

## Chapter 16 Electrolyte Solutions

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### Framework of the Chapter

This chapter provides a comprehensive and multi-level discussion for the equilibrium, transport and reaction-rate properties of the electrolyte solutions, and all the three methods used for obtaining these properties, experimental, semi-empirical and theoretical. In discussing the theoretical methods, the transition level from microscopic to macroscopic is involved. This Chapter is divided into three parts:

**I. Equilibrium Properties of Electrolyte Solutions** The emphasis is put on the activities and the corresponding theories.

(1) **Diversity of Activities of Electrolyte Solutions** An electrolyte solution normally contains undissociated electrolyte, cations, anions, and solvents, their activities should be defined separately, leading to the diversity of the activities such as the electrolyte activity, the ionic activity and the solvent activity. Besides, due to some practical reasons, the mean ionic activity and the osmotic factor are introduced (16.2).

(2) **Debye-Hückel Theory and Semi-Empirical Methods** A brief derivation based on the statistical mechanics and the electrostatics is provided. The semi-empirical methods developed are also introduced (16.3).

(3) **Applications** For heterogeneous systems containing electrolyte solutions, in applications, the phase equilibria, the chemical equilibria and the electro-neutrality principle should be considered jointly (16.4).

**II. Transport Properties of Electrolyte Solutions** The electric conductance and the diffusion are mainly discussed.

(1) **Mechanism of Electric Conductance of Electrolyte Solutions** Different from the metals, the electric conductance of the electrolyte solutions relies mainly on the ionic migration and the electrode reaction, the former is characterized by the mobility, the transference number is its relative measure,

the latter will be discussed in the next Chapter. Various transport properties are all determined by the mobility (16.6).

(2) **Molar Electric Conductivity and Ionic Molar Electric Conductivity** They are a measure of the conductive ability and have definite relations with the mobility (16.7). The applications of their measurements to the dissociation equilibria are illustrated by examples (16.8).

(3) **Diffusion Coefficients of Electrolytes** Diffusion is determined by the ionic migration and restricted by the electro neutrality. The diffusion coefficients have definite relations with the mobilities and the ionic molar electric conductivities (16.9).

(4) **Theoretical and Semi-Empirical Methods** A brief introduction is provided (16.10).

### **III. Reaction-Rate Properties of Electrolyte Solutions**

**Ionic Reactions in Solution** The effect of the relative permittivity and the ionic strength on the reaction rate is discussed (16.11).

## **16.1 Introduction**

**Electrolytes and Electrolyte Solutions** A solution in which the solute is completely or partially dissociated into ions after dissolving in solvent is called an electrolyte solution. The solute is called the electrolyte. Two categories can be distinguished for electrolyte solutions:

**First-Kind Electrolyte Solutions** In this category, the solute dissociates completely, neither the undissociated solute molecules nor the associates of cation and anion are found in the solution. The aqueous solutions of the halides of the alkaline, alkaline-earth and transition metals, as well as some perchlorates belong to this category.

**Second-Kind Electrolyte Solutions** In this category, the solute dissociates partially. The undissociated solute molecules with atoms combined by covalent bonds such as the aqueous solutions of the strong acids, weak acids and weak bases, or the ionic pairs formed by the association of cation and anion such as the aqueous solutions of the sulphates of bivalent metals and the strong bases, are found in the solution.

**Strong Electrolytes and Weak Electrolytes** Usually, the electrolytes in the solutions of the second kind in which the undissociated solute molecules can be found in dilute concentration such as the acetic acid, ammonia and sulfurous acid, are called the weak electrolytes. Others are called the strong electrolytes.

**Significance of Studies of Electrolyte Solutions** Many

manufacturing processes and nature phenomena involve electrolyte solutions. Acids, bases and salts are raw materials that are mostly often met. Seawater, salt-lake water and brine are also electrolyte solutions with various concentrations. The biochemical processes carried out in living organs concern mostly with electrolytes, for example, the liquid in cells is usually an aqueous solution containing  $K^+$  and  $Na^+$  ions. Besides water, the applications of the non-aqueous solvents have special significance, such as alcohols, carboxylic acids, ketones, as well as benzene, DMF and so on. For example, the non-aqueous titration can be used to estimate the quantities of substances with very small dissociation constant such as weak acids and weak bases.

**Properties of Electrolyte Solutions** The general principles concerning equilibria and rates have been discussed in the Part I and Part II of this book. However, electrolyte solutions have many special properties different from ordinary substances. In this Chapter, we will introduce: (1) **Equilibrium Properties.** The activities of the electrolyte solutions are mainly determined by the electrostatic interactions among ions and have many peculiarities. (2) **Transport Properties.** The most prominent is the ionic migration in the electric field. Correspondingly, a series of important properties are exhibited such as the mobility, the transference number and the molar electric conductance. Even without electric field, for the diffusion of ions, besides being motivated by the concentration gradient, it is also restricted by the demand of electro neutrality in solution. (3) **Reaction Properties.** The rate constants of ionic reactions are also closely related with the ionic charges.

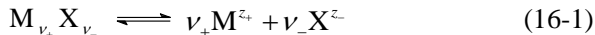
## I. Equilibrium Properties of Electrolyte Solutions

### 16.2 Activities of Electrolyte Solutions

#### 1. Activities of Various Components in Electrolyte Solutions

**Components** The electrolyte solutions of the first kind in strict sense actually do not exist. Besides solvent and ions, there should be at least a few undissociated electrolyte molecules or ionic pairs. Therefore, generally

speaking, all electrolyte solutions are the second-kind. Suppose the electrolyte is  $M_{\nu_+}X_{\nu_-}$ , which dissociates in solution in terms of the following equation,



where  $z_+$ (positive) and  $z_-$ (negative) are the **ionic charge numbers** (the ratio of the ionic charge to the elementary charge) for the cation  $M^{z_+}$  and anion  $X^{z_-}$  respectively,  $\nu_+$  and  $\nu_-$  are the corresponding stoichiometry numbers. According to the electro neutrality,

$$\nu_+z_+ + \nu_-z_- = 0 \quad (16-2)$$

For example,  $H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$ ,  $\nu_+=2$ ,  $\nu_-=1$ ,  $z_+=+1$ ,  $z_-=-2$ , as symbols of ions, the latter two are represented by  $1+$  or  $+$  and  $2-$  respectively. There are four components in the solution, the solvent, the undissociated electrolyte, the cation and anion, represented by A, Bu,  $+$  and  $-$  respectively.

**Chemical Potentials of Components** Chemical potentials of the solvent, undissociated electrolyte, cation and anion are  $\mu_A$ ,  $\mu_{Bu}$ ,  $\mu_+$  and  $\mu_-$  respectively. In terms of the criterion of chemical equilibrium, Eq.(3-58),

$$\mu_{Bu} = \nu_+\mu_+ + \nu_-\mu_- \quad (16-3)$$

**Activities of Components** As accepted through common practice: The selection I is adopted for the solvent activity,  $\mu_A^*$  is the chemical potential of the reference state in terms of the selection I (the pure solvent at the system temperature and pressure). The selection III is adopted for the activities of the undissociated electrolyte, cation and anion,  $\mu_{b,Bu}^{**}$ ,  $\mu_{b,+}^{**}$ ,  $\mu_{b,-}^{**}$  are the chemical potentials of the corresponding reference states in terms of the selection III (the solute in an ideal dilute solution with  $b^\ominus = 1\text{mol}\cdot\text{kg}^{-1}$ ). According to Eqs.(3-99, 3-125), the chemical potentials of various components can be expressed by activities as follows:

$$\mu_A = \mu_A^* + RT \ln a_A \quad (16-4)$$

$$\mu_{Bu} = \mu_{b,Bu}^{**} + RT \ln a_{b,Bu} \quad (16-5)$$

$$\mu_+ = \mu_{b,+}^{**} + RT \ln a_{b,+}, \quad \mu_- = \mu_{b,-}^{**} + RT \ln a_{b,-} \quad (16-6)$$

According to Eqs.(3-102, 3-126), relations between the activities and the corresponding activity factors are respectively:

$$a_A = x_A \gamma_A \quad (16-7)$$

$$a_{b,\text{Bu}} = (b_{\text{Bu}}/b^\circ) \gamma_{b,\text{Bu}} \quad (16-8)$$

$$a_{b,+} = (b_+/b^\circ) \gamma_{b,+}, \quad a_{b,-} = (b_-/b^\circ) \gamma_{b,-} \quad (16-9)$$

where  $x_A$  is the mole fraction of the solvent,  $b_{\text{Bu}}$ ,  $b_+$  and  $b_-$  are the molarities of the undissociated electrolyte, cation and anion, respectively. An alternative is the adoption of  $a_{c,\text{Bu}}$ ,  $a_{c,+}$  and  $a_{c,-}$  in terms of the selection IV.

**Standard Equilibrium Constant of Dissociation Equilibrium** In terms of the discussion in 5.5, for Eq.(16-1), we can write:

$$K^\circ \approx K_a = \frac{a_{b,+}^{v_+} a_{b,-}^{v_-}}{a_{b,\text{Bu}}} \quad (16-10)$$

## 2. A Phenomenological Approach

In this approach, the electrolyte is regarded as a whole whether it dissociates or not.

**Chemical Potential  $\mu_B$  of Electrolyte as a Whole** It can be proved that (the prove is omitted here),

$$\mu_B = \mu_{\text{Bu}} = v_+ \mu_+ + v_- \mu_- \quad (16-11)$$

The chemical potential  $\mu_B$  of the electrolyte as a whole equals that of the undissociated electrolyte  $\mu_{\text{Bu}}$ , also equals the sum of the products of the ionic chemical potential and the corresponding stoichiometry number of the cation and the anion,  $v_+ \mu_+$  and  $v_- \mu_-$ .

**Activity  $a_B$  of Electrolyte as a Whole** It is simply called the electrolyte activity. The relation between it and  $\mu_B$  is

$$\mu_B = \mu_B^{**} + RT \ln a_B \quad (16-12)$$

Since the electrolyte as a whole includes both the undissociated and the dissociated ones, the reference state should be specially chosen. As a common practice, the reference state is selected in the same way as that of the undissociated electrolyte, i.e., the solute of an ideal dilute solution of an undissociated electrolyte with a molarity of  $b^\circ = 1 \text{ mol} \cdot \text{kg}^{-1}$ . With this choice,  $\mu_B^{**} = \mu_{b,\text{Bu}}^{**}$ , the activity  $a_B$  is also the same as that of the undissociated electrolyte  $a_{b,\text{Bu}}$ . In terms of Eq.(16-10),

$$a_B = a_{b,\text{Bu}} = \frac{a_{b,+}^{v_+} a_{b,-}^{v_-}}{K_a} \quad (16-13)$$

## 3. Mean Ionic Activity

In electrolyte solutions, cations and anions always exist

simultaneously, it is difficult to determine the activity of a single kind of ions. In practice, the mean ionic activity is adopted with a symbol of  $a_{\pm}$  defined by

$$a_{\pm} \stackrel{\text{def}}{=} (a_{b,+}^{v_+} a_{b,-}^{v_-})^{1/\nu} \quad (16-14)$$

where  $\nu = \nu_+ + \nu_-$ . Define the **mean ionic molarity**  $b_{\pm}$  and the **mean ionic activity factor**  $\gamma_{\pm}$ ,

$$b_{\pm} \stackrel{\text{def}}{=} (b_+^{v_+} b_-^{v_-})^{1/\nu} \quad (16-15)$$

$$\gamma_{\pm} \stackrel{\text{def}}{=} (\gamma_+^{v_+} \gamma_-^{v_-})^{1/\nu} \quad (16-16)$$

Substituting Eq.(16-9) into Eq.(16-14), using Eqs.(16-15, 16-16), we have

$$a_{\pm} = (b_{\pm}/b^{\circ}) \gamma_{\pm} \quad (16-17)$$

Substitution of Eqs.(16-13, 16-14) into Eq.(16-10) yields  $K_a$  expressed by  $a_{\pm}$ ,

$$K_a = \frac{a_{\pm}^{\nu}}{a_B} = \frac{a_{\pm}^{\nu}}{a_{b,\text{Bu}}} \quad (16-18)$$

$$a_B = a_{b,\text{Bu}} = \frac{a_{\pm}^{\nu}}{K_a} \quad (16-19)$$

#### 4. Special Common Practice for First-Kind Electrolyte Solutions

Although theoretically the undissociated electrolyte molecules always exist, if the degree of dissociation is too large to detect practically the undissociated electrolyte, the solution can be regarded as a first-kind electrolyte solution. On this occasion, talking about the chemical potential or the activity of an undissociated electrolyte is actually meaningless. The following common practice is adopted:

(1) **Activities of Solvent and Ions** They are still defined by Eqs.(16-4,16-6).

(2) **Activity of Electrolyte as a Whole** Eqs.(16-11, 16-12) are still valid,

$$\mu_B = \mu_B^{**} + RT \ln a_B = \nu_+ \mu_+ + \nu_- \mu_- \quad (16-20)$$

The reference state should be specially chosen as usual. Since the undissociated electrolyte does not exist, as a common practice, the solute of an ideal dilute solution of a completely dissociated electrolyte with a molarity of  $b^{\circ} = 1 \text{ mol} \cdot \text{kg}^{-1}$  is selected as the reference state, which contains  $\nu_+$   $\text{mol} \cdot \text{kg}^{-1}$  of cation  $M^{z_+}$  and  $\nu_-$   $\text{mol} \cdot \text{kg}^{-1}$  of anion  $X^{z_-}$ .

Therefore,

$$\mu_B^{**} = \nu_+ \mu_{b,+}^{**} + \nu_- \mu_{b,-}^{**} \quad (16-21)$$

Substitution of  $\mu_+$ ,  $\mu_-$  of Eq.(16-6) and Eq.(16-21) into Eq.(16-20) yields

$$a_B = a_{b,+}^{\nu_+} a_{b,-}^{\nu_-} = a_{\pm}^{\nu} \quad (16-22)$$

Comparing with Eq.(16-13),  $a_B = a_{b,+}^{\nu_+} a_{b,-}^{\nu_-} / K_a$ , indicates that this practice is equivalent to the artificial designation of 1 for the  $K_a$ .

Since the electrolyte dissociates completely for the first-kind electrolyte solutions, we have

$$b_+ = \nu_+ b \quad , \quad b_- = \nu_- b \quad (16-23)$$

Table 16-1 Relations between  $b_{\pm}$ ,  $a_{\pm}$  and  $b$  for electrolyte solutions of various valence types

Type	Electrolyte	$b_{\pm} = b(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu}$	$a_{\pm} = (b_{\pm}/b^{\Theta}) \gamma_{\pm}$	$a_{\pm}^{\nu}$
1-1	NaCl	$b$	$(b/b^{\Theta}) \gamma_{\pm}$	$(b/b^{\Theta})^2 \gamma_{\pm}^2$
2-1	CaCl <sub>2</sub>	$4^{1/3} b$	$4^{1/3} (b/b^{\Theta}) \gamma_{\pm}$	$4(b/b^{\Theta})^3 \gamma_{\pm}^3$
2-2	CuSO <sub>4</sub>	$b$	$(b/b^{\Theta}) \gamma_{\pm}$	$(b/b^{\Theta})^2 \gamma_{\pm}^2$
3-1	LaCl <sub>3</sub>	$27^{1/4} b$	$27^{1/4} (b/b^{\Theta}) \gamma_{\pm}$	$27(b/b^{\Theta})^4 \gamma_{\pm}^4$

where  $b$  is the molarity of the electrolyte as a whole, correspondingly, Eqs.(16-15, 16-17) can be expressed by  $b$  as

$$b_{\pm} = b(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \quad , \quad a_{\pm} = (b/b^{\Theta}) (\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/\nu} \gamma_{\pm} \quad (16-24)$$

Table 16-1 gives relations between  $b_{\pm}$ ,  $a_{\pm}$  and  $b$  for the first-kind electrolyte solutions of various valence types.

### 5. Osmotic Factor of Solvent

When the concentration is not too high, the solvent activity factor is not too far from 1. For example, an aqueous KCl solution of  $b=2\text{mol}\cdot\text{kg}^{-1}$  at  $25^{\circ}\text{C}$ ,  $\gamma_{b,\pm}=0.573$ , but  $x_A=0.9328$ ,  $a_A=0.9364$ ,  $\gamma_A=1.004$ . To reflect the departure from the ideal more sensitively for the solvent, the osmotic factor is defined with two versions:

**Rational Osmotic Factor  $\phi_x$**  Refer to Eq.(3-132) in 3.12.6,

$$\phi_x \stackrel{\text{def}}{=} \frac{\mu_A - \mu_A^*}{RT \ln x_A} = \frac{\ln a_A}{\ln x_A} = \frac{\ln(x_A \gamma_A)}{\ln x_A} \quad (16-25)$$

**Practical Osmotic Factor  $\phi_b$**  It is defined by the molarity  $b$ ,

$$\phi_b \stackrel{\text{def}}{=} \frac{\mu_A - \mu_A^*}{-RT \nu b M_A} = -\frac{\ln a_A}{\nu b M_A} = -\frac{\ln(x_A \gamma_A)}{\nu b M_A} \quad (16-26)$$

For the aqueous KCl solution above,  $\phi_x=0.945$ ,  $\phi_b=0.912$ , obviously, they are more sensitive than  $\gamma_A$ . In practice,  $\phi_b$  is more often adopted.

**Relation between  $\phi_b$  and  $\phi_x$**  Combining Eqs.(16-25, 16-26), we have

$$\phi_x \ln x_A = -\phi_b \nu b M_A \quad (16-27)$$

When the solution is very dilute, expanding  $\ln x_A$  and taking only the first term,  $\ln x_A = x_A - 1 - (x_A - 1)^2 / 2 + \dots \approx x_A - 1$ . If the solute dissociates completely,  $\nu$  ions are formed by one solute molecule,  $x_A$  can be expressed as

$$x_A = \frac{M_A^{-1}}{M_A^{-1} + \nu b} = \frac{1}{1 + \nu b M_A} \approx 1 - \nu b M_A \quad (16-28)$$

where  $M_A$  is the molar mass of the solvent. Substituting into Eq.(16-27),  $\ln x_A \approx x_A - 1 \approx -\nu b M_A$ ,  $\phi_b \approx \phi_x$ , the two versions of the osmotic factor are consistent. In the case of infinite dilution,  $\phi_b = \phi_x = 1$ .

## 6. Sources of Activity

### Factors and Osmotic Factors

There are three ways, experimental, semi-empirical and theoretical. The latter two will be introduced in the next section.

### Experimental Determinations

There are **electromotive-force method** (referring to Chapter 17), **solubility method** and so on. For the volatile electrolytes such as HCl and HNO<sub>3</sub>, the vapor-liquid-equilibrium method discussed in Chapter 3 can be used. As for  $\phi$ , it can be calculated from  $\gamma_{\pm}$  by using the Gibbs-Duhem equation.

**Examples** Practical osmotic factors and mean activity coefficients of

Table 16-2 Practical osmotic factors and mean activity coefficients of KCl, MgCl<sub>2</sub> solutions at 25°C

$b$ mol · kg <sup>-1</sup>	KCl		MgCl <sub>2</sub>	
	$\phi_b$	$\gamma_{\pm}$	$\phi_b$	$\gamma_{\pm}$
0.1	0.927	0.770	0.861	0.528
0.2	0.913	0.718	0.877	0.488
0.7	0.897	0.626	1.004	0.505
1.2	0.899	0.593	1.184	0.630
2.0	0.912	0.573	1.523	1.051
4.5	0.980	0.583	2.783	8.72

Cited from: Robinson R A, Stokes R H. Electrolyte Solutions. 2nd ed. Butterworth, 1970

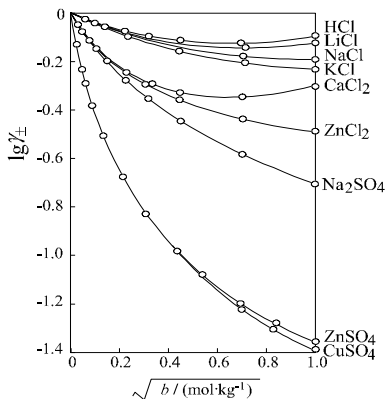


Figure 16-1  $\lg \gamma_{\pm} \sim \sqrt{b}$  curves for electrolyte solutions at 25°C



aqueous KCl and MgCl<sub>2</sub> solutions at 25°C are listed in Table 16-2. The results indicate that  $\gamma_{\pm}$  first depresses then elevates with increasing electrolyte concentration. Figure 16-1 depicts relations of  $\lg \gamma_{\pm}$  with  $\sqrt{b}$  at 25°C for various electrolyte solutions. The results indicate that in the dilute region,  $\gamma_{\pm}$  is mainly determined by the concentration and the valence type of the electrolyte, irrelevant to the nature of the ions. As the concentration increases, the differences among various electrolyte of the same valence type are then gradually prominent.

**Ionic Strength** In 1921, Lewis G N and Randall M proposed the concept of the ionic strength  $I$ ,

$$I \stackrel{\text{def}}{=} \frac{1}{2} \sum_i b_i z_i^2 \quad \text{or} \quad I \stackrel{\text{def}}{=} \frac{1}{2} \sum_i c_i z_i^2 \quad (16-29)$$

For a single first-kind electrolyte solution, due to  $b_i = \nu_i b$ , we can write

$$I = \frac{1}{2} (\nu_+ z_+^2 + \nu_- z_-^2) b \quad (16-30)$$

The equation indicates that  $I$  is proportional to  $b$ . Figure 16-1 gives that  $\lg \gamma_{\pm}$  has a linear relation with  $\sqrt{b}$  approximately in the dilute region with different slopes for different valence types, then departs from the linearity as the concentration further increases. It was found that by replacing  $b$  with  $I$ , an empirical relation exists in the dilute region,

$$\lg \gamma_{\pm} = -B\sqrt{I} \quad (16-31)$$

where  $B$  is a constant at a certain temperature with a unit of (mol·kg<sup>-1</sup>)<sup>-1/2</sup> or (mol·dm<sup>-3</sup>)<sup>-1/2</sup> irrelevant to the valence type. This empirical equation has played an important role in the development of electrolyte-solution theories.

**Activity of a Single Ion** The theoretical methods and computer simulation can provide activities of single ions in principle. Experimentally, because of the ion-selective electrodes, referring to 17.6.6, direct measurements are possible, however, the problem of the liquid-junction potential still remains, referring to 17.2.3, the participation of the theoretical or semi-empirical methods is still needed. For a numerical example: For a HCl solution of  $b_{\text{HCl}}=0.002\text{mol}\cdot\text{kg}^{-1}$ ,  $\gamma_{\pm}$ ,  $\gamma_+$ ,  $\gamma_-$  are 0.962, 0.970 and 0.954 respectively. When  $b_{\text{HCl}}=1.002\text{mol}\cdot\text{kg}^{-1}$ , they are respectively 0.825, 1.201 and 0.567, the discrepancies among the activity factors of single ions and the mean activity factor are serious. (Schneider A C et al. J Solution Chem, 2004, 33(3):257-273.)

**Example 1** Calculate the mean ionic concentration, the mean ionic activity, the electrolyte activity, the solvent activity and activity factor of an aqueous KCl solution of  $b=1.20\text{mol}\cdot\text{kg}^{-1}$  at  $25^\circ\text{C}$ .

**Solution:** For KCl,  $\nu_+=\nu_-=1$ ,  $\nu=2$ . From Table 16-2,  $\gamma_{\pm}=0.593$ ,  $\phi_b=0.899$ . According to Eq.(16-28),

$$x_A = (1 + \nu b M_A)^{-1} = (1 + 2 \times 1.20 \times 0.0180)^{-1} = 0.959, \quad b_{\pm} = b = 1.20\text{mol}\cdot\text{kg}^{-1}$$

$$a_{\pm} = (b_{\pm}/b^{\circ}) \gamma_{\pm} = 1.20 \times 0.593 = 0.712, \quad a_B = a_{\pm}^{\nu} = 0.712^2 = 0.507$$

According to Eq.(16-26),

$$\ln a_A = -\phi_b \nu b M_A = -0.899 \times 2 \times 1.20 \times (18.02 \times 10^{-3}) = -0.0389,$$

$$a_A = 0.962, \quad \gamma_A = a_A/x_A = 0.962/0.959 = 1.003$$

**Example 2** Calculate the mean ionic concentration, the mean ionic activity, the electrolyte activity, the solvent activity and activity factor of an aqueous  $\text{MgCl}_2$  solution of  $b=1.20\text{mol}\cdot\text{kg}^{-1}$  at  $25^\circ\text{C}$ .

**Solution:** For  $\text{MgCl}_2$ ,  $\nu_+=1$ ,  $\nu_-=2$ ,  $\nu=3$ . From Table 16-2,  $\gamma_{\pm}=0.630$ ,  $\phi_b=1.184$ .

$$x_A = (1 + \nu b M_A)^{-1} = (1 + 3 \times 1.20 \times 0.0180)^{-1} = 0.939$$

$$b_{\pm} = (b_+ b_-^2)^{1/3} = [b \cdot (2b)^2]^{1/3} = 4^{1/3} b = 4^{1/3} \times 1.20\text{mol}\cdot\text{kg}^{-1} = 1.905\text{mol}\cdot\text{kg}^{-1}$$

$$a_{\pm} = (b_{\pm}/b^{\circ}) \gamma_{\pm} = 1.905 \times 0.630 = 1.20, \quad a_B = a_{\pm}^{\nu} = 1.20^3 = 1.73$$

$$\ln a_A = -\phi_b \nu b M_A = -1.184 \times 3 \times 1.20 \times (18.02 \times 10^{-3}) = -0.0768, \quad a_A = 0.926$$

$$\gamma_A = a_A/x_A = 0.926/0.939 = 0.986$$

**Example 3** Calculate the ionic strength of the two aqueous solution of the Examples 1 and 2.

**Solution:** According to Eq.(16-30), for the two aqueous solutions,

$$\text{KCl} \quad I = \frac{1}{2} (\nu_+ z_+^2 + \nu_- z_-^2) b = \frac{1}{2} (1 \times 1^2 + 1 \times 1^2) 1.20\text{mol}\cdot\text{kg}^{-1} = 1.20\text{mol}\cdot\text{kg}^{-1}$$

$$\text{MgCl}_2 \quad I = \frac{1}{2} (1 \times 2^2 + 2 \times 1^2) 1.20\text{mol}\cdot\text{kg}^{-1} = 3.60\text{mol}\cdot\text{kg}^{-1}$$

## 16.3 Theories and Semi-Empirical Methods

### 1. Debye-Hückel Theory

Since Arrhenius S presented the ionization theory in 1887, the most important progress is the theory of electrolyte solutions proposed by Debye P J W and Hückel E in 1923 and named after them. The departure of the electrolyte solutions from the ideal dilute solution is solely attributed to the electrostatic attraction forces occurring among the ions by this theory. By applying the principles of the statistical mechanics and the electrostatics, the connections between the macroscopic equilibrium properties and the microscopic electrostatic interactions can be established. The Debye-Hückel theory can be well applied to the very dilute electrolyte solutions in which the electrolyte molecules dissociate completely and without ionic

association.

(1) **Concept of Ionic Atmosphere** In this sub-section, we directly give the final results of the Debye-Hückel theory based on the concept of the ionic atmosphere. Then introduce the clues of the derivation in the next few sub-sections.

Because of the electrostatic interactions among ions, from the point of view of statistical average, the probability of appearance of anions surrounding any one cation is higher than that of cations; the probability of

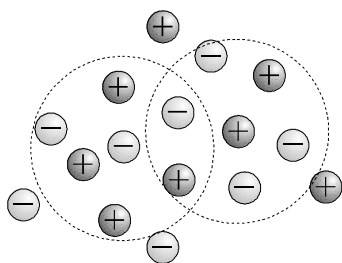


Figure 16-2 Ionic-atmosphere model of Debye and Hückel

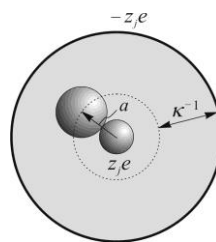


Figure 16-3 Mean effective ionic diameter and the thickness of ionic atmosphere

appearance of cations surrounding any one anion is higher than that of anions. On the other hand, the whole solution should be electro neutral. Therefore, it is reasonable to consider that every ion in the solution is surrounded by an ionic atmosphere with opposite charge, and the absolute quantity of the charge equals that of the central ion. Every ion plays the role of the central ion of the ionic atmosphere, also plays the role of the members of the ionic atmospheres of other ions, referring to Figure 16-2. The ionic atmosphere is not fixed, it renews continuously due to the thermal movement of ions.

**Electrostatic Interaction Energy between the Central Ion and the Ionic Atmosphere** Suppose that the charge number of the central ion  $j$  is  $z_j$ , the limit or the closest distance other ions can approach this central ion is  $a$  which is called the **mean effective ionic diameter**. The Debye-Hückel theory gives by derivation that the electric potential exerted by the ionic atmosphere at the central ion is equivalent to the potential  $\phi$  formed by a spherical shell of opposite charges at a distance of  $a + \kappa^{-1}$  with a quantity of

$-z_j e$ , referring to Figure 16-3.  $\kappa$  is a function of the ionic strength and  $\kappa^{-1}$  can be considered as the thickness of the ionic atmosphere. According to the principle of the electrostatics, this potential  $\phi$  and the corresponding electrostatic interaction energy  $E$  can be written respectively as:

$$\phi = -\frac{z_j e}{4\pi\epsilon(a + \kappa^{-1})} \quad (16-32)$$

$$E = \frac{1}{2} z_j e \phi = -\frac{z_j^2 e^2}{8\pi\epsilon(a + \kappa^{-1})} \quad (16-33)$$

where  $\epsilon$  is the **permittivity**,  $\epsilon = \epsilon_r \epsilon_0$ ,  $\epsilon_r$  is the **relative permittivity**,  $\epsilon_0$  is the **permittivity of vacuum**,  $4\pi\epsilon_0 = 1.11265 \times 10^{-10} \text{C}^2 \cdot \text{N}^{-1} \cdot \text{m}^{-2}$ .

**Ionic Activity Factor** The electrostatic interaction energy  $E$  of Eq.(16-33) is just the reason causing the departure of the electrolyte solutions from the ideal dilute solution. It equals the difference between the chemical potential of an ion in the electrolyte solution and that in the ideal dilute solution (isol), in the latter, interactions among ions are absent,

$$\mu_j - \mu_j(\text{isol}) = LE = -\frac{Lz_j^2 e^2}{8\pi\epsilon(a + \kappa^{-1})} \quad (16-34)$$

where  $\mu_j - \mu_j(\text{isol}) = RT \ln \gamma_j$ . Because the solution studied is very dilute, the difference between the activity factors in terms of the second, the third and the fourth selections can be neglected, the ionic activity factor can then be obtained theoretically,

$$\ln \gamma_j = -\frac{z_j^2 e^2}{8\pi\epsilon kT(a + \kappa^{-1})} \quad (16-35)$$

In the above results, the derivation of Eq.(16-32) which includes an unknown  $\kappa^{-1}$  is remained. Then the following we introduce the clues of the derivation and the expression for the thickness of the ionic atmosphere  $\kappa^{-1}$ .

## (2) Ions in Ionic Atmosphere Observe Boltzmann Distribution

For an element apart from the central ion  $j$  with a distance  $r$ , referring to Figure 16-4, the electric potential  $\psi(r)$  at this position is composed of that created by the central ion,  $z_j e / 4\pi\epsilon r$ , and that formed by the ionic atmosphere,  $\phi(r)$ ,

$$\psi(r) = \frac{z_j e}{4\pi\epsilon r} + \phi(r) \quad (16-36)$$

Because of the effect of  $\psi(r)$ , an ion of a kind of  $i$  with a charge number of  $z_i$  possesses a potential energy  $z_i e \psi(r)$ . At different distance apart from  $j$ , the potential energy is different leading to the different probability of appearance of ions. According to the Boltzmann distribution, Eq.(12-35), the number density  $C_i$  of ions of the kind  $i$  (number of ions  $i$  in unit volume) at the distance  $r$  should be:

$$C_i = C_{i0} \exp\left(-\frac{z_i e \psi(r)}{kT}\right) \quad (16-37)$$

where  $C_{i0}$  is the number density when the potential energy is zero ( $r=\infty$ ). It is the average number density of the ions  $i$ . The charge density  $\rho(r)$  at  $r$  can be obtained by summing up the charges of various kinds of ions,

$$\rho(r) = \sum_i C_i z_i e = \sum_i C_{i0} z_i e \exp\left(-\frac{z_i e \psi(r)}{kT}\right) \quad (16-38)$$

However, this equation can not be solely used to solve  $\psi(r)$ , another independent equation connecting  $\rho(r)$  and  $\psi(r)$  is needed.

**(3) Poisson Equation Should Be Observed between Charge Density and Electric Potential According to Electrostatics** The equation is:

$$\frac{1}{r} \frac{d^2 [r \psi(r)]}{dr^2} = -\frac{\rho(r)}{\epsilon} \quad (16-39)$$

Coupled this Poisson equation with Eq.(16-38), a differential equation of  $\psi(r)$  is obtained which can be used to solve  $\psi(r)$  in principle, and further to obtain  $\phi(r)$  by Eq.(16-36). (Details are neglected.)

Due to the fact that other ions can not enter the region of  $r < a$ , the potential in this region is a constant  $\phi(a)$ . By substituting  $r=a$  into  $\phi(r)$ , finally we obtain Eq.(16-32),  $\phi = \phi(a) = -z_j e / 4\pi\epsilon(a + \kappa^{-1})$ , and  $\kappa$  is expressed as:

$$\kappa = \left( \sum_i \frac{C_{i0} z_i^2 e^2}{\epsilon kT} \right)^{1/2} = \left( \frac{2e^2 L \rho_s I}{\epsilon kT} \right)^{1/2} \quad (16-40)$$

where  $\rho_s$  is the solvent density (strictly, it should be the solution density, for dilute solutions, this is a good approximation),  $I$  is the ionic strength defined

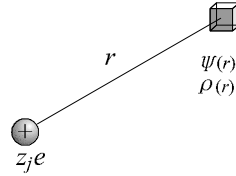


Figure 16-4 Potential at  $r$  from the central ion

by Eq.(16-29),  $I = \sum_i b_i z_i^2 / 2$ .

(4) **Debye-Hückel Equation of Activity Factor** Substitution of Eq.(16-40) into Eq.(16-35) yields

$$\ln \gamma_j = - \frac{A z_j^2 \sqrt{I}}{1 + B a \sqrt{I}} \quad (16-41)$$

$$\text{with } A = \frac{e^3 L^{1/2} \rho_s^{1/2}}{4\pi\sqrt{2}(\varepsilon kT)^{3/2}},$$

$$B = \left( \frac{2e^2 L \rho_s}{\varepsilon kT} \right)^{1/2} \quad (16-42)$$

If the solvent is water, at 25°C,  $\varepsilon=78.54$ ,  $\rho_s=997.07\text{kg}\cdot\text{m}^{-3}$ ,

$$A=1.1709\text{mol}^{-1/2}\cdot\text{kg}^{1/2},$$

$$B=0.32816\times 10^{10}\text{mol}^{-1/2}\cdot\text{kg}^{1/2}\cdot\text{m}^{-1}$$

Eq.(16-41) is the Debye-Hückel activity-factor equation. Correspondingly, the mean ionic activity factor is:

$$\ln \gamma_{\pm} = \frac{A z_+ z_- \sqrt{I}}{1 + B a \sqrt{I}} \quad (16-43)$$

If the solution is very dilute,  $Ba\sqrt{I}$  in the denominator can be omitted, we have the **Debye-Hückel limiting law**,

$$\ln \gamma_{\pm} = A z_+ z_- \sqrt{I} \quad (16-44)$$

Using the Gibbs-Duhem equation, the corresponding expression for the practical osmotic factor for the solvent can be derived as:

$$\phi_b = 1 + \frac{1}{3} A z_+ z_- \sqrt{I} \quad (16-45)$$

**Example** Figure 16-5 shows the variation of the mean ionic activity factor of an aqueous NaCl solution with the ionic strength at 25°C. The results indicate that in the dilute region the predicted  $\gamma_{\pm}$  by the Debye-Hückel theory is well consistent with the experimental data. The concentration range that the theory can apply by using Eq.(16-43) is wider than that by using the limiting law, Eq.(16-44). However, as the concentration further increases, the departure is more and more serious.

## 2. Further Development of the Theories

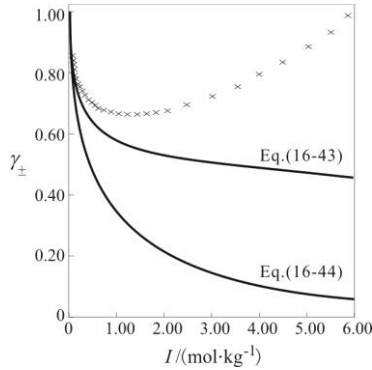
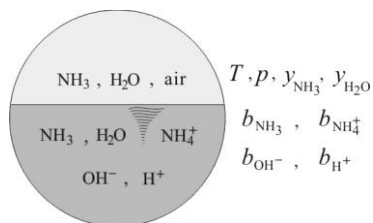


Figure 16-5 Variation of  $\gamma_{\pm}$  with  $I$  for aqueous NaCl solution at 25°C.  
×-experiment data,  $a = 0.45 \times 10^{-9}\text{m}$

Stokes R H and Robinson R A proposed an **ionic hydration theory** by introducing the **solvation number**. They applied the Debye-Hückel theory to the solvated ions, the prediction of the activity factors is notably improved, the concentration range of application for the 1-1 type electrolyte solutions has extended to as high as  $5 \sim 6 \text{ mol}\cdot\text{kg}^{-1}$ . Besides the improvements of the Debye-Hückel theory, another kind of very prosperous theory based on the integral-equation theory of the statistical mechanics has been proposed, among them, the **mean spherical approximation theory** developed since 1970s by Blum L is the focus of people's attention.

Figure16-6  $\text{NH}_3\text{-H}_2\text{O}$  equilibrium

### 3. Semi-Empirical Methods

Many semi-empirical methods have been developed based on the Debye- Hückel theory and widely used in engineering. The electrostatic interactions among ions considered in the Debye-Hückel theory are long-range interactions. The method developed by Pitzer K S in 1970s takes into account the short-range interactions among two and three different ions, has very good functions for predicting the activity factors and the osmotic factors.

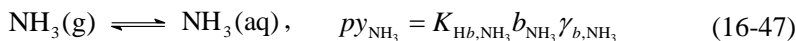
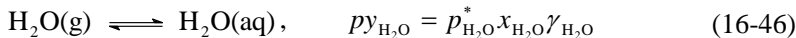
## 16.4 Applications

**Example** To elucidate the peculiarities in applications for the equilibrium properties of electrolyte solutions, take the absorption of ammonia in gas phase by water for example, referring to Figure 16-6. This example seems simple but shows a certain complexities because  $\text{NH}_3$  dissociates in water. As is shown in the Figure, altogether there are eight variables involved:  $T$  and  $p$ ,  $y_{\text{NH}_3}$  and  $y_{\text{H}_2\text{O}}$  of the gas phase,  $b_{\text{NH}_3}$ ,  $b_{\text{NH}_4^+}$ ,  $b_{\text{OH}^-}$  and  $b_{\text{H}^+}$  of the liquid phase. The questions are: How many independent variables are there? Then, how are those dependent variables calculated?

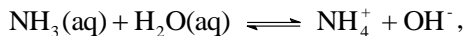
The following equilibrium relations and special independent relation

are involved: For simplicity, the gaseous non-ideality is neglected.

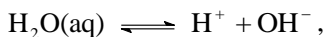
**(1) Phase Equilibria:**



**(2) Chemical Equilibria:**



$$K_{a1} = \frac{a_{b, \text{NH}_4^+} a_{b, \text{OH}^-}}{a_{b, \text{NH}_3} a_{\text{H}_2\text{O}}} = \frac{(b_{\text{NH}_4^+}/b^\circ) \gamma_{b, \text{NH}_4^+} (b_{\text{OH}^-}/b^\circ) \gamma_{b, \text{OH}^-}}{(b_{\text{NH}_3}/b^\circ) \gamma_{b, \text{NH}_3} \cdot x_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \quad (16-48)$$



$$K_{a2} = \frac{a_{b, \text{H}^+} a_{b, \text{OH}^-}}{a_{\text{H}_2\text{O}}} = \frac{(b_{\text{H}^+}/b^\circ) \gamma_{b, \text{H}^+} (b_{\text{OH}^-}/b^\circ) \gamma_{b, \text{OH}^-}}{x_{\text{H}_2\text{O}} \gamma_{\text{H}_2\text{O}}} \quad (16-49)$$

$$(3) \text{ Electro Neutrality: } b_{\text{NH}_4^+} + b_{\text{H}^+} = b_{\text{OH}^-} \quad (16-50)$$

**Number of Independent Variables** According to the phase rule,  $f = K - \pi + 2 - R - R'$ . For this system, there are: Six components,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , air (regarded as a component),  $\text{NH}_4^+$ ,  $\text{OH}^-$  and  $\text{H}^+$ ,  $K=6$ . Two phases, gas and liquid,  $\pi=2$ . Two chemical reactions,  $R=2$ . One special independent relation, the electro neutrality,  $R'=1$ . Therefore,  $f = 6 - 2 + 2 - 2 - 1 = 3$ , the degree of freedom is 3, there are three independent variables in intensive properties.

**Dependent Variables** Suppose  $T$ ,  $y_{\text{NH}_3}$  and  $y_{\text{H}_2\text{O}}$  are given, to calculate the other five variables,  $p$ ,  $b_{\text{NH}_3}$ ,  $b_{\text{NH}_4^+}$ ,  $b_{\text{OH}^-}$  and  $b_{\text{H}^+}$ , five equations are needed. The above Eqs.(16-46,...,16-50) just provide five equations, the five variables can be solved. This corresponds to a dew-point calculation. In using the five equations, the ionic activity factors  $\gamma_{b, \text{NH}_4^+}$ ,  $\gamma_{b, \text{OH}^-}$ ,  $\gamma_{b, \text{H}^+}$ , and the activity factor of water  $\gamma_{\text{H}_2\text{O}}$  or the osmotic factor, should be provided, for obtaining these factors, those principles, experimental, semi-empirical or theoretical methods introduced above have to be used. The dissociation constant  $K_a$  can be found in handbooks or calculated by using the methods in Chapter 5. As those non-ionic properties such as the activity factor  $\gamma_{b, \text{NH}_3}$  and the Henry's constant  $K_{\text{Hb}, \text{NH}_3}$  of  $\text{NH}_3$ , they have been discussed in Chapters 3 and 4.

## II. Transport Properties of Electrolyte Solutions



## 16.5 Mechanism of Electric Conductance of Electrolyte Solutions

**Two Categories of Conductors** Metals rely on the free electrons to conduct the electricity; they are the **first-kind conductor**. Electrolyte solutions are different; they rely on the ionic migration and the electrode reactions to conduct the electricity, they are the **second-kind conductor**.

**Sketch Example** Take the electrolysis of water for example, referring to a sketch diagram shown in Figure 16-7. For enhancing the conductance, the electrolyte such as KOH is usually added. The concentration of  $H^+$  ions is very small that can be neglected. The whole solution is imaginarily to be divided into three compartments with equal volume, the cathode, intermediate and anode compartments. Figure 16-7(a) shows the situation before the external power is connected to the two electrodes, the same number of  $K^+$  and  $OH^-$  ions exists in each of the three compartments. After the power is connected, because of the electric field,  $K^+$  ions transfer toward the cathode (Fe plate),  $OH^-$  ions transfer toward the anode (Ni plate). The migration speeds toward the two electrodes for cations and anions are generally different, in this example, the migration speed of  $OH^-$  ions is about three time as high as that of the  $K^+$  ions. Therefore, for each one  $K^+$  ion transferring and leaving the anode compartment, three  $OH^-$  ions transfer leaving the cathode compartment simultaneously as shown in Figure 16-7(b). As a result, except the intermediate compartment, the cathode compartment has 4  $K^+$  ions more and the anode compartment has 4  $OH^-$  ions excessive. At the same time, these excessive cations and anions should take part in the electrode reactions on the corresponding electrode surfaces. The reaction on the anode surface is:

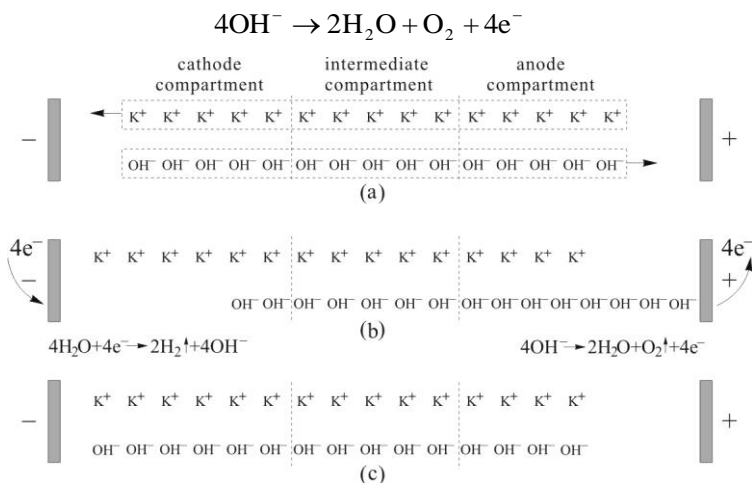
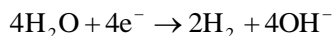


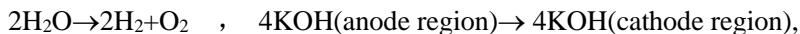
Figure 16-7 Mechanism of electric conduction of electrolyte solutions

That on the anode surface is not  $4\text{K}^+ + 4\text{e}^- \rightarrow 4\text{K}$ , but



$4\text{K}^+$  are then pairing with  $4\text{OH}^-$ . The reason will be clear in the next Chapter.

As is shown in Figure 16-7(c), the total result of the process is:



Meanwhile, the electrolyte solution gains 4 electrons from the cathode and gives 4 electrons to the anode, the whole circuit is then put through.

Although the anode compartment consumes 4  $\text{OH}^-$  ions, that of the cathode creates 4  $\text{OH}^-$  ions, various compartments of the electrolyte solution still keep electro neutrality after the electric conduction, the quantities of ions in the anode and cathode compartments are then changed.

The second-kind conductor conducts the electricity just relying on this mechanism of the ionic migration and the electrode reactions. The wire of the external circuit concerning only the electron flow is the first-kind conductor.

**Faraday's Law** In 1833, Faraday M found by experiment that: When a current is passing through an electrolyte solution, the reaction extent  $\xi$  of the electrode reaction is proportional to the amount of electricity  $Q$  passed and inversely proportional to the **reaction charge number**  $z$  (which is the absolute value of the change of number of electrons in an electrode reaction). This is the Faraday's Law, expressed by equation:

$$\zeta = \frac{n_B - n_{B0}}{\nu_B} = \frac{Q}{zF} \quad (16-51)$$

where  $n_B - n_{B0}$  is the amount of change of a substance B,  $\nu_B$  is the corresponding stoichiometry number.  $F$  is the **Faraday constant**,

$$\begin{aligned} F &\stackrel{\text{def}}{=} Le = 6.0221367 \times 10^{23} \text{ mol}^{-1} \times 1.60217733 \times 10^{-19} \text{ C} \\ &= 96485.309 \text{ C} \cdot \text{mol}^{-1} \end{aligned}$$

Usually,  $96485 \text{ C} \cdot \text{mol}^{-1}$  is adopted for  $F$ . Eq.(16-51) can be used for both the galvanic cell and the electrolysis cell.

**Example** For the electrode reaction  $\frac{1}{2} \text{Cu}^{2+} + \text{e}^- \rightarrow \frac{1}{2} \text{Cu}$ ,  $z=1$ , if Cu is taken as B,  $\nu_B=1/2$ , an electricity of  $2 \times 96485 \text{ C}$  should be passed to obtain 1mol of Cu. If Cu/2 is taken as B,  $\nu_B=1$ , 96485C should be passed to obtain 1mol of Cu/2. As another example, the above electrolysis of water, the total reaction is composed of the two electrode reactions. If  $\text{H}_2\text{O}$  is taken as B,  $\nu_B=-2$ ,  $z=4$ , if 1mol of  $\text{H}_2\text{O}$  is decomposed,  $n_B - n_{B0} = -1 \text{ mol}$ ,  $Q = -1 \text{ mol} \times 4F / (-2)$ , an electricity of  $2 \times 96485 \text{ C}$  should be passed.

## 16.6 Mobility and Transference Number of Ions

### 1. Mobility of Ions

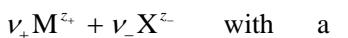
**Definition** As is shown in the above example of the electrolysis of water, three of the 4 electrons transferred in solution are contributed by  $\text{OH}^-$  ions transferring toward the anode, one of them by  $\text{K}^+$  ion toward the cathode. The contributions of different ions are different. To express this difference, a concept of **mobility** with a symbol of  $u_B$  is introduced which is defined by the ionic migration speed in unit electric field intensity, B represents an ion,

$$u_B \stackrel{\text{def}}{=} \nu_B / E \quad (16-52)$$

The units of the migration speed  $\nu_B$ , the electric field intensity  $E$  and  $u_B$  are  $\text{m} \cdot \text{s}^{-1}$ ,  $\text{V} \cdot \text{m}^{-1}$  and  $\text{m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$  respectively. The mobility is a basic parameter characterizing the ionic migration in an electric field. It is a characteristic property of ions. Later we will see that various transport properties of electrolyte solutions such as the transference number, the molar electric conductance, the diffusion coefficient, are all relevant to the mobility.

**Relation between Current and Mobility** Suppose the concentration of an electrolyte  $M_{\nu_+} X_{\nu_-}$  is  $c$ .

The electrolyte is dissociated in terms of Eq.(16-1),  $M_{\nu_+} X_{\nu_-}$



degree of dissociation  $\alpha$ . The solution is filled in a conductance cell; the area of its electrode is  $A_s$ , referring to Figure 16-8. Imagine taking an arbitrary section  $abcd$ . At a time interval of  $\tau$ , the cations on the right side to a distance of  $\nu_+ \tau$  from the section in a volume of  $\nu_+ \tau A_s$  can all transfer through the section to the left side, the amount of them is  $\nu_+ \tau A_s c \alpha \nu_+$ ,

multiplying by  $z_+ F$  is the amount of electricity carried by cations. Meanwhile, the anions on the left side to a distance of  $\nu_- \tau$  from the section in a volume of  $\nu_- \tau A_s$  can all transfer through the section to the right side, the amount of them is  $\nu_- \tau A_s c \alpha \nu_-$ , multiplying by  $|z_-| F$  gives the corresponding amount of electricity carried by anions. These two migrations compose the flow of charges, divided by  $\tau$ , the charge flow in unit time is obtained, i.e., the current. According to Eq.(16-52),  $\nu_+ = u_+ E$ ,  $\nu_- = u_- E$ . The current carried by cations and anions are respectively:

$$I_+ = A_s c \alpha \nu_+ z_+ u_+ E F, \quad I_- = A_s c \alpha \nu_- |z_-| u_- E F \quad (16-53)$$

$$I = I_+ + I_- = A_s c \alpha (\nu_+ z_+ u_+ + \nu_- |z_-| u_-) E F \quad (16-54)$$

where  $z_-$  is negative therefore the absolute value is taken. The current carried by each kind of ions is proportional to its mobility.

**Mobility at Infinite Dilution** The symbol used is  $u^\infty$ . It can be regarded as independent irrelevant to other ions. Table 16-3 lists  $u_+^\infty$  and

Table 16-3 Mobility of ions at 25°C and infinite dilution

Ion	$\frac{u_+^\infty \times 10^8}{\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}}$	Ion	$\frac{u_-^\infty \times 10^8}{\text{m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}}$
H <sup>+</sup>	36.25	OH <sup>-</sup>	20.55
Li <sup>+</sup>	4.01	F <sup>-</sup>	5.74
NH <sub>4</sub> <sup>+</sup>	7.61	Cl <sup>-</sup>	7.92
Na <sup>+</sup>	5.19	Br <sup>-</sup>	8.09
K <sup>+</sup>	7.62	I <sup>-</sup>	7.96
Ag <sup>+</sup>	6.42	NO <sub>3</sub> <sup>-</sup>	7.40
Ca <sup>2+</sup>	6.17	CH <sub>3</sub> COO <sup>-</sup>	4.24
La <sup>3+</sup>	7.21	CO <sub>3</sub> <sup>2-</sup>	7.18

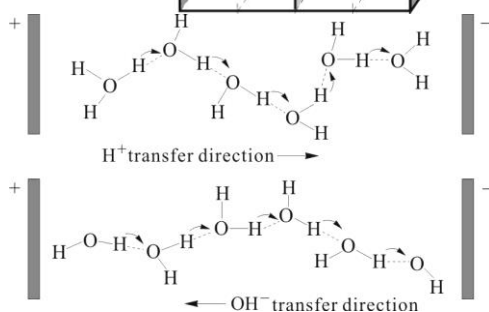


Figure 16-9 Conductance mechanism of  $H_3O^+$  and  $OH^-$

$u_-^\infty$  for some ions at 25°C indicating a notable difference among different ions. For the alkaline metal ions, the ionic radius of  $\text{Li}^+$  is the smallest. The ion then exerts a strong field on the surrounding polar water molecules resulting in a close hydration layer formed which enhances the resistance to the migration of  $\text{Li}^+$  in water. Therefore, although Li is the lightest element in that series,  $u^\infty$  is the smallest. The  $u^\infty$  of  $\text{H}^+$  ion (usually exists in the form of  $\text{H}_3\text{O}^+$ ) and that of  $\text{OH}^-$  ion in aqueous and alcoholic solutions are very large. This is because that there exists a fast proton-transfer chain mechanism in between ions and the surrounding solvent molecules, referring to Figure 16-9.

**Affecting Factors** Ionic mobility depends on the ionic concentration in solution and the temperature. The higher the concentration, the stronger the interaction among ions, the smaller is the mobility. The higher the temperature, the lower the viscosity leading to the smaller resistance to the migration, the larger mobility will be.

## 2. Transference Number

**Definition** Conduction of electricity is carried by cations and anions jointly. To estimate their relative contribution to the electric conductance, the ionic transference number  $t$  is introduced which is defined as the ratio of the current transmitted by a certain ions to the total current,

$$t_+ \stackrel{\text{def}}{=} \frac{I_+}{I_+ + I_-}, \quad t_- \stackrel{\text{def}}{=} \frac{I_-}{I_+ + I_-} \quad (16-55)$$

The sum of the transference numbers of all the cations and anions should be equal to 1. For the above example of the electrolysis of water,  $t_{\text{K}^+} = 1/4$ ,  $t_{\text{OH}^-} = 3/4$ ,  $t_{\text{K}^+} + t_{\text{OH}^-} = 1$ .

**Relation between Transference Number and Mobility** According to Eq.(16-53),

$$t_+ = \frac{u_+}{u_+ + u_-}, \quad t_- = \frac{u_-}{u_+ + u_-} \quad (16-56)$$

## Experimental Determination of Transference Number

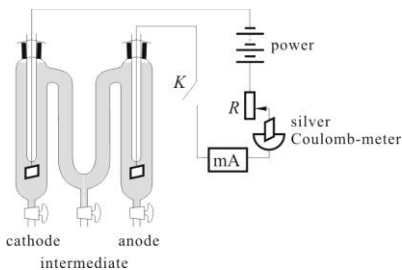


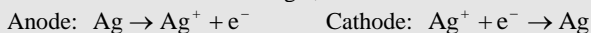
Figure 16-10 Transference number measurement by Hittorf method

(1) **Hittorf Method** Figure 16-10 shows the apparatus of the method named after Hittorf J W, the principle of it can be made clear by referring to the conductance mechanism shown in Figure 16-7. The electrolyte solution with a known concentration is filled in the apparatus. After electrolysis, the samples are taken through the cocks and analyzed. The change of the amount of a certain ion is then obtained. Carry out material balance before and after the electrolysis for a certain ion in the anode and cathode compartments in terms of the following equation,

$$n_{\text{after electrolysis}} = n_{\text{before electrolysis}} + \Delta n_{\text{electrode reaction}} + \Delta n_{\text{transfer}} \quad (16-57)$$

where  $\Delta n_{\text{electrode reaction}}$  takes positive or negative values respectively, for the cases when the ion is created or removed during the reaction, and  $\Delta n_{\text{transfer}}$  takes positive or negative values respectively, for the cases when the ion enters or leaves. According to the Faraday's law, the absolute value of  $\Delta n_{\text{transfer}}$  gives  $|\Delta n_{\text{transfer}}| zF$ , the amount of electricity carried or transmitted by the ion. The total amount of electricity can be calculated by the amount of silver deposited in the cathode of the silver Coulomb meter. The transference numbers of the anion and the cation are then obtained.

**Example** A silver nitrate solution is electrolyzed using the silver electrodes. The initial concentration is  $b=0.04356\text{mol}\cdot\text{kg}^{-1}$ , the electrode reactions are:



Analysis the whole solution in the anode compartment after electrolysis, the result is: it contains  $1.391 \times 10^{-3}\text{mol}$  of  $\text{AgNO}_3$  and  $23.14\text{g}$  of  $\text{H}_2\text{O}$ . The silver deposited in the Coulomb meter is  $0.723 \times 10^{-3}\text{mol}$ . Calculate the transference numbers of  $\text{Ag}^+$  and  $\text{NO}_3^-$ .

**Solution:** (1) Carry out material balance for  $\text{Ag}^+$  ions in the anode compartment. Suppose that the amount of water keeps unchanged during the electrolysis, water can then be set as the reference of the balance.

$$n_{\text{before electrolysis}} = (23.14 \times 0.04356 / 1000) \text{mol} = 1.008 \times 10^{-3} \text{mol}$$

$$n_{\text{after electrolysis}} = 1.391 \times 10^{-3} \text{mol}$$

Because the anode reaction creates  $\text{Ag}^+$ ,  $\Delta n_{\text{electrode reaction}} = +0.723 \times 10^{-3}\text{mol}$ , substituting into Eq.(16-57),

$$\Delta n_{\text{transfer}} = 1.391 \times 10^{-3} \text{mol} - 1.008 \times 10^{-3} \text{mol} - 0.723 \times 10^{-3} \text{mol} = -0.340 \times 10^{-3} \text{mol}$$

$\Delta n_{\text{transfer}}$  is negative, indicating that  $\text{Ag}^+$  transfers and leaves the anode compartment. Its absolute value is proportional to the amount of electricity carried by  $\text{Ag}^+$  ions. On the other hand,  $0.723 \times 10^{-3}\text{mol}$  of  $\text{Ag}$  is deposited in the Coulomb-meter, which is proportional to the total amount of electricity. Therefore,

$$t_{\text{Ag}^+} = 0.340 / 0.723 = 0.470, \quad t_{\text{NO}_3^-} = 1 - 0.470 = 0.530.$$

(2) An alternative way is to carry out material balance for  $\text{NO}_3^-$  ions in the anode compartment. On this occasion,  $\Delta n_{\text{electrode reaction}} = 0$ , because the electrode reaction is

irrelevant to  $\text{NO}_3^-$ . Due to the electro neutrality,  $n_{\text{before electrolysis}}$  and  $n_{\text{after electrolysis}}$  for  $\text{NO}_3^-$  ions are the same as those for  $\text{Ag}^+$  ions. Substituting into Eq.(16-57),

$$\Delta n_{\text{transfer}} = 1.391 \times 10^{-3} \text{ mol} - 1.008 \times 10^{-3} \text{ mol} = 0.383 \times 10^{-3} \text{ mol}$$

$\Delta n_{\text{transfer}}$  is positive, indicating that  $\text{NO}_3^-$  transfers and enters the anode compartment. Its value is proportional to the amount of electricity carried by  $\text{NO}_3^-$  ions. Therefore,

$$t_{\text{NO}_3^-} = 0.383 / 0.723 = 0.530, \quad t_{\text{Ag}^+} = 1 - 0.530 = 0.470$$

The results are the same as those in (1).

**(2) Moving Boundary Method** For determining the transference numbers of ions in an electrolyte solution MX, a solution NX with a higher density than MX solution, containing a common anion  $\text{X}^-$  with MX and  $u_{\text{N}^+} < u_{\text{M}^+}$ , is first placed in a vertical tube, then the MX solution is carefully filled in above the NX with a clear liquid-liquid interface maintained, referring to Figure 16-11. After passing the electricity, cations move toward the cathode (-). Because of the smaller mobility of  $\text{N}^+$  ions, they will not chase the  $\text{M}^+$  ions to blur the interface. At time  $t$ , the interface has moved from  $AB$  to  $CD$ , the volume scanned is  $V$ , an amount of  $c_{\text{M}^+}V$  of  $\text{M}^+$  ions in this volume has passed through  $CD$  before the time  $t$  carrying an electricity of  $z_{\text{M}^+}c_{\text{M}^+}VF$ . If the electric current is  $I$ , the total amount of electricity passed before the time  $t$  is  $It$ . The transference numbers of  $\text{M}^+$  and  $\text{X}^-$  can be calculated as:

$$t_{\text{M}^+} = z_{\text{M}^+}c_{\text{M}^+} \frac{VF}{It}, \quad t_{\text{X}^-} = 1 - t_{\text{M}^+} \quad (16-58)$$

## 16.7 Electric Conductivity

### 1. Electric Conductivity

**Definition** The electric conductivity  $\kappa$  of electrolyte solutions is defined as the reciprocal of the electric resistivity  $\rho$ , the same as that of the first-kind conductors,

$$\kappa \stackrel{\text{def}}{=} 1/\rho$$

$$\rho \stackrel{\text{def}}{=} RA_{\text{s}}/l$$

where  $R$ ,  $A_{\text{s}}$ ,  $l$  are the electric resistance, area

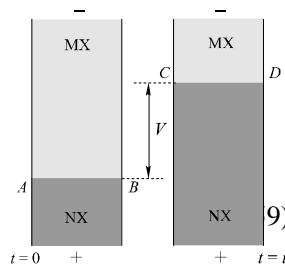


Figure 16-11 Moving Boundary method determining transference number

and length respectively. Because the conductance  $G$  is the reciprocal of the resistance  $R$ ,  $G=1/R$ , therefore, the electric conductivity can also be expressed as:

$$\kappa = Gl/A_s \quad (16-61)$$

This equation indicates that the electric conductivity is the conductance of a solution in unit electrode area and unit distance between electrodes. Because  $G=I/V$ ,  $I$  and  $V$  are the current and the voltage,  $j=I/A_s$ ,  $j$  is the current density,  $E=V/l$ ,  $E$  is the electric field intensity, Eq.(16-61) turns to

$$\kappa = j/E \quad (16-62)$$

Therefore, the electric conductivity can also be defined as the current density in unit electric field intensity. The unit of the electric conductivity  $\kappa$  is  $S \cdot m^{-1}$ ,  $S$  is called siemens equivalent to  $\Omega^{-1}$ .

**Features of Electric Conductance of Electrolyte Solutions** The electric conductivity is a characteristic property of electrolyte solutions. Figure 16-12 shows the variations of electric conductivity with concentration at  $18^\circ C$  for some electrolyte solutions.

(1) The electric conductivities of the strong acids and bases are among the largest, followed are those of the salts. Those of the weak electrolytes such as acetic acid (HAc) are the smallest due to their incomplete dissociation in solution.

(2) Whether they are strong or weak electrolytes, the variation of their electric conductivity  $\kappa$  with the concentration  $c$  has the same trend that  $\kappa$  first increases with increasing  $c$ , after surpassing the maximum, it decreases. This is because that with the increasing concentration, the number of ions in unit volume also rises favoring the conductance, on the other hand, the interactions among ions strengthen weakening the conductive ability.

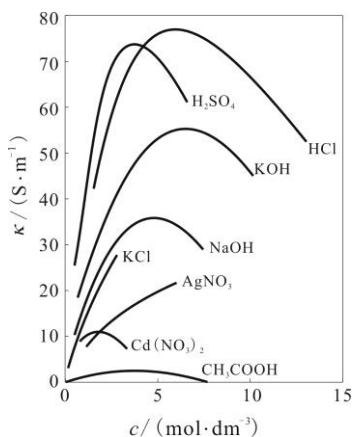


Figure 16-12 relation between electric conductivity and concentration

## 2. Molar Electric Conductivity



**Definition** The molar electric conductivity  $\Lambda_m$  of electrolyte solutions is defined as the electric conductivity in unit concentration,

$$\Lambda_m \stackrel{\text{def}}{=} \kappa / c \quad (16-63)$$

where the unit of concentration  $c$  is  $\text{mol} \cdot \text{m}^{-3}$ , the unit of  $\Lambda_m$  is therefore  $\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ . Suppose a solution of concentration  $c$  with an amount of the electrolyte of  $n$  is placed in a conductance cell shown in Figure 16-13, the volume of the solution is  $c^{-1} \times n$ , the electrode area occupied is  $c^{-1} \times n / l$ ,  $l$  is the distance between the electrodes. According to Eq.(16-61), the conductance of the solution is

$$G = \kappa A_s / l = \kappa c^{-1} n / l^2 = \Lambda_m n / l^2, \quad \Lambda_m = (G/n) l^2,$$

If  $G/n$  is regarded as the molar conductance, it is shown that  $\Lambda_m$  is proportional to the so called molar conductance.

### Specify Elementary Entity

Because the concentration is involved in the molar electric conductivity, the elementary entity of the electrolyte should be specified. For examples,  $\Lambda_m(\text{HCl})$ ,  $\Lambda_m(\text{NaOH})$ ,  $\Lambda_m(\text{CuSO}_4)$ ,  $\Lambda_m(\frac{1}{2}\text{CuSO}_4)$ ,  $\Lambda_m[\text{Al}(\text{NO}_3)_3]$ ,  $\Lambda_m[\frac{1}{3}\text{Al}(\text{NO}_3)_3]$ . Obviously,

$$\Lambda_m(\text{CuSO}_4) = 2 \Lambda_m(\frac{1}{2}\text{CuSO}_4), \quad \Lambda_m[\text{Al}(\text{NO}_3)_3] = 3 \Lambda_m[\frac{1}{3}\text{Al}(\text{NO}_3)_3]$$

For the electrolytes with the valence of an ion higher than 1, if the specified elementary entity is selected to be equivalent to the ion with a valence of 1, for example, the electrolyte  $\text{Al}_2(\text{SO}_4)_3$ , by selecting  $\frac{1}{6}\text{Al}_2(\text{SO}_4)_3$  as the specified entity, the corresponding ions are  $\frac{1}{3}\text{Al}^{3+}$  and  $\frac{1}{2}\text{SO}_4^{2-}$ , this will bring a certain convenience to the calculations. This selection of the molar electric conductivity corresponds to adopting the **equivalent conductance** which was accustomed to being used in the past.

**Features of Molar Electric Conductance** Figure 16-14 shows the

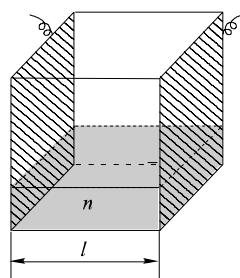


Figure 16-13 Conductance cell

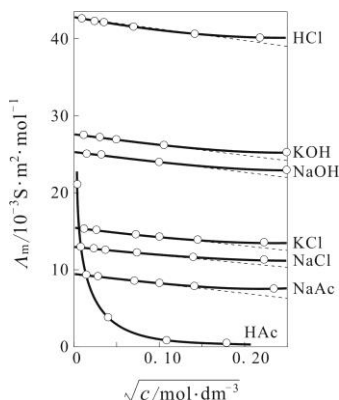


Figure 16-14 Variations of molar electric conductivity at 25°C for several electrolyte solutions with square root of concentration

variations of  $\Lambda_m$  with  $\sqrt{c}$  at 25°C for some electrolyte solutions. It is shown that regardless of strong or weak electrolytes,  $\Lambda_m$  diminishes monotonically with increasing  $c$ . For the strong electrolytes, the phenomenon attributes solely to the enhancement of ionic interactions with increasing  $c$ . For the weak electrolytes, it is mainly because of the lowering of the degree of dissociation. Take HAc for example, notably different from the strong electrolyte, in the very dilute region,  $\Lambda_m$  sharply drops with increasing  $c$  because of the rapid decrease of the degree of dissociation.

**Kohlrausch Relation** For the dilute solution of strong electrolytes, Kohlrausch F discovered by experiment that the molar electric conductivity has a linear relation with the square root of the concentration, referring to Figure 16-14,

$$\Lambda_m = \Lambda_m^\infty - A\sqrt{c} \quad (16-64)$$

where  $\Lambda_m^\infty$  is the  $\Lambda_m$  when the concentration approaches zero. It is called the **molar electric conductivity at infinite dilution**.

**Relation between Molar Electric Conductivity and Mobility** The electric conductance of electrolyte solutions relies on the ionic migration under the electric field. Therefore,  $\Lambda_m$  is related with  $u_B$ . According to Eqs.(16-63, 16-62),

$$\Lambda_m = \frac{\kappa}{c} = \frac{j}{Ec} = \frac{I}{EcA_s} \quad (16-65)$$

With  $v_+z_+ = v_-|z_-|$ , substitution of Eq.(16-54) yields

$$\Lambda_m = \alpha \left( v_+z_+u_+ + v_-|z_-|u_- \right) F = \alpha v_+z_+ (u_+ + u_-) F \quad (16-66)$$

This equation relates the molar electric conductivity with the mobilities of cations and anions. If the specified elementary entities for electrolyte and ions are all selected to be equivalent to the ion with a valence of 1, on this occasion,  $v_+ = v_- = 1$ ,  $z_+ = |z_-| = 1$ , Eq.(16-66) can be simplified as

$$\Lambda_m = \alpha (u_+ + u_-) F \quad (16-67)$$

Notice that  $u_+$  and  $u_-$  are a kind of speed irrelevant to the selection of specified entity. Take  $\text{Al}_2(\text{SO}_4)_3$  for example,  $v_+ = 2$ ,  $z_+ = 3$ ,  $v_- = 3$ ,  $z_- = -2$ , according to Eqs.(16-66, 16-67), we can write respectively:

$$\Lambda_m[\text{Al}_2(\text{SO}_4)_3] = 6\alpha[u(\text{Al}^{3+}) + u(\text{SO}_4^{2-})]$$

$$\Lambda_m \left[ \frac{1}{6} \text{Al}_2(\text{SO}_4)_3 \right] = \alpha [u(\text{Al}^{3+}) + u(\text{SO}_4^{2-})]$$

**Calculate Mobilities by Molar Electric Conductivity and Transference Numbers** Substitution of Eq.(16-66) into Eq.(16-65) yields

$$u_+ = t_+ (u_+ + u_-) = \frac{t_+ \Lambda_m}{\alpha v_+ z_+ F} \quad (16-68)$$

$$u_- = t_- (u_+ + u_-) = \frac{t_- \Lambda_m}{\alpha v_- |z_-| F} \quad (16-69)$$

Data in Table 16-3 are provided by this method.

### Calculate Dissociation Constant by Molar Electric Conductivity

When the solution is very dilute, the degree of dissociation  $\alpha$  approaches 1, Eq.(16-66) turns to

$$\Lambda_m^\infty = v_+ z_+ (u_+^\infty + u_-^\infty) F \quad (16-70)$$

If neglecting the difference between  $u_+$ ,  $u_-$  and  $u_+^\infty$ ,  $u_-^\infty$ , dividing Eq.(16-66) by the above equation, the degree of dissociation is obtained.

$$\alpha = \Lambda_m / \Lambda_m^\infty \quad (16-71)$$

### 3. Ionic Molar (Electric) Conductivity

**Definition** The ionic molar (electric) conductivity  $\lambda_B$  (B represents ion) is defined as:

$$\lambda_B \stackrel{\text{def}}{=} |z_B| u_B F \quad (16-72)$$

$\lambda_B$  is proportional to the mobility  $u_B$ . Due to a unit of  $\text{C} \cdot \text{mol}^{-1}$  for  $F$ , the unit of  $\lambda_B$  is  $\text{C} \cdot \text{mol}^{-1} \cdot \text{m}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1} = \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$  ( $\text{C} \cdot \text{s}^{-1} \cdot \text{V}^{-1} = \text{S}$ ), the same as that of  $\Lambda_m$ .

**Relation between  $\Lambda_m$  and  $\lambda_B$**  Substitution of Eq.(16-72) into Eq.(16-66) yields

$$\Lambda_m = \alpha (v_+ \lambda_+ + v_- \lambda_-) \quad (16-73)$$

The molar electric conductivity of an electrolyte is the sum of the products of the ionic conductivity and the stoichiometry number of the corresponding ions, further multiplying the degree of dissociation. If the specified elementary entities for electrolyte and ions are all selected to be equivalent to the ion with a valence of 1, the equation is simplified as:

$$\Lambda_m = \alpha (\lambda_+ + \lambda_-) \quad , \quad v_+ = v_- = 1 \quad (16-74)$$

Take  $\text{Al}_2(\text{SO}_4)_3$  for example, in terms of Eqs.(16-73, 16-74) respectively,

$$\begin{aligned} \Lambda_m[\text{Al}_2(\text{SO}_4)_3] &= \alpha[2\lambda(\text{Al}^{3+}) + 3\lambda(\text{SO}_4^{2-})] \\ \Lambda_m[\frac{1}{6}\text{Al}_2(\text{SO}_4)_3] &= \alpha[\lambda(\frac{1}{3}\text{Al}^{3+}) + \lambda(\frac{1}{2}\text{SO}_4^{2-})] \end{aligned}$$

Table 16-4 lists ionic molar conductivities at infinite dilution and 25°C for various ions.

**Independent Migration Law of Ions** For very dilute solutions, the degree of dissociation is close to 1, Eqs.(16-73, 16-74) turn to respectively:

$$\Lambda_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty \quad (16-75)$$

$$\Lambda_m^\infty = \lambda_+^\infty + \lambda_-^\infty, \quad \nu_+ = \nu_- = 1 \quad (16-76)$$

where  $\lambda_+^\infty$  and  $\lambda_-^\infty$  are the ionic molar conductivities of cation and anion respectively. They are determined by the solvent, the temperature and the nature of the ion, irrelevant to other ions in solution. Eqs.(16-75, 16-76) are called the independent migration law of ions discovered by Kohlrausch F based on experiment. For example, the difference between the molar electric conductivities at infinite dilution of chloride and nitrate solutions with the same cation is a constant at a certain temperature irrelevant to the nature of the cation. For the cations  $\text{Li}^+$ ,  $\text{K}^+$  and  $\text{H}^+$ , we have

Table 16-4 Ionic molar conductivities at infinite dilution and 25°C for various cations and anions  
(The specified elementary entity is selected to be equivalent to the ion with a valence of 1)

Cation	$\frac{\lambda_+^\infty \times 10^4}{\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}}$	Cation	Same as 2rd col.	Anion	$\frac{\lambda_-^\infty \times 10^4}{\text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1}}$	Anion	Same as 6th col.
$\text{H}^+$	349.8	$\frac{1}{2}\text{Ni}^{2+}$	53	$\text{OH}^-$	198.3	$\text{ClO}_4^-$	67.4
$\text{Li}^+$	38.7	$\frac{1}{2}\text{Cu}^{2+}$	53.6	$\text{F}^-$	55.4	$\text{MnO}_4^-$	61
$\text{NH}_4^+$	73.4	$\frac{1}{2}\text{Zn}^{2+}$	52.8	$\text{Cl}^-$	76.4	$\text{HCOO}^-$	54.6
$\text{Na}^+$	50.1	$\frac{1}{2}\text{Ba}^{2+}$	63.6	$\text{Br}^-$	78.1	$\text{CH}_3\text{COO}^-$	40.9
$\text{K}^+$	73.5	$\frac{1}{2}\text{Hg}^{2+}$	63.6	$\text{I}^-$	76.8	$\text{C}_2\text{H}_5\text{COO}^-$	35.8
$\text{Ag}^+$	61.9	$\frac{1}{2}\text{Pb}^{2+}$	59.4	$\text{HCO}_3^-$	44.5	$\frac{1}{2}\text{CO}_3^{2-}$	69.3
$\text{Tl}^+$	74.7	$\frac{1}{3}\text{Al}^{3+}$	63.0	$\text{CN}^-$	82	$\frac{1}{2}\text{SO}_4^{2-}$	79.8
$\frac{1}{2}\text{Mg}^{2+}$	53.1	$\frac{1}{3}\text{Fe}^{3+}$	68.4	$\text{NO}_3^-$	71.4	$\frac{1}{3}\text{PO}_4^{3-}$	80
$\frac{1}{2}\text{Ca}^{2+}$	59.5	$\frac{1}{3}\text{La}^{3+}$	69.6	$\text{HSO}_4^-$	52	$\frac{1}{3}\text{Fe}(\text{CN})_6^{3-}$	101.0
$\frac{1}{2}\text{Fe}^{2+}$	54			$\text{ClO}_3^-$	64.6	$\frac{1}{4}\text{Fe}(\text{CN})_6^{4-}$	110.5

$$\begin{aligned} \Lambda_m^\infty(\text{LiCl}) - \Lambda_m^\infty(\text{LiNO}_3) &= \Lambda_m^\infty(\text{KCl}) - \Lambda_m^\infty(\text{KNO}_3) \\ &= \Lambda_m^\infty(\text{HCl}) - \Lambda_m^\infty(\text{HNO}_3) = 0.49 \times 10^{-3} \text{S} \cdot \text{m}^2 \cdot \text{mol}^{-1} \end{aligned}$$

Similar relation can be observed for lithium and potassium salt solutions

with the same anion.

**Applications of Independent Migration Law of Ions** For weak electrolyte solutions, Eq.(16-64) is not valid, as shown in Figure 16-14, the molar electric conductivity at infinite dilution  $\Lambda_m^\infty$  of them (for example HAc) can not be given simply by extrapolation. By using Eq.(16-76), the relation between  $\Lambda_m^\infty$  of HAc and that of strong electrolytes can be obtained,

$$\begin{aligned}\Lambda_m^\infty(\text{HAc}) &= \lambda^\infty(\text{H}^+) + \lambda^\infty(\text{Ac}^-) \\ &= \lambda^\infty(\text{H}^+) + \lambda^\infty(\text{Cl}^-) + \lambda^\infty(\text{Na}^+) + \lambda^\infty(\text{Ac}^-) - \lambda^\infty(\text{Na}^+) - \lambda^\infty(\text{Cl}^-) \\ &= \Lambda_m^\infty(\text{HCl}) + \Lambda_m^\infty(\text{NaAc}) - \Lambda_m^\infty(\text{NaCl})\end{aligned}$$

where  $\Lambda_m^\infty$  of HCl, NaAc and NaCl can be obtained by the extrapolation of experimental data using Eq.(16-64).

**Example 1** For an aqueous solution of  $\text{AgNO}_3$  at  $25^\circ\text{C}$ , experiment gives  $\Lambda_m^\infty = 133.3 \times 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ . Combining with the experimental transference number in the Example in 16.6, calculate the mobilities at infinite dilution,  $u_+^\infty$  and  $u_-^\infty$  for  $\text{Ag}^+$  and  $\text{NO}_3^-$  at  $25^\circ\text{C}$ .

**Solution:** From the example in 16.6,  $t_{\text{Ag}^+} = 0.470$ ,  $t_{\text{NO}_3^-} = 0.530$ . Suppose these transference numbers can be used at infinite dilution, substituting into Eqs.(16-68, 16-69),

$$\begin{aligned}u_+^\infty &= t_+^\infty \Lambda_m^\infty / F = (0.470 \times 133.3 \times 10^{-4} / 96485) \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1} = 6.49 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1} \\ u_-^\infty &= t_-^\infty \Lambda_m^\infty / F = (0.530 \times 133.3 \times 10^{-4} / 96485) \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1} = 7.32 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}\end{aligned}$$

**Example 2** Calculate  $u_+^\infty$  and  $u_-^\infty$  for  $\text{Ag}^+$  and  $\text{NO}_3^-$  using the data of ionic molar conductivities listed in Table 16-4.

**Solution:**  $\lambda^\infty(\text{Ag}^+) = 61.9 \times 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$ ,

$$\lambda^\infty(\text{NO}_3^-) = 71.4 \times 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1}$$

Substituting into Eq.(16-72),

$$\begin{aligned}u_+^\infty &= \lambda_+^\infty / F = 61.9 \times 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1} / (96485 \text{ C} \cdot \text{mol}^{-1}) = 6.42 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1} \\ u_-^\infty &= \lambda_-^\infty / F = 71.4 \times 10^{-4} \text{ S} \cdot \text{m}^2 \cdot \text{mol}^{-1} / (96485 \text{ C} \cdot \text{mol}^{-1}) = 7.40 \times 10^{-8} \text{ m}^2 \cdot \text{s}^{-1} \cdot \text{V}^{-1}\end{aligned}$$

## 16.8 Other Applications of Electric Conductance

(1) **Degree of Dissociation and Dissociation Constant of Weak Electrolytes** The degree of dissociation of weak electrolytes is very small. The effect of the ionic interactions to the ionic mobilities can be neglected. Therefore,  $u_+ \approx u_+^\infty$ ,  $u_- \approx u_-^\infty$ , Eq.(16-71)  $\alpha = \Lambda_m / \Lambda_m^\infty$  can be used directly

to calculate the degree of dissociation,

**Ostwald Dilution Law** For a 1-1 type electrolyte MX, the dissociation constant can be expressed as:

$$K_c = \frac{c_{M^+} c_{X^-}}{c_{MX}} = \frac{c\alpha^2}{1-\alpha} \quad (16-77)$$

where  $c$  is the total concentration of the electrolyte. Substitution of Eq.(16-71) yields

$$K_c = \frac{cA_m^2}{A_m^\infty(A_m^\infty - A_m)} \quad (16-78)$$

or

$$cA_m = \frac{K_c A_m^{\infty 2}}{A_m} - K_c A_m^\infty \quad (16-79)$$

This is the dilution law named after Ostwald W. Eq.(16-79) is a linear equation, plotting  $cA_m$  against  $1/A_m$  should give a straight line, the slope and intercept of it can be used to calculate  $A_m^\infty$  and  $K_c$ . Figure 16-15 is a plot by the experimental  $A_m$  at 25°C for aqueous HAc solutions of various concentrations. The slope and the intercept are:

$$K_c A_m^{\infty 2} / S^2 \cdot m^4 \cdot mol^{-1} \cdot dm^{-3} = 0.2740 \times 10^{-7},$$

$$-K_c A_m^\infty / S \cdot m^2 \cdot dm^{-3} = -0.6998 \times 10^{-6},$$

Results are:  $A_m^\infty = 3.916 \times 10^{-2} S \cdot m^2 \cdot mol^{-1}$ ,  $K_c = 1.787 \times 10^{-5} mol \cdot dm^{-3}$ .

## (2) Solubility and Solubility Product of Sparingly Soluble Salts

For the sparingly soluble salts such as  $BaSO_4$ ,  $AgCl$  and so on, the solubility in water is too small to determine. The electric conductance can be applied. By Eq.(16-63)  $c = \kappa / A_m$ , due to the small solubility  $c$ , we have approximately  $A_m \approx A_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$ . However, because the water also has electric conductance comparable to that of the sparingly soluble salt, the contribution to the electric conductance by the salt should be that of the solution measured minus that of the water at the same temperature,  $\kappa = \kappa_{\text{expt}} - \kappa_{\text{water}}$ . Combining the above two equations, the solubility and the solubility product can be obtained,

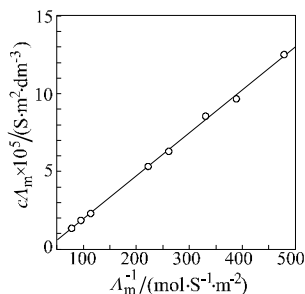


Figure 16-15 Dissociation constant of HAc in aqueous solution by electric conductance measurement.

$$c = \frac{\kappa_{\text{expt}} - \kappa_{\text{water}}}{\nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty} \quad (16-80)$$

$$K_{\text{sp}} = c_{\text{M}^{z+}}^{\nu_+} c_{\text{X}^{z-}}^{\nu_-} = (\nu_+ c)^{\nu_+} \cdot (\nu_- c)^{\nu_-} = \nu_+^{\nu_+} \cdot \nu_-^{\nu_-} \cdot c^{(\nu_+ + \nu_-)} \quad (16-81)$$

For the 1-1 type sparingly soluble salt,  $K_{\text{sp}} = c_+ \cdot c_- = c^2$ .

**Example 1** The electric conductivity of the saturated AgCl solution at 25°C is  $3.41 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$  by experiment, that of the pure water at the same temperature is  $1.60 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$ . Calculate the solubility product of AgCl.

**Solution:** Taking  $\lambda^\infty$  from Table 16-4, according to Eq.(16-80), the solubility of AgCl in water is

$$c = \frac{\kappa_{\text{expt}} - \kappa_{\text{water}}}{\nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty} = \frac{3.41 \times 10^{-4} - 1.60 \times 10^{-4}}{(61.9 + 76.4) \times 10^{-4}} \text{ mol} \cdot \text{m}^{-3}$$

$$= 1.31 \times 10^{-2} \text{ mol} \cdot \text{m}^{-3} = 1.31 \times 10^{-5} \text{ mol} \cdot \text{dm}^{-3}$$

$$K_{\text{sp}} = c_{\text{Ag}^+} \cdot c_{\text{Cl}^-} = c^2 = (1.31 \times 10^{-5})^2 \text{ mol}^2 \cdot \text{dm}^{-6} = 1.72 \times 10^{-10} \text{ mol}^2 \cdot \text{dm}^{-6}$$

**Example 2**  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CrO}_4$  in water at 25°C is  $9 \times 10^{-12} \text{ mol}^3 \cdot \text{dm}^{-9}$ . (a) Calculate the solubility of  $\text{Ag}_2\text{CrO}_4$  in water. (b) Calculate the solubility of  $\text{Ag}_2\text{CrO}_4$  in a  $\text{Na}_2\text{CrO}_4$  solution of  $0.1 \text{ mol} \cdot \text{dm}^{-3}$ .

**Solution:**  $\text{Ag}_2\text{CrO}_4(\text{s}) \rightleftharpoons 2\text{Ag}^+ + \text{CrO}_4^{2-}$

(a) According to Eq.(16-81),  $K_{\text{sp}} = (c_{\text{Ag}^+})^2 c_{\text{CrO}_4^{2-}} = (2)^2 (1)c^3$

Therefore,  $c = \sqrt[3]{K_{\text{sp}}/4} = 1.3 \times 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$

(b) Suppose the concentration of  $\text{Na}_2\text{CrO}_4$  is  $c'$ , the solubility of  $\text{Ag}_2\text{CrO}_4$  is  $c$ . Because the two salts have the same anion, the concentration of  $\text{Ag}^+$  is  $2c$ , that of  $\text{CrO}_4^{2-}$  is  $c' + c$ , the solubility product is:

$$K_{\text{sp}} = (2c)^2 (c' + c), \quad 9 \times 10^{-12} \text{ mol}^3 \cdot \text{dm}^{-9} = 4c^2 (0.1 \text{ mol} \cdot \text{dm}^{-3} + c)$$

Due to the fact that  $c$  is far less than  $0.1 \text{ mol} \cdot \text{dm}^{-3}$ ,  $c$  in the bracket can be neglected. The solution is:

$$c = 4.7 \times 10^{-6} \text{ mol} \cdot \text{dm}^{-3}.$$

This example indicates that the common-ion effect leads to the lowering of the solubility of the solid electrolyte.

(3) **Ionic Product of Water** Water has the following dissociation equilibrium:  $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ . Water is a weak electrolyte, although the degree of dissociation is very small, water does have a certain electric conductivity. Using a special apparatus to distillate the water in vacuum repeatedly, the impurities such as  $\text{CO}_2$  can be removed. The obtained pure water usually called the **conductance water** can reach an electric conductivity as low as  $5.5 \times 10^{-4} \text{ S} \cdot \text{m}^{-1}$ . Treating  $\text{H}^+$  and  $\text{OH}^-$  obtained by dissociation as infinite dilution, applying  $\Lambda_{\text{m}} = \Lambda_{\text{m}}^\infty = \lambda_+^\infty + \lambda_-^\infty$ , combining with Eq.(16-63), their concentrations can be obtained,

$$c = c_{\text{H}^+} = c_{\text{OH}^-} = \frac{\kappa}{\lambda_+^\infty + \lambda_-^\infty} = \frac{5.5 \times 10^{-6}}{(349.8 + 198.3) \times 10^{-4}} \text{ mol} \cdot \text{m}^{-3}$$

$$= 1.003 \times 10^{-4} \text{ molm}^{-3} = 1.003 \times 10^{-7} \text{ mol} \cdot \text{dm}^{-3}$$

The ionic product of water is:  $K_w = c_{\text{H}^+} \cdot c_{\text{OH}^-} = 1.01 \times 10^{-14} \text{ mol}^2 \cdot \text{dm}^{-6}$ .

## 16.9 Diffusion in Electrolyte Solutions

### 1. Features of Diffusion in Electrolyte Solutions

(1) **Fick's Law Is Still Observed** When without external electric field, macroscopically, the ions in solution can diffuse motivated by the concentration gradient  $\partial c_B / \partial x$ , Eq.(6-1) of the Fick's law is still observed,

$$j_{B,x} = -D_B \frac{\partial c_B}{\partial x} \quad (16-82)$$

where B represents the electrolyte as a whole or the cation and anion,  $j_{B,x}$  and  $D_B$  are the flux in the  $x$  direction and the diffusion coefficient for the substance B respectively. The difference of the diffusion from the electric conductance lies in: The cations and anions move in the same direction in diffusion but transfer in the opposite directions in electric conductance.

(2) **Electro Neutrality is Maintained All the Time** The diffusion of ions is motivated by the concentration or the chemical-potential gradient the same as that of the ordinary solutes. What is special is that the electrolyte solution should maintain the electro neutrality. As is shown in 16.6.1 above, different ions have notably different mobilities. Suppose the cation and the anion have the same valence of 1, in the same electric field, they bear the same magnitude of force. The different mobilities mean that the resistances met should be different. When the cations and the anions are motivated by the same concentration gradient, because of the different resistances, the moving speeds should be different leading to the broken of electro neutrality. However, experiment reveals that the electro neutrality is maintained in various parts of the solution all the time indicating that the cations and anions have the same moving speed.



(3) **Local Electric Field** The above phenomenon looks like contradictory. The reason lies in the local electric field  $E$  formed between cations and anions with different moving speeds, referring to Figure 16-16. This field makes the rapid ions be retarded and the slow ions accelerate, finally, they reach the same speed. The special character of the diffusion in electrolyte solutions compared with that in ordinary solutions is that the former is affected by the additional local electric field; as a result, the electro neutrality is maintained.

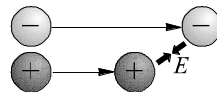


Figure 16-16 Local electric field

## 2. Nernst-Hartley Equation

The aim of the studies on the diffusion in electrolyte solutions is to establish the relation between the diffusion coefficients and the mobilities which reflect the transfer characteristics of ions, as well as the non-ideality which reflects the molecular interactions.

**Clues for Derivation** The forces experienced by ions in solution come from the concentration or the chemical-potential gradient on the one hand, on the other hand, originated from the local electric field  $E$ . To solve the problem of the magnitude of  $E$ , the condition of electro neutrality should be used. Restricted by this condition,  $E$  and the ionic moving speed can be solved simultaneously. Correspondingly, the flux and the diffusion coefficient are obtained.

**Nernst-Hartley Equation** The equation named after Nernst W and Hartley G S was derived in 1930s and is expressed as:

$$D_B = \frac{1}{L} \frac{u_+ u_- (v_+ + v_-) RT}{v_+ z_+ e u_- - v_- z_- e u_+} \left( 1 + \frac{d \ln \gamma_{\pm}}{d \ln (c_B / c^\ominus)} \right) \quad (16-83)$$

The equation relates the diffusion coefficient of electrolyte in solution and the mobilities  $u_+$  and  $u_-$  of ions, the contribution of the non-ideality of the solution  $\gamma_{\pm}$  is also included. Using Eq.(16-72)  $\lambda_B = |z_B| u_B F$ ,  $F = Le$ , the molar electric conductivity can also be connected.

## 3. Ionic Diffusion Coefficients

The ionic diffusion coefficients of cations and anions  $D_+$  and  $D_-$  can be defined according to the diffusion of a single ion in the chemical-potential gradient. The relation between them and  $D_B$  of the electrolyte is:

$$D_B = \frac{v_+ + v_-}{v_+ D_+^{-1} + v_- D_-^{-1}} \quad (16-84)$$

Values of  $D_+$  and  $D_-$  at infinite dilution and 25°C are about in the range of  $0.5 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1} \sim 2 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ . Diffusion coefficients of  $\text{H}^+$  and  $\text{OH}^-$  are  $9.31 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$  and  $5.28 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$  respectively. The abnormally large values are also attributed to the fast proton-transfer chain mechanism, referring to Figure 16-9.

**Example** Calculate the diffusion coefficient of electrolyte  $\text{LaCl}_3$  in a dilute solution at 25°C. Given that  $D_{\text{La}^{3+}}^\infty = 0.62 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ ,  $D_{\text{Cl}^-}^\infty = 2.03 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$ .

**Solution:** Treated as infinite dilution, substituting the data given into Eq.(16-84) with  $v_+=1$  and  $v_-=3$ ,

$$D^\infty = 4 \times [(0.62 \times 10^{-5})^{-1} + 3(2.03 \times 10^{-5})^{-1}]^{-1} \text{ cm}^2 \cdot \text{s}^{-1} = 1.29 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$$

## 16.10 Theoretical and Semi-Empirical Methods

### 1. Debye-Hückel-Onsager Theory of Electric Conductance

Debye P J W and Hückel E, as the first time, applied the concept of the ionic atmosphere to the electric conductance of dilute solutions. In 1926, Onsager L improved the theory and obtained the correct concentration dependence of the molar electric conductivity. The theoretical derivation is based on the analysis of the forces experienced by

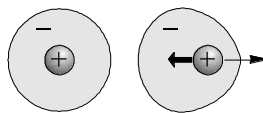


Figure 16-17 Relaxation effect

ions in electric field which include the **electric-field force**, the **frictional force**, the **relaxation force** and the **electrophoresis force**. When an ion moves forward, the symmetry of the ionic atmosphere is broken, as shown in Figure 16-17. The retardation effect caused by the unsymmetrical ionic atmosphere with opposite charge on the moving ion is called the relaxation force. On the other hand, all the ions are solvated. When an ion moves forward, the counter ions carrying their solvation layers move in the opposite direction. Therefore, the ion is not moving in the immobile solvent but in a counter stream of solvent, the resistance formed is called the electrophoresis force. The following equation is finally derived:

$$\Lambda_m = \Lambda_m^\infty - (A\Lambda_m^\infty + B)\sqrt{c} \quad (16-85)$$

where  $A$  is the relaxation parameter,  $B$  is the electrophoresis parameter, they

all depend on the temperature and the relative permittivity of the solvent,  $B$  also depends on the viscosity. The empirical Kohlrausch relation, Eq.(16-64) is then elucidated theoretically.  $A$  in Eq.(16-64) is the  $AA_m^\infty + B$  in Eq.(16-85). Later, many further improvements have appeared.

## 2. Semi-Empirical Methods

The methods conveniently used are: The FHFP (Fuoss-Hsia-Fernandez- Prini) equation and a rule named after Walden P for electric conductance. The method named after Jones G and Dole M for viscosity. The group-contribution method named after Riedel L for thermal conductivity.

# III. Reaction-Rate Properties of Electrolyte Solutions

## 16.11 Ionic Reactions in Solution

### 1. Effect of Relative Permittivity of Solvent

When a reaction happens between a pair of ions A and B, in terms of the transition-state theory, an activated complex  $A\cdots B$  should be firstly formed, referring to Figure 16-18. When reactants are neutral molecules, there is a standard molar Gibbs function of activation  $\Delta^\ddagger G_m^\circ$  which relates with the reaction rate constant  $k$  by Eq.(14-50),  $k = (k_B T / hc^\circ) e^{-\Delta^\ddagger G_m^\circ / RT}$ . Now A and B are ions, an additional energy originated from the electrostatic interaction should be considered during the formation of an activated complex. The Gibbs function will be lowered if A and B are charged with opposite signs, and increased if they have charges with the same sign. For the additional value  $\Delta^\ddagger G_m^\circ(e)$  with respect to the standard molar Gibbs function of activation  $\Delta^\ddagger G_m^\circ$ , electrostatics gives:

$$\Delta^\ddagger G_m^\circ(e) = Lz_A z_B \frac{e^2}{4\pi\epsilon d_{AB}} \quad (16-86)$$

where  $d_{AB}$  is the distance between A and B in the activated complex,  $\epsilon$  is the permittivity. Suppose  $\Delta^\ddagger G_m^\circ(z=0)$  is the standard molar Gibbs function of

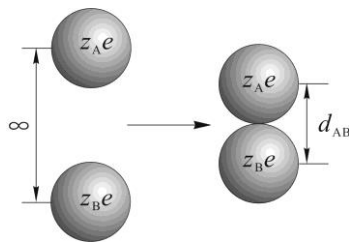


Figure 16-18 Activated complex formed in ionic reaction

activation for the corresponding neutral molecules, for the ionic reaction, we have  $\Delta^\ddagger G_m^\circ = \Delta^\ddagger G_m^\circ(z=0) + \Delta^\ddagger G_m^\circ(e)$ , substitution of Eq.(16-86) yields

$$\Delta^\ddagger G_m^\circ = \Delta^\ddagger G_m^\circ(z=0) + Lz_A z_B \frac{e^2}{4\pi\epsilon d_{AB}} \quad (16-87)$$

Substituting into Eq.(14-50), the ratio of  $k$  for the ionic reaction to that of the corresponding molecular reaction  $k(z=0)$  can be obtained:

$$\ln \frac{k}{k(z=0)} = -\frac{Lz_A z_B e^2}{4\pi\epsilon d_{AB} RT} \quad (16-88)$$

**Example** Figure 16-19 shows the relation between the rate constant of the reaction of bromoacetate ion and thiosulphate ion,  $\text{CH}_2\text{BrCOO}^- + \text{S}_2\text{O}_3^{2-}$ , with the relative permittivity  $\epsilon_r = \epsilon/\epsilon_0$ . The variation of  $\epsilon_r$  is realized by changing the composition of the mixed solvent. Plotting  $\lg\{k\}$  against  $1/\epsilon_r$ , except for very small  $\epsilon_r$ , a good straight line is exhibited. The slope gives  $d_{AB}=0.510\text{nm}$ .

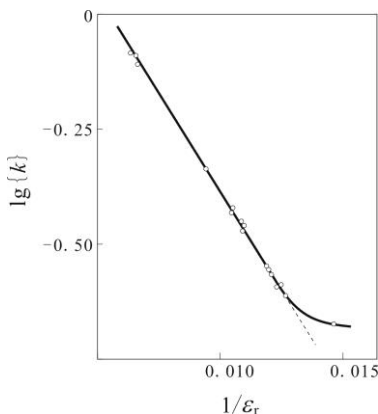


Figure 16-19 Variation of rate constant with relative permittivity of solvent for the reaction of  $\text{CH}_2\text{BrCOO}^- + \text{S}_2\text{O}_3^{2-}$

## 2. Effect of Ionic Strength

In discussing the reaction problem for electrolyte solutions, concerning the ionic activities, the selection IV, selecting the solute of an ideal dilute solution with a concentration of  $c^\circ = 1\text{mol}\cdot\text{dm}^{-3}$  as the reference state is the most convenient choice. Similar to Eq.(14-53) in discussing the effect of solvent, we can write:

$$k = k_\infty \frac{\gamma_{c,A} \gamma_{c,B}}{\gamma_{c,\ddagger}} \quad (16-89)$$

where  $\gamma_{c,A}$ ,  $\gamma_{c,B}$ ,  $\gamma_{c,\ddagger}$  are the activity factors of A, B and the activated complex respectively.  $k_\infty$  is the corresponding rate constant in an infinite dilute solution with  $\gamma_{c,i}=1$ .

As is mentioned in 16.3, the ionic activity factors are affected by the ionic strength. Their relation can be described by the Debye-Hückel limiting law, Eq.(16-44). For an ion  $i$ ,  $\ln \gamma_{c,i} = -Az_i^2 \sqrt{I}$ . For the activated complex,

$z_x = z_A + z_B$ . Substituting into Eq.(16-89),

$$\ln k - \ln k_\infty = -A(z_A^2 + z_B^2 - z_x^2)\sqrt{I} = 2Az_A z_B \sqrt{I} \quad (16-90)$$

This equation indicates that plotting  $\ln(k/k_\infty)$  against  $\sqrt{I}$  gives a straight line with a slope of  $2Az_A z_B$ . The variation of the rate coefficient with the ionic strength of this kind is called the **primary kinetic salt effect**. The ionic strength affects the rate coefficients though affecting the activity factors, and changing the equilibrium between the reactants and the activated complex.

**Example** Figure 16-20 gives the rate coefficients of six ionic reactions plotted in terms of Eq.(16-90). Good straight lines are obtained for all the six reactions. They can be distinguished as three cases:

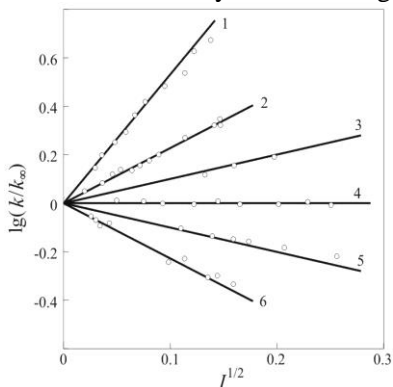
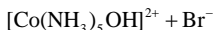
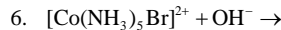
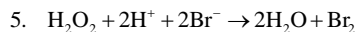
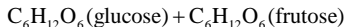
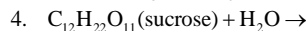
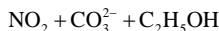
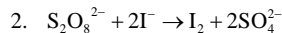
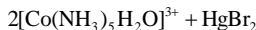
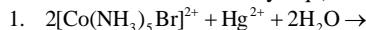


Figure 16-20 Variations of rate coefficients of some ionic reactions with ionic strength

Open circles are experimental values.

Solid lines are calculated by Eq.(16-90).



(1)  $z_A$  and  $z_B$  have the same sign,  $z_A z_B > 0$ ,  $k$  increases with increasing  $\sqrt{I}$ , referring to the reactions 1, 2 and 3.

(2)  $z_A$  and  $z_B$  have the opposite signs,  $z_A z_B < 0$ ,  $k$  decreases with increasing  $\sqrt{I}$ , referring to the reactions 5 and 6.

(3) Reactant molecules are neutral without charge,  $z_A z_B = 0$ ,  $k$  is irrelevant to  $\sqrt{I}$ , referring to the reaction 4.

### 3. Microscopic-Diffusion Control

For ionic reactions,  $R_{\text{eff}}$  in Eq.(8-9),  $k = k_d = 4\pi(D_A + D_B)R_{\text{eff}}L$ , is expressed as  $R_{\text{eff}} = (r_A + r_B)f$ ,  $f$  is called the **electrostatic factor**. Theoretical analysis gives that at 25°C and  $r_A + r_B = 0.2\text{nm}$ , when  $z_A z_B = -1, -2, 1$  and  $2$ ,  $f = 3.65, 7.08, 0.106$  and  $0.006$  respectively. The results indicate that  $k_d$  enhances for the ionic reactions of ions with opposite charges, and depresses

when ions are with charges of the same sign.

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### Brief History

The electrolyte solutions started to attract people's attention since the discovery of the electrolysis phenomena. In 1800, Nicholson W and Carlisle A of England (referring also to Chapter 17) for the first time observed the hydrogen and oxygen produced by the electrolysis of a dilute aqueous solution of sulfuric acid. To explain this phenomenon, in 1805, von Grotthuss T, a German chemist, proposed that the molecules form chains connected by the positive and negative ends of different molecules due to the orientation effect in the electric field. On the electrode, the molecules are ruptured with positive end and negative end separated forming products. However, Clausius R J E of Germany raised an objection. He thought that the energy needed for the rupture of a molecule is too high disproportional to that for the electrolysis. In 1857, he proposed that the positive end and the negative end of a molecule do not connect firmly but can separate in a short period forming ions. It is just these shortly occurred ions who take the responsibility of conducting current and discharge on the electrode forming electrolysis products. In 1886, Van't Hoff J H of the Netherlands (also referring to Chapters 4, 5, 7) developed the osmotic-pressure equation and established the theory of colligative properties of dilute solutions. But it was found that large deviations appear for those systems which were later called electrolyte solutions. For these solutions, it seems that one molecule plays the role of several molecules. On the basis of these works, Arrhenius S (also referring to Chapters 7, 14) developed the ionization theory: An electrolyte can partly be ionized into ions in the aqueous solution,  $MX \rightleftharpoons M^+ + X^-$ , chemical equilibrium exists between the molecule and the ions, the more dilute the solution, the larger the degree of dissociation is. The theory of Arrhenius has settled the foundation of the modern theory of electrolyte solutions. Through the studies of the deviations from the ideal dilute solution for the electrolyte solutions, in 1921, Lewis G N and Randall M (also referring to Chapter 3) raised the concept of the ionic strength. In 1923, Debye P J W of the Netherlands and Hückel E of Germany combined the Boltzmann distribution of the statistical mechanics and the Poisson equation of the electrostatics, raised the concept of ionic atmosphere and established the Debye-Hückel theory, successfully obtained the relations between the activity factor, the electric conductivity and the ionic strength theoretically. Up to then, the theory of the dilute electrolyte solutions was nearly perfect. The works later are focused on the extension of the concentration range. Among them, the prominent one is the theory of mean sphere approximation based on the integral-equation theory of the statistical mechanics. The analytical equations for the activity factor and the excess properties of the single and mixed electrolyte solutions are obtained. More studies on this direction are being developed continuously.

### Concluding Remarks

The most fundamental characteristic of the electrolyte solutions is the solvated ions occurred in solution with electrostatic interactions among them

leading to a series of peculiarities different from ordinary solutions. For the equilibrium properties, the activity does exhibit certain diversity such as that of the undissociated electrolyte, of the cations and anions, of the solvent and the electrolyte as a whole, as well as the mean ionic activity and the osmotic factor. The relations of them with the concentration are symbolized by using the square root of the ionic strength. For the transport properties, the ionic migration plays the key role, not only it determines the electric conductivity, but also affects the diffusion coefficient, even for the viscosity and the thermal conductivity which are not involved in this Chapter, theoretical analysis indicates that they are also related to the ionic migration. For reaction properties, they are also affected by the interactions among ions. By adjusting the relative permittivity and the ionic strength, the rate constant or coefficient can be notably changed. The diversity of the electrolyte solutions is yet displayed on the selection of the special elementary entity. For the activity and activity factor, the selection is usually natural, for the electric conductivity and the diffusion coefficient of the electrolyte as a whole, they are irrelevant to the selection, for the molar electric conductivity and ionic molar conductivity, if it is selected to be equivalent to the ion with a valence of 1, the equations might be greatly simplified indeed.

This characteristic of electrolyte solutions not only brings complexity but also opportunity. The development of electrostatics in physics is nearly perfect. The rule of the interactions among charges is well established on the basis of the Coulomb's law. Therefore, as early as 1920s, the theory of dilute solutions of electrolyte including the activity and the electric conductance has been almost perfectly developed. On the contrary, for ordinary solutions, because of the complexity of the intermolecular forces, even for the activity factors of dilute solutions, the theoretical prediction is still not satisfactory. Take the Lennard-Jones potential for example, the attractive and repulsive energies are inversely proportional to  $r^6$  and  $r^{12}$  respectively, whereas the electrostatic energy is simply inversely proportional to  $r$ , not to mention that the Lennard-Jones potential is only a rough approximation of the intermolecular forces.

However, the favor we have enjoyed is only limited to the dilute solutions. As the concentration increases, the trouble of the intermolecular forces in treating the ordinary solutions does puzzle the electrolyte solutions as well. What is more is that in dilute solutions of electrolyte, the solvent is regarded as a homogeneous medium with a certain relative permittivity in which the ions are moving, the Boltzmann distribution of the independent-particle systems can then be approximatedly applied. For more concentrated solutions, the Boltzmann distribution can not be used again, the canonical ensemble or the grand canonical ensemble should be adopted. Regarding the solvent as a homogeneous medium is also too rough. On this occasion, the interactions between the ions and the solvent, the interactions among the solvated ions besides the electrostatic, are gradually prominent. It is also worth mentioning that although water is the most popular and important solvent well-known to every one of us, the understanding of its basic structure is still incomplete. The density of water exhibits a maximum at 4°C, can be considered as a unique example in nature. The progress of the theory of electrolyte solutions relies on the progress of the theory of water structure, also on overcoming the mathematical difficulties in statistical mechanics. In applications, those semi-empirical methods for the activity, the electric conductivity and the viscosity are mainly adopted. They are all developed by the empirical revisions based on the current theories.

Finally, we have to mention the **ionic liquids**, a kind of salt exhibiting liquid appearance at ambient temperature which are composed of organic cations and inorganic or organic anions, for example,  $[\text{emin}]^+[\text{BF}_4]^-$ , where *emin* is *N*-ethyl-*N*-methyl imidazole ion. Because the liquid state covers a wider temperature range, also because of the low vapor pressure, a fine dissolving ability, moderate conductive and dielectric properties, as well as some special functions such as the catalytic performance, the acidity, the coordination ability and the chirality, the ionic liquids have attracted great attention which can be used as the medium of the chemical reactions, the electrochemical reactions and the separation processes, for developing the new technological processes with high efficiency, clean and energy-saving potentials.

## General Problems

1. Why is the activity  $a_B$  of the electrolyte as a whole the same as the activity  $a_{b,\text{Bu}}$  of the undissociated electrolyte?
2. How do we distinguish the first-kind and the second-kind electrolyte solutions, the strong and the weak electrolytes? What peculiarities do their properties have such as the activity factor, the osmotic factor, the electric conductivity and the molar electric conductivity?
3. What are the similarities and dissimilarities for the selection of the reference state of the activity for the first-kind and the second-kind electrolyte solutions?
4. Suppose a substance B can form a dimer in terms of  $2B \rightleftharpoons B_2$ . Using the concept of the electrolyte as a whole, deduce that the chemical potential of an electrolyte as a whole equals that of the unassociated monomer B and equals one half of that of the dimer.
5. Why should the osmotic factor be defined for the solvent? Is it true that the osmotic factor equals the ratio of the activity to the mole fraction?
6. What is the ionic atmosphere? How does it affect the ionic activity?
7. Why can  $\kappa^{-1}$  be understood as the thickness of the ionic atmosphere? By what factors is it affected?
8. Comparing the calculations in 16.4 and that in Chapters 3 and 4, sum up the essentials of the phase-equilibrium calculations.
9. How does a conductor conduct the current?
10. The migration speeds are different for cations and anions. Why can an electrolyte solution still keep electro neutrality?
11. What are the relations among the mobility, the transference number, the electric conductivity, the molar electric conductivity and the ionic molar electric conductivity?
12. Why is the mobility the basic parameter to represent the ionic migration characteristics?
13. In those properties such as the mobility, the electric conductivity, the molar electric conductivity, the ionic molar electric conductivity, the electrolyte diffusion coefficient and the ionic diffusion coefficient, which of them depends on the selection of the specified elementary entity? Which of them is irrelevant to the selection?
14. What is your understanding toward the condition of electro neutrality? In which part of this Chapter does it play an important role?
15. What is the difference between the effects of the ionic atmosphere to the ionic conductance and to the ionic activity?
16. What are the peculiarities of the ionic reactions in solution?



## Numerical Problems

1. Write the relations between the mean ionic concentration  $c_{\pm}$  and the molarity  $b$  for the electrolyte solutions of  $\text{CuSO}_4$ ,  $\text{K}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$  respectively.

2. Calculate the ionic strength for a solution composed of 1kg of water and 0.025mol of  $\text{NaCl}$ ,  $\text{CuSO}_4$  and  $\text{LaCl}_3$ , respectively.

3. The ionic mean activity factor of a  $\text{NaCl}$  aqueous solution of  $1.00\text{mol}\cdot\text{kg}^{-1}$  at 298K is  $\gamma_{\pm}=0.659$ , the practical osmotic factor of solvent is  $\phi=0.936$ . Calculate the mean ionic concentration, the mean ionic activity, the electrolyte activity, the solvent activity and activity factor of this solution.

4. Suppose the relation between the mean ionic activity factor and the ionic strength of a  $\text{ZnSO}_4$  aqueous solution of  $0.001\text{mol}\cdot\text{kg}^{-1}$  observes the Debye-Hückel limiting equation. Calculate the mean ionic activity factor and the practical osmotic factor of solvent at 298K.

5. Electrolyze a copper sulfate solution with a current of 0.1A. How much copper in mass will be deposited on the cathode in 10min? How much oxygen in volume at 298K and 100kPa could be obtained on the platinum anode?

6. How much is the amount of electricity consumed to produce  $1\text{m}^3(\text{STP})$  of dried hydrogen using the method of electrolysis of water? How long is it needed if the current is 10A?

7. Copper is used as electrodes to electrolyze a copper sulfate solution. Before the electrolysis, each 100g of solution contains 10.06g of  $\text{CuSO}_4$ . After the electrolysis, the solution in the anode compartment has a mass of 54.565g containing 5.726g of  $\text{CuSO}_4$ . The silver deposited in the silver Coulomb meter is 0.5008g. Calculate the transference numbers of  $\text{Cu}^{2+}$  and  $\text{SO}_4^{2-}$ .

8. Silver is used as electrodes to electrolyze a  $\text{KCl}$  solution. Before the electrolysis, each 100g of solution contains 0.7422g of  $\text{KCl}$ . After the electrolysis, the solution in the anode compartment has a mass of 117.51g containing 0.6659g of  $\text{KCl}$ . The silver deposited in the silver Coulomb meter is 0.6136g. The anode reaction is:  $\text{Ag} + \text{Cl}^- \rightarrow \text{AgCl(s)} + \text{e}^-$ . Calculate the transference numbers of  $\text{K}^+$  and  $\text{Cl}^-$ .

9. In a symmetrical glass transference tube with a section area of  $3.25\text{cm}^2$ , a  $\text{CdCl}_2$  solution is placed in the bottom and an  $\text{HCl}$  solution of  $0.0100\text{mol}\cdot\text{dm}^{-3}$  on the top. A clear interface is formed between the two solutions. When a current of 3.00mA is passed, the interface is observed to be moved 2.13cm upward after 45min. Calculate the transference number  $t_{\text{H}^+}$  of the hydrogen ion.

10. A conductance cell is filled with a  $\text{KCl}$  solution of  $0.01\text{mol}\cdot\text{dm}^{-3}$ . The electric resistance at 298K is measured as  $161.5\Omega$ . Replaced by a  $\text{K}_2\text{SO}_4$  solution of  $2.50\times 10^{-3}\text{mol}\cdot\text{dm}^{-3}$ , the resistance is  $326\Omega$ . The electric conductivity of the above  $\text{KCl}$  solution is given as  $0.14114\text{S}\cdot\text{m}^{-1}$ . Calculate the electric conductivity and the molar electric conductivity of the  $\text{K}_2\text{SO}_4$  solution.

11. The electric resistances of a  $\text{KCl}$  solution of  $0.01\text{mol}\cdot\text{dm}^{-3}$ , a  $\text{K}_2\text{SO}_4$  solution of  $0.5\times 10^{-3}\text{mol}\cdot\text{dm}^{-3}$  and the distilled water used to prepare the solutions in the same cell at 291K are measured as  $97.8\Omega$ ,  $937\Omega$  and  $10000\Omega$  respectively. (The conductivity of the distilled water is a little higher than that of the pure water because of the tiny amount of impurities such as carbonic acid and ammonia dissolved.)

(1) Calculate the electric conductance of the two solutions and the distilled water. If the distilled water is considered as without impurities completely, calculate the conductance of the two solutions again.

(2) The electric conductivity of the KCl solution of  $0.01\text{mol}\cdot\text{dm}^{-3}$  at 291K is given as  $0.12227\text{S}\cdot\text{m}^{-1}$ , calculate the electric conductivity of the  $\text{K}_2\text{SO}_4$  solution of  $0.5\times 10^{-3}\text{mol}\cdot\text{dm}^{-3}$  using the results of (1).

12. The electric conductivity of a  $\text{BaCl}_2$  solution of  $0.01\text{mol}\cdot\text{dm}^{-3}$  at 298K is given as  $0.2382\text{S}\cdot\text{m}^{-1}$ , the transference number of  $\text{Ba}^{2+}$  in the solution is 0.4375. Calculate the mobilities of  $\text{Ba}^{2+}$  and  $\text{Cl}^-$ .

13. The molar electric conductivity at infinite dilution of an  $\text{NH}_4\text{Cl}$  solution at 298K is  $14.97\times 10^{-3}\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$ , the transference number of the cation at infinite dilution is 0.4907. Calculate the molar electric conductivities and the mobilities of  $\text{NH}_4^+$  and  $\text{Cl}^-$  at infinite dilution.

14. The molar electric conductivities at infinite dilution for  $\text{NaIO}_3$ ,  $\text{CH}_3\text{COONa}$  and  $\text{CH}_3\text{COOAg}$  at 291K are  $7.694\times 10^{-3}\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$ ,  $7.816\times 10^{-3}\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$  and  $8.88\times 10^{-3}\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$  respectively. Calculate the molar electric conductivity at infinite dilution for  $\text{AgIO}_3$  at 291K.

15. The molar electric conductivity of a HAc solution of  $1.028\times 10^{-3}\text{mol}\cdot\text{dm}^{-3}$  at 298K is measured as  $4.815\times 10^{-3}\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}$ . Calculate the degree of dissociation  $\alpha$  and the dissociation constant  $K_c$  of the acetic acid in this concentration.

16. The electric conductivity of pure water at 298K is given as  $5.5\times 10^{-6}\text{S}\cdot\text{m}^{-1}$ , the density is  $997\text{kg}\cdot\text{m}^{-3}$ . Calculate the degree of dissociation of water at 298K.

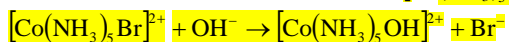
17. The electric conductivity of the saturated solution of  $\text{AgBr}$  at 298K subtracted by that of pure water is  $1.174\times 10^{-5}\text{S}\cdot\text{m}^{-1}$ . Calculate the solubility and the solubility product of  $\text{AgBr}$ . The molar electric conductivity at infinite dilution and at 298K for  $\text{Ag}^+$  and  $\text{Br}^-$  can be found in Table 16-4.

18. The electric conductivity at 291K of the saturated solution of  $\text{CaF}_2$  is measured as  $38.6\times 10^{-4}\text{S}\cdot\text{m}^{-1}$ , that of the water is  $1.5\times 10^{-4}\text{S}\cdot\text{m}^{-1}$ . Suppose  $\text{CaF}_2$  is completely dissociated. Calculate the solubility product of  $\text{CaF}_2$ . It is given that:

$$\Lambda_{\text{m}}^{\infty}\left(\frac{1}{2}\text{CaCl}_2\right)=0.01167\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}, \Lambda_{\text{m}}^{\infty}(\text{NaCl})=0.01089\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1},$$

$$\Lambda_{\text{m}}^{\infty}(\text{NaF})=0.00902\text{S}\cdot\text{m}^2\cdot\text{mol}^{-1}.$$

19. The alkaline hydrolysis reaction of a complex ion  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+}$  is:



The rate coefficient depends on the ionic strength of the solution. Calculate the ratio of the rate coefficients at 298K when the ionic strength is raised to twice as much as the original  $I=0.01\text{mol}\cdot\text{kg}^{-1}$ .