

28

Electrical Conduction in Liquids and Solids

28-1 Conductivity of Liquids. Electrolytes

We have seen that electrical conduction in solids is associated with the drift of free electrons in the solid, a process which will be examined in greater detail in Section 28-4. A similar mechanism may be used to account for the conduction of electricity in liquid metals. In other liquids electricity is conducted by the migration of positive and negative *ions* through the liquid.

When two terminals, or *electrodes*, are immersed in a liquid and a source of emf is connected to them, there will be a current through the liquid. Under the influence of the electric field established between the positive terminal, or *anode*, and the negative terminal, or *cathode*, the ions drift through the liquid. In general, if n_+ is the number of positive ions per unit volume moving with an average drift velocity v_+ , and n_- is the number of negatively charged ions per unit volume moving with a drift velocity v_- , we find the current density J in the liquid to be

$$J = n_+q_+v_+ - n_-q_-v_-.$$

The drift of the positive ions is in the direction of the current, while the drift of negative ions is opposite to the direction of the current.

The electrical conductivity of a liquid depends upon the number of ions per unit volume and upon their drift velocity. The drift velocity of an ion varies with the electric field intensity, with the mass of the ion, and with other factors as well. Thus the electrical conductivity of different liquids may be expected to have widely different values.

Oily substances are very poor conductors of electricity, with conductivity of about 10^{-10} mho/m. Such oils find application as insulating oils in electrical apparatus. Pure solvents such as water or alcohol are relatively poor conductors, with a conductivity of about 10^{-4} mho/m. The conduc-

tivity of solutions of chemical salts in water is much higher, being about 10 mho/m. Such solutions are generally classed as good conductors and are called *electrolytic* solutions. The dissolved substance, or *solute*, is known as the *electrolyte*. While the conductivity of electrolytes is quite high compared to the conductivity of the pure solvent, their conductivity is small compared to a metallic conductor such as copper whose conductivity is about 10^8 mhos/m. The electrical conductivity of different liquids is shown in Table 28-1.

TABLE 28-1 ELECTRICAL CONDUCTIVITY OF LIQUIDS

Substance	Conductivity (mhos/m)
KCl solution (0.1 <i>n</i>)	1.05 (at 15°C)
NaCl solution (saturated)	20.14 (at 15°C)
Ethyl alcohol	3.3×10^{-4} (at 15°C)
Paraffin oil	10^{-14}
Distilled water	2×10^{-4} (at 18°C)
Mercury	1.04×10^6 (at 20°C)

Our present understanding of the conduction of electricity by electrolytic solutions indicates that electrolytes are materials which are held together by strong electrical forces in the solid state. In crystalline sodium chloride, positively charged sodium ions and negatively charged chlorine ions occupy adjacent places in the crystal lattice. These ions are firmly anchored in position in the solid phase. Solid sodium chloride is a non-conductor of electricity. At high temperatures the ions have sufficient thermal energy to overcome the attractive forces holding them in place, and the substance melts. Molten sodium chloride is a good conductor of electricity, having a conductivity about one twentieth that of a solution of sodium chloride in water. The sodium ions and the chlorine ions in molten sodium chloride drift under the action of the electric field. The sodium ions migrate toward the cathode, and the chlorine ions migrate toward the anode, so that pure sodium and pure chlorine may be separated in an electrolytic cell. Free electrons do not traverse the cell.

When sodium chloride is placed in water, there are strong forces of attraction between the water molecules and the ions of sodium and chlorine. The water molecule is highly polar. The positive or hydrogen end of the water molecule tends to attach itself to the negative chlorine ion, while the negative or oxygen end of the water molecule tends to attach itself to the positive sodium ion, as shown in Figure 28-1. A shell of water molecules tends to surround each ion, and we say that the ions are *hydrated* in solution. This shell of water molecules tends to separate the sodium and

chlorine ions and to reduce the electrical force of attraction between them, both as a result of the physical separation and as a result of the reduction in electric field intensity of a point charge in a medium of high dielectric constant (see Section 25-7).

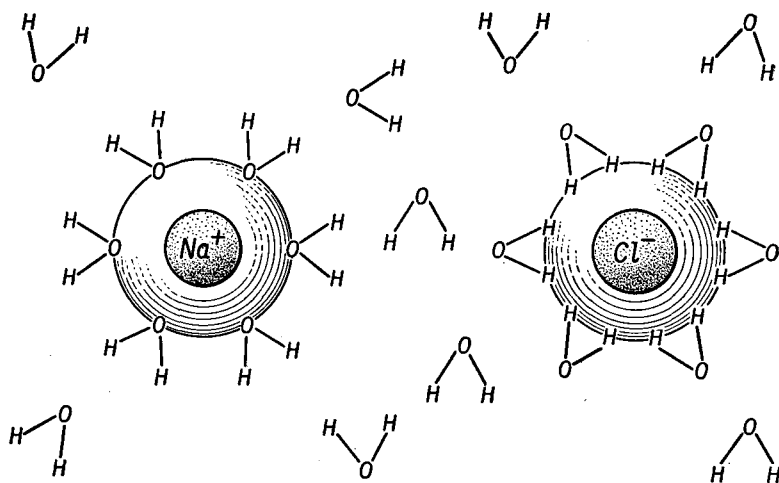


Fig. 28-1 Sodium and chlorine ions and associated water molecules.

It is interesting that ionic substances dissolve only in polar solvents. The process of solution is evidently furthered by the manner in which the molecules of the solvent are able to attach themselves to the ions of the solute. Ionic substances are relatively insoluble in nonpolar solvents, such as benzene. When electrodes are immersed in an electrolytic solution, the ion and its associated water of hydration drift as a unit through the liquid, so that the effective mass of the ion is the mass of the entire assemblage.

28-2 Faraday's Laws of Electrolysis

The flow of electricity through an electrolytic solution is associated with the transport of ions through the solution. If two silver electrodes are immersed in a solution of silver nitrate in water, it is observed that the mass of the anode diminishes as current is passed through the cell, while the mass of the cathode increases. The total mass of the two electrodes remains constant; that is, the effect of the passage of current is to transport silver from anode to cathode. Silver atoms from the anode go into solution as ions at the anode, replacing those ions which have left the solution as atoms at the cathode. Electric charges are thus transported between the electrodes. The concentration of the electrolyte in the solution remains