$\Lambda^o(\text{NaCl}) = \lambda_{\text{Na}^+}^o + \lambda_{\text{Cl}^-}^o = 126.5 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1} \text{ (see table 1)}$$

$$\lambda_{\text{K}^+}^o - \lambda_{\text{Na}^+}^o = (149.9 - 126.5) \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

Therefore,  $\lambda_{\text{K}^+}^o - \lambda_{\text{Na}^+}^o = 23.4 \, \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  difference, which will be the same whatever the nature of the anion.

### Ionic mobility and transference/transport number of ions

The ability of an electrolyte to conduct electric current is dependent upon the product of the total charge carried by the ion and its velocity under the influence of the electric field between the electrodes. If the electrochemical valence ( $n_e = n \times z$ ) and concentration of two ions are the same, then at infinite dilution, when all the molecules are completely dissociated, the conductivity of the ions would depend solely on their velocities.

For example:



For  $\text{Na}^+$ ,  $n = n_{\text{Na}^+} = 2$ ,  $z_{\text{Na}^+} = 1$

$$\text{i.e. } n_e = n_{\text{Na}^+} \times z_{\text{Na}^+} = 2 \times 1 = 2$$

For  $\text{SO}_4^{2-}$ ,  $n = n_{\text{SO}_4^{2-}} = 2$ ,  $z_{\text{SO}_4^{2-}} = 2$

$$\text{i.e. } n_e = n_{\text{SO}_4^{2-}} \times z_{\text{SO}_4^{2-}} = 1 \times 2 = 2$$

In the above example, both ions have the same value of  $n_e$ , hence their conductivity would depend only on their velocities.

It thus follows that:

$$\lambda_+^o = F U_+^o \text{ and } \lambda_-^o = F U_-^o \quad (15)$$

where  $F$ ,  $U_+^o$  and  $U_-^o$  are the Faraday's constant, and velocities at infinite dilution (or ionic mobilities) of the cation and anion respectively. *The mobility of an ion,  $U$ , is defined as the speed with which the ion moves under a unit potential gradient.*

Thus, from equation 14 we can write,

$$\Lambda^o = \lambda_+^o + \lambda_-^o = F(U_+^o + U_-^o)$$

$$\text{therefore, } \Lambda^o = F(U_+^o + U_-^o) \quad (16)$$

Dividing equation 14 by 15:

$$\frac{\lambda_+^o}{\Lambda^o} = \frac{U_+^o}{U_+^o + U_-^o} = t_+^o \quad \text{and} \quad \frac{\lambda_-^o}{\Lambda^o} = \frac{U_-^o}{U_+^o + U_-^o} = t_-^o \quad (17)$$

where  $t_+^o$  and  $t_-^o$  are the transport number of the cation and anion at infinite dilution respectively.

Transport/transference number is the fraction of the current carried by each ion present in solution.

### Question:

**Describe the experimental procedure for the determination of transport number of ions in a named electrolyte.**

The effect of solvent drag on moving ion is represented by the Stokes' law as;

$$U_i = \frac{z_i e}{6\pi\eta r_i} \quad (18)$$

where  $U_i$ ,  $\eta$ ,  $e$ ,  $z_i$ , and  $r_i$  are mobility of ion, viscosity of solvent, electronic charge, valency and ionic radius respectively. In place of  $U_+$  and  $U_-$  in equation 16, put the value of  $U_i$ , we will then have;

$$\Lambda^o = \frac{Fe}{6\pi\eta} \left( \frac{z_+}{r_+} + \frac{z_-}{r_-} \right) \quad (19)$$

$$\Lambda^o \eta = \frac{Fe}{6\pi} \left( \frac{z_+}{r_+} + \frac{z_-}{r_-} \right) = \text{constant} \quad (20)$$

$\Lambda^o \eta = \text{constant}$  is known as the Walden's rule. This rule holds for large ions only, because of complication of hydration. The Stokes' law can be used to explain  $\lambda_+^o$  and  $\lambda_-^o$  given in equation 14, by separating the Stokes' law as follows:

$$\lambda_+^o = \frac{Fe}{6\pi\eta} \left( \frac{z_+}{r_+} \right) \quad (21)$$

Since  $\frac{Fe}{6\pi\eta}$  is a constant, it follows that  $\lambda_+^o \propto 1/r_+$  which is consistent with the data given in

Table 2 below.

| Ions  | H <sup>+</sup>  | Li <sup>+</sup> | Na <sup>+</sup> | K <sup>+</sup> | Rb <sup>+</sup>               | Cs <sup>+</sup>               |                              |
|---|-----------------|-----------------|-----------------|----------------|-------------------------------|-------------------------------|------------------------------|
| $\lambda_+^o$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) | 349.8           | 38.66           | 50.11           | 73.52          | 77.80                         | 77.30                         |                              |
| Ions  | OH <sup>-</sup> | Cl <sup>-</sup> | Br <sup>-</sup> | I <sup>-</sup> | ClO <sub>3</sub> <sup>-</sup> | BrO <sub>3</sub> <sup>-</sup> | IO <sub>3</sub> <sup>-</sup> |
| $\lambda_-^o$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ ) | 198.6           | 76.35           | 78.20           | 76.90          | 64.60                         | 55.80                         | 40.50                        |

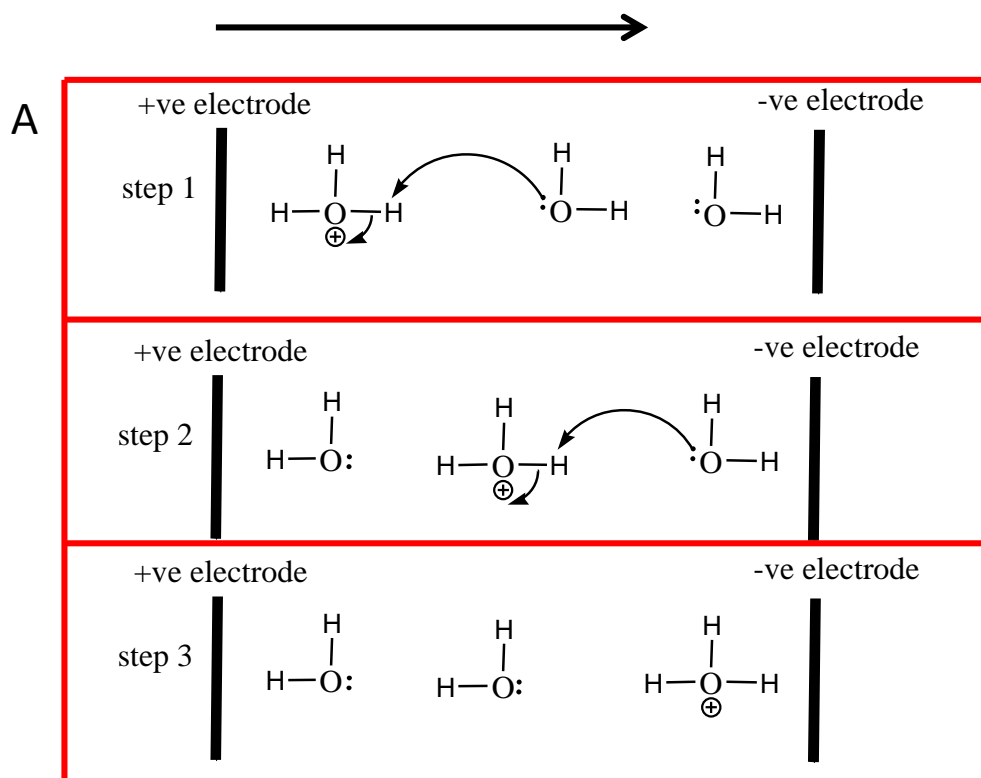


Small positive ions are known to be more highly hydrated than large +ve ions, therefore, large ions are more conducting than small ions. The hydration number of  $\text{Li}^+ = 6$ ,  $\text{Na}^+ = 4$ ,  $\text{K}^+ = 2$ ,  $\text{Rb}^+ = 1$ , implying that hydration numbers decrease as ion sizes increase, and so the effective ionic radius is very large for small ions due to their large hydration numbers.

The case of the -vely charged ions can be understood, since it is generally agreed that they are less hydrated (due to electron cloud), and hence, large ions are less conducting. The  $\lambda_{-/+}^0$  values for  $\text{OH}^-$  and  $\text{H}^+$  are much larger than the others (highlighted in yellow). These large values can be explained on the basis of Proton-Jump Mechanism.

Proton-Jump mechanism illustration for positive and negative ions:

For positive ions, e.g.  $\text{H}^+$ :  $\text{H}^+$  exists in  $\text{H}_2\text{O}$  as  $\text{H}_3\text{O}^+$



For negative ions, e.g.  $\text{OH}^-$  :

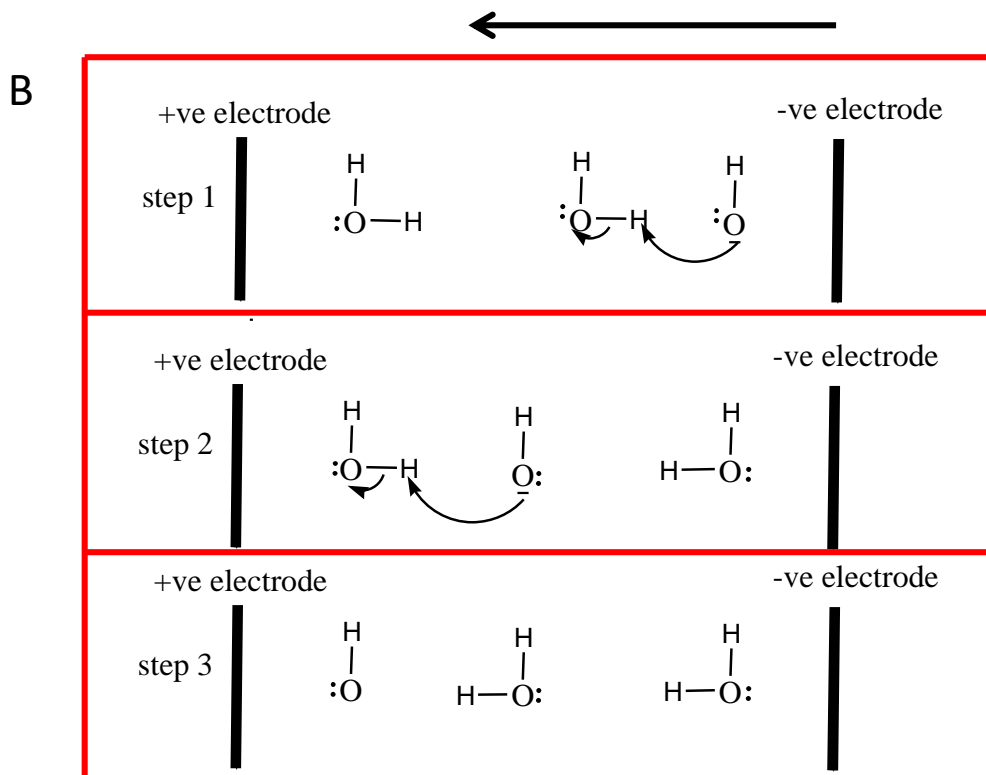


Fig. 6: These figures show the Proton-Jump mechanism by which (A) positive ion migrates towards the  $-ve$  electrode of the cell. (B) negative ion migrates towards the positive electrode of the cell.

This process of hydrogen transfer results in more rapid transfer of  $+ve$  charge from one region to another (hence the high value of  $\lambda_+^0$ ) than will be possible if the  $\text{H}_3\text{O}^+$  ion has to push its way through the solution as the other ions.

### Application of Conductivity Measurement

The conductance of electrolytes depends on the number of ions and their speeds. The measurements of conductivity have been utilized for determining –

- (a) the endpoints of acid-base titrations,
- (b) the endpoints of precipitation titrations;

(c) the solubility of sparingly soluble salts and

(d) the kinetics of reactions.

For conductometric titration experiments, a known volume of the solution to be titrated is placed in a beaker and a conductivity cell dipped into it. The conductivity cell is now connected to one end of the Wheatstone's bridge. The other solution is then added to the solution in the beaker in installments and the conductance is measured after each addition. This is continued beyond a sharp change in conductance value. The conductance values are then plotted against the volumes of the titrant added. In each case, the straight-line portions of the graph are extrapolated and the point at which the straight lines intersect is taken as the end point of the titration.

Practical application of this is found when the conductivity of natural water is required. Conductivity is mostly used to estimate the concentrations of dissolved salts in natural water, which then provide insights into processes affecting the water. In coastal areas, the conductivity of water might change with assimilation with saltwater, and the conductivity of water might rise when it becomes contaminated with road salt in areas with cool climates.

***Other Common Application of conductance measurements:***

- Determination of dissociation constant of weak electrolytes, e.g. HAc
- Determination the solubility of a sparingly soluble salt: Conductance offers a very simple and convenient means of determining the solubility of a sparingly soluble salt such as AgCl.
- Water Treatment and Industrial Applications: Water treatment may be used to make water safe to drink or suitable for industrial use. In many industrial applications, corrosion might be a source of heavy contamination. Conductivity can be used to monitor the level of this contamination before desalinization or other techniques for the removal of the ions are employed.

In some other industrial applications, conductivity measurements may be used to identify leaks, where the leaking water might have higher conductivity value. Conductivity may also be used to check the efficiency of rinsing procedures, where a low conductivity of water in contact with the rinsed object indicates an efficient rinse.

- Agricultural and hydroponics applications: For irrigation, the salinity of the water is a significant factor. If the salinity is too high, salts will build up in the soil as the water evaporates which might demean soil eminence and inhibit plant growth.
- Conductivity can also be used to observe nutrient concentrations in liquid fertilizers: Comparable to fertilizer application, conductivity is used in hydroponics to monitor the concentrations of nutrient solutions. If the conductivity gets too high, indicating a nutrient concentration at toxic levels, plant growth might be inhibited or the plant dies. Low

conductivities can designate insufficient nutrient supply. Conductivity monitoring can be used as a component of mechanized nutrient supply systems.

### Exercises

1. The electrolytic conductivity of a  $0.1 \text{ mol.dm}^{-3}$  solution of acetic acid (corrected for the conductivity of water) was found to be  $5.3 \times 10^{-4} \text{ } \Omega^{-1}.\text{cm}^{-1}$ . Calculate the molar conductivity.
2. A conductivity cell was filled with  $0.0100 \text{ mol.dm}^{-3}$  KCl which was known to have a conductivity of  $0.001413 \text{ } \Omega^{-1}.\text{cm}^{-1}$  at  $25^{\circ}\text{C}$ . Its measured resistance was  $94.3 \text{ } \Omega$ . When the cell was filled with  $0.0200 \text{ mol.dm}^{-3}$   $\text{AgNO}_3$ , its resistance was  $50.3 \text{ } \Omega$ . Calculate the conductivity of the  $\text{AgNO}_3$  solution.
3. A conductivity cell whose constant is  $22.81 \text{ m}^{-1}$  was filled with  $0.0025 \text{ mol.dm}^{-3}$   $\text{K}_2\text{SO}_4$  solution. The resistance of the solution is  $326.0 \text{ } \Omega$ . If the  $\text{K}_2\text{SO}_4$  dissociates completely in solution, what is the molar conductivity of  $\text{K}_2\text{SO}_4$ ?
4. (a) Calculate the molar conductivity at infinite dilution for acetic acid at  $298 \text{ K}$  given the following data obtained by extrapolation from the graph of  $\Lambda$  vs  $c$ :  
 $\Lambda^{\circ}(\text{HCl}) = 426.1 \times 10^{-4} \text{ m}^2 \text{ } \Omega^{-1}.\text{mol}^{-1}$   
 $\Lambda^{\circ}(\text{AcNa}) = 91.0 \times 10^{-4} \text{ m}^2 \text{ } \Omega^{-1}.\text{mol}^{-1}$   
 $\Lambda^{\circ}(\text{NaCl}) = 126.5 \times 10^{-4} \text{ m}^2 \text{ } \Omega^{-1}.\text{mol}^{-1}$   
  
 (b) The molar conductivity of a  $0.001028 \text{ mol.dm}^{-3}$  acetic acid solution was found to be  $48.15 \times 10^{-4} \text{ m}^2 \text{ } \Omega^{-1}.\text{mol}^{-1}$  at  $298 \text{ K}$ , from the molar conductivity at infinite dilution obtained from (a), calculate the degree of dissociation of acetic acid at this concentration and its ionization constant.
5. The molar conductivity at infinite dilution at  $25^{\circ}\text{C}$  for KCl is  $150 \text{ cm}^2.\Omega.\text{mol}^{-1}$ , and the transport number of  $\text{K}^{+}$  at infinite dilution is  $0.491$ . Calculate  $\lambda_{+}^{\circ}$  for  $\text{K}^{+}$  and  $\lambda_{-}^{\circ}$  for  $\text{Cl}^{-}$  at the same temperature.
6. The mobility of a sodium ion in water at  $25^{\circ}\text{C}$  is  $5.19 \times 10^{-4} \text{ cm}^2.\text{V}^{-1}.\text{s}^{-1}$ . Calculate the molar conductivity of the sodium ion.

**END OF LECTURE I**