

An Introduction to Electrochemical Engineering

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By

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FOREWORD

Since the early days of the 20th century, when chlor-alkali industry and metal electrowinning were, with lead-acid and Leclanché batteries, almost the only economically significant electrochemical processes, a dramatic change has taken place.

In fact, the impact and span of electrochemistry in modern industry has evolved since then at an astonishing pace. New inorganic and organic products have been synthesized, surface treatments by electrochemical techniques are a keystone in the production of electronic devices, the mechanisms of corrosion have been understood and consequently the development of techniques for its prevention and control are now available, the introduction of new techniques for producing mechanical pieces that were not amenable to traditional methods and new techniques for energy production by electrochemical methods are some of the present day industrial activities under the scope of electrochemistry.

This impressive development has posed unexpected challenges for young engineers that, when entering their first job, feel that they have landed on *terra incognita*, where the introduction of an electric field in the realm of chemical reactions shakes their foundations.

University curricula on industrial chemistry and chemical engineering have traditionally considered that electrochemical engineering is just limited to the analysis of reactors similar to those studied for chemical processes, on which reaction kinetics is governed by the Tafel equation. This is clearly an oversimplification whose consequences, that stem from the fact that undergraduate physical – chemistry courses do not afford knowledge on the fundamentals of electrode processes, are apparent when *terra incognita* opens its unknown grounds to the newcomer.

After more than 25 years teaching electrochemical engineering at the undergraduate and graduate level in the Chemical Engineering Department of the Buenos Aires University, and following many discussions lead with R&D and plant managers of different companies on the expected profile of young engineers, we decided that it was worthwhile to write an introductory

book on Electrochemical Engineering that, in the first place, offers an adequate physical – chemistry background on electrochemistry and, on this basis, considers five broad areas of professional activity for engineers.

We hope that the present book, whose content has evolved from the quite traditional view our course had in the late 90's to its present form, will help to improve undergraduate curricula in chemical engineering and, also, be a valuable asset for graduate courses in other engineering branches.

PART 1

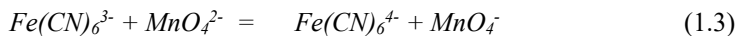
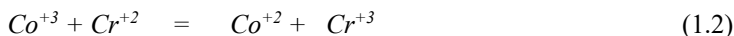
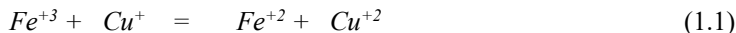
FUNDAMENTALS

CHAPTER ONE

INTRODUCTION

In many cases processes, called *reactions*, occur in which a well-defined number of substances, generally named *reagents*, interact transferring atoms between molecules, thus producing a set of new substances which are called *products*. If the transferred atom shows no change in its oxidation state the process is called a *chemical reaction*; on the other hand, if the atom transfer includes a change in its oxidation state, because electrons are also exchanged, the process is called an *electrochemical reaction*.

Electrochemical reactions can be classified in two groups according to the way in which electrons are transferred. Thus, the electrochemical reaction is called *homogeneous* when electron transfer occurs between two species that are dissolved in the same phase. Many reactions between ions in water correspond to this group such as:



These reactions might take place in several steps but in all cases, as shown in Figure 1.1, electron transfer is produced when the involved species collide with enough energy to overcome the activation barrier.

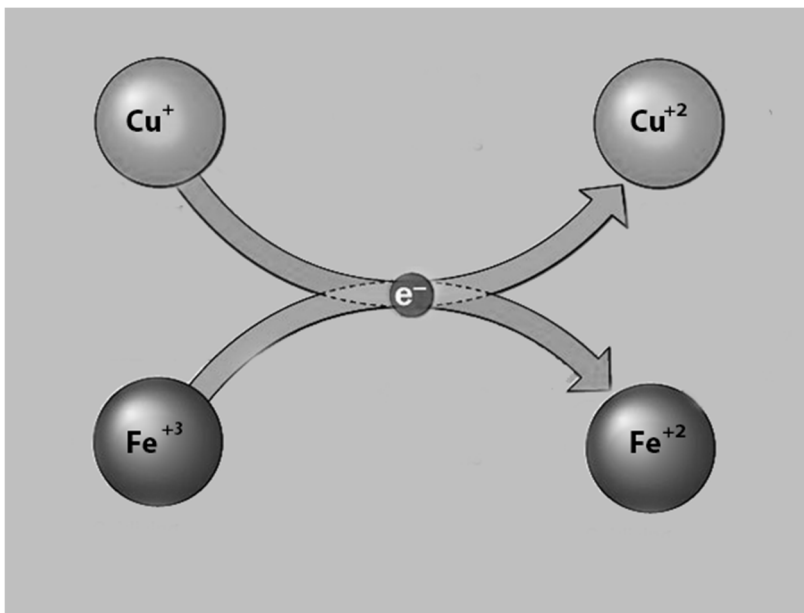


Figure 1.1: Schematic representation of the reduction of an Fe^{+3} ion and the oxidation of Cu^{+} ion.

An electrochemical reaction is *heterogeneous* when electron transfer does not occur by direct contact of the reactants but takes place, **separately**, at two independent interphases in which an electronic conductor, the *electrode*, is in contact with an ionic conductor, the *electrolyte*, and an electric potential difference exists between them. When the reaction proceeds spontaneously such arrangement is called an *electrochemical cell* and the electric potential difference is generated by the reaction. When the process is not spontaneous, an electric potential difference must be applied to the electrodes in order that the reaction can occur, in which case the arrangement is called an *electrochemical reactor*.

Two reactions that occur heterogeneously are:



Figures 1.2a and 1.2b schematically show the way in which electron transfer between reagents takes place in both cases.

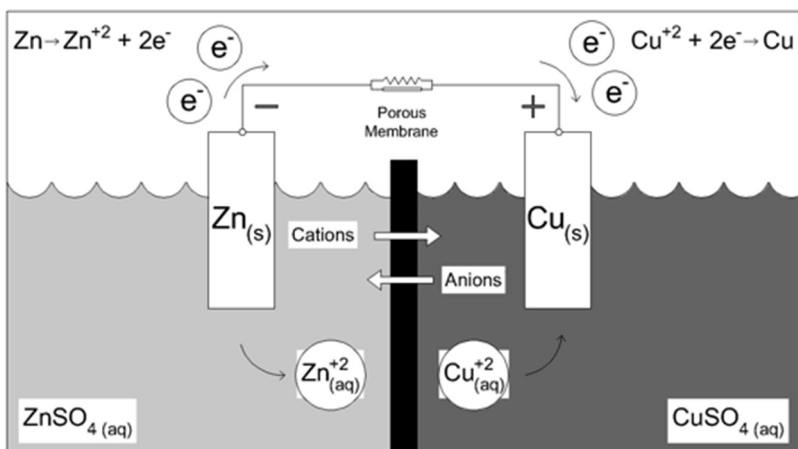


Figure 1.2.a: Spontaneous reduction of Cu^{+2} to Cu and oxidation of Zn to Zn^{+2} in an electrochemical cell.

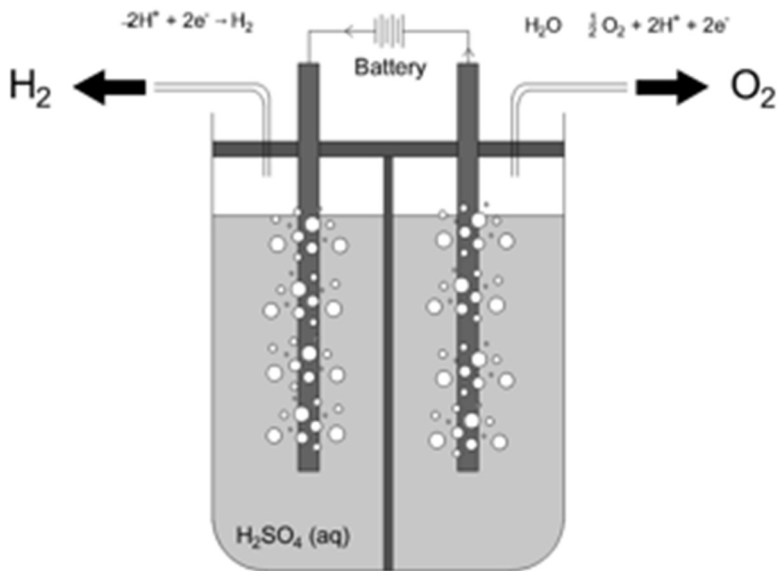
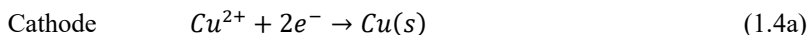


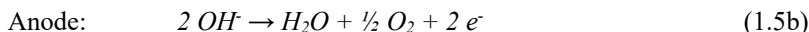
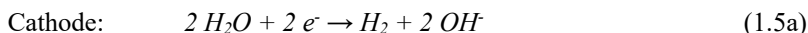
Figure 1.2.b: Water decomposition into hydrogen and oxygen in an electrochemical reactor.

It is to be pointed out, hence, that heterogeneous electrochemical reactions imply that reduction and oxidation processes occur separately on the electrodes. The electrode on which the reduction reaction takes place is the *cathode* and the electrode on which the oxidation reaction occurs is the *anode*.

Taking into consideration the electrochemical reaction (1.4) the processes occurring at each electrode are:



while for reaction (1.5) the electrode processes are



Considering now the general electrode reaction:



Faraday's law indicates that the number of electrodes that flow through the circuit per unit time is proportional to the reaction rate and, hence, we have:

$$\frac{dn_A}{dt} = \frac{I}{\nu^*\mathcal{F}} \quad (1.7)$$

where n_A is the number of moles of A, I is the electric current, ν^* is the number of electrons exchanged and \mathcal{F} is Faraday's constant ($\mathcal{F} = 96487$ Coulomb).

If the electric current I is to be maintained, an electric potential difference $\Delta\Psi$ between both electrodes must be established and the product $|I\Delta\Psi|$ indicates the electric power that must be exchanged. When the reaction occurs spontaneously this electric power is obtained from the reaction energy itself while, if the reaction is not spontaneous, electric power must be provided by an external source.

In the first case, the transformation of reactants into products results in the production of electrical energy:

$$\text{Zn} + \text{Cu}^{2+} = \text{Zn}^{2+} + \text{Cu} + I \cdot \Delta\Psi \quad (1.8)$$

In the second case, electrical energy must be applied in order to obtain the products:



Heterogeneous electrochemical reactions are of practical interest since it is possible, by controlling the electric current, a direct management of reaction rate. Hence, a central goal for the electrochemical engineer will be to optimise the electric current value: in the case of industrial production of substances the aim is to minimise energy consumption per kilogram of product whereas, in the case of electricity generation by means of electrochemical reactions, the goal is to maximise the amount of energy obtained per kilogram of reactant.

The energy balance of the process is, thus, the core problem to be solved by the engineer and, on a first analysis, the following contributions can be identified for a process occurring at a given current value:

- The amount of energy that, according to the reaction spontaneity, will be produced or required, which depends on the thermodynamic electric potential difference, $\Delta\Psi_{\text{therm}}$
- The amount of energy required to overcome the activation barriers involved in electrode reaction kinetics, which depends on the “*activation overpotential*”, $\Delta\Psi_{\text{act}}$.
- The amount of energy required to keep reactants flowing to, and products flowing from, the electrodes, which depends on the “*mass transfer overpotential*” $\Delta\Psi_{\text{mt}}$.
- Finally, the amount of energy employed in overcoming the electrical resistance of the medium that separates the electrodes, which depends on the “*resistance overpotential*”, $\Delta\Psi_{\Omega}$,

Consequently, the total potential difference in an electrochemical cell can be described by the equation:

$$\Delta\Psi = \Delta\Psi_{\text{therm}} - \Delta\Psi_a - \Delta\Psi_{\text{mt}} - \Delta\Psi_{\Omega} \quad (1.10)$$

where the value of $\Delta\Psi_{\text{therm}}$ might be positive or negative. If $\Delta\Psi$ is positive, the cell will be able provide energy while, if $\Delta\Psi$ is negative, an external energy source will be needed in order that reaction occurs.

The purpose of this book is to provide the reader with the basic knowledge required to understand the main factors that impact on the different contributions shown in Eqn. (1.10) and apply it to some cases of practical interest.

CHAPTER TWO

THE ELECTROLYTE RESISTANCE

2.1. Introduction

In order to sustain an electric current through a piece of matter an electric potential difference must be applied. The relationship between electric current and potential is given by Ohm's law:

$$\Delta\Psi_{\Omega} = I \cdot R \quad (2.1)$$

where R is the electrical resistance and $\Delta\Psi_{\Omega}$ is the electric potential difference required to maintain the current flow I .

When electrochemical reactions are employed to produce substances or to obtain energy at industrial scale, large currents are needed and, consequently, a critical goal is to reduce the resistance of the electrolyte in the cell as much as possible.

In order to give an idea of the importance of this fact, Table 2.1 shows some typical current values for several industrial processes.

Process	Production (kg/h)	Current (A)
Aluminium production	32	100,000
Copper refining	23	20,000
Chlorine production	185	150,000
Hydrogen production	0.34	10,000

Table 2.1: Typical current values in industrial cells for some important industrial processes.

With these current values, applying equation 2.1 and assuming that electric energy is provided at a cost of 0.02 US\$/kWh, Table 2.2 shows the cost per kilogram of product, for three electrolyte resistance values.

Process	R = 1 Ω	R = 0,1 Ω	R = 0,01 Ω
Aluminium production	6,250	625	62.5
Copper refining	349	34.9	3.49
Chlorine production	2,432	243.2	24.32
Hydrogen production	5,882	588.2	58.82

Table 2.2: Energy cost in US\$ per kilogram due to electrolyte resistance.

As it is clearly seen, minimizing electrolyte resistance is of utmost economic importance and, therefore, it is necessary to understand its causes.

2.2. Electrical conductivity of solutions: Basic concepts

The electrical resistance of a homogeneous piece of a given material, with length \mathcal{L} and cross-sectional area \mathcal{A} , is given by:

$$R = \rho \frac{\mathcal{L}}{\mathcal{A}} \quad (2.2)$$

where ρ is the *specific resistance*, or *resistivity*, which is usually expressed in $\Omega \cdot \text{cm}$.

The *specific conductance*, or *conductivity*, of a material is defined as:

$$\kappa = \rho^{-1} = \frac{\mathcal{L}}{\mathcal{A}R} \quad (2.3)$$

with units $\mathcal{S} \cdot \text{cm}^{-1}$ where \mathcal{S} = Siemens = Ω^{-1} . Table 2.3 shows resistivity and conductivity values for several electronic and ionic conductors.

Material	ρ ($\Omega \cdot \text{cm}$)	κ ($\mathcal{S} \cdot \text{cm}^{-1}$)
Silver	$1.6 \cdot 10^{-6}$	$6.3 \cdot 10^5$
Copper	$1.7 \cdot 10^{-6}$	$5.9 \cdot 10^5$
Gold	$2.2 \cdot 10^{-6}$	$4.5 \cdot 10^5$
Aluminium	$2.6 \cdot 10^{-6}$	$3.8 \cdot 10^5$
Tungsten	$5.1 \cdot 10^{-6}$	$1.9 \cdot 10^5$
Zinc	$5.6 \cdot 10^{-6}$	$1.8 \cdot 10^5$
Steel	$11.9 \cdot 10^{-6}$	$8.4 \cdot 10^4$
Lead	$21.9 \cdot 10^{-6}$	$4.6 \cdot 10^4$
Titanium	$46.2 \cdot 10^{-6}$	$5.9 \cdot 10^4$
Mercury	$95.8 \cdot 10^{-6}$	$2.1 \cdot 10^4$
Graphite	$700 \cdot 10^{-6}$	$1.4 \cdot 10^3$

NaCl (molten at 1000 °C)	$2.43 \cdot 10^{-3}$	$4.2 \cdot 10^2$
H ₂ SO ₄ 3.5 M (18 °C)	$1.35 \cdot 10^{-2}$	73.9
NaCl (saturated at 18 °C)	$4.67 \cdot 10^{-2}$	21.4
KOH 1 M (18 °C)	$5.43 \cdot 10^{-2}$	18.4
NaCl 1 M (18 °C)	0.134	7.44
LiCl 1 M (18 °C)	0.158	6.34
Zirconia (85% ZrO ₂ 15% Y ₂ O ₃) a 1000 °C	0.20	5.0
Water (25 °C)	$1.82 \cdot 10^5$	$5.5 \cdot 10^{-6}$
Methanol (25 °C)	$1.43 \cdot 10^6$	$7 \cdot 10^{-7}$
Benzene (25 °C)	$2 \cdot 10^{11}$	$5 \cdot 10^{-12}$

Table 2.3: Resistivity and conductivity values for several materials.

In metals electric current flows because of the movement of electrons in the conduction band, but in an electrolyte solution electrical conductivity is due to the movement of dissolved ions and any attempt to understand the mechanisms which lead to the observed resistance values must be based on this fact.

A first intuitive analysis suggests that the conductivity of an electrolyte will depend on the concentration of ionic species: a larger number of ions able to contribute to electricity transport should yield a larger conductivity value. A second intuitive assumption is that, since the kinetic energy of dissolved ions increases with temperature, the electrolyte conductivity should be enhanced at higher temperature values. In Table 2.4 results obtained in highly precise measurements on KCl solutions are shown which confirm both points.

Molality g KCl/1000 g solution	K273.15K S.cm⁻¹	K291.15K S.cm⁻¹	K298.15K S.cm⁻¹
71.1352	0.065176	0.097838	0.111342
7.41913	0.007137	0.011167	0.012857
0.745263	0.0007736	0.0012205	0.0014087

Table 2.4: Conductivity of KCl solutions at three temperature values.

A careful look at data of Table 2.4 indicates that conductivity increases with concentration and therefore one might assume that in a first, coarse, approximation the conductivity of a mixture of ionic compounds should be the sum of the conductivity of each component of the mixture. Thus, if we

have measured the conductivity of several solutions, say CuCl_2 at concentration c_1 ; NaNO_3 at concentration c_2 and K_2SO_4 at concentration c_3 whose values are, respectively, κ_1 , κ_2 and κ_3 the conductivity of a mixture of the three compounds at these concentrations could be assumed to be given by:

$$\kappa \approx \kappa_1 + \kappa_2 + \kappa_3 \quad (2.4)$$

This approach, however, is only valid at highly dilute solutions and, if applied to solutions with component concentrations of practical interest, significant errors will be committed. Such errors can be particularly serious, as shown in Figure 2.1, where it is seen that when ionic concentrations increase the slope of the conductivity vs concentration curves diminishes and, eventually, reaches a maximum.

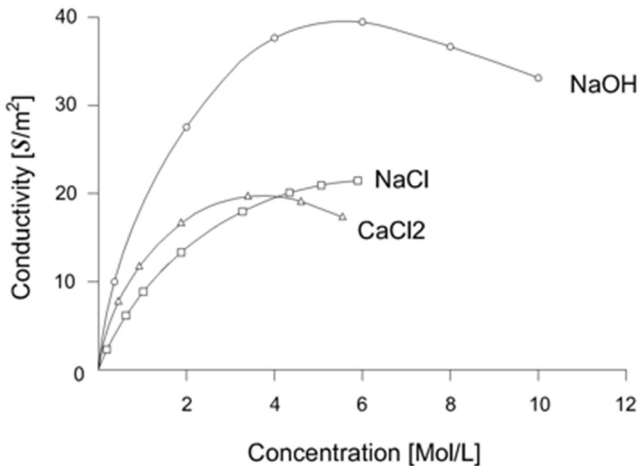


Figure 2.1 Conductivity vs concentration curves for several ionic compounds.

2.3. Equivalent conductance

If the resistance of a given solution is to be directly obtained from experimental conductivity values it will be necessary to have specific data for each compound and, moreover, for each mixture over a given concentration range. Thus, a large number of costly and time-consuming measurements should be performed. However, and as suggested by the additivity rule of conductivity at highly dilute solutions, we might conclude that each ionic species makes a well defined contribution to the conductivity

of a mixture. Hence, the idea is to look for a method that allow to express conductivity of a solution in such a way that its dependence with concentration be described by means of general equations in which the individual contribution of each ion can be identified.

With this goal in mind the *molar conductance*, Λ_m , of a solution of an electrolyte with concentration c is defined as:

$$\Lambda_m = \frac{\kappa}{c} \quad (2.5)$$

Clearly, molar conductance units are $\mathcal{S} \cdot \text{cm}^2 \text{mol}^{-1}$.

When studying a mixture containing ions of different electrical charge, the direct use of molar conductance has some drawbacks and, for this reason, the use of the concept of *equivalent conductance*, Λ , defined as:

$$\Lambda = \frac{\kappa}{c \cdot n_{eq}} \quad (2.6)$$

has been customary where, for a solution of the ionic compound $A_{n_A}B_{n_B}$, $n_{eq} = n_A z_A = -n_B z_B$, is the number of equivalents in a mole of electrolyte, n_A and n_B indicate the stoichiometric number of cations and anions in the electrolyte molecule, and z_A and z_B their charge. Λ units are, then, $\mathcal{S} \cdot \text{cm}^2 \cdot \text{eq}^{-1}$.

By the end of the 19th century Kohlrausch (Kohlrausch, 1874) performed a systematic experimental study on solution conductivity variation with concentration for a large number of 1 – 1 electrolytes and found that, if concentrations were kept below 0.001 M, in all cases it was verified that:

$$\Lambda = \Lambda^\circ - A \cdot c^{1/2} \quad (2.7)$$

which is known as Kohlrausch's equation, where Λ° is the equivalent conductance at infinite dilution of the electrolyte and A is a positive parameter. Considering (2.6) it comes that:

$$\kappa = \Lambda^\circ \cdot c - A \cdot c^{3/2} \quad (2.8)$$

From the obtained experimental data Kohlrausch showed that, for a binary ionic compound, the electrolyte equivalent conductance at infinite dilution could be described as the sum of two independent contributions, one from the cation and other from the anion:

$$\Lambda^\circ = \lambda_+^\circ + \lambda_-^\circ \quad (2.9)$$

and thus, recording the λ° values for the different ions, it is possible to obtain the equivalent conductance at infinite dilution of any ionic compound. Table 2.5 shows the equivalent conductance at infinite dilution for some of the most usual ions in aqueous solution.

Ion	$\lambda^\circ/(\text{S}\cdot\text{cm}^2\cdot\text{eq}^{-1})$
H^+	349.8
OH^-	199.1
Li^+	38.6
Na^+	50.1
K^+	73.5
Rb^+	77.8
Cs^+	77.2
Ag^+	61.9
NH_4^+	73.5
F^-	55.4
Cl^-	76.4
Br^-	78.1
I^-	76.8
NO_3^-	71.5
ClO_4^-	67.3
Mg^{2+}	53.0
Ca^{2+}	59.5
Sr^{2+}	59.4
Ba^{2+}	63.6
Cu^{2+}	53.6
Zn^{2+}	52.8
Pb^{2+}	69.5
Co^{2+}	55.0
Al^{3+}	69.8
La^{3+}	69.7
SO_4^{2-}	80.0
CO_3^{2-}	69.3

Table 2.5.: Equivalent conductance at infinite dilution of several ions at 298.15 K.

2.4. Ionic mobility and transport numbers

In the absence of an electric field ions move randomly in an electrolytic solution and, if concentration gradients are nil, the net ionic flow at any point is zero. However, if an electric field is applied, a force will operate on each ion whose value depends on the electric field intensity and the ion electric charge, z_j . If the electric field is not extraordinarily high, this force will be almost instantaneously balanced by the solution viscosity and ions will attain a limiting velocity \vec{v}_j that, according to Stoke's law, is:

$$\vec{v}_j = \frac{\vec{F}}{6\pi r_j \nu} \quad (2.10)$$

where \vec{F} is the applied force, r_j the effective ionic radius and ν the solution viscosity.

Defining ionic mobility, u_j , as the velocity attained by the ion under unit force:

$$u_j = \frac{|\vec{v}_j|}{|\vec{F}|} \quad (2.11)$$

and since the applied force on an ion is:

$$\vec{F} = z_j \cdot \vec{E} = z_j (-\nabla\psi) \quad (2.12)$$

where \vec{E} is the electric field, the electrical mobility of an ion, u'_j , is defined as the velocity attained by the ion under a unit electric field:

$$u'_j = \frac{|\vec{v}_j|}{|\vec{E}|} = \frac{|\vec{v}_j|}{|\nabla\psi|} \quad (2.13)$$

Ionic electrical mobility clearly has a direct link with ionic equivalent conductance as can be seen if a volume element with unit length and cross-sectional area, containing a solution of the ionic compound $A_a B_b$ with concentration c is considered. In this volume the ionic total charge for each species is:

$$|Q_A| = |Q_B| = \mathcal{F} \cdot |z_A a| \cdot c = \mathcal{F} \cdot |z_B b| \cdot c \quad (2.14)$$

Applying a unit potential difference ($|\Delta\psi| = 1V$) on this volume the electrical current I is:

$$I = \kappa. \Delta \Psi = \kappa. 1V \quad (2.15)$$

Now, since conductivity can be expressed in terms of ionic electrical mobility by:

$$\kappa = \mathcal{F}(z_A. u'_A. a. c + z_B. u'_B. b. c) \quad (2.16)$$

and since $|z_A a| = |z_B b| = n_{eq}$, from (2.6):

$$\kappa = \Lambda. n_{eq}. c = (\lambda_A + \lambda_B). n_{eq}. c \quad (2.17)$$

and it comes that:

$$\mathcal{F}. u'_A = \lambda_A \quad (2.18)$$

and

$$\mathcal{F}. u'_B = \lambda_B \quad (2.19)$$

Under no concentration gradients, the current fraction carried by each ion is:

$$\tau_A = \frac{u'_A}{u'_A + u'_B} \quad (2.20)$$

for species A and

$$\tau_B = \frac{u'_B}{u'_A + u'_B} \quad (2.21)$$

for species B. τ_A and τ_B are the *transport numbers* of A and B.

In the general case it can be shown that in a solution with several ionic components with concentrations and charges c_i and z_i , the transport number for each species is:

$$\tau_j = \frac{|z_j|.c_j.u'_j}{\sum_i (|z_i|.c_i.u'_i)} \quad (2.22)$$

where the sum is performed over all the ionic species.

2.5. Equivalent conductance dependence on ionic concentration

When the equivalent conductance of an electrolyte solution is measured at very low concentrations, there is a linear dependence with $c^{1/2}$, as shown in Eqn. (2.7). However, as concentration increases the Λ vs $c^{1/2}$ curve deviates from linearity and this deviation is larger when ionic charges are higher and, also, if the electrolyte is only partially dissociated. Figure 2.2 shows experimental results for some specific cases.

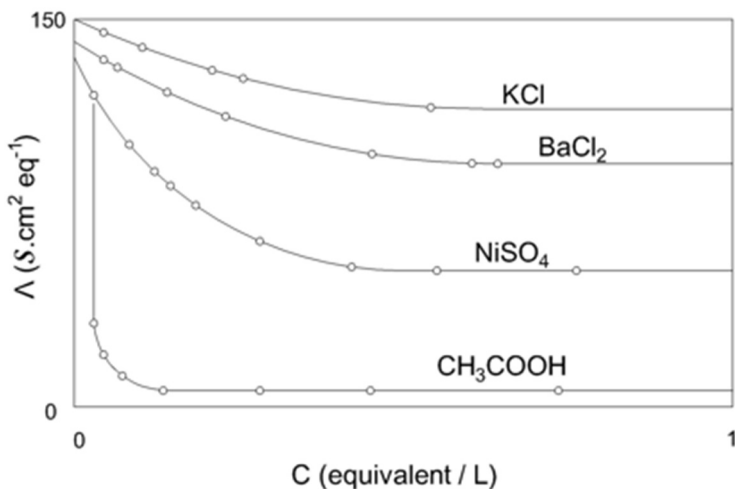


Figure 2.2: Equivalent conductance dependence on concentration for several electrolytes at concentrations below 1 M.

In order to understand this behaviour, it is necessary to consider the fact that ions in solution are not free but associated with solvent molecules through charge – dipole and chemical interactions. In the case of aqueous solutions, hydrated ions are the entities that move under an electric field and, consequently, their mobility is related to the hydration sphere radius. In turn, hydration sphere radii depend on the hydration number, *i.e.*, the number of water molecules attached to the particular ion, which is a function of both charge and size of the ion: for two ions with the same charge value the polarizing effect on water dipoles will be more intense for species with lower ionic radius. Thus, hydration number of alkali ions increases as $K^+ < Na^+ < Li^+$ and, correspondingly, equivalent ionic conductance at infinite dilution shows the reverse behaviour $\lambda_{K^+}^o > \lambda_{Na^+}^o > \lambda_{Li^+}^o$.

On a first approximation an electrolytic solution might be described as a dielectric continuum in which charged spheres, whose radii depend on the hydration number, interact through electrostatic forces. Hence, if an observer is installed on a hydrated positive ion, the charge distribution around it will not be homogeneous, because the ion density of negative hydrated ions will exceed that of positive ions, and a negative *ionic atmosphere* is built.

From this description, the behaviour of the equivalent conductance vs concentration curve is explained on the basis of three contributions:

- The electrophoretic effect
- The relaxation effect
- Specific interactions between ions

The electrophoretic effect is the consequence of the fact that when a hydrated ion moves in a viscous medium it tends to drag other ions of the solution in its vicinity. Conversely, dragged ions will affect the original ion, restraining its advance, an effect whose impact will increase with ionic concentration.

In understanding the relaxation effect, it can be mentioned that the function that describes the distribution of charges in the neighbourhood of a given ion, which was calculated by Debye and Hückel (Debye and Hückel, 1923) for dilute solutions, is, in the absence of an electric field, spherically symmetric. Thus, when an electric field is applied, ions with opposite charge are attracted in opposite directions, and the consequence of this fact is that the *ionic atmosphere* loses its symmetry and exerts a force, against that induced by the field, which will depend on concentration.

Finally, as the concentration of an electrolyte increases, the probability that an anion and a cation get near enough to generate an electrostatic attractive force that overcomes thermal agitation is enhanced and “ionic pairs” with net zero charge can be formed, which will not contribute to conductivity. Furthermore, specific chemical interactions might exist, forming molecules with net zero charge. Weak electrolytes are a typical case of chemical interactions that affect conductivity. Figure 2.2 illustrates how equivalent conductance of acetic acid solutions briskly falls from the infinite dilution value because of the strong chemical interaction between the acetate anion and the H^+ cation that impedes the complete dissociation of the acid.

For dilute electrolytic solutions, in which ionic pair formation can be dismissed, the equations describing the electrophoretic and the relaxation effects were obtained by Onsager (Onsager, 1927) employing the distribution function of Debye and Hückel and the equivalent conductance is expressed as:

$$\Lambda = \Lambda^\circ - [A \cdot \Lambda^\circ + B] \cdot \mathcal{I}^{1/2} \quad (2.23)$$

where A and B are constants, and \mathcal{I} is the solution ionic force defined by:

$$\mathcal{I} = \frac{1}{2} \sum_i c_i z_i^2 \quad (2.24)$$

where c_i is the molar concentration of species i , z_i its charge, and the sum is carried over all ionic components. Obviously, Kohlrausch's equation is a particular case of Eqn. (2.24) for 1 – 1 electrolytes.

As said above, Onsager's equation is valid only at highly dilute solutions which are not typical of those found in electrochemical processes of practical interest. Therefore, several modifications have been proposed to be used at higher concentrations which can be considered approximate forms of the polynomial:

$$\Lambda = \Lambda^\circ - [B_1 \cdot \Lambda^\circ + B_2] \cdot \mathcal{I}^{1/2} + B_3 \mathcal{I} - B_4 \mathcal{I}^{3/2} + \dots \quad (2.25)$$

In concentrated mixtures of ionic compounds, it is usual to work employing *ad hoc* correlations developed on the basis of (2.25).

2.6. Anomalous conductance in aqueous media. Conductance in non-aqueous media and molten salts

If the values of equivalent ionic conductance at infinite dilution in water, shown in Table 2.5, are examined, it is clear that those corresponding to H^+ and OH^- are considerably larger than what can be expected from the arguments given in the previous section. This “anomalous” behaviour can be understood if the particular structure of liquid water is considered. In fact, and as demonstrated by spectroscopical measurements and computational models, water molecules interact through hydrogen bonds as shown in Figure 2.3