

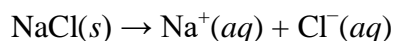
Chapter one

1. Electrolytic Solutions

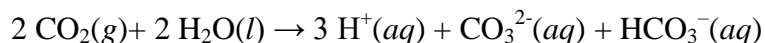
1.1. Introduction

Electrolyte solutions are solutions which can conduct electricity. The word *electrolyte* is used to describe ionic solutes. The word *nonelectrolyte* is used to describe those solutes whose solutions do not conduct electricity. An electrolyte is any salt or ionizable molecule that, when dissolved in solution, will give that solution the ability to conduct electricity. This is because when a salt dissolves, its dissociated ions can move freely in solution, allowing a charge to flow..

For example, when table salt, NaCl, is placed in water, the salt (a solid) dissolves into its component ions, according to the dissociation reaction:



It is also possible for substances to react with water to yield ions in solution. For example, carbon dioxide gas, CO₂, will dissolve in water to produce a solution that contains hydrogen ions, carbonate, and hydrogen carbonate ions:



The resulting solution will conduct electricity because it contains ions. It is important to keep in mind, however, that CO₂ is *not* an electrolyte, because CO₂ itself does not dissociate into ions. Only compounds that dissociate into their component ions in solution qualify as electrolytes.

In considering how charged particles interact, we have to understand the work involved in moving charged particles together and apart, and the energy required performing that work. Energy and work - these are concepts of thermodynamics. Therefore, our understanding of the chemistry of electrically charged particles, *electrochemistry*, is based on thermodynamics.

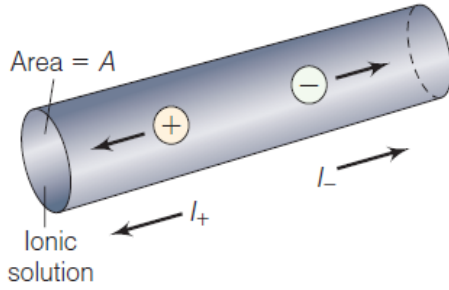
The concepts of ionic strength, activity, and activity coefficients correlate the amount of charge with the behavior of the system.

Note:- Arrhenius (1884) actually proposed that electrolytes are compounds composed of oppositely charged ions that separate when they dissolve, thereby allowing them to conduct electricity.

1.2. Transport properties and Conductance

The conductivity of ionic solutions is due to movement of both cations and anions which are move in opposite directions The currents are due to positive ions, I_+ , and a current due to negative ions, I_- . Furthermore, the current depends on the change in the amount of ions passing

through a cross-sectional area A per unit time, as shown in Figure below. Then , the current can be written as



$$I_+ = \frac{\partial q_+}{\partial t} \text{ and } I_- = \frac{\partial q_-}{\partial t} \quad (1.1)$$

Fig.1.1. Ionic current travels in two directions, and is measured in terms of how many ions pass through some cross-sectional area A per unit time.

In molar amounts, the total charge (positive or negative) equals the magnitude of the charge times the fundamental unit of charge (e) times the number of moles of ions

$$I_i = e \cdot |z_i| \cdot \frac{\partial N_i}{\partial t} \quad (1.2)$$

Where N_i represents the number of ions of species i .

Assuming that the ions are moving with some velocity v_i through the cross-sectional area A , and expressing the concentration of the ion as N/V . Thus, the change in amount per unit time, $\partial N_i / \partial t$, as the concentration times the area times the velocity expressed as

$$\frac{\partial N_i}{\partial t} = \frac{N_i}{V} A \cdot v_i \quad (1.3)$$

Thus, substituting into equation into Eqn(1.2)

$$I_i = e \cdot |z_i| \cdot \frac{N_i}{V} \cdot A \cdot v_i \quad (1.4)$$

Ions conducting current in solution are moving in response to an electromotive force acting across the solution. There is a relationship between force F and the electric field E :

$$F_i = q_i \cdot E = e \cdot |z_i| \cdot E \quad (1.5)$$

In solution, there is also a force of friction due to movement through the solvent. This force of friction always works against the direction of motion, and is proportional to the velocity of the ion. Therefore,

$$\text{force of friction on ions} = f \cdot v_i \quad (1.6)$$

where f is the proportionality constant. The force on the ion, F_i , becomes

$$F_i = e \cdot |z_i| \cdot E - f \cdot v_i \quad (1.7)$$

Because of the force of friction, at some velocity the net force on the ion will drop to zero and the ion will no longer accelerate. Its velocity will remain constant and terminal velocity can be derived as follows:

$$\begin{aligned} 0 &= e \cdot |z_i| \cdot E - f \cdot v_i \\ v_i &= \frac{e \cdot |z_i| \cdot E}{f} \end{aligned} \quad (1.9)$$

But what is f , the frictional proportionality constant? According to *Stokes's law*, the frictional constant of a spherical body with radius r_i moving through a fluid medium with a viscosity η is

$$f = 6\pi\eta r_i \quad (1.10)$$

Using the expression for Stokes's law, the velocity of the ions becomes

$$v_i = \frac{e \cdot |z_i| \cdot E}{6\pi\eta r_i} \quad (1.11)$$

Substituting into the expression eqn. (1.4) for current, I_i becomes

$$I_i = e^2 \cdot |z_i|^2 \cdot \frac{N_i}{V} \cdot A \cdot \frac{E}{6\pi\eta r_i} \quad (1.12)$$

This equation shows that the ionic current is related to the square of the charge on the ion. For virtually all ionic solutions, the ionic currents of the positive and negative ions I_+ and I_- will be different. In order to maintain overall electrical neutrality, the oppositely charged ions have to move at different velocities.

Finally, the basic relationship between the voltage V across a conductor and the current I flowing through the conductor is known as *Ohm's law*:

$$V \propto I \quad (1.13)$$

The proportionality constant is defined as the *resistance*, R , of the system

$$V = IR \quad (1.14)$$

Measurements of the resistances of ionic solutions show that the resistance is directly proportional to the distance, l , between two electrodes and inversely proportional to the area A of the electrodes :

$$R = \rho \cdot \frac{l}{A} \quad (1.15)$$

The proportionality constant ρ is called the *specific resistance* or the *resistivity* of the solution, and has units of ohm·meter or ohm·cm. The *conductivity* K (also called the *specific conductance*) defined as the reciprocal of the resistivity:

$$K = \frac{1}{\rho} \quad (1.16)$$

Conductivities have units of $\text{ohm}^{-1} \cdot \text{m}^{-1}$. Resistivities and conductivities are quite variable because ρ would depend not only on the charge on the ions but also on the concentration of the solution. Taking these factors into account, the *equivalent conductance* of an ionic solute, Λ , is defined as

$$\Lambda = \frac{K}{N} \quad (1.7)$$

where N is the normality of the solution (Λ is the capital Greek letter lambda). **Recall** that **normality** is defined in terms of number of equivalents per liter of solution.

Note:- The use of equivalents rather than moles *takes ionic charge into account*.

For dilute (less than about 0.1 normal) solutions, Λ varied with the square root of the concentration, and the y-intercept of the straight line of Λ versus \sqrt{N} was a value of Λ that was characteristic of the ionic solute. This characteristic, infinitely diluted value is given the symbol Λ_0 . Mathematically, the relationship between the equivalent conductance versus concentration can be expressed as

$$\Lambda = \Lambda_0 + K \cdot \sqrt{N} \quad (1.8)$$

where K is a proportionality constant that relates the slope of the straight line and the equation is called *Kohlrausch's law* after Friedrich Kohlrausch, a German chemist who first proposed it in the late 1800s after a detailed study of the electrical properties of ionic solutions. Debye and Hückel, and later the Norwegian chemist Lars Onsager, derived an expression for K :

$$K = -(60.32 + 0.2289\Lambda_0) \quad (1.19)$$

When combined, equations (1.18) and (1.19) are called the *Onsäger equations* for the conductance of ionic solutions.

1.3 Activity and activity Coefficients

For ions in dilute solution, the presence of oppositely charged ions will affect the expected properties of the solution. *Dilute* ionic solutions have concentrations of 0.001 M or even less.

For non-ideal chemical systems, to know about ionic solutions there is the need to understand the concepts of chemical potentials and activities

The chemical potential μ_i of a material is defined as the change in the Gibbs free energy versus the molar amount of that material:

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T,p} \quad (1.20)$$

The activity a_i of a component in a multicomponent system defined as some non-ideal parameter that defines the actual chemical potential μ_i in terms of the standard chemical potential μ_i^0 :

$$\mu_i = \mu_i^0 + RT \ln a_i \quad (1.21)$$

In the case of gas mixtures, activity related to the partial pressure p_i of the gas. For ions in solution, the activity of the ionic solute is related to the concentration of the solute, in this case the molality:

$$a_i \propto m_i \quad (1.22)$$

In order to remove the unit of molality, divide the right side of equation by some standard concentration m^0 , which set as exactly 1 molal. The proportionality constant γ_i , called the *activity coefficient*, for an ion:

$$a_i = \gamma_i \cdot \frac{m_i}{m^0} \quad (1.23)$$

The value of the activity coefficient γ_i varies with concentration, so tabulate either the values versus concentration or have a way of calculating them. However, in the limit of infinite dilution, ionic solutions should behave as if their molal concentration is directly related to the chemical potential; that is,

$$\lim_{m_i \rightarrow 0} \gamma_i = 1 \quad (1.24)$$

As concentrations of ions get larger, γ_i gets smaller, and the activity gets progressively smaller and smaller than the true molal concentration of the ions. The subscript i on the variables in the above equations implies that each individual species has its own molality, activity, activity coefficient, and so on.

The fact that the total positive charge must equal the total negative charge implies a relationship between the charges on the ions and their molal concentrations. For a simple binary salt $A_{n+}B_{n-}$, where n_+ and n_- are the formula subscripts for the cation and anion, respectively, ionic solutions require that the molalities of the cation and anion satisfy the formula shown below.

$$\frac{m_+}{n_+} = \frac{m_-}{n_-} \quad (1.25)$$

Example

Verify the expression for 1.00-molal solution of sodium sulfate (Na_2SO_4)

$$m_{\text{Na}^+} = 2.00 \, m \quad \text{and} \quad m_{\text{SO}_4^{2-}} = 1.00 \, m$$

$$n_+ = 2 \quad \text{and} \quad n_- = 1$$

$$\text{Thus, } \frac{2.00 \, m}{2} = \frac{1.00m}{1}$$

The activity potential of the cation and anion are

$$\left. \begin{aligned} \mu_+ &= \mu_+^0 + RT \ln \gamma_+ \frac{m_+}{m^0} \\ \mu_- &= \mu_-^0 + RT \ln \gamma_- \frac{m_-}{m^0} \end{aligned} \right\} \quad (1.26)$$

The total chemical potential of the ionic solution depends on the number of moles of each ion which are given by the ionic formula variables n_+ and n_- . The total free energy is

$$G = (n_+ \cdot \mu_+) + (n_- \cdot \mu_-) \quad (1.27)$$

Substituting for μ_+ and μ_- from Eqn (1.26):

$$G = (n_+ \cdot \mu_+^0) + (n_- \cdot \mu_-^0) + \left(n_+ \cdot RT \ln \gamma_+ \frac{m_+}{m^0} \right) + \left(n_- \cdot RT \ln \gamma_- \frac{m_-}{m^0} \right) \quad (1.28)$$

This equation is simplified by defining the *mean ionic molality* m_{\pm} and the *mean ionic activity coefficient* γ_{\pm} as

$$m_{\pm} \equiv (m_+^{n_+} \cdot m_-^{n_-})^{1/(n_+ + n_-)} \quad (1.29)$$

$$\gamma_{\pm} \equiv (\gamma_+^{n_+} \cdot \gamma_-^{n_-})^{1/(n_+ + n_-)} \quad (1.30)$$

Further, if $n_{\pm} = n_+ + n_-$ and $\mu_{\pm}^0 = n_+ \mu_+^0 + n_- \mu_-^0$, and rewrite the expression for total chemical potential as

$$G = \mu_{\pm}^0 + n_{\pm} RT \ln \gamma_{\pm} \frac{m_{\pm}}{m^0} \quad (1.31)$$

By correspondence to eqn (1.21), using the properties of logarithms the mean ionic activity a_{\pm} of an ionic solute $A_{n^+}B_{n^-}$ can be define as

$$a_{\pm} = \left(\gamma_{\pm} \frac{m_{\pm}}{m^0} \right)^{n_{\pm}} \quad (1.32)$$

These equations indicate how ionic solutions will really behave.

Example

Determine the mean ionic molality and activity for a 0.200-molal solution of $\text{Cr}(\text{NO}_3)_3$ if its mean activity coefficient γ_{\pm} is 0.285.

Answer

For chromium(III) nitrate, the coefficients n_+ and n_- are 1 and 3, respectively, so that n_{\pm} is 4. The ideal molality of Cr^{3+} (aq) is 0.200 m , and the ideal molality of NO_3^- (aq) is 0.600 m . The mean ionic molality is therefore,

$$m_{\pm} = (0.200^1 \cdot 0.600^3)^{1/4} m \Rightarrow m_{\pm} = 0.456 m$$

Using this and the given mean activity coefficient, we can determine the mean activity of the solution:

$$a_{\pm} = \left(0.285 \cdot \frac{0.456 m}{1.00 m} \right)^4 \Rightarrow a_{\pm} = 2.85 \times 10^{-4}$$

The behavior of this solution is based on a mean activity of 2.85×10^{-4} , rather than a molality of 0.200. This makes a big difference in the expected behavior of the solution.

Solutions containing ions that have larger absolute charges have greater coulombic effects affecting their properties. One way to keep track of this is by defining the *ionic strength*, I , of the solution

$$I = \frac{1}{2} \sum_{i=1}^{\text{Number of ions}} m_i \cdot z_i^2 \quad (1.33)$$

Where z_i is the charge on the i^{th} ion. Ionic strength was originally defined in 1921 by Gilbert N. Lewis. Recall that for ionic solutes that do not have a 1:1 ratio of cation and anion, the individual molalities m_i will not be the same.

Example

- Calculate the ionic strengths of 0.100 m NaCl, Na₂SO₄, and Ca₃(PO₄)₂.
- What molality of Na₂SO₄ is needed to have the same ionic strength as 0.100 m Ca₃(PO₄)₂?

Answer

Using
$$I = \frac{1}{2} \sum_{i=1}^{\text{Number of ions}} m_i \cdot z_i^2$$

$$I_{\text{NaCl}} = \frac{1}{2} [(0.100 \text{ } m)(+1)^2 + (0.100 \text{ } m)(-1)^2] = 0.100 \text{ } m$$

$$I_{\text{Na}_2\text{SO}_4} = \frac{1}{2} [(2 \cdot 0.100 \text{ } m)(+1)^2 + (0.100 \text{ } m)(-2)^2] = 0.300 \text{ } m$$

$$I_{\text{Ca}_3(\text{SO}_4)_2} = \frac{1}{2} [(3 \cdot 0.100 \text{ } m)(+2)^2 + (2 \cdot 0.100 \text{ } m)(-3)^2] = 1.50 \text{ } m$$

Note:- The ionic strength gets when the charges on the individual ions increase.

- This part asks what molality of Na₂SO₄ is needed to get an ionic strength the same as 0.100 m Ca₃(PO₄)₂, which found in part a to be 1.50 m and use 1.50 m for the value and set the molality as the unknown. Thus

$$I_{\text{Na}_2\text{SO}_4} = 1.50 \text{ } m = \frac{1}{2} [(2 \cdot m)(+1)^2 + (m)(-2)^2]$$

$$1.50 \text{ } m = \frac{1}{2} (2m + 4m) = \frac{1}{2} \cdot 6m = 3m$$

Therefore, $m = 0.500\ m$

So we need a solution of Na_2SO_4 with five times the molality to have the same ionic strength as $\text{Ca}_3(\text{PO}_4)_2$. As an exercise, what molality of NaCl would be needed to have this same ionic strength?

1.4. Application of Electrolytic Cells

Electrochemical cells in which faradaic currents are flowing are classified as either *galvanic* or *electrolytic* cells. A *galvanic cell* is one in which reactions occur spontaneously at the electrodes when they are connected externally by a conductor (Figure below(a)). These cells are often employed in converting chemical energy into electrical energy. Galvanic cells of commercial importance include *primary (nonrechargeable) cells* (e.g., the Leclanche Zn-MnO_2 cell), *secondary (rechargeable) cells* (e.g., a charged Pb-PbO_2 storage battery), and *fuel cells* (e.g., an $\text{H}_2\text{-O}_2$ cell). An *electrolytic cell* is one in which reactions are effected by the imposition of an external voltage greater than the open-circuit potential of the cell (Figure (b)). These cells are frequently employed to carry out desired chemical reactions by expending electrical energy. Commercial processes involving electrolytic cells include electrolytic syntheses (e.g., the production of chlorine and aluminum), electrorefining (e.g., copper), and electroplating (e.g., silver and gold). The lead-acid storage cell, when it is being "recharged," is an electrolytic cell.

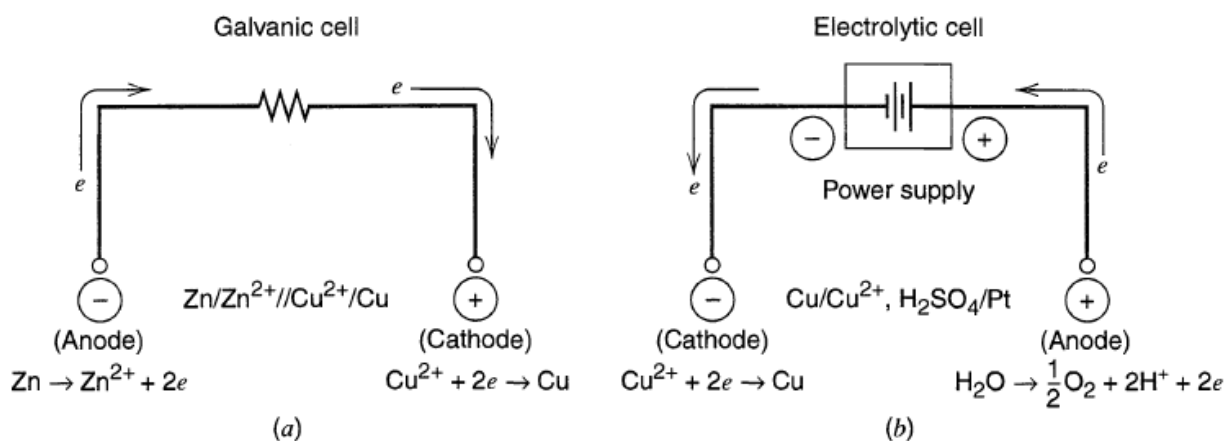


Fig1.2 (a) Galvanic cell and (b) Electrolytic cells