

PHYSICAL  
PHARMACY

ALFRED MARTIN

FOURTH EDITION

# Physical Pharmacy

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PHYSICAL CHEMICAL PRINCIPLES IN THE PHARMACEUTICAL SCIENCES

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# 6

## Solutions of Electrolytes

Properties of Solutions of Electrolytes  
Arrhenius Theory of Electrolytic Dissociation  
Theory of Strong Electrolytes

Coefficients for Expressing Colligative  
Properties

The first satisfactory theory of ionic solutions was that proposed by Arrhenius in 1887. The theory was based largely on studies of electric conductance by Kohlrausch, colligative properties by van't Hoff, and chemical properties such as heats of neutralization by Thomsen. Arrhenius<sup>1</sup> was able to bring together the results of these diverse investigations into a broad generalization known as the theory of electrolytic dissociation.

Although the theory proved quite useful for describing weak electrolytes, it was soon found unsatisfactory for strong and moderately strong electrolytes. Accordingly, many attempts were made to modify or replace Arrhenius's ideas with better ones, and finally, in 1923, Debye and Hückel put forth a new theory. It is based on the principles that *strong electrolytes* are completely dissociated into ions in solutions of moderate concentration and that any deviation from complete dissociation is due to interionic attractions. Debye and Hückel expressed the deviations in terms of activities, activity coefficients, and ionic strengths of electrolytic solutions. These quantities, which had been introduced earlier by Lewis, are discussed in this chapter together with the theory of interionic attraction. Other aspects of modern ionic theory and the relationships between electricity and chemical phenomena are considered in following chapters.

We begin with a discussion of some of the properties of ionic solutions that led to Arrhenius theory of electrolytic dissociation.

### PROPERTIES OF SOLUTIONS OF ELECTROLYTES

**Electrolysis.** When, under a potential of several volts, a direct electric current (dc) flows through an electrolytic cell (Figure 6-1), a chemical reaction occurs. The process is known as *electrolysis*. Electrons enter the

cell from the battery or generator at the *cathode* (road down); they combine with positive ions or *cations*, in the solution, and the cations are accordingly reduced. The negative ions, or *anions*, carry electrons through the solution and discharge them at the *anode* (road up), and the anions are accordingly oxidized. *Reduction* is the addition of electrons to a chemical species, and *oxidation* is removal of electrons from a species. The current in a solution consists of a flow of positive and negative ions toward the electrodes, whereas the current in a metallic conductor consists of a flow of free electrons migrating through a crystal lattice of fixed positive ions. Reduction occurs at the cathode, where electrons enter from the external circuit and are added to a chemical species in solution. Oxidation occurs at the anode where the electrons are removed from a chemical species in solution and go into the external circuit.

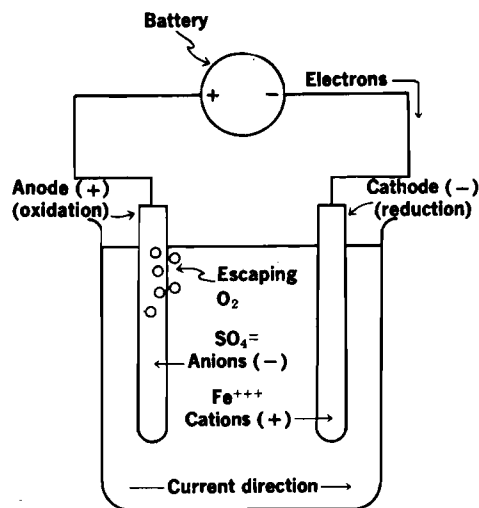
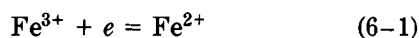
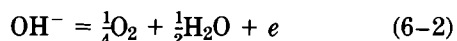


Fig. 6-1. Electrolysis in an electrolytic cell.

In the electrolysis of a solution of ferric sulfate in a cell containing platinum electrodes, a ferric ion migrates to the cathode where it picks up an electron and is reduced:

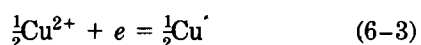


The sulfate ion carries the current through the solution to the anode, but it is not easily oxidized; therefore, hydroxyl ions of the water are converted into molecular oxygen, which escapes at the anode, and sulfuric acid is found in the solution around the electrode. The oxidation reaction at the anode is



Platinum electrodes are used here since they do not pass into solution to any extent. When *attackable* metals, such as copper or zinc, are used as the anode, their atoms tend to lose electrons, and the metal passes into solution as the positively charged ion.

In the electrolysis of cupric chloride between platinum electrodes, the reaction at the cathode is



while at the anode, chloride and hydroxyl ions are converted respectively into gaseous molecules of chlorine and oxygen, which then escape. In each of these two examples, the net result is the transfer of one electron from the cathode to the anode.

**Transference Numbers.** It should be noted that the flow of electrons through the solution from right to left in Figure 6-1 is accomplished by the movement of cations to the right as well as anions to the left. The fraction

of total current carried by the cations or by the anions is known as the *transport* or *transference number*  $t_+$  or  $t_-$ .

$$t_+ = \frac{\text{current carried by cations}}{\text{total current}} \quad (6-4)$$

$$t_- = \frac{\text{current carried by anions}}{\text{total current}} \quad (6-5)$$

The sum of the two transference numbers is obviously equal to unity:

$$t_+ + t_- = 1 \quad (6-6)$$

The transference numbers are related to the velocities of the ions, the faster-moving ion carrying the greater fraction of current. The velocities of the ions in turn depend on hydration as well as ion size and charge. Hence, the speed and the transference numbers are not necessarily the same for positive and for negative ions. For example, the transference number of the sodium ion in a 0.10-*M* solution of NaCl is 0.385. Because it is greatly hydrated, the lithium ion in a 0.10-*M* solution of LiCl moves slower than the sodium ion and hence has a lower transference number, viz., 0.317.

**Electrical Units.** According to Ohm's law, the strength

metallic conductor is related to the difference in applied potential or voltage  $E$  and the resistance  $R$  in ohms, as follows:

$$I = \frac{E}{R} \quad (6-7)$$

The current strength  $I$  is the rate of flow of current or the quantity  $Q$  of electricity (electronic charge) in coulombs flowing per unit time:

$$I = \frac{Q}{t} \quad (6-8)$$

and

$$\begin{aligned} \text{Quantity of electric charge, } Q \\ = \text{current, } I \times \text{time, } t \end{aligned} \quad (6-9)$$

The quantity of electric charge is expressed in coulombs (1 coul =  $3 \times 10^9$  electrostatic units of charge, or esu), the current in amperes, and the electric potential in volts.

Electric energy consists of an intensity factor, electromotive force or voltage, and a quantity factor, coulombs.

$$\text{Electric energy} = E \times Q \quad (6-10)$$

**Faraday's Laws.** In 1833 and 1834, Michael Faraday announced his famous laws of electricity, which may be summarized in the statement, *the passage of 96,500 coulombs of electricity through a conductivity cell produces a chemical change of 1 gram equivalent weight of any substance.* The quantity 96,500 is known as the faraday,  $F$ . The best estimate of the value today is  $9.648456 \times 10^4$  coulombs per gram equivalent.

A univalent negative ion is an atom to which a valence electron has been added; a univalent positive ion is an atom from which an electron has been removed. Each gram equivalent of ions of any electrolyte carries Avogadro's number ( $6.02 \times 10^{23}$ ) of positive or negative charges. Hence, from Faraday's laws, the passage of 96,500 coulombs of electricity results in the transport of  $6.02 \times 10^{23}$  electrons in the cell. A faraday is an Avogadro's number of electrons, corresponding to the mole, which is an Avogadro's number of molecules. The passage of 1 faraday of electricity causes the electrolytic deposition of the following number of gram atoms or "moles" of various ions:  $1\text{Ag}^+$ ,  $1\text{Cu}^+$ ,  $\frac{1}{2}\text{Cu}^{2+}$ ,  $\frac{1}{2}\text{Fe}^{2+}$ ,  $\frac{1}{3}\text{Fe}^{3+}$ . Thus, the number of positive charges carried by 1 gram equivalent of  $\text{Fe}^{3+}$  is  $6.02 \times 10^{23}$ , but the number of positive charges carried by 1 gram atom or 1 mole of ferric ions is  $3 \times 6.02 \times 10^{23}$ .

Faraday's laws can be used to compute the charge on an electron in the following way. Since  $6.02 \times 10^{23}$  electrons are associated with 96,500 coulombs of electricity, each electron has a charge  $e$  of

$$e = \frac{96,500 \text{ coulombs}}{6.02 \times 10^{23} \text{ electrons}}$$

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