Ionic mobilities

The velocity of an ion in a solution depends upon the applied potential ~~graduen~~ gradient ~~of~~ 1 volt cm^{-1} The velocity with which an ion moves under a potential gradient of 1 volt cm^{-1} in a solution is called ionic mobility.

The approach of the equivalent conductances of all electrolytes to a limiting value at very high dilution may be ascribed to the fact that under these conditions, all the ions from 1 g ~~eq~~ eq are taking part in conducting the current. At high dilutions, therefore, solutions containing 1 g eq of various electrolytes will contain equivalent no of ions, the total charge carried by all the ions will thus be the same in every case. The ability of an ~~elect~~ electrolyte to transport current is determined by the product of no. of ions and charge carried by each i.e the total charge is constant for equivalent solutions at high dilution. Therefore the limiting ~~value~~ equivalent conductance of an electrolyte must depend on ionic velocities. It is the difference in the speeds of the ions which is consequently responsible for the different values of ion conductances. The speed with which a charged particle moves is proportional to the potential gradient i.e fall of potential per cm. So, the speeds of ions are specified under a potential gradient of unity i.e $1 \, V \, cm^{-1}$. These speeds are known as ionic mobilities.

If u° and v° are actual velocities of cation and anion of the given electrolyte at infinite dilution under $1 \, volt \, cm^{-1}$, the equivalent conductance at infinite dilution is given by

$$\Lambda_0 = K(u^\circ + v^\circ)$$

where K is proportionality constant which is same for all electrolyte. Again, $\Lambda_0 = \lambda_+ + \lambda_-$

Therefore, $\lambda_+^\circ = ku^\circ$ and $\lambda_-^\circ = kv^\circ$

where λ_+° and λ_-° are ionic conductances of cation anion at infinite dilution respectively

The $\lambda_{Na^+} = 50.1$ mho cm² mol⁻¹ the ionic mobility of Na^+ ion is therefore

$$\text{Ionic mobility} = \frac{\text{Ionic conductance}}{96500}$$

$$= \frac{50.1 \text{ mho cm}^2 \text{mol}^{-1}}{96500 \text{ c mol}^{-1}}$$

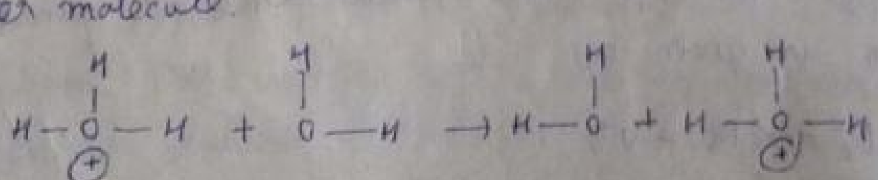
$$= 5.1917 \times 10^{-4} \text{ cm}^2/\text{ohm C}$$

$$= 5.1917 \times 10^{-4} \frac{\text{cm}^2 \text{s}^{-1}}{\text{ohm ampere}}$$

$$= 5.1917 \times 10^{-4} \text{cm}^2 \text{s}^{-1} \text{V}^{-1} \text{ (volt = ohm amp.)}$$

$$= 5.1917 \times 10^{-8} \text{ m}^2 \text{V}^{-1} \text{s}^{-1}$$

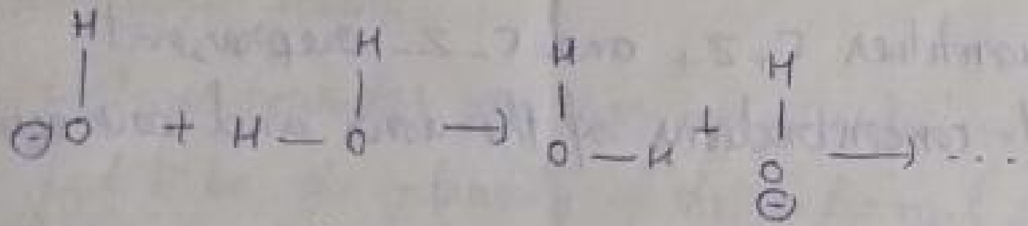
The ionic mobilities of H^+ and OH^- are very high. The high conductance of H^+ and OH^- are due to a type of GROTTHUSS conduction. It is supposed that the H^+ ion in water is H_3O^+, when a potential gradient is applied to an aqueous solution containing H^+ ions, the H^+ ions travel to some extent by the same mechanism as do other ions, there is an addition another mechanism which permits of a more rapid movement. The second process is believed to involve the transfer of a proton from H_3O^+ to an adjacent water molecule



The resulting H_3O^+ ion can now transfer a proton to another water molecule and in this way

+ve charge transferred a considerable distance in a short time. It is estimated that the proton has to jump a distance of 0.86×10^{-8} cm from one H_3O^+ to another H_2O molecule. As a result, the +ve charge is effectively transferred through 3.1×10^{-8} cm. The electr electrical conductance will thus be much greater than due to normal mechanism. The abnormal conductivity of H^+ in CH_3OH and C_2H_5OH which are some what less than in water can also be explained by the similar mechanism

The conductance of OH^- in water is less than that of the H^+ ion. It can also be explained as the transfer of proton shown as



The H^+ and OH^- are transferred from one end to other end without migrating through the solution.