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Author(s)	Goh Ngoh Khang and Chia Lian Sai
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The Concept of Conductivity and Molar Conductivity of an Aqueous Solution

Introduction

In most of the Pre-University Chemistry textbooks, the definitions of conductivity and molar conductivity are presented in an understandable and well-formulated way. However the authors' own teaching experiences reveal that many pre-university students do not understand the real physical meanings of conductivity and molar conductivity and even confuse the difference between the two terms. The purpose of this article is therefore to introduce a more basic concept and to give certain physical meanings for the conductivity, molar conductivity and molar conductivity at infinite dilution.

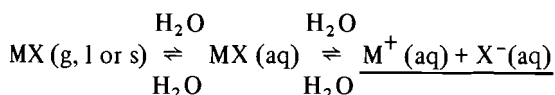
What causes the conductivity of an aqueous solution?

To answer the above question, we might first think what would happen to the electrolytes regardless of whether they are strong or weak, when placed in water. In fact, interactions of various particles would take place. These include

- (i) interaction of compound with polar water molecules,
- (ii) interaction of ions with water molecules (hydration effect), and
- (iii) interaction of ions themselves.

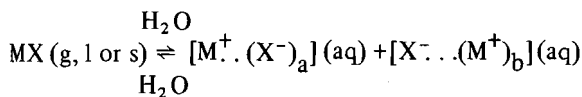
The process can be summarised as follows:

For weak electrolytes:



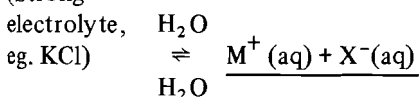
(Weak electrolyte, eg. HAc)

For strong electrolytes:



(Strong

electrolyte, eg. KCl)



Normally, the interaction (ii) is accompanied with the interaction (i). The action of water will finally cause the dissociation of either strong or weak electrolytes into the ionic species.

Consider now the processes by which water is gradually added into weak as well as strong electrolytes.

- (a) Weak electrolyte: The electrolyte will form hydrated molecules together with some ions which are dissociated from the molecules. The electrolyte is weak because the dissociation is very small in quantity. If more water is added, more water molecules will separate the ions and prevent the recombination of ions and hence the dissociation will increase with increasing dilution.

This fact can also be explained by Le Chatelier's Principle that the addition of water will make the equilibrium shift to the right hand side. Such phenomenon is also known as Ostwald's dilution law.

- (b) Strong electrolyte: Strong electrolytes might dissolve in water completely because the hydration energy produced is usually sufficient to overcome the lattice energy or bond energy of the compound. If the hydration energy is insufficient, the entropy effect plays an important role in the dissolving process.

In the case when a small amount of water is added to the strong electrolyte, it can be imagined that the ions are crowded together. Since the attractive forces of ions to those oppositely charged are non-directional and unsaturated, positive ions tend to attract a number of negative ions and vice versa, with the formation of ionic atmosphere. With increasing dilution, i.e. addition of water, the ionic atmosphere will be destroyed due to more hydration, possibly between ions and water molecules. Eventually no more ionic atmosphere is left.

In fact, these two processes could be identical if the numerical values of a and b are both equal to unity. As a result, the term degree of dissociation can also be given to the strong electrolyte in such a state, in order to indicate how free the ions are. Since we still consider strong electrolytes to be completely dissociated, the term "apparent degree of dissociation" will be used for strong electrolytes. With this term, it seems more suitable for our purpose to distinguish strong electrolytes from weak electrolytes. But for convenience, degree of dissociation could commonly be used for weak electrolytes as well as for strong electrolytes.

The interaction (iii), i.e. the interaction of ions themselves, is responsible for the backward reaction. Such backward reaction, which is the reverse of dilution, indicates that the more concentrated the solution is, the greater is the effect it has. In a concentrated solution, the ions with opposite charges have more opportunity to approach each other and hence the chances to recombine together will be greater.

Those ions present, which are underlined, are responsible for conducting a current in the aqueous solution of an electrolyte.

The manner of conduction in a metal, i.e. its conductivity, is so much different from that of an aqueous solution because in the case of metal, the free electrons in the metallic lattice play the role of conducting the current. Its mechanism is shown in the following figure:

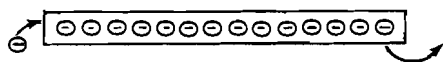


Figure 1

While one electron is put in from one end, immediately one electron will move out from the other end. In the case of an aqueous solution, the ions carry charges and move through the water molecules and oppositely charged ions, under the applied potential difference, towards the electrodes where the ions are discharged (see Figure 2).

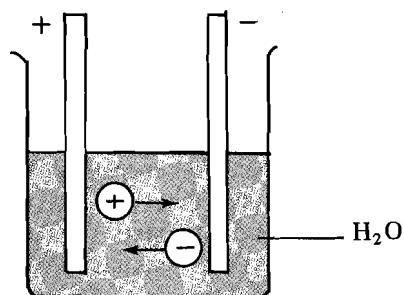


Figure 2

It can be expected that the conductivity of an aqueous solution will be very small in comparison to that of metal. Indeed it is so! In general, the electrolytic conductance is of the order of one hundred-fold less than metallic conductance.

Factors affecting the conductivity

The conductivity of an aqueous solution will be affected by some factors. These are:

- (I) number of charged particles i.e. ions, which are responsible for the carrying of current.
- (II) movement of charged particles under the applied electric field.
- (III) magnitude of charge on the ions.

More detailed discussions on these factors will be given below.

- (I) **Number of charged particles** — The total number of ions present depends on
 - (a) Whether the compound is weak or strong electrolyte — Due to the nature of the electrolyte, it is clear that with the same molar concentration, the aqueous solution of the strong electrolyte will contain more ions than that of the weak electrolyte. As a result, the strong electrolyte has generally a higher conductivity than the weak one.
 - (b) Concentration of the strong electrolyte — When the concentration of a solution of a strong electrolyte increases, the concentration of the ions present in solution increases. But the effect of interaction forces of ions also becomes more and more pronounced as the concentration of ions increases. This implies that the conductivity of a strong electrolyte, in very concentrated solution, is relatively low. With dilution, the conductivity increases rapidly up to a certain maximum value. With further dilution, the concentration of the solution, i.e. the number of ions per unit volume, drops accompanied by a fall in conductivity (See Figure 3)

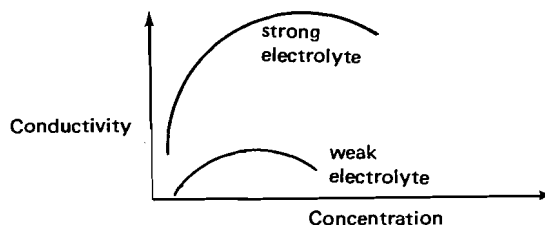


Figure 3

- (c) **Concentration of the weak electrolyte** – When the concentration of a weak electrolyte is increased, the concentration of the ions in solution and hence its conductivity would not increase very much because the degree of dissociation is limited.

As the dilution of a solution containing a weak electrolyte causes an increase in the degree of dissociation of the electrolyte, there is a steady increase of conductivity with dilution. But the gradient of this increase should be smaller in comparison to those for strong electrolytes. This is due to the fact that the interaction forces of the ions fall rapidly with the dilution of strong electrolyte solutions, while this is not the case with the dilution of weak electrolyte solutions. Analogous to the strong electrolyte, if the dilution exceeds a certain extent, a fall of conductivity should be expected. The increase of dissociation by dilution would likely to be compensated by the reduction of the total concentration caused by dilution (see Figure 3).

(II) **Movement of charged particles** – The movement of charged particles (ions) depends on the following conditions.

- (a) **Size of the ions** – The velocity with which ions move under the influence of an electric field is inversely proportional to the mass and the size of the ions. But the size of ions should be defined carefully since ions possess higher charges or smaller sizes, and attract water molecules so strongly and firmly that the water envelope formed should be taken as part of the size of the ion (see Figure 4, dotted line in the case of Na^+ ion)

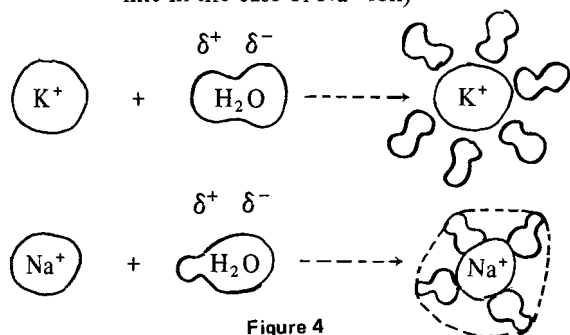


Figure 4

This explains the fact why Na^+ ions, although smaller in gaseous state (i.e. $\text{Na}^+(\text{g})$) than that of K^+ ions, has a lower conductivity.

- (b) **Concentration of strong electrolyte solutions and interaction of oppositely charged ions** – In a concentrated solution, the attraction of oppositely charged ions tends to shield one another from the electric field applied and these ions thereby move more slowly towards the respective electrode. The more concentrated the solution, the greater is the opportunity for the ions of opposite charge to come closer together and hence the greater the shielding effect. In a very dilute solution, the ions are separated from one another by distances which are very great compared with the sizes of the ions. Here the movement of ions through the solution under the influence of an applied electric field could be more or less independent of one another. Therefore, the conductivity increases as the concentration of a strong electrolyte solution decreases.
- (c) **Concentration of the weak electrolyte solution** – The dilution of a weak electrolyte solution generally causes an increase in conductivity due to an increase in the degree of dissociation, as discussed above. Although there is an increase of ions, the dilution might compensate more than the effect of interaction between two ions of opposite charge. So the movement of ions could still be independent.
- (d) **The effect of hydration** – As mentioned before, cations and anions are moving against a counter movement of anions and cations respectively. All these ions are hydrated with some water molecules and therefore the ions are in fact “swimming against the current”. As the concentration increases the effect would be more pronounced.

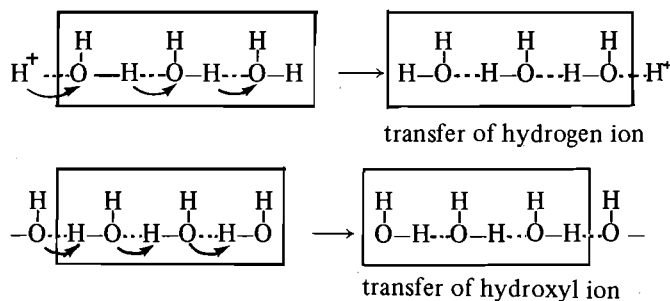
- (III) **Magnitude of charge on the ions** – We would expect that with ions of higher charge there is an increase of conductivity because the ions will be strongly affected by an external electric field. However the hydration effect and interaction forces will also increase with an increase in the charges of the ions. This provides a compensatory effect which

causes the resultant conductivity of all sorts of ions, except H^+ and OH^- ions, to be comparable.

Conductivities of hydrogen and hydroxyl ions.

The conductivities of hydrogen and hydroxyl ions are unexpectedly high, being about 7 and 3 times that of the average value for other ions respectively. It is known that water is polymerised in chains $(H_2O)_n$ [where $n = 2 - 5$] and that hydrogen

and hydroxyl ions are highly hydrated in aqueous solutions. Thus the very high conductivities of these two ions cannot be accounted for by the actual ease of motion of the ions themselves. It seems likely that a special mechanism takes place so that these ions do not actually have to move through the solution. It is thought that these ions are able to pass on their charge from one water molecule to another by the transfer of a hydrogen ion or a hydroxyl ion in the following way:



(The dotted lines indicate hydrogen bonds)

Figure 5

These processes can occur very rapidly and can be continued through the solution, causing the charge to transfer through the solution faster than the speed at which the ions can move, and hence resulting in abnormal conduction. This mechanism is similar to the manner of conducting electricity in metal, i.e. "one end in and the other end out."

However such mechanism involves the chain reactions of bond breaking and bond forming and hence the conductivity of hydrogen ion and hydroxyl ion respectively is still much smaller than conduction in metals.

Molar Conductivity

From the above discussion, it would be meaningless to compare conductivities under various concentrations, since any comparison should be on a certain common basis. So we introduce the concept of molar conductivity. The relationship of conductivity and molar conductivity is generally given by the following mathematical expression:

$$\Lambda(\text{Molar conductivity}) = \frac{k(\text{conductivity or specific conductivity}) \text{ m}^2/\text{mol. } \Omega.}{C(\text{concentration in molarity})}$$

In most chemistry textbooks, the meaning of molar conductivity is given as follows: "The value of molar conductivity is equivalent to the conductance caused by all the ions in a volume of solution (φm^3) containing 1 mol. of the electrolyte, the electrodes being 1 m apart". They can be imagined as parallel electrodes, each having a very large area and immersed into a solution. The conductance of the solution, confined between the cut-out surfaces of such electrodes having an area of φm^2 , is the molar conductivity of the solution. The volume of the solution between these electrode areas is obviously equal to φm^3 . It contains one gramme mole of electrolyte. The stand point of the above consideration is derived from the unit of molar conductivity and the measurement technique of conductance.

Physical Meaning of Molar Conductivity

For the respective concentration, the conductivity k includes the resultant effect of all the factors affecting the conductivity. Now the change of the various concentrations to the same unified molar concentration (1 molar solution) shows that the number of particles initially would be the same and this is what we have mentioned earlier, the common basis. The corresponding numerical

magnitude of the molar conductivity at certain concentration indicates only the change of conductivity which relates the increase (or decrease) of concentration to the unified one. In considering

those factors affecting conductivity just mentioned, the meaning of molar conductivities then could have the following two approaches (refer also to Figure 6):

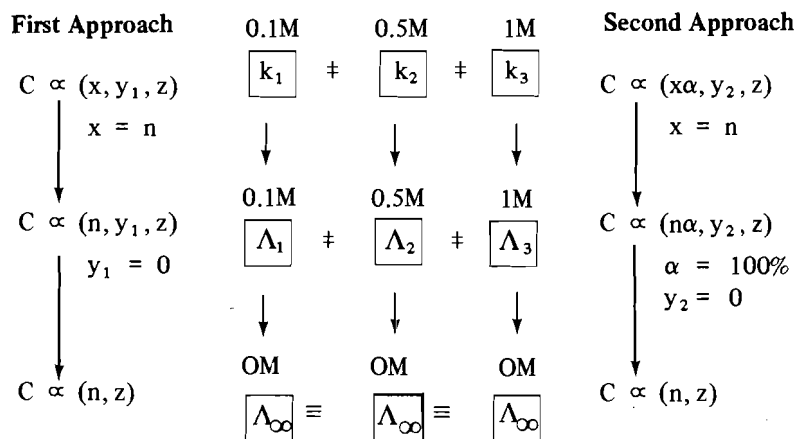


Figure 6

Legend

C = conductivity, x = no. of mol of ions, n = no. of mol of ions in φ m³ of solution which contains 1 mol of electrolyte, α = degree of dissociation, y_1 = interaction of ions in terms of degree of dissociation, y_2 = interaction of ions, z = hydration effect, k = specific conductivity, Λ = molar conductivity, Λ_∞ = molar conductivity at infinite dilution, \propto : is proportional to, \neq : is not equal to, \equiv : is identical to.

Approach 1. If we assume that all sorts of electrolytes whether strong or weak dissociate completely in water, then the molar conductivity shows only the measurement of interaction of ions-ions and ions-water molecules (hydration effect) at the corresponding concentrations.

The difference between strong electrolyte and weak electrolyte could be considered to be based on the interaction forces of ions-ions. At normal concentration, the interaction of ions and ions for the weak electrolyte would be much greater than the strong electrolyte and hence it exists more in the molecular form.

Approach 2. If we want to have a distinction between the strong and weak electrolytes, then the molar conductivity should also include the measurement of the degree of dissociation besides the interactions of ions-ions and ions-water molecules at the corresponding concentration.

The second approach seems to be more related to the real situation. We can express the approach in another way.

For strong electrolytes: The molar conductivity is the proportional change of the conductivity from C concentration to 1 molar concentration, whereas hydration effect and interaction of ions themselves still remain the same as at C concentration.

The molar conductivity at infinite dilution is hence the molar conductivity at such a condition that the interaction of ions among themselves is eliminated.

For weak electrolytes: The molar conductivity of a weak electrolyte has exactly the same meaning as that of a strong electrolyte except that the dissociation is incomplete and the interaction of ions among themselves is eliminated (since the weak electrolyte exists mostly in the molecular form). The molar conductivity at infinite dilution is hence the molar conductivity at the condition which could be considered as 100% dissociation.

In fact, at infinite dilution, strong and weak electrolytes have exactly the same properties, i.e. 100% dissociation and no interaction of ions among themselves, except that the interaction of ions and water molecules might be different.

With the concept of molar conductivity and molar conductivity at infinite dilution, it is not difficult to understand the physical meaning of "conductance ratio" or non-committal term "apparent degree of dissociation", i.e. the ratio Λ_v/Λ_∞ and the ionic conductance.

Furthermore, the figures for the ionic conductance which is throwing some light on the extent to which ions in solution are hydrated can be well understood. ☞