CHAPTER TWELVE

SOLUTIONS OF ELECTROLYTES

12-1 Introduction

The historical development of electrochemistry constitutes one of the more interesting stories of science. It begins, for us, with observations made in 1600 by W. Gilbert, physician to Queen Elizabeth, on the ability of amber to attract pith or other light objects when rubbed with a piece of fur. Gilbert coined the word electric (from the Greek for amber) in describing such behavior. Benjamin Franklin became interested in the subject and suggested, around 1750, that the different behavior of electrostatically charged glass and amber was not due to two kinds of electricity, but rather to an excess or deficiency of an electric "fluid." Thus began the subject of electrostatics, which culminated around 1890 with the identification of the electron as the unit of electricity.

Another chain of events led to the discovery of a second kind of electricity. The story traces back to 1678 when Swammerdam demonstrated before the Grand Duke of Tuscany that a frog’s leg resting on a copper support would twitch when touched with a silver wire connected to the copper. We are more familiar with the experiments of L. Galvani in 1790, who observed that a frog’s leg (again) would twitch when connected to a static electricity generator or when the nerve was merely touched with a metal strip which was connected to the end of the leg. The terms galvanic electricity and galvanometer honor this discovery. By 1800 A. Volta succeeded in producing visible sparks from a stack of alternate silver and zinc plates. This was the first battery, then called a voltaic pile or a galvanic cell. The first definite experiment in electrochemistry appears to have been made by W. Nicholson and A. Carlisle in 1800, who used a galvanic cell to electrolyze water. By 1807 H. Davy had isolated sodium and potassium by the electrolysis of their hydroxides.

The foundation of modern electrochemistry was laid by M. Faraday, working around 1830 at the Royal Institution. He showed that a given quantity of electricity produced a fixed amount of electrolysis and formulated the following now well-known laws:¹

¹ Faraday's law is not always experimentally obvious; for a puzzling discrepancy see Palit (1975).

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1. The amount of chemical decomposition produced by a current is proportional to the quantity of electricity passed.

2. The amounts of different substances deposited or dissolved by a given quantity of electricity are proportional to their chemical equivalent weights.

Faraday's contribution is of an importance comparable to that of Joule in finding the mechanical equivalent of heat. In modern language, Faraday determined the electrochemical equivalence, or the amount of electricity corresponding to one mole of electrons. This equivalence, which we call the Faraday constant $F$ is

$$F = N_0 e = (6.02252 \times 10^{23})(1.6021 \times 10^{-19}) = 96,487 \text{ C mole}^{-1},$$

where $N_0$ is Avogadro's number and $e$ is the charge on the electron; C is the abbreviation for the coulomb. Our name for the natural unit of charge, the electron, was proposed, incidentally, by G. Stoney in 1874.

A great number of interesting and perceptive experiments have been passed over in this account. Much of our basic nomenclature originated during Faraday's time: anode and cathode for the positive and negative pole, respectively, of a battery; ion (Greek for wanderer) for the carrier of electricity in solution; ampere for the unit of current; and ohm for the measure of electrical resistance. The latter two terms are, of course, in recognition of the pioneer investigations of A.M. Ampère and G.S. Ohm.

The mechanism whereby current is transported through solutions of salts took nearly a century to be understood after the first observations of the phenomenon by Davy and others. An early idea was that of T. von Grotthus, who suggested in 1805 that an electrolyte consisted of polar molecules which lined up in an electric field and, by exchanging ends, passed electricity down a chain. He was trying to explain how electricity could go through a solution and yet cause electrolysis only at the electrodes. As illustrated in Fig. 12-1, his thought was that application of a potential across the electrodes caused the polar molecules to break and reform in such a way as to leave a negative piece of one at the anode and a positive piece of another at the cathode. The idea was clever, and will be invoked in more modern language in explanation of the motion of hydrogen ions.

As originally stated, the Grotthus mechanism was untenable on various grounds: Electrolyte "molecules" are not that close together in solution; why should even the weakest potential be able to cause strong molecules to break up; and so on. The hypothesis was largely demolished in 1857 by R. Clausius. Clausius proposed instead that the positive and negative parts of the electrolyte molecule were always partially present as fragments or ions, which then carried the current. We would

FIG. 12-1. Illustration of the original Grotthus mechanism.
call his proposal one of partial dissociation. It was a compromise in the sense that it was very difficult to accept that a molecule could break up or dissociate, and Clausius theorized that only a small fraction of the molecules actually did so.

We come now to the last quarter of the nineteenth century. J. van't Hoff and his group made colligative property measurements on sugar solutions and then on aqueous electrolytes. They reported large \( i \) factors [Eq. (10-58)] in the latter case. Thus \( i \) was close to two for NaCl solutions. S. Arrhenius drew heavily on van't Hoff's work in proposing the theory of electrolytic dissociation in 1883. The theory amounted to an assertion that electrolytes were mostly and not just partially dissociated into ions. During this last period the giants of electrochemistry were Arrhenius, F. Kohlrausch, W. Ostwald, and van't Hoff. Kohlrausch and his school carried out a monumental number of experiments on the conductance of electrolyte solutions, establishing that they obeyed Ohm's law. Thus the terms \textit{specific conductivity} and \textit{equivalent conductivity} were defined, and the major rules governing the variation of conductance with concentration were formulated. Ostwald did much to clarify the behavior of what we now call \textit{weak electrolytes}, or ones which behave essentially as Clausius had proposed much earlier.

The basic framework of electrochemistry was thus in place by the turn of the century. The early 1900's were spent in more and more precise studies of electrolyte solutions. The next major advances were made in the 1920's, in the treatment of the forces between ions, which determined the quantitative aspects of their motion through a solvent and their thermodynamic properties. A major theory by P. Debye and E. Hückel led, in 1923, to an enduring picture of dilute electrolyte solutions. Each ion tends to have around it an excess concentration of oppositely charged ions, which form a statistical or diffuse \textit{atmosphere}. This atmosphere contributes to the thermodynamic chemical potential of the ion and hence to its activity coefficient. At about the same time, J. Brensted and N. Bjerrum (in Copenhagen) made lasting contributions both to the understanding of acid and base strengths and in establishing that ions could form \textit{ion pairs} in more concentrated solutions.

Late in the same decade, L. Onsager extended the Debye–Hückel theory to treat dynamic effects such as conductance and diffusion. Later, with I. Prigogine, he was a leader in developing the general thermodynamic treatment of irreversible processes. Still later, R. Tolman and J. Kirkwood pioneered the development of the statistical mechanical theory of solutions—a task yet to be finished.

We begin the subject of electrochemistry with the important new property of electrolyte solutions—that of conductance. The separate behavior of each kind of ion is then discussed in terms of ionic mobilities and of transference numbers. The chapter moves on to a presentation of the Debye–Hückel treatment of the non-ideality of electrolyte solutions and concludes with a study of ionic equilibria.

### 12-2 Conductivity—Experimental Definitions and Procedures

#### A. Defining Equations

The various systems of electrical units were reviewed in Section 3-CN-2. It was noted there that international commissions have recommended the uniform adoption of the SI system of units, one of the main advantages being that the esu
and emu systems are merged into a single one. Experimental electrochemistry makes use of the volt (V), ampere (A), coulomb (C), and ohm (Ω)—all accepted in the SI recommendations.

As noted in Section 3-CN-2, the ampere is defined in terms of the magnetic field produced by current i flowing in a loop of wire. The coulomb is the quantity of electricity q corresponding to a current of 1 A flowing for 1 sec, or in general, \( q = \int i \, dt \). The unit of potential \( V \) is the volt; it requires 1 J (joule) of energy to transport 1 C of charge across 1 V potential difference. Resistance \( R \) is defined in terms of Ohm’s law,

\[
V = iR. \tag{12-1}
\]

A current of 1 A flowing through a resistance of one ohm produces a voltage drop of 1 V. The resistance \( R \) is, of course, a function of temperature and, in the case of electrolyte solutions, of concentration.

Ohm’s law can be thought of both as an ideal law and as the limiting law for small \( V \) and \( i \). It is well obeyed by all substances, provided the energy dissipated does not result in appreciable local heating. In the case of electrolyte solutions Ohm’s law begins to fail at high voltages because ionic velocities become large enough that the distortion of the diffuse ion atmosphere around each ion ceases to be proportional to its velocity. In the case of metals current is carried by electrons, and there is no problem in this last respect. The same is true for semiconductors, which differ from metals mainly in that the concentration of conduction electrons is small and increases exponentially with temperature so that the resistance is very temperature-dependent.

The resistance of a substance is proportional to its thickness \( l \) and inversely proportional to the cross-sectional area \( A \). One therefore generally reports a specific resistance or resistivity \( \rho \) defined by

\[
R = \frac{l}{\rho}. \tag{12-2}
\]

The resistivity \( \rho \) is given in ohm centimeter in the cgs system and in ohm meter in the SI system. Although resistance is the measured quantity, its reciprocal, the conductance, is more useful in dealing with electrolyte solutions. Conductance \( L \) is defined as

\[
L = \frac{1}{R}. \tag{12-3}
\]

and specific conductivity \( \kappa \) as

\[
\kappa = \frac{1}{\rho} = \frac{l}{A} \frac{1}{R}. \tag{12-4}
\]

As will be seen later, the ratio \( l/A \) is usually treated as an apparatus or cell constant and is given the symbol \( k \). Thus

\[
R = kp, \tag{12-5}
\]

\[
\kappa = kL. \tag{12-6}
\]

(A considerable range of symbols will be found for these quantities; the ones here are the SI ones, except that \( L \) rather than \( G \) is used to denote conductance.)

An electrolyte solution conducts electricity by several paths. Each ion contributes, including those from the self-ionization of the solvent. The situation is therefore
one of resistances in parallel so that the total resistance obeys the law

$$\frac{1}{R_{\text{obs}}} = \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \cdots.$$  

Conductances are thus additive, that is,

$$L_{\text{obs}} = L_1 + L_2 + L_3 + \cdots,$$  

(12-7)

hence their great utility in this situation. One is ordinarily interested just in the contribution to the observed conductance by the electrolyte and therefore subtracts out that due to the medium \(L_0\):

$$L = L_{\text{obs}} - L_0.$$  

(12-8)

The same relation will, of course, apply to specific conductivities:

$$\kappa = \kappa_{\text{obs}} - \kappa_0.$$  

(12-9)

One of the first quantitative observations was that the net specific conductivity of a solution is approximately proportional to the electrolyte concentration. It should be exactly so if each ion were a completely independent agent since each would then make its separate, additive contribution to \(\kappa\). A very useful quantity is therefore the equivalent conductivity, \(\Lambda\), which is the value of \(\kappa\) contributed by 1 equiv of ions of either charge. We consider a portion of the electrolyte solution which is 1 cm deep and of area such that the volume contains one mole of charge due to the ions of the electrolyte (with only the positive or only the negative ions being considered). The number of moles of such charge per liter will be designated by \(C^*\), the concentration in equivalents of ions per liter whenever we wish to emphasize the distinction between actual ion concentration and equivalents of electrolyte per liter, \(C\). The volume (in cubic centimeters) required to contain one mole of ions is \(1000/C^*\) and the area (in square centimeters) of the required portion of solution is then \(1000/C^*\). It follows from Eq. (12-6) that

$$\Lambda \ (= L \text{ for 1 equiv}) = \frac{\kappa}{\kappa_0} = \frac{\kappa}{C^*},$$  

or, since \(C^* = 1000/C\) and \(l = 1\),

$$\Lambda = \frac{1000}{C^*} \kappa.$$  

(12-10)

The above language is somewhat carefully phrased. We want \(\Lambda\) to be the conductivity ascribable to 1 equiv of actual ions. For a strong electrolyte, such as NaCl or Na\(_2\)SO\(_4\), \(C^* = M_{\text{NaCl}} = 2M_{\text{Na}_2\text{SO}_4}\), and so on, where \(M\) is the molarity. That is, \(C^*\) is the molarity multiplied by the number of positive ion charges (or the number of negative ion charges) per formula weight, and corresponds to the usual definition of equivalents per liter. In the case of a weak electrolyte, such as acetic acid, however, \(C^*\) should be the concentration of actual ions present per liter of solution; the concentration of undissociated acetic acid is not to be included. If the solute is not fully dissociated or if there is doubt on the matter, one may write

$$\Lambda_{\text{app}} = \frac{1000}{C} \kappa,$$  

(12-11)
where \( \Lambda_{\text{app}} \) is the apparent equivalent conductivity, obtained with \( C \), the formal concentration in equivalents per liter. “Formal” means the number of gram equivalent weights of the solute present.

In the SI system, Eqs. (12-10) and (12-11) do not contain the factor of 1000. Remember, however, that \( \kappa \) (SI) = 100\( \kappa \) (cgs) and that \( C \) and \( C^* \) are now in equivalents per cubic meter, so that \( \Lambda \) (SI) = \( 10^{-4} \Lambda \) (cgs). If \( C \) is in moles \( m^{-3} \), the SI designation for \( \Lambda \) is *molar conductivity*.

The various defining equations are summarized in Table 12-1.

### B. Measurement of Conductance

The actual quantity measured for an electrolyte solution is its electrical resistance \( R \). This is usually done by means of a Wheatstone bridge, the basic scheme of which is shown in Fig. 12-2. In its simplest form, the galvanometer \( G \) shows no current flow when \( R_x/R_1 = R_y/R_3 \). In practice, it is very important first of all that the electrodes of the cell used have identical electrode potentials; otherwise a voltage change across the cell will be present in addition to the voltage drop due to Ohm’s law. This requirement is usually met by the use of identical reversible electrodes, such as platinized platinum, and an alternating source of potential. This last avoids having any appreciable net electrolysis at the electrodes and hence buildup of electrolysis products. The use of the ac bridge introduces another problem, however, namely that due to the capacitance of the cell. There must now be a means for balancing out capacity differences across the two legs of the bridge, or otherwise the ac galvanometer (often an oscilloscope) will not register a point of zero current. The reader is referred to experimental texts for further details.

### TABLE 12-1. Definitions of Electrical Quantities

<table>
<thead>
<tr>
<th>Quantity</th>
<th>Symbol</th>
<th>Cgs</th>
<th>SI</th>
<th>Defining relationship(^a)</th>
<th>Equation number</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance</td>
<td>( R )</td>
<td>ohm</td>
<td>ohm</td>
<td>( V = iR )</td>
<td>(12-1)</td>
</tr>
<tr>
<td>Specific resistance</td>
<td>( \rho )</td>
<td>ohm cm</td>
<td>ohm m</td>
<td>( \rho = \frac{\sigma}{l} R )</td>
<td>(12-2)</td>
</tr>
<tr>
<td>Conductance</td>
<td>( L )</td>
<td>ohm(^{-1}) (or mho)</td>
<td>ohm(^{-1}) ohm</td>
<td>( L = \frac{1}{R} )</td>
<td>(12-3)</td>
</tr>
<tr>
<td>Specific conductivity</td>
<td>( \kappa )</td>
<td>ohm(^{-1}) cm(^{-1})</td>
<td>ohm(^{-1}) m(^{-1})</td>
<td>( \kappa = \frac{1}{\rho} = \frac{l}{\sigma R} )</td>
<td>(12-4)</td>
</tr>
<tr>
<td>Cell constant</td>
<td>( k )</td>
<td>cm(^{-2})</td>
<td>m(^{-1})</td>
<td>( k = \frac{l}{\sigma} )</td>
<td></td>
</tr>
<tr>
<td>Equivalent conductivity</td>
<td>( \Lambda )</td>
<td>cm(^2) equiv(^{-1}) ohm(^{-1})</td>
<td>m(^2) equiv(^{-1}) ohm(^{-1})</td>
<td>( \Lambda = \frac{1000}{C^* \kappa} )</td>
<td>(12-10)</td>
</tr>
</tbody>
</table>

\(^a\) Here \( V \) is the potential difference and \( i \) the current between electrodes of effective area \( \sigma \) and separation \( l \).

\(^b\) The SI unit of conductance is called the *siemens*, S, and has the dimensions A\(^2\) sec\(^{-3}\) kg\(^{-1}\) m\(^{-2}\).
The typical measurement, then, is of $R_x$, the resistance of the cell, first when filled with the solvent medium and then when filled with the electrolyte solution. Application of Eq. (12-8) then gives the net conductance $L$ due to the solute.

The second experimental problem is the reduction of $L$ to a specific conductivity $\kappa$. The defining equation (12-4) is not easily applied in practice since $l$ is not exactly the distance between the electrodes and $A$ is not exactly the area of the electrodes. The reason is that ions lying outside of the cylinder defined by the two electrodes still experience potential gradients and contribute to the conductivity. Extensive and careful studies have allowed for this contribution, with the result that accurate specific conductivities are known for several standard electrolyte solutions. One such standard is a solution containing 0.74526 g KCl per 1000 g of solution, whose specific conductivity at 25°C is 0.0014088 ohm$^{-1}$ cm$^{-1}$. [See Daniels et al. (1956) for further details.] Alternatively, the specific conductivities of 0.1 M and 0.01 M KCl are 0.012886 and 0.0014114 ohm$^{-1}$ cm$^{-1}$ at 25°C, respectively.

The availability of precise, absolute specific conductivities allows the problem of determining the $l$ and $A$ values for a cell to be by-passed. One measures the resistance of the cell when filled with a standard solution and calculates the cell constant $k$ by means of Eq. (12-5). The same cell constant applies to a measurement with any other solution (in very precise work, the standard and unknown solutions should have about the same resistance). One then uses $k$ to calculate $\rho$ or $\kappa$ from the measured resistance $R$ or conductance $L$.

Resistances can be measured with great precision, and conductance determinations can therefore be extended to very dilute solutions. At this point, however, one must take major precautions to rinse the cell clean of any impurities adsorbed on the wall or on the electrodes and to free the solvent of all traces of electrolytes. Kohlrausch and co-workers, for example, were able to obtain water virtually free of ionic impurities and found a residual specific conductivity of $6.0 \times 10^{-8}$ ohm$^{-1}$ cm$^{-1}$ at 25°C. As discussed in Section 12-4A this residual value is due to the $\sim 10^{-7}$ mole liter$^{-1}$ of H$^+$ and OH$^-$ ions from the dissociation of the water itself. This concentration then represents the upper limit of dilution possible with an aqueous electrolyte before its contribution to the conductivity of the solution is swamped by that of the solvent water.
12-3 Results of Conductance Measurements

The decades preceding and following 1900 were ones in which the conductance of aqueous salt solutions was studied in great detail. Most soluble mineral salts, such as NaCl or KNO₃, show a pattern of behavior which led Arrhenius to propose his theory of electrolytic dissociation, namely that salts are largely dissociated in aqueous solution and fully dissociated at extreme dilution. We agree with this interpretation today and call such substances strong electrolytes.

Other salts, and especially some acids and bases, behave quite differently from strong electrolytes. It is necessary to suppose that only a small degree of dissociation takes place; such substances are known as weak electrolytes. We take up these two categories of electrolytes in turn and then consider some of the more modern treatments of their behavior.

**FIG. 12-3.** (a) Specific conductivity is approximately proportional to C. (b) Equivalent conductivity for strong electrolytes decreases with increasing C and (c) is nearly linear in $\sqrt{C}$. (d) Equivalent conductivity decreases strongly with increasing C in the case of a weak electrolyte. All data are for 25°C.
TABLE 12-2. Some Equivalent Conductivities for Aqueous Electrolytes at 25°C\(^a\)

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>(\Lambda_0)(^b) (cm(^2) equiv(^{-1}) ohm(^{-1}))</th>
<th>Electrolyte</th>
<th>(\Lambda_0)(^b) (cm(^2) equiv(^{-1}) ohm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>426.16</td>
<td>CaCl(_2)</td>
<td>135.84</td>
</tr>
<tr>
<td>LiCl</td>
<td>115.03</td>
<td>Ca(NO(_3))(_2)</td>
<td>130.94</td>
</tr>
<tr>
<td>NaCl</td>
<td>126.45</td>
<td>BaCl(_2)</td>
<td>139.98</td>
</tr>
<tr>
<td>KCl</td>
<td>149.86</td>
<td>Na(_2)SO(_4)</td>
<td>129.9</td>
</tr>
<tr>
<td>NH(_4)Cl</td>
<td>149.7</td>
<td>Na(_2)C(_2)O(_4)</td>
<td>124</td>
</tr>
<tr>
<td>KBr</td>
<td>151.9</td>
<td>CuSO(_4)</td>
<td>133.6</td>
</tr>
<tr>
<td>NaNO(_3)</td>
<td>121.55</td>
<td>ZnSO(_4)</td>
<td>132.8</td>
</tr>
<tr>
<td>KNO(_3)</td>
<td>144.96</td>
<td>LaCl(_3)</td>
<td>145.8</td>
</tr>
<tr>
<td>AgNO(_3)</td>
<td>133.36</td>
<td>K(_4)Fe(CN)(_6)</td>
<td>184.5</td>
</tr>
<tr>
<td>NaOOCCH(_3)</td>
<td>91.0</td>
<td>NaOH</td>
<td>248.1</td>
</tr>
<tr>
<td>MgCl(_2)</td>
<td>129.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>


\(^b\) To convert to SI units, multiply by 10\(^4\); thus \(\Lambda_0(\text{HCl}) = 426.6 \times 10^{-4}\) m\(^2\) equiv\(^{-1}\) ohm\(^{-1}\).

### A. Strong Electrolytes

It is typical of a strong electrolyte solution that its specific conductivity is proportional to its concentration, to a first approximation. This behavior is illustrated in Fig. 12-3(a), and its observation led to the introduction of equivalent conductivity \(\Lambda\) as a useful quantity. According to Eq. (12-10), \(\kappa\) should be a linear function of concentration if \(\Lambda\) is an intrinsic property of the electrolyte, independent of its concentration. The linearity law is not exact, however; as shown in Fig. 12-3(b), \(\Lambda\) for typical strong electrolytes decreases noticeably with increasing concentration. It was found very early that the decrease was proportional to \(\sqrt{C}\); that is,

\[
\Lambda = \Lambda_0 - \Lambda \sqrt{C^*}, \tag{12-12}
\]

where, in the case of a strong electrolyte, we take \(C = C^*\). Figure 12-3(c) shows that Eq. (12-12) is well obeyed up to about 0.1 M uni-univalent electrolyte concentration. Deviations set in much earlier, however, with more highly charged ions.

As is discussed in more detail in the Commentary and Notes and Special Topics sections, Eq. (12-12) has been explained theoretically as a consequence of interionic attractions and repulsions, that is, as a result of long-range Coulomb forces between ions. The effect is, in a sense, an incidental one arising from the charge on ions rather than from more chemical properties. The most important specific characteristic of an electrolyte is therefore \(\Lambda_0\), its equivalent conductivity at infinite dilution, since in this limit interionic attraction effects have vanished. Table 12-2 summarizes some \(\Lambda_0\) values for common electrolytes.

One of the early observations that helped to establish the concept of a strong electrolyte was that their \(\Lambda\) values are approximately additive. By this is meant that, for example, \(\Lambda_{\text{KCl}}\) is due to independent contributions from K\(^+\) and Cl\(^-\) ions, and similarly for \(\Lambda_{\text{NaNO}_3}\) and \(\Lambda_{\text{KNO}_3}\). An example of additivity behavior would then be

\[
\Lambda_{\text{NaCl}} = \Lambda_{\text{KCl}} + \Lambda_{\text{NaNO}_3} - \Lambda_{\text{KNO}_3}. \tag{12-13}
\]
Values at 25°C are

\[ 0.1 \text{ M} \quad 106.74 = 128.96 + 98.7 - 120.40 - 107.26, \]
\[ \Lambda_0 \quad 126.45 = 149.86 + 121.55 - 144.96 - 126.45. \]

The first line of these data shows that the additivity rule holds to within a percent or so for 0.1 M solutions. Our interpretation of \( \Lambda_0 \) requires that the rule hold exactly at infinite dilution, and this expectation is confirmed by the second line.

The additivity rule allows the indirect calculation of \( \Lambda \) for an electrolyte. For example,

\[ \Lambda_{\text{AgCl}} = \Lambda_{\text{AgNO}_3} + \Lambda_{\text{KCl}} - \Lambda_{\text{KNO}_3} \]
\[ = 133.36 + 149.86 - 144.96 = 138.26. \]

This type of calculation is greatly simplified in Section 12-6 since it turns out that absolute values for the individual ion contributions to \( \Lambda_0 \) can be determined. One then obtains the value for an electrolyte by adding the separate ion values.

**B. Weak Electrolytes**

One of the early problems was that not all electrolytes behaved as illustrated in Fig. 12-3(a–c). Thus, unlike HCl and NaOH, acetic acid and aqueous ammonia give the results shown in Fig. 12-3(d). In this case, however, the behavior was explainable on the basis of a dissociation equilibrium. For a binary electrolyte AB whose formal concentration is \( C \) we write

\[ \text{AB} = \text{A}^+ + \text{B}^- , \]
\[ (1 - \alpha)C \quad \alpha C \quad \alpha C \]

where \( \alpha \) is the degree of dissociation. The equilibrium constant is

\[ K = \frac{(\alpha C)^2}{(1 - \alpha)C} = \frac{\alpha^2 C}{1 - \alpha} . \]  
(12-14)

Alternatively, the quotient of Eqs. (12-10) and (12-11) gives

\[ \frac{\Lambda_{\text{app}}}{\Lambda} = \frac{C^*}{C} = \alpha . \]  
(12-15)

The ratio \( C^*/C \) is that of the concentration of ions, \( \alpha C = C^* \), to the formal concentration \( C \), and hence is equal to \( \alpha \). Substitution of this result into Eq. (12-14) gives

\[ K = \frac{\Lambda_{\text{app}} C}{\Lambda (\Lambda - \Lambda_{\text{app}})} . \]  
(12-16)

If interionic attraction effects (see Section 12-3C) can be neglected, as is often true for weak electrolyte solutions if their actual ionic concentrations are low, then \( \Lambda \) is identified with \( \Lambda_0 \); Eqs. (12-15) and (12-16) then become

\[ \frac{\Lambda_{\text{app}}}{\Lambda_0} = \alpha \]  
(12-17)

and

\[ K = \frac{\Lambda_{\text{app}} C}{\Lambda_0 (\Lambda_0 - \Lambda_{\text{app}})} . \]  
(12-18)
Equation (12-18) is known as the *Ostwald dilution law*, after W. Ostwald, who proposed it. It allows a determination of the dissociation constant of a weak electrolyte from conductance data.

### C. General Treatment of Electrolytes

The great success of Eq. (12-18) in accounting for the behavior of weak electrolytes such as acetic acid led Ostwald, Arrhenius, and others to apply the same equation to salts such as KCl and to acids such as HCl. The results were confusing. Although the $K$ values computed on the basis of Eq. (12-18) were reasonably constant for a weak electrolyte, they would vary 10- or 20-fold when so computed for strong electrolytes over a range of concentration.

It was eventually realized that two different effects are present. The predominant one in the case of a weak electrolyte is that of its partial dissociation into ions. Superimposed on this, however, is the effect of interionic attraction, which causes the value of $\Lambda$ (as distinct from $\Lambda_{\text{app}}$) to vary with concentration. If the electrolyte is largely or fully dissociated, then the interionic attraction aspect becomes the dominant one. This is the situation with strong electrolytes.

Neither effect can be neglected for any electrolyte. In the case of a weak electrolyte the correct equation to use is Eq. (12-16), where $\Lambda$ must have the value corresponding to the actual ionic environment that is present. That is, the dissociation produces an ion concentration $C^*$, which in turn affects $\Lambda$ according to Eq. (12-12). The constant $A$ of this equation,

$$\Lambda = \Lambda_0 - A \sqrt{C^*} \quad \text{[Eq. (12-12)]},$$

has been evaluated theoretically (see Special Topics), and is given by

$$A = 0.2289 \Lambda_0 + 60.19. \quad (12-19)$$

Equation (12-19) is valid for aqueous univalent ions at 25°C at concentrations below about 0.1 $M$.

### 12-4 Some Sample Calculations

#### A. Calculation of Dissociation Constants

The first two examples are ones in which interionic attraction effects are neglected. That is, we assume that $\Lambda_0$ gives the equivalent conductivity of the ions. We obtain the data in Table 12-3.

<table>
<thead>
<tr>
<th>Solution</th>
<th>Measured resistance at 25°C (ohms)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent water</td>
<td>$1 \times 10^4$</td>
</tr>
<tr>
<td>0.1 $M$ KCl</td>
<td>24.96</td>
</tr>
<tr>
<td>0.01 $M$ acetic acid</td>
<td>1982</td>
</tr>
</tbody>
</table>


We wish to calculate the dissociation constant of acetic acid. It is first necessary to obtain the cell constant. The net conductance due to the KCl is

\[
\frac{1}{24.96} - \frac{1}{10^6} = 0.04006.
\]

The specific conductivity of 0.1 M KCl is known to be 0.012886 ohm\(^{-1}\) cm\(^{-1}\), and use of Eq. (12-6) gives the cell constant:

\[
k = \frac{\kappa}{L} = \frac{0.012886}{0.04006} = 0.3217 \text{ cm}\(^{-1}\).
\]

The net conductance of the acetic acid is

\[
L = \frac{1}{1982} - \frac{1}{10^6} = 5.035 \times 10^{-4},
\]

from which we find

\[
\kappa = (5.035 \times 10^{-4})(0.3217) = 1.620 \times 10^{-4}.
\]

The apparent equivalent conductivity is therefore

\[
\Lambda_{\text{app}} = \frac{1000}{0.01} \times 1.620 \times 10^{-4} = 16.20 \text{ cm}^2 \text{ equiv}^{-1} \text{ ohm}^{-1}.
\]

We may obtain \(\Lambda_0\) for the ions of acetic acid from the additivity rule, using the values 91.0, 426.2, and 126.5 for the \(\Lambda_0\) values of sodium acetate NaAc, HCl, and NaCl, respectively:

\[
\Lambda_{0,\text{HAc}} = \Lambda_{0,\text{NaAc}} + \Lambda_{0,\text{HCl}} - \Lambda_{0,\text{NaCl}} = 91.0 + 426.2 - 126.5 = 390.7.
\]

The degree of dissociation is then

\[
\alpha = \frac{16.20}{390.7} = 0.0415
\]

and the dissociation constant is

\[
K = \frac{(0.0415)^2(0.01)}{1 - 0.0415} = 1.797 \times 10^{-5}.
\]

The resistance of 1 \(\times 10^6\) quoted for the solvent water was deliberately picked as a somewhat low value. It corresponds to a specific conductivity of

\[
\kappa = (10^{-6})(0.3217) = 3.217 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}.
\]

The value for pure water was quoted in Section 12-2B as 6.0 \(\times 10^{-8}\) ohm\(^{-1}\) cm\(^{-1}\), and the difference, 2.62 \(\times 10^{-7}\), is therefore to be attributed to impurities. Taking NaCl as a typical impurity, we get the corresponding concentration from Eq. (12-10) using \(\Lambda_0 = 126\):

\[
C = \frac{1000}{\Lambda} \kappa = \frac{1000}{126} (2.62 \times 10^{-7}) = 2.08 \times 10^{-6} \text{ M}.
\]

This concentration of ionic impurity is not likely to affect the dissociation of the
0.01 M acetic acid, so the slightly impure water used is acceptable for the particular experiment.

A value of $6.0 \times 10^{-8} \text{ohm}^{-1} \text{cm}^{-1}$ for the specific conductivity of pure water at 25°C was obtained by Kohlrausch and co-workers in 1894; the measurement allows a calculation of the dissociation constant for water itself. We write

$$
\text{H}_2\text{O} = \text{H}^+ + \text{OH}^-,
$$

$$
K_w = (\text{H}^+)(\text{OH}^-).
$$

(12-20)

The concentration of water does not appear in $K_w$ since we take pure liquid water to be the standard state for water substance, and hence of unit activity. The limiting equivalent conductivity for the electrolyte $\text{H}^+$, $\text{OH}^-$ may again be calculated from the additivity rule:

$$
\Lambda_{\text{H}^+,\text{OH}^-} = \Lambda_{0, \text{HCl}} + \Lambda_{0, \text{NaOH}} - \Lambda_{0, \text{NaCl}}
$$

$$
= 426.16 + 248.1 - 126.45 = 547.81.
$$

Equation (12-10) then gives the concentration of ions present:

$$
C = \frac{1000}{547.81} (6.0 \times 10^{-8}) = 1.10 \times 10^{-7}.
$$

The value of $K_w$ at 25°C is therefore

$$
K_w = (1.10 \times 10^{-7})^2 = 1.20 \times 10^{-14}.
$$

It is very difficult to remove the last traces of ionic impurities from water and this value for $K_w$ is a little high; a better (modern) value is

$$
K_w = 1.01 \times 10^{-14}.
$$

(12-21)

B. Correction for the Interionic Attraction Effect

We can improve the preceding calculation of the dissociation constant for acetic acid if we correct for the error introduced by using $\Lambda_{0, \text{HAc}}$ rather than $\Lambda_{\text{H}^+, \text{Ac}^-}$ in determining it (we write $\Lambda_{\text{H}^+, \text{Ac}^-}$ as a reminder that this is the actual equivalent conductivity of the ions $\text{H}^+$ and $\text{Ac}^-$). The value of 0.0415 for $\alpha$ is now regarded as a first approximation, giving an ion concentration

$$
C^* = (0.0415)(0.01) = 4.15 \times 10^{-4} \text{ M}.
$$

The constant $A$ of Eq. (12-12) is as given by Eq. (12-19),

$$
A = (0.2289)(390.7) + 60.19 = 149.62.
$$

Equation (12-12) then gives

$$
\Lambda_{\text{H}^+, \text{Ac}^-} = 390.7 - (149.62)(4.15 \times 10^{-4})^{1/2} = 387.7.
$$

The second approximation to $\alpha$ is therefore

$$
\alpha = \frac{16.20}{387.7} = 0.0418.
$$
C. Calculation of Solubility Products

A useful application of conductivity measurements is to the calculation of the solubility of slightly soluble salts. Consider the following set of data: The resistance of a cell is 227,000 ohms when filled with water and is 21,370 ohms when filled with saturated calcium oxalate solution. The cell constant is 0.25 cm⁻¹.

We calculate first the net specific conductivity of the calcium oxalate. The specific conductivity of the water is, by Eq. (12-4), \( \frac{0.25}{227,000} = 1.10 \times 10^{-6} \) (the water is again somewhat impure), and that of the saturated solution is \( \frac{0.25}{21,370} = 1.170 \times 10^{-5} \). The net value is \( 1.060 \times 10^{-5} \) ohm⁻¹ cm⁻¹. The value of \( \Lambda_0 \) for \( \text{Ca}^{2+} \) and oxalate, \( \text{Ox}^{2-} \), ions is obtained through use of the additivity rule:

\[
\Lambda_{0, \text{Ca}^{2+}, \text{Ox}^{2-}} = \Lambda_{0, \text{Ca(NO}_3)_2} + \Lambda_{0, \text{Na}_2\text{Ox}} - \Lambda_{0, \text{NaNO}_3} = 130.94 + 124 - 121.55 = 133.
\]

An equivalent conductivity for a salt such as \( \text{Ca(NO}_3)_2 \) will often be written as \( \Lambda_{1, \text{Ca(NO}_3)_2} \) as a reminder that 1 equiv and not one mole of salt is present in the defining experiment for \( \Lambda \). We will take this point to be implicit in the writing of a \( \Lambda \) value, and will insert such fractions only when the reminder seems desirable.

The concentration of \( \text{Ca}^{2+} \) and \( \text{Ox}^{2-} \) ions is then

\[
C = \frac{1000}{133} 1.060 \times 10^{-5} = 7.97 \times 10^{-5} \text{ N}.
\]

The solubility product is, of course

\[
\text{CaOx(s)} = \text{Ca}^{2+} + \text{Ox}^{2-}, \quad K_{sp} = (\text{Ca}^{2+})(\text{Ox}^{2-}).
\]

The concentration of \( \text{CaOx(s)} \) does not appear in \( K_{sp} \) since solid calcium oxalate is in its standard state and hence has unit activity. The concentration is in equivalents per liter, so the molar concentration of ions in the saturated solution is \( 3.99 \times 10^{-5} \text{ M} \). The value of \( K_{sp} \) is therefore \( (3.99 \times 10^{-5})^2 = 1.59 \times 10^{-9} \text{ mole}^2 \text{ liter}^{-2} \).

12-5 Ionic Mobilities

The conductance of an electrolyte solution is understood to be due to the motion of ions through the solution as a result of the applied potential. Positive ions move toward the electrode which is negatively charged in solution, or the cathode, and negative ions move toward the electrode which is positively charged in solution, or the anode. The current due to each ion is given by the product of the velocity of
the ion and its charge. We consider first the quantitative aspect of this motion of ions under the influence of an applied potential, and then methods for measuring ion velocities.

A. Defining Equations

The motion of a particle in solution when subjected to some force \( f \) was discussed in Section 10-7A. To review the situation, we recall that a limiting velocity \( v \) is quickly reached such that

\[
v = \frac{f}{f'}.
\]

(12-23)

where \( f' \) is the friction coefficient. In the case of spherical particles, recall that a relationship due to Stokes gives \( f = 6\pi \eta r \), where \( \eta \) is the viscosity of the medium and \( r \) is the particle radius. It has become customary when dealing with ions to use the reciprocal of \( f \), called the mobility \( \omega \). Equation (12-23) thus becomes

\[
v = \omega f.
\]

(12-24)

We want now to consider the case of an ion in solution which experiences a force due to the imposed potential difference between the electrodes. The potential energy \( \phi \) of a charge \( q \) in a potential \( V \) is, by the definition of potential, just \( qV \) (and will be in joules if \( q \) is in coulombs and \( V \) in volts). The force acting on a particle of this charge is then \( \frac{d\phi}{dx} \) or \( qF \), where \( F \) is the field and is equal to \( \frac{dV}{dx} \). The force in dynes is then

\[
f = 10^7 F z e,
\]

(12-25)

where \( F \) is in volts per centimeter, \( z \) is the valence number of the ion, and \( e \) is the electronic charge in coulombs, \( e = 1.602 \times 10^{-19} \text{ C} \). If the charge is given in esu, Eq. (12-25) becomes

\[
f = F z \frac{e}{300}.
\]

(12-26)

The velocity of the \( i \)th ion is

\[
v_i = 10^7 F z_i \omega_i e
\]

(12-27)
or

\[
v_i = u_i F,
\]

(12-28)

where \( u_i \) is called the electrochemical mobility, usually expressed as (cm sec\(^{-1}\))/ (V cm\(^{-1}\)) or cm\(^2\) V\(^{-1}\) sec\(^{-1}\), and

\[
u_i = 10^7 z_i \omega_i e.
\]

(12-29)

We now want to determine the equivalent conductivity of this ion. According to the definition of equivalent conductivity, the electrodes are to be 1 cm apart and of area such that the enclosed volume contains 1 equiv. The conductance so measured is then the equivalent conductivity. In the present case the current carried will be

\[
i_i = v_i \mathcal{F},
\]

(12-30)
since Faraday's number gives the charge per equivalent. The potential difference is just \( F \), since the electrodes are 1 cm apart, and we find from Ohm's law

\[
\lambda_i = \frac{1}{R_i} = \frac{i_i}{F} = \frac{v_iF}{F} = u_iF
\]

or

\[
\lambda_i = u_iF. \quad (12-31)
\]

It is customary to use the lower case lambda, \( \lambda \), to designate the equivalent conductivity of an individual ion.

In the SI system, \( f \) is in newtons so that Eq. (12-25) becomes \( f = Fze \), and Eqs. (12-27) and (12-29) are correspondingly changed. The various conversion factors are: \( \eta (SI) = 0.1 \eta (cgs) \), \( \omega (SI) = 10^3 \omega (cgs) \), and \( \lambda (SI) = 10^{-4} \lambda (cgs) \).

The equivalent conductivity for an electrolyte is the sum of the contributions of the separate ions. Ordinarily only one kind of positive and one kind of negative ion are involved, so

\[
\Lambda = \lambda_+ + \lambda_-. \quad (12-32)
\]

Since \( \Lambda \) can be determined from conductance measurements, if \( \lambda_+ \) can be found by some independent means, then \( \lambda_- \) may be calculated, and vice versa. One way that this may be done is by measurement of the velocity \( u \) of an ion per unit field.

It should be emphasized that this velocity of an ion is not very large under ordinary potential gradients. The \( \Lambda \) values for electrolytes are around 100 cm\(^2\) equiv\(^{-1}\) ohm\(^{-1}\) (Table 12-2) and \( \lambda \) values for individual ions are about 50 cm\(^2\) equiv\(^{-1}\) ohm\(^{-1}\). A typical ion mobility is then 50/96,500 or about 5 \( \times \) 10\(^{-4}\) cm\(^2\) V\(^{-1}\) sec\(^{-1}\). The potential gradient is not apt to be more than perhaps 1 V cm\(^{-1}\) in experimental conductance measurements and so actual ion velocities would be less than 5 \( \times \) 10\(^{-4}\) cm sec\(^{-1}\). Such a velocity is far less than the kinetic energy velocity at room temperature, about 10\(^4\) cm sec\(^{-1}\), and the effect of the imposed electric field is evidently to give a very minor net bias to the random motion of ions in solution.

### B. Measurement of Ionic Mobilities

The rate of motion of a given kind of ion under an imposed electric field may be observed directly if a boundary is present between two kinds of electrolytes. The method, called the moving boundary method, is illustrated schematically in Fig. 12-4. A vertical tube is layered with a solution of MX' (sodium acetate in this example) on top of one of MX (sodium chloride), which in turn is on top of one of M'X (lithium chloride). The concentrations are such that the solutions decrease in density upward, so that convectional mixing will not occur. The applied potential is such as to cause positive and negative ions to move in the directions shown. The lower boundary is one between M'X and MX, and hence between two types of positive ions, while the upper boundary is between MX and MX', or between two types of negative ions. The positions of these boundaries can be measured optically (and would also be visible to the eye) because of the change in refractive index.

A further requirement is that the mobility of \( M \) be greater than that of \( M' \) and that the mobility of \( X \) be greater than that of \( X' \). In terms of the particular example, \( u_{Na^+} > u_{Li^+} \) and \( u_{Cl^-} > u_{Ac^-} \). If this condition is met, then \( M' \) cations will not
overtake the M cations but will lag behind slightly until enough extra potential drop occurs locally to bring them just up to the velocity of the M cations. The boundary between MX and M'X then remains sharp and its motion is determined by the velocity of the cations M. Similarly, the upper boundary remains sharp and its motion is determined by that of the anions X.

On application of a potential across the electrodes, after a time \( t \) the lower boundary has moved up a distance \( d_+ \) and the upper one down a distance \( d_- \). The velocities of the M and X ions are then proportional to \( d_+ \) and \( d_- \), respectively, and since the ions experience the same potential gradient, the velocities are in turn proportional to the respective mobilities, and, by Eq. (12-31), to the respective \( \lambda \) values. Thus

\[
\frac{\lambda_M}{\lambda_X} = \frac{d_+}{d_-}.
\]  

By Eq. (12-32),

\[
\Lambda_{MX} = \lambda_M + \lambda_X = \lambda_X \left( \frac{d_+}{d_-} + 1 \right)
\]

or

\[
\lambda_X = \Lambda_{MX} \left( \frac{d_-}{d_+ + d_-} \right),
\]

and

\[
\lambda_M = \Lambda_{MX} \left( \frac{d_+}{d_+ + d_-} \right). \tag{12-34}
\]

One can therefore determine \( \lambda_X \) and \( \lambda_M \) from the motions of the two boundaries if \( \Lambda_{MX} \) is known.

The restrictions on this type of procedure are somewhat severe, and act to limit the number of systems that can be studied. An alternative is to deal with just one boundary, say the one between MX and M'X. The motion of this boundary through distance \( d_+ \) sweeps out a volume \( d_+A \), where \( A \) is the cross-sectional area of the
tube. If the concentration of MX is \( C \) equivalents per liter, then the total quantity of electricity carried by the M cations is

\[
q_M = \frac{C_{MX}}{1000} (d_+ \mathcal{A}) \mathcal{F}.
\]  

(12-35)

Had the motion of the upper boundary been observed, then, similarly,

\[
q_X = \frac{C_{MX}}{1000} (d_- \mathcal{A}) \mathcal{F}.
\]  

(12-36)

It follows that

\[
\lambda_M = \lambda_{MX} \frac{q_M}{q_M + q_X} 
\]  

(12-37)

since \( q_M \) and \( q_X \) are proportional to \( d_+ \) and \( d_- \), respectively. However, \( q_M + q_X = q_{\text{tot}} = it \), where \( i \) is the current through the system and \( t \) is the elapsed time. Equation (12-37) can therefore be written

\[
\lambda_M = \lambda_{MX} \frac{(C_{MX}/1000)(d_+ \mathcal{A}) \mathcal{F}}{it} 
\]  

(12-38)

It is thus possible to determine the ratio \( \lambda_M/\lambda_{MX} \) from measurements of the motion of just one of the two boundaries. This ratio is known as the transference number for the ion M in salt MX (see Section 12-6).

### C. Experimental Results

Ionic mobilities may be determined by the preceding method or indirectly, through the measurement of transference numbers, discussed in the next section. Some representative values are given in Table 12-4, extrapolated to infinite dilution. As suggested in the numerical example of Section 12-5A, the values are of the order of \( 10^{-4} \) cm\(^2\) V\(^{-1}\) sec\(^{-1} \). We can use Eq. (12-29) to relate \( u \) to the absolute mobility \( \omega \) and if, further, we invoke Stokes' law so that \( \omega = 1/\rho = 1/6\pi\eta r \), then we find

\[
u_i = \frac{10^7 z_i e^2}{6\pi\eta r},
\]  

(12-39)

<table>
<thead>
<tr>
<th>Cation</th>
<th>Mobility ((\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \times 10^4))</th>
<th>Anion</th>
<th>Mobility ((\text{cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \times 10^4))</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(^+)</td>
<td>36.30</td>
<td>OH(^-)</td>
<td>20.50</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>4.01</td>
<td>F(^-)</td>
<td>5.70</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>5.19</td>
<td>Cl(^-)</td>
<td>7.91</td>
</tr>
<tr>
<td>K(^+)</td>
<td>7.62</td>
<td>Br(^-)</td>
<td>8.13</td>
</tr>
<tr>
<td>Rb(^+)</td>
<td>7.92</td>
<td>I(^-)</td>
<td>7.95</td>
</tr>
<tr>
<td>Ag(^+)</td>
<td>6.41</td>
<td>NO(_3^-)</td>
<td>7.40</td>
</tr>
<tr>
<td>Cs(^+)</td>
<td>7.96</td>
<td>CH(_3)COO(^-)</td>
<td>4.23</td>
</tr>
<tr>
<td>NH(_4^+)</td>
<td>7.60</td>
<td>CO(_3^2-)</td>
<td>7.46</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>6.16</td>
<td>SO(_4^{2-})</td>
<td>8.27</td>
</tr>
<tr>
<td>La(^{3+})</td>
<td>7.21</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
where \( e \) is in coulombs. Equation (12-39) predicts that \( u \) should vary inversely with solvent viscosity, a statement known as **Walden's rule**.

One may also calculate the apparent or hydrodynamic radius of an ion. As an example, the mobility of \( \text{Na}^+ \) ion is \( 5.19 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1} \), and the viscosity of water is 0.894 cP; hence at 25°C

\[
\begin{align*}
\rho_{\text{Na}^+} &= \frac{(1)(1.602 \times 10^{-19})(10^7)}{(6)(3.142)(0.00894)(5.19 \times 10^{-4})} \\
&= 1.83 \times 10^{-8} \text{ cm}.
\end{align*}
\]

The radius of the \( \text{Na}^+ \) ion in a crystal of NaCl is found to be 0.95 Å, so, to the extent that Stokes' law is accurate, it appears that \( \text{Na}^+ \) ion is larger in solution than its true size. The accepted explanation is that the ion strongly binds a sphere of water molecules around it, so that the size of the hydrodynamic unit is thereby increased. This interpretation is supported by the fact that the corresponding calculation for a large ion such as \( \text{N(CH}_3)_4^+ \) gives essentially the crystallographic radius. Tetramethylammonium ion is large and nonpolar so that its interaction with water molecules is not expected to be so strong as to bind them to it as a kinetic unit.

This example illustrates that quite reasonable ionic radii result from calculations based on mobility measurements, provided that ions are regarded as capable of binding water molecules so as to increase the size of the effective hydrodynamic unit. Table 12-4 shows that the order of increasing mobility is

\[
\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+.
\]

Since by Eq. (12-39) mobility should vary inversely with the ion radius, the series is just opposite to what might be expected in terms of the actual ion sizes—\( \text{Li}^+ \) should be the smallest and the most mobile of the series. The accepted explanation is that the binding of water molecules by a cation is strongly affected by the charge density at the surface of the ion and therefore varies along the series. The potential of a point charge \( q \) is \( q/r \) at a distance \( r \) (as discussed in Section 8-ST-1), and is consequently larger at the surface of a \( \text{Li}^+ \) ion than at the surface of a \( \text{Cs}^+ \) ion, to consider the extremes. Aqueous \( \text{Li}^+ \) ion probably carries about six water molecules with it, tightly held by the strong local field. The surface potential for \( \text{Cs}^+ \) is small enough that it appears to carry few if any water molecules with it. The mobility series for the alkali metal ions thus provides one of the strong evidences for the hydration of ions in solution.

Independent methods confirm that aqueous ions hold or coordinate solvent water molecules around them. In the case of divalent and trivalent ions the rate of exchange between coordinated and free water is slow enough to be followed as a chemical reaction. The coordination chemist thus regards an aqueous cation in much the same light as any other complex ion; the ion holds water more or less tightly in its coordination sphere, and this water must leave if some other group or ligand is to be coordinated in its place.

The case of the \( \text{H}^+ \) ion is a very interesting one. The simple ion, is, of course, just a proton, and its radius on this basis would be about \( 10^{-13} \text{ cm} \). We know that this is not the situation and that \( \text{H}^+ \) is coordinated to a water molecule, so that it is more appropriately written as \( \text{H}_2\text{O}^+ \). However, as discussed in Section 8-CN-2, liquid water is a very complex mixture of individual molecules and clusters of hydrogen-bonded molecules. These last were described as “flickering clusters” since they form, break up, and reform elsewhere very rapidly. It is therefore difficult to assign \( \text{H}^+ \) to any one single unit and the formulation \( \text{H}_2\text{O}^+ \) is used here
in the same way that \( \text{H}_2\text{O} \) is used to describe the molecular unit of liquid water.

The formula \( \text{H}_3\text{O}^+ \) is, however, the minimum size of the positively charged unit, and the observed mobility for \( H^+ \) ion is much too large to be explainable in terms of Eq. (12-39). It seems very likely that a variation of the Grotthus mechanism of Fig. 12-1 is operative in this case. As an illustration of the proposed mechanism, one of the clusters of Fig. 8-21 may be stretched out in linear form and imagined to carry an extra proton:

\[
\begin{array}{cccccccccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} \\
\end{array}
\]

The long spacings represent hydrogen bonds, and the short ones, regular bonds. The proton is shown as first assigned to the left-hand oxygen, but hydrogen bonds are mobile in that the hydrogen atom can easily jump from a \( \text{O}--\text{H} \) position to a \( \text{O}--\text{H}--\text{O} \) position. Such a shift down the chain then puts the extra proton on the right-hand oxygen. Thus in this case a unit of positive charge has moved four molecular distances without any appreciable molecular motion being required.

This process is not quite complete, however, since after the charge transfer each water molecule has, in effect, been rotated 180°. The following elementary steps illustrate the point:

\[
\begin{array}{cccccccccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} \\
\end{array}
\]

It may be that either the rotation time for a water molecule or the rate of formation and disruption of clusters determines the speed at which charge can move through the solution. M. Eigen, from his studies of very fast reactions in aqueous solutions, has been led to suggest that rather than being associated randomly with molecules and clusters, a special unit is the most stable one:

\[
\begin{array}{cccccccccccc}
\text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} & \text{H} \\
\text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} & \text{O} & \text{H} \\
\end{array}
\]

If so, the rate of reformation of \( \text{H}_3\text{O}^+ \) may be the slow step that determines the mobility of protons in water. The subject is as complicated as the structure of water itself.

The mobility of the \( \text{OH}^- \) ion is also unusually high, and mechanisms have been proposed that are similar to those for proton migration.

### D. Electrophoresis

A special case of the moving boundary method should be discussed briefly. It has been very highly developed for use in the study of proteins and other large
molecules and the process is now called *electrophoresis*. As an example, a boundary is formed between two buffer solutions, one of which contains protein. The boundary is observed to move on application of a potential between the electrodes and one thus obtains the rate of motion of the protein and, from the potential gradient, a value for its electrochemical mobility. The temperature is often set at about 4°C or at the point of maximum density of the solution. In this way convection currents due to temperature fluctuations are largely eliminated. Alternatively, a gel matrix may be used to eliminate convection. See Fig. 12-5 for some representative results.

Electrophoresis measurements serve to distinguish protein molecules qualitatively since each shows a characteristic rate of motion. If a mixture is initially present as a thin band, separation into several distinct zones will occur. The method may thus be used for the analysis of a protein or other mixture. On a more quantitative level the determination of the mobility \( u \) allows us to estimate the charge \( \zeta \) that is carried. If the size of the protein molecule is known, then Eq. (12-39) may be used for the calculation of \( z \). The more elegant approach is to determine the friction coefficient \( \gamma \) by means of sedimentation or diffusion measurements (see Section 10-7) and to write the more general expression

\[
\gamma = -uy^+.
\] (12-40)

The charge may then be computed without making any assumptions about molecular size or shape.

It should be noted that in the case of amino acids and proteins, the charge on a given molecule fluctuates with time as it adds or loses protons in rapid acid–base equilibria (note Section 12-CN-3). The electrophoretic velocity depends on the average charge, and is therefore very \( \rho H \)-dependent.

Electrophoretic measurements may be extended to particles large enough to be visible under a microscope, that is, to colloidal systems. For reasons that are not discussed until Section 21-ST-1, the equipment is now called a *zetameter*, but the method is essentially the same as that just described. One applies a known potential gradient and observes the slow motion of the colloidal particle along the gradient. We can then calculate the mobility from the rate of such motion and the field and use Eq. (12-39) to obtain the total charge on the particle.

---

**12-6 Transference Numbers—Ionic Equivalent Conductivities**

The direct measurement of ionic mobilities was discussed in the preceding section. An alternative approach is to determine directly the fraction of current carried by a particular ion, rather than its actual velocity.

**A. Defining Equations**

The *transference* (or *transport*) number of an ion in an electrolyte solution is defined as the fraction of the total current which that ion carries when a potential
Further separations are possible by electrophoresis first in one direction and then at right angles. Human serum proteins: ACG, β-L-A/C-globulin; ACh, α1-antichymotrypsin; AGP, acid-α1-glycoprotein; Alb, albumin; AT, α2-antitrypsin; HSGP, α2-HS-glycoprotein; GcG, Gc-globulin; Hp, haptoglobins; Hpx, hemopexin; IgA, immunoglobulin A; IgG, immunoglobulin G; MG, α2-macroglobulin; mHp, haptoglobin monomer; oAlb, albumin oligomere; oAT, α1-antitrypsin oligomere; Pa, prealbumin; Tf, transferrin. [From W. Giebel in “Electrophoresis and Isoelectric Focusing in Polyacrylamide Gel” (R. C. Allen and H. R. Maurer, eds.), De Gruyter, Berlin, 1974. See Giebel and Saechting (1973).]
gradient is applied. We can write Eq. (12-35) in the form

\[ i_i = \frac{C_i}{1000} v_i \Phi, \]  

(12-41)

where \( v_i = \frac{dd_i}{dt} \) and is the velocity of the \( i \)th ion. Since each velocity is proportional to the field, Eq. (12-41) reduces to the form

\[ i_i = k u_i C_i, \]  

(12-42)

where \( k \) is a proportionality constant common to all the ions present. The total current is then \( \sum_i i_i = \sum_i u_i C_i \), so the transference number of the \( i \)th ion is

\[ t_i = \frac{u_i C_i}{\sum u_i C_i}. \]  

(12-43)

Further, the mobility of an ion is proportional to its equivalent conductivity, by Eq. (12-31), so that

\[ t_i = \frac{\lambda_i C_i}{\sum \lambda_i C_i}. \]  

(12-44)

Equation (12-44) is a general one, valid for a mixture of electrolytes. If a single electrolyte is present, then \( C_+ = C_- \) and the special form for this case is therefore

\[ t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-} \]

or

\[ t_+ = \frac{\lambda_+}{A}, \quad t_- = \frac{\lambda_-}{A}. \]  

(12-45)

Some representative transference numbers are given in Table 12-5. Note that these vary with concentration. The reason is that \( \lambda_+ \) and \( \lambda_- \) vary differently with concentration.

### B. Transference Numbers by the Hittorf Method

The fraction of current carried by each ion of an electrolyte, and hence the transference numbers, may be determined directly with a special type of electrolysis cell. The procedure is known as the Hittorf method (introduced in 1853)

Table 12-5. Cation Transference Numbers in Aqueous Solutions at 25°C

<table>
<thead>
<tr>
<th>Concentration C</th>
<th>HCl</th>
<th>NaCl</th>
<th>KCl</th>
<th>Na₂SO₄</th>
<th>LaCl₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.8251</td>
<td>0.3918</td>
<td>0.4902</td>
<td>0.3848</td>
<td>0.4625</td>
</tr>
<tr>
<td>0.02</td>
<td>0.8266</td>
<td>0.3902</td>
<td>0.4901</td>
<td>0.3836</td>
<td>0.4576</td>
</tr>
<tr>
<td>0.05</td>
<td>0.8292</td>
<td>0.3876</td>
<td>0.4899</td>
<td>0.3829</td>
<td>0.4482</td>
</tr>
<tr>
<td>0.10</td>
<td>0.8314</td>
<td>0.3854</td>
<td>0.4898</td>
<td>0.3828</td>
<td>0.4375</td>
</tr>
<tr>
<td>0.20</td>
<td>0.8337</td>
<td>0.3821</td>
<td>0.4894</td>
<td>0.3828</td>
<td>0.4233</td>
</tr>
</tbody>
</table>

Hittorf cell is sketched in Fig. 12-6. The cell is constructed so that the three compartments may be isolated from each other and drained separately. The basis of the method is that the change in the amount of electrolyte in either end compartment depends both on the electrolysis reaction and on the number of ions that have migrated in or out in the process of carrying current.

The cell shown in the figure is filled with silver nitrate solution and has silver electrodes. The general situation is that since the mobilities of $\text{Ag}^+$ and $\text{NO}_3^-$ ions are about equal, each carries about half the current. Thus for each faraday of electricity put through the cell, $\frac{1}{2}$ equiv of $\text{Ag}^+$ ions will pass from left to right across the dividing line $I-II$ between cells $I$ and $II$ and $\frac{1}{2}$ equiv of $\text{NO}_3^-$ ions will pass across the line $I-II$ from right to left. Oxidation occurs at the anode, so that, per faraday, 1 equiv of $\text{Ag}^+$ ions is delivered into cell $I$ by the silver electrode. Between the gain by electrolysis and the loss by migration, there is a net gain of $\frac{1}{2}$ equiv of $\text{Ag}^+$ ions in cell $I$. Since the $\text{NO}_3^-$ ion is not involved in the electrode reaction, the gain of $\frac{1}{2}$ equiv by migration is net. Cell $I$ will thus show an overall gain of $\frac{1}{2}$ equiv of silver nitrate per faraday.

The details of the analysis of the Hittorf method are given in the Special Topics section. It is sufficient here to note that analysis of the changes in amounts present in the electrode compartments of a Hittorf cell allows the calculation of the fraction of current carried by each ion, and hence the determination of its transference number.

C. Ionic Equivalent Conductivities

There are two principal methods for obtaining ionic equivalent conductivities. The first is by direct measurement of the ionic mobility, as in the moving boundary experiment, and the second is through a determination of the cation or anion transference number for an electrolyte of known equivalent conductivity, as by means of the Hittorf method.

As in the case of the equivalent conductivity of an electrolyte, the usual quantity tabulated is the equivalent conductivity of the ion at infinite dilution. This value
12-7 Activities and Activity Coefficients of Electrolytes

A. Introductory Comments

An electrolyte, like any other solute, tends to give nonideal solutions, approaching Henry's law behavior at infinite dilution. We know that at high dilution the positive and negative ions act independently. The colligative property effects report, for example, the number of particles expected from the complete dissociation of the electrolyte. On the other hand, it is not possible to vary a single ion concentration, keeping everything else constant. An attempt to do so would immediately result in the solution acquiring an enormous electrostatic charge. An excess of even $10^{-10}$ mole liter$^{-1}$ of one kind of ion over another would result in a static charging of the solution to a potential of about $10^6$ V! In other words, we cannot prepare a solution containing only one kind of ion and therefore cannot determine individual ion activities or activity coefficients; we can only observe a mean value for the positive and negative ions present.

The situation is illuminated if we consider the case of a solubility product.

### TABLE 12-6. Equivalent Conductivities of Aqueous Ions at 25°C

<table>
<thead>
<tr>
<th>Cation</th>
<th>Equivalent conductivity$^b$ (cm$^2$ equiv$^{-1}$ ohm$^{-1}$)</th>
<th>Anion</th>
<th>Equivalent conductivity$^b$ (cm$^2$ equiv$^{-1}$ ohm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$^+$</td>
<td>349.7</td>
<td>OH$^-$</td>
<td>198</td>
</tr>
<tr>
<td>Li$^+$</td>
<td>38.7</td>
<td>F$^-$</td>
<td>55</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>50.1</td>
<td>Cl$^-$</td>
<td>76.3</td>
</tr>
<tr>
<td>K$^+$</td>
<td>73.5</td>
<td>Br$^-$</td>
<td>78.4</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>76.4</td>
<td>I$^-$</td>
<td>76.8</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>76.8</td>
<td>NO$_2^-$</td>
<td>71.44</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>61.9</td>
<td>HSO$_3^-$</td>
<td>50</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>73.7</td>
<td>SO$_4^{2-}$</td>
<td>72</td>
</tr>
<tr>
<td>Be$^{2+}$</td>
<td>45</td>
<td>HCO$_3^-$</td>
<td>44.5</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>53.06</td>
<td>CO$_3^{2-}$</td>
<td>72</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>59.50</td>
<td>SO$_4^{2-}$</td>
<td>79.8</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>63.7</td>
<td>HCOO$^-$</td>
<td>56</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>69.6</td>
<td>HC$_2$O$_4^-$</td>
<td>40.2</td>
</tr>
<tr>
<td>Co(NH$_3)_6^{3+}$</td>
<td>102</td>
<td>C$_2$O$_4^{2-}$</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CH$_3$COO$^-$</td>
<td>40.9</td>
</tr>
</tbody>
</table>


$^b$ To convert to SI units, multiply by $10^{-4}$. Thus $\lambda$(Na$^+$) = 50.1 cm$^2$ equiv$^{-1}$ ohm$^{-1}$ = $50.1 \times 10^{-4}$ m$^2$ equiv$^{-1}$ ohm$^{-1}$.
equilibrium. We write for a slightly soluble salt MX the solubility equilibrium

$$MX(s) = MX(\text{solution}) = M^+ + X^-.$$  \hspace{1cm} (12-46)

The thermodynamic criterion for equilibrium is satisfied if we write

$$\mu_{MX}(s) = \mu_{MX}(\text{solution})$$

as required by Eq. (9-44). We can introduce the activity of the electrolyte species:

$$\mu_{MX}(\text{solution}) = \mu_{MX}(\text{solution}) + RT \ln a_{MX}.$$  \hspace{1cm} (12-47)

The activity $a_{MX}$ corresponds to the solute activity $a_2$ in the equations of Chapter 10. It can be obtained, for example, by application of the Gibbs-Duhem integration procedure to solvent activities as determined from colligative property measurements. As with solutes generally, we use a Henry's law standard state, usually the one based on molality as a concentration unit (see Section 10-6).

The treatment up to this point is rather unsatisfactory, however. It does not tell us that the electrolyte is dissociated or how $a_{MX}$ is apt to be influenced by the presence of a common ion in the solution. Returning to the solubility equilibrium, the normal way of writing the equilibrium constant for process (12-46) is in terms of a solubility product:

$$K_{sp} = (M^+)(X^-).$$  \hspace{1cm} (12-48)

We know that the constant $K_{sp}$ is well-behaved in dilute solutions. For example, while we cannot avoid having essentially equal numbers of positive and negative ions present in any solution, we can, by using mixed electrolytes, vary the concentrations of specific kinds of ions, such as $M^+$ or $X^-$, independently. If $S$ denotes the solubility of $MX(s)$, then in pure water we have

$$K_{sp} = S^2.$$  \hspace{1cm} (12-49)

If added $X^-$ ion is present, as in the form of a concentration $C$ of NaX, then Eq. (12-48) becomes

$$K_{sp} = (S)(S + C).$$  \hspace{1cm} (12-50)

We now have the common ion effect whereby added $X^-$ ion depresses the solubility of $MX(s)$. Since the solution is still in equilibrium with the solid, $a_{MX}$ must not have changed, even though the individual values of $(M^+)$ and $(X^-)$ are now quite different from before. Thus observation tells us that in dilute solution

$$a_{MX} = (M^+)(X^-).$$  \hspace{1cm} (12-51)

Use of Eq. (12-51) allows a more realistic treatment of colligative effects in dilute solution. The Gibbs-Duhem integration gives $\ln a_{MX}$, and for a single electrolyte solute MX, $(M^+) = (X^-) = m$. We then have $\ln a_{MX} = m^2 = 2 \ln m$, and the experimentally observed factor of 2 has now appeared.

Consider, for example, the osmotic pressure effect. The basic equation is

$$-\ln a_i = \frac{V_i}{RT} IT \quad [\text{Eq. (10-20)}]$$
and this is to be used with the Gibbs–Duhem relation

\[ x_1 \, d(\ln a_1) + x_2 \, d(\ln a_2) = 0 \quad \text{[Eq. (9-79)]}, \]

where \( x_1 \) and \( x_2 \) must denote the mole fraction of components 1 (solvent) and 2 (salt MX). It is simpler for the present illustration to use mole fraction rather than molality for the salt concentration, and so we write \( a_{\text{MX}} = (x_{\text{MX}}^+) (x_{\text{MX}}^-) = x_2^2 \) (rather than \( a_{\text{MX}} = m^2 \)). This amounts to using the first of the Henry’s law conventions of Section 10-6. Since \( d(\ln a_{\text{MX}}) = 2 \, d(\ln x_2) \), combination of Eqs. (10-20) and (9-79) gives

\[ 2x_2 \, d(\ln x_2) = -x_1 \, d(\ln a_1) = \frac{V_1}{RT} \, x_1 \, d\Pi \]

or

\[ \frac{V_1}{RT} \, \Pi = 2 \int_0^{x_2} \frac{x_2}{x_1} \, d(\ln x_2) = 2 \int_0^{x_2} \frac{dx_2}{x_1} . \]

The integral of \( dx_2/x_1 \) is \(-\ln(1 - x_2)\) and since the solution is to be dilute, this becomes just \( x_2 \). The final result is

\[ \frac{V_1}{RT} \, \Pi = 2x_2 . \]

Thus the osmotic pressure is predicted to be twice the value expected just from the mole fraction of the salt, or the van’t Hoff factor comes out equal to 2, as observed.

### B. Defining Equations for Activity and Activity Coefficient

The preceding analysis was presented to show that the activity of an electrolyte is equal to the product of the ion concentrations in very dilute solutions. For the more general case of a nonideal solution we therefore write

\[ a_2 = a_+ a_- , \]

(12-54)

where \( a_2 \) denotes the electrolyte activity and \( a_+ \) and \( a_- \) the individual ion activities, which become equal to \( m_+ \) and \( m_- \), respectively, in the limit of infinite dilution. We then further define the activity coefficients \( \gamma_+ \) and \( \gamma_- \):

\[ a_+ = \gamma_+ m_+ \quad \text{and} \quad a_- = \gamma_- m_- . \]

(12-55)

Since \( a_2 \) involves the square of a concentration, it is convenient to define a new activity \( a_\pm \) as the square root of \( a_2 \):

\[ a_2 = a_\pm^2 . \]

(12-56)

The activity \( a_\pm \) is known as the mean activity. Similarly, \( \gamma_\pm \) is called the mean activity coefficient:

\[ \gamma_\pm^2 = \gamma_+ \gamma_- , \]

(12-57)

and \( m_\pm \) the mean molality:

\[ m_\pm^2 = m_+ m_- . \]

(12-58)
Then
\[ a_\pm = \gamma_\pm m_\pm. \] (12-59)

This set of definitions is for the specific case of a 1–1 electrolyte, that is, for an electrolyte which produces 1 mole of ions of each kind per formula weight. The general treatment is suggested by consideration of the solubility product for a salt \( M_vX_{v^-} \):

\[ M_vX_{v^-} = \nu_+ M^{v+} + \nu_- X^{v^-} , \quad K_{SP} = (M^{v+})^{\nu_+} (X^{v^-})^{\nu_-} , \] (12-60)

where \( z_+ \) and \( z_- \) are the respective ion charges and \( \nu_+ \) and \( \nu_- \) are the numbers of ions of each type. Electroneutrality requires that

\[ \nu_+ z_+ = \nu_- z_- . \] (12-61)

We want to define the activity of this general electrolyte in terms of individual ion activities such that in the limit of infinite dilution we obtain the expression on the right-hand side of Eq. (12-60). The definitions are then

\[ a_\pm = a_\pm^0 a_\pm^- , \] (12-62)

\[ a_\pm = a_\pm^0 a_\pm^- , \quad \text{where} \quad \nu = \nu_+ + \nu_- , \] (12-63)

\[ a_+ = \gamma_+ m_+ , \quad a_- = \gamma_- m_- \quad [\text{Eq. (12-55)}] , \]

\[ \gamma_\pm = \gamma_\pm^0 \gamma_\pm^- , \] (12-64)

\[ m_\pm = m_\pm^0 m_\pm^- , \] (12-65)

and, as before,

\[ a_\pm = \gamma_\pm m_\pm \quad [\text{Eq. (12-59)}] . \]

The complications introduced by these definitions are regrettable. They develop naturally, however, when we deal with nonideal electrolyte solutions.

**C. Activity Coefficients from Solubility Measurements**

The preceding material allows us to write the thermodynamic equilibrium constant for the solubility equilibrium of an electrolyte. Thus for AgCl we have

\[ \text{AgCl}(s) = \text{Ag}^+ + \text{Cl}^- , \] (12-66)

\[ K_{th} = a_{\text{Ag}^+} a_{\text{Cl}^-} = (\text{Ag}^+) (\text{Cl}^-) \gamma_{\text{Ag}^+} \gamma_{\text{Cl}^-} , \] (12-67)

or

\[ K_{th} = K_{SP} \gamma_\pm^0 \] (12-68)

where \( K_{th} \) is the thermodynamic solubility product and \( K_{SP} \) is the usual form in which concentrations are used. The solubility of AgCl in water is about \( 10^{-5} \, m \) and it seems likely that \( \gamma_\pm \) will be unity for so low a concentration. We can investigate the situation by adding some neutral or noncommon-ion electrolyte. We find experimentally that on doing so the solubility of AgCl increases, and hence
so does its \( K_{sp} \) value. Evidently \( \gamma_{\pm} \) is varying with the concentration of added neutral electrolyte, since \( K_{th} \) must remain a constant.

A useful way of graphing such data follows if we write Eq. (12-68) in the form

\[
\log K_{sp} = \log K_{th} - 2 \log \gamma_{\pm}.
\]  

(12-69)

We then plot \( \log K_{sp} \) against some function of concentration. Figure 12-7 gives the results of measurements that show the effect of added KNO\(_3\) and MgSO\(_4\) on the solubility and hence the \( K_{sp} \) for AgCl. As with equivalent conductivity, the experimental observation is that a plot is nearly linear if the square root of the added electrolyte concentration is used. The theoretical explanation is given in the next section, as is the definition of ionic strength, \( I \).

Since we are using the Henry's law convention for activities and activity coefficients, \( \gamma_{\pm} \) approaches unity at infinite dilution. The intercept of Fig. 12-7 therefore gives \( \log K_{th} = -9.790 \), or \( K_{th} = 1.62 \times 10^{-10} \). We may then calculate \( \gamma_{\pm} \) for the ions Ag\(^+\) and Cl\(^-\) in the presence of added KNO\(_3\) by inserting \( K_{th} \) and the measured \( K_{sp} \) into Eq. (12-69). Thus \( K_{sp} = -9.645 \) at \( \sqrt{m} = 0.175 \) or \( m = 0.0306 \); then \( \log \gamma_{\pm} = [(−9.790) - (−9.645)]/2 = −0.0725 \), whence \( \gamma_{\pm} = 0.846 \). The data allow a tabulation of \( \gamma_{\pm} \) versus concentration of added KNO\(_3\) (strictly speaking, \( m \) includes the contribution of the dissolved AgCl to the total salt concentration).

D. The Ionic Strength Principle

Studies such as the preceding were carried out for a number of systems, especially by V. LaMer and co-workers, and these confirmed an earlier observation by G. Lewis that the activity coefficient of an electrolyte depends mainly on the total concentration of ions and only secondarily on their specific chemical natures. Thus for concentrations below about 0.05 \( m \), the data of Fig. 12-7 would be essentially the same if NaNO\(_3\), KClO\(_4\), and so on were used instead of KNO\(_3\). The

![Diagram](image-url)  

**FIG. 12-7.** Variation of \( K_{sp} \) for AgCl at 25°C with increasing KNO\(_3\) concentration (plotted as \( \sqrt{m} \)) and increasing MgSO\(_4\) concentration (circles, plotted as \( \sqrt{T} \)).
results, incidentally, would also have been the same if NaCl were the added electrolyte. Although there is now a common-ion effect, depressing the solubility of the AgCl, the experimental $K_{sp}$ values will still show the same variation with concentration of total electrolyte present.

Empirical observation showed, however, that if other than uni-univalent salts were used, there was an increased effect on activity coefficients. It was found that all types of electrolytes can be put on a common basis by expression of the ionic concentration in terms of a quantity called the ionic strength $I$, where

$$I = \frac{1}{2} \sum_i m_i z_i^2.$$  \hspace{1cm} (12-70)

In the case of a uni-univalent electrolyte, $I = m$, but for, say $K_2SO_4$, $I = \frac{1}{2}(2m + 4m) = 3m$, while for MgSO$_4$, $I = \frac{1}{2}(4m + 4m) = 4m$. The increase in solubility of a salt in the presence of any electrolyte is nearly the same if the results are plotted in terms of $I$ rather than $m$. The circles in Fig. 12-7 are the points obtained with MgSO$_4$ as the neutral salt and with the abscissa reading $\sqrt{I}$ rather than $\sqrt{m}$.

The discovery of the ionic strength principle was a major step toward the understanding of nonideality effects in dilute electrolyte solutions. The principle constituted strong evidence that it was the charges on ions and not their particular chemical natures that determined activity coefficients. It paved the way for the development of the interionic attraction theory (described in Section 12-8).

### E. Methods of Determining Activity Coefficients

The change in solubility of a salt with ionic strength provides one means for determination of the activity coefficient of the salt in the presence of some other electrolyte. The method is not applicable to soluble salts, and, moreover, necessarily gives activity coefficients in mixed electrolyte solutions. The activity coefficient of an electrolyte in solutions containing no other ionic species is of more general importance.

As indicated in Section 12-7A, $a_x$, the solute activity, may be obtained from colligative property measurements through use of the Gibbs–Duhem equation. Equation (12–52) would be written with $d(\ln a_x)$ rather than $d(\ln x_3)$, and then

**TABLE 12-7. Dissociation Constant of Acetic Acid at 25°C**

<table>
<thead>
<tr>
<th>$C \times 10^3$ (M)</th>
<th>$aC \times 10^4$</th>
<th>$K \times 10^6$ (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.028014</td>
<td>0.151</td>
<td>1.768</td>
</tr>
<tr>
<td>0.2184</td>
<td>0.540</td>
<td>1.781</td>
</tr>
<tr>
<td>2.4140</td>
<td>2.00</td>
<td>1.809</td>
</tr>
<tr>
<td>9.8421</td>
<td>4.12</td>
<td>1.834</td>
</tr>
<tr>
<td>20.000</td>
<td>5.96</td>
<td>1.840</td>
</tr>
<tr>
<td>50.000</td>
<td>9.50</td>
<td>1.849</td>
</tr>
</tbody>
</table>

manipulated into the form of Eq. (9-80). The detailed procedures for simplifying
the handling of this integration may be found in more specialized texts [for example,
Lewis and Randall (1961)]. Much of our activity coefficient data comes from
measurements of the emf of electrochemical cells. This approach is discussed
in detail in Chapter 13 and will not be reviewed here.

Activity coefficients may also be obtained from a study of ionic equilibrium. As
a specific example, Table 12-7 gives the concentration equilibrium constant for
the dissociation of acetic acid as determined from conductivity measurements at
various concentrations. The concentration equilibrium constant is

\[ HAc = H^+ + Ac^- \]

\[ K = \frac{\alpha^2 C}{1 - \alpha} \]  

(12-71)

and \( \alpha \) in the table has been corrected for the ion atmosphere effect on \( \mathcal{I} \), as described
in Section 12-3C. The residual variation in \( K \) is attributed to nonideality, and
Eq. (12-71) is written

\[ K_{th} = K \frac{\gamma_{H^+} \gamma_{Ac^-}}{\gamma_{HAc}} = KK_v \]  

(12-72)

The solutions are dilute enough that, as a nonelectrolyte, HAc is probably in the
Henry's law region of behavior, so \( \gamma_{HAc} = 1 \). Therefore \( K_v = \gamma_{\pm} \), and Eq. (12-72)
may be plotted according to the form

\[ \log K = \log K_{th} - 2 \log \gamma_{\pm} \]  

(12-73)

The ionic strength derives entirely from the \( H^+ \) and \( Ac^- \) ions, whose concentra-
tion is \( \alpha C \), and the plot of \( \log K \) versus \( (\alpha C)^{1/2} \) is shown in Fig. 12-8. Extrap-
olation to zero \( \alpha C \) gives \( \log(10^6 K_{th}) = 0.2440 \), or \( K_{th} = 1.754 \times 10^{-5} \). Insertion
of this value into Eq. (12-72) allows \( K_v \), and hence \( \gamma_{\pm} \), to be calculated for each
concentration. Thus for 0.050 \( m \) HAc, \( \gamma_{\pm} = 1.754 \times 10^{-8}/1.849 \times 10^{-5} = 0.949 \),
or \( \gamma_{\pm} = 0.97 \).

The same approach would be used in the case of an equilibrium not involving
ionic species. Thus for the esterification reaction in aqueous solution,

\[
\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} = \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O},
\]

one again writes

\[
K_{th} = \frac{(\text{CH}_3\text{COOC}_2\text{H}_5)(\text{H}_2\text{O})\gamma_{\text{CH}_3\text{COOC}_2\text{H}_5}\gamma_{\text{H}_2\text{O}}}{(\text{CH}_3\text{COOH})(\text{C}_2\text{H}_5\text{OH})\gamma_{\text{CH}_3\text{COOH}}\gamma_{\text{C}_2\text{H}_5\text{OH}}} = KK_y
\]

and extrapolates the measured values of \(K\) to infinite dilution. Pure water is taken to be in its standard state so that \(\gamma_{\text{H}_2\text{O}}\) approaches unity at infinite dilution of the other species, and the extrapolated value of \(K\) is then equal to \(K_{th}\). We are primarily concerned with rather dilute solutions in this chapter, and activity coefficients for nonionic species are close to unity. It is only in the case of ions that the long-range Coulomb interactions lead to nonideal behavior even in quite dilute solutions (\(C < 0.1m\)).

**F. Activity Coefficients of Electrolytes**

As noted earlier, a number of methods may be used for the determination of the activity coefficient of an electrolyte. The results have been collected and tables of standard activity coefficients are available. A selection of such results is given in Table 12-8 and the mean activity coefficients of some typical electrolytes are plotted against concentration in Fig. 12-9.

The points to notice are the following. First, of course, even 0.1 \(m\) solutions can be drastically nonideal in their behavior. Second, electrolytes of a given charge type tend to show similar variations of \(\gamma_{\pm}\) with concentration at first but deviate from each other at higher concentrations. Third, the higher the product \(z_+ z_-\), the earlier the deviations from ideality set in. The differences within a given family

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>0.001 (m)</th>
<th>0.005 (m)</th>
<th>0.01 (m)</th>
<th>0.05 (m)</th>
<th>0.1 (m)</th>
<th>0.5 (m)</th>
<th>1.0 (m)</th>
<th>2.0 (m)</th>
<th>4.0 (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>0.965</td>
<td>0.928</td>
<td>0.904</td>
<td>0.830</td>
<td>0.796</td>
<td>0.757</td>
<td>0.809</td>
<td>1.009</td>
<td>1.762</td>
</tr>
<tr>
<td>NaCl</td>
<td>0.966</td>
<td>0.929</td>
<td>0.904</td>
<td>0.823</td>
<td>0.778</td>
<td>0.682</td>
<td>0.658</td>
<td>0.671</td>
<td>—</td>
</tr>
<tr>
<td>KCl</td>
<td>0.965</td>
<td>0.927</td>
<td>0.901</td>
<td>0.815</td>
<td>0.769</td>
<td>0.650</td>
<td>0.605</td>
<td>0.575</td>
<td>0.582</td>
</tr>
<tr>
<td>HNO₃</td>
<td>0.965</td>
<td>0.927</td>
<td>0.902</td>
<td>0.823</td>
<td>0.785</td>
<td>0.715</td>
<td>0.720</td>
<td>0.783</td>
<td>0.982</td>
</tr>
<tr>
<td>KNO₃</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.733</td>
<td>0.542</td>
<td>0.548</td>
<td>0.481</td>
<td>—</td>
</tr>
<tr>
<td>AgNO₃</td>
<td>—</td>
<td>0.92</td>
<td>0.90</td>
<td>0.79</td>
<td>0.72</td>
<td>0.51</td>
<td>0.40</td>
<td>0.28</td>
<td>—</td>
</tr>
<tr>
<td>NaOH</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.82</td>
<td>—</td>
<td>0.69</td>
<td>0.68</td>
<td>0.70</td>
<td>0.89</td>
</tr>
<tr>
<td>H₂SO₄</td>
<td>0.830</td>
<td>0.639</td>
<td>0.544</td>
<td>0.340</td>
<td>0.265</td>
<td>0.154</td>
<td>0.130</td>
<td>0.124</td>
<td>0.171</td>
</tr>
<tr>
<td>K₂SO₄</td>
<td>0.89</td>
<td>0.78</td>
<td>0.71</td>
<td>0.52</td>
<td>0.43</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>BaCl₂</td>
<td>0.88</td>
<td>0.77</td>
<td>0.72</td>
<td>0.56</td>
<td>0.49</td>
<td>0.39</td>
<td>0.39</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>CuSO₄</td>
<td>0.74</td>
<td>0.53</td>
<td>0.41</td>
<td>0.21</td>
<td>0.16</td>
<td>0.068</td>
<td>0.047</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>K₄Fe(CN)₆</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.19</td>
<td>0.14</td>
<td>0.067</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

of the same $z_+z_-$ product appear to be due to several causes. Extensive hydration of the ions ties up the solvent water and makes the true mole fraction higher than the apparent one; a similar explanation was offered for the behavior of aqueous sucrose solutions (note Table 10-3). This may be a major reason for the rather high activity coefficients of electrolytes such as HCl in concentrated solutions. A second factor is that many electrolytes are not fully dissociated. Although a chemical bond is not ordinarily expected to form in the case of electrolytes involving a rare gas type of ion such as $K^+$, ions may associate strongly as an ion pair. Salts such as $CuSO_4$, however, may actually form a coordinate bond in their association. Acids such as $H_2SO_4$ are relatively weak, and are not fully dissociated except in dilute solution. If association occurs for any of these reasons, the result is generally to lower the activity coefficient of the electrolyte.

A less chemically specific effect is that the actual size of the ion becomes important in concentrated solutions. The result is an increase in activity coefficient over what it would otherwise be.

These various explanations are important in the sense that they provide some rationale for an otherwise bewildering variety of behavior. They are discussed in somewhat more detail in the Commentary and Notes section. On the other hand, an activity coefficient is a \textit{phenomenological} quantity; when multiplied by the mean molality, it gives the mean activity of the electrolyte and therefore its chemical potential, regardless of explanation.

### 12-8 The Debye–Hückel Theory

Repeated remarks have been made throughout this chapter about the effect of the long-range Coulomb interactions between ions on both their transport behavior or mobilities and their activity coefficients. The theoretical approach to the former effect is mentioned further in the Special Topics section. The same interactions that affect ion mobilities also affect their activity coefficients, and the treatment of this second effect is important enough to cover here.
The theory of Debye and Hückel (1923) constituted a major breakthrough. Earlier observations, especially by G. Lewis, had shown that the activity coefficients of electrolytes were, in dilute solutions, determined more by ionic strength than by any specific chemical property. The implication that nonideality effects are due mainly to long-range Coulomb interactions between ions was accepted, but the problem of treating a collection of ions seemed insurmountable. The normal statistical mechanical approach would require one somehow to list the energy states of each ion while recognizing that its energy was affected by the location of all other ions.

The path that Debye and Hückel found was through the assumption that there exists some average potential around each ion and that each potential field is independent, that is, one does not perturb another. Further assumptions were that the electrolyte is completely dissociated and, at first, that the ions are of negligible size. It was also assumed that electrical interactions are solely responsible for deviations from nonideality. The treatment is therefore limited to rather dilute solutions.

We proceed as follows, taking for simplicity the electrolyte to be of the uni-univalent type. It is assumed that there is some average potential $\psi$ which is a function of distance $r$ from any particular ion. The potential energy of an ion in this potential is $e\psi$, where $e$ is the electronic charge. Since we are dealing with Coulomb’s law, $\psi$ will be in esu units and likewise $e$. The probability of finding a positive ion in a region of potential $\psi$ around a particular ion of like charge is given by the Boltzmann principle:

$$n_+ = n e^{-e\psi/kT}, \quad (12-74)$$

where $n$ is the average concentration in molecules per cubic centimeter. Similarly

$$n_- = n e^{e\psi/kT}. \quad (12-75)$$

The net charge density $\rho$ is then

$$\rho = (n_+ - n_-)e = ne(e^{-e\psi/kT} - e^{e\psi/kT}). \quad (12-76)$$

The next major assumption, without which further progress would have stopped, was that a theorem from electrostatics, known as the Poisson equation, could be used. This states that the rate of change or the divergence of the gradient of the electrostatic potential at a given point is proportional to the charge density at that point. The equation is valid for a continuous medium of uniform dielectric constant $D$ and the equation for spherical coordinates is

$$\nabla^2 \psi = \frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = -\frac{4\pi \rho}{D}. \quad (12-77)$$

This implies that the random motion of ions gives a smeared-out charge density to which Eq. (12-77) can be applied.

We now combine Eqs. (12-76) and (12-77) to obtain what has come to be known as the Poisson–Boltzmann equation:

$$\nabla^2 \psi = -\frac{4\pi n e}{D} (e^{-e\psi/kT} - e^{e\psi/kT}). \quad (12-78)$$

The assumptions implicit up to this point (such as the independence of the potential
fields around each ion) require that the effect not be a large one, that is, that $e\psi/kT$ be a small number. We therefore proceed to expand the exponentials, keeping only the first term, to obtain

$$\nabla^2 \psi = \left( \frac{8\pi ne^2}{DkT} \right) \psi.$$  \hspace{1cm} (12-79)

The collection of quantities multiplying $\psi$ on the right-hand side of Eq. (12-79) is assembled into a single parameter $\kappa$, defined as

$$\kappa^2 = \frac{4\pi e^2}{DkT} \sum_i z_i^2 n_i.$$  \hspace{1cm} (12-80)

Equation (12-80) applies to the general case of a collection of ions of charges $z_i$ and reduces to $\kappa^2 = 8\pi ne^2/DkT$ for a uni-univalent electrolyte. Equation (12-79) then becomes

$$\nabla^2 \psi = \kappa^2 \psi.$$  \hspace{1cm} (12-81)

The solution to Eq. (12-81) is

$$\psi(r) = \frac{ze}{Dr} e^{-kr}. \hspace{1cm} (12-82)$$

This may be verified by insertion of the expression for $\psi(r)$ back into Eq. (12-81). Thus

$$\frac{d\psi}{dr} = -\frac{ze}{Dr^2} e^{-kr} - \frac{ze}{Dr} e^{-kr},$$

$$r^2 \frac{d\psi}{dr} = -\frac{ze}{D} e^{-kr} - \frac{ze}{D} e^{-kr},$$

$$\frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = \frac{ze}{D} e^{-kr} - \frac{ze}{D} e^{-kr} + \frac{ze}{D} e^{-kr},$$

$$= \frac{ze}{D} e^{-kr},$$

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\psi}{dr} \right) = \frac{ze}{D} e^{-kr} = \kappa^2 \psi \hspace{1cm} \text{Q.E.D.}$$

We again expand the exponential, keeping only the first terms, to get

$$\psi(r) = \frac{ze}{Dr} - \frac{ze}{D} \kappa. \hspace{1cm} (12-83)$$

The first term on the right is just the potential due to the charge on the ion itself, and we are interested only in the second term, $-ze\kappa/D$, which gives the alteration in the potential due to the distribution of other ions around the given ion. Notice that this second term corresponds to the potential of a charge $-ze$ as observed at a distance $1/\kappa$. The quantity $1/\kappa$ has the dimensions of distance (centimeters in the cgs system) and has come to be known as the effective or equivalent radius of the ion atmosphere. The simple physical picture, illustrated in Fig. 12-10, is thus one of an ion of charge $ze$ having a statistical excess of ions of opposite charge around it, the excess amounting to just $-ze$ and behaving as though it were located on a spherical shell of radius $1/\kappa$.

It is next necessary to find the free energy associated with this extra potential
originating from the ion atmosphere. This is done by calculating the reversible work needed to form the atmosphere: We integrate the product of potential times charge as the ion is allowed to build up its charge from zero to the full value:

\[
\text{electrical work} = \int_0^{\varepsilon e} \psi_{\text{atm}} d(ze) = \int_0^{\varepsilon e} \left( -\frac{ze\kappa}{D} \right) d(ze)
\]

or

\[
w_{\text{el}} = -\frac{1}{2} \frac{\kappa}{D} (ze)^2.
\]

This electrical work then contributes to the chemical potential \(\mu_i\) of the \(i\)th ion:

\[
\mu_i = \mu_i^0 + kT \ln a_i + w_{\text{el}}.
\]

Since the whole derivation is for a very dilute solution, it seems safe to assume \(a_i = m_i\), that is, that the ion obeys Henry’s law apart from the electrical contribution. This last is the source of the observed deviation from ideality, reported experimentally in terms of an activity coefficient. The conclusion is then

\[
w_{\text{el}} = kT \ln \gamma_i = -\frac{z_i^2 e^2 \kappa}{2D}
\]

or

\[
\ln \gamma_i = -\frac{z_i^2 e^2 \kappa}{2DkT}.
\]  

(12-84)

We next need to find the mean activity coefficient for the case of an electrolyte
having just two kinds of ions. From Eq. (12-64) we have

\[ \ln \gamma_\pm = \frac{v_+}{v} \ln \gamma_+ + \frac{v_-}{v} \ln \gamma_- . \] (12-85)

Algebraic manipulation of Eqs. (12-85) and (12-61) gives

\[ \ln \gamma_\pm = -|z_+z_-| \frac{e^2\kappa}{2DKT}. \] (12-86)

Finally, \( \kappa \) can be related to the ionic strength \( I \) [Eq. (12-70)] since \( n_i = (C_i/1000)N_0 \) and in dilute solution \( C_i = m_i \rho_0 \), where \( \rho_0 \) is the solvent density. Equation (12-80) becomes

\[ \kappa^2 = \frac{8\pi e^2 N_0^2 \rho_0}{1000 DRT} I \] (12-87)

and so Eq. (12-86) becomes

\[ \ln \gamma_\pm = -|z_+z_-| \frac{e^2 N_0^2}{DRT} \left( \frac{2\pi \rho_0}{1000 DRT} \right)^{1/2} I^{1/2} \] (12-88)

\[ = -A |z_+z_-| I^{1/2}. \]

Insertion of the values for the general constants (\( e \) in esu and \( R \) in erg mole\(^{-1} \) K\(^{-1} \)) gives

\[ \ln \gamma_\pm = -4.198 \times 10^6 |z_+z_-| \left( \frac{\rho_0}{D^2 T^2} \right)^{1/2} I^{1/2}. \] (12-89)

For water at 25°C, \( D = 78.54 \) and Eq. (12-89) reduces to

\[ \ln \gamma_\pm = -1.172 |z_+z_-| I^{1/2}. \] (12-90)

The Debye–Hückel treatment leads, first of all, to a theoretical explanation of the empirical observation that the activity coefficient of an electrolyte is determined by the ionic strength \( I \) of the medium. The quantitative predictions, as for example, from Eq. (12-90), have been well verified for uni-univalent electrolytes. The theoretical slopes are included in Figs. 12-7 and 12-8, and the experimental points approach agreement at low concentrations. One may make a more direct check by plotting the activity coefficient data of Table 12-7 according to Eq. (12-90). This is done in Fig. 12-11, and it is apparent that the uni-univalent electrolytes approach agreement with theory. It is less clear whether accurate agreement occurs in the case of the higher charge types. Equation (12-90) is a limiting law in that various approximations restrict its validity to dilute solutions, and it has been assumed that activity coefficients for the more highly charged electrolytes will approach the theoretical predictions at sufficiently low concentrations. This aspect is discussed further in the Commentary and Notes section.

\[ ^{\dagger} \] The preceding derivation has been made in the cgs system, as the more natural one to use. The equations are the same in the SI system except that \( D \) is everywhere multiplied by \( 4\pi \varepsilon_0 (8.854 \times 10^{-12} \text{—see Section 3-CN-1}) \) and the factor of 1000 disappears from the denominators of Eqs. (12-87) and (12-88). Ionic strength remains in \( m \) (mole kg\(^{-1} \) solvent) but \( \rho_0 \) is now in kg m\(^{-3} \) and \( 1/\kappa \), the ion atmosphere radius, in meters.
CHAPTER 12: SOLUTIONS OF ELECTROLYTES

12-9 Ionic Equilibria

There are two somewhat separate aspects of the treatment of ionic equilibria. The first, introduced in Section 12-7, is that of the determination of the true or thermodynamic equilibrium constant. Recall that the basic procedure is the extrapolation of a concentration equilibrium constant, $K_{sp}$ in the case of solubility and $K$ in the case of homogeneous equilibrium, to infinite dilution. To review this aspect briefly, we write for each species $\mu_i = \mu_i^0 + RT \ln a_i$, and, following the derivation of Eq. (7-10), obtain

$$AG = (m\mu_M + n\mu_N + \cdots) - (a\mu_A + b\mu_B + \cdots)$$

or

$$AG = AG^0 + RT \ln Q_{th}, \quad Q_{th} = \frac{a_M^{\alpha_M}a_N^{\alpha_N} \cdots}{a_A^{\alpha_A}a_B^{\beta_B} \cdots}.$$  \hspace{50pt} (12-91)

At equilibrium $AG = 0$, and $Q_{th}$ becomes the thermodynamic equilibrium constant $K_{th}$:

$$AG^0 = -RT \ln K_{th}.$$  \hspace{50pt} (12-92)

It is convenient for us to write each activity as a product of concentration and activity coefficient, to obtain

$$K_{th} = \frac{(M)^m(N)^n \cdots \gamma_M^m \gamma_N^n \cdots}{(A)^a(B)^b \cdots \gamma_A^a \gamma_B^b} = KK_y,$$

or

$$K = \frac{K_{th}}{K_y}.$$  \hspace{50pt} (12-93)
where $K$ is the concentration equilibrium constant, using mole fraction, molality, or molarity, and $K_y$ is the activity coefficient constant using the corresponding activity coefficients.

Solution equilibria are usually studied in fairly dilute solutions, and one commonly assumes that nonionic species obey Henry's law, that is, have unit activity coefficients. However, we have seen that electrolytes show serious departures from ideality even at high dilution, and quite appreciable error can result if we treat ionic equilibria without considering $K_y$. Several procedures are possible. First, as already discussed, one may extrapolate $K$ values to infinite dilution so as to obtain $K_{th}$, and then back calculate the $K_y$ value for each equilibrium condition. One may estimate $K_y$ by evaluating each ion activity coefficient from the Debye–Hückel equation (12-89) or (12-90). One may, alternatively, use an experimental mean activity coefficient from some independent source. Thus if $K_{th}$ is for a solubility equilibrium, then, as discussed in Section 12-7, $K_y$ will correspond to the mean activity coefficient of the electrolyte raised to the power $\nu$, and standard tables of activity coefficients, such as Table 12-8, can be used. In the case of an equilibrium such as

$$\text{Ac}^- + \text{H}_2\text{O} = \text{HAc} + \text{OH}^-, \tag{12-94}$$

where ions of more than one electrolyte are involved, it is always possible to give $K$ in terms of mean activity coefficient ratios. Thus in this case, we have

$$K_y = \frac{\gamma_{\text{OH}^-}}{\gamma_{\text{Ac}^-}} \tag{12-95}$$

and if the cation present in the solution is $\text{Na}^+$, multiplication of the numerator and denominator of Eq. (12-94) gives

$$K_y = \frac{\gamma_{\text{NaOH}}^{\pm}}{\gamma_{\text{NaAc}}^{\pm}} \tag{12-96}$$

It is usually acceptable to take activity coefficients in mixed electrolytes, $\gamma_{\text{NaOH}}^{\pm}$ and $\gamma_{\text{NaAc}}^{\pm}$ in this case, to be the same as for the pure electrolyte species at the same overall ionic strength, although specific effects would have to be allowed for in accurate work.

A remaining device that is employed is to examine the equilibrium in the presence of a large excess of nonparticipating electrolyte, often $\text{NaClO}_4$. The nature of the solvent medium is in this way made essentially independent of the concentrations of the species and $K_{th}/K_y$ is therefore constant. The use of a swamping electrolyte is very common, for example, in the study of reaction kinetics involving ionic species.

The second aspect of the treatment of ionic equilibria, and the principal subject of this section, is that of the algebraic relationships and manipulations that are useful. These are for the most part standard, and the discussion here will be cursory except for some special cases. Table 12-9 gives some representative ionic equilibrium constants, and we now proceed to consider the use of solubility products in calculating solubilities under various circumstances, and then the treatment of simple acids and bases. A more detailed approach to acid–base equilibria is given in the Special Topics section.
### TABLE 12-9. Ionic Equilibrium Constants

<table>
<thead>
<tr>
<th>Solubility products</th>
<th>$K_{sp}$</th>
<th>Salt</th>
<th>$K_{sp}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCl</td>
<td>$1.0 \times 10^{-6}$</td>
<td>Ag(C$_2$H$_3$O$_2$)</td>
<td>$1.8 \times 10^{-2}$</td>
</tr>
<tr>
<td>PbCl$_2$</td>
<td>$1.0 \times 10^{-4}$</td>
<td>AgCl</td>
<td>$1.55 \times 10^{-10}$</td>
</tr>
<tr>
<td>PbCrO$_4$</td>
<td>$1.8 \times 10^{-14}$</td>
<td>AgBr</td>
<td>$7.7 \times 10^{-13}$</td>
</tr>
<tr>
<td>Mg(C$_2$O$_4$)</td>
<td>$8.6 \times 10^{-6}$</td>
<td>AgI</td>
<td>$7.1 \times 10^{-17}$</td>
</tr>
<tr>
<td>PbCl$_2$</td>
<td>$2.6 \times 10^{-16}$</td>
<td>Ag$_2$CrO$_4$</td>
<td>$9 \times 10^{-12}$</td>
</tr>
<tr>
<td>HgCl$_2$</td>
<td>$2 \times 10^{-18}$</td>
<td>TlCl</td>
<td>$2.7 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

**Dissociation of simple acids and bases**

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_a$</th>
<th>Base</th>
<th>$K_b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>$1.01 \times 10^{-14}$</td>
<td>NH$_4$OH</td>
<td>$1.8 \times 10^{-5}$</td>
</tr>
<tr>
<td>CH$_3$COOH</td>
<td>$1.75 \times 10^{-5}$</td>
<td>C$_6$H$_5$NH$_3$OH</td>
<td>$3.8 \times 10^{-10}$</td>
</tr>
<tr>
<td>CH$_3$ClCOOH</td>
<td>$1.38 \times 10^{-3}$</td>
<td>C$_2$H$_5$NH$_3$OH</td>
<td>$5.6 \times 10^{-4}$</td>
</tr>
<tr>
<td>CCl$_3$COOH</td>
<td>$0.13$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>C$_6$H$_5$COOH</td>
<td>$6.3 \times 10^{-5}$</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>HCN</td>
<td>$7.2 \times 10^{-10}$</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

**Dissociation of polybasic acids**

<table>
<thead>
<tr>
<th>Acid</th>
<th>$K_1$</th>
<th>$K_2$</th>
<th>$K_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$CO$_3$</td>
<td>$4.31 \times 10^{-7}$</td>
<td>$5.6 \times 10^{-11}$</td>
<td>—</td>
</tr>
<tr>
<td>H$_2$C$_2$O$_4$</td>
<td>$6.5 \times 10^{-3}$</td>
<td>$6.1 \times 10^{-5}$</td>
<td>—</td>
</tr>
<tr>
<td>C$_6$H$_5$O$_4$</td>
<td>$6.4 \times 10^{-5}$</td>
<td>$2.7 \times 10^{-4}$</td>
<td>—</td>
</tr>
<tr>
<td>Succinic acid</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>$9.1 \times 10^{-8}$</td>
<td>$1.2 \times 10^{-15}$</td>
<td>—</td>
</tr>
<tr>
<td>H$_2$SO$_4$</td>
<td>Strong</td>
<td>0.012</td>
<td>—</td>
</tr>
<tr>
<td>H$_2$SO$_3$</td>
<td>$0.0172$</td>
<td>$6.24 \times 10^{-4}$</td>
<td>—</td>
</tr>
<tr>
<td>H$_3$PO$_4$</td>
<td>$7.5 \times 10^{-3}$</td>
<td>$6.2 \times 10^{-4}$</td>
<td>$4.8 \times 10^{-13}$</td>
</tr>
<tr>
<td>H$_3$AsO$_4$</td>
<td>$5 \times 10^{-3}$</td>
<td>$8.3 \times 10^{-4}$</td>
<td>$6 \times 10^{-10}$</td>
</tr>
</tbody>
</table>

* Aqueous solution at 25°C.

*18°C.

### A. Solubility Equilibria

The solubility product expression for a 1-1 electrolyte is

$$MX(s) = M^{z_+} + X^{z_-}, \quad K_{sp} = (M^{z_+})(X^{z_-})$$

and, for the general case,

$$M_{v_+}X_{v_-} = v_+M^{z_+} + v_-X^{z_-}, \quad K_{sp} = (M^{z_+})^{v_+}(X^{z_-})^{v_-} \quad [\text{Eq. (12-60)}].$$

The solid salt is taken to be in its standard state and hence to have unit activity, but we must remember that for $K_{sp}$ to apply, the solid must in fact be in equilibrium with the solution.

The solubility $S$ of an electrolyte is defined as the number of gram formula weights that dissolve in the particular medium. If there is no added common ion, then $S = (M^{z_+})/v_+ = (X^{z_-})/v_-$, so in the general case

$$K_{sp} = (v_+)^{v_+}(v_-)^{v_-} S^v.$$
As an example, \( K_{sp} = 9 \times 10^{-12} \) for \( Ag_2CrO_4 \) at 25°C, so we have
\[
9 \times 10^{-12} = (2)^2 (1) S^3, \quad S = 1.3 \times 10^{-4}.
\]
If, however, an electrolyte is present which furnishes a common ion, say \( X^{\pm} \), then the solubility is given by \( (M^{\pm})/\nu_{+} \). The expression for \( K_{sp} \) becomes
\[
K_{sp} = (\nu_{+} S)^{\nu_{+}} (C + \nu_{-} S)^{\nu_{-}},
\]
where \( C \) is the concentration of added \( X^{\pm} \).

Continuing this example, if 0.1 m \( Na_2CrO_4 \) is also present, then
\[
9 \times 10^{-12} = (2S)^2(0.1 + S).
\]
The resulting cubic equation is best solved by successive approximations:
\[
S_1 \approx \left( \frac{9 \times 10^{-12}}{4(0.1)} \right)^{1/3} = 4.7 \times 10^{-4}.
\]
The first approximation, \( S_1 \), gives a result small compared to 0.1, and is therefore adequate. A more serious calculation would now proceed to the estimation of \( K_y \) for a solution \( S \) molar in \( Ag_2CrO_4 \) and 0.1 m in \( Na_2CrO_4 \) as the medium, so as to obtain a more nearly correct \( K_{sp} \) using Eq. (12-93).

Another type of complication is that the dissolved salt may not be fully dissociated. For example, appreciable amounts of \( CoOx \) (where \( Ox \) denotes oxalate ion) are present in solution as the undissociated molecule. If the solution is saturated with respect to \( CoOx(s) \), the concentration \( S_0 \) of undissociated \( CoOx \) in solution is a constant. The observed solubility \( S \) is then \( S_0 + (Co^{2+}) \), and if \( Na_2Ox \) is added, \( S \) decreases due to the common ion effect. With further addition of \( Na_2Ox \), however, the complex \( Co(Ox)_{\frac{2}{2}}^{2-} \) begins to form and the solubility, that is, total dissolved \( CoOx(s) \), increases. Other cases of complex formation with slightly soluble salts include the well-known example of \( Ag(CN)_{2}^{2-} \), as well as that of \( AgCl_{2}^{-} \) and other silver halide complexes.

Finally, if the anion of the slightly soluble salt is one of a weak acid, then the solubility will depend on the \( pH \) of the solution. Thus in the case of silver acetate the following simultaneous equilibria would hold:
\[
AgAc(s) = Ag^{+} + Ac^{-}, \quad K_{sp} = 1.8 \times 10^{-3},
\]
\[
HAc = H^{+} + Ac^{-}, \quad K = 1.75 \times 10^{-5}.
\]
If the \( pH \) is known, this determines the degree of dissociation \( \alpha \) of the acid, and
\[
K_{sp} = (Ag^{+})(Ac^{-}) = S(\alpha S).
\]
In this case the total acetic acid substance is given by the solubility \( S \), but the actual \( Ac^{-} \) concentration is only \( \alpha S \).

**B. Equilibrium across a Semipermeable Membrane**

An important type of ionic equilibrium is that across a membrane which is permeable only to certain of the ions present. The situation is known as one of Donnan
equilibrium. As an example, consider the arrangement shown in Fig. 12-12. The membrane is permeable to solvent and to M\(^+\) and X\(^-\) ions, but not to N\(^+\) ions. Such selectivity is shown, for example, by the membranes of living nerve cells.

The condition for ionic equilibrium is that the activity \(a_2\) [see Eq. (12-52)] be the same on both sides of the membrane for that electrolyte to which it is permeable, in this case M\(^+\), X\(^-\). Thus

\[
\prod a_i = \prod a_i' ,
\]

(12-96)

If the solutions are dilute, activities may be replaced by concentrations. Also, electroneutrality requires that \((M^+)_1 = (X^-)_1 = C\) and \((M^+)_2 + (N^+)_2 = (X^-)_2\) . Equation (12-96) thus reduces to

\[
C^2 = (M^+)_2 [(M^+)_2 + (N^+)_2] .
\]

(12-97)

Suppose that \(C = 0.01\) m and that \((N^+) = 0.1\) m. We find \((M^+)_2 = 9.9 \times 10^{-4}\) m
and see that the Donnan effect acts to exclude M\(^+\) from side II. If \(C = 10^{-3}\) m, \((M^+)_2\) drops to \(1 \times 10^{-5}\) m, and the exclusion ratio \((M^+)_2/(M^+)_1\) increases from 10.1 to 100.

The physical basis for the exclusion effect is that a potential difference, the Donnan potential \(\phi\), makes side II positive relative to side I. It can be shown that

\[
\phi = \frac{RT}{F} \ln \left( \frac{(M^+)_1}{(M^+)_2} \right) ,
\]

(12-98)

where \(F\) is Faraday's number [see Eq. (13-12)]. In the numerical example, \(\phi\) is 0.0594 V and 0.118 V for \(C\) values of 0.01 m and 0.001 m, respectively, for 25°C.

Donnan potentials are important in biology. For example, nerve cells or axons appear to be permeable to K\(^+\) but not to Na\(^+\) ions and application of Eq. (12-88) gives about the observed potential across the resting cell membrane. Reduction of this potential by more than a certain threshold amount makes the membrane permeable to Na\(^+\) ions and a wave of local depolarization races along from cell to cell. Such nerve impulses travel at some 100 ft sec\(^{-1}\). The contraction of muscle cells also involves changes in cell membrane potential and in ratio of permeability to Na\(^+\) versus K\(^+\) ions.

### C. Weak Acids and Bases

The treatment of dissociation equilibria involving weak acids and bases will be limited here to the cases of a simple acid HA and a simple base BOH. Even so, the general solutions can involve rather complex algebraic manipulations. A powerful alternative approach is given in the Special Topics section.
We consider first the weak monobasic acid HA:

$$HA = H^+ + A^-,$$

$$K_b = \frac{(H^+)(A^-)}{(HA)}.$$  \hspace{1cm} (12-99)

The general situation is one of a solution prepared by dissolving amounts of HA and of the salt MA so as to give the formalities $f_{HA}$ and $f_{MA}$. The cation $M^+$ is assumed not to hydrolyze. With the solvent taken to be water, we have

$$H_2O = H^+ + OH^-,$$

$$K_w = (H^+)(OH^-).$$  \hspace{1cm} (12-100)

The solution must be electrically neutral, and so

$$(M^+) + (H^+) = (A^-) + (OH^-),$$  \hspace{1cm} (12-101)

where $(M^+) = f_{MA}$. Finally, by material balance

$$(HA) + (A^-) = f_{HA} + f_{MA}.$$  \hspace{1cm} (12-102)

Note that $(HA)$ and $(A^-)$ denote the actual concentrations of these species, whereas $f_{HA}$ and $f_{MA}$ are the amounts weighed out per 1000 g of water when the solution is made up.

The preceding four equations must be solved simultaneously, and it is helpful to reduce them as follows. From Eq. (12-101) we have

$$(A^-) = f_{MA} + (H^+) - (OH^-)$$

and insertion of this result into Eq. (12-102) gives

$$(HA) = f_{HA} - (H^+) + (OH^-).$$

Equation (12-99) then becomes

$$K_b = \frac{(H^+)[f_{MA} + (H^+) + (OH^-)]}{f_{HA} - (H^+) + (OH^-)}.$$  \hspace{1cm} (12-103)

The simultaneous solution of Eqs. (12-100) and (12-103) then gives $(H^+)$ and $(OH^-)$ for any formal composition.

Equation (12-103) simplifies considerably under various special conditions.

**Case 1.** $f_{MA} = 0$. Then

$$K_b = \frac{(H^+)(H^+) - (OH^-)}{f_{HA} - (H^+) + (OH^-)}.$$  \hspace{1cm} (12-104)

If $(OH^-) \ll (H^+)$, then $K_b = (H^+)^2/[f_{HA} - (H^+)]$. This condition holds if $(H^+)^2 > 10^{-12}$ and hence if $K_b f_{HA} > 10^{-12}$. If also $f_{HA} \gg (H^+)$, then $K_b = (H^+)^2/f_{HA}$. This condition holds if $f_{HA} > 100 (H^+)$ and hence if $f_{HA} > 10^4 K_b$.

As examples, for $0.1 \text{ m HAc}$, $K_b f_{HA} = 1.75 \times 10^{-6}$ and is much greater than $10^{-12}$. Since $f_{HA}$ is about $10^4 K_b$, the last approximation can just be used (to $1\%$ error) and $(H^+)^2 = 1.75 \times 10^{-6}$, $(H^+) = 1.32 \times 10^{-3}$. However, if $f_{HA}$ were $10^4 \text{ m}$, then $K_b f_{HA}$ would be $1.75 \times 10^{-12}$, and the full equation (12-103) would be needed.

**Case 2.** $f_{HA} = 0$. Then

$$K_b = \frac{(H^+)[f_{MA} + (H^+) - (OH^-)]}{-(H^+) + (OH^-)}.$$
If we divide \( K_a \) by \( K_w \) to give \( K_h \), the hydrolysis constant, we obtain

\[
K_h = \frac{K_w}{K_a} = \frac{(OH^-)[(OH^-) - (H^+)]}{f_{MA} + (H^+) - (OH^-)}.
\]  

(12-105)

This is of the same form as Eq. (12-104), and the same two types of approximation follow:

\[
\text{If } K_h f_{MA} > 10^{-12}, \quad \text{then } K_h = \frac{(OH^-)^2}{f_{MA} - (OH^-)}.
\]

\[
\text{If } f_{MA} > 10^4 K_h, \quad \text{then } K_h = \frac{(OH^-)^2}{f_{MA}}.
\]

For example, \( K_h = 1.01 \times 10^{-14}/1.75 \times 10^{-5} = 5.77 \times 10^{-10} \). For 0.1 m NaAc, \( K_h f_{MA} = 5.77 \times 10^{-11} \), or more than 10^{-12}, and \( f_{MA} = 0.1 \), or more than \( 10^4 K_h \). The simplest form may then be used and \( (OH^-)^2 = (0.1)(5.77 \times 10^{-10}) \), \( (OH^-) = 7.6 \times 10^{-6} \), \( (H^+) = 1.3 \times 10^{-9} \).

Case 3. If \( f_{MA} \) and \( f_{HA} \) are each greater than \( (H^+) \) or \( (OH^-) \), then Eq. (12-103) reduces to

\[
K_a = \frac{(H^+)f_{MA}}{f_{HA}}.
\]  

(12-106)

The solution is now said to be buffered. That is, in order to change \( (H^+) \) appreciably, we must add sufficient acid or base to change \( f_{MA} \) or \( f_{HA} \) appreciably. Thus in a solution 0.1 \( f \) in HAc and 0.1 \( f \) in NaAc, \( (H^+) \) will be \( 1.75 \times 10^{-5} \). Addition of 0.01 \( f \) HCl changes \( f_{HAc} \) to 0.11 and \( f_{NaAc} \) to 0.09, and hence \( (H^+) \) only changes to \( 2.1 \times 10^{-5} \).

A parallel set of relationships holds for the weak base BOH:

\[
BOH = B^+ + OH^-; \quad K_b = \frac{(B^+)(OH^-)}{(BOH)}.
\]

The analog of Eq. (12-103) is

\[
K_b = \frac{(OH^-)[f_{BX} + (OH^-) - (H^+)]}{f_{BOH} - (OH^-) + (H^+)},
\]  

(12-107)

where \( X^- \) is a nonhydrolyzing anion. The various special cases are similarly analogous to those for the weak acid.

We can find the equilibrium concentrations in a solution containing HA, MA, BOH, and BX, by solving Eqs. (12-100), (12-103), and (12-107) simultaneously. If all of the concentrations \( (HA), (A^-), (BOH), \) and \( (B^+) \) are much larger than that of \( (H^+) \) or \( (OH^-) \), then these ions may be ignored in the charge balance, and the simultaneous equations to be solved are

\[
BOH + HA = B^+ + A^- + H_2O, \quad K_{ab} = \frac{(B^+)(A^-)}{(BOH)(HA)} = \frac{K_a K_b}{K_w},
\]

\[
(B^+) + f_{MA} = (A^-) + f_{BX}, \quad f_{HA} + f_{MA} = (HA) + (A^-),
\]

\[
f_{BOH} + f_{BX} = (BOH) + (B^+).
\]

D. Titration Curves

An acid–base titration consists of adding successive amounts of a base to a solution of an acid, or of an acid to a solution of a base, and noting how the
hydrogen ion concentration [or $pH = -\log(H^+)$] varies. We will consider only the first situation here.

The calculation of a titration curve is clarified if one recognizes that a solution which initially has a formality $f_{HA}$ in acid is converted into one having formalities $f'_{HA}$ and $f'_{MA}$ by addition of a strong base, where $f'_{MA}$ is the formality of the added base and $f'_{HA} + f'_{MA} = f_{HA}$. As a specific example, consider a solution that initially is 0.1 m in acetic acid. Addition of sodium hydroxide sufficient to make the solution 0.05 m in NaOH must yield an equilibrium mixture identical to that which would be obtained if the solution were 0.05 m in HAc and 0.05 m in NaAc. In effect, the formal composition of the solution may be expressed in two alternative ways:

$$
0.1 \text{m in HAc} \sim \begin{cases} 
0.05 \text{m in HAc}, \\
0.05 \text{m in NaOH} \sim 0.05 \text{m in NaAc}.
\end{cases}
$$

Both statements specify the same amount of acetic acid substance and sodium ion.

The general procedure for finding such alternative ways of expressing a formal composition is to consider species that would tend to react and then to suppose that the reaction goes to completion. The new formal composition is expressed in terms of the products. Thus HAc and NaOH tend to react:

$$
\text{HAc} + \text{Na}^+ + \text{OH}^- = \text{Na}^+ + \text{Ac}^- + \text{H}_2\text{O}. \quad (12-108)
$$

The alternative expression of formal composition follows if we suppose that the neutralization of the 0.1 m HAc by 0.05 m NaOH goes to completion, giving 0.05 m NaAc and residual 0.05 m HAc. The reaction does not in fact go entirely to completion, but the formal composition can be given as 0.05 m NaAc and 0.05 m HAc.

With this preamble, the calculation of a titration curve reduces to the calculation of $(H^+)$ from Eq. (12-103) for various ratios of $f_{MA}$ to $f_{HA}$, with their total kept constant. The equivalence point is that for which $f_{HA} = 0$. The result of such a calculation for a 0.002 m acetic acid solution is shown in Fig. 12-13, where $F_N$ is the degree of neutralization. (It has been assumed that the added sodium hydrox-

\[\text{FIG. 12-13. Titration curve for acetic acid using a strong base.}\]
ide solution is sufficiently concentrated that dilution effects can be neglected.

Calculations of this type can be quite tedious, and as in the preceding subsection, the reader is reminded that a more general and powerful approach is given in the Special Topics section.

A titration may be followed conductimetrically. In a neutralization reaction such as that of Eq. (12-108), each portion of NaOH added converts an equivalent amount of HAc into Na$^+$ + Ac$^-$. The conductance of the solution therefore increases since a weak electrolyte is being replaced by a strong one. At the end point, further addition of NaOH adds Na$^+$ and OH$^-$ ions to those of the NaAc, and the conductance increases more rapidly, as illustrated in Fig. 12-14. If the acid being titrated is a strong acid, then the neutralization converts the ions H$^+$ + A$^-$ into Na$^+$ + A$^-$ or, in effect, substitutes sodium ion for hydrogen ion. Since the equivalent conductivity of sodium ions is much less than that of hydrogen ions, the result is that the conductance drops during the titration until the end point is reached, and then rises as before.

Example. Suppose that 0.1 m HCl is being titrated with concentrated NaOH (we therefore neglect volume changes) and that the conductance is followed using an immersion-type conductivity cell of cell constant 0.2. The initial conductance is $L_0 = (CA)/1000k = (0.1)(426)/(1000)(0.2) = 0.213 \text{ ohm}^{-1}$. When enough NaOH has been added to make the solution 0.05 m in NaOH or, alternatively, 0.05 m in NaCl and 0.05 m in residual HCl, the conductance $L_1$ is

$$L_1 = \frac{(0.05)(426) + (0.05)(126)}{(1000)(0.2)} = 0.138 \text{ ohm}^{-1}.$$  

At the end point the formality of the added NaOH is 0.1, and the solution consists of just 0.1 m NaCl. The conductance $L_2 = (0.1)(126)/(1000)(0.2) = 0.063 \text{ ohm}^{-1}$. When the end point is overshot with 0.15 m added NaOH, the system is 0.1 m in NaCl and 0.05 m in NaOH, and $L_3$ is now

$$L_3 = \frac{(0.1)(126) + (0.05)(248)}{(1000)(0.2)} = 0.125 \text{ ohm}^{-1}.$$  

Thus the series of $L$ values 0.213, 0.138, 0.063, and 0.125 goes through a minimum at the end point.

**FIG. 12-14.** Conductimetric titration curves for a strong acid (upper left line) and a weak acid (lower left line).
COMMENTARY AND NOTES

12-CN-1 Electrolytic Dissociation

A brief further discussion of the theory of electrolytic dissociation seems worthwhile. This is something we now take for granted, yet the reasons for the original resistance to Arrhenius' proposal were serious ones and should be appreciated. It must be remembered that in 1890 the electron as such had not yet been discovered; it would be many years before x-ray crystallography revealed the crystal structures of solids; and, of course, wave mechanics was not imagined. Mineral solids, such as NaCl, were known as hard, high-melting materials, similar in these respects to metals, and evidently held together by strong chemical forces. It seemed incredible that the mere dissolving of such a salt in water would break it up into fragments. The heat of solution of most salts is relatively small, and so it appeared that little play of energy was present; the most natural supposition was that solutions of mineral salts consisted of the molecular units.

Two types of observations led Arrhenius to attack this very reasonable picture. The first was the difficulty in accounting for Ohm's law being obeyed by electrolyte solutions. The original Grotthus idea of salt molecules exchanging polar parts (Fig. 12-1) implied that even the most minute applied potential would induce a chain of bond breaking and making. This was contrary to experimental evidence, which strongly indicated that electrical charge carriers were ever-present, waiting to carry current, and did not have to be created by an applied potential.

The second type of observation was that of the colligative behavior of electrolyte solutions. Van't Hoff, in particular, had found it necessary to introduce his (now famous) i factor into the osmotic equation [Eq. (10-58)]. The experimental result is that \( i \approx 2 \) for aqueous NaCl and this was entirely mysterious until electrolytic dissociation was proposed. The early situation was clouded by what we now consider to be a combination of interionic attraction and partial dissociation effects, the consequence of which is that \( i \) factors are not found to be simple integers except at extreme dilution. Nonetheless, it was the combined impact of colligative property and conductance measurements that established the theory of electrolytic dissociation.

As noted in Section 12-3, it is now useful to class electrolytes as strong or as weak. Weak electrolytes obey the Ostwald dilution law well, and their behavior is thus determined primarily by a dissociation equilibrium. Strong electrolytes, however, do not obey a dissociation equilibrium constant at all well, and it was not until the development of interionic attraction theory that they could be understood.

We can also now explain how it is possible that strongly bonded salt crystals can so readily dissociate in water solution. X-ray crystallography tells us that crystalline NaCl consists of a closely packed array of alternate Na\(^+\) and Cl\(^-\) ions and not of molecular Na–Cl units (Section 19-3). The strong forces that hold the crystal together are primarily Coulomb attractions between unlike charged ions. The Coulomb attractive potential between one Na\(^+\) and an adjacent ion is

\[
\phi = \frac{e^2}{r},
\]
where \( r \) is the distance between the centers of the ions. The picture is essentially that of Fig. 8-5, and a summation of all of the mutual Coulomb interactions gives the total crystal or so-called lattice energy. Such calculations (see Section 20-ST-3) agree well with the observed heats of sublimation, 186 kcal mol\(^{-1}\) in the case of NaCl.

Equation (12-109) applies if the medium in which the ions are present is vacuum; otherwise the dielectric constant enters in the denominator. Water has a dielectric constant of about 80, so the energy to dissociate NaCl would be reduced to about 1.5 kcal mol\(^{-1}\). Thus by inserting itself between the ions, water reduces their mutual attraction to a point where the gain in entropy on dissolution can make the process occur. The 125 kcal mol\(^{-1}\) or other analogous quantity has not disappeared. This much energy is still required to take the aqueous Na\(^+\) and Cl\(^-\) ions into the gas phase. In other words, the strong mutual binding in the crystal has, in solution, been replaced by a strong binding to water. We speak of this binding as the hydration energy and ionic crystals may be said to dissolve in water because the hydration energy nearly balances the lattice energy. It is interesting, for example, that the heat of solution of an anhydrous salt is generally more negative (more heat is evolved) than that of a corresponding hydrate. Thus the heat of solution of Na\(_2\)SO\(_4\) is \(-0.5\) kcal mol\(^{-1}\), while that of Na\(_2\)SO\(_4\)·10H\(_2\)O is 19 kcal mol\(^{-1}\); the presence of water of hydration in the crystal has noticeably diminished the amount of hydration energy available when the crystal dissolves.

The Coulomb forces between ions in aqueous solution, although greatly reduced from those between ions in the crystal, are still important; they give rise to the interionic attraction effects in conductance and in the Debye–Hückel treatment of nonideality. It seems certain that ion pairs and possibly ion clusters form in concentrated solutions as discussed in the next section.

**12-CN-2 Activity Coefficients for Other than Dilute Aqueous Solutions**

It was noted in Section 12-8 that the activity coefficients of uni-univalent electrolytes approach the Debye–Hückel limiting law in dilute solutions, and that the values for other valence types also would do so at extreme dilution. In effect, however, the simple Debye–Hückel treatment is valid only for slightly “contaminated” water, and a great deal of effort has been devoted to the physical chemical treatment of more concentrated aqueous solutions and of nonaqueous solutions. The first improvement was with the recognition of the finite size of ions, based on the assumption that there is some distance \( a \) of closest approach; the effect is to modify \( \psi \) in such a way as to lead to the following equation:

\[
\ln \gamma_i = -\frac{z_i^2 e^2}{2DKT} \frac{\kappa}{1 + \kappa a}
\]  

(12-110)

or

\[
\log \gamma \pm = -\frac{AI^{1/2}}{1 + BI^{1/2}},
\]  

(12-111)
where $A$ is as defined in Eq. (12-88) and $B$ is given by

$$B = \frac{35.56}{(DT)^{1/2}} \bar{a}$$

(12-112)

where $\bar{a}$ is now in Angstroms. For water at 25°C, $B = 0.232 \bar{a}$. Equation (12-111) fits activity coefficient data for uni-univalent electrolytes, up to perhaps 0.1 $m$, with reasonable values for $\bar{a}$.

The next efforts were in various different directions. V. LaMer and others attempted to solve the Poisson–Boltzmann equation (12-78) more exactly, but encountered great mathematical difficulties. Although major departures from the simple theory were shown to be expected, especially for asymmetric electrolytes, such as those of the 1–2 type, the extended terms that they obtained are hard to use and are not very satisfactory. A semiempirical equation due to Brønsted suggested that at higher concentrations $\log \gamma \pm$ should be proportional to $m$, and a commonly used form today is

$$\log \gamma \pm = -\frac{A11/2}{1 + B11/2} + Cm.$$  

(12-113)

Now $B$ and $C$ are treated as empirical constants. A more stimulating approach was that of N. Bjerrum, also of the Copenhagen school, who pointed out that in terms of the Debye–Hückel model, the probability of finding an ion of opposite charge near a given ion went through a minimum at a characteristic distance $q$:

$$q = \frac{e^{2}\bar{z}_{1}\bar{z}_{2}}{DkT}.$$  

(12-114)

For a 1–1 electrolyte at 25°C, $q$ is about 3.5 Å and Bjerrum suggested that ions closer than this distance should be regarded as ion pairs. The existence of a distance $q$ arises as somewhat of an accident, however; $\psi(r)$ decreases steadily outward, but the volume of space increases with $r^3$ and it is the combination of these opposite factors that leads to $q$ as the radius of the spherical shell having a minimum probability of finding a counter ion. The approach, however, established a pattern of thought that has been very useful.

At this point a distinction should be made between ion pairing and chemical association. Acetic acid is highly associated, but as a result of chemical bond formation between $H^+$ and Ac$^-$. Transition metal ions form coordinate bonds (see Section 12-ST-3) with anionic ligands; the case of CoOx and Co(Ox)$_3^{2-}$—mentioned in Section 12-9A is but one example. As just one further example, the Fe$^{3+}$ ion forms the complex FeX$^{2+}$, where $X$ may be a halogen, pseudohalogen, or hydroxide ion. In fact, transition metal ions have a solvation shell of coordinated water, and the formation of FeX$^{2+}$ would more properly be written

$$\text{Fe(H}_2\text{O)}_6^{5+} + X^- = \text{Fe(H}_2\text{O)}_6^{2+} + \text{H}_2\text{O}.$$  

Many of these ligand substitution reactions are in rapid equilibrium, and the apparent nonideality of, say, aqueous FeCl$_3$ is largely due to complex formation.
On the other hand, an ion such as Na\(^+\) does not have much ability to form coordinate bonds, and the attraction between Na\(^+\) and Cl\(^-\) is, as noted in the preceding section, mainly of Coulombic origin. We speak of ion association (or ion pairing), then, when we wish to think of the unit as consisting of the intact ions. The distinction between ion pairing and coordinative association is not always easy to make. The association which occurs with, say, Zn\(^{2+}\) and SO\(_4^{2-}\) may be partly Coulombic and partly coordinative—Zn\(^{2+}\) does, after all, form well-known complex ions. In the case of Co(NH\(_3\))\(_6^{3+}\), however, the coordination sphere is saturated, and the association constant of 1000 observed between this ion and SO\(_4^{2-}\) is therefore spoken of confidently as due to ion pairing.

To return to the matter of activity coefficients, we find that there is no question that ion pairing does occur in more concentrated solutions, and even in dilute ones if the ions are highly charged. R. M. Fuoss and C. A. Kraus have estimated ion pair dissociation constants for a number of electrolytes from conductivity measurements. For uni-univalent electrolytes values are of the order of unity and for di-divalent ones they are around 0.01 or less. Thus the estimated dissociation constants are about 1.4 for KNO\(_3\), 0.15 for KSO\(_4\)\(^-\), and 5.3 \times 10^{-3} for ZnSO\(_4\) (aqueous solutions at 25°C). The conclusion is that the Debye–Hückel theory must be used with great caution for other than dilute solutions of uni-univalent electrolytes. Semiempirical equations such as Eq. (12-113) are very helpful, but it must be remembered that the constants B and C of the equation depend on the total ionic makeup of a solution and not just on the particular electrolyte in question.

Ion pairing, important in aqueous solutions, becomes a dominant feature in nonaqueous systems. As the dielectric constant of a medium is reduced, the Coulomb forces between ions increase, and the degree of dissociation of an electrolyte drops dramatically. As an example, the dissociation constant of KI is only about 2 \times 10^{-4} in pyridine as solvent. There are a few nonaqueous solvents, of fairly high dielectric constant, in which electrolytes having large ions may be moderately dissociated. The salt K\(^+\)[Cr(NH\(_3\))\(_2\)(NCS)\(_4\)]\(^-\) is fully dissociated in nitromethane, and similar complex ions are moderately dissociated in dipolar aprotic solvents such as dimethylsulfoxide, dimethylformamide, and the like.

### 12-CN-3 Acids and Bases

#### A. Aqueous Solutions

There are many interesting regularities in the dissociation constants of weak acids and bases. The following are a few examples which draw on the data of Table 12-9. Carboxylic acids tend to have \(K_a\) values of around \(10^{-5}\), except that as the carbon atom adjacent to the carboxyl group is substituted with electronegative groups, such as halogens, the acidity increases. For CCl\(_3\)COOH, \(K_a = 0.13\), for example. This appears to be an inductive effect by which the carboxyl carbon atom is made more positive and the O—H bond is electrostatically weakened. A large number of acids of this type have been studied, and L. P. Hammett has used the data to characterize substituents. Thus in the case of substituted benzoic acids a substituent is assigned a parameter \(\sigma\), defined as \(\sigma = pK_o - pK_s\), where \(pK_o = -\log K_o\), with \(K_o\) the dissociation constant of benzoic acid, and \(pK_s = -\log K_s\), with \(K_s\) the dissociation constant of the sub-
stituted acid. The σ values are then found to correlate with the behavior of the compounds in other equilibria or in their reaction kinetics.

The electrostatic effect appears to be very important in determining the pK values of oxyacids. The approximately $10^5$-fold reduction in successive $K$ values for $H_3PO_4$ is one example. The three protons should be essentially equivalent, except for the increased electrostatic work of dissociation in the series $H_3PO_4$, $H_2PO_4^-$, $HPO_4^{2-}$. A useful empirical rule is that for an oxyacid of the general formula MO$_m$(OH)$_n$, $pK_1$ is approximately $7 - 5n$, $pK_2$ is $12 - 5n$, and so on. Thus for $H_3PO_4$, $pK_1$ should be $7 - 5 = 2$, $pK_2$ should be about $12 - 5 = 7$, and so on; for $H_2SO_4$, $pK_1$ is predicted to be $-3$, in agreement with the observation that the first dissociation is that of a strong acid, while $pK_2$ should be 2, again about as observed.

Another type of situation is that in which two acid functions are sufficiently separated in a molecule that they should be essentially free of the preceding electrostatic effects. An example is HOOC—(CH$_2$)$_n$—COOH, where $n$ is two or more. It might be supposed that $K_1$ and $K_2$ should be the same since the two groups are independent. A statistical factor remains, however. If the acid is represented by $H_1H_2A$, there are two ways for the first-stage dissociation to occur, namely to give $H_1A^-$ or $H_2A^-$. There is only one choice of hydrogen to dissociate in the second stage, but the association reaction $H^+ + A^{2+}$ can occur on either position. Thus $K_1$ is enhanced and $K_2$ is diminished by this effect. In the case of succinic acid, HOOC—(CH$_2$)$_2$—COOH, $K_1 = 6.4 \times 10^{-5}$, or somewhat more than twice $K_a$ for acetic acid, and $K_2 = 2.7 \times 10^{-6}$, or about half $K_a$ for acetic acid.

A related behavior is that of amino acids, typifying electrolytes having separated weakly acidic and weakly basic groups. An amino acid is sometimes shown in the form $H_2N—R—COOH$, but it appears certain that internal proton transfer is largely complete, so that $^+H_2N—R—COO^-$ is the actual species in aqueous solution. This last is known as a zwitterion. The behavior of an amino acid is then represented in terms of the two stages of dissociation of a dibasic acid:

$$^+H_2N—R—COOH = H^+ + ^+H_2N—R—COO^-,$$
$$K_1 = \frac{(H^+)(A^+)}{(A^+)} ,$$

$$^+H_2N—R—COO^- = H^+ + H_2N—R—COO^-,$$
$$K_2 = \frac{(H^+)(A^-)}{(A^-)} .$$

In the case of glycine, $H_2NCH_3COOH$, $K_1 = 4.5 \times 10^{-3}$ and $K_2 = 2.24 \times 10^{-12}$ at $25^\circ C$.

The isoelectric point is a state of special importance for an amino acid. This is the pH value such that $(A^+) = (A^-)$. Acid–base equilibria are rapid, which means that an individual amino acid molecule rapidly samples all its possible states of dissociation and at the isoelectric point it therefore spends equal times as $A^+$ and as $A^-$. The effect is that the amino acid behaves as though it were electrically neutral, even though it is still a conducting electrolyte; it displays essentially no net motion in an electrophoresis experiment, for example. Analysis of the preceding equilibrium relationships shows that at the isoelectric point $(H^+) = (K_1K_2)^{1/4}$. It can also be shown that at this pH the total degree of ionization of the amino acid is at a minimum. For this reason many of the physical properties of an amino acid solution exhibit maxima or minima at the isoelectric point.
B. Brønsted Treatment of Acids and Bases

The phenomenology of electrolyte behavior in aqueous solutions made it natural for Arrhenius and Ostwald to define an acid as a substance furnishing $\text{H}^+$ ions and a base as one furnishing $\text{OH}^-$ ions. Neutralization then consisted of the reaction of these ions to give water. This formalism is an adequate and functioning one for the treatment of acid-base equilibria in water solution, although it is somewhat misleading chemically. The $\text{H}^+$ ion exists in water at least as $\text{H}_3\text{O}^+$, if not in more complex forms, and the dissociation of a weak acid is more correctly written as

$$\text{HA} + \text{H}_2\text{O} = \text{A}^- + \text{H}_3\text{O}^+ \quad (12-115)$$

than as $\text{HA} = \text{H}^+ + \text{A}^-$. Similarly, a weak base may produce $\text{OH}^-$ ions by the reaction

$$\text{H}_2\text{O} + \text{B} = \text{OH}^- + \text{HB}^+ \quad (12-116)$$

(as, for example, with $\text{B} = \text{NH}_3$).

Brønsted and Lowry illuminated the chemistry of weak acids and bases by recognizing (in 1923) that the degree of a reaction such as those given by Eqs. (12-115) and (12-116) must depend on the natures of both reactants and that the reactions are really symmetric. They introduced the more general definitions that an acid is a proton donor and a base is a proton acceptor. Equations (12-115) and (12-116) now fall into the common form

$$\text{acid} + \text{base} = \text{conjugate base} + \text{conjugate acid}$$

$$\begin{align*}
\text{HA} + \text{H}_2\text{O} & = \text{A}^- + \text{H}_3\text{O}^+ \\
\text{H}_2\text{O} + \text{B} & = \text{OH}^- + \text{HB}
\end{align*}$$

An acid, on yielding a proton, becomes its conjugate base, and a base, on accepting a proton, becomes its conjugate acid.

The Brønsted picture has been useful in two major ways. First, it emphasizes that the anion of a weak acid is a proton acceptor, or a base, as well as $\text{OH}^-$ ion and may be capable of reacting directly with a proton donor without going through the route of accepting an $\text{H}^+$ ion released by it. There are a number of cases of acid- or base-catalyzed reactions in which direct reaction evidently occurs. The rate of reaction in such cases is found to depend on the specific acid or base present and not just on the $\text{pH}$ of the solution.

The second important feature of the Brønsted picture is that it relates aqueous to nonaqueous systems. Other solvents can now be seen in striking analogy to water. Liquid ammonia, for example, autoionizes to give $\text{NH}_4^+$ and $\text{NH}_2^-$ ions, in analogy to the $\text{H}_3\text{O}^+$ and $\text{OH}^-$ ions of water. Acetic acid in liquid ammonia solution then dissociates according to the reaction

$$\text{HAc} + \text{NH}_3 = \text{Ac}^- + \text{NH}_4^+. \quad (12-117)$$

This dissociation is virtually complete. That is, acetic acid is a strong acid in liquid ammonia solvent, and the reason is clearly that $\text{NH}_3$ is a much better...
proton acceptor than is H$_2$O. Acids that are too weak to be studied in water solution can be observed easily in liquid ammonia.

Pure acetic acid may be used as a solvent, and the autoionization reaction gives CH$_3$CO$_2$H$_2^+$ and CH$_3$CO$_2^-$ ions. Then HCl in acetic acid solution dissociates according to the reaction

$$\text{HCl} + \text{HAc} = \text{Cl}^- + \text{H}_2\text{Ac}^+$.$$

(12-118)

However, HAc is a weak base and this dissociation is not complete. That is, HCl behaves as a weak acid in acetic acid solvent. In this solvent, the series of acid strengths

$$\text{HClO}_4 > \text{HBr} > \text{H}_2\text{SO}_4 > \text{HCl} > \text{HNO}_3$$

is established. All of these acids are so completely dissociated in water that distinctions among them cannot be made and it is only by balancing their proton-donating ability against a rather poor acceptor that the real differences become apparent.

Other acid–base systems have some value. In molten oxide mixtures an acid and a base may be defined as an acceptor and a donor, respectively, of oxide ion. In the reaction BaO + CO$_2$ = BaCO$_3$, BaO is then the base and CO$_2$ the acid.

G. N. Lewis proposed the rather general definitions of an acid as an electron pair acceptor and a base as an electron pair donor. The designations are consistent with the Bronsted scheme in that a Bronsted base has an unshared pair of electrons capable of bonding with H$^+$. The Lewis definition also allows the reaction BF$_3$ + (CH$_3$)$_3$N = (CH$_3$)$_3$N·BF$_3$ to be characterized as an acid–base one, BF$_3$ being the acid. The Lewis formalism does not provide the symmetry of the Brønsted formalism, however, and really is more a notation indicating that an important type of chemical bond is that in which the electron pair derives from one of the associating molecules. Such a bond is also often called a coordinate bond, and in the Lewis sense coordination chemistry is a study of acid–base reactions. More recently, Lewis acids and bases have been subdivided into categories A and B, alternatively known as "hard" and "soft," depending roughly on their charges and polarizabilities. This author feels that it is more profitable to study the coordinate bond as it is, rather than in terms of often hypothetical acid plus base reactions. Thus in the case of Cr(CO)$_6$, Cr is supposedly the acid and CO the base, but this approach does not seem very illuminating of the actual wave-mechanical description of the Cr—CO bond.

**SPECIAL TOPICS**

**12-ST-1 Ionic Diffusion Coefficients**

It was shown in Section 10-7B that the diffusion coefficient for a particle in solution is given by

$$D = \frac{kT}{\gamma} \quad [\text{Eq. (10-41)}],$$

where $\gamma$ is the friction coefficient. The same treatment applies to individual ions,
and writing $\omega = 1/\nu$, Eq. (10-41) becomes

$$D_i = \omega_i kT.$$  \hfill (12-119)

It is now possible to relate $D_i$ and electrochemical mobility $u_i$, using Eq. (12-29):

$$D_i = 10^{-7} \frac{u_i kT}{z_i e}$$

or, using Eq. (12-31),

$$D_i = 10^{-7} \frac{\lambda_i kT}{z_i e z^2} = \frac{\lambda_i RT}{z_i e z^2},$$  \hfill (12-120)

where $R$ is now in joules per degree Kelvin per mole.

Equation (12-120) gives the diffusion coefficient for a single ion, as might be observed in a self-diffusion experiment. Ordinarily, however, one studies the diffusion of an electrolyte as a whole, and the electroneutrality requirement enforces the same diffusional velocity on both ions. The intrinsically slower diffusing type of ion will lag behind the faster one until a local potential (called the diffusion potential) builds up. This potential $\phi$ acts to retard the faster ions and speed up the slower ones, and Eq. (2-67) for the diffusional flux therefore becomes

$$J_1 = -D_1 \frac{dC_1}{dx} + \phi \omega_1 C,$$  \hfill (12-121)

$$J_2 = -D_2 \frac{dC_2}{dx} - \phi \omega_2 C,$$  \hfill (12-122)

where 1 and 2 denote the two kinds of ion present and $C$ is the ion concentration assuming a 1–1 electrolyte. In other words, $\phi \omega$ gives the increment in velocity due to the local field and $\phi \omega C$ gives the corresponding increment to the molecular flow across a unit area. We require that $J_1 = J_2$, that is, that no excess of one ion build up over the other during the diffusion, and on equating (12-121) and (12-122), we obtain

$$\phi = \frac{(D_1 - D_2) dC/dx}{(\omega_1 + \omega_2) C}.$$

Substitution of this result into Eq. (12-121) [or (12-122)] gives

$$J_1 = - \left( -D_1 + \frac{D_1 - D_2}{\omega_1 + \omega_2} \omega_1 \right) \frac{dC}{dx}.$$  \hfill (12-123)

Since $\omega_i$ is proportional to $D_i$ and $J_1$ is now the flux for the diffusion of the electrolyte as a whole, we have

$$J_1 = -D \frac{dC}{dx}.$$

Equation (12-123) reduces to

$$D = \frac{2D_1 D_2}{D_1 + D_2} = \frac{2RT \lambda_1 \lambda_2}{z^2 A}.$$  \hfill (12-124)

Equation (12-124) is known as the Nernst diffusion equation; it permits the calcula-
tion of the diffusion coefficient for an electrolyte if the equivalent conductivities are known.

The more complete form of Eq. (12-124) allows for nonideality in the same manner as does Eq. (10-40):

\[ \mathcal{D} = \frac{2RT}{zFr^2} \frac{\lambda_1\lambda_2}{A} \left[ 1 + \frac{d(ln \gamma_c)}{d(ln C)} \right]. \]  

(12-125)

Strictly speaking, interionic attractions affect the equivalent conductivities differently from the diffusional mobilities. In the former case the two kinds of ion are moving in opposite directions, whereas in diffusion they are moving in the same direction. In brief, two kinds of effects are recognized in conductance. The motion of a given ion in a direction opposite to its atmosphere produces an electrical drag or relaxation effect, given by the first term of Eq. (12-19). In addition, the ion atmosphere entrains solvent, so that each ion is in effect swimming in a countercurrent of moving solvent. This is known as the electrophoretic effect and is given by the second term of Eq. (12-19). In diffusion, there is no relaxation effect, but there is still an electrophoretic one. The theories of these effects are approximate, and the treatment of the electrophoretic effect is open to certain objections, particularly for other than uni-univalent electrolytes. Also, the derivations are intimately tied to the Debye–Hückel assumptions, and show these approximations. [See Harned and Owen (1950) for further details.]

### 12-ST-2 The Hittorf Method

The analysis of the Hittorf method for the determination of transference numbers was greatly abridged in Section 12-6, and the more detailed presentation appears here.

We consider first the system shown in Fig. 12-6, for which a qualitative analysis was given. The more exact bookkeeping is as follows, based on 1 \( \mathcal{F} \) of electricity passing through the cell.

#### Cell I. Anode compartment

Anode reaction: \( \text{Ag} = \text{Ag}^+ + e^- \): gain of 1 equiv of \( \text{Ag}^+ \)
migration of \( \text{Ag}^+ \): loss of \( t_+ \) equiv of \( \text{Ag}^+ \)
migration of \( \text{NO}_3^- \): gain of \( t_- \) equiv of \( \text{NO}_3^- \).  

Net change: Gain of \( 1 - t_+ \) or \( t_- \) equiv of \( \text{Ag}^+ \), gain of \( t_- \) equiv of \( \text{NO}_3^- \); or gain of \( t_- \) equiv of \( \text{AgNO}_3 \).

#### Cell III. Cathode compartment

Cathode reaction: \( \text{Ag}^+ + e^- = \text{Ag} \): loss of 1 equiv of \( \text{Ag}^+ \)
migration of \( \text{Ag}^+ \): gain of \( t_+ \) equiv of \( \text{Ag}^+ \)
migration of \( \text{NO}_3^- \): loss of \( t_- \) equiv of \( \text{NO}_3^- \).  

Net change: Loss of \( 1 - t_+ \) or \( t_- \) equiv of \( \text{Ag}^+ \), loss of \( t_- \) equiv of \( \text{NO}_3^- \); or loss of \( t_- \) equiv of \( \text{AgNO}_3 \).

The overall change per faraday is that the anode compartment gains \( t_- \) equiv of \( \text{AgNO}_3 \) and the cathode compartment loses \( t_- \) equiv. The middle compartment should not change in content since the gains and losses due to the migration of ions past the dividing lines I–II and II–III exactly compensate.
This analysis applies to any cell containing a single electrolyte and having electrodes that generate or consume the cation of the electrolyte. The cell of Fig. 12-6 might have been filled with \( \text{CuSO}_4 \) solution, for example, and have copper electrodes. We would conclude that, per faraday, the anode compartment would gain \( t_+ \) equiv of \( \text{CuSO}_4 \) and the cathode compartment would lose \( t_- \) equiv.

Alternatively, the electrodes might be reversible to the anion, that is, the electrode reaction might produce and consume anion. This would be the case if, for example, the cell were filled with \( \text{NaCl} \) solution, and the electrodes were silver coated with silver chloride. The bookkeeping is now as follows:

Cell I. Anode compartment

\[
\text{Anode reaction: } \text{Ag} + \text{Cl}^- = \text{AgCl} + e^-:
\]

- migration of \( \text{Na}^+ \): loss of \( t_+ \) equiv of \( \text{Na}^+ \)
- migration of \( \text{Cl}^- \): gain of \( t_- \) equiv of \( \text{Cl}^- \).

Net change: Loss of \( t_+ \) equiv of \( \text{Na}^+ \), loss of \( 1 - t_- \) or \( t_+ \) equiv of \( \text{Cl}^- \);

or loss of \( t_+ \) equiv of \( \text{NaCl} \).

Cell III. Cathode compartment

\[
\text{Cathode reaction: } \text{AgCl} + e^- = \text{Ag} + \text{Cl}^-:
\]

- migration of \( \text{Na}^+ \): gain of \( t_+ \) equiv of \( \text{Na}^+ \)
- migration of \( \text{Cl}^- \): loss of \( t_- \) equiv of \( \text{Cl}^- \).

Net change: Gain of \( t_+ \) equiv of \( \text{Na}^+ \), gain of \( 1 - t_+ \) or \( t_- \) equiv of \( \text{Cl}^- \);

or gain of \( t_+ \) equiv of \( \text{NaCl} \).

The opposite working of the electrode reaction thus has the effect of making the anode compartment undergo a net loss of \( t_+ \) equiv of \( \text{NaCl} \) and the cathode compartment undergo a net gain of \( t_+ \) equiv of \( \text{NaCl} \), in contrast to the preceding example.

It is not necessary, of course, that the electrode reaction involve either of the ions of the electrolyte. If platinum electrodes were used in the example just given, the analysis would be as follows:

Cell I. Anode compartment

\[
\text{Anode reaction: } \frac{1}{2}\text{H}_2\text{O} = \frac{1}{2}\text{O}_2 + \text{H}^+ + e^-:
\]

- migration of \( \text{Na}^+ \): loss of \( t_+ \) equiv of \( \text{Na}^+ \)
- migration of \( \text{Cl}^- \): gain of \( t_- \) equiv of \( \text{Cl}^- \).

Net change: Gain of 1 equiv of \( \text{H}^+ \), loss of \( t_+ \) equiv of \( \text{Na}^+ \), gain of \( t_- \) equiv of \( \text{Cl}^- \);

or gain of 1 equiv of \( \text{HCl} \), loss of \( t_+ \) equiv of \( \text{NaCl} \).

Cell III. Cathode compartment

\[
\text{Cathode reaction: } e^- + \text{H}_2\text{O} = \frac{1}{2}\text{H}_2 + \text{OH}^-:
\]

- migration of \( \text{Na}^+ \): gain of \( t_+ \) equiv of \( \text{Na}^+ \)
- migration of \( \text{Cl}^- \): loss of \( t_- \) equiv of \( \text{Cl}^- \).

Net change: Gain of 1 equiv of \( \text{OH}^- \), gain of \( t_+ \) equiv of \( \text{Na}^+ \), loss of \( t_- \) equiv of \( \text{Cl}^- \);

or gain of 1 equiv of \( \text{NaOH} \), loss of \( t_- \) equiv of \( \text{NaCl} \).

This last example illustrates some further points. First, the net change can be expressed either in terms of gains and losses of individual types of ions or in terms of gains and losses of complete electrolytes; the alternative statements are seen on examination to be entirely equivalent. The purpose of the middle compartment now becomes apparent. The analysis assumes that only \( \text{Na}^+ \) and \( \text{Cl}^- \) ions carry current past the I–II and II–III dividing lines. The electrode reactions are producing \( \text{H}^+ \) and \( \text{OH}^- \) ions, however, and if mixing occurs in compartments I and III
during the electrolysis, then these electrode products will carry part of the current between compartments. The gains and losses of Na\(^+\) and Cl\(^-\) ions would then be less than expected, and the overall analysis would be in error. The test of whether electrolysis products reached compartment II would, in this case, be whether the pH of II changed or not.

Notice that all of these analyses are couched in terms of amounts gained or lost during electrolysis. The concentrations present do not enter directly. The transference numbers are themselves concentration-dependent, however, since \(\lambda_+\) and \(\lambda_-\) will in general change differently with concentration. It is desirable for this reason that no great change in composition occur during the electrolysis. Ordinarily, then, the amount of electricity passed through the cell will be some small fraction of a faraday.

It is, of course, necessary to measure the quantity of electricity involved in a Hittorf experiment so that the results can be put on a per faraday basis. It is not necessary, however, to know the applied potential or the actual current—only the total quantity of electricity. One usually obtains this by determining the amount of an electrode reaction that has occurred. Thus in the first example, the loss in weight of the silver anode gives the number of faradays used. It would be possible in the third example to titrate the solution in the anode compartment to find the amount of H\(^+\) ion produced. However, it is generally more convenient to have a second cell in series with the Hittorf cell, which functions as a coulometer. This might consist of a silver anode dipping into silver nitrate solution and a platinum cathode. Either the loss in weight of the anode or the amount of silver deposited on the cathode would show the number of faradays that had passed through the cell. A numerical example is as follows.

**Example.** We can construct an illustrative problem using the cell in which an NaCl solution was electrolyzed with platinum electrodes. Suppose that the initial NaCl solution is 0.1000 \(m\), and thus contains 5.844 g of NaCl per 1000 g of water. The electrolysis is carried out until 1.92 g of silver have been deposited in a coulometer in series with the cell, at which point the anode compartment is drained and then rinsed with some of the original NaCl solution, so that a total of 301.35 g of solution results which is found to contain 0.02315 equiv of NaCl. Calculate \(\lambda_+\) and \(\lambda_-\).

First, 1.92 g of silver corresponds to \(1.92/107.87 = 0.01780\) equiv so that \(0.01780\) of electricity passed through the cell. At the end of the experiment, the 0.02315 equiv of NaCl present in the anode solution plus rinse corresponds to 1.35 g, and so the amount of water in the solution was 301.3 \(-\) 1.35 = 300.0 g. Now the amount of NaCl associated originally with 300 g of water is \(0.1(300)/1000 = 0.03000\) equiv. There has been a loss of \(0.03000 - 0.02315 = 0.00685\) equiv of NaCl.

This loss becomes, per faraday, \(0.00685/0.01780 = 0.385\). From the earlier bookkeeping analysis, the loss should be \(\lambda_+\) equiv of NaCl per faraday. The transference number of Na\(^+\) is therefore 0.385 and that of Cl\(^-\) is 0.615. The equivalent conductivity of 0.1 \(m\) NaCl is 106.74, so that \(\lambda_{Na^+} = (0.385)(106.74) = 41.09\) and \(\lambda_{Cl^-} = (0.615)(106.74) = 65.65\).

The use of a rinse of original solution is a characteristic procedure in a transference experiment. The purpose of the rinsing, of course, is to displace all of the electrolyzed solution, and the use of original solution for the rinse simplifies the ensuing calculation. We are not interested in concentrations and need only to compare the amount of NaCl present in electrolyzed solution plus rinse with the amount originally associated with the quantity of water in the combined solutions. It is thus not necessary to know exactly how much solution was originally present in the anode compartment.

An alternative but less accurate procedure would have been to fill the anode compartment with a known volume of the 0.1 \(m\) solution and to determine the change in concentration resulting from the electrolysis. For example, had the anode compartment originally contained 200 cm\(^3\) of solution, or approximately 0.02 equiv of NaCl, then at the end of the electrolysis the amount remaining would have been \(0.02 - 0.00685 = 0.01315\) equiv, corresponding to a 0.0657 \(m\).
NaCl solution. The solution would also have contained 0.01780 equiv of HCl, or 0.0890 \( m \) HCl.

When we calculate transference numbers by the Hittorf method we implicitly assume that the solvent water does not migrate during the electrolysis. The water of hydration of the ions should move with them, however, and Washburn suggested the ingenious experiment of adding a sugar to the solutions in a Hittorf cell and referring the calculations to the sugar as the non-migrating species. The result showed that several molecules of water do in fact migrate with each ion.

12-ST-3 Treatment of Complex Ionic Equilibria

The treatment of the dissociation of a weak acid or a weak base is developed along standard lines in Section 12-9 but stops at the point of simple acids and bases, HA and BOH. The solution of the simultaneous equations for \((H^+)^-\) or \((OH^-)^-\) becomes very unwieldy if more than one stage of dissociation can occur or if there is a mixture of weak electrolytes. An alternative procedure becomes much more practical.

A. Acid HA or Base BOH

We first illustrate the method for a monobasic acid HA before proceeding to more complex situations. The material balance equation (12-102) is now written in the form

\[
 f_{tot} = f_{HA} + f_{MA} = (HA) + \frac{(HA) K_a}{(H^+)^-},
\]

using Eq. (12-99) to eliminate \((A^-)^-\). Rearrangement gives

\[
 F_{HA} = \frac{1}{[K_a/(H^+)] + 1},
\]

(12-126)

where \( F_{HA} = (HA)/f_{tot} \) and is the fraction of the total acid-substance which is present as undissociated acid HA. Alternatively, we may eliminate (HA) to obtain

\[
 F_{A^-} = \frac{1}{1 + [(H^+)^-]/K_a}.
\]

(12-127)

Equations (12-126) and (12-127) are usually displayed as a plot of log \( F \) versus pH. Such a plot is called a logarithmic diagram. That for acetic acid is shown in Fig. 12-15. Notice that if the pH is much less than \( pK_a \), Eq. (12-127) reduces to

\[
 \log F_{A^-} = pH - pK_a
\]

and so the plot of \( \log F_{A^-} \) versus \( pH \) becomes a straight line of slope +1 and intercept \(-pK_a\) in the region of high acidity. Similarly, if \( pH \gg pK_a \), then the plot of \( \log F_{HA} \) versus \( pH \) becomes a straight line of slope \(-1\) and intercept \( pK_a \).

The logarithmic diagram for a weak electrolyte resembles a phase diagram. It provides a map of the \( pH \) domain of each species so that one can tell at a glance the general makeup of a solution at any given \( pH \). The diagram is used quantita-
tively as follows. The charge balance equation

\[(M^+) + (H^+) = (A^-) + (OH^-) \quad \text{[Eq. (12-101)]}\]

can be put in the form

\[(M^+) + (H^+) = F_{A^-} + (OH^-). \quad (12-128)\]

One knows \(f_{HA}\) and \(f_{MA}\) and hence \(f_{tot}\) and \((M^+)\), and Eq. (12-128) is solved by successive approximations. A first guess at \((H^+)\) allows \(F_{A^-}\) to be read off the logarithmic diagram, and substitution into the equation will indicate whether the value is too high or too low. This guides a second choice of \((H^+)\), and so on, until a self-consistent answer is reached.

**Example.** We can calculate the pH of a solution which is 0.002 \(f\) in HAc and 0.001 \(f\) in NaAc; \(f_{tot}\) is then 0.003 and Eq. (12-128) becomes

\[0.001 + (H^+) = F_{A^-}(0.003) + (OH^-)\]

or

\[F_{A^-} = 0.333 + \frac{(H^+) - (OH^-)}{0.003}.\]

We can guess immediately a pH of 4.45, at which \(F_{A^-} = \frac{1}{3}\). The test of the equation is then

\[0.333 = 0.333 + \frac{3.54 \times 10^{-5}}{0.003} = 0.345.\]

\(F_{A^-}\) is slightly too small, and we next try a pH of 4.46, \(F_{A^-} = 0.345\). The test is now

\[0.345 = 0.333 + \frac{3.45 \times 10^{-5}}{0.003} = 0.345.\]
The desired pH is then close to 4.46. One may also calculate a titration curve. In Eq. (12-128), \( f_{\text{tot}} \) is now the initial formality of the acid, and \( (M^+) \) gives the concentration of added strong base. One may now insert successive choices for \( (H^+) \) and calculate \( (M^+) \) for each. The fraction of neutralization \( F_N \) is just

\[
F_N = \frac{(M^+)}{f_{\text{tot}}}.
\]

Several points on the titration curve for 0.002 M HAc are summarized thus. Equation (12-128) becomes \( (M^+) + (H^+) = 0.002 f_A - (OH^-) \), or \( F_N = f_A - ((H^+) - (OH^-))/0.002 \); some sample calculations are given in Table 12-10. The calculation illustrates several items. The first two values for \( F_N \) are negative, meaning that excess strong acid must be present. The third line gives the actual starting point of the titration; the relatively rapid change in \( F_N \) between pH 4 and 6 characterizes the buffer region, and the asymptotic approach to \( F_N = 1 \) marks the endpoint. The last entry shows that 5.3% excess base has been added. The curve is plotted in Fig. 12-13.

The logarithmic diagram approach offers little advantage in speed over the straight attack in the case of a simple acid. Being graphical, it is also less precise, but this is not a matter of great importance since the overriding uncertainty will be in the value for \( K_y \), that is, in the size of the activity coefficient correction.

The treatment of a simple weak base BOH is analogous to that just given:

\[
F_{BOH} = \frac{1}{[K_b/(OH^-)] + 1}, \quad F_{B^+} = \frac{1}{1 + [(OH^-)/K_b]}.
\] (12-129)

The logarithmic diagram is still a plot of log \( F \) versus pH, and the associated charge balance equation is

\[
F_{B^+} f_{\text{tot}} + (H^+) = (X^-) + (OH^-),
\] (12-130)

where \( f_{\text{tot}} = f_{BOH} + f_{BX} \), where X is a nonhydrolyzing anion. The plots for ammonium hydroxide are included in Fig. 12-18.

Logarithmic diagrams may be used for any mixture of weak electrolytes. Thus, for a mixture which contains both a weak acid and a weak base, the charge balance equation becomes

\[
(M^+) + F_{B^+} f_{(BOH+BX)} + (H^+) = (X^-) + F_A - f_{(HA+MA)} + (OH^-)
\] (12-131)

and the correct pH for a given mixture is found by trial-and-error solution. As an example, a solution which is 0.002 M in HAc, 0.001 M in NaAc, 0.003 M in \( NH_4OH \),

<table>
<thead>
<tr>
<th>( pH )</th>
<th>( (H^+) )</th>
<th>( (OH^-) )</th>
<th>( f_{A^-} )</th>
<th>( (H^+) - (OH^-)/0.002 )</th>
<th>( F_N )</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.01</td>
<td>—</td>
<td>( 1.7 \times 10^{-3} )</td>
<td>5</td>
<td>—5</td>
</tr>
<tr>
<td>3</td>
<td>0.001</td>
<td>—</td>
<td>( 1.7 \times 10^{-2} )</td>
<td>0.5</td>
<td>—0.483</td>
</tr>
<tr>
<td>3.75</td>
<td>( 1.78 \times 10^{-4} )</td>
<td>—</td>
<td>0.089</td>
<td>0.089</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>( 1 \times 10^{-4} )</td>
<td>—</td>
<td>0.149</td>
<td>0.05</td>
<td>0.099</td>
</tr>
<tr>
<td>4.75</td>
<td>( 1.75 \times 10^{-5} )</td>
<td>—</td>
<td>0.500</td>
<td>0.009</td>
<td>0.491</td>
</tr>
<tr>
<td>6</td>
<td>( 1 \times 10^{-6} )</td>
<td>( 1.05 \times 10^{-8} )</td>
<td>0.9461</td>
<td>—</td>
<td>0.9461</td>
</tr>
<tr>
<td>8</td>
<td>( 1 \times 10^{-8} )</td>
<td>( 1.05 \times 10^{-4} )</td>
<td>( 1 - (6 \times 10^{-4}) )</td>
<td>—</td>
<td>0.9994</td>
</tr>
<tr>
<td>10</td>
<td>( 1 \times 10^{-10} )</td>
<td>( 1.05 \times 10^{-4} )</td>
<td>1.000</td>
<td>—0.053</td>
<td>1.053</td>
</tr>
</tbody>
</table>
and 0.005 M in NH₄Cl would have a pH such that the equation

\[ 0.001 + 0.008F_{NH_4^+} + (H^+) = 0.005 + 0.003F_{A_2^-} + (OH^-) \]

is obeyed. In this case, \((H^+)\) and \((OH^-)\) will be negligible compared to the other terms, and so

\[ F_{NH_4^+} = 0.5 + 0.375F_{A_2^-}. \]

A few successive choices of pH should serve to locate the value such that \(F_{NH_4^+}\) and \(F_{A_2^-}\) as read off the logarithmic diagrams satisfy the equation.

**B. Successive Dissociations of a Weak Acid**

In the case of a dibasic acid \(H_2A\) the equilibrium constants are

\[ K_1 = \frac{(H^+)(HA^-)}{(H_2A)} \quad \text{and} \quad K_2 = \frac{(H^+)(A^{2-})}{(HA^-)}, \quad (12-132) \]

and substitution into the material balance statement \(\Sigma = (H_2A) + (HA^-) + (A^{2-})\) gives

\[ F_{H_2A} = \frac{1}{1 + [K_1/(H^+)] + [K_1K_2/(H^+)^2]}, \quad (12-133) \]

\[ F_{HA^-} = \frac{1}{[K_1/(H^+)] + 1 + [K_2/(H^+) ]}, \quad (12-134) \]

\[ F_{A^{2-}} = \frac{1}{[(H^+)^2/K_1K_2] + [(H^+)/K_2] + 1}. \quad (12-135) \]

The logarithmic diagram for \(H_2CO_3\) is shown in Fig. 12-16. Its use follows the

**FIG. 12-16. Logarithmic diagram for \(H_2CO_3\) at 25°C.**
same scheme as before, the charge balance equation now being

\[(M^+) + (H^+) = F_{HA-} f_{tot} + 2F_{A_2-} f_{tot} + (OH^-). \quad (12-136)\]

Figure 12-17 shows the titration curve for 0.1 \(M\) \(\text{H}_2\text{CO}_3\) calculated by the same procedure as before. That is, each assumed pH provides a value for \((M^+)\) through Eq. (12-136) and hence for the degree of neutralization.

The treatment for a tribasic acid \(\text{H}_3\text{A}\) yields the equation

\[F_{\text{H}_3\text{A}} = \frac{1}{1 + [K_1/(H^+)] + [K_1K_2/(H^+)^2] + [K_1K_2K_3/(H^+)^3]}, \quad (12-137)\]

and so on. The logarithmic diagram for phosphoric acid is given in Fig. 12-18. Phosphate buffers are much used and the figure allows the calculation of the pH of any mixture of phosphoric acid and its various salts. The dashed curves are for ammonium hydroxide, so the combined plots can be used for mixtures that include ammonium salts as well as phosphates.

\[\text{FIG. 12-17. Titration curve for } \text{H}_2\text{CO}_3.\]

\[\text{FIG. 12-18. Logarithmic diagrams for } \text{H}_3\text{PO}_4 \text{ (full lines) and NH}_4\text{OH (dashed lines).}\]
C. Complex Ions

The logarithmic diagram approach is not limited to weak acids and bases but may be applied to any set of successive dissociations. For example, Co²⁺ forms a succession of ammine complexes:

\[
H_2O + Co(NH_3)_6^{2+} = Co(NH_3)_5(H_2O)^{2+} + NH_3, \quad pK_6 = -0.74, \\
H_2O + Co(NH_3)_5(H_2O)^{2+} = Co(NH_3)_4(H_2O)_2^{2+} + NH_3, \quad pK_5 = 0.06,
\]

and so on. The values of \( pK_4, pK_3, pK_2 \), and \( pK_4 \) are 1.99, 1.51, 0.93, and 0.64, respectively. Note that the reactions have been written as interchanges of water for ammonia in the coordination sphere, in recognition of our belief that Co²⁺ is octahedrally coordinated.

Application of the standard procedure leads to

\[
F_{Co(NH_3)_6^{2+}} = \frac{1}{1 + [K_6/(NH_3)] + [K_5K_6/(NH_3)^2] + [K_4K_5K_6/(NH_3)^3] + \cdots},
\]

and similarly for the other species. The logarithmic diagram now consists of plots of the log \( F \)'s against \( p(NH_3) \), that is, against \( -\log(NH_3) \). Application of the charge balance equation then allows the calculation of the composition of any mixture of ammonia and a cobalt salt.

**GENERAL REFERENCES**


**CITED REFERENCES**


**EXERCISES**

Neglect interionic attraction effects in the following Exercises and Problems unless specifically directed otherwise. Take as exact numbers given to one significant figure.

12-1 The measured resistance of a 0.02 M solution of NaCl is 793 ohm in a cell whose path length can be taken to be 10 cm. Calculate (a) the specific conductivity of the solution, (b) its conductance, (c) the effective area of the electrodes, and (d) the cell constant.

\[ \text{Ans.} \]

(a) \( 2.53 \times 10^{-3} \) ohm\(^{-1}\) cm\(^{-1}\), (b) \( 1.26 \times 10^{-4} \) ohm\(^{-1}\), (c) 5.0 cm\(^2\), (d) 2.01 cm\(^{-1}\).
12-2 The resistance of electrolyte solution A is 45 ohm in a given cell and that of electrolyte solution B is 100 ohm in the same cell. Equal volumes of solutions A and B are then mixed. Calculate the resistance of this mixture, again in the same cell.

Ans. 62.1 ohm.

12-3 Calculate the resistance of a 0.03 M solution of Na₂SO₄ in a cell of cell constant 1.50 cm⁻¹.

Ans. 192 ohm.

12-4 The specific conductivity of a saturated solution of AgCl in pure water at 25°C is 1.79 × 10⁻⁶ ohm⁻¹ cm⁻¹ while that of the water used is 6.0 × 10⁻⁸ ohm⁻¹ cm⁻¹. From Table 12-2, calculate λ for Ag⁺, Cl⁻ and thence the solubility of AgCl.

Ans. 138.26 cm² ohm⁻¹ equiv⁻¹, 1.26 × 10⁻⁵ M.

12-5 Calculate λ for (a) Na₄Fe(CN)₆, (b) Cu(NO₃)₂, and (c) the double salt (Na)(NH₄)SO₄, using the data of Table 12-2.

Ans. (a) 161.1, (b) 125.3, (c) 141.5 (cm² ohm⁻¹ equiv⁻¹).

12-6 The solubility product for barium oxalate is 2.00 × 10⁻⁷ at 25°C. Calculate the specific conductivity of the saturated solution.

Ans. 1.23 × 10⁻⁴ ohm⁻¹ cm⁻¹.

12-7 The dissociation constant for NH₄OH is 1.80 × 10⁻⁵ at 25°C. Calculate A_app and the specific conductivity of a 0.02 M solution.

Ans. 8.0 cm² ohm⁻¹ equiv⁻¹, 1.60 × 10⁻⁴ ohm⁻¹ cm⁻¹.

12-8 Calculate the specific conductivity of 0.05 M sodium chloride at 25°C, allowing for interionic attraction effects.

Ans. 5.33 × 10⁻³ ohm⁻¹ cm⁻¹.

12-9 The equivalent conductivity of a cation M⁺ is determined at 25°C by means of a moving boundary experiment. A 0.005 M solution of MCl is used, and after 30 min of passing a current of 0.2 mA the cation boundary has moved 0.208 cm; the area of the column of solution is 1.50 cm². Calculate λ⁺, (A_MCI = 132 cm² ohm⁻¹ equiv⁻¹.)

Ans. 55.2 cm² ohm⁻¹ equiv⁻¹.

12-10 Calculate the electrochemical mobility and the effective radius of (a) an ion M⁺ whose equivalent conductivity is 55.0 cm² ohm⁻¹ equiv⁻¹, and (b) Fe(CN)₆³⁻, whose λ value is 95.0 cm² ohm⁻¹ equiv⁻¹ (both for 25°C).

Ans. (a) 5.70 × 10⁻⁴ cm² V⁻¹ sec⁻¹ and 1.67 Å, (b) 9.85 × 10⁻⁴ cm² V⁻¹ sec⁻¹ and 6.45 Å.

12-11 Calculate the transference number at 25°C for NO₃⁻ in 0.1 M KNO₃ and in a solution which is also 0.05 M in NaCl.

Ans. 0.493, 0.343.

12-12 The solubility of Pb(IO₃)₂ in water at 25°C is 4.00 × 10⁻⁶ m and the Kₛₚ = 5.00 × 10⁻¹⁸ in an aqueous KNO₃ solution. Calculate (a) the solubility product, (b) the mean molarity of the saturated solution, (c) the solubility in the KNO₃ solution, (d) the mean activity coefficient for the electrolyte Pb(IO₃)₂, IO₃⁻ in the KNO₃ solution.

Ans. (a) 2.56 × 10⁻¹⁸, (b) 6.35 × 10⁻⁴ m, (c) 5.00 × 10⁻⁵ m, (d) 0.800.

12-13 If the aqueous KNO₃ solution of Exercise 12-12 was 0.02 m, in what concentration of LaCl₃ should the solubility of Pb(IO₃)₂ be 5.00 × 10⁻⁶ m, according to the ionic strength principle?

Ans. 0.00333 m.
12-14 Calculate $\gamma_+$ for 0.02 m acetic acid at 25°C using Table 12-7.

Ans. 0.976.

12-15 Assuming the ionic strength principle, estimate $\gamma_+$ for 0.0333 m Cu(NO$_3$)$_2$ using the data of Table 12-8 (and assuming that the principle is obeyed by each ion separately).

Ans. 0.52.

12-16 Calculate $\gamma_{K^+}$ and $\gamma_{SO_4^{2-}}$ (separately) at 25°C in 0.05 m K$_2$SO$_4$ using the Debye–Hückel theory and compare the resulting $\gamma_+$ with the value in Table 12-8.

Ans. 0.635, 0.163, 0.404.

12-17 What is the Debye–Hückel value for $\gamma_+$ of 0.5 m NaCl at 50°C?

Ans. 0.42.

12-18 The solubility product of Ag$_2$CrO$_4$ is $2.0 \times 10^{-7}$ at 25°C; calculate the solubility of this salt in 0.1 m silver nitrate, recognizing nonideality.

Ans. $1.85 \times 10^{-4}$ m.

12-19 Obtain the degree of dissociation of 0.1 m chloroacetic acid in 0.05 m HCl at 25°C.

Ans. 0.0256.

12-20 What would the pH of the solution in Exercise 12-19 be if 0.06 mole liter$^{-1}$ of NaOH were added to it?

Ans. 1.91.

Some exercises in SI units.

12-21 The equivalent conductivity of Na$_2$SO$_4$ is $1.299 \times 10^{-2}$ m$^2$ equiv$^{-1}$ ohm$^{-1}$. Calculate the resistance of a 0.005 M solution in a cell whose cell constant is 150 m$^{-1}$.

Ans. $1.155 \times 10^8$ ohm.

12-22 Calculate the specific conductivity of a saturated solution of AgCl. Assume the water used has a specific conductivity of $70 \times 10^{-4}$ ohm$^{-1}$ m$^{-1}$.

Ans. $2.42 \times 10^{-4}$ ohm$^{-1}$ m$^{-1}$.

12-23 Calculate the ion atmosphere radius for a 0.02 m solution of a 1-1 electrolyte.

Ans. 2.155 nm.
Calculate $K_a$ for H$_2$S (relevant data are available in the text, but should be corrected to 18°C with the use of Walden’s rule).

**12-3** The specific conductivity of a saturated solution of silver iodate at 80°C is $1.25 \times 10^{-6}$ ohm$^{-1}$ cm$^{-1}$; that of the water used is $1.4 \times 10^{-4}$ ohm$^{-1}$ cm$^{-1}$ and the equivalent conductivity of silver iodate is 89 cm$^2$ ohm$^{-1}$ equiv$^{-1}$. Calculate the solubility product for silver iodate.

**12-4** The specific conductivities at 25°C were measured for the following solutions:

<table>
<thead>
<tr>
<th>Solution</th>
<th>Specific conductivity (ohm$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$10^{-3} M$ Phenanthrolinium chloride (BHC1)</td>
<td>$1.360 \times 10^{-4}$</td>
</tr>
<tr>
<td>$10^{-3} M$ BHC1 plus a large excess of phenanthroline (B)</td>
<td>$1.045 \times 10^{-4}$</td>
</tr>
<tr>
<td>$10^{-3} M$ HCl</td>
<td>$4.21 \times 10^{-4}$</td>
</tr>
</tbody>
</table>

Phenanthrolinium chloride is a strong electrolyte, that is, it exists as BH$^+$ and Cl$^-$ ions. Phenanthroline is a nonelectrolyte. Calculate $K_a$ for the acid dissociation BH$^+ = B^- + H^+$.

**12-5** Calculate the mobilities of H$^+$ and Cl$^-$ ions at 0°C using Walden’s rule, and the velocity with which each ion should move in a moving boundary experiment if the field is 0.1 V cm$^{-1}$. Calculate also the current if the solution is 0.02 $M$ and the cross section of the tube is 0.5 cm$^2$.

**12-6** One hundred cubic centimeters of 0.10 $N$ sodium acetate solution is titrated with 0.1 $N$ HCl solution. Calculate the specific conductivity of the resulting solution when 90, 99, 101, and 110 cm$^3$ of the HCl solution has been added. Bear in mind that acetic acid is only slightly ionized in the presence of HCl and NaAc; in these calculations neglect the variation of equivalent conductivity with concentration and use the value for infinite dilution. Your answers need be correct to only 1%. Make a semiquantitative plot of your calculated specific conductivities (as ordinate) versus the volume of HCl solution added.

**12-7** If pure water has a conductivity of $4.5 \times 10^{-8}$ ohm$^{-1}$ cm$^{-1}$ at 20°C, calculate the specific conductivity of a saturated solution of CO$_2$ in water at 20°C if the CO$_2$ pressure is maintained at 20 Torr and the equilibrium constant for the reaction H$_2$O(l) + CO$_2$(ag) = HCO$_3^-$ + H$^+$ is $4.35 \times 10^{-7}$. The solubility of CO$_2$ in water follows Henry’s law with a constant of 0.03353 mole liter$^{-1}$ atm$^{-1}$.

**12-8** Given that the equivalent conductivities for NaCl, KNO$_3$, and KCl are 126.4, 144.9, and 149.8 cm$^2$ equiv$^{-1}$ ohm$^{-1}$, respectively, and that $t_+ = 0.39$ for NaCl, calculate $\Lambda$ for NaNO$_3$ and $t_+$ for Na$^+$ in NaNO$_3$ solution.

**12-9** For an incompletely dissociated electrolyte the Onsager equation is

$$A = \alpha\left[A_0 - (A + BA_0)(\alpha C)^{1/2}\right] = \alpha\Lambda',$$

where $A = 82.4/\eta(DT)^{1/2}$, $B = 8.2 \times 10^6/(DT)^{3/2}$, $D$ is the dielectric constant, and $\eta$ is the viscosity. The equivalent conductivity of dichloroacetic acid in 0.03 $M$ solution is 273 cm$^2$ equiv$^{-1}$ ohm$^{-1}$. For dichloroacetic acid, $\Lambda_0 = 388.5$. Calculate the degree of dissociation $\alpha$ from the Onsager equation. [Hint: use a procedure of successive approximations, starting with $\alpha = \Lambda/\Lambda_0$.] Assume 25°C.

**12-10** In a transport experiment in 0.02 $M$ NaCl solution at 25°C, using the moving boundary method, Longsworth found the boundary between NaCl and CdCl$_2$ solutions to...
move 6.0 cm in 2070 sec with a current of 0.00160 A. Tube cross section was 0.12 cm². Calculate $t$.

12-11 Longsworth determined the transference number of sodium ion by the following moving boundary experiment. The data refer to the movement of a rising boundary between solutions of sodium and cadmium chlorides; the lower electrode was a cadmium anode and the upper a silver/silver chloride cathode. The temperature was 25°C, the current was maintained constant at $16.00 \times 10^{-4}$ A, the cross section of the tube was 0.1115 cm², and the concentration of the sodium chloride 0.02 mole liter⁻¹. The table gives some corresponding readings of the time $t$ and the distance of traverse of the boundary $x$:

<table>
<thead>
<tr>
<th>$t$ (sec)</th>
<th>172</th>
<th>344</th>
<th>2757</th>
<th>3104</th>
<th>3454</th>
</tr>
</thead>
<tbody>
<tr>
<td>$x$ (cm)</td>
<td>0.5</td>
<td>1.0</td>
<td>8.0</td>
<td>9.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>

Calculate the transference number of sodium ion. [Note: For the most accurate value of $x/t$ divide the difference between the average of the last three distances and that of the first two by the difference between the average of the last three values of $t$ and that of the first two.]

12-12 Ion-exchange particles exhibit the Donnan effect. Here, the porous particle corresponds to the left side of Fig. 12-12 in the case of an anion exchanger. That is, $N^+$ denotes the positively charged exchange sites that are attached to the ion-exchange polymer matrix. Suppose that the concentration of exchange sites is 2.5 $M$ for a certain ion exchanger. Calculate the interior concentration of Na⁺ and of Cl⁻ when the exchanger is immersed in 0.01 $M$ NaCl solution.

12-13 Calculate the concentration of $H_2S$, $HS^-$, $S^{2-}$, and $H^+$ in a 0.200 $M$ NaHS solution (to an accuracy of about 1%). [Note: The solution to this problem can be much simplified by making judicious approximations at each stage.]

12-14 Calculate the concentrations of acetate ion, benzoate ion, and $H^+$ in a solution made up of 0.0100 mole of acetic acid and 0.0100 mole of benzoic acid dissolved in water and then diluted to 1 liter.

12-15 A total of 0.01 mole of NaCl and 0.01 mole of solid $Ag_4CrO_4$ are shaken with a liter of water. Calculate the equilibrium constant for the reaction

$$Ag_4CrO_4 + 2Cl^- = 2AgCl + CrO_4^{2-}.$$ 

Calculate also the concentrations of each ion at equilibrium and the number of moles of any solids present. The $K_{sp}$ values are $1.8 \times 10^{-10}$ for AgCl and $1.2 \times 10^{-13}$ for $Ag_4CrO_4$.

12-16 Derive Eq. (12-90) from Eq. (12-84).

12-17 The following are mixed until equilibrium is achieved: 0.02 mole of AgCl, 0.02 mole of AgCN, 0.01 mole of NaCN, and 1 liter of water. Calculate within 1 or 2% relative accuracy the final concentration of each species in solution and the amounts of each solid present given the following data: final $pH$ is 7.00; $K_{sp}$ for AgCl is $1.8 \times 10^{-10}$; $K_{sp}$ for AgCN is $7 \times 10^{-13}$; $K_a$ for HCN is $1 \times 10^{-10}$; $K = (Ag(CN)_{2-})/[(Ag^+)(CN^-)]^2$ is $2.6 \times 10^{18}$.

12-18 Solid NaOH is added to 1 liter of a 0.1 M solution of $H_2S$ until the $pH$ rises to 12. Taking $K_1$ and $K_2$ as $10^{-3}$ and $10^{-14}$, respectively, calculate the initial $pH$ and the number of moles of NaOH added and the concentration of all species present in this final solution.

12-19 Leucylglycine is an amino acid which dissociates into both hydrogen and hydroxide ions.
At 25°C the constant for the dissociation into anions and hydrogen ions is $1.51 \times 10^{-8}$. The apparent dissociation constant for the dissociation into cations and hydroxyl ions is $3.02 \times 10^{-11}$. Calculate the pH at which the degree of dissociation into hydrogen ions and hydroxyl ions is the same.

12-20 How many millimoles of HA should be added to 100 cm$^3$ of a 0.01 M solution of base BOH in order to give a solution with a pH of 8.90? $pK_a$ for HA is 4.76, $pK_b$ for BOH is 5.40. How many cubic centimeters of 0.01 M HA would one have to add to 100 cm$^3$ of 0.01 M BOH to obtain this pH?

12-21 One hundred cubic centimeters of 0.1 M H$_2$SO$_4$ is mixed with 100 cm$^3$ of 0.025 M NaOH. Calculate the pH of the resulting solution. The second dissociation constant of sulfuric acid is 0.015 and the first corresponds to a strong acid.

12-22 Barney et al. obtained data on the solubility of cobaltous oxalate (CoOx) as a function of added potassium oxalate concentration. The solubility is at first depressed due to the common ion effect, then increased, due to the complex formation:

$$\text{Co}^{2+} + 2\text{Ox}^2- \rightleftharpoons K \text{Co(Ox)}_2^{2-}.$$

The minimum in solubility occurs at $S = 9.2 \times 10^{-5}$ and $(K_{\text{Ox}}) = 4.5 \times 10^{-4}$; the solubility of CoOx in pure water is $1.44 \times 10^{-4}$. Derive the equation whereby $K$ can be calculated from the solubility minimum, and calculate $K$.

12-23 The solubility of lead chloride is 0.005 mole liter$^{-1}$ at 25°C. Calculate the activity product (that is, make correction for activity coefficients). Calculate also the solubility of PbCl$_2$ in 0.02 M sodium nitrate solution.

12-24 Chlorine dissolved in water reacts according to the equation

$$\text{Cl}_2(\text{aq}) + \text{H}_2\text{O} = \text{H}^+ + \text{Cl}^- + \text{HClO}.$$

Since all the forms present are essentially nonconducting with the exception of the HCl, the concentration of this last may be determined by measuring the conductance of the solution. If the total dissolved chlorine is known, then the equilibrium constant for the reaction may be determined. Given the following data, calculate this equilibrium constant: The specific conductivity of 0.01 M Cl$_2$ solution is 0.00351 ohm$^{-1}$ cm$^{-1}$. The equivalent conductivities of 0.01 M HCl and 0.005 M HCl solutions are 412 and 415.6, respectively. Using Eq. (12-12) and the data given, calculate the hydrolysis constant (do not use conductivity values other than the ones given).

12-25 At 25°C, $pK$ for the dissociation of Ag(NH$_3$)$_2^+$ into its components is 7.22. For AgCl, AgBr, and AgI, $pK_{sp}$ is 9.77, 12.48, and 16.07, respectively. Calculate how many milligrams of these salts are dissolved by 1 liter of 1.0 M NH$_3$. Neglect Ag(NH$_3$)$_2^+$, NH$_4^+$, and OH$^-$. 

### SPECIAL TOPICS PROBLEMS

12-1 Calculate the limiting value for the diffusion coefficient of aqueous NaCl at 25°C.

12-2 The equivalent conductivity for 0.01 M KCl is 146 cm$^2$ ohm$^{-1}$ equiv$^{-1}$ at 25°C. Calculate the diffusion coefficient for 0.01 M KCl using Eq. (12-125).

12-3 A solution containing 0.14941 wt % KCl is electrolyzed in a Hittorf cell at 25°C with
silver/silver chloride electrodes. After the electrolysis, which deposits 0.16024 g of silver in a silver nitrate coulometer, one of the end cells is analyzed and found to contain 120.99 g of solution of 0.19404 wt % KCl. Calculate the transference number for K⁺.

12-4 A 0.01 m solution of HCl is electrolyzed in a Hittorf cell with a Pt/H₂ anode and a silver/silver chloride cathode. Each compartment contains 50 cm³ of solution. A current of 2 mA is passed through the cell for 1 hr. Calculate the final concentrations of the various species present in the anode and cathode compartments.

12-5 A famous early experiment by Washburn attempted to find the amount of water of hydration carried by ions. The procedure was to carry out an electrolysis in a Hittorf cell with solutions containing a sugar. The sugar, being neutral, was assumed not to move during the electrolysis (an assumption later found not to be quite correct). In one experiment a solution contained 4.939 wt % of LiCl and 4.73 % of a sugar and an amount of electricity corresponding to 0.0464 F was passed through the cell with a silver/silver chloride cathode and a silver anode. After the electrolysis the cathode solution weighed 81.47 g and contained 5.565 % of LiCl and 4.619 % of sugar, while the anode solution weighed 104.4 g and contained 4.440 % of LiCl and 4.806 % of sugar. Find n as a function of nₐ, the number of water molecules bound per cation and per anion, respectively.

12-6 By means of a logarithmic diagram, find the pH of a solution 0.1 M in ammonia and 0.1 M in KHCO₃.

12-7 The acid dissociation constants for monochloroacetic acid (HM) and acetic acid (HAC) are 1.55 × 10⁻³ and 1.8 × 10⁻⁵, respectively.
(a) Make a semilogarithmic plot of the fractions of HM, M⁺, HAc, and Ac⁻ versus pH.
(b) Using this plot, calculate the pH of a solution 0.01 m in HM (total concentration of acid) and 0.02 m in HAc (again total concentration of acid).
(c) Calculate the pH if 0.01 mole of solid NaOH is added to a liter of the solution in (b).
(d) Calculate the pH if 0.02 mole of solid NaOH is added to a liter of the solution in (b).

12-8 The acids HA and HB have pKₐ values of 4.5 and 7.5; pKₜ is 14.0. Find by means of a logarithmic diagram the pH for solutions that have been mixed so as to contain: (a) 10 mM of HA; (b) 10 mM of HA, 5 mM of HB; (c) 10 mM of Naₐ, 5 mM of HB; (d) 10 mM of Naₐ, 5 mM of NaB, 5 mM of NaOH; (e) 5 mM of HB, 10 mM of HA, 2 mM of HCl. (These are formalities.)

12-9 Calculate the pH of a 0.025 M solution of Na₂HPO₄.

12-10 Solution A contains 9.08 g liter⁻¹ of KH₂PO₄; solution B contains 11.88 g liter⁻¹ of Na₂HPO₄ · 2H₂O. Calculate the pH of the solution that results when 95 cm³ of A are mixed with 5 cm³ of B.

12-11 Ethylenediaminetetraacetic acid is a tetrabasic acid H₄Y. The successive pK's are 2.00, 2.67, 6.16, and 10.26. It forms a stable complex with Co ion, CoY²⁻ + Y⁴⁻ = CoY₄²⁻. For this complex formation K = 10¹⁴; Ba²⁺ forms a similar complex with K = 10⁷. Both CoY²⁻ and BaY²⁻ are the anions of strong acids, that is, one does not get H₂CoY and so on in acid solution (although the solids are known). Calculate and plot the logarithmic diagram for the various forms of ethylenediaminetetraacetic acid for the pH range from 0 to 7, and the similar diagram for the distribution of cobalt and barium between CoY²⁻ and BaY²⁻ as a function of pH, C, where C is the concentration of Y⁻. Calculate the percentage of complexing of CoY⁻ and BaY⁻ in solutions of (a) 0.01 f Co(NO₃)₉, 0.01 f Ba(NO₃)₉, 0.1 f Na₂H₄Y; (b) the same as (a) but also 0.1 f NaOH. Also give the pH's of these solutions.

12-12 Derive Eq. (12-98). Calculate the osmotic pressure at 25°C if C = 0.01 m and (N⁺) = 0.1 m, neglecting activity coefficient effects.