# Ionic Equilibria

# Dissociation of Electrolytes in Solution

The dissociation of electrolytes – be it partial or total – in water releases ions, which lend the medium particular properties.

The ionic solution is characterized by the presence in the medium (generally a liquid) of ions carrying positive and negative charges, with the whole being electrically neutral. These ions may or may not be accompanied by:

– neutral dissolved molecules;

– molecules of solvent.

## 1.1. Strong electrolytes – weak electrolytes

Starting with neutral molecules in solid- or gaseous form, there are three main ways to obtain a liquid ionic solution: dissolution, solvolysis and melting.

### 1.1.1. *Dissolution*

When we place sodium chloride crystals in water, they dissolve according to the reaction:

$$NaCl_{(solid)} = Na^+_{(aqu)} + Cl^-_{(aqu)} \hspace{2cm} [1R.1]$$

In fact, the ionic solution obtained is the result of three phenomena: dissociation into ions, solvation of ions (in this case, hydration), which is the

fixation of a certain number of polar molecules of solvent onto the ions and the separation of the charges of opposite signs because of the high electrical permittivity of the solvent.

## 1.1.2. *Solvolysis*

Solvolysis is the decomposition of a molecule by a solvent. In the case of water, we speak of hydrolysis. Take the example of gaseous hydrogen chloride composed of HCl molecules, whose reaction with water leads to the formation of ions by the following reaction, which is indeed a solvolysis:

$$HCl_{(gas)} + H_2O = H_3O^+_{(aqu)} + Cl^-_{(aqu)} \qquad [1R.2]$$
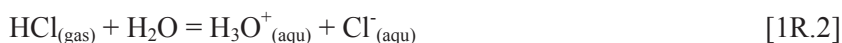
The result is the presence of ions, which are also solvated and separated from one another for the same reasons as in dissolution.

## 1.1.3. *Melting*

Raising the temperature of a solid such as sodium chloride leads to its melting, which leads to the dissociation into ions, according to the reaction:

$$NaCl_{(solid)} = Na^+_{(liq)} + Cl^-_{(liq)} \qquad [1R.3]$$

We again obtain a solution of ions (and neutral molecules), which are obviously not solvated, because the solution does not contain any solvent in the true sense of the word.

When a solution is obtained by one of the methods described above, we obtain a solution with multiple interactions between the ions, which can be described in one of two ways:

– a complex solution of ions with activity coefficients using a more or less elaborate model;

– a quasi-chemical model using the model of associated solutions, which leads us to divide the species in the solution into two categories:

- neutral associated molecules,

- ions.

Remember that the associated solution model consists of replacing a non-perfect solution of ions or molecules, generally complex, with a less complex solution (a perfect solution, a dilute ideal solution or a relatively-simple model), formed of the same ions and accompanied by ionic or molecular associated species at equilibrium with the ions.

Depending on the nature of the species in question, we are then led to distinguish two types of solutions:

– solutions which practically contain only ions;

– solutions which, alongside the ions, contain a not-insignificant amount of non-dissociated neutral molecules. These molecules may be molecules of the solvent or of a solute.

If the amount of non-dissociated neutral molecules is negligible in comparison to that of the dissociated molecules, we say that we have a strong electrolyte; such is the case of the aqueous solutions of sodium chloride and hydrogen chloride gas seen earlier. If, on the other hand, the number of molecules not dissociated is significant, we say that we are dealing with a weak electrolyte; such is the case of molten sodium chloride at a temperature a little above the melting point. It is also the case with the aqueous solution of ethanoic acid or ammonia, for example.

In practice, a strong electrolyte is an ionic solution whose formation reaction is complete toward the right; it no longer contains any neutral molecules. Meanwhile, a weak electrolyte is characterized by states of thermodynamic equilibrium between the ions and the neutral molecules – i.e. ultimately characterized by equilibrium constants.

In aqueous solution, practically all salts are strong electrolytes, whilst acids and bases are divided into strong acids and bases, on the one hand, and weak acids and bases, on the other.

## 1.2. Mean concentration and mean activity coefficient of ions

The methods for measuring the activity coefficients are unable to give us the activity coefficients of the individual ions, so it is useful to introduce, for

an electrolyte $A_{v_+} B_{v_-}$, the idea of the *mean activity coefficient* which gives us the same Gibbs energy. We can show that this coefficient is defined by:

$$\gamma_\pm = \left( \gamma_+^{v_+} \gamma_-^{v_-} \right)^{1/(v_+ + v_-)} \tag{1.1}$$

One might also define a *mean concentration* using a similar relation. If $C$ is the molar concentration of the solute, the concentrations of the different ions (for entirely-dissociated strong electrolytes) will be:

$$C_+ = v_+ C \tag{1.2a}$$

and

$$C_- = v_- C \tag{1.2b}$$

and the mean concentration will be:

$$C_\pm = C \left( v_+^{v_+} v_-^{v_-} \right)^{1/(v_+ + v_-)} \tag{1.3}$$

The mean activity coefficient obeys the same convention as the individual activity coefficients – generally convention (III) – but we know that in a dilute solution, the activity coefficients in conventions (II) and (III) are identical.

In particular, for a so-called 1–1 electrolyte, such as potassium chloride (the dissociation of the neutral molecule yields one anion and one cation), we have $v_+ = v_- = 1$ and the above expressions take the following forms:

$$C_+^{1/2} = C_-^{1/2} = C^{1/2} = C_\pm \tag{1.4}$$

$$\gamma_\pm = \left( \gamma_+ \gamma_- \right)^{1/2} \tag{1.5}$$

## 1.3. Dissociation coefficient of a weak electrolyte

Consider an electrolyte A which dissociates according to reaction [1R.4], giving rise to $v_+$ cations $A^{z_+ +}$ and $v_-$ anions $A^{z_- -}$:

$$A = v_+ A^{z_+} + v_- A^{z_- --} \tag{1R.4}$$

Electrical neutrality must be preserved:

$$v_+ z_+ = v_- z_-$$  [1.6]

The dissociation constant is defined as the equilibrium constant of [1R.4]; which is expressed on the basis of the activities of the species (ions and non-dissociated molecules):

$$K_d = \frac{\left|A^{z+}\right|^{v_+} \left|A^{z-}\right|^{v_-}}{|A|}$$  [1.7]

We know that, in a dilute solution, the molar concentrations are practically equal to the ratio of the molar fractions to the volume molar of the solvent, generally the water. However, at ambient temperature, the molar volume of water is basically 1 kg/l. Thus, we keep the same equilibrium constant where the concentrations, expressed in moles/l, replace the molar fractions. In addition, if we separate the concentrations of the activity coefficients, we can write:

$$K_d = \frac{\gamma_{A^{z+}}^{v_+} \gamma_{A^{z-}}^{v_-}}{\gamma_A} \frac{\left[A^{z+}\right]^{v_+} \left[A^{z-}\right]^{v_-}}{[A]} = K_d^{(\gamma)} K_d^{(C)}$$  [1.8]

Thus, relation [1.8] defines two pseudo-constants – one relative to the concentrations:

$$K_d^{(C)} = \frac{\left[A^{z_+}\right]^{v_+} \left[A^{z_-}\right]^{v_-}}{[A]}$$  [1.9]

and the other relative to the activity coefficients:

$$K_d^{(\gamma)} = \frac{\gamma_{A^+}^{v_+} \gamma_{A^-}^{v_-}}{\gamma_A}$$  [1.10]

If we bring in the mean activity coefficient of the ions, then by applying relation [1.1], we find:

$$K_d^{(\gamma)} = \frac{\gamma_{A^{z+}}^{v_+} \gamma_{A^{z--}}^{v_-}}{\gamma_A} = \frac{\gamma_\pm^{(v_+ + v_-)}}{\gamma_A}$$  [1.11]

NOTE.– If we look at relation [1.7], it seems that the dissociation constants do not depend on the solvent. In reality, the reaction written in the form [1R.4] is not correct, because it ignores all the solvation processes which we shall discuss in Chapter 2, which yield the fact that the constant for equilibrium [1.7] truly depends on the solvent.

For weak electrolytes, we define the *dissociation coefficient* or *ionization coefficient* $\alpha$ by the fraction of the molecules of electrolyte that are actually dissociated into the solution.

If we begin with $C_0$ moles of the molecular compound A, the dissociation represented by the reaction [1R.4] gives us a residual concentration of A of $C_0(1-\alpha)$, a concentration of $A^{z_++}$ which is $C_0 v_+ \alpha$ and a concentration of $A^{z_--}$ which is $C_0 v_- \alpha$. The law of mass action in the form [1.8], replacing the concentrations of the different species with their values as a function of $\alpha$, is written:

$$K_d = \frac{\gamma_\pm^{(v_++v_-)}}{\gamma_A} \frac{C_0^{(v_++v_--1)} \alpha^{(v_++v_-)} v_+^{v_+} v_-^{v_-}}{1-\alpha}$$

[1.12]

With very dilute solutions, the activity coefficients are equal to 1 and the law of mass action is expressed as a function of the dissociation coefficient thus:

$$K_d = K_d^{(C)} = \frac{C_0^{(v_++v_--1)} \alpha^{(v_++v_-)} v_+^{v_+} v_-^{v_-}}{1-\alpha}$$

[1.13]

Later on, we use expressions [1.12] and [1.13] to determine the dissociation constant of a weak electrolyte.

NOTE.– If the concentration $C_0$ tends toward zero, we can use relation [1.13], and we see that in order for the equilibrium constant to remain finite, the denominator must tend toward zero, and thus the dissociation coefficient $\alpha$ must tend toward 1. Hence, the dissociation of a weak electrolyte tends to be complete if dilution becomes infinite. In other words, at infinite dilution, weak electrolytes behave like strong electrolytes.

## 1.4. Conduction of electrical current by electrolytes

Electrolytic solutions containing electrically-charged ions conduct electricity which they are subjected to a potential difference – i.e. when the ions are placed in an electrical field. A portion $I_+$ of the intensity of the current is delivered by the cations, which move in the direction of the field; the other portion $I_-$ is carried by the anions, which move in the opposite direction to the field. The total intensity of the current is the sum of the cationic and anionic contributions:

$$I = I_+ + I_-$$

[1.14]

The study of the conductivity of electrolytes does not, strictly speaking, fall within the field of thermodynamics. Nonetheless, here, we shall discuss the essential elements that are necessary to make use of that conductivity to determine the dissociation coefficients.

### 1.4.1. *Transport numbers and electrical conductivity of an electrolyte*

We use the term *cationic transport number* to denote the portion of the current transported by the cations. It is defined by:

$$\tau_+ = \frac{I_+}{I_+ + I_-}$$

[1.15]

In parallel, we define the *anionic transport number* as:

$$\tau_- = \frac{I_-}{I_+ + I_-}$$

[1.16]

Of course, by virtue of relation [1.14], we have:

$$\tau_+ + \tau_- = 1$$

[1.17]

If we consider a cell containing the electrolytical solution, of length $l$ and section area $s$, the resistance obeys the law:

$$R = \rho \frac{l}{s} = \frac{1}{\chi} \frac{l}{s}$$

[1.18]

$\chi$ is the electrical conductivity of the electrolyte, and we deduce:

$$\chi = \frac{1}{R}\frac{l}{s}$$
[1.19]

We can write, in view of Ohm's law, that if $Q$ is the quantity of electricity which has passed through the cell uniformly during the time $t$, the voltage $U$ at the terminals of the cell is:

$$U = RI = \frac{RQ}{t}$$
[1.20]

Thus, by comparing with relation [1.19]:

$$\chi = \frac{Q}{ts\dfrac{U}{l}}$$
[1.21]

The conductivity thus appears as the quantity of electricity per second passing across a 1 cm$^2$ section with a potential drop of 1 v/cm. According to relation [1.19], it is expressed in $\Omega^{-1}$cm$^{-1}$.

NOTE.– Above, we chose commonly-used units. Obviously, in the international system of units (SI), conductivity is expressed in $\Omega^{-1}$m$^{-1}$.

## 1.4.2. Equivalent conductivity and limiting equivalent conductivity of an electrolyte

Experience tells us that the conductivity of a solution depends on the concentration of electrolyte which it contains. Thus, it has become common practice to express the conductivity in relation to the concentration – i.e. the amount of dissolved salt (in moles) per cm$^3$ of solution.

Thus, let $C$ be the concentration of a solution in moles/l. Thus, the quantity per cm$^3$ would be $C/1000$, and we define the *equivalent conductivity* $\Lambda$ as the ratio of the conductivity to the number of equivalents per cm$^3$:

$$\Lambda = \frac{1000\chi}{Cz}$$
[1.22]

The equivalent conductivity is expressed in $\Omega^{-1} \text{moles}^{-1} \text{cm}^2$.

NOTE.– Sometimes, although it is not widely used, we encounter the definition of the *molar conductivity* as the ratio of the conductivity to the concentration expressed in moles per liter:

$$\Lambda_m = \frac{\chi}{C} \qquad [1.23]$$

This molar conductivity is expressed in $l.\Omega^{-1} \text{mole}^{-1} \text{cm}^{-1}$.

Experience shows us that the equivalent conductivity increases as the concentration decreases, tending toward a limit as the concentration tends toward zero (infinite dilution). We define the *limiting equivalent conductivity* $\Lambda_0$ as being the conductivity at infinite dilution. Thus, we write:

$$\Lambda_0 = \lim_{C \to 0} \Lambda \qquad [1.24]$$

## 1.4.3. *Ionic mobility*

We know that each ion, supposed to be punctual, with a charge $ze$, placed in an electrical field $\vec{E}$ experiences a force $\vec{F}$ such that:

$$\vec{F} = ze\vec{E} \qquad [1.25]$$

That force imbues the ion with a velocity $\vec{V}$ in the direction of $\vec{E}$ or the opposite direction, depending on whether it is a cation or an anion. In its motion, the ion encounters resistance, which slows it down. If the solution is sufficiently dilute for it not to be influenced at all by the other ions, it only experiences a counter force on the part of the solvent. This is known as the Stock force, and is proportional to its velocity, in accordance with:

$$\vec{F}' = 6\pi\eta \, r_A \vec{V} \qquad [1.26]$$

In this expression, $\eta$ is the viscosity of the solvent. If $I$ is the ionic strength of the medium and $\varepsilon$ is the electrical permeability of the medium, $r_A$ is the ionic radius defined by the relation:

$$r_A = \sqrt{\frac{1000\varepsilon\, k_B T}{2 N_a e^2 I}} \qquad [1.27]$$

The action of the two forces in opposite directions lends the ion a limiting velocity $\vec{V}_0$ such that:

$$6\pi\eta\, r_A \vec{V}_0 = ze\vec{E} \qquad [1.28]$$

Consider the ratio $\vec{V}_0/\vec{E}$, written as $u_{0+}$ or $u_{0-}$. This velocity per unit field strength, depending on whether it is a cation or an anion, is called the *ionic mobility of the cation or of the anion*. Thus, for the respective mobilities of the cation and the anion, we have:

$$u_{0+} = \frac{z_+ e}{6\pi\eta r_+} \qquad [1.29a]$$

and

$$u_{0-} = \frac{z_- e}{6\pi\eta r_-} \qquad [1.29b]$$

Mobility is expressed in $cm^2 s^{-1} V^{-1}$. The mobilities of the different ions in water range between $2.10^{-4}$ and $10^{-3}$, with the exception of those of the $H^+$ and $OH^-$ ions, which are much higher, with $3.10^{-3}$ for the proton and $2.10^{-3}$ for the hydroxide ion.

The mobilities defined above were to be understood in a sufficiently-dilute (or infinitely-dilute) solution, so that the ion is influenced only by the solvent. In a less dilute solution, each ion is influenced by its neighbors, as it is surrounding by an ionic atmosphere whose electrical charge is of the opposite sign to its own. Whilst at rest, the two centers of symmetry – of the ion and of its ionic atmosphere – coincide; the same is no longer true when

the ion is subjected to the electrical field. The ion is then subject to two additional forces of resistance:

– the relaxation of the ionic atmosphere due to the fact that the ion tends to move in one direction and its ionic atmosphere in the other direction;

– the electrophoretic effect: the counter-flow movement of the positive and negative ions increases the difficulty for the ions to move in the solution.

It follows that in a non-infinitely-dilute solution, the mobilities $u_+$ and $u_-$ of the ions are less than their values observed at infinite dilution, i.e. at zero concentration, denoted by $u_{0+}$ and $u_{0-}$.

Debye and Hückel, alongside Onsager, showed that the mobility at concentration $C$ can be obtained by dividing the mobility at zero concentration by the same corrective term as that used for the activity coefficients in the Debye–Hückel model of a solution, meaning that, if we consider the Debye–Hückel limiting law (see section A.5, in the Appendix), we have:

$$u_+ = \frac{u_{0+}}{1 + Br_+ \sqrt{I}} \qquad\qquad [1.30a]$$

and

$$u_- = \frac{u_{0-}}{1 + Br_- \sqrt{I}} \qquad\qquad [1.30b]$$

The coefficient $B$ is always given by the expression:

$$B = 2.303 \frac{e^2 \sqrt{\dfrac{2N_a e^2}{1000\,\varepsilon_0 D k_B T}}}{2D\varepsilon_0 k_B T} \qquad\qquad [1.31]$$

where, in water, $B = 0.511\ l^{1/2}\mathrm{mole}^{-0.5}$.

NOTE.– Relations [1.30a] and [1.30b] are valid within the same range of concentrations as the Debye–Hückel relation.

### 1.4.4. *Relation between equivalent conductivity and mobility – Kohlrausch's law*

Consider a solution of a completely ionized electrolyte (strong electrolyte) at a concentration $C$ that is sufficiently low so that the mobilities of the ions are the limiting mobilities $u_{0+}$ and $u_{0-}$. The cationic concentration is $v_+C$, whilst that of the anions is $v_-C$.

– the number of cations per cm$^3$ is, therefore: $v_+C/1000$;

– the number of anions per cm$^3$ is: $v_-C/1000$.

The numbers of moles of ions per second which traverse a 1 cm$^2$ section are given:

– for cations, by: $u_{0+}v_+C/1000$;

– for anions, by: $u_{0-}v_-C/1000$.

Thus, the amount of electricity passing across that surface each second is:

$$\chi_0 = \left( u_{0+}v_+ + u_{0-}v_- \right)\frac{C\mathcal{F}}{1000} \qquad [1.32]$$

In view of relations [1.22] and [1.24], we obtain the following for the limiting equivalent conductivity:

$$\Lambda_0 = \left( u_{0+}v_+ + u_{0-}v_- \right)\mathcal{F} \qquad [1.33]$$

This limiting equivalent conductivity is the sum of two contributions:

– one contribution made by the cations:

$$\lambda_{0+} = u_{0+}\mathcal{F} \qquad [1.34]$$

– one contribution from the anions:

$$\lambda_{0-} = u_{0-}\mathcal{F} \qquad [1.35]$$

The values $\lambda_{0+}$ and $\lambda_{0-}$ are called the *limiting equivalent ionic conductivities*. These two contributions are independent of one another,

because the limiting mobilities are values which are intrinsic to each individual ion. It follows that the limiting equivalent conductivity is the sum:

$$\Lambda_0 = \nu_+ \lambda_{0+} + \nu_- \lambda_{0-}$$  [1.36]

This is known as Kohlrausch's law, which was discovered through experimentation.

Based on tables showing the limiting mobilities, or the limiting equivalent ionic conductivities $\lambda_{0+}$ and $\lambda_{0-}$, it is possible to calculate the limiting equivalent conductivity for a given fully-dissociated electrolyte. Table 1.1 gives an extract of such a table.

| Cation | $\lambda_{0+}$ ($\Omega^{-1}.mol^{-1}.cm^2$) | Anions | $\lambda_{0-}$ ($\Omega^{-1}.mol^{-1}.cm^2$) |
|--------|------|--------|------|
| $H^+$ | 349.60 | $OH^-$ | 199.1 |
| $Li^+$ | 38.69 | $Cl^-$ | 76.34 |
| $Na^+$ | 50.11 | $Br^-$ | 78.40 |
| $K^+$ | 73.50 | $I^-$ | 76.80 |
| $Mg^{++}$ | 106.12 | $SO_4^{--}$ | 159.60 |
| $Ca^{++}$ | 119.00 | $NO_3^-$ | 71.40 |
| $Ba^{++}$ | 127.28 | $CH_3CO_2^-$ | 40.90 |

**Table 1.1.** *Limiting equivalent ionic conductivities of a number of ions*

To establish the individual values of the limiting ionic mobilities (Table 1.1), we combine the use of relation [1.36] and the measurement of the limiting conductivity of a strong electrolyte with a measurement of the transport numbers in that same electrolyte. We then use the following relation, which is easy to prove:

$$\frac{\lambda_{0+}}{\lambda_{0-}} = \frac{\tau_+}{\tau_-} \frac{\nu_-}{\nu_+}$$  [1.37]

NOTE.– The only hypotheses made in this section are complete dissociation of the electrolyte and a concentration which tends toward zero, so relations [1.33] and [1.36] apply both the completely-dissociated strong electrolytes and to weak electrolytes because we know that, at infinite dilution, the dissociation coefficient tends toward 1, and that the weak electrolyte tends toward complete dissociation and becomes a strong electrolyte.

### 1.4.5. *Apparent dissociation coefficient and equivalent conductivity*

We use the term *apparent dissociation coefficient* $\alpha_a$ to denote the dissociation coefficient of a weak electrolyte whose ions have the same mobility at a given concentration $C$ as at zero dilution. The number of moles of ions per second crossing a $1\text{cm}^2$ cross-section under the influence of the unit field is:

– for cations: $u_{0+}\nu_+C\alpha_a/1000$;

– for anions: $u_{0-}\nu_-C\alpha_a/1000$.

From this, we deduce a conductivity as follows:

$$\chi = \left(u_{0+}\nu_+ + u_{0-}\nu_-\right)\frac{C\alpha_a\mathcal{F}}{1000} \qquad [1.38]$$

and an equivalent conductivity at concentration $C$:

$$\Lambda_0 = \left(u_{0+}\nu_+ + u_{0-}\nu_-\right)\alpha_a\mathcal{F} \qquad [1.39]$$

By comparing relations [1.33] and [1.39], we can deduce the apparent dissociation coefficient:

$$\alpha_a = \frac{\Lambda}{\Lambda_0} \qquad [1.40]$$

Whilst we have hitherto considered the mobilities to be independent of the concentration, it has long been held that this apparent degree of dissociation is the true degree of dissociation at concentration $C$. Thus, the variation of the equivalent conductivity values was attributed to dissociation alone.

### 1.4.6. *Variations of equivalent conductivities with the concentrations*

We shall now take a look at the variations of the mobility values with concentration, using expressions [1.30a] and [1.30b]. In turn, we examine

the cases of completely-dissociated strong electrolytes and of weak electrolytes exhibiting a true dissociation coefficient $\alpha$ at concentration $C$.

### 1.4.6.1. *Case of strong electrolytes*

Let us begin by considering a strong electrolyte at concentration $C$, completely dissociated. The ionic mobilities of its ions at that concentration are $u_+$ and $u_-$, and its equivalent conductivity is $\Lambda$. We can employ exactly the same reasoning as in section 1.2.3, giving us the following relation, which is valid for the concentration $C$:

$$\Lambda = \left(u_+ v_+ + u_- v_-\right)\mathfrak{F} \qquad [1.41]$$

Thus, by defining ionic mobilities at concentration $C$ by $\lambda_+ = u_+\mathfrak{F}$ and $\lambda_- = u_-\mathfrak{F}$, we obtain the relation:

$$\Lambda = v_+\lambda_+ + v_-\lambda_- \qquad [1.42]$$

Kohlrausch's law therefore remain valid at the concentration $C$ for completely dissociated electrolytes.

If we feed expressions [1.32] back into relation [1.41], and recall that in the case of a single electrolyte, the ionic strength is proportional to the concentration of that electrolyte $C$, we can use the Debye, Hückel and Onsager law to show that, within the limits of concentrations of validity of the Debye–Hückel solution limiting law, the conductivity of the strong (completely dissociated) electrolyte is given by:

$$\Lambda = \Lambda_0 - \left(B_1\Lambda_0 + B_2\right)\sqrt{C} \qquad [1.43]$$

In this relation, the coefficients $B_1$ and $B_2$ are constants which depend only on the solvent (through its dielectric constant and its viscosity), the charges of the ions and the temperature.

For example, for a 1-1 electrolyte – i.e. an electrolyte for which we have $v_+ = v_- = z_+ = z_- = 1$, those coefficients are given in water by Table 1.2 at two temperatures.

| T (°C) | $B_1$ | $B_2$ |
|--------|-------|-------|
| 18°C | 0.224 | 50.5 |
| 20°C | 0.229 | 59.5 |

**Table 1.2.** *Coefficients $B_1$ and $B_2$ from relation [1.43] in water at two temperatures*

NOTE.– Relation [1.43] can also be written in the form:

$$\frac{\Lambda}{\Lambda_0} = \varphi = 1 - \left( B_1 + \frac{B_2}{\Lambda_0} \right) \sqrt{C} \qquad [1.44]$$

In this expression, which is only valid for a strong electrolyte, the coefficient $\varphi$, which is called the conductivity coefficient, no longer represents an apparent dissociation coefficient. It merely enables us to compare the equivalent conductivity at concentration $C$ to the limiting equivalent conductivity of a completely dissociated electrolyte, this coefficient actually quantifies the effect of dilution.

From relation [1.43], we see that it is possible to determine the limiting equivalent conductivity of a strong electrolyte by extrapolation to zero concentration of the straight line showing the equivalent conductivity as a function of the square root of the concentration. Figure 1.1 shows the example, in curve *a*, of such a determination for potassium chloride solutions.
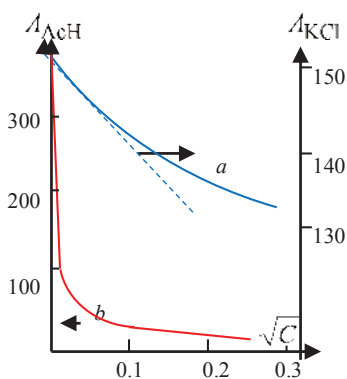


**Figure 1.1.** *Equivalent conductivity a) of potassium chloride – b) of acetic acid as a function of the square root of the concentration*

### 1.4.6.2. *Case of weak electrolytes*

In the case of weak electrolytes that are not completely dissociated, we can no longer apply relation [1.44]. To solve the problem we shall use the MacInnes and Shedlovsky method. Those authors introduce a completely-dissociated fictitious electrolyte containing the same ions as the weak electrolyte under study. This electrolyte would be the effective concentration $C_e$ which is the same as the concentration of the ions in the real electrolyte, so if $\alpha$ is the dissociation coefficient of our electrolyte, the effective concentration will be:

$$C_e = \alpha C \tag{1.45}$$

The equivalent conductivity of that strong electrolyte at the concentration $C_e$ is $\Lambda_e$. To calculate it, as we are dealing with a strong electrolyte, we can apply relation [1.44], which gives us:

$$\frac{\Lambda_e}{\Lambda_0} = \varphi_e = 1 - \left( B_1 + \frac{B_2}{\Lambda_0} \right) \sqrt{\alpha C} \tag{1.46}$$

The ratio $\Lambda/\Lambda_e$ for our weak electrolyte will only take account of the effect dissociation, as the effect of dilution is canceled out because the two electrolytes with equivalent conductivity values $\Lambda$ and $\Lambda_e$ are at the same concentration.

Thus, for the weak electrolyte under study here with equivalent conductivity $\Lambda$, we can write the following, if $\alpha$ is the dissociation coefficient:

$$\frac{\Lambda}{\Lambda_0} = \frac{\Lambda}{\Lambda_e} \frac{\Lambda_e}{\Lambda_0} = \alpha \varphi_e = \alpha \left[ 1 - \left( B_1 + \frac{B_2}{\Lambda_0} \right) \sqrt{\alpha C} \right] \tag{1.47}$$

This relation can also be written thus:

$$\Lambda = \Lambda_0 \alpha - \left( A_1 \Lambda_0 + A_2 \right) \alpha^{3/2} \sqrt{C} \tag{1.48}$$

We can see that the function [1.48] giving $\varLambda$ as a function of $\sqrt{C}$ is, in fact, more complex than it appears, because the dissociation coefficient is itself a function of $C$. Figure 1.1 shows the curve $b$ which represents $\varLambda$ for ethanoic acid.

It stems from the shape of the curve $b$ that $\varLambda_0$ cannot be determined by extrapolation. We can, however, determine this value using Kohlrausch's law – e.g. in the case of ethanoic acid AcH, we can write:

$$\varLambda_0(\text{HAc}) = \lambda_0(\text{H}^+) + \lambda_0(\text{Ac}^-) \tag{1.49}$$

This sum can be broken down as follows:

$$\begin{aligned}\varLambda_0(\text{HAc}) = \lambda_0(\text{H}^+) + \lambda_0(Cl^-) + \left(\lambda_0(\text{Na}^+) + \lambda_0(\text{Ac}^-)\right)\\ - \left(\lambda_0(\text{Na}^+) + \lambda_0(Cl^-)\right)\end{aligned} \tag{1.50}$$

In the pairs of terms, we recognize the limiting equivalent conductivities of the three compounds $\text{HCl}$, $\text{NaAc}$ and $\text{NaCl}$, so we have:

$$\varLambda_0(\text{HAc}) = \varLambda_0(\text{HCl}) + \varLambda_0(\text{NaAc}) - \varLambda_0(\text{NaCl}) \tag{1.51}$$

The three necessary values $\varLambda_0(\text{HCl})$, $\varLambda_0(\text{NaAc})$ and $\varLambda_0(\text{NaCl})$, are easy to determine separately on the basis of the pure electrolytes, using the extrapolation method, described in section 1.4.6.2, because $\text{HCl}$, $\text{NaAc}$ and $\text{NaCl}$ are strong electrolytes and therefore obey relation [1.43].

## 1.5. Determination of the dissociation coefficient

We shall now describe two generally methods which can theoretically be used to determine the dissociation coefficients. One is based on cryometry, and the other on electrical conductivity. In Chapter 7 (section 7.7.2) we shall see a method for determining the dissociation constant of a weak electrolyte on the basis of the voltage of a battery.

### 1.5.1. *Determination of the dissociation coefficient by the cryometric method*

The first method is thermodynamic, because the ionic dissociation has a direct influence on Raoult's laws of ebullioscopy and cryoscopy. Indeed, in the case of cryoscopy, the drop in the melting point of the solvent (index 0) is given by the relation:

$$\Delta T_{0(F)} = \frac{RT_{0(F)}^2}{\Delta_F h_0^0} x_1 \qquad [1.52]$$

If the solution now contains not one but several solutes $i$, we can easily show that the drop of the melting point becomes:

$$\Delta T_{0(F)} = \frac{RT_{0(F)}^2}{\Delta_F h_0^0} \sum_i x_i \qquad [1.53]$$

Suppose that the molecule dissociating gives rise to $v$ ions, and $\alpha$ is the degree of ionization. If we initially consider $n_s$ moles of non-dissociated solute, the total amount of solute $n_t$ after partial dissociation is:

$$n_t = n_s (1-\alpha) + \alpha n_s v = n_s \left[1+(v-1)\alpha\right] \qquad [1.54]$$

The sum of the molar fractions of the solutes is therefore:

$$\sum_i x_i = \frac{n_s \left[1+(v-1)\alpha\right]}{n_0 + n_s \left[1+(v-1)\alpha\right]} \qquad [1.55]$$

If the solution is sufficiently dilute, the second term in the denominator in the previous fraction is small in relation to $n_0$ (amount of solvent) and thus the sum of the molar fractions is approximately:

$$\sum_i x_i = x_s \left[1+(v-1)\alpha\right] \qquad [1.56]$$

We see the emergence of a factor $j$ defined by:

$$j = \left[1+(v-1)\alpha\right] \qquad [1.57]$$

This factor $j$ is called the *van 't Hoff factor*. It can be measured by comparing the cryoscopic drop measured with the electrolyte solution with the calculated value which would be obtained without dissociation – i.e. for $j = 1$.

We supposed, when using relation [1.53], that the solution was sufficiently dilute, meaning that it exhibited ideal behavior. If this is not the case, and we know that this is more common with ionic solutions than for molecular solutions, we must take account of the mean activity coefficient of the ions $\gamma_{\pm}$.

In practice, the differences between the theoretical value and the experimental value are too low for the cryometric method to be able to be used to accurately determine a degree of ionization. Cryometry in a molten-salt medium is able to deliver a more precise result.

## 1.5.2. *Determination of the dissociation coefficient on the basis of the conductivity values*

To determine the degree of ionization, it is preferable to use a dynamic method based on measuring the equivalent conductivity of the electrolytical solution at the desired concentration and calculating the limiting equivalent conductivity. This method is limited to a concentration domain below 0.02 moles per liter, which is the domain of validity of the Debye–Hückel theory for modeling strong electrolytes.

To determine the dissociation coefficient of an electrolyte at a concentration $C$, we measure its equivalent conductivity and calculate its limiting equivalent conductivity by an addition reaction similar to expression [1.50]. We then use expression [1.48] to calculate $\alpha$.

In practice, to determine $\alpha$ on the basis of relation [1.48], which cannot be expressed in terms of $\alpha$, we carry out a succession of approximations.

We determine a first approximate value for $\alpha$: $\alpha_1$ by making $\alpha = 1$, so:

$$\alpha_1 = \frac{\Lambda}{\Lambda_0} \qquad\qquad\qquad [1.58]$$

We feed this value back into the expression of $\alpha$, which enables us to calculate a second approximation $\alpha_2$ by using the relation:

$$\alpha_2 = \frac{\Lambda}{\Lambda_0} \frac{1}{1 - \left( B_1 \Lambda_0 + B_2 \right) \sqrt{\alpha_1 C}}$$   [1.59]

The operation is repeated as many times as necessary. In practice, usually, the second calculated value of $\alpha$ is sufficient and therefore $\alpha = \alpha_2$.

It is the application of relation [1.59], using the Debyean terms $B_1$ and $B_2$, which limits the method to solutions containing concentrations lower than 0.02 moles/l, i.e. within the bounds of application of Debye's model.

## 1.6. Determination of the number of ions produced by dissociation

We shall now describe two experimental methods that can be used to determine the number of ions produced by the dissociation of an electrolyte. These methods, which can be used for strong (i.e. completely dissociated) electrolytes, are again based on measurements of the conductivity and cryometric measurements.

### 1.6.1. *Use of limiting molar conductivity*

We have seen (section 1.4.3) that the ionic mobilities do not vary within a very large range (between $2 \times 10^{-4}$ and $10^{-3}$ cm$^2$s$^{-1}$V$^{-1}$, with the exception of the ions H$^+$ ($3 \times 10^{-3}$ cm$^2$s$^{-1}$V$^{-1}$) and OH$^-$ ($2 \times 10^{-3}$ cm$^2$s$^{-1}$V$^{-1}$). The same is true of the limiting equivalent conductivities. Consequently, the limiting molar conductivity will increase with the number of ions provided by the molecule. Table 2.1 shows the ranges of the molar conductivities depending on the number of ions supplied by the decomposition of the molecule.

Obviously, this method lacks precision and can only be applicable for dissociated species. Thus, if we consider the three complexes in platinum – [Pt(NH$_3$)$_4$Cl$_2$]Cl$_2$, [Pt(NH$_3$)$_3$Cl$_3$]Cl and [Pt(NH$_3$)$_4$Cl$_4$] – upon dissociation they can only furnish chlorine ions and complex ions. For these three complexes, we find the limiting molar conductivities 228, 97 and 1. The first value belongs to the range 200–300 and thus there will by three ions (one complex

ion and two chlorine ions). The second value belongs to the range 100–200, so there are two ions (one complex ion and one chlorine ion). Finally, for the last complex, the value belongs to the range < 100, so it gives no ions at all.

| Number of ions | Molar conductivity |
|:---:|:---:|
| 2 | 100–150 |
| 3 | 200–300 |
| 4 | 400–450 |
| 5 | > 500 |

**Table 1.3.** *Molar conductivity values and number of ions*

### 1.6.2. *Use of cryometry*

The method presented here applies to completely dissociated (i.e. strong) electrolytes. We employ the same reasoning as in section 1.5.1 but adapt it to the decomposition of an electrolyte, which ionizes to produce $n$ ions. By virtue of relations [1.53] and [1.56], we can write the following for the variation of the melting point of the solvent:

$$\Delta T_{0(F)} = \frac{RT_{0(F)}^2}{\Delta_F h_0^0} x_s \left[1+(n-1)\alpha\right] \qquad [1.60]$$

Let us introduce the quantity $q_s$ (number of moles) of solute for 1000 g of solvent. It is easy to show that, for a dilute solution ($x_s \approx 1$), this quantity is given as a function of the molar fraction of the solute and the molar mass of the solvent by the relation:

$$q_s = \frac{100x_s}{M_0} \qquad [1.61]$$

Thus, the variation in melting point is written as:

$$\Delta T_{0(F)} = \frac{RT_{0(F)}^2 M_0}{1000\Delta_F h_0^0} q_s \left[1+(n-1)\alpha\right] \qquad [1.62]$$

We see the emergence of the cryoscopic constant of the solvent, which is defined by:

$$K_{0(Cryo)} = \frac{R T_{0(F)}^2 M_0}{1000 \Delta_F h_0^0} \qquad [1.63]$$

The variation in temperature of the solvent therefore becomes:

$$\Delta T_{0(F)} = K_{0(Cryo)} q_s \left[ 1 + (n-1) \alpha \right] \qquad [1.64]$$

If there were no ionization of the electrolyte, that variation in the melting point would be, where $(n = 0)$:

$$\Delta T_{0(F)} = K_{0(Cryo)} q_s \qquad [1.65]$$

Let us examine the limit of the *molecular drop* $\dfrac{\Delta T_{0(F)}}{q_s}$, when $q_s$ tends toward 0. In these conditions, when dilution tends toward infinity, we know that the fraction of dissociation of the complex tends toward 1, so we have:

$$\lim_{q_s \to 0} \frac{\Delta T_{0(F)}}{q_s} = K_{0(Cryo)} n \qquad [1.66]$$

If the electrolyte were not dissociated, that ratio would be constant:

$$\frac{\Delta T_{0(F)}}{q_s} = K_{0(Cryo)} \qquad [1.67]$$

Figure 1.2 shows the variations in the molecular drop with the quantity of complex dissolved.

In the case of non-dissociation, the curve is not a horizontal because the variations of the activity coefficients with dilution come into play.

In the case of dissociation, the ordinate at the origin is used to calculate the coordination number if we know the cryoscopic constant of the solvent, which can be calculated.
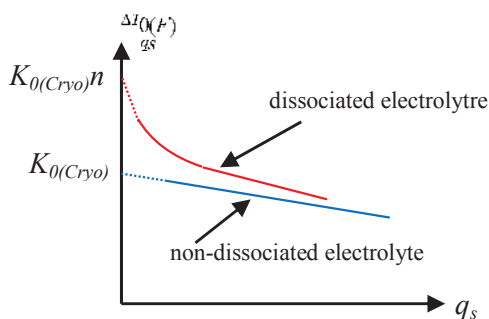
**Figure 1.2.** *Variation of the molecular drop with the quantity of complex dissolved*

In practice, the variation of the activity coefficients, which is very significant at high dilution, renders the above extrapolation very difficult. It is preferable to operate in conditions such that the activity coefficients practically do not vary. With this in mind, we carry out cryoscopy in a molten-salt medium.

Numerous saline hydrates behave like cryoscopic solvents when we dissolve a substance in the molten hydrate. We observe a cryoscopic drop of the melting point. We also see a cryoscopic drop in the temperature of the hydrate-to-anhydrous transformation and the temperature of a eutectic, e.g. between a salt and ice.

In this case, the activity coefficients of the ions practically no longer vary with dilution. Indeed, we know that these activity coefficients vary not with the composition of an ionic solution but with the ionic strength of the solvent. Molten salts are composed of a large quantity of ions so that the addition of a solute does not alter the ionic strength of the medium.

In these conditions, the molecular drop varies little with the quantity of dissolved salt, and therefore it is easy to extrapolate to the situation of zero dissolved quantity. In addition, if the solvent contains a common ion with the solute, that ion is inactive from the point of view of cryoscopy, because its quantity practically does not vary when the complex is dissociated.

The method applies both to the dissociation of complexes and that of the ions.

For example, with cryoscopies at the transition temperature between sodium sulfate and sodium sulfate decahydrate, it has been possible to measure the following values of $n$:

$- n = 1$; for sodium chloride NaCl (the common sodium ion has no influence), and for magnesium sulfate $MgSO_4$ (with a common sulfate ion). The true value of the coordination number is 2;

$- n = 2$, for potassium nitrate $KNO_3$ and potassium sulfate $K_2SO_4$ (common sulfate ion). The true value of the coordination number is 3;

$- n = 3$, for magnesium chloride $MgCl_2$.

## 1.7. Thermodynamic values relative to the ions

In order to study the ionic medium, we need to know the enthalpies and entropies of the reactions, and therefore the enthalpies and entropies of formation of the ions. This is the topic of our discussion in this section.

Note, firstly, that it is not possible to deduce the values we seek from the known values for the atoms and molecules because, in view of the necessity to respect the electrical neutrality of the balance equations, it is impossible to design reactions which involve only the ions of one species.

### 1.7.1. *The standard molar Gibbs energy of formation of an ion*

Consider, for instance, the reaction of formation of a pair of dissolved ions:

$$A_{pure} + B_{\,pure} + solvent = A^+ \,(dissolved) + B^- \,(dissolved) \qquad [1R.5]$$

The Gibbs energy associated with that reaction is given by:

$$\Delta_5 G_T = \mu_T^0(A^+) - \mu_T^0(B^-) + RT \ln \frac{\left| A^+ \right|}{\left| B^- \right|}$$

$$= \mu_T^0(A^+) - \mu_T^0(B^-) + RT \ln \frac{\left[ A^+ \right]}{\left[ B^- \right]} + RT \ln \left( \gamma_\pm \right)^{(\nu_+ + \nu_-)} \qquad [1.68]$$

The standard chemical potentials of the ions cannot be found individually. At most, by placing ourselves in conditions such that the mean activities of the ions are equal to 1, and considering the Gibbs energy associated with the dilution, we can determine the difference between the two standard potentials $\mu_T^0(A^+) - \mu_T^0(B^-)$.

To find an individual value, it is necessary, by convention, to attribute a particular value to the standard chemical potential of an ion, and then, starting with that chosen value, little by little, calculate a complete scale of the standard potentials of the ions.

To choose the base, we consider the electrochemical reaction associated with the neutralization of the proton, which is written thus:

$$H^+ + e^- = 1/2H_2 \qquad\qquad\qquad [1R.6]$$

The standard Gibbs energy associated with this reaction is:

$$\Delta_6 g_{298}^0 = \frac{1}{2}\mu_{298}^0(H_2) - \mu_{298}^0(H^+) \qquad\qquad [1.69]$$

By convention, this standard Gibbs energy is chosen as being equal to 0 at 25°C. This is known as *Latimer's first convention*. Thus:

$$\Delta_6 g_{298}^0 = 0 \qquad\qquad\qquad [1.70]$$

By combining relations [1.69] and [1.70], we immediately obtain:

$$\mu_{298}^0(H^+) = \frac{1}{2}\mu_{298}^0(H_2) \qquad\qquad\qquad [1.71]$$

As the standard enthalpy of formation of the hydrogen molecule is zero at 25°C, we can deduce that:

$$\mu_{298}^0(H^+) = -\frac{298}{2}s_{298}^0(H_2) \qquad\qquad\qquad [1.72]$$

Thus, the standard chemical potential of the hydrogen ion is directly linked to the standard entropy of the dihydrogen molecule.

At a temperature other than 25°C, relation [1.71] still holds true, but the standard enthalpy of formation of the hydrogen molecule is no longer zero.

### 1.7.2. *Standard enthalpy of formation of ions*

By convention, and for the same reasons as for the Gibbs energy, *Latimer's second convention* is to posit that the standard enthalpy of formation of $H^+$ ions is 0 at any given temperature.

$$h_T^0(H^+) = 0 \qquad [1.73]$$

This convention is the same as that of neutral molecules of simple substances, which is normal because relation [1.71] can be transposed to apply to enthalpies.

### 1.7.3. *Absolute standard molar entropy of an ion*

In view of convention [1.73], relation [1.72] becomes:

$$s_T^0(H^+) = \frac{1}{2} s_T^0(H_2) \qquad [1.74]$$

Hence, at 25°C:

$$s_{298}^0(H^+) = \frac{1}{2} s_{298}^0(H_2) = 65\ 342\ \text{J.mole}^{-1}\text{K}^{-1} \qquad [1.75]$$

Note that the entropy of formation of the $H^+$ ions is not zero, contrary to another convention which Latimer had chosen and which thus proved to be inconsistent with the first two.

In this chapter, we have examined the behavior of an electrolyte placed in water. The study would have been performed in the same way if, instead of water, we had used another solvent, provided that, like water, that solvent has a high dielectric constant. In the case of a solvent with a lower dielectric constant, we see that the solution behaves as though the number of ions were less. The conductivity decreases. Not only are the coefficients $B_1$ and $B_2$ from relation [1.41] different, but it is as if the concentration too were lower – even in the case of a strong electrolyte in the solvent at hand. In

Chapter 3, when we study acids, we shall see the role of the dielectric constant of the solvent on the dissociation of an acid. Then, we introduce the ion pair model.

### 1.7.4. *Determination of the mean activity of a weak electrolyte on the basis of the dissociation equilibrium*

Suppose we know the dissociation constant of the weak electrolyte AH and its dissociation coefficient $\alpha$ at the chosen concentration $C$. The dissociation constant is written as:

$$K = \frac{\alpha^2 C}{1-\alpha} \frac{\left(\gamma_{\pm}\right)^2}{\gamma_{AH}} \qquad [1.76]$$

Adopting the hypothesis of a solution sufficiently dilute in terms of electrolyte AH, we know that as the concentration decreases, neutral molecules approach an ideal state much more quickly than do ions. Thus, we shall posit $\gamma_{AH} = 1$. Immediately, we find;

$$\gamma_{\pm} = \sqrt{\frac{K(1-\alpha)}{\alpha^2 C}} \qquad [1.77]$$

We shall see other methods for measuring the mean activity of an electrolyte in Chapter **7**.