CHAPTER 7
SOLID-ELECTROLYTE JUNCTIONS AND MEMBRANE TRANSPORT

When two different pieces of matter are brought into contact, very often new physico-chemical properties originate at their interface. These properties can be foreseen by the designer, as in the case of the junction between a p-type semiconductor and an n-type semiconductor (as described in the previous chapter), or they can rather be a complex problem to deal with, as in the case of an artificial structure to be interfaced to the human body (i.e., a prosthesis). Broadly speaking, the appropriate operation of all kinds of hybrid bioelectronic devices, e.g., biosensors, critically rests on the precise characterization of the junction between biological and artificial structures.

To make a junction, two solids (as described in Chap. 6), or a solid and a liquid solution (as we will describe in this chapter) are brought into contact. Another interesting situation is produced when two liquid regions are separated by a thin structure designed (by human beings or nature) to selectively distribute specific molecules among the two liquid regions. These "thin structures" are named *membranes* (the structure of a biological membrane has been already introduced in Chap. 4). Examples of membranes relevant to two quite separate research fields include the ion-selective membrane of a neuron and the artificial membranes designed for dialysis purposes. To summarize, solid-liquid junctions and membranes are two very important topics for any student or researcher dealing with bioelectronics and, more generally, with bioengineering.

In the following, the basic properties of solid-liquid interfaces and the transport properties of membranes will be considered in detail.

7.1 ELECTRODE-ELECTROLYTE INTERFACES

Electrical potential differences can develop across the boundary between a solid phase and a liquid phase, in particular an electrolyte. There are several ways in which this potential difference can arise. If one of the phases is an electronic conductor, i.e., an electrode, and the other is an ionic conductor (electrolyte), electron-transfer reactions can occur at the boundary and lead to the development of a potential difference. Alternatively, the electronic conductor can be deliberately charged by a flow of electrons from an external source of electricity. Even without deliberate charging or steady electron-transfer reactions, a potential difference can develop across a solid-electrolyte boundary, typically due
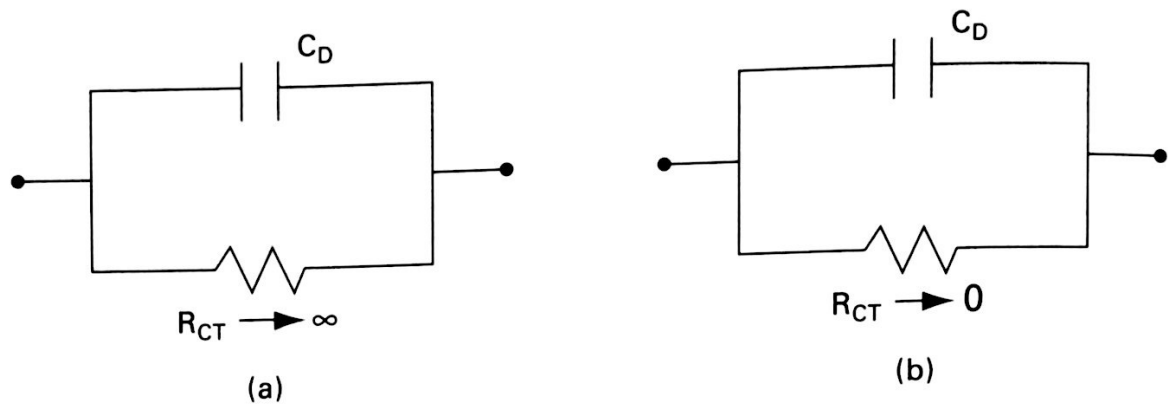
FIGURE 7.1 Equivalent circuit of (*a*) ideally polarizable interface and (*b*) ideally nonpolarizable interface. R_{CT} = charge-transfer resistor and C_D = double-layer capacitor.

to an initial (very small and transient) charge exchange between electrode and electrolyte solution.

In consideration of the vastness of the topic, we will start with a classification of different electrode-electrolyte interfaces. Then, the general scheme of the Poisson-Boltzmann equation will be considered. Finally, the relevance of this topic to the study of biosensors (see Chap. 10) will be briefly discussed.

7.1.1 Nonpolarizable and Polarizable Interfaces

To polarize an interface means to alter the potential difference across it. Thus, an ideally *nonpolarizable* interface is characterized by the fact that the potential difference across it is virtually fixed. On the contrary, in an ideally *polarizable* (or *blocking*) interface, the potential difference changes as a consequence of any variation of the potential difference across the whole system which includes the interface (the system consisting of an electrode immersed in an electrolyte solution, a "reference" electrode, and a power supply). A way to visualize the properties of polarizable/nonpolarizable interfaces is to make use of the simple equivalent circuit representation of Fig. 7.1.

Suppose the capacitor-resistor configuration in Fig. 7.1 is connected to a source of potential difference. Then, if the resistor is very high, the capacitor charges up to the value of the potential difference set by the source; this is the behavior of a polarizable interface (Fig. 7.1*a*). On the other hand, if the resistance in parallel with the capacitor is low, then any attempt to change the potential difference across the capacitor is compensated by charge leaking through the low-resistance path; this is the behavior of a nonpolarizable interface (Fig. 7.1*b*). This description can be generalized to the frequency domain by writing down the frequency-dependent equivalent impedance Z of the circuit, in the presence of a periodic potential:

$$Z(\omega) = \frac{R_{CT}}{j\omega R_{CT} C_D + 1} \tag{7.1}$$

where R_{CT} stands for charge-transfer resistance, C_D for double layer capacitance, and $\omega = 2\pi \times$ frequency. The meaning of the resistance and capacitance will be clarified in the following.

Examples of nonpolarizable interfaces are the so-called *reference electrodes* (e.g., the calomel electrode and the Ag/AgCl electrode). These electrodes guarantee a constant potential drop at their interface and consequently they act as a "reference."

At the other extreme, the classic example of a polarizable interface is the interface between mercury (Hg) and electrolyte solution. Mercury is a liquid at ordinary temperatures. For (solid) metals other than mercury, ideal polarizability (i.e., infinite resistance R_{CT}) is not obtained. Only the softer metals, such as lead, tin, and gallium have large (e.g., 1 V) ranges of applied potential in which the interface can be considered an ideal capacitor. Let us briefly analyze in the following sections the behavior of the various kinds of interfaces.

7.1.2 An Ideally Polarizable Electrode (Hg) in an Electrolyte Solution

In an ideally polarizable interface (connected to an external voltage source), a separation of charges happens at the interface between electrode and solution and a potential difference develops across the interface. The separation of charge in the metal implies redistribution of electrons, the separation of charge in the electrolyte implies redistribution of ions (which can be either hydrated or bare) and of water dipoles.

It should be underlined that no electrons leave the ideally polarized metal to cross the interface and no ions and water dipoles leave the electrolyte to cross the interface. Redistribution of charge on one side is immediately paralleled by redistribution of charge on the other side. This is the behavior of a capacitor and the resulting interface is known as an *electrified interface*. The charging of this interface can be controlled by an appropriate external circuit including a voltage source. Electrons inside the metal are free to move as a kind of gas (see Chap. 1). The charge distribution in the electrolyte is more complex: bare ions can approach the surface of the metal, as water dipoles do. They form a kind of layer, known as the *inner Helmholtz plane* (IHP) (von Helmholtz was one of the first to introduce the concept of electrified interface, around 1879). Hydrated ions form a kind of second layer, known as *outer Helmholtz plane* (OHP). The planes IHP and OHP are sketched in Fig. 7.2.

In summary, as a result of immersing an ideally polarizable metal (e.g., Hg) in an electrolyte, a redistribution of charge occurs both in the metal and in the electrolyte. The charge at the metal side of the interface is *partially* balanced by the IHP and OHP planes. This is a *partial* balance because diffusion processes take place inside the electrolyte; therefore also a *diffuse excess of charge* has to be taken into account. This diffuse layer, where the potential decays exponentially, is known as the *Gouy-Chapman (G-C) layer*. A classical way of describing this diffuse layer is by solving the Poisson-Boltzmann equation. This will be done in Sec. 7.2.

7.1.3 A Solid Metal in an Electrolyte Solution

There is always leakage of charge across the interface with metals other than mercury.
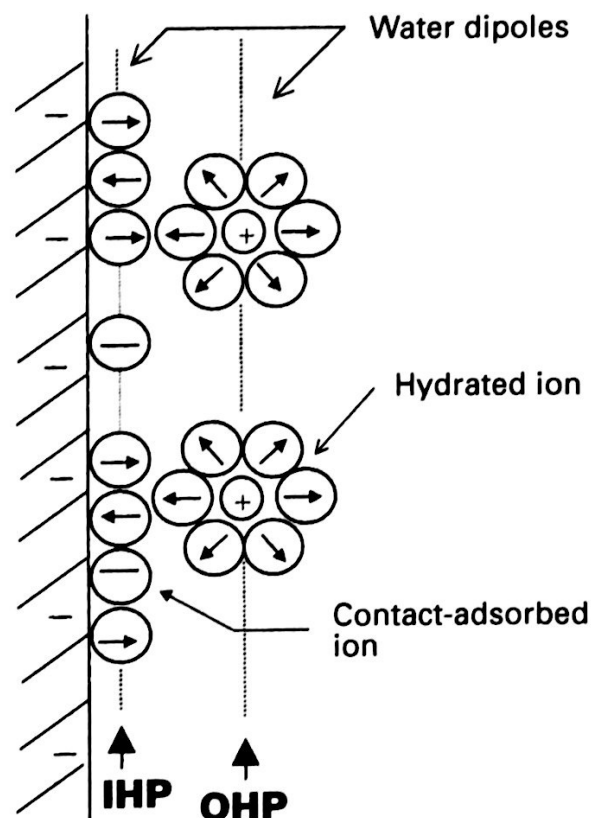
FIGURE 7.2 The inner Helmholtz plane (IHP) and the outer Helmholtz plane (OHP) are shown. The diffuse layer (Gouy-Chapman) is not shown.

Thus, as already mentioned, only mercury and a few of the softer metals can be considered as ideally polarizable over a large (e.g., 1 V) range of potentials. In all the other cases, exchange of electrons does happen across the interface as a result of *reduction* or *oxidation* of dissolved species in solution. A reaction such as

$$O + ne \rightleftharpoons R \tag{7.2}$$

with O the reactant and R the product on a Pt electrode, for example, will allow a current to flow (in electrochemical books this current is named *faradaic*). The movement of electrons (ne) should be imaged as a kind of "hopping," better described by quantum rather than classic physics.[1] Under equilibrium conditions, electrons cross the electrified interface in both directions. The result is that there is no net current, but two processes, an *electronation* (or reduction) and a *de-electronation* (or oxidation), continue to occur, *at the same rate,* in the presence of an equilibrium potential difference $\Delta\phi_e$ across the interface, which is characteristic of the specific redox process.

In conclusion, at *equilibrium* (i.e., almost immediately after immersing a metal in solution without any external difference in potential applied) there are two currents equal in magnitude and opposite in direction and, as a result, no net current. It can be shown[1,2] that their magnitude i_0 depends exponentially on the potential difference $\Delta\phi_e$. A *net* current can then be produced if the system is taken out of equilibrium, i.e., if an overpotential drop η is added to the equilibrium potential drop resulting in the overall potential difference

$$\Delta\phi = \Delta\phi_e + \eta \tag{7.3}$$

The net current takes the form[1,2]

$$I = I_0[e^{(1-\beta)\eta z q/kT} - e^{-\beta\eta z q/kT}] \tag{7.4}$$

where the *overpotential* η is the "extra part" by which the potential of the electrode departs from that at equilibrium; β is a factor greater than zero but less than unity, known as the *symmetry factor*.[1,2] Of course, if $\eta = 0$, then $I = 0$. Equation (7.4) is known as the *Butler-Volmer* equation, and it represents the starting point for any study concerning nonideal polarized electrodes in electrolyte solutions. Similarities with the diode equation [Eq. (6.53)] should be evident to the reader. By the way, an electrical equivalent circuit of Eq. (7.4) is given by two diodes connected in reverse-parallel, as shown in Fig. 7.3.

7.1.4 A Semiconductor-Insulator Structure in an Electrolyte Solution

Inside a semiconductor facing an electrolyte, the charge carriers will redistribute according to the rules described in Chap. 6. By adding an insulator (e.g., SiO_2 or Si_3N_4), an elec-
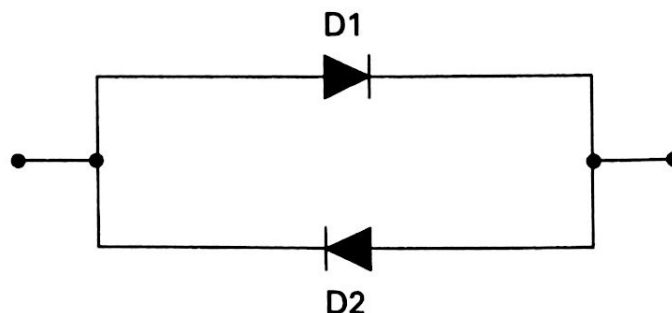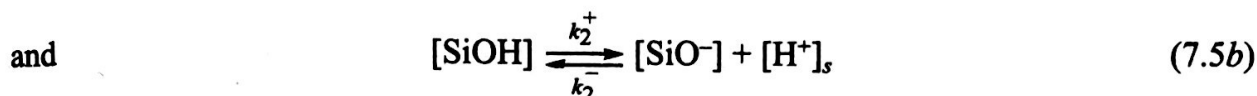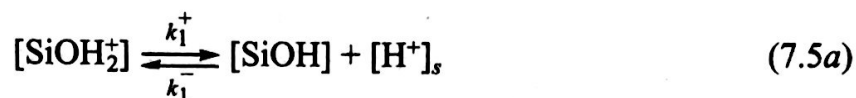

FIGURE 7.3 Two diodes connected in reverse-parallel.

trolyte-insulator-semiconductor (EIS) structure is generated, which is analogous to the metal-oxide-semiconductor (MOS) capacitor, considered in detail in Chap. 8. The two structures are shown for comparison in Fig. 7.4. Note that, in order to polarize the EIS structure, a reference electrode—that is, a virtually nonpolarizable interface—must be inserted to close the circuit.

The presence of an insulator in contact with the electrolyte solution introduces a new kind of charge distribution, which is caused by the formation of *surface groups* that transform the EIS structure into a *pH sensor*. Let us consider this process in some detail.

Let us first consider an SiO_2 insulator exposed to an aqueous solution interacts with H^+ ions in the following way:

$$[SiOH_2^+] \underset{k_1^-}{\overset{k_1^+}{\rightleftharpoons}} [SiOH] + [H^+]_s \qquad (7.5a)$$

and

$$[SiOH] \underset{k_2^-}{\overset{k_2^+}{\rightleftharpoons}} [SiO^-] + [H^+]_s \qquad (7.5b)$$

The subscript s in $[H^+]_s$ means that the concentration of protons is *near* the surface of the insulator, and $[SiOH_2^+]$, $[SiOH]$, and $[SiO^-]$ are the concentrations of the proton *binding sites* present on the oxide surface. Under equilibrium conditions, the kinetic reactions (7.5a), (7.5b) result in the equilibrium constants

$$K_+ = \frac{[SiOH][H^+]_s}{[SiOH_2^+]} \qquad (7.6a)$$

and

$$K_- = \frac{[SiO^-][H^+]_s}{[SiOH]} \qquad (7.6b)$$

By multiplying together the two equilibrium constants, we obtain

$$K_+ K_- = \frac{[SiO^-][H^+]_s^2}{[SiOH_2^+]} \qquad (7.7)$$

Concentrations of binding sites can be transformed into *fractions of sites* θ_+, θ_0, θ_- giving

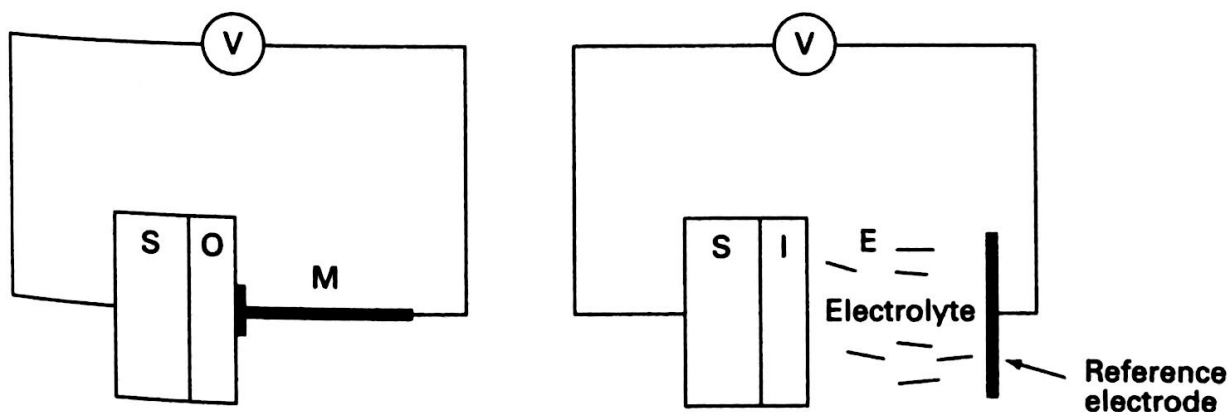$$\frac{[SiO^-]}{[SiOH_2^+]} = \frac{\theta_-}{\theta_+} \qquad (7.8)$$

FIGURE 7.4 (a) Metal-oxide-semiconductor (MOS) structure and (b) electrolyte-insulator-semiconductor (EIS) structure. A reference electrode is present to close the circuit of the EIS. Note that the electrolyte solution plays the role of the conductor.

where θ_-, θ_+, and θ_0 satisfy the constraint

$$\theta_- + \theta_+ + \theta_0 = 1 \tag{7.9}$$

Moreover, under equilibrium conditions, the concentration of protons at the surface of the insulator can be related to the one in the bulk via the Boltzmann equation

$$[H^+]_s = [H^+]_b \, e^{q(\phi_b - \phi_0)/kT} \tag{7.10}$$

where $(\phi_b - \phi_0)$ is the potential drop between electrolyte bulk and insulator surface. By assuming $\phi_b = 0$, Eq. (7.10) reduces to

$$[H^+]_s = [H^+]_b \, e^{-q\phi_0/kT} \tag{7.11}$$

By substitution of Eqs. (7.8) and (7.11) into (7.7), we obtain

$$K_+ K_- = \frac{\theta_-}{\theta_+} [H^+]_b^2 \, e^{-2q\phi_0/kT} \tag{7.12}$$

and, by taking logarithms of both sides and dividing by 2, we obtain

$$\frac{1}{2} \ln (K_+ K_-) = \frac{1}{2} \ln \frac{\theta_-}{\theta_+} + \ln [H^+]_b - \frac{q\phi_0}{kT} \tag{7.13}$$

Note that

$$\ln [H^+]_b \simeq 2.303 \log [H^+]_b = -2.303 \, pH_b \tag{7.14}$$

Then Eq. (7.13) can be written in pH terms as follows (we drop the subscript b from now on):

$$\frac{1}{2} \ln (K_+ K_-) = \frac{1}{2} \ln \frac{\theta_-}{\theta_+} - 2.303 \, pH - \frac{q\phi_0}{kT} \tag{7.15}$$

Equation (7.15) holds true for *any* pH value, and, for a given insulator, the ratio θ_-/θ_+ is a given function of pH. In other words, for a given insulator, there is a specific pH value for which

$$\theta_- = \theta_+ \tag{7.16}$$

This specific value is known as the *point of zero charge* of the material and is indicated as pH_{pzc}.

By setting $\phi_0 = 0$ for $pH = pH_{pzc}$ (since only differences in potential are ever physically meaningful), we obtain

$$\frac{1}{2} \ln (K_+ K_-) = -2.303 \, pH_{pzc} \tag{7.17}$$

Thus, we can finally write Eq. (7.17) as

$$2.303(pH - pH_{pzc}) = \frac{1}{2} \ln \frac{\theta_-}{\theta_+} - \frac{q\phi_0}{kT} \tag{7.18}$$

or

$$\phi_0 = -2.303 \frac{kT}{q} \Delta pH + \frac{1}{2} \frac{kT}{q} \ln \frac{\theta_-}{\theta_+} \tag{7.19}$$

where

$$\Delta pH = pH - pH_{pzc} \tag{7.20}$$

At room temperature we have

$$2.303 \, \frac{kT}{q} \simeq 59 \, \text{mV} \tag{7.21}$$

Equation (7.19) relates the potential ϕ_0 and pH and is the basis for utilizing an EIS structure as a pH sensor. The value of ϕ_0 can be deduced by knowing the profile of the potential in the electrolyte, and this will be considered in more detail in the next section. The same procedure followed for SiO_2, can then be utilized for other insulators, such as Si_3N_4. Unfortunately, for Si_3N_4 the reactions are slightly more complicated. On the other hand, Si_3N_4 is much more appropriate than SiO_2 for designing a silicon-based pH meter, so it is worth considering it. At the surface of the Si_3N_4 insulator, *silanol sites, tertiary amine sites, secondary amine sites,* and *primary amine sites* are present. The picture can be approximated by assuming that only silanol sites and basic primary amine sites are present on the surface of the insulator after oxidation.[3,4] Thus the equilibrium constants are

$$K_+ = \frac{[SiOH][H^+]_s}{[SiOH_2^+]} \tag{7.22a}$$

$$K_- = \frac{[SiO^-][H^+]_s}{[SiOH]} \tag{7.22b}$$

$$K_{N+} = \frac{[SiNH_2][H^+]_s}{[SiNH_3^+]} \tag{7.22c}$$

Concentrations of binding sites can again be transformed into fractions of sites as follows:

$$K_+ = \frac{\theta_0}{\theta_+}[H^+]_s \tag{7.23a}$$

$$K_- = \frac{\theta_-}{\theta_0}[H^+]_s \tag{7.23b}$$

$$K_{N+} = \frac{\theta_{N0}}{\theta_{N+}}[H^+]_s \tag{7.23c}$$

with the normalization conditions

$$\theta_+ + \theta_- + \theta_0 = \frac{N_{sil}}{N_s} \tag{7.24}$$

$$\theta_{N+} + \theta_{N0} = \frac{N_{nit}}{N_s} \tag{7.25}$$

$$\theta_0 + \theta_+ + \theta_- + \theta_{N+} + \theta_{N0} = 1 \tag{7.26}$$

where N_{sil} and N_{nit} are the numbers of silanol sites and primary amine sites per unit area, respectively, and N_s is the total number of available binding sites per unit area. The charge density σ_0 of the surface sites on the insulator is given by[4]

$$\sigma_0 = qN_s(\theta_+ + \theta_{N+} - \theta_-) \tag{7.27}$$

By combining Eqs. (7.22) and (7.27), we get

$$\frac{\sigma_0}{qN_s} = \left(\frac{[H^+]_s^2 - K_+ K_-}{[H^+]_s^2 + K_+[H^+]_s + K_+ K_-}\right)\frac{N_{sil}}{N_s} + \left(\frac{[H^+]_s}{[H^+]_s + K_{N+}}\right)\frac{N_{nit}}{N_s} \qquad (7.28)$$

As for the previously considered SiO_2 insulator, $[H^+]_s$ can then be related to the concentration of protons in the bulk, $[H^+]_b$, via the equilibrium Boltzmann equation:

$$[H^+]_s = [H^+]_b\, e^{-q\phi_0/kT} \qquad (7.29)$$

where ϕ_0 is the potential of the electrolyte-insulator interface, referred to the bulk value of the potential. The condition of charge neutrality for the EIS system is

$$\sigma_d + \sigma_0 + \sigma_s = 0 \qquad (7.30)$$

where σ_d is the charge density diffuse in the electrolyte, σ_0 is the charge density on the insulator surface, and σ_s is the charge density inside the semiconductor.

As already anticipated for the SiO_2 insulator, the above equations represent the starting point to relate the potential ϕ_0 to the pH of the electrolyte solution. This will be further considered in Sec. 7.2 and then again in Chap. 10, in dealing with ion-sensitive field-effect transistors (ISFETs) and related biosensors.

7.1.5 Colloidal Particles

The *sizes* of the materials in contact with the electrolyte have not quantitatively entered the picture so far. Basically, we can assume that we dealt with single, macroscopic (i.e., at least in the millimeter range) electrodes. The picture becomes quite different if we consider many micrometer-sized particles, each of them generating an electrified interface around itself. Such particles are known as *colloidal particles*. They include inert objects, for example, a suspension of metallic microspheres and living objects such as red blood cells. Micrometer-sized particles belong to the category of "mesoscopic" objects undergoing Brownian motion (see Chap. 5).

Let us consider a population of metallic spheres. As already noticed in Chap. 5, the smaller they are (in the range of micrometers), the more they react to the thermal collisions from the ions and water molecules of the electrolyte; they undergo a random walk through the solution. Large (centimeter-sized) spheres, too, exchange momentum with the particles of the solution, but their masses are huge compared with those of ions or molecules, so that the velocities imparted (to the spheres) from such collisions are essentially zero.

Once the microspheres begin to move in a *Brownian fashion* in the solution, some of them collide with each other. Many aspects of colloidal chemistry are clarified by a consideration of this subject. Each metal sphere feels its environment through its charged interface; each sphere is enveloped in a double layer. All the concepts of the electrified interface developed so far are of relevance to the colliding microspheres. For the sake of simplicity, we will not take into account that we are now dealing with spherical surfaces and not planes. Considering dilute solutions and no contact-adsorbing ions, one can visualize each metal sphere surrounded by a G-C region of diffuse charge. Note, however, that the *G-C layers* of both colliding spheres contain charges of the same sign. Thus, there is Coulomb repulsion as the two spheres come close. The repulsion energy depends on the distance r between the spheres and varies with distance in the same way as the G-C potential. This dependence on distance is approximately given by $\phi_0 e^{-\chi r}$, where χ is the inverse of the *Debye length* and it increases with the ion concentrations (see Sec. 7.2).

Double layers interact with double layers and the metal of one sphere also interacts with the metal of the second sphere. There is what is called the *Van der Waals attraction,* essentially a dispersion interaction, which depends on r^{-6}, and the electron overlap *repulsion,* which varies as r^{-12} (Ref. 1). These interactions between the bulk of the two colloidal metal spheres shall be represented together by a term $(-Ar^{-6} + Br^{-12})$, where A and B depend essentially on the chemical composition of the phase which is dispersed in the solution.

The total interaction between the two metal spheres can then be considered composed of two parts, (1) the surface, or double-layer, interaction determined by the Gouy-Chapman potential $\phi_0 e^{-\chi r}$ and (2) the volume, or bulk, interaction $(-Ar^{-6} + Br^{-12})$. The interaction between double layers becomes repulsive as the particles approach. The bulk interaction leads to an attraction unless the spheres get too close, when there is a sharp repulsion (Fig. 7.5). The total interaction energy U_{total} depends on the interplay of the surface (double-layer) and volume (bulk) effects and may be represented as

$$U_{\text{total}} = \phi_0 e^{-\chi r} + (-Ar^{-6} + Br^{-12}) \qquad (7.31)$$

This approximate formula contains information concerning what happens when two colloidal particles collide. Consider one type of energy-distance diagram (Fig. 7.5). It is seen that, for the first type of behavior where the electrostatic repulsion predominates, the net energy U_{total} is always positive; this means that two metal spheres under this condition cannot stick together stably. Note from Fig. 7.5 that, if the spheres did not wrap themselves in double layers, the interaction between the particles themselves, neglecting the double-layer repulsion, would predominate and have a minimum in a negative potential energy region corresponding, therefore, to a favoring of the aggregation of colloidal particles.

Thus, particles of colloidal dimensions survive aggregation into macroscopic phases only because their boundaries develop electrified interfaces. The repulsion between double layers is the key to the stability of colloids.

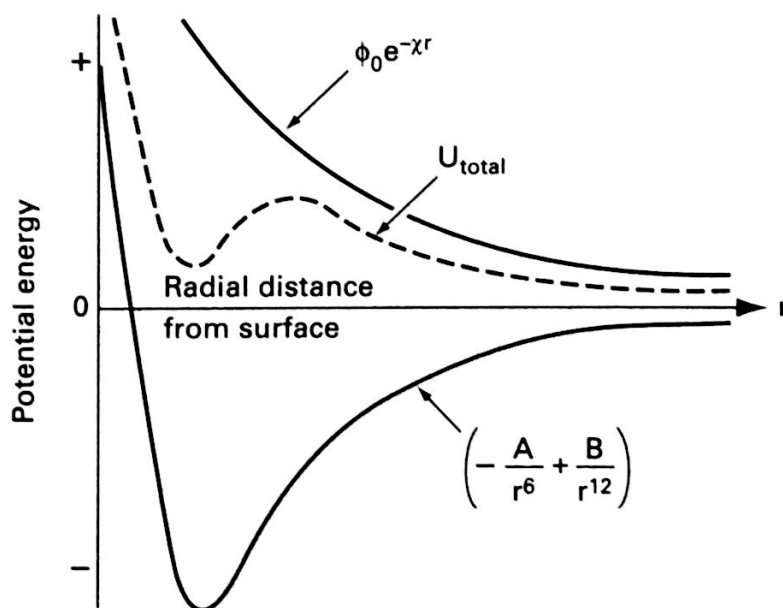The structure of an electrified interface and therefore the potential drop across it de-

FIGURE 7.5 The energy of interaction between two colloidal particles as a function of their distance apart, in the case of conditions favoring stability of the colloid. (*From O. M. Bockris and A. K. N. Reddy.*[1] *Used by permission.*)

pends on the composition of the electrolyte. The diffuse region can be reduced in thickness and the potential made to fall sharply by concentrating the solution with the addition of some electrolyte. Moreover, contact-adsorbing ions can be added to increase the IHP contribution. All this means that one has, by variation of the solution composition, an indirect control over the double-layer contribution and therefore the total interaction energy for two colloidal particles. In this way, one can control the stability of the colloids.

Aggregation happens by lowering Gouy-Chapman potentials at the r_{min} distance. This is obtained by adding more electrolyte to the solution. As a consequence, χ increases (see Sec. 7.2.1), and, since $\phi = \phi_0 e^{-\chi r}$, ϕ falls more sharply with distance. In other words, the Gouy-Chapman region is compressed, and the total interaction curve becomes negative and shows a minimum at r_{min} (Fig. 7.6). The colloid *has lost its stability*. This is known as *coagulation* or *flocculation*.[1]

Flocculation can be brought about in another way. By contact adsorption of ions, most of the potential drop across the interface can be made to occur between the metal and the IHP. Thus, by the addition of contact-adsorbing ions, the value of ϕ_0 can be reduced without significantly changing the concentration of the bulk electrolyte. The effect of this will be qualitatively similar to that shown in Fig. 7.6 and is shown in Fig. 7.7. The value of U_{total} again comes into the negative potential energy region; i.e., a stable configuration of particles in contact may exist, and a flocculation thus again occurs.

The characteristic behavior of the colloidal state is that double-layer interactions are as significant as bulk interactions. This condition can therefore be realized in all systems where the surface-to-volume ratios are high, i.e., at microscopic dimensions.

A colloidal suspension consisting of discrete, separate particles immersed in a continuous phase is known as a *sol*. A colloidal suspension can also consist of filamentous particles (i.e., macromolecules) dispersed in solution.

Instead of having one phase discontinuous and in the form of separate particles, it is possible to have the phase as a continuous matrix with pores of very fine dimensions through it. This is a porous mass, or membrane, also known as a *gel*. In such membranes, interactions inside the pores become highly dependent on double-layer interactions.
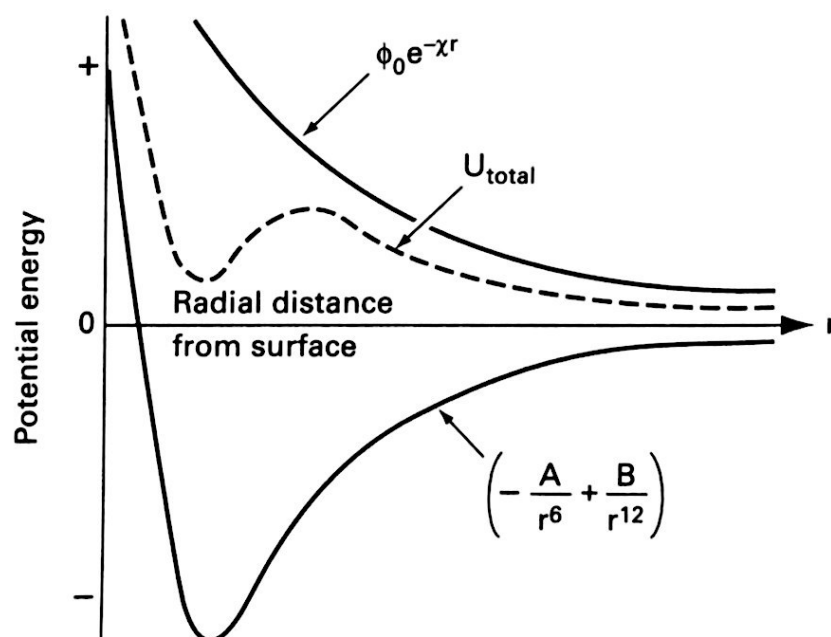

FIGURE 7.6   The energy of interaction between two colloidal particles as a function of their distance apart, for conditions favoring coagulation. (*From O. M. Bockris and A. K. N. Reddy.[1] Used by permission.*)
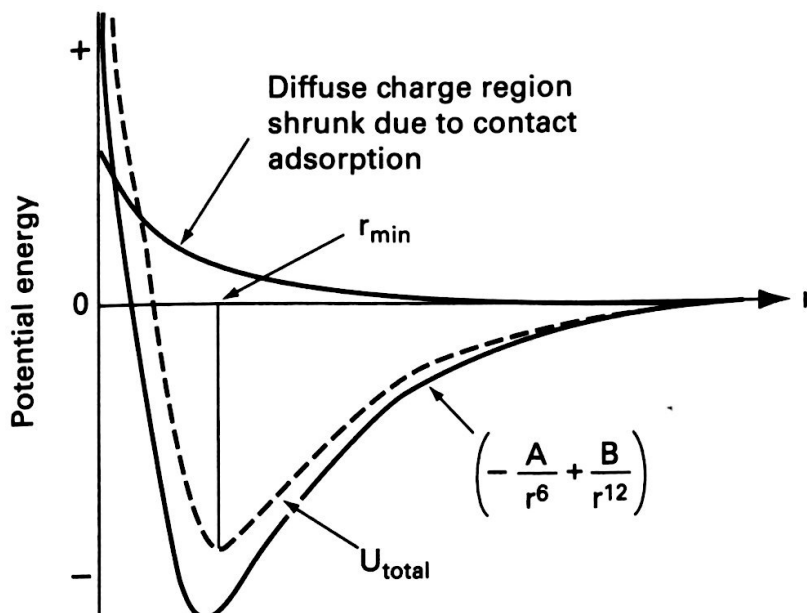
FIGURE 7.7 The effect of the contact adsorption of ions on the condition of the stability of a colloid. (*From O. M. Bockris and A. K. N. Reddy.*[1] *Used by permission.*)

Sols and gels are of great relevance in biological processes. A living cell is separated from the outside by a membrane and inside it can be viewed as a collection of colloidal particles held in suspension by interacting Gouy-Chapman layers. An example of this is given by the electrochemical mechanism of the clotting of blood.

The reader should be aware of the fact that, in comparison to the initial example of metallic microspheres, biological membranes are much more sophisticated objects. With specific reference to interfaces, biological membranes allow us to introduce one more way of charging a surface, i.e., by the adsorption (*binding*) of ions from solution onto a previously uncharged surface. This is the case, for example, of the binding of Ca^{2+} onto the zwitterionic headgroups (i.e., dipole ions) of the surfaces of the lipid bilayer. As a final consideration on living cells, let us conclude that electrified interfaces are essential for them, but charge transfer through them is even more important. This statement will be expanded in the last section of this chapter, when we will consider the flux of matter through membranes.

7.2 SOLUTION OF THE POISSON-BOLTZMANN EQUATION UNDER VARIOUS BOUNDARY CONDITIONS

It should be clear from the previous section that one of the key points for the characterization of an electrode-solution junction is the calculation of the profile of the electrical potential inside the electrolyte. The classical way to obtain this is to solve the *Poisson-Boltzmann equation*. We will do it in the following by first (Sec. 7.2.1) obtaining an expression for $\phi(x)$ from $x = 0$ to $x \to \infty$. The reader should be already aware of the fact that, in accordance with the arguments developed in the previous section, a more appropriate picture should consider solving the Poisson-Boltzmann equation from the *outer Helmholtz plane* to infinity. Moreover, in most practical problems, it is of interest to calculate the potential profile between *two* (or several, as already seen in the case of col-

loidal particles) electrodes separated by a *finite* distance. This will be considered in Sec. 7.2.2.

7.2.1 Electrical Potential Profile in an Electrolyte in the Presence of an Electrode

Let us consider a lamina in the electrolyte parallel to the electrode and at a distance x from it in the absence of any charge transfer (Fig. 7.8). As for the *pn* junction, the charge density ρ_x can be expressed in two ways: (1) In terms of the Poisson equation, which, for the x dimension in rectangular coordinates reads

$$\rho_x = -\varepsilon_0 \varepsilon_r \frac{d^2 \phi(x)}{dx^2} \qquad (7.32)$$

where $\phi(x)$ is the potential difference between the lamina and the bulk of the solution (taken as $\phi(x)_{x \to \infty} = 0$) and (2), in terms of the Boltzmann distribution,

$$\rho_x = \sum_i c_i z_i q = \sum_i c_i^b z_i q e^{-z_i q \phi / kT} \qquad (7.33)$$

where c_i and c_i^b are the concentrations of the ith ionic species in the lamina and in the bulk of the solution, respectively, z_i is the valence of the species i, and q is the electronic charge. The factor $z_i q \phi(x)/kT$ represents the ratio of the electrical and thermal energies of an ion at the distance x from the electrode. From the two expressions for the charge density ρ_x in Eqs. (7.32) and (7.33), we obtain the *Poisson-Boltzmann equation* (see also Sec. 8.7)

$$\frac{d^2 \phi}{dx^2} = -\frac{1}{\varepsilon_0 \varepsilon_r} \sum_i c_i^b z_i q e^{-z_i q \phi / kT} \qquad (7.34)$$

A simple transformation can now be used, namely

$$\frac{d^2 \phi}{dx^2} = \frac{1}{2} \frac{d}{d\phi} \left(\frac{d\phi}{dx} \right)^2 \qquad (7.35)$$
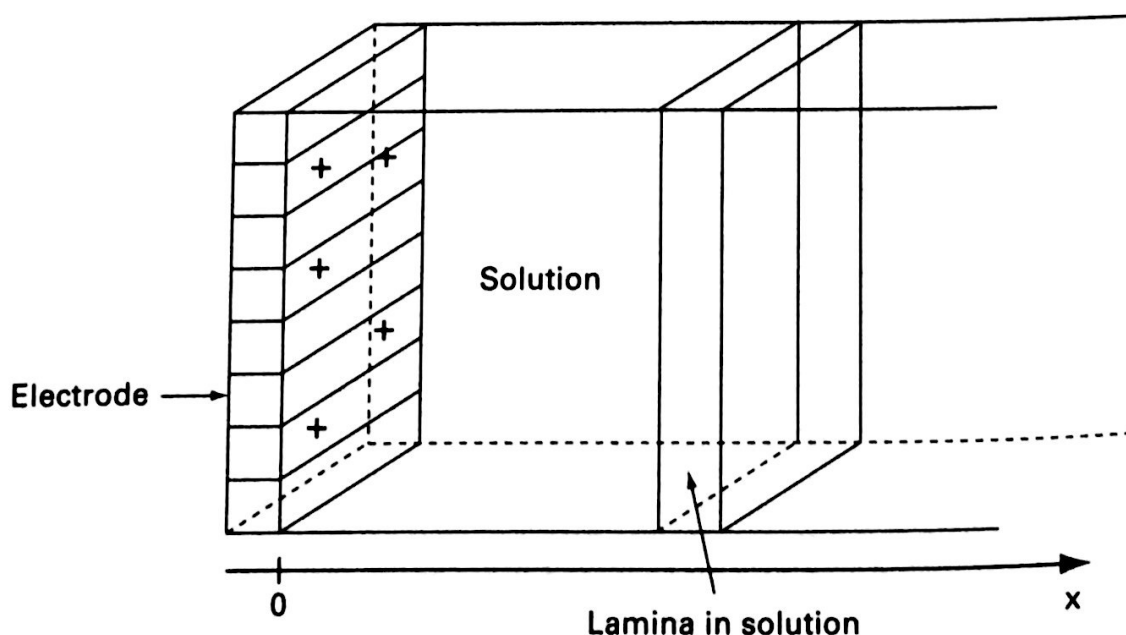

FIGURE 7.8 A lamina in the solution, parallel to a plane electrode.

This identity can be used in the differential Eq. (7.34) to give

$$\frac{d}{d\phi}\left(\frac{d\phi}{dx}\right)^2 = -\frac{2}{\varepsilon_0\varepsilon_r}\sum_i c_i^b z_i q e^{-z_i q\phi/kT} \tag{7.36}$$

or

$$d\left(\frac{d\phi}{dx}\right)^2 = -\frac{2}{\varepsilon_0\varepsilon_r}\sum_i c_i^b z_i q e^{-z_i q\phi/kT} d\phi \tag{7.37}$$

By integrating Eq. (7.37), we obtain

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2\,kT}{\varepsilon_0\varepsilon_r}\sum_i c_i^b e^{-z_i q\phi/kT} + \text{constant} \tag{7.38}$$

The integration constant can be evaluated by assuming that, deep in the bulk of the solution, i.e., at $x \to \infty$, not only is $\phi(x) = 0$, but the field $d\phi/dx$ is also zero, i.e.,

$$\phi|_{x\to\infty} = \frac{d\phi}{dx}\bigg|_{x\to\infty} = 0 \tag{7.39}$$

Under these conditions,

$$\text{Constant} = -\frac{2kT}{\varepsilon_0\varepsilon_r}\sum_i c_i^b \tag{7.40}$$

and, therefore

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2kT}{\varepsilon_0\varepsilon_r}\sum_i c_i^b(e^{-z_i q\phi/kT} - 1) \tag{7.41}$$

Considering the simplest case of one z:z-valent electrolyte, then

$$|z_+| = |z_-| = z \tag{7.42}$$

and

$$c_+^b = c_-^b = c^b \tag{7.43}$$

Therefore Eq. (7.41) becomes

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2kT}{\varepsilon_0\varepsilon_r}c^b(e^{zq\phi/kT} - 1 + e^{-zq\phi/kT} - 1) \tag{7.44}$$

or

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{2kT}{\varepsilon_0\varepsilon_r}c^b(e^{zq\phi/2kT} - e^{-zq\phi/2kT})^2 \tag{7.45}$$

Since

$$e^x - e^{-x} = 2\sinh(x) \tag{7.46}$$

hence Eq. (7.45) becomes

$$\left(\frac{d\phi}{dx}\right)^2 = \frac{8kT}{\varepsilon_0\varepsilon_r}c^b\sinh^2\left(\frac{zq\phi}{2kT}\right) \tag{7.47}$$

From Eq. (7.47), we can obtain the field $d\phi/dx$ in the solution by taking square roots on both sides. To decide which root is to be taken, we recall that, at the positively charged electrode, $\phi > 0$, $\sinh(\phi) > 0$ and $d\phi/dx < 0$, while, at the negatively charged electrode,

$\phi < 0$, sinh $(\phi) < 0$, and $d\phi/dx > 0$. Hence, only the negative root of Eq. (7.47) corresponds to the physical situation, i.e.,

$$\frac{d\phi}{dx} = -\left(\frac{8kTc^b}{\varepsilon_0\varepsilon_r}\right)^{1/2} \sinh\left(\frac{zq\phi}{2kT}\right) \tag{7.48}$$

From Eq. (7.32) we can derive the diffuse charge density in the electrolyte. To fix ideas, and in analogy with the procedure utilized for the MOS capacitor (see Chap. 8), let us assume that the electrode was charged by connecting it to an external source of electricity and that a charge density σ_e was added to the electrode. Then, the diffuse charge in the solution can be obtained as follows. We can choose a gaussian box of unit area, extended from $x = 0$ to $x \to \infty$, where ϕ and $d\phi/dx = 0$. Now, the charge density $\sigma_d = (-\sigma_e)$ inside this box will be given by Gauss' law

$$\sigma_d = \varepsilon_0\varepsilon_r \frac{d\phi}{dx}\bigg|_{x=0} \tag{7.49}$$

Thus, by using Eq. (7.48) we obtain

$$\sigma_d = -(8\varepsilon_0\varepsilon_r c^b kT)^{1/2} \sinh\left(\frac{zq\phi_0}{2kT}\right) \tag{7.50}$$

Starting from Eq. (7.48), the potential drop in the diffusion layer can also be estimated. To make the derivation simpler, let us approximate (a complete solution can be found in Ref. 5)

$$\sinh\left(\frac{zq\phi}{2kT}\right) \approx \frac{zq\phi}{2kT} \tag{7.51}$$

Then,
$$\frac{d\phi}{dx} \approx -\left(\frac{8c^b kT}{\varepsilon_0\varepsilon_r}\right)^{1/2} \frac{zq\phi}{2kT} \tag{7.52}$$

or
$$\frac{d\phi}{dx} \approx -\left(\frac{2c^b(zq)^2}{\varepsilon_0\varepsilon_r kT}\right)^{1/2} \phi \tag{7.53}$$

The square root of the quantity in parentheses on the right-hand side of Eq. (7.53) is the inverse of a length and it is customary to indicate it with the Greek letter χ. The inverse of χ is known as the *Debye length*.

In terms of χ, Eq. (7.53) becomes

$$\frac{d\phi}{dx} = -\chi\phi \tag{7.54}$$

and, by integration, we obtain

$$\phi = \phi_0 e^{-\chi x} \tag{7.55}$$

where ϕ_0 is the value of the potential at the electrode surface ($x = 0$).

The reader should note that the Poisson-Boltzmann equation considers ions as *point charges*. As a consequence, they are allowed to concentrate on the surface of the electrode up to unreasonable values. As suggested by Fig. 7.2, a more realistic picture can be obtained by assuming that the outer Helmholtz plane, which crosses the centers of

the first row of hydrated ions, identifies a plane of maximum approach for hydrated ions. Thus, the diffuse charge density should be calculated by solving the Poisson-Boltzmann equation from the OHP and not from the electrode surface. The layer delimited by electrode and OHP is referred to as the *Stern layer*.

In closing this section, let us finally address the question of the numerical value of the water relative dielectric permittivity ε_r. Its value is dependent on the electric field strength of the environment. *Bulk* water, where the average electric field strength can be assumed to be zero and no permanent dipole orientation is present, has a corresponding ε_r value around 80. On the other hand, on a charged electrode, water dipoles would orient and attain saturation orientation if the charge density on the electrode is large enough. This oriented water is sometimes termed the *primary hydration sheath* of the electrode and its dielectric permittivity can be assumed to have a numerical value around 6. Here, fully oriented water dipoles and adsorbed ions form the IHP. Away from the electrode, but still near it, water will be partially oriented, most of its dipoles contributing to the hydration sheath of ions. A mean value around 40 can be assumed for its dielectric permittivity. This is the value of ε_r which can be assigned to the OHP.[1]

7.2.2 Two Charged Planar Surfaces in Water

As a last example, in the following we shall consider the ion distribution between two similarly charged planar surfaces in water, where (apart from H^+ and OH^- ions) the only ions in the solution are those that have come off the two surfaces (that is, *no added* electrolyte is present). Such systems occur when, for example, colloidal particles (see Sec. 7.1.5) or bilayers with ionizable groups interact in water. To find the ion distribution, we solve again the Poisson-Boltzmann equation. To do so, we need two boundary conditions. In Sec. 7.2.1, when considering *one* electrode facing a *semi-infinite electrolyte solution*, we chose that both the potential ϕ and its space derivative $d\phi/dx$ approached zero as $x \rightarrow \infty$ [Eq. (7.39)]. In the present case, one boundary condition follows from the symmetry requirement that the electric field must vanish at the midplane between the two surfaces (see Fig. 7.9).

The second boundary condition follows from the requirement of overall *electroneutrality*, i.e., that the total charge of the ions (which came from the electrodes) in the gap between the two electrodes must be opposite to the charge on the surfaces. If σ_l is the surface charge density on each surface, d is the distance between the surfaces and l is a thickness which takes into account the finite size of the ions approaching the surfaces (Stern layer, see the discussion at the end of the previous section and in Ref. 5), then the condition of electroneutrality implies that

$$\sigma_l = -\int_0^{(d/2)-l} \rho \, dx = \varepsilon_0 \varepsilon_r \int_0^{(d/2)-l} \left(\frac{d^2\phi}{dx^2} \right) dx \qquad (7.56)$$

or

$$\sigma_l = \varepsilon_r \varepsilon_0 \left(\frac{d\phi}{dx} \right)\bigg|_{(d/2)-l} = -\varepsilon_r \varepsilon_0 E_{s+l} \qquad (7.57)$$

where E_{s+l} is the value of the electric field on a plane inside the solution at a distance l from the surface s. Note that this value is independent of the gap width d.

Turning now to the calculation of the ionic distribution, we can write down the Boltzmann distribution of the charge density ρ as

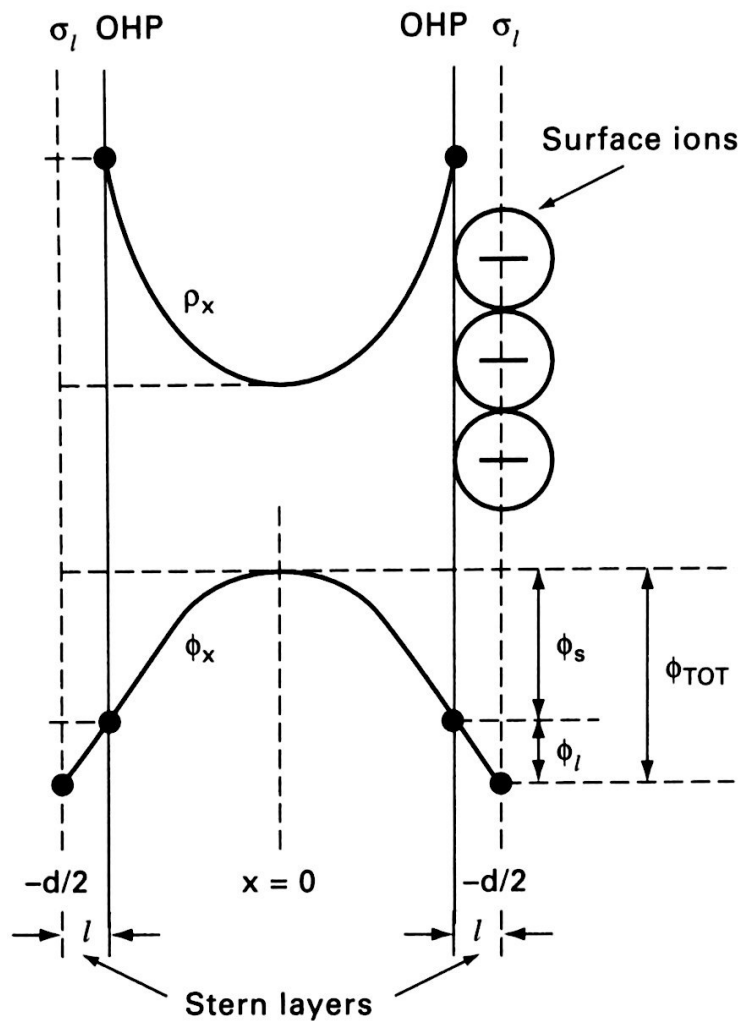$$\rho = \rho_0 e^{-zq\phi/kT} \qquad (7.58)$$

FIGURE 7.9 Stern layers of thickness l at each surface dividing the planes of fixed charge density σ_l from the boundary of the aqueous solution. (*Adapted from Israelachvili.*[5] *Used by permission.*)

ρ_0 being the charge density at the midplane, where $d\phi/dx = 0$ by symmetry and we may set also $\phi = 0$ (since only *differences* in potential are ever physically meaningful). Differentiating Eq. (7.58) and utilising the Poisson-Boltzmann equation, we obtain

$$\frac{d\rho}{dx} = -\frac{zq\rho_0}{kT} e^{-zq\phi/kT}\left(\frac{d\phi}{dx}\right) = \frac{\varepsilon_0\varepsilon_r}{2kT}\frac{d}{dx}\left(\frac{d\phi}{dx}\right)^2 \tag{7.59}$$

hence
$$\rho_x - \rho_0 = \int_{\rho_0}^{\rho(x)} d\rho = \frac{\varepsilon_r\varepsilon_0}{2kT}\int_0^{d\phi/dx} d\left(\frac{d\phi}{dx}\right)^2 = \frac{\varepsilon_r\varepsilon_0}{2kT}\left(\frac{d\phi}{dx}\right)^2 \tag{7.60}$$

or
$$\rho_x = \rho_0 + \frac{\varepsilon_r\varepsilon_0}{2kT}\left(\frac{d\phi}{dx}\right)^2 \tag{7.61}$$

which gives ρ at any point x in terms of ρ_0 at the midplane and $(d\phi/dx)^2$ at x.

Starting from the results obtained so far, an expression for the *pressure* existing between two charged surfaces in water can be derived. Moreover, similar equations can be obtained for two charged surfaces in the presence of *added* electrolytes. The interested reader can find treatment of these topics in Ref. 5.

7.3 MEMBRANE TRANSPORT

The characterization of solute movement across a barrier separating two solutions is a topic of great relevance in several scientific fields dealing with biomedical and biotechnological issues. The concept of "barrier" can be used to indicate such different objects as an inert homogeneous material or the highly inhomogeneous membrane of a living neuron. In the following we will begin with continuous transport by introducing the *Nernst-Planck equation* and the so-called constant-field equation. Diffusive potentials and equivalent electric circuits will be then considered. Finally, a short description of discontinuous transport will be given.

7.3.1 The Nernst-Planck Equation

Let us consider the one-dimensional motion of a solute i crossing in the x direction a homogeneous membrane separating two homogeneous solutions in the same solvent and at the same temperature. In order to describe the flux of this solute, we can start by writing the current density J in any point x of the solution as (no time dependence)

$$J_i(x) = -\tilde{D}_i z_i q \frac{dC_i(x)}{dx} + \tilde{\mu}_i z_i q \, C_i(x)E(x) \qquad (7.62)$$

where $C_i(x)$ is the *molecular* concentration of the solute i at x, z_i is its valence, q is the (positive) elementary charge, $\tilde{D}_i$ and $\tilde{\mu}_i$ are the molecule diffusion and mobility coefficients, respectively, and $E(x)$ is the electric field value at x. The two terms of the right side of Eq. (7.62) are clearly the diffusion and drift current density terms already introduced for electrons and holes in Chap. 3.

We can then transform Eq. (7.62) into a *molar* current density as follows:

$$J_{m,i}(x) = -D_i z_i \mathscr{F} \frac{dc_i(x)}{dx} + \mu_i z_i \mathscr{F} c_i(x)E(x) \qquad (7.63)$$

where $\mathscr{F}$ is the *Faraday constant* (see App. A) and $c_i(x)$ is the *molar* concentration of the solute i at x.

We can now introduce the *molar* flux F_{ci} of the solute i, defined as the moles of solute that cross the membrane (unit area) in the x direction per unit time

$$F_{ci}(x) = -D_i \frac{dc_i(x)}{dx} + \mu_i c_i(x)E(x) \qquad (7.64)$$

Let us now define the "generalized" mobility u_i as

$$u_i = \frac{\mu_i}{z_i \mathscr{F}} \qquad (7.65)$$

Then Eq. (7.64) can be written as, dropping (x) reference for simplicity,

$$F_{ci} = -D \frac{dc_i}{dx} + u_i c_i z_i \mathscr{F} E \qquad (7.66)$$

The Einstein relationship gives (for molar quantities)

$$D_i = RTu_i \qquad (7.67)$$

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where R, the gas constant, is defined as

$$R = N_{AV}k \tag{7.68}$$

and N_{AV} and k are the *Avogadro* and *Boltzmann constants*, respectively. By making use of Eq. (7.67), we transform Eq. (7.66) to

$$F_{ci} = -u_i RT \frac{dc_i}{dx} + u_i c_i z_i \mathscr{F} E \tag{7.69}$$

which can be easily transformed into

$$F_{ci} = -u_i c_i \frac{d}{dx} [RT \ln c_i + z_i \mathscr{F} \phi(x)] \tag{7.70}$$

where
$$\frac{d\phi}{dx} = -E \tag{7.71}$$

Equation (7.70) is a simplified version of the *Nernst-Planck equation,* first introduced by Nernst (1888) and Planck (1890). The term inside the brackets can be recognized as a simplified expression of the *electrochemical potential energy* Π. (More general expressions of Π can be found in Refs. 6 and 7). Accordingly, we can write

$$F_{ci} = -u_i c_i \frac{d\Pi}{dx} \tag{7.72}$$

Moreover the gradient of an energy can be always related to a force f as follows:

$$f = -\frac{d\Pi}{dx} \tag{7.73}$$

In conclusion, we arrive at the *flux-force relationship*

$$F_{ci} = -u_i c_i f \tag{7.74}$$

   In most books dealing with membrane transport, the Nernst-Planck Eq. (7.70) is deduced starting from Eq. (7.74). In concluding this section, two points can be stressed, namely:

1. Equation (7.62) is equivalent to Eqs. (3.46) and (3.47) derived for the current density of holes and electrons.

2. The generalized mobility u_i can be thought as a proportionality constant between the mean velocity v_i of particles i subject to a frictional drag and *any* force, acting on them, i.e.

$$v_i = u_i f \tag{7.75a}$$

For example, for a body freely moving in the atmosphere, Eq. (7.75a) becomes

$$v_i = u_i m_i g \tag{7.75b}$$

where m_i is the body mass and g the gravitational acceleration.

7.3.2 Solutions of the Nernst-Planck Equation

The Nernst-Planck equation is the starting point for several calculations, which are done by integration under appropriate boundary conditions and assumptions on charge and

electric field. When applied to a concentration c_i of uncharged molecules (e.g., glucose), Eq. (7.70) reduces to

$$F_{ci} = -u_i c_i \frac{d}{dx}(RT \ln c_i) \qquad (7.76)$$

or

$$F_{ci} = -u_i RT \frac{dc_i}{dx} \qquad (7.77)$$

Let us assume that Eq. (7.77) describes the flux of the molecule i in the x direction at some point inside a homogeneous membrane of thickness Δx. Then, if the system under study is in a *steady state*, F_{ci} should have the same values at all points within the membrane. By assuming u_i also constant through the membrane, Eq. (7.77) can be easily integrated across the thickness Δx of the membrane separating two semi-infinite solutions of concentration c_a and c_b, respectively. Thus,

$$F_{ci} \int_0^{\Delta x} dx = -RTu_i \int_{\bar{c}_{i,a}}^{\bar{c}_{i,b}} dc \qquad (7.78)$$

The quantity $\bar{c}_{i,a}$ represents the concentration of the solute "just inside" the membrane, on the side in contact with concentration $c_{i,a}$. Similarly, $\bar{c}_{i,b}$ represents the concentration of the solute "just inside" the membrane, on the side in contact with concentration $c_{i,b}$.

The meaning of the above definitions is that there is a discontinuity in matter when a particle is crossing a solution/membrane boundary. Concentrations "just inside" are linked[6] to concentrations "just outside" via *partition coefficients* $\beta(c_i)$.

The simplest hypothesis on the partition coefficients is to assume them independent of the actual concentration, i.e.,

$$\frac{\bar{c}_{i,b}}{c_{i,b}} = \beta_i = \frac{\bar{c}_{i,a}}{c_{i,a}} \qquad (7.79)$$

Under conditions given by Eq. (7.79), Eq. (7.78) yields

$$F_{ci} = -RTu_i \beta_i \frac{\Delta c}{\Delta x} \qquad (7.80a)$$

or, according to Eq. (7.67),

$$F_{ci} = -D_i \beta_i \frac{\Delta c}{\Delta x} \qquad (7.80b)$$

Equation (7.80b) is easily recognized as the *Fick first law of diffusion* (see also Chaps. 3 and 5). By introducing the *permeability coefficient P_i* defined as

$$P_i = \frac{D_i \beta_i}{\Delta x} \qquad (7.81)$$

Equation (7.80b) can be finally written as

$$F_{ci} = -P_i \Delta c_i \qquad (7.82)$$

When the solute is charged (i.e., $z_i \neq 0$) and there is an electrical potential difference across the membrane, the situation is more complex, in consideration of the fact that Eq.

(7.70) *cannot* be integrated, unless the dependence of the electric potential ϕ on x is known.

Before making any choice on such a dependence, let us rewrite Eq. (7.70) as

$$F_{ci} = -D_i\left(\frac{dc_i}{dx} + \frac{c_i z_i \mathscr{F}}{RT}\frac{d\phi}{dx}\right) \qquad (7.83)$$

Then, by multiplying both sides by $\exp(z_i\mathscr{F}\phi/RT)$ and rearranging, we obtain

$$F_{ci}e^{z_i\mathscr{F}\phi/RT}\,dx = -D_i d(c_i e^{z_i\mathscr{F}\phi/RT}) \qquad (7.84)$$

Assuming a steady state and that D_i is constant through the membrane, the integration of Eq. (7.84) across the membrane thickness gives

$$F_{ci}\int_0^{\Delta x} e^{z_i\mathscr{F}\phi/RT}\,dx = -D_i\int_{\bar{c}_{i,a},\bar{\phi}_a}^{\bar{c}_{i,b},\bar{\phi}_b} d(c_i e^{z_i\mathscr{F}\phi/RT}) \qquad (7.85)$$

The right-hand side of Eq. (7.85) can be immediately integrated. On the other hand, in order to accomplish the integration of the left-hand side, the dependence of ϕ on x within the membrane must be known or assumed. A simple and most frequently used assumption, first proposed by Goldman in 1943, is that ϕ is a linear function of x, i.e. (with the overbar meaning the quantity "just inside" the membrane),

$$\bar{\phi} = \bar{\phi}_0 + \frac{\overline{\Delta\phi}}{\Delta x}x \qquad (7.86)$$

where

$$\overline{\Delta\phi} = \bar{\phi}(\Delta x) - \bar{\phi}(0) \qquad (7.87a)$$

or equivalently,

$$\overline{\Delta\phi} = \bar{\phi}(b) - \bar{\phi}(a) \qquad (7.87b)$$

Equation (7.86) is known as the *constant field assumption*. By virtue of this assumption, Eq. (7.85) becomes

$$F_{ci}\int_0^{\Delta x} e^{z_i\mathscr{F}\bar{\phi}_a/RT} e^{z_i\mathscr{F}\overline{\Delta\phi}x/RT\Delta x}\,dx = -D_i(\bar{c}_{i,b}e^{z_i\mathscr{F}\bar{\phi}_b/RT} - \bar{c}_{i,a}e^{z_i\mathscr{F}\bar{\phi}_a/RT}) \qquad (7.88)$$

Multiplying both sides by $\exp(-z_i\mathscr{F}\phi_a/RT)$, integrating and rearranging yields:

$$F_{ci} = -\frac{D_i z_i \mathscr{F}}{RT}\frac{\overline{\Delta\phi}}{\Delta x}\left[\frac{\bar{c}_{i,b}e^{z_i\mathscr{F}\overline{\Delta\phi}/RT} - \bar{c}_{i,a}}{e^{z_i\mathscr{F}\overline{\Delta\phi}/RT} - 1}\right] \qquad (7.89)$$

Equation (7.89) is usually referred as the *constant field flux equation* and it refers to *intramembrane* properties. However, by assuming again partition coefficients independent of the concentrations [Eq. (7.79)], it can be shown (see Sec. 7.3.4) that

$$\overline{\Delta\phi} = \Delta\phi \qquad (7.90)$$

Under these conditions, and making use of Eq. (7.81), we finally arrive at

$$F_{ci} = -\frac{P_i z_i \mathscr{F}}{RT}\Delta\phi\left[\frac{c_{i,b}e^{z_i\mathscr{F}\Delta\phi/RT} - c_{i,a}}{e^{z_i\mathscr{F}\Delta\phi/RT} - 1}\right] \qquad (7.91)$$

Equation (7.91) has been widely employed for the description of ion transport across biological membranes (a different approach will be shortly described in the next section).

Let us analyze some relevant features of Eq. (7.91). First of all, it should be appreciated that when $c_{i,a} \neq c_{i,b}$, the relation between F_{ci} and $\Delta\phi$ is clearly nonlinear. In other words, the membrane offers a different *resistance* to the flow of an ion depending on the direction of the flow. This asymmetric behavior is an example of *rectification*. The only exception to the rectifying behavior is given when $c_{i,a} = c_{i,b}$. The reader can easily verify that under this condition the relation between F_{ci} and $\Delta\phi$ is a straight line passing through the origin. The resulting equation is

$$F_{ci} = -\frac{P_i z_i \mathscr{F} \Delta\phi \, c_i}{RT} \tag{7.92}$$

By multiplying Eq. (7.92) by the ion charge $z_i \mathscr{F}$ and rearranging, we obtain a form of *Ohm's law:*

$$I_i = \left(-\frac{P_i z_i^2 \mathscr{F}^2 \, c_i}{RT} \right) \Delta\phi \tag{7.93}$$

Going back to the general case [Eq. (7.91)] when $c_{i,a} \neq c_{i,b}$, the condition of zero flux gives (see Sec. 6.2.1) the *Nernst equilibrium potential:*

$$\Delta\phi = \frac{RT}{z_i \mathscr{F}} \ln \left(\frac{c_{i,a}}{c_{i,b}} \right) \tag{7.94}$$

Finally, letting the potential drop $\Delta\phi$ go to zero, the resulting flux approaches the Fick law of diffusion (see Prob. 7.3),

$$F_{ci} = -P_i \, \Delta c_i = -D_i \beta_i \frac{\Delta c_i}{\Delta x} \tag{7.95}$$

The reader should be aware of the fact that Eq. (7.91) is obviously an incomplete picture of any real situation in the sense that it describes the flux of a *single* ion, not taking into account the fact that other ion species (at least one of opposite sign) should be present in the solution.

The general problem is faced at an elementary level when it is restricted to univalent anions and cations. Then, the flow of *each* cation c_+ is given by

$$F_{c+} = -\frac{P_+ \mathscr{F} \Delta\phi}{RT} \left[\frac{c_{+,b} e^{\mathscr{F} \Delta\phi/RT} - c_{+,a}}{e^{\mathscr{F} \Delta\phi/RT} - 1} \right] \tag{7.96a}$$

and the flow of *each* anion c_- is given by

$$F_{c-} = \frac{P_- \mathscr{F} \Delta\phi}{RT} \left[\frac{c_{-,b} e^{-\mathscr{F} \Delta\phi/RT} - c_{-,a}}{e^{-\mathscr{F} \Delta\phi/RT} - 1} \right] \tag{7.96b}$$

The steady-state condition implies the *zero current condition*, i.e.,

$$I = \mathscr{F} \left(\sum_c F_{c+} - \sum_a F_{c-} \right) = 0 \tag{7.97}$$

where $\Sigma_c F_{c+}$ is the sum of the flows of all cations and where $\Sigma_a F_{c-}$ is the sum of the flows of all anions.

Combining Eqs. (7.96) and (7.97) and solving for $\Delta\phi$, we obtain the *Goldman-Hodgkin-Katz (GHK) equation*

$$\Delta\phi = \frac{RT}{\mathscr{F}} \ln\left(\frac{\sum_c P_+ c_{+,o} + \sum_a P_- c_{-,i}}{\sum_c P_+ c_{+,i} + \sum_a P_- c_{-,o}}\right) \tag{7.98}$$

where the subscript a has been replaced by o (outside) and b by i (inside).

In most biological membranes, where the predominant permeant ions are Na^+, K^+ and Cl^-, Eq. (7.98) reduces to

$$\Delta\phi = \frac{RT}{\mathscr{F}} \ln\left(\frac{P_{Na}c_{Na,o} + P_K c_{K,o} + P_{Cl}c_{Cl,i}}{P_{Na}c_{Na,i} + P_K c_{K,i} + P_{Cl}c_{Cl,o}}\right) \tag{7.99}$$

Equation (7.99) is frequently used to estimate the potential drop across a biological membrane.

Example 7.1   Let us give an estimate of the membrane potential under conditions typical of an electrophysiology experiment (squid axon in seawater).

Answer   Let us assume:

$$P_K:P_{Na}:P_{Cl} = 1:0.03:0.1$$

$$c_{K,o} = 10 \text{ mM} \qquad c_{Na,o} = 460 \text{ mM} \qquad c_{Cl,o} = 540 \text{ mM}$$

$$c_{K,i} = 400 \text{ mM} \qquad c_{Na,i} = 50 \text{ mM} \qquad c_{Cl,i} = 40 \text{ mM}$$

Then Eq. (7.99) gives

$$\Delta\phi \simeq -70 \text{ mV} \tag{E7.1}$$

On the other hand, we can easily verify (see Prob. 7.4) that Cl is approximately at equilibrium. Therefore, Eq. (7.99) can be approximated with

$$\Delta\phi \simeq \frac{RT}{\mathscr{F}} \ln\left(\frac{P_{Na}c_{Na,o} + P_K c_{K,o}}{P_{Na}c_{Na,i} + P_K c_{K,i}}\right) \simeq -71 \text{ mV} \tag{E7.2}$$

Before closing this section, let us finally consider a very simple case, where a homogeneous membrane separates two solutions a and b of a single $z{:}z$ salt. In this very special case the flux potential drop relation can be deduced by directly integrating the Nernst-Planck equation. According to this equation, we can write

$$F_{c+} = -c_+ u_+ \left[RT\left(\frac{d\ln c_+}{dx} + z_+ \mathscr{F}\left(\frac{d\phi}{dx}\right)\right)\right] \tag{7.100}$$

and

$$F_{c-} = -c_- u_- \left[RT\left(\frac{d\ln c_+}{dx}\right) - z_+ \mathscr{F}\left(\frac{d\phi}{dx}\right)\right] \tag{7.101}$$

Since bulk electroneutrality of each solution must be preserved, it follows that

$$c_+ = c_- = c \tag{7.102}$$

and

$$F_{c+} = F_{c-} = F_c \tag{7.103}$$

Equating Eqs. (7.100) and (7.101), making use of Eqs. (7.102) and (7.103), and rearranging, we obtain

$$\frac{d\phi}{dx} = -\left(\frac{u_+ - u_-}{u_+ + u_-}\right)\left(\frac{RT}{z\mathscr{F}}\right)\left(\frac{d}{dx}\ln c\right) \tag{7.104}$$

Assuming again constant partition coefficients, integration of Eq. (7.104) across the thickness of the membrane gives

$$\Delta\overline{\phi} = \Delta\phi = -\left(\frac{u_+ - u_-}{u_+ + u_-}\right)\left(\frac{RT}{z\mathscr{F}}\right)\ln\left(\frac{c_a}{c_b}\right) \tag{7.105}$$

Substituting Eq. (7.104) into Eq. (7.100) and combining terms yields

$$F_c = -\left(\frac{2RTu_+u_-}{u_+ + u_-}\right)\frac{dc}{dx} \tag{7.106}$$

By taking into account Eq. (7.103), we can finally write

$$F_c = -D_\pm\left(\frac{dc}{dx}\right) \tag{7.107}$$

where $D_\pm$, the diffusion coefficient of the *salt,* is

$$D_\pm = \frac{2RTu_+u_-}{u_+ + u_-} \tag{7.108}$$

This simple case allows us to discuss a relevant principle which is fundamental to the understanding of the origin of diffusion potentials in more complex systems. The principle is that, in the absence of an externally applied current, electroneutrality can be preserved only by the equivalent flow of anions and cations across a membrane. In the simple system just considered, this zero current condition (which does *not* imply equilibrium conditions) implies the constraint

$$F_{c+} = F_{c-} \tag{7.109}$$

and, therefore

$$I = z_+\mathscr{F}F_{c+} + z_-\mathscr{F}F_{c-} = 0 \tag{7.110}$$

The reader should note that, if $u_+ \neq u_-$, then Eq. (7.110) can be satisfied only if an electrical potential difference is generated with a magnitude proportional to the difference in mobilities and with an orientation appropriate to slow down the movement of the ion with the greater mobility and to speed up the movement of the ion with the lower mobility.

On the other hand, if

$$u_+ = u_- \tag{7.111}$$

then

$$\Delta\phi = 0 \tag{7.112}$$

In the limiting condition in which one of the mobilities is zero, e.g.,

$$u_+ = 0 \tag{7.113}$$

then, according to Eq. (7.105), we obtain

$$\Delta\phi = -\frac{RT}{z_+\mathscr{F}}\ln\left(\frac{c_b}{c_a}\right) \tag{7.114}$$

where $\Delta\phi$ is clearly the Nernst equilibrium potential. A similar result, with opposite orientation, would be obtained with $u_- = 0$.

Equation (7.114) means that, if an ion cannot cross the membrane, then *neither ion* is permitted to cross the membrane, otherwise electroneutrality would be violated. Thus, if

$$u_+ = 0 \tag{7.115a}$$

or

$$u_- = 0 \tag{7.115b}$$

then

$$F_{c+} = F_{c-} = 0 \tag{7.116a}$$

and

$$D_\pm = 0 \tag{7.116b}$$

In this *limiting* condition there is no ion flux and the system is in a state of equilibrium. We wish to underline that this equilibrium condition is never globally satisfied by living biological systems, which behave under *out-of-equilibrium* conditions.

7.3.3 Electrical Circuit Analogs

Let us rearrange the Nernst-Planck equation [Eq. (7.70)] of a *single ion i* in the form

$$F_{ci} = -u_i c_i z_i \mathscr{F} \left[\left(\frac{RT}{z_i \mathscr{F}} \right) \left(\frac{d}{dx} \ln c_i \right) + \left(\frac{d\phi}{dx} \right) \right] \tag{7.117}$$

The corresponding (molar) current density is then

$$J_{ci} = -u_i c_i z_i^2 \mathscr{F}^2 \left[\left(\frac{RT}{z_i \mathscr{F}} \right) \left(\frac{d \ln c_i}{dx} \right) + \left(\frac{d\phi}{dx} \right) \right] \tag{7.118}$$

and, rearranging, we obtain

$$\frac{J_{ci}}{u_i z_i^2 \mathscr{F}^2 c_i} = -\left(\frac{RT}{z_i \mathscr{F}} \right) \left(\frac{d \ln c_i}{dx} \right) - \left(\frac{d\phi}{dx} \right) \tag{7.119}$$

Assuming steady state (i.e., J_{ci} constant), Eq. (7.119) can be formally integrated over the thickness of the membrane Δx, yielding

$$J_{ci} \int_0^{\Delta x} \frac{dx}{u_i z_i^2 \mathscr{F}^2 c_i} = \frac{RT}{z_i \mathscr{F}} \ln \frac{c_{i,o}}{c_{i,i}} - \Delta\phi \tag{7.120}$$

Now we can define the integral resistance of the membrane to the ion i as

$$R_i = \int_0^{\Delta x} \frac{dx}{u_i z_i^2 \mathscr{F}^2 c_i} \tag{7.121}$$

and the voltage source of ion i as the Nernst potential

$$E_i = \frac{RT}{z_i \mathscr{F}} \ln \left(\frac{c_{i,o}}{c_{i,i}} \right) \tag{7.122}$$

By making use of Eqs. (7.121) and (7.122), we write Eq. (7.120) as

$$J_{ci} R_i = E_i - \Delta\phi \tag{7.123}$$

The circuital representation of Eq. (7.123) is given in Fig. 7.10.

Clearly, the equilibrium condition, when $J_{ci} = 0$, is given by

$$\Delta\phi = E_i = \frac{RT}{z_i\mathscr{F}} \ln\left(\frac{c_{i,o}}{c_{i,i}}\right) \qquad (7.124)$$

The flow of *two ions* which, according to the Nernst-Planck equation, move independently of each other, can be represented as a two-branch parallel circuit (Fig. 7.11). Its current is given by

$$I = g_1(E_1 - \Delta\phi) + g_2(E_2 - \Delta\phi) \qquad (7.125)$$

where

$$g_1 = \frac{1}{R_1} \qquad (7.126a)$$

is the *conductance* of ion 1 and

$$g_2 = \frac{1}{R_2} \qquad (7.126b)$$

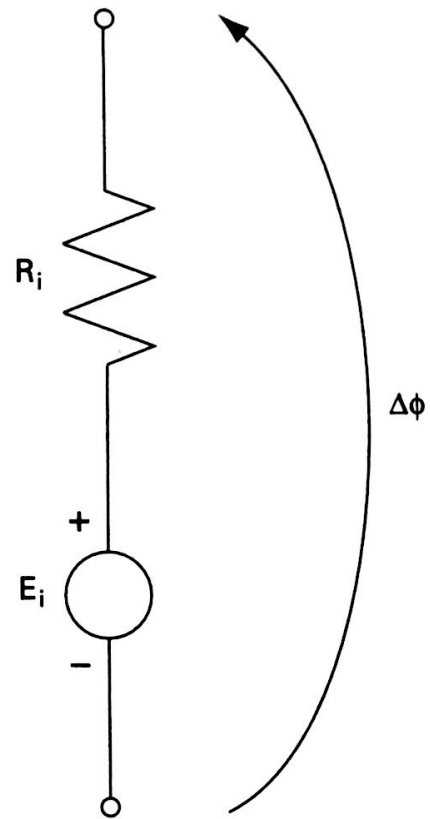is the conductance of ion 2; E_1 and E_2 are the two Nernst potentials.

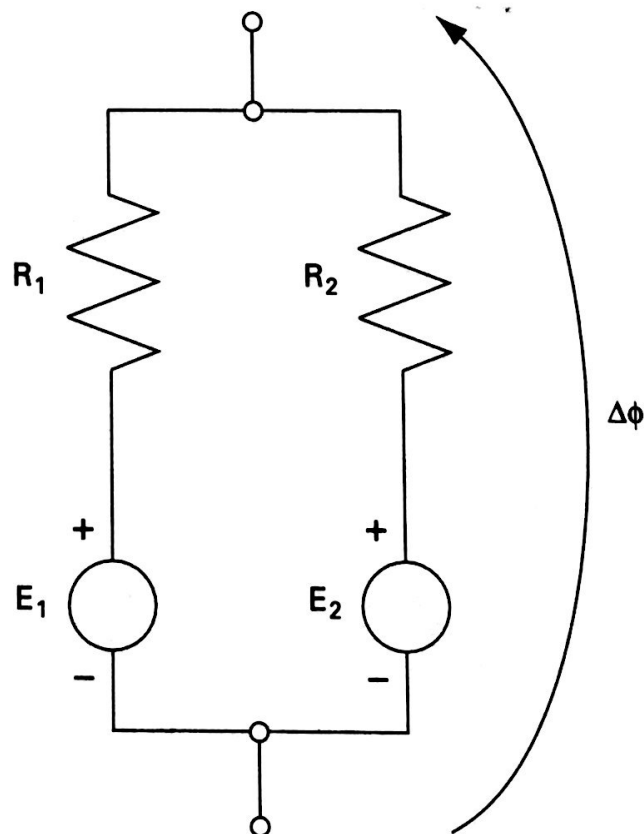**FIGURE 7.10** Equivalent circuit representation of the flow of a single ion.

FIGURE 7.11 Equivalent circuit representation of the parallel flow of two ions.
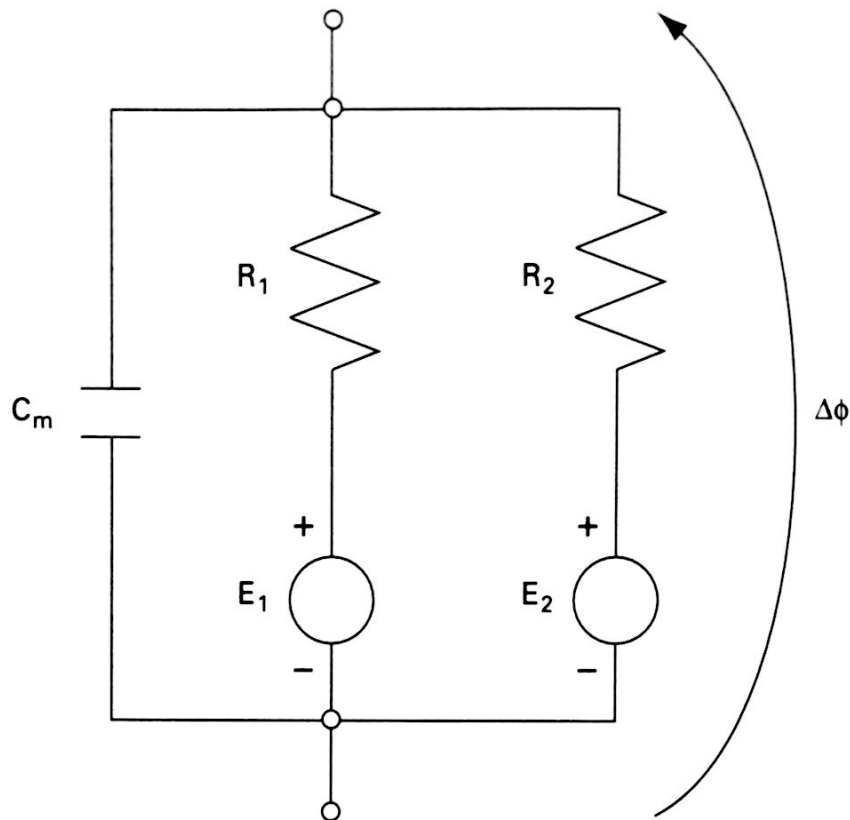
FIGURE 7.12   As Fig. 7.11, but now including the charging capability of the membrane.

If a charging process is also present on the membrane, a *capacitor* has to be inserted in parallel to the resistive branches (Fig. 7.12). The current density is now

$$I = C_m \frac{d}{dt}(\Delta\phi) + g_1(E_1 - \Delta\phi) + g_2(E_2 - \Delta\phi) \tag{7.127}$$

where C_m is the membrane capacitance per unit area.[9] These schemes will be further considered in Chap. 11 where the convention $(\Delta\phi - E_i)$ is chosen.

In closing this section, we wish to underline that electrical circuit rules, such as those routinely used in electrical engineering, deal with flux of *electrons* and *do not* recognize *different* ionic species. On the contrary, artificial and biological membranes *make these distinctions*. This consideration should be kept in mind when using the very valuable equivalent-circuit approach, to avoid misleading results.[6]

7.3.4 Modeling Transport through Structured Membranes

Fixed charges can be present on biological membranes (see Chap. 4). Moreover, particles crossing the membrane can interact with specific sites along their path, for example, inside a narrow channel (see Chap. 4). These situations, which have not been taken into account so far, will be considered in this section.

Donnan Equilibrium.   Let us first consider the effect of *fixed charges* present on a membrane. In order to do so, let us first reconsider in greater detail the movement of an ion across a membrane. We can always imagine this motion as a three-step process: the first step is the crossing of the membrane's first border (i.e., the outer solution-membrane interface). Let us call this border the outside (*o*) border. The second step is the movement

through the thickness of the membrane. The last step is the crossing of the inside (i) border (i.e., the membrane–inner solution interface). Consistent with this description, the potential drop across the membrane can be split into three parts, i.e.,

$$\Delta\phi = \Delta\phi_{o,\bar{o}} + \overline{\Delta\phi} + \Delta\phi_{\bar{i},i} \tag{7.128}$$

where $\Delta\phi_{o,o}$ is the potential drop at the outside border, $\overline{\Delta\phi}$ is the potential drop through the interior of the membrane and $\Delta\phi_{\bar{i},i}$ is the potential drop at the inside border.

In contrast to the movement through the membrane thickness, the two border crossings can reasonably be assumed to be equilibrium phenomena.[6] Therefore we can indicate them as two Nernst equilibrium potentials, namely

$$\Delta\phi_{o,\bar{o}} = \frac{RT}{z\mathscr{F}} \ln\left(\frac{c_o}{\bar{c}_o}\right) \tag{7.129}$$

and

$$\Delta\phi_{\bar{i},i} = \frac{RT}{z\mathscr{F}} \ln\left(\frac{\bar{c}_i}{c_i}\right) \tag{7.130}$$

In accordance to Eq. (7.79), if the ratio at the borders is independent of the concentrations, we can then write

$$\frac{c_o}{\bar{c}_o} = \frac{1}{\beta} \tag{7.131a}$$

$$\frac{\bar{c}_i}{c_i} = \beta \tag{7.131b}$$

Therefore, under conditions expressed by Eqs. (7.131),

$$\Delta\phi = \overline{\Delta\phi} \tag{7.132}$$

We remind the reader that Eq. (7.132) was assumed without justification in the previous section [see Eq. (7.90)].

The situation becomes slightly more complex if we assume the presence of a concentration of a fixed molecular species in the membrane structure. As we already discussed in Chap. 4, this is a very reasonable assumption for biological membranes. In the presence of a fixed negative charge concentration, the electroneutrality condition, applied at any of the membrane borders to a monovalent salt of concentration c, reads

$$c_+ = c_- = c \tag{7.133}$$

and

$$c_{+,m} = c_{-,m} + |z|M \tag{7.134}$$

where c_+ and c_- represent the cation and anion concentration outside the membrane, the subscript m identifies ion concentrations in the membrane, and z is the valence of the negative chemical components fixed to the membrane, with concentration M. As compared to previous use of the electroneutrality condition, Eq. (7.134) is a *new* constraint, imposed by the presence of the fixed charged component of concentration M.

By assuming again an equilibrium condition at the solution-membrane interface, we can write

$$\Delta\phi = \frac{RT}{\mathscr{F}} \ln\left(\frac{c_{+,m}}{c_+}\right) = \frac{RT}{\mathscr{F}} \ln\left(\frac{c_-}{c_{-,m}}\right) \tag{7.135}$$

which implies

$$\beta = \frac{c_{+,m}}{c_+} = \frac{c_-}{c_{-,m}} \tag{7.136}$$

By using Eqs. (7.133) and (7.134), we transform Eq. (7.136) into

$$c\beta = \frac{c}{\beta} + |z|M \tag{7.137}$$

or

$$c\beta^2 - |z|M\beta - c = 0 \tag{7.138}$$

which gives

$$\beta = \frac{|z|M + (|z|^2M^2 + 4c^2)^{1/2}}{2c} \tag{7.139}$$

The equilibrium system just considered is referred to as the *Donnan equilibrium.* It depicts a situation where the partition coefficient β is a function of the salt concentration c. Therefore, indicating with β_i and β_o the partition coefficients at the two sides of the membrane, it is

$$\beta_i \neq \beta_o \tag{7.140}$$

Under these conditions, Eq. (7.128) becomes

$$\Delta\phi = -\frac{RT}{\mathscr{F}} \ln \beta_o + \overline{\Delta\phi} + \frac{RT}{\mathscr{F}} \ln \beta_i \tag{7.141}$$

and the first and third terms on the right-hand side of Eq. (7.141) do not cancel each other.

In the limiting case of $|z|M$ much greater than c, Eq. (7.141) reduces to

$$\Delta\phi = \frac{RT}{\mathscr{F}} \ln \beta_i - \frac{RT}{\mathscr{F}} \ln \beta_o = \frac{RT}{\mathscr{F}} \ln \frac{c_o}{c_i} \tag{7.142}$$

In this instance, $\Delta\phi$ is the sum of two equilibrium potentials that arise solely at the interfaces of the membrane through which no net flux occurs. This is the origin of the electrical potential differences generated in glass pH electrodes.

Obviously, the considerations made so far can be applied to *any* system made of two equilibrium compartments separated by a membrane, one of which contains charged species that cannot cross the membrane.

Discontinuous Flow. Biological (and also artificial) membranes often display saturation, transeffects, and competitive behavior that cannot be described by Nernst-Planck–type equations, where P_i, the permeability coefficient, is a constant and is not influenced by the concentration of the diffusing species or by the presence of other permeant ions.

In other words, the Nernst-Planck approach is not appropriate for describing very important entities such as ion channels. For these entities a quite different approach, based on the *absolute reaction rate theory* (proposed by Eyring in 1935), must be used. This approach will be illustrated with a simple example in the following. The reader can find further details in Refs. 6 and 8.

The fundamental assumption of this approach is that the movement of a particle inside a membrane is discontinuous, and the membrane can be viewed as a series of potential energy barriers, depicted as a series of peaks and valleys, that a particle must cross in order

to pass from the outer (o) to the inner (i) solution. The key actor in the absolute rate theory is the rate constant K_{ij} which has the dimension of frequency [s^{-1}] and governs the movement of a particle from a minimum in energy (i.e., the "valley" i) to another minimum in energy (i.e., the "valley" j) over a maximum (i.e., the "peak" ij).

Without further justifications (which are provided in Ref. 6), let us assume that K_{ij} is given by the following Boltzmann (molar) distribution:

$$K_{ij} = \frac{kT}{h} e^{-\Delta G_{ij}/RT} \qquad (7.143)$$

where k is the Boltzmann constant, T the absolute temperature, h the Planck constant, ΔG_{ij} a molar energy indicating the height of the peak from the valley i, and R the gas constant. The reader can easily verify that K_{ij} has the dimension of frequency and that its numerical value increases with the absolute temperature T. Equation (7.143) originated from considerations of the average frequency ν of the vibrations (i.e., the movement) of a molecule at temperature T. This frequency ν can be estimated by equating

$$h\nu = kT \qquad (7.144)$$

or

$$\nu = \frac{kT}{h} \qquad (7.145)$$

At room temperature ν is in the order of 10^{12} s^{-1}.

The rate coefficient K_{ij} is obtained by weighting the frequency ν by a Boltzmann distribution.[10] The rate K_{ij} can then be related to a mean free path l in such a way that the mean velocity of a particle moving or rather "hopping" (the situation is similar to the one describing the electrode-solution interface; see Sec. 7.1.3) from valley i to valley j is given by

$$v_{ij} = K_{ij} l \qquad (7.146)$$

Consequently, the flux F_c of a particle is given by

$$F_c = K_{ij} lc \qquad (7.147)$$

Let us apply this approach to a simple two-barrier representation of a membrane as depicted in Fig. 7.13. Let us further assume that we are dealing with an uncharged molecule of concentrations c_0 (outside compartment) and c_i (inside compartment), so that no drift component has to be taken into account. Then, using the notation of Fig. 7.13, the flux from the outer compartment into the membrane (concentration c_m) is

$$F_{c,om} = K_{om} c_o l - K_{mo} c_m l \qquad (7.148)$$

Similarly, we can write the flux of exit from the membrane into solution i as

$$F_{c,mi} = K_{mi} c_m l - K_{im} c_i l \qquad (7.149)$$

When the diffusion of the molecules reaches a steady state, then we have

$$F_{c,om} = F_{c,mi} = F_c \qquad (7.150)$$

Also, if the barriers have the same amplitude, then

$$K_{om} = K_{im} \qquad (7.151)$$

and

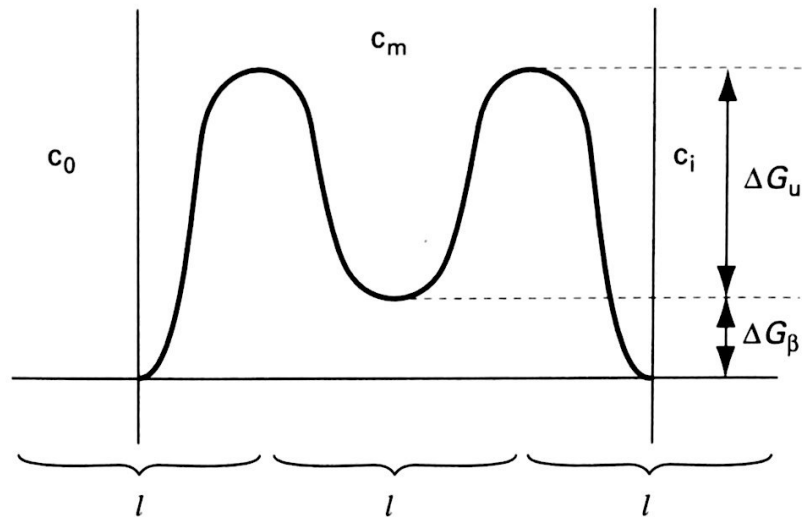$$K_{mo} = K_{mi} \qquad (7.152)$$

FIGURE 7.13   A symmetrical double energy barrier model for diffusion across a membrane.

Therefore, solving Eqs. (7.148) and (7.149), with constraints given by Eqs. (7.150) to (7.152), we obtain

$$F_c = \frac{K_{om}l}{2}(c_o - c_i) \tag{7.153}$$

The reader can note that Eq. (7.153) has the form of a diffusion equation, so that we may write

$$P = \frac{K_{om}l}{2} \tag{7.154}$$

where P is the permeability coefficient of the molecule.

Let us indicate with Δx the thickness of the membrane. Then, from Fig. 7.13, we can write

$$\Delta x = 2l \tag{7.155}$$

Therefore, since from Eq. (7.81)

$$P = \frac{D\beta}{\Delta x} \tag{7.156}$$

we can also write, taking into account Eq. (7.154),

$$D\beta = K_{om}\,l^2 \tag{7.157}$$

According to Eq. (7.143), the rate constant K_{om} can be written as

$$K_{om} = \frac{kT}{h}\,e^{-\Delta G/RT} \tag{7.158}$$

Moreover (see Fig. 7.13), we can split ΔG as

$$\Delta G = \Delta G_\beta + \Delta G_u \tag{7.159}$$

and, therefore we can write

$$K_{om} = \frac{kT}{h} e^{-\Delta G_\beta/RT} e^{-\Delta G_u/RT} \tag{7.160}$$

and

$$D\beta = \frac{l^2 kT}{h} e^{-\Delta G_\beta/RT} e^{-\Delta G_u/RT} \tag{7.161}$$

with the following identifications

$$\beta = e^{-\Delta G_\beta/RT} \tag{7.162}$$

$$D = l^2 \frac{kT}{h} e^{-\Delta G_u/RT} \tag{7.163}$$

Equation (7.163) could be further compared to the *Einstein-Smolucowsky relation*

$$D = \frac{\langle x^2 \rangle}{2} \frac{1}{t} \tag{7.164}$$

The reader should appreciate that, unlike the approaches that involve integration of the Nernst-Planck equation, the rate theory allows, at least in principle, the parameters β and D to be expressed in terms of the physical and chemical structural details of the diffusion pathway.

The approach just introduced can be extended to (more realistic) multibarrier systems and also to charged species moving through channels containing binding sites.[6,8]

PROBLEMS

7.1 Discuss the frequency dependence of the double-layer equivalent impedance (Eq. 7.1).

7.2 Find out the expression for the minimum in the potential energy between two colloidal particles (see Sec. 7.1.5)

7.3 Deduce the Fick diffusion law from the constant field flux equation (Eq. 7.89).

7.4 By using the numerical values given in Example 7.1, find the numerical values of the Nernst equilibrium potential for Na^+, K^+ and Cl^-.

7.5 Find the expression for the membrane potential under steady-state conditions by making use of the equivalent circuit model (Eq. 7.127).

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