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# IONS, ELECTRODES AND MEMBRANES

Jiří Koryta

BLM RESEARCH LAB.

# *Ions, Electrodes, and Membranes*

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*A Wiley-Interscience Publication*



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# Preface

The present book is an introduction to electrochemistry destined particularly for people coming from other fields of science. Electrochemistry is one of the oldest branches of physical chemistry and, in fact, of chemistry at all. The first great electrochemist was the Italian Luigi Galvani (1737–1798) who made his main discovery as early as 1791! In spite of this it took a considerable time, about three-quarters of a century, before two large regions formed in electrochemistry: one of them dealing with ion-containing liquids and the other one concerned with processes at electrodes. Later, particularly under the influence of the study of living cells, a new region emerged—the study of membranes. As I expect that at present this field has greatest chance for important discoveries, I reserve a special chapter for it.

In view of its great age, electrochemistry has an entrenched kind of language which makes its study rather difficult, both for a biologist and a physicist. Therefore I have tried to approach each problem in a simple physical manner keeping in mind that electrochemistry is an experimental discipline. At the beginning I always describe a simple (sometimes rather idealized) experiment and only then formulate a more general law and discuss its consequences. In my opinion this is a more suitable way of explanation than to postulate a certain law of nature and only use the experiments to illustrate its consequences. Needless to say, the choice of detailed information shows how much I stress the importance of electrochemistry, particularly for biology.

The reader will find additional information on various topics in this book in the books and reviews quoted in the text, also in the textbooks on electrochemistry: D. A. McInnes, *The Principles of Electrochemistry*, Reinhold, New York, 1961; G. Kortüm, *Treatise on Electrochemistry*, Elsevier, Amsterdam, 1965; J. O'M. Bockris and A. K. N. Reddy, *Modern Electrochemistry*, Plenum, New York, 1970; and J. Koryta, J. Dvořák, and V. Boháčková, *Electrochemistry*, Science Paperbacks, Chapman and Hall, London, 1973, and in three series of 'Advances', i.e. *Advances in Electrochemistry and Electrochemical Engineering* (ed. by P. Delahay, H. Gerischer, and C. W. Tobias), Wiley-Interscience, New York; *Modern Aspects of Electrochemistry* (J. O'M. Bockris and B. E. Conway, eds.), Butterworths, London, and Plenum, New York; and *Electroanalytical Chemistry* (A. J. Bard, ed.), M. Dekker, New York. Furthermore, there are three compendia of electrochemistry, C. A. Hampel (Ed.), *The Encyclopedia of Electrochemistry*, Reinhold Publishing Co., New York, 1964, A. J. Bard (Ed.), *Electrochemistry of Elements* (a series in publication since 1973), Marcel Dekker, New York, and J. O'M. Bockris, B. E. Conway and E. Yeager (Eds.), *Comprehensive Treatise of*

*Electrochemistry* (a ten volume series in publication since 1980), Plenum Press, New York.

I am much indebted to Dr. A. Ryvolová-Kejharová, Mrs. D. Tůmová, and my wife for their help with the manuscript and to Mrs. Kozlová for drawing the figures. Dr. M. Hyman-Štulíková kindly revised the English.

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# Chapter 1

## Ions

### Origin

A simple experiment will demonstrate how ions are formed: gaseous sodium can be obtained by evaporation of metallic sodium in an evacuated tube at a sufficiently high temperature (above  $883^{\circ}\text{C}$ ). The radiation from a light bulb is then passed through this gas and a spectroscope is used to observe the line absorption spectrum of sodium (Fig. 1). Each line corresponds to the radiation energy necessary for transferring the outer electron of sodium to a higher energy level after absorbing a photon with an energy  $h\nu$ . The Planck constant, which is a universal physical constant, is denoted by  $h$  and the frequency of light waves corresponding to the line in the absorption spectrum by  $\nu$ . Close examination of the spectrum reveals a conspicuous feature, i.e. the distances between the lines gradually become smaller in the direction toward higher frequencies (or smaller wave-lengths) and finally reach a limiting value, called the edge of the spectrum. The energy corresponding to the edge of the spectrum is just sufficient for tearing-off the outer electron to form the sodium ion



This process is called ionization and can be brought about by a number of other mechanisms. For example, a high-energy photon can knock out one of the inner electrons of the sodium atom which then restores the stable structure with

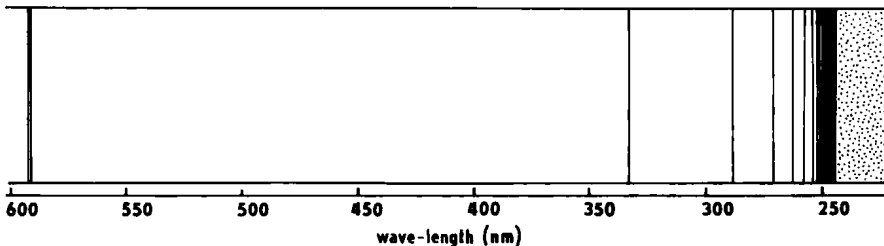


Fig. 1. The absorption spectrum of gaseous sodium. The adsorption lines are ordered according to their wave-length  $\lambda$  in nanometres. The frequency is  $\nu = c/\lambda$ , where  $c$  is the velocity of light in a vaccum. The line doublet on the left-hand side corresponds to the intense yellow colour in the emission spectrum of sodium. On the right-hand side the lines become denser until the edge of the series of lines is reached, corresponding to the ionization of sodium

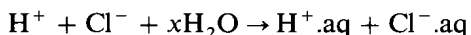


occupied K and L shells by regrouping the other electrons. The final structure is again the  $\text{Na}^+$  ion. Ionization can also be caused by collision of the atom with an elementary particle (electron, neutron, proton, etc.) or with other ions or atoms, etc. Ions are formed from molecules in the same way as from atoms. Negatively charged ions originate from reactions with an electron (for example,  $\text{O}_2 + e \rightarrow \text{O}_2^-$ ).

There are simpler, more “chemical” methods of forming ions. Consider feeding gaseous hydrogen chloride, which consists of  $\text{HCl}$  molecules, into water. The resulting electrically conducting solution of hydrochloric acid contains exclusively chloride ions  $\text{Cl}^-$  and hydrogen ions (which we shall provisionally denote as  $\text{H}^+$ ) and virtually no  $\text{HCl}$  molecules. In contrast to pure water, this solution is an excellent conductor of electricity. During dissolution of  $\text{HCl}$  in water the reaction



obviously took place. Why could this happen so easily—at room temperature and without the influence of radiation? The answer can be found in the effect of the solvent. The solvent molecules form a stabilizing *hydration sheath* around each ion. The ionization of hydrogen chloride is followed and, in fact, made possible, by hydration of the ions formed from  $\text{HCl}$ . In general, for an arbitrary solvent, this process is called *solvation*. The reaction of ionization of  $\text{HCl}$  is accompanied by a further process



where the symbol aq indicates that the ions are solvated.

A similar electrically conductive solution consisting of hydrated ions is obtained by dissolving solid sodium chloride in water. This is somewhat different from dissolving hydrogen chloride in water. It has been proven by various physical measurements that the crystal lattice of sodium chloride consists of the sodium and chloride ions. The regular structure of rock salt, a typical ionic crystal (see Fig. 2), is a result of electrical forces attracting the  $\text{Na}^+$  cations and  $\text{Cl}^-$  anions and repulsing ions with the same sign ( $\text{Cl}^-$  and  $\text{Cl}^-$ , for example) and the electron sheaths of all the ions. This interaction determines the effective dimensions of the ions. The effective crystallographic ionic radii given by Goldschmidt and somewhat modified values from Pauling are listed in Table 1. During dissolution the ions are only set free from the lattice and hydrated (see Fig. 3).

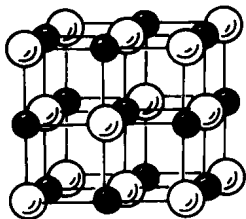


Fig. 2. The structure of the cubic crystal lattice of sodium chloride. The sodium ions are represented by black spheres while the chloride ions correspond to white spheres

Table 1 Comparison of Pauling's ionic radii with Goldschmidt's values  $G$  in nanometers

		Li	Be <sup>2+</sup>		
		0.06	0.031		
		$G$ 0.078	0.034		
O <sup>2-</sup>	F <sup>-</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	Al <sup>3+</sup>	Si <sup>4+</sup>
0.14	0.136	0.095	0.065	0.05	0.041
$G$ 0.132	0.133	0.098	0.078	0.057	0.039
S <sup>2-</sup>	Cl <sup>-</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Sc <sup>3+</sup>	Ti <sup>4+</sup>
0.184	0.181	0.133	0.099	0.081	0.068
$G$ 0.174	0.181	0.133	0.106	0.083	0.064
Se <sup>2-</sup>	Br <sup>-</sup>	Rb <sup>+</sup>	Sr <sup>2+</sup>	Y <sup>3+</sup>	Zr <sup>4+</sup>
0.198	0.195	0.148	0.113	0.093	0.08
$G$ 0.191	0.196	0.149	0.127	0.106	0.087
Te <sup>2-</sup>	I <sup>-</sup>	Cs <sup>+</sup>	Ba <sup>2+</sup>	La <sup>3+</sup>	Ce <sup>4+</sup>
0.221	0.216	0.169	0.135	0.115	0.101
$G$ 0.211	0.22	0.165	0.143	0.122	0.102

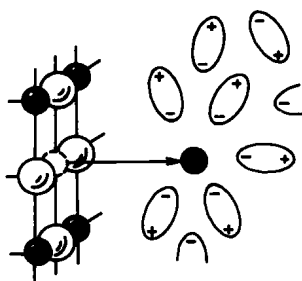


Fig. 3. The sodium ion leaves the crystal lattice of NaCl and is solvated by water molecules

### Conduction of Electric Current

If two metal plates are placed parallel in a vacuum and connected to a d.c. source, then the electric current forms a positive charge on one of the plates and a negative charge on the other one, but no charge is transported between the plates—only the voltage (or, as it will be called here, the electrical potential difference) increases. Such a device is called a *condenser*, since it helps the charge to become “denser” on the plates.

The ratio of the charge brought to the positive plate of the condenser and the resulting electrical potential difference  $\Delta V$  is called the capacity of the condenser  $C$

$$C = Q/\Delta V \quad (1.1)$$

When the plates of the condenser are connected to a low-voltage source, like an automobile storage battery (voltage 12 V) or to an electric grid (the a.c. voltage has to be first transformed to d.c. by a rectifier), the condenser is charged instantaneously and the current flowing to the plates rapidly decreases. When the condenser is connected to a high-voltage source like a Wimshurst machine or van de Graaf generator, an electric discharge appears between the plates. The electrons jump from the negative to the positive plate and an electric current starts to flow.

In a subsequent experiment the space between the plates is filled with a substance having a high *electric dipole*<sup>1</sup> like, for example, 1-chloropropane  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$ . Chlorine is an element with high electronegativity (the tendency to attract electrons), therefore the end of the molecule carrying a chlorine atom exhibits a slightly excessive negative charge, while the other end becomes slightly positive. As a whole the chloropropane molecule is electroneutral.

The electric field which exists in the space between the plates of a charged condenser acts on the chloropropane molecules so that their positive ends are deflected somewhat towards the negative plate and the negative ends in the opposite direction. Complete orientation along the lines of force of the electric field is prevented by the thermal motion of the molecules—in a weak electric field the dipoles are aligned only slightly. The electric field also influences the distribution of charge inside some molecules to form new dipoles. The dipoles originally present in the molecule are called *permanent* while the new ones are *induced*. The dipoles partially compensate the electric effect of the charge present on the plates and the electric field (and thus also the voltage) decreases. Equation (1.1) indicates that, at constant charge  $Q$  and decreased voltage  $\Delta V$ , the capacity  $C$  increases.

When the space between the plates is filled, for example with paraffin (which is a mixture of long-chain hydrocarbons), the capacity of the condenser increases very little. Such a substance is *non-polar* and the space inside the condenser behaves almost in the same way as in a vacuum.

Any type of matter which prevents an electric current from flowing between the plates of a condenser is called a *dielectric* (including a vacuum); the substances which have so far replaced the vacuum in the condenser are termed *insulators*. Various dielectrics increase the capacity of the condenser to a different degree. Thus, it seems suitable to express this ability quantitatively. For this purpose a quantity called the *relative dielectric constant* or, better, the *relative permittivity*, denoted  $D$ , is used. The relative permittivity indicates the degree to which a given dielectric increases the capacity of the condenser compared with a vacuum condenser with the same size and distance between the plates. The values of the relative permittivities of some liquids are listed in Table 2. The relative permittivity decreases with increasing temperature and is almost independent of the electric field (for weak fields).

The relative permittivity appears in the equation for the capacity of the plate condenser

$$C = (D\epsilon_0 S)/d \quad (1.2)$$

where  $\epsilon_0$  is the permittivity of a vacuum,  $\epsilon_0 = 8.85 \times 10^{-12} \text{ Fm}^{-1}$ ,  $S$  is the area of one plate, and  $d$  is the distance between the plates.

Table 2 Relative permittivities of selected solvents

Solvent	$D$	°C	Solvent	$D$	°C
Water	78.4	25	Ethanol	24.6	25
(Ice)	94	−2	1-Butanol	17.5	25
Formamide	109	20	Terc-Butanol	2.7	25
HCN (liq.)	95	21	1,2-dichloro- benzene	9.8	20
Formic acid	47.9	18.5	Chloroform	4.8	20
Dimethyl- sulphoxide	46.7	25	Tetrachloro- methane	2.23	20
Acetonitrile	37.5	20	Benzene	2.23	20
Dimethylform- amide	36.7	25	Dioxane	2.28	20
Nitrobenzene	36.1	20	Pentane	1.8	20.3
Methanol	32.7	25	Ammonia (liq.)	21	−34

The effect of replacing the dielectric by a piece of metal touching both plates is not surprising. After the plates come into contact, an electric current starts to flow through the metal—the charge cannot be retained on the plates because they are conductively connected. Thus, metal is an *electric conductor*.

There are various kinds of conductors. They may be distinguished according to the type of electric particles which carry the current through them. In metals these particles are electrons—metals are electronic conductors. In the crystal lattice of a metal the metal atoms are ionized, the electrons are set free and the electron clouds (orbitals) overlap in such a way that all the electrons are common to all the ions. Under these conditions the electrons in the metal behave in a way similar to molecules in a gas. (This follows from Fermi–Dirac statistics governing the behaviour of electrons in solids.) Thus, we speak of an ‘electron gas’ where the probable position of an electron changes in the same irregular manner as the position of a molecule in a gas, where it is constantly under the influence of collisions with other molecules.

Like electrons in an isolated atom, the electrons in a metal follow Pauli’s principle which states that an energy level in the system can be filled by a maximum of two electrons with different spins.<sup>2</sup> In a metal, the energy levels of the electrons differ very little from each other. Thus, they form a continuous band which we call the *conductivity band* (Fig. 4). The probability of an electron

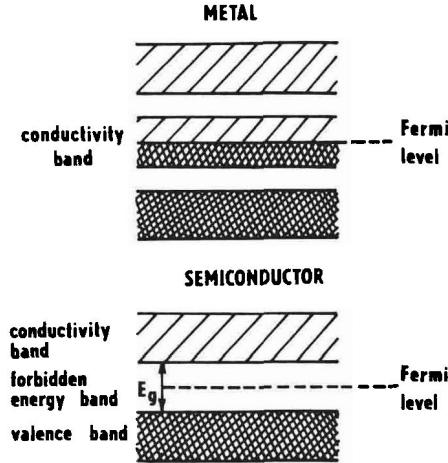


Fig. 4. The band structure of a metal and of a semiconductor. Simply hatched areas are not occupied but can be occupied by electrons while void areas are not accessible to electrons. Double hatched areas are occupied by electrons. The vertical coordinate of the scheme corresponds to the energy of the electrons.  $E_g$  denotes the energy difference between the upper and the lower edge of the forbidden energy gap (the gap width). In a metal half of the conductivity band is filled with electrons. In a semiconductor the conductivity band is empty. Between this and the valence band the forbidden energy gap is situated; the Fermi level lies in the middle of the gap

occupying a level with energy  $\varepsilon$  is given by the Fermi function

$$P = \frac{1}{1 + \exp [(\varepsilon - \varepsilon_F)kT]}$$

where  $\varepsilon_F$  is the energy of the Fermi level. This level has the probability of occupation exactly one-half.  $k$  is the Boltzmann constant and  $T$  is the absolute temperature (for details, see Fig. 5).

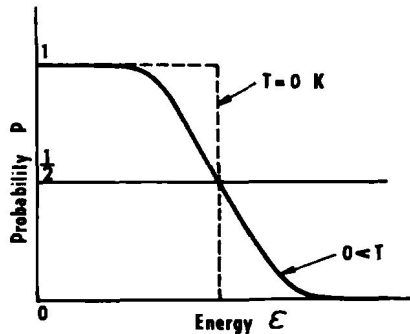


Fig. 5. The Fermi function for the energy distribution in a metal.  $\varepsilon_F$  denotes the energy of the Fermi level. At a temperature of absolute zero (0 K), the energy levels below  $\varepsilon_F$  are completely filled while those above  $\varepsilon_F$  are empty. At higher temperatures the levels in the neighbourhood of  $\varepsilon_F$  are only partly filled

We already know that the electrons in the metal move in various directions and with various velocities. Connection of a voltage source to a metallic conductor will result in a slight change in the motion of the electrons—the component of the velocity in the direction of the field (i.e. from the negative to the positive pole) will prevail somewhat over the component in the opposite direction. This preference of the velocity in a certain direction is very small compared with the absolute magnitudes of the velocities of the irregular motion, but is just sufficient to cause the flow of an electric current. This is a typical property of many physical and chemical processes. They proceed in various directions with high velocities but in the equilibrium state all these ‘partial’ processes cancel each other out and no change is observed. When a partial process in one direction is slightly faster than in the opposite direction, a change in the physical or chemical system becomes apparent (current flow in the present case). Under these circumstances the rate of change (here the flow of electric charge, i.e. electric current) is proportional to the generalized force which causes the change (applied voltage or electric potential difference in the present case). Thus, we have deduced Ohm’s Law in a simple intuitive way, stating that electric current  $I$  is proportional to electric potential difference  $V$

$$I \sim \Delta V$$

The proportionality constant is the conductance  $G$  which is equal to the reciprocal of the resistance  $R$ .

As mentioned above, the charge carriers in metallic conductors are electrons, while metal ions in the lattice do not transfer electric charge because they occupy fixed positions. These positions are not in fact completely fixed because they vibrate around average lattice positions. The frequency as well as the amplitude of these vibrations increases when the temperature of the metal increases. The more the lattice ions vibrate, the more they hinder the free movement of the electrons, so that the resistance of a metallic conductor increases with increasing temperature.

When a piece of very pure elemental germanium is placed between two metal plates (the purification of such materials has been highly perfected during the past few decades) and a voltage source is connected to the plates, a very tiny electric current starts to flow. This current increases when the temperature is increased. In appearance, germanium is much like a metal, being grey with a metallic sheen, but it conducts electricity very imperfectly. It belongs among the *semiconductors*.

The electronic structure of a semiconductor is different from that of a metal. The energies of the outer electrons in the electron sheath of the atoms in the semiconductor almost completely fill the valence band (Fig. 4). Above this band lies the conductivity band, which is almost empty. There is no energy level which could be occupied by the electrons of the semiconductor in the energy interval between these two bands. This property is described by the appropriate term ‘forbidden energy gap’. The thermal vibration of the electrons can be so great that they can ‘jump up’ to the conductivity band and participate in the conduction of electricity. When the temperature is increased, more electrons reach the

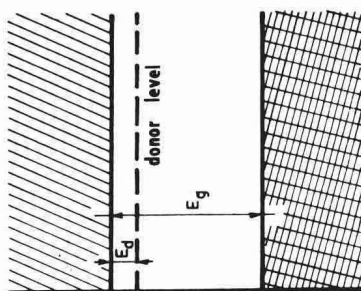
conductivity band, so that the conductivity of a semiconductor increases with increasing temperature. The electron which has 'jumped' up from the valence band has added a negative charge to the conductivity band. According to the law of conservation of charge, when a charge of a definite sign is formed, another charge of opposite sign must emerge at the same time. Thus, the electron has left a vacant position in the valence band—a hole or vacancy—with a positive charge. 'Chemically' speaking this means that an electron has been set free from a germanium atom and can freely move in the crystal lattice, while the resulting  $\text{Ge}^+$  ion can exchange its positive charge for an electron from the neighbouring atoms.

If an electric field is applied to pure germanium, the electrons migrate in one direction and the holes in the opposite direction (again the velocity of the electrons or holes in this particular direction slightly prevails over the velocities in the other directions). Such 'intrinsic' semiconductors conduct electric current poorly and are technologically relatively unimportant. A revolution in electronics, marked by the progress from simple rectifying diodes to microprocessors with integrated circuits, was based on the discovery of semiconductors with artificially implanted impurities, i.e. of semiconductors doped with minute quantities of admixtures.

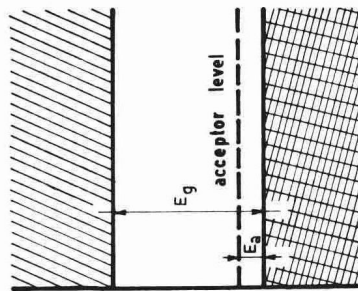
A very small amount of arsenic can be added to pure germanium, leading to the following 'chemical' process: an electron is split off from the outer shell of the electron sheath of arsenic and is added to the neighbouring germanium atoms in such a way that it can move freely in the germanium lattice. Because of its ability to donate electrons, arsenic is termed an 'electron-donor'. In the band scheme of germanium this phenomenon is demonstrated as shown in Fig. 6. The admixture of arsenic brings about a new donor energy level just below the conductivity band. The electrons need only a small amount of energy  $E_d$  to move up to the conductivity band, thus increasing the conductivity of germanium. The semiconductor that contains a donor admixture and has conductivity based on the motion of electrons (negative charge carriers) is termed an n-type semiconductor.

The opposite process occurs when germanium is doped with boron instead of with arsenic. Boron is an electronegative element with a tendency to complete its electron shell. It receives one electron from germanium and is converted to the negative ion  $\text{B}^-$ . At the same time, a hole is formed in the electron structure of germanium. This situation is depicted in Fig. 6. Boron is an 'electron-acceptor' and, when present as an admixture in germanium, gives rise to a new acceptor energy level just above the valence band. The transfer of an electron from the valence band to the acceptor band requires a small energy  $E_a$ . The hole remaining in the valence band contributes to the conductivity of the semiconductor. Because it is a positive charge carrier, this material is called a p-type semiconductor. Increasing the temperature has the same influence on doped semiconductors as on intrinsic semiconductors, because the thermal energy of the electrons permits them to reach the donor or acceptor levels.

In the next experiment, two plates made of a certain metal, for example, copper,



A



B

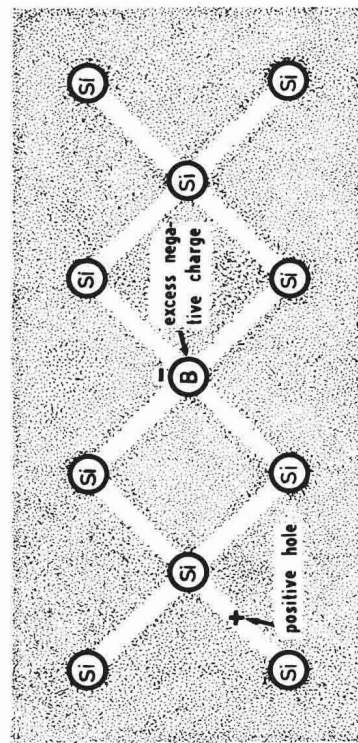
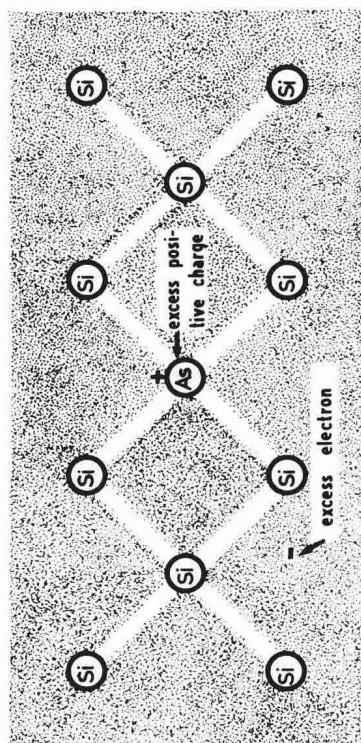
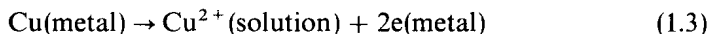


Fig. 6. Schematic representation of a semiconductor (germanium) with impurities. Doping with an electropositive element (As) results in a new 'donor' level immediately below the conductivity band. The electrons jumping from this level to the conductivity level induce n-type conductivity in the semiconductor (the charge carriers are the electrons with a negative charge). By doping with an electronegative element (B) a new 'acceptor' level is formed just above the valence band. The electrons jumping from the valence band into this new band leave holes (positive charge carriers) in the valence band. Thus, the material becomes a p-type semiconductor. From C. Kittel

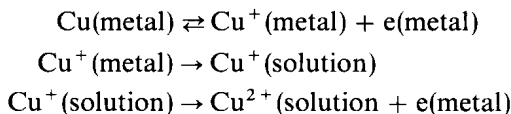


are immersed in a copper sulphate solution. When a source of d.c. voltage is connected to the plates, an electric current starts to flow, accompanied by chemical changes at the copper plates, which will be termed *electrodes*.

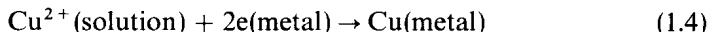
The copper plate through which the positive charge from an external source of electricity enters the solution is dissolved. This process can be described by the equation



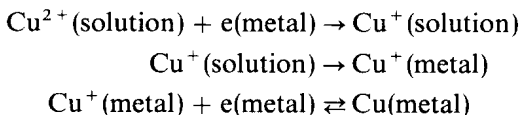
In fact, copper ions were already present in the metal lattice, so that equation (1.3) can be broken down into several partial steps



Metallic copper is deposited on the other electrode, where the electrons enter the solution, apparently in the process



This reaction again takes place as a sequence of partial steps



The last step must always involve transfer of electrons to the metal because the electrode must remain electroneutral (even if copper remains in the ionic form in the lattice).

The electrode which accepts a positive charge from the solution or injects a negative charge into the solution is termed the *cathode*, while the other electrode injecting a positive charge into the solution or accepting a negative charge from the solution is the *anode*.

Close examination of equations (1.3) and (1.4) reveals that the substances present in the solution which are formed at the electrodes as a result of the flow of electric current through the solution, or from which the final products originate, are exclusively ions. We can assume (and other experiments have justified our doing so) that only ions participate in the conduction of electric current in the  $\text{CuSO}_4$  or, in other words, only ions function as *charge carriers*. The conductor where electricity is communicated by the ions is termed an *electrolyte*.

The whole process described above is called *electrolysis*. This term, as well as *electrode*, *anode*, *cathode*, and *electrolyte*, were introduced by M. Faraday in 1835 (see Appendix A).

Electrolysis can be separated into two principal processes:

(1) The processes taking place directly at the electrodes which are connected with charge transfer between the electrode and the electrolyte solution.