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## ***Physics*, Chapter 28: Electrical Conduction in Liquids and Solids**

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# 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	$3.3 \times 10^{-4}$ (at 15°C)
Paraffin oil	$10^{-14}$
Distilled water	$2 \times 10^{-4}$ (at 18°C)
Mercury	$1.04 \times 10^6$ (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).

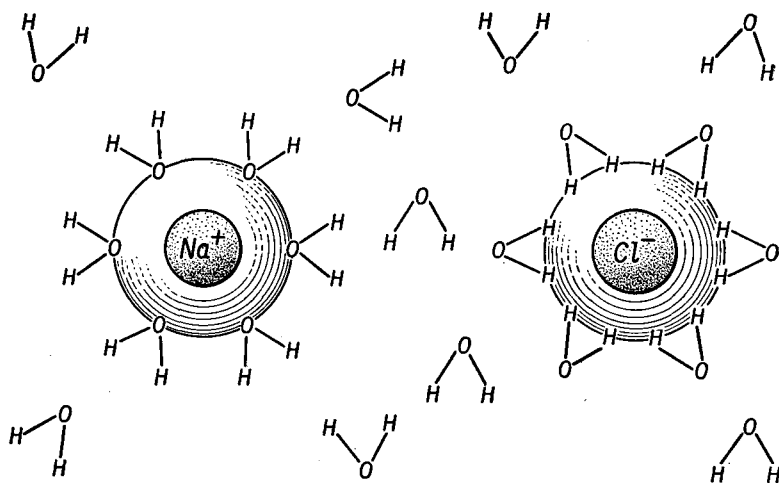


Fig. 28-1 Sodium and chlorine ions and associated water molecules.

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

unchanged. When a cathode of some metal other than silver is used, this process results in *electroplating* silver onto the other metal.

The results of experiments with electrolytic cells can be summarized in terms of two laws first formulated by Faraday, which state:

(1) *The mass of any substance liberated from the solution is proportional to the total quantity of charge passing through the circuit.*

(2) *If the same quantity of electric charge passes through a series of cells, the masses of the elements deposited or liberated are in the ratio of their respective chemical equivalents.*

The *chemical equivalent* of an element is defined as the atomic weight divided by the valence. The direct implication of Faraday's laws is that the flow of electric charge through a cell is always accompanied by the movement of ions, and that no charge is transported through the solution by the motion of free electrons.

Faraday's two laws of electrolysis can be combined into the following single equation:

$$M = Q \frac{A}{v} \frac{1}{\mathcal{F}}, \quad (28-1)$$

where  $M$  is the mass of an element deposited or liberated by the transfer of a quantity of electricity  $Q$  through an electrolytic cell,  $A$  is the atomic weight of the element,  $v$  is its valence, and  $\mathcal{F}$  is a constant known as the *faraday*. The faraday is equal to the quantity of electricity transferred through the cell in depositing or liberating a gram chemical equivalent of an element. The gram chemical equivalent is the number of grams numerically equal to the chemical equivalent.

The best experimental value of the faraday is

$$\mathcal{F} = 96,496 \text{ coul/gm atomic wt,}$$

using the chemical scale of atomic weights in which the atomic weight of oxygen is taken as 16. The faraday has a slightly different value on the physical scale of atomic weights in which the atomic weight of a particular isotope of oxygen containing 16 nucleons (8 protons and 8 neutrons) is taken as 16.

It is possible to make use of Faraday's laws of electrolysis to measure the charge transferred in a circuit by the passage of an electric current. Thus, a silver *coulombmeter*, an electrolytic cell having silver electrodes and a solution of a silver salt as electrolyte, may be placed in an electric circuit, and the charge transferred may be determined by measuring the mass of silver plated onto the cathode or liberated from the anode.

The results of experiments in electrolysis enable us to determine the

charge carried by ions. The faraday represents the total charge transferred by the ions when a gram atomic weight of an element of unit valence is liberated from the solution. Since there are  $N_0$  atoms in a gram atomic weight of an element, where  $N_0$  is the Avogadro number, this means that  $N_0$  ions, each carrying a charge  $e$  equivalent to the charge of an electron, are transferred in the process. We can write

$$\mathcal{F} = N_0 e. \quad (28-2)$$

The Avogadro number  $N_0$  has been determined by other experiments and its presently accepted value is

$$N_0 = 6.023 \times 10^{23} \text{ atoms/gm atomic wt.}$$

Equation (28-2) therefore yields the value

$$e = 1.602 \times 10^{-19} \text{ coul}$$

for the electronic charge.

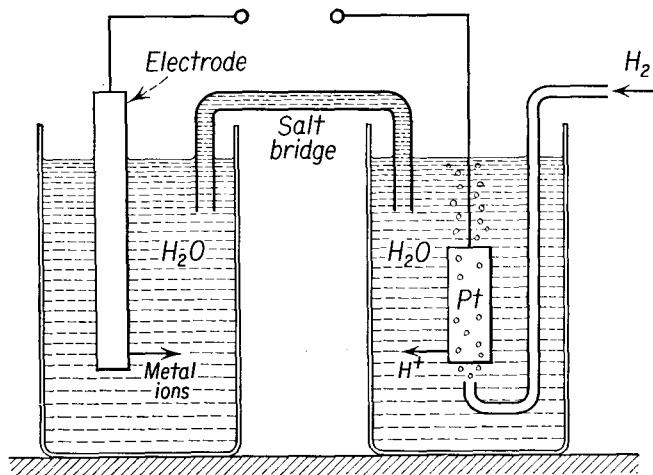
The above procedure is one of the most accurate methods for the determination of the charge of the electron. The first demonstration of the unique value of the electronic charge was made by Robert Andrews Millikan, who measured the charge on small droplets of oil suspended between two horizontal brass plates, by studying the speed with which the charged droplets fell through air under the combined action of gravitation and the imposed electric field between the two plates.

### 28-3 Electrochemical Cells

In an electrochemical cell chemical energy is transformed into electrical energy. When electrodes of two different materials are immersed in an electrolyte and no current is permitted to flow to any external circuit, it is found that there is a potential difference between them, called the emf of the cell. When a metallic electrode is immersed in an electrolyte, there is a tendency for ions of the metal to go into solution, and, since ions formed by a metal are generally positively charged, the electrode becomes negatively charged. The negatively charged electrode tends to attract ions onto itself as a precipitate. Equilibrium is reached when the number of ions leaving the electrode to go into solution in a given time interval is equal to the number attracted to the electrode in that time interval. The charge on the electrode when equilibrium is reached depends upon the chemical activity between the electrode and the solvent. Since chemical activity varies with temperature, the charge on the electrode, and hence its potential, vary with temperature.

The potential acquired by an electrode cannot itself be measured without some reference potential. It is customary to measure the potential

difference between a particular electrode and a *hydrogen electrode*. The hydrogen electrode consists of a piece of platinum foil, coated with finely divided platinum, immersed in water. Hydrogen gas is bubbled over the platinum electrode and tends to collect at the surface of the platinum. An electrode potential is reached which is a measure of the tendency for hydrogen ions to accumulate in the solution. The potential of this reference



**Fig. 28-2** Cell made of a metal electrode and a hydrogen electrode for measurement of electrode potentials.

electrode is arbitrarily assigned the value zero. The potentials of other electrodes are then determined by measuring the potential difference between the hydrogen electrode and another electrode when these are made part of a cell, as shown in Figure 28-2. The results of such measurements with different electrodes are shown in Table 28-2. The algebraic difference in potential between two values in the table then gives approximately the emf of a cell made up of the two electrodes.

The values of electrode potentials given in Table 28-2 represent the potential of a particular electrode, when in equilibrium with ions of that electrode, referred to the potential of a hydrogen electrode in equilibrium with hydrogen ions. The position of a substance in the table therefore represents the tendency of an electrode to go into solution. The more negative the electrode potential, the greater the tendency of the substance to go into solution. Since zinc has a more negative electrode potential than copper, we find that, if a zinc strip is placed in a copper sulphate solution, zinc ions will tend to replace copper ions in the solution, and the zinc strip will acquire a coating of copper.

We shall describe briefly only a few of the many practical cells in common use:

The *Daniell cell* consists of an amalgamated zinc electrode immersed in a solution of zinc sulphate and a copper anode immersed in a saturated solution of copper sulphate. The emf is approximately 1.06 volts, which may be compared to a value of 1.10 volts obtained from Table 28-2. The

TABLE 28-2 ELECTRODE POTENTIALS AT 25°C

Element	Reaction	Electrode Potential (volts)
Li	$e^- + \text{Li}^+ \rightarrow \text{Li}$	-3.05
Zn	$e^- + \frac{1}{2}\text{Zn}^{++} \rightarrow \frac{1}{2}\text{Zn}$	-0.76
Cd	$e^- + \frac{1}{2}\text{Cd}^{++} \rightarrow \frac{1}{2}\text{Cd}$	-0.40
H	$e^- + \text{H}^+ \rightarrow \frac{1}{2}\text{H}_2$	0.00
Cu	$e^- + \frac{1}{2}\text{Cu}^{++} \rightarrow \frac{1}{2}\text{Cu}$	+0.34
	$e^- + \text{Cu}^+ \rightarrow \text{Cu}$	+0.52
Hg	$e^- + \frac{1}{2}\text{Hg}_2^{++} \rightarrow \text{Hg}$	+0.79
Pd	$e^- + \frac{1}{2}\text{Pd}^{++} \rightarrow \frac{1}{2}\text{Pd}$	+0.99

zinc sulphate solution is of lower density than the copper sulphate solution, so that the two solutions remain apart by gravity, or may be separated by a porous diaphragm. The zinc electrode is negative in this cell.

One type of *dry cell* has a zinc cylindrical shell which forms the outer container of the cell and is the negative electrode. The positive electrode

is a carbon rod which is inside, but which does not touch the cylinder. The dry cell is shown in Figure 28-3. The rest of the cell is filled with a paste of carbon powder, manganese dioxide, and ammonium chloride solution. The ammonium chloride solution acts as the electrolyte. The manganese dioxide reacts with the hydrogen liberated at the carbon anode when current is drawn from the cell. The top of the cell is sealed with a cement so that the cell does not leak. The emf of this cell is about 1.55 volts when new. The dry cell is capable of

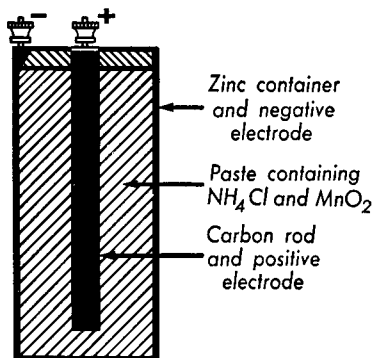


Fig. 28-3 Dry cell.

supplying small amounts of current, of the order of tens of milliamperes for steady use, and larger currents in intermittent use.

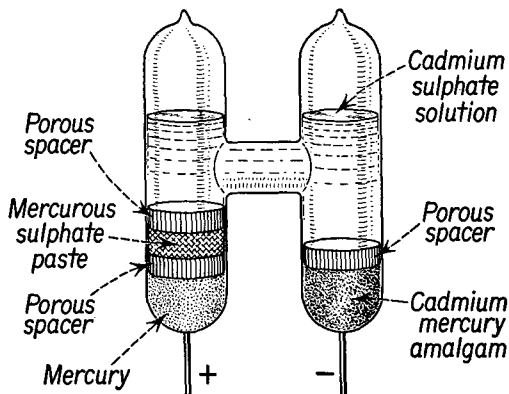
A cell which is widely used as a secondary standard of potential is the *Weston standard cell* shown in Figure 28-4. If the current drawn from the



cell is very small, the cell maintains a very stable emf. The Weston cell has an anode of mercury, in contact with a paste of mercurous sulphate. The cathode consists of a cadmium amalgam in contact with a layer of cadmium sulphate crystals. The electrolyte consists of a saturated solution of cadmium sulphate.

The *lead storage cell* has a positive electrode made of lead dioxide and a negative electrode of lead, with a dilute solution of sulphuric acid as the electrolyte. When the cell is delivering current to an external circuit, the

**Fig. 28-4** Weston standard cell. (Courtesy of Weston Electrical Instrument Corporation.)



chemical reaction forms lead sulphate on both plates and makes the solution more dilute. The specific gravity of a fully charged lead cell is 1.285 when the emf of the cell is 2.1 volts. When the cell is discharged, the specific gravity of the electrolyte falls to 1.1, and the emf of the cell is about 1.8 volts. Thus a hydrometer may be used to measure the specific gravity of the electrolyte and to determine the state of charge of the cell. The chemical action in a storage cell is reversed when current flows through the cell in a direction opposite to the normal discharge direction. A storage cell may be repeatedly charged and discharged in normal operation.

## 28-4 Conduction in Solids

The most important feature of atomic structure is that there is a discrete set of energy levels in an atom. For our present purposes we may divide the electrons of an atom into two groups. We shall call one group of electrons the *core* electrons. These consist of electrons which are relatively close to the nucleus and which occupy energy levels in which they are tightly bound to the atom. The other group of electrons are called the *valence* electrons. These are the outermost electrons of the atom and are the least tightly bound to the atom. The valence electrons may be shared

by other atoms in the formation of molecules. In general, an atom may have up to 8 valence electrons. These valence electrons occupy energy levels which may be designated as  $s$  levels and  $p$  levels. The  $s$  levels are more tightly bound than the  $p$  levels. The energy separation of the levels of the different classes is of the order of several electron volts of energy.

No more than 2 electrons may be in any one  $s$  level and no more than 6 electrons may be in any one  $p$  level. An element in the first column of the periodic table has a valence of 1; this means that it has 1 electron outside a closed core. This valence electron is in an  $s$  level. Elements in the second column of the periodic table have 2 valence electrons. These fill the  $s$  levels outside the core. An element of valence greater than 2 will have 2 electrons in the  $s$  level and the additional electrons in the  $p$  level.

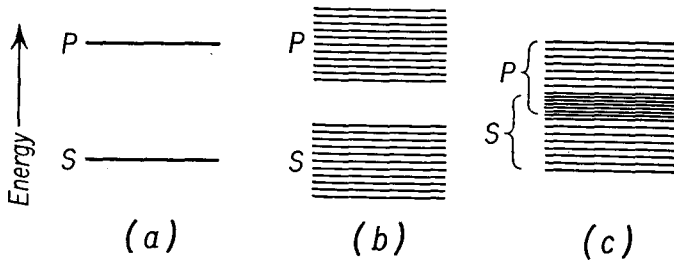
The energy levels of an atom are associated with the fact that the electric field experienced by the valence electrons has a well-defined center of attraction. Each valence electron is bound to its parent nucleus, as long as the atom is distant from all other atoms. When two different atoms combine to form a molecule, as in the case of molecular hydrogen  $H_2$ , the valence electrons of both atoms experience two centers of attraction, so that these electrons are shared by the two nuclei, and it is no longer possible to say which electron belongs to which nucleus. When a number of identical atoms are assembled in a periodic lattice structure to form a crystal, the valence electrons of the atoms of the crystal may no longer experience a well-defined center of attraction. In this case these electrons are sometimes free to drift through the crystal as *conduction* electrons.

We may gain additional insight into the problem of the conduction of electricity in solids by considering what happens to the energy levels of the atoms when the crystal is assembled. The presence of adjacent nuclei may alter the energy associated with the  $s$  levels and the  $p$  levels of an atom. The total number of levels in the system remains the same, but the position of the levels may be altered. The collection of  $s$  levels of the crystal may then be thought of as a continuous band, called the  $s$  band. In a similar way the  $p$  levels spread out into a  $p$  band. Depending upon the position of adjacent atoms in the crystal, these bands may remain far apart, they may be brought relatively close together, and, in some cases, they may even overlap, as shown in Figure 28-5.

If the atom is divalent, there are two  $s$  electrons in each atom. When the  $s$  band is relatively far from the  $p$  band in energy, all the  $s$  levels are occupied, and the electrons cannot move readily to the  $p$  band except by the addition of large amounts of energy. This band structure then describes an insulator, for the electrons are not free to alter their velocities. If the atom is monovalent, only half of the available  $s$  levels are occupied. The application of an electric field can influence the direction and magnitude of the velocity of the electrons, and the material is a conductor. Thus the

monovalent metals such as copper, silver, and so on, are good conductors of electricity.

In the general case of a metallic conductor, the bands overlap. Thus there are a large number of available energy levels, and the valence electrons of the crystal are free to alter their velocities in accordance with an applied electric field.

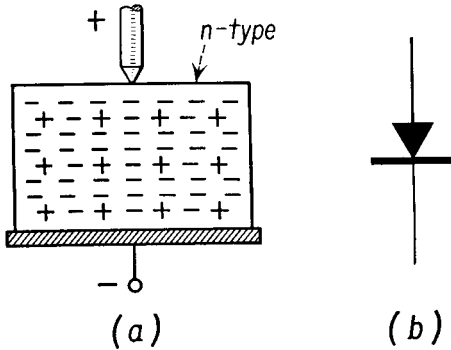


**Fig. 28-5** (a) Energy levels of an atom. (b) Energy levels of a solid (nonoverlapping). (c) Overlapping energy bands of a conductor.

When the  $s$  band is only a few tenths of an electron volt distant from the  $p$  band, the energy associated with small changes in temperature may be sufficient to raise an electron from a filled  $s$  band to an unfilled  $p$  band. The resistivity of such a material is markedly affected by temperature. Such a material is an *intrinsic semiconductor*. An electron may be raised from the filled  $s$  band to the  $p$  band by absorbing energy from incident light. In this case the material is called *photoconductive*.

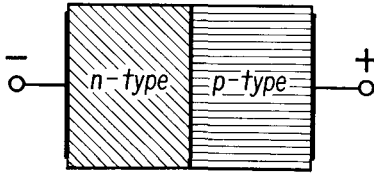
If there are distortions in the crystal lattice, or if there are impurities present, the structure of the bands may be altered. In the vicinity of these impurity sites, the level structure may be altered, and the material may become partially conducting, as in an *impurity semiconductor*. As an example, let us consider the effect of impurities in a germanium crystal. Atoms of germanium have 4 outer electrons each. If one atom of antimony which has 5 outer electrons replaces one atom of germanium, there will be 1 excess electron in this region. The energy-level structure is locally altered, and this electron may be set in motion by the application of a small electric field. A germanium crystal with this type of impurity is called an  $n$ -type crystal, the  $n$  standing for negative charge. On the other hand, if an atom of indium, which has only 3 outer electrons, replaces a germanium atom, there will be a deficiency of electrons, or a *hole* left in this part of the crystal. Again the energy-level structure is locally altered, and if an electric field is applied to such a crystal, electrons from other parts of the crystal flow toward the holes, leaving holes in other parts of the crystal. Thus the current in this type of crystal may be considered as the motion of holes.

A hole in a region which would be normally occupied by an electron is equivalent to the addition of a positive charge at this place. A germanium crystal with a type of impurity which produces holes is called a *p*-type crystal, where *p* stands for positive charge.



**Fig. 28-6** (a) Point contact rectifier, direction of easy conductor. (b) Conventional symbol of rectifier; the arrow is in the direction of the forward current.

When a point contact is made between a metal wire and an *n*-type semiconductor, as shown in Figure 28-6(a), it is found that the resistance of the contact is comparatively low when the wire is made positive relative to the semiconductor, but the resistance is considerably higher when the wire is negative.



**Fig. 28-7** *p*-*n* junction; direction of easy conduction.

In such a semiconductor there are relatively few energy levels available to the conduction electrons. When the wire is made positive, electrons from the semiconductor are attracted to the wire, so that there is a continuous supply of available levels in the vicinity of the contact for other electrons in the semiconductor to occupy. These electrons diffuse toward the contact point, establishing a current sometimes called the forward current. When the wire is made negative, electrons are injected from the wire into the available levels in the semiconductor in the vicinity of the contact point. All available levels become occupied, and additional electrons can no longer flow into the semiconductor until the excess of electrons in the vicinity of the contact point has diffused through the body of the semiconductor into the opposite terminal. Thus the resistance of the contact depends upon the direction of the current. Such a point contact may be used as a *diode* or *rectifier*; the conventional symbol is shown in Figure 28-6(b); the arrow shows the direction of the forward current.

In a similar way, when an *n*-type semiconductor is placed in contact with a *p*-type semiconductor, as shown in Figure 28-7, the direction of easy

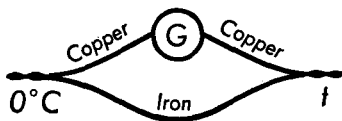
electron flow is from  $n$  to  $p$ , that is, when the  $p$ -type semiconductor is made positive. Once again, when electrons flow from the  $p$  to the  $n$  material, the available energy levels in the  $n$  material in the vicinity of the contact become occupied, and no additional electrons may flow until these diffuse away.

### 28-5 Thermoelectric Effects

One thermoelectric effect with which we are already familiar is the liberation of heat due to the passage of electric current through a conductor. This is an irreversible process, for heating a conductor to uniform temperature does not generate an electric current. Besides the Joule effect, there are several reversible thermoelectric effects of interest.

The most frequently applied of these effects is called the *Seebeck effect*, after its discoverer Thomas Johann Seebeck (1770–1831). If wires of two

Fig. 28-8 Thermocouple circuit.



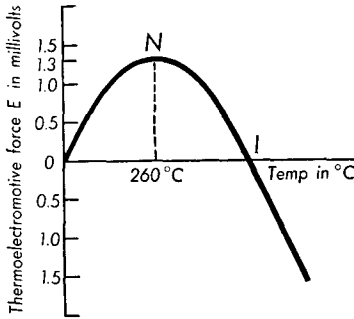
dissimilar metals are joined at their ends, and these ends are maintained at different temperatures, a current may be observed in the wires of the circuit. It is possible to analyze the current in terms of a *thermal emf* developed at the junctions of the wires and the resistance of the circuit. In general, the interposition of a third metal into the circuit does not affect the thermal emf if the third metal is maintained at a constant temperature.

The primary application of the Seebeck effect is in the measurement of temperature through a device called a *thermocouple*. In practice, one junction of a thermocouple is kept at the temperature of melting ice, while the other junction is immersed in the medium whose temperature is being measured. In some applications a galvanometer is inserted into the thermocouple circuit, as shown in Figure 28-8, but more generally the thermal emf is measured with a potentiometer, and the unknown temperature is determined by comparison with a calibration chart. This application of the potentiometer is one of its principal uses in industry, where the measurement of temperature is of great importance in metallurgy, in chemical engineering, and so on.

Figure 28-9 shows the thermoelectromotive force as a function of the temperature of the hot junction when the cold junction is kept at  $0^{\circ}\text{C}$ . The thermoelectromotive force at first increases with increasing temperature until the point  $N$ , known as the neutral point, is reached, and then decreases as the temperature of the hot junction is increased still further

until the point *I*, known as the inversion point, is reached, when the emf reverses direction as the temperature is increased still further. The neutral point for a copper-iron thermocouple is about 260°C; it varies with the purity of the metals.

When there is a current in a thermocouple circuit because of a difference in temperatures at the two junctions, heat is absorbed at the higher-temperature junction, and a smaller quantity of heat is emitted at the cooler junction, the difference between the two quantities of heat being converted into electrical energy.



**Fig. 28-9** Thermoelectromotive force of a copper-iron thermocouple as a function of the temperature of the hot junction.

Thermocouples can be made of any combination of metals. The electromotive force  $\mathcal{E}$  of a thermocouple depends upon the nature of the two metals used and the temperatures of the junctions. If one junction is kept at a fixed temperature and the other at any other temperature *T*, the emf of

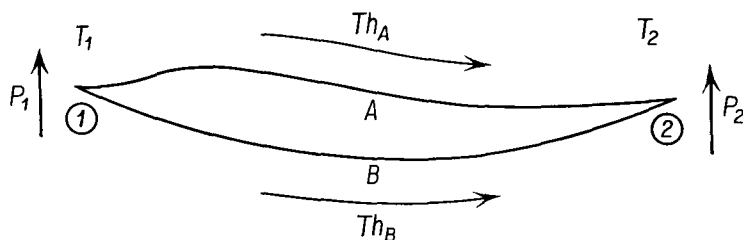
the thermocouple will be given, to a very close approximation, by the equation

$$\mathcal{E} = a + bT + cT^2, \quad (28-3)$$

where *a*, *b*, and *c* are constants for the particular thermocouple and have to be determined experimentally from the measurements at known temperatures. Once these constants have been determined, the thermocouple may be used as a thermometer. A thermocouple thermometer, one wire of which is made of platinum and the other of an alloy of 90 per cent platinum and 10 per cent rhodium, is used for measuring temperatures on the international scale in the range from 660°C to 1063°C. Special alloys have been developed for use in thermocouples. One of the advantages of a thermocouple thermometer is that only one junction need be heated, and since this can be made very small, only very small quantities of heat are needed to produce a measurable effect. Because of its small size and mass, the thermocouple junction will follow very rapid changes in temperature.

More recently, there has been considerable research into the possibility of exploiting the Seebeck effect as a means of generating electrical energy directly from heat energy without the use of rotating machinery. One unit, developed in 1954, was capable of converting solar energy into electrical energy with an efficiency of 3.35 per cent, as compared to an efficiency of about 5.8 per cent for a conventional gasoline-powered 1-kw generator.

A second thermoelectric effect was discovered by Jean C. A. Peltier (1785–1845). The *Peltier effect* is the inverse of the Seebeck effect. When there is a current through the junction of two dissimilar metals, the temperature of the junction changes. An emf is developed at the junction as electrons from one metal diffuse into the other to fill vacant energy levels in the other metal. When the current is in the direction of the emf, the temperature of the junction falls, while if it is in the opposite direction, the temperature of the junction rises. This effect is superimposed upon the usual Joule heating of a conductor, and, in spite of the Joule heating, it is possible to cool a suitably designed junction to a temperature lower



**Fig. 28-10** Peltier emf's  $P_1$  and  $P_2$  at the junctions 1 and 2 respectively, and the Thomson emf's  $Th_A$  and  $Th_B$  in the wires A and B of a thermocouple. The junctions are maintained at temperatures  $T_1$  and  $T_2$  respectively.

than that of the surroundings. The Peltier effect in an arrangement of wires of two dissimilar metals similar to a thermocouple may be thought of as an electrically operated heat pump, albeit a very inefficient one at present.

A third thermoelectric effect, called the *Thomson effect*, was predicted from thermodynamic considerations by Sir William Thomson (Lord Kelvin, 1824–1907). When different parts of the same metallic conductor are maintained at different temperatures, differences of potential may be observed in the conductor. The Thomson emf's are of the order of millivolts (abbreviated mv). The Thomson effect may be interpreted on the assumption that the free, or conduction, electrons within a metal behave like the molecules of a gas. Like the molecules of a gas, the electron density is highest where the temperature is lowest. The low-temperature portions of the conductor become negatively charged and thus are at lower potentials with respect to regions of the conductor at higher temperature.

Thermoelectric effects occur in all conductors. In electrical apparatus of high sensitivity, it is desirable to avoid temperature differences in different parts of the apparatus to avoid difficulties associated with the thermal electromotive force.

The three thermal emf's discussed above are not independent of each

other. When the junctions of two wires of dissimilar metals are maintained at different temperatures  $T_1$  and  $T_2$ , respectively, there are Thomson emf's in both wire  $A$  and wire  $B$ ; these are designated as  $Th_A$  and  $Th_B$  respectively, as shown in Figure 28-10. There are Peltier emf's  $P_1$  and  $P_2$  at the junctions 1 and 2. The Seebeck emf  $\mathcal{E}$  is the sum of the emf's around the thermocouple. Thus

$$\mathcal{E} = P_1 + Th_A - P_2 - Th_B.$$

### Problems

28-1. Determine the mass of silver which is deposited on a cathode from a silver nitrate solution by a current of 2 amp in 15 min.

28-2. When a current is passed through water containing a small amount of sulphuric acid to make it conducting, the water is decomposed into hydrogen and oxygen. (a) How large an electric charge must pass through the solution to liberate 1 gm atomic wt of oxygen? (b) How much hydrogen will be liberated at the same time? The chemical formula for water is  $H_2O$ .

28-3. A dry cell having an emf of 1.55 volts and an internal resistance of 0.08 ohm supplies current to a 4-ohm resistor. (a) Determine the current in the circuit. (b) Calculate the terminal voltage of the cell.

28-4. A lead storage battery whose emf is 6.3 volts, when being charged with a current of 12 amp, has a terminal voltage of 7.2 volts. (a) Determine the internal resistance of the battery. (b) How much energy is supplied to the battery in 30 min? (c) How much of this energy is converted into heat? (d) What becomes of the rest of this energy?

28-5. Two storage cells having the same emf of 2.1 volts, but having different internal resistances of 0.2 and 0.4 ohms, respectively, are connected in parallel. The parallel combination of cells is connected to a 10-ohm resistor. Determine (a) the current through the resistor and (b) the terminal voltage across either cell.

28-6. When a pure metal is immersed in an electrolyte, ions of the metal form in the solution until equilibrium is reached and the electrode attains its equilibrium electrode potential. Explain why a commercial metal such as iron or aluminum continues to corrode when it is immersed in salt water.

28-7. The emf of a silver-platinum thermocouple when one junction is at  $0^\circ\text{C}$  and the other at  $100^\circ\text{C}$  is 0.74 mv; when the second junction is at  $200^\circ\text{C}$ , the emf is 1.77 mv. (a) Determine the constants of Equation (28-3). (b) Calculate the temperature of the second junction when the emf is 1.30 mv.

28-8. A Pt—Pt-10 per cent Rh thermocouple is used as a standard for the determination of temperature. The following table gives the emf in millivolts when one junction is at  $0^\circ\text{C}$  and the other junction is at the temperature given in the table. (a) Plot a graph of emf against temperature. (b) Determine the temperature of the second junction when the emf is 5.00 mv. (c) Determine the constants of Equation (28-3) for this range of temperatures.

emf	0.643	1.436	2.316	3.251	4.221	5.224	6.260	7.329	8.432	9.570
temp ( $^\circ\text{C}$ )	100	200	300	400	500	600	700	800	900	1000