

« *Department of Process and Environmental Engineering”*

Electrochemistry course

Level:L3+ING3 Process Engineering

Chapter I: electrolyte solutions

Presented by :

Pr NEDJHIOUI MOHAMMED

Agenda



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Introduction

- Electrochemistry is the study of the physical and chemical phenomena occurring when an "electrode" and an electrolyte come into contact. Such contact constitutes what is called a "half-cell."

Electrochemistry is divided into two main parts:

Thermodynamics and Kinetics of Electrolytes;

Electrochemical Thermodynamics and Kinetics.

The first part generally concerns the properties of electrolyte solutions, especially aqueous ones. (Non-aqueous solutions are also considered).
The second part concerns the study of the thermodynamics and kinetics of electrode processes and the theories of batteries and electrolytic cells.

I.2 ELECTROLYTES

I.2.1 Definition of an Aqueous Electrolytic Solution

- An aqueous electrolytic solution (or aqueous electrolyte) is obtained by dissolving an ionic substance or compound in water, which acts as a solvent.
- The definition of electrolytes is based on the "quantitative theory of electrolytic dissociation," which concerns salts capable of conducting an electric current.

I.2.2 Classification of electrolytes

Certain substances called electrolytes, dissolved in suitable solvents, can dissociate into particles called ions of opposite signs.

There are different types of electrolytes:

1. Binary electrolytes, or mono-monovalent electrolytes, dissociate into two ions
   They are symbolized by 1.1 ($HCl \rightarrow H^{+} + Cl^{-}$).
2. Di-divalent electrolytes are symbolized by 2.2 ($CuSO^{4-} \rightarrow Cu^{2+} + SO4^{2-}$).
3. Ternary electrolytes, dissociate into three ions. We distinguish:

Mono-divalent electrolytes, symbolized by 2.1 ($Na_2SO4 \rightarrow 2Na^{+} + SO4^{2-}$)

1. Di-monovalent electrolytes, symbolized by 1.2 ($CaCl_2 \rightarrow Ca^{2+} + 2Cl^{-}$).
2. Quaternary electrolytes dissociate into four ions, and are divided into:
3. Mono-trivalent electrolytes, symbolized by 1.3 ($K_3PO_4 \rightarrow 3K^{+} + PO4^{3-}$).
4. Tri-monovalent electrolytes, symbolized by 3.1 ($Al(NO_3)_3 \rightarrow Al^{3+} + 3(NO3)^{-}$)

Electrolytic solutions are solutions that conduct electrical current, the flow of which is ensured by ions. We distinguish:

Solid salts ($10^{+3} < \text{Resistivity} < 10^{+8}$) Ω.cm

Molten substances ($0.1 < \text{Resistivity} < 10$) Ω.cm

Electrolyte solutions Resistivity < 10^{+6}Ω.cm



I.2.3 the strength of electrolytes



Electrolytes can be divided into two groups:

Those that, despite the electrostatic attractions between ions of opposite signs, are completely dissociated are called "strong electrolytes," and their dissociation is a complete reaction.

$$AB \rightarrow A^{+} + B^{-}$$

Exemple: ($HCl \rightarrow H^{+} + Cl^{-}$).

a) Those that are imperfectly dissociated are weak electrolytes; their dissociation is reversible.

b) $AB \rightleftharpoons A^+ + B^-$ ($CH_3COOH \rightleftharpoons CH_3COO^- + H^+$)

c) The previous relationship can be applied to a weak binary electrolyte AB of concentration C.

d) The dissociation is not complete, and the number of B- and A+ ions would be αC.

e) α is called the dissociation coefficient. It gives the number of electrolyte molecules that are dissociated at equilibrium. It is given by:

f) $$\propto = \frac{n}{N} = \frac{\text{number of dissociated electrolyte molecules}}{\text{number of dissolved electrolyte molecules}}$$

I.5 ELECTRICAL CONDUCTIVITY OF SOLUTIONS

I.5.1 Conductance

- Consider the same electrolyte column of cross-section S and length l (Figure).
- Resistance (in Ω or Ohm) can be defined for an electrolyte as for a metal, and therefore the specific resistance or resistivity ρ can be defined as the resistance of an electrolyte column of cross-section S=1 cm2 and length 1 cm where the field is uniform.

We will measure the resistivity ρ in Ohm-cm. We then have:

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

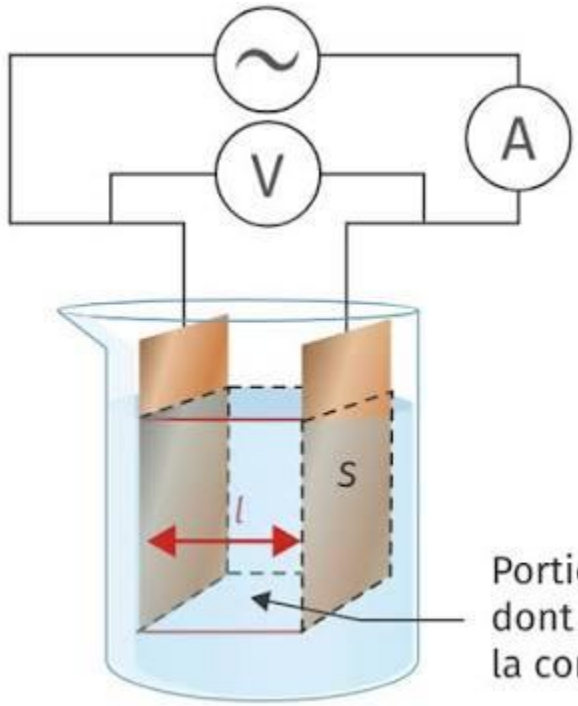
For an electrolyte, the inverse of resistance is more often used.

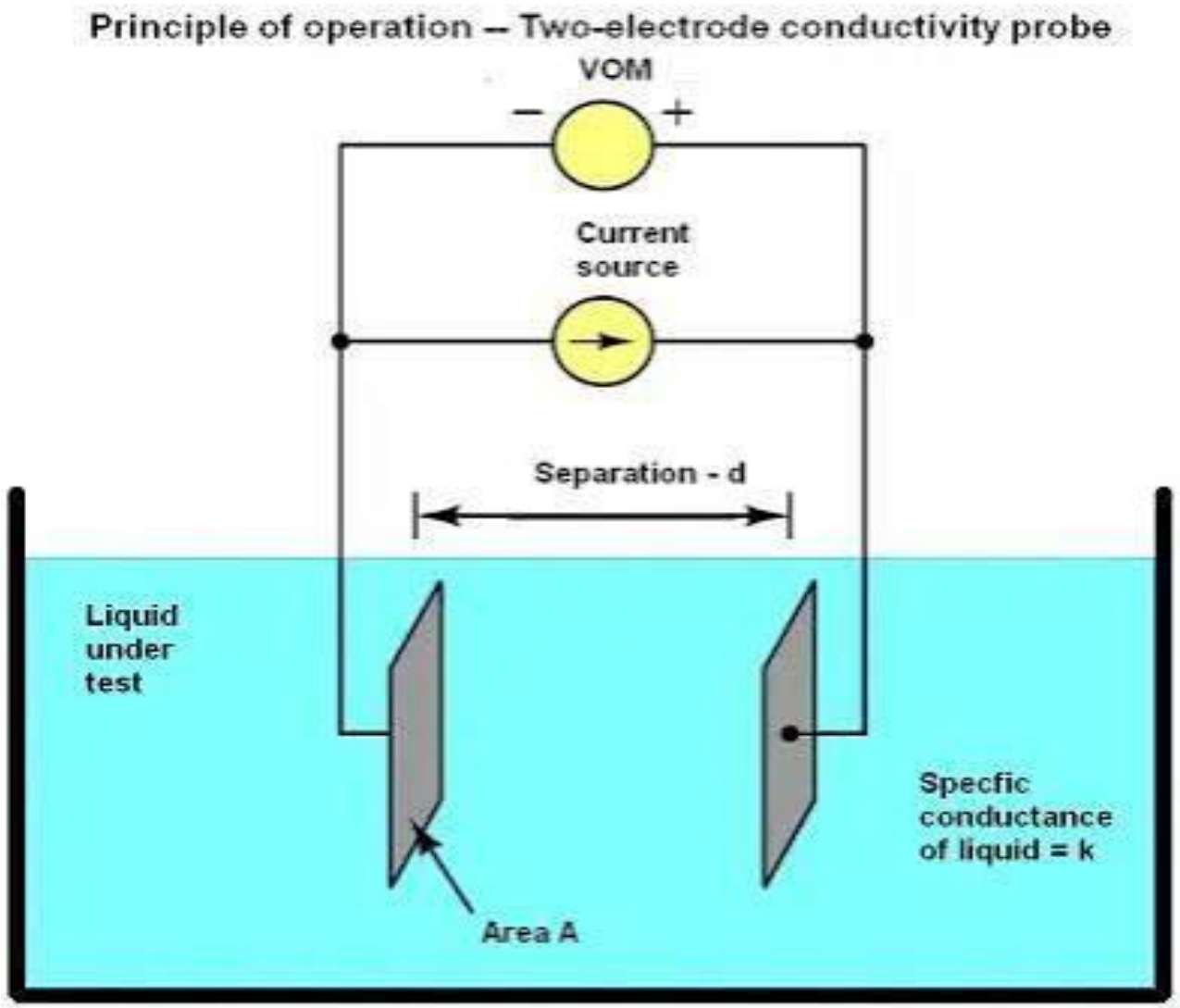
$$G=\frac{1}{R}=\frac{S}{\rho l}$$

This is the conductance of the solution. It is expressed in Siemens S or Ω-1.



Presentation ti


A
V
S
l
Portion de solution
dont on mesure
la conductance G


Principle of operation -- Two-electrode conductivity probe
VOM
−
+
Current
source
Separation - d
Liquid
under
test
Specfic
conductance
of liquid = k
Area A

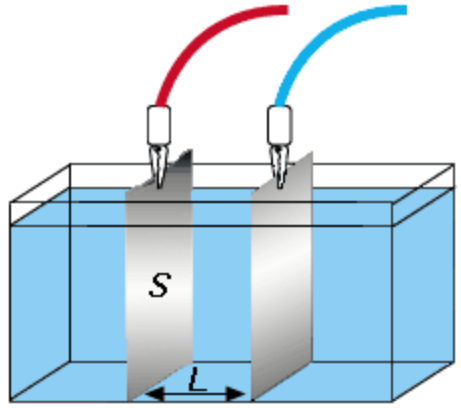
La conductance G est définie **sur une portion de solution**, caractérisée par une largeur L (en m) et une section S (en m^2).

G dépend de L et de S ; G est proportionnelle à $\frac{S}{L}$:

$$G = \sigma \times \frac{S}{L}.$$

[*G* en S ; S en m^2 ; L en m et **σ en $S.m^{-1}$**.]

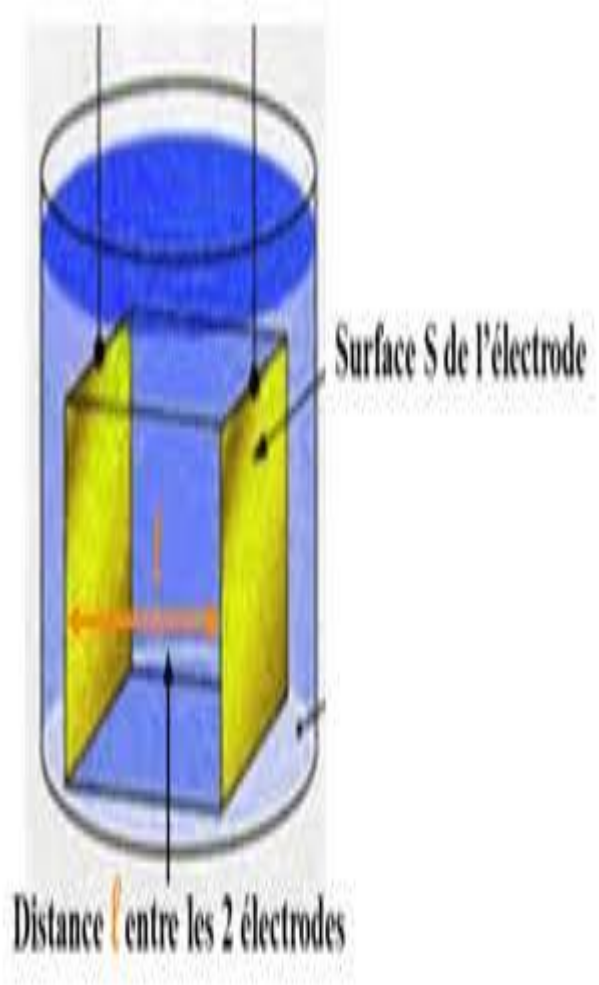
Le coefficient de proportionnalité **σ** (sigma) **représente la conductivité de la solution électrolytique.**



La conductivité traduit aussi la **capacité** qu'a une solution électrolytique à conduire le courant électrique.
La conductivité se mesure en **$S.m^{-1}$**.

Remarques : Plus la conductivité est grande, plus la solution est conductrice. La valeur de la conductivité dépend de la nature de la solution utilisée :

Electrolyte	NaCl	KCl	NaOH
Conductivité ($\mu S.m^{-1}$)	126,4	149,8	248,7


Surface S de l'électrode
Distance l entre les 2 électrodes

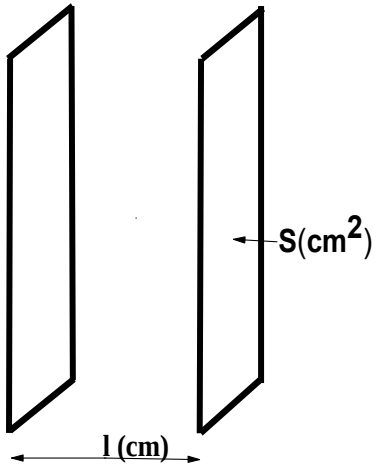
Dimensional Formulas in Physics

Electricity & Electrostatics (91 – 100)

91. Electric Charge → $[IT]$
92. Electric Potential → $[ML^2T^{-3}I^{-1}]$
93. EMF → $[ML^2T^{-3}I^{-1}]$
94. Electric Field → $[MLT^{-3}I^{-1}]$
95. Electric Flux → $[ML^3T^{-3}I^{-1}]$
96. Electric Displacement → $[ITL^{-2}]$
97. Capacitance → $[M^{-1}L^{-2}T^4I^2]$
98. Resistance → $[ML^2T^{-3}I^{-2}]$
99. Resistivity → $[ML^3T^{-3}I^{-2}]$
100. Conductance → $[M^{-1}L^{-2}T^3I^2]$

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In practice, the l/S ratio is called the conductivity cell constant.



I.5.1 Specific Conductivity.

- The conductivity of an electrolyte solution is a quantity that defines the solution's ability to conduct current.
- Let's consider the same electrolyte column as before.
- We will measure ρ in Ohm-cm. For an electrolyte, the inverse of the resistivity is also most often used.

$$\sigma = \frac{l}{\rho}$$

This is the specific conductivity. It is expressed in Ohm-cm-1.

Comparison with Ohm's formula:

$$U = RI$$

With:

$$R = \rho\, l/S = 1/\, c\, l/S$$

This is the specific conductivity. It is expressed in Ohm-cm-1.

Comparison with Ohm's formula:

$$U = RI$$

With:

$$R=\rho \frac{l}{s} = \frac{l}{\sigma \frac{l}{s}}$$

1.5.2 Equivalent conductivity

a) The equivalent conductivity Λ of an electrolyte solution is defined as the conductivity of the electrolyte per unit of charge concentration. This charge concentration will be noted as “Ceq”.

b) According to the previous formulas, the specific conductivity σ varies with the concentration and obviously vanishes when C=0, that is to say when there is no electrolyte.

$$\Lambda = \frac{1000}{C_{eq}} \sigma \qquad \text{(I.26)}$$

With σ in Ohm.cm^{-1} et C_{eq} in equivalent g/l

a) Exemples :

b1) Consider a solution containing a binary electrolyte: NaCl with a concentration of C0 (mol/l). Calculate the equivalent conductivity of this solution.

We have:

$C_{eq} = |Z_{Na^+}|.C_{Na^+} = |Z_{Cl^-}|.C_{Cl^-} = C_0$ (mole/l) = 1. C_0 =|−1|. C_0= C_0 (mole/l) et

$$\sigma_{solution} = \sigma_{Na^+} + \sigma_{Cl^-}$$

hence: $\Lambda = \frac{\kappa_{solution}}{C_{eq}} = \frac{\kappa_{Na^+} + \kappa_{Cl^-}}{C_0}$

b2) Consider a solution containing a binary electrolyte: $CaCl_2$ with a concentration of C_0 (mol/l). Calculate the equivalent conductivity of this solution.

We have:

$$C_{eq} = |Z_{Ca^{2+}}|.C_{Ca^{2+}} = |Z_{Cl^-}|.C_{Cl^-} = 2C_0 \text{ (mole/l)} = 2.C_0 = |-1|.2C_0 = 2C_0 \text{ (mole/l)}.$$

Hence :

$$\Lambda = \frac{\kappa_{solution}}{C_{eq}} = \frac{\kappa_{Ca^{2+}} + \kappa_{Cl^-}}{2\,C_0}$$

1.5.3 Ionic equivalent conductivity

In an electrolyte solution, when the latter contains two or more ions, we define the ionic equivalent conductivity (noted λ_i)
b) Example: either to determine the equivalent conductivity of a solution containing $ZnCl_2$ at C_0 (mole/l) from the ionic equivalent conductivities of this compound.

The equivalent conductivity of the solution is:

$$\Lambda = \lambda_{Zn^{2+}} + \lambda_{Cl^-}$$

From the above, we have:

$$C_{Zn^{2+}eq} = |Z_{Zn^{2+}}|. C_{Zn^{2+}} = 2\ C_0 \ \text{et}$$

$$C_{Cl^-}\ eq\ = |Z_{Cl^-}|. C_{Cl^-}\ = 2\ C_0$$

hence :

$$\lambda_{Zn^{2+}} = \frac{\sigma_{Zn^{2+}}}{2C_0} \text{ et } \lambda_{Cl^-} = \frac{\sigma_{Cl^-}}{2C_0}$$

La conductivité équivalente de la solution est :

$$\Lambda = \lambda_{Zn^{2+}} + \lambda_{Cl^-}$$

Dans notre exemple : $\Lambda = \frac{\sigma_{Zn^{2+}}}{2C_0} + \frac{\sigma_{Cl^-}}{2C_0} = \frac{\sigma_{Zn^{2+}} + \sigma_{Cl^-}}{2C_0} = \frac{\kappa_{solution}}{2C_0}$

Note: The value of the limiting equivalent conductivity for infinite dilution, Λ_0 (or Λ_∞), can be considered as the sum of the contributions to the conductivity of the individual ions λ_{0i} (or $\lambda_{\infty i}$)

hence:

$$\Lambda_0 \text{ (or } \Lambda_\infty) = \lambda_\infty^+ + \lambda_\infty^-$$

This is Kohlrauch's law of independent ion migration, and is valid for all electrolytes.

Table I.1 below lists some values of equivalent ionic conductivities at infinite dilution of a few ions.

Cations	λ_{0i} en S.cm^2. mole^{-1}	anions	λ_{0i} en S.cm^2. mole^{-1}
H_30^+	350	OH^-	198
Li^+	38.7	F^-	55.4
Na^+	50.11	Cl^-	76
K^+	73.5	I^-	76.5
NH_4^+	73.55	CN^-	57
Mg^+	53	NO_3^-	71.5
Ca^{2+}	59.5	CH_3COO^-	41
Zn^{2+}	53	HCO_3^-	44.5
Ba^{2+}	63.5	CO_3^{2-}	69.5
Ag^+	62	SO_4^{2-}	80
Cu^{2+}	54	HSO_4^-	72.5
Al^{3+}	189	$HC_2O_4^-$	53
Pb^{2+}	139	PO_4^{3-}	69.5

Example: to determine the limiting equivalent conductivity of ethanoic acid from the following chemical reaction:

$$NaCl + CH_3COOH \rightleftharpoons CH_3COONa + HCl$$

From equation I.29 and table I.1, we can write:

$$\Lambda_\infty(CH_3COOH) = \Lambda_\infty(CH_3COONa) + \Lambda_\infty(HCl) - \Lambda_\infty(NaCl)$$

$\Lambda_\infty(CH_3COOH)$= 91+425-128,1= 387,1 $S.cm^2.\ mole^{-1}$

The value obtained from the table gives $\Lambda_\infty(CH_3COOH) = \lambda^+_\infty(H_30^+) + \lambda^-_\infty(CH_3COO^-)$ =391 $S.cm^2.\ mole^{-1}$.

Or ∝ obeys Ostwald's dilution law:

$$k = \frac{\propto^2 C}{1 - \propto}$$

From which we deduce another expression for ∝:

$$\propto = \frac{\Lambda}{\Lambda_\infty}$$

- This is the Arrhenius relation, a relation that allows us to measure $\propto$ at any concentration if we can determine Λ_∞ more precisely by extrapolation.

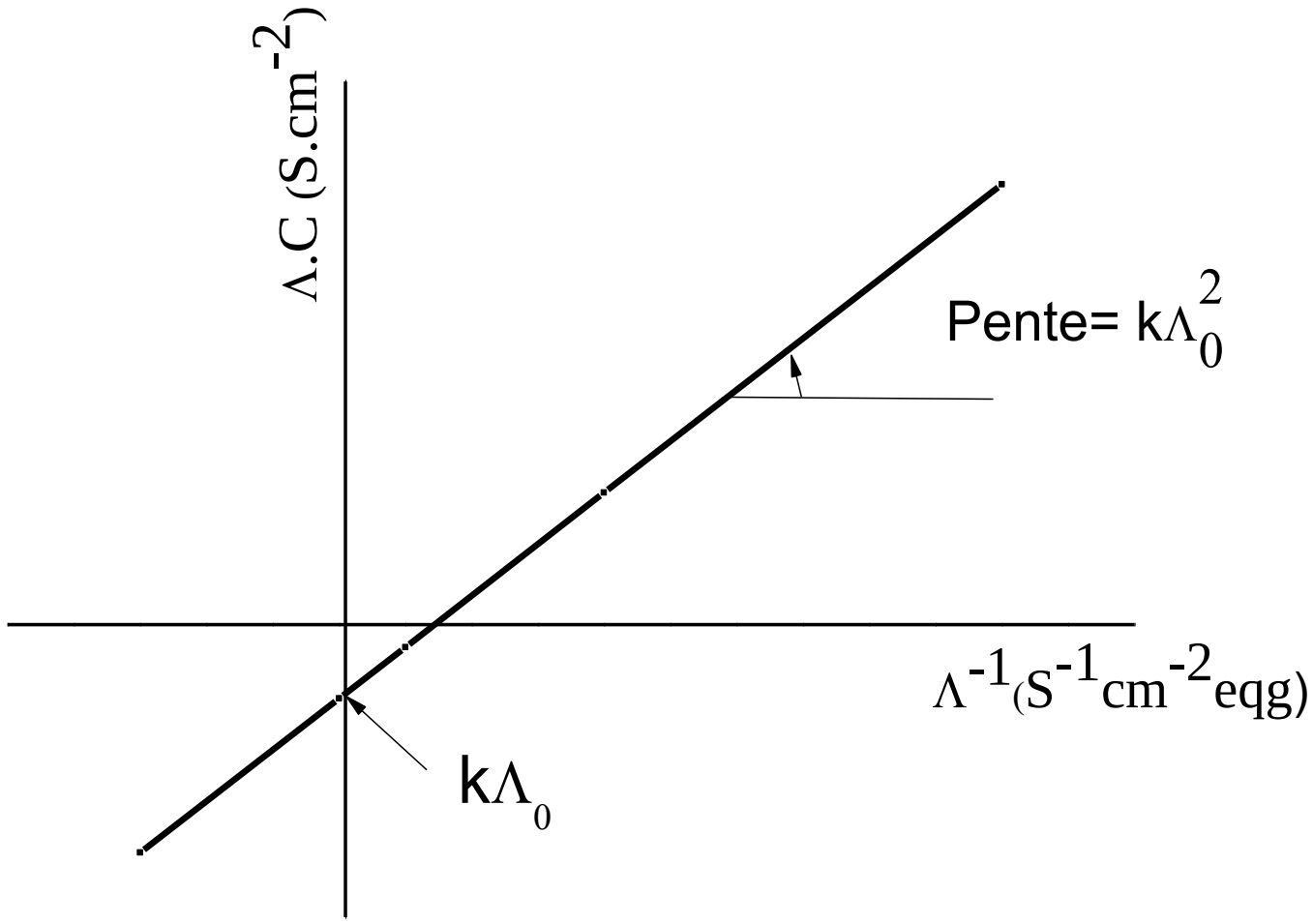
- On the other hand, by replacing $\propto$ with this expression in the Ostwald formula, we have:

$$k = \frac{C\frac{\Lambda^2}{\Lambda_\infty}}{\Lambda - \frac{\Lambda}{\Lambda_\infty}}$$

$$k\Lambda_\infty = \frac{C\Lambda^2}{\Lambda_\infty - \Lambda}$$

$$k = \frac{C\frac{\Lambda^2}{\Lambda_\infty}}{\Lambda - \frac{\Lambda}{\Lambda_\infty}} = \frac{\Lambda^2 C}{\Lambda_\infty - \Lambda\Lambda_\infty} \Rightarrow \Lambda^2 C = k\Lambda_\infty^2 - k\Lambda\Lambda_\infty$$

Plotting the curve $\Lambda C = k\frac{\Lambda_\infty^2}{\Lambda} - k\Lambda_\infty$ gives a straight line whose slope gives the value of $k\Lambda_\infty^2$ and the ordinate at the origin gives - $k\Lambda_\infty$ (figure I.4).


Λ.C (S.cm-2)
Pente= kΛ0 2
Λ-1(S-1cm-2eqg)
kΛ0

I.2.5 Electrolyte Activity:

- Consider an electrolyte $A_m B_n$ that is totally or partially dissociated according to the relationship

$$\text{Am Bn} \rightleftharpoons \text{m(ions A)+n(ions B)}$$

- The activity of this compound in solution can be defined as a function of the chemical potential.

I.2.5.1 Expression of chemical potential:

The chemical potential of the two ionic species in solution is given as a function of the activity "a" and the activity coefficient by: a=f.C. We have:

$$a_A = f_A . C_A \; et \; a_B = f_B . C_B$$

f_A and f_B are the activity coefficients of A and B. They tend toward 1 in dilute solution and their value is equal to 1 if the species considered is a molecule or a solid.

We then have:

$$\begin{cases} \mu_A = \mu_A^0 + RTLoga_A \\ \mu_B = \mu_B^0 + RTLoga_B \end{cases}$$

Therefore, for a solution containing "i" ionic species in solution, the chemical potential denoted "μ_i"will be given by the expression:

$$\mu_i = \mu_i^0 + RTLoga_i$$

with:

a_i= the activity of species i in solution given by $a_i = f_i.C_i$:

C_i= concentration of i

f_i= the activity coefficient of i.

Hence:

$\mu_i = \mu_i^0 + RTLoga_i = \mu_i^0 + RTLogc_i = RTLogf_i$, μ_i^0 is called:

standard chemical potential of i.

I.2.5.2 Mean Activity

- There are many methods for measuring ionic activities, but they generally do not allow for the assessment of individual activities.
- This is because an electrolyte cannot release one ion species without simultaneously releasing the other species.
- Therefore, it is convenient to introduce the concept of mean activity, which is the geometric mean of the individual activities.

Let us take the dissociation of the compound A_mB_n from equation (I.6):

$$A_mB_n \rightleftharpoons m(ionsA) + n(ionsB)$$

We define the average activity $a_\pm$ of the compound A_mB_n by:

$$a_\pm = \sqrt[m+n]{(a_A^m a_B^n)} = (a_A^m a_B^n)^{\frac{1}{m+n}}$$

From the above, regarding the definition of activity a=f.C, we can define the average concentration and the average activity coefficient:

$$a_{\pm} = (f_A^m f_B^n)^{\frac{1}{m+n}} \cdot (C_A^m C f_B^n)^{\frac{1}{m+n}} \cdot$$

Finally the average concentration is given by:

$$C_{\pm} = (C_A^m C_B^n)^{\frac{1}{m+n}} \qquad \text{(I.9)}$$

And the average activity coefficient is given by:

$$f_{\pm} = (f_A^m f_B^n)^{\frac{1}{m+n}}$$

I.2.5.3 definition of ionic strength

The ionic strength of a solution represents a quantity that characterizes the intensity of the interaction forces exerted between ions, which depend on the respective concentrations of various ions present in solution.

The ionic strength, noted "I", is defined by the relation:

$$I = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2$$

In which C_i is the concentration of the ion i and *Zi* its electrovalence.

Example 1: either to calculate the ionic strength of a solution $FeCl_3$ 10^{-2}N.

Applying equation (I.6) gives:

$$I = \frac{1}{2}\sum_{i=1}^{n} C_i Z_i^2 = \frac{1}{2}[C_{Fe^{3+}}.(Z_{Fe^{3+}})^2 + C_{Cl^-}(Z_{Cl^-})^2]$$

Hence :

$$I = \frac{1}{2}[0.01.3^2 + 3.0.01.1^2] = 0.06 \text{ N}$$

Example 2: Calculate the ionic strength of a solution containing 0.01N in HCl et 0.01 N in $FeCl_2$.

From the above we have:

$$I = \frac{1}{2}\left[C_{Fe^{2+}}.(Z_{Fe^{2+}})^2 + C_{H^+}.(Z_{H^+})^2 + C_{Cl^-\,Total}(Z_{Cl^-})^2\right]$$

$$C_{Cl^-\,Total} = (C_{Cl^-})_{in\,HCl} + (C_{Cl^-})_{in\,FeCl_2} = 0.01 + 2.0.01 = 0.03\ \text{N}$$

hence :

$$\text{I} = 0.04\text{N}$$

I.2.5.3 Thermodynamic and apparent dissociation constants

Consider a binary electrolyte of type AB, the dissociation of AB is given according to equation (I.2):

$$AB \rightleftharpoons A^- + B^+$$

The equilibrium constant K_{AB} of this equilibrium is given by:

$$K_{AB} = \frac{a_{A^-} a_{B^+}}{a_{AB}}$$

where

a_{A^-} : Activiy of A^- in solution = $C_{A^-} f_{A^-}$;

a_{B^+} : Activity of B^+ en solution = $C_{B^+} f_{B^+}$;

a_{AB} : Activity of the molecule AB.

C_{A^-}, C_{B^+} are the concentrations of A and of B respectivelyt

f_{A^-}, f_{B^+} are the activity coefficients of A and of B respectively

If we replace these factors in equation (I.9) becomes:

$$K_{AB} = \frac{a_{A^-} a_{B^+}}{a_{AB}} = \frac{C_{A^-} f_{A^-} . C_{B^+} f_{B^+}}{C_{AB} f_{\mathrm{AB}}} = \underbrace{\frac{C_{A^-} . C_{B^+}}{C_{AB}}}_{\mathrm{I}} . \frac{f_{A^-} f_{B^+}}{f_{\mathrm{AB}}}$$

Term I of this last equation defines the apparent dissociation constant, it is given by the law of mass action by:

$$k_{AB} = \frac{\propto^2 \mathrm{C}}{1-\propto}$$

(I.10)

hence:

$$K_{AB} = k_{AB}.\frac{f_{A^-} f_{B^+}}{f_{\mathrm{AB}}}$$

Consider a sparingly soluble salt that is stirred with conductance water until saturation, and the conductivity σ of the resulting solution is measured. Applying equation (I.34) gives, neglecting the term in $\sqrt{C}$, since C tends towards 0: from which we can write C≈S (solubility) and $\Lambda \approx \Lambda_\infty$

$$\frac{1000\kappa}{S} = \Lambda \approx \Lambda_\infty$$

This relationship makes it possible to determine the solubility of poorly soluble salts by simply knowing the limiting equivalent conductivity Λ_∞.

Exemple

1. The limiting equivalent conductivities of the following compounds are given:

Composé	$AgNO_3$	$K NO_3$	KCl
Λ_∞ ($S.cm^2. eq^{-1}$)	115, 3	125.8	129.4

Deduce the equivalent conductivity from AgCl

A saturated aqueous solution of AgCl has a conductivity of $2.40.10^{-6}$ $S.cm^2. eq^{-1}$; that of the conductance water being de $1.16.10^{-6}$ $S.cm^2. eq^{-1}$, deduce, using the given result, the solubility of AgCl in water

1°) the application of the equation giving conductivity and from the table I.1 gives :

$$\Lambda_\infty(AgCl) = \Lambda_\infty(AgNO_3)_{+} \Lambda_{\infty(KCl)} _{-} \Lambda_{\infty(}K\,NO_3)$$

D'où :

$$\Lambda_\infty(AgCl) = 119\ \Lambda_\infty\ (S.cm^2.\ eq^{-1}).$$

2°) the natural conductivity of AgCl can be deduced from the equation1.24 that's to say $\sigma(AgCl) = (2.40\text{-}1.16)\ 10^{-6} = 1.24\ 10^{-6}\ S.cm^2.\ eq^{-1}$. on a:

$$\Lambda_\infty(AgCl) = \frac{1000.1.24\ 10^{-6}}{S}$$

Hence:

$$S = 1.04.10^{-5}\ eq/l.$$

Thank you

Pr NEDJHIOUI MOHAMMED

nedjhioui@gmail.com

www.univ.medea.dz