Physical pharmacy I
2nd stage

Solution of Electrolytes

2025-2026

Objectives

- Properties Solution of electrolytes
- Arrhenius theory of dissociation
- Theory of strong electrolytes
- Ionic strength
- Debye-Huckle theory
- Coefficients for expressing colligative properties.

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Electrolytes solution

- *An electrolyte* solution is a solution that generally contains ions, atoms or molecules that have **lost or gained electrons**, and is **electrically conductive.**
- Ionic solutions are studied by several scientists such as Arrhenius (1887), van't Hoff, Lewis, Faraday,

$$H_2O + \underset{\text{[Ionic compound]}}{Na^+Cl^-} \rightarrow Na^+ + Cl^- + H_2O$$

[Strong electrolyte]

$$H_2O + \underset{\text{[Covalent compound]}}{HCl} \rightarrow H_3O^+ + Cl^-$$

[Strong electrolyte]

$$H_2O + \underset{\text{[Covalent compound]}}{CH_3COOH} \rightleftharpoons H_3O^+ + CH_3COO^-$$

[Weak electrolyte]

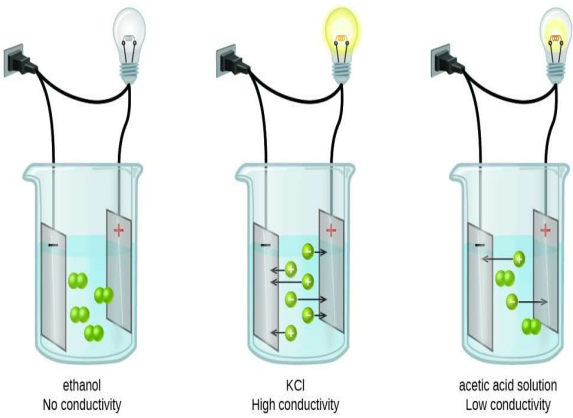
- Arrhenius theory was **not satisfactory** for strong and moderately strong electrolyte; its **only satisfactory** for weak electrolytes

- Debye and Huckel (1923) put **forth** a new theory
- Debye and Huckel define ***strong electrolytes*** as
  - molecules those **completely** dissociated into ions in solutions of **moderate** concentration which **depend on** the interionic attractions and solution properties.
- Debye and Hückel expressed the deviations from complete dissociation in terms of :

1. activities
2. activity coefficient
3. and ionic strengths of electrolytic solutions.

Properties of electrolyte solutions

- ➢Electrolysis
- ➢Transference numbers
- ➢Faraday's laws
- ➢Electrolytic Conductance
- ➢Colligative properties



Electrolysis

- **Electrolysis** is a **chemical reaction** occurs when a direct electric current (dc) flows through an electrolytic cell.
- The ionic solutions show a direct electrical current through an electrolytic cell in which
  - **cations** are reduced
  - and **anions** are oxidized.

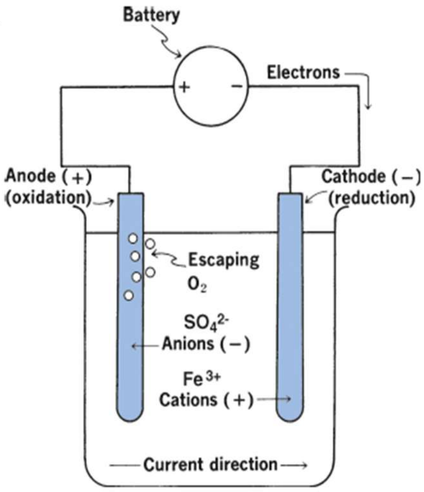


FIG. 6-1 Electrolysis in an electrolytic cell.

Electrolytic cell consist of

1. battery (or electron generator).
2. Two **platinum** electrodes (cathode and anode)

$$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + e$$

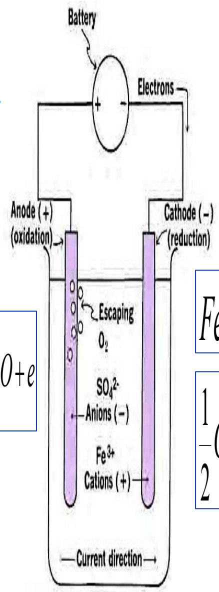


Fig. 6-1. Electrolysis in an electrolytic cell.

$$Fe^{3+} + e = Fe^{2+}$$

$$\frac{1}{2}Cu^{2+} + e = \frac{1}{2}Cu$$

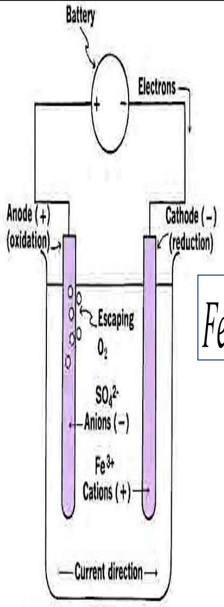


Fig. 6-1. Electrolysis in an electrolytic cell.

$$Fe^{3+} + e = Fe^{2+}$$

- Electrons enter the Cathode **(road down)** and combine with positive ions (cations) in the solution (Reduction reaction).
- **Reduction occurs** at the cathode, where electrons enter from the external circuit and are added to a chemical species in solution.
- In the electrolysis of a solution of ferric sulfate in a cell containing platinum electrodes, a ferric ion migrates to the cathode, where it picks up an electron and is **reduced**

- **Anions** will carry electrons through solution and discharge them at the Anode(road up).
- Oxidation reaction takes place in the anode and hydroxyl ion converted to oxygen that leaves the solution at the Anode
- The sulfate ion carries the current through the solution to the anode, but it is **not easily** oxidized; **therefore**, hydroxyl ions of the water are converted into molecular oxygen, which escapes at the anode, and sulfuric acid is found in the solution around the electrode.

$$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + e$$

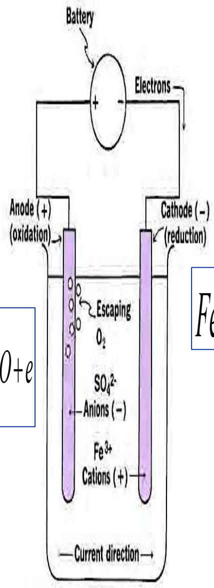


Fig. 6-1. Electrolysis in an electrolytic cell.

$$Fe^{3+} + e = Fe^{2+}$$

$$OH^- = \frac{1}{4}O_2 + \frac{1}{2}H_2O + e$$

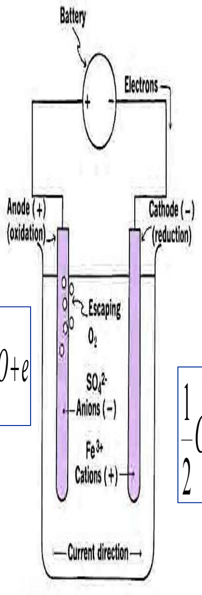


Fig. 6-1. Electrolysis in an electrolytic cell.

$$\frac{1}{2}Cu^{2+} + e = \frac{1}{2}Cu$$

In the electrolysis of **cupric chloride** between platinum electrodes,

whereas at the anode, chloride and hydroxyl ions are converted, respectively, into gaseous molecules of chlorine and oxygen, which then escape.

- In each of these two examples, the net result is the transfer of one electron from the cathode to the anode

Why?

- The electrodes made up from Platinum.?
- Hydroxyl ion oxidized instead of Sulfate ion.?
- Sulfuric acid solution is found around the anode.
- In the oxidation process there is an increase in oxidation number.?
- In the reduction process there is a decrease in the oxidation number.?

Transference Numbers

- The fraction of total current carried by the cations or by the anions is known as the **transport or transference number t+ or t–:**

$$t_+ = \frac{\text{Current carried by cations}}{\text{Total current}}$$

$$t_- = \frac{\text{Current carried by anions}}{\text{Total current}}$$

The sum of the two transference numbers is obviously equal to unity:

$$t_+ + t_- = 1$$

- The transference numbers are related to the **velocities** of the ions,
  - the **faster-moving** ion carrying the **greater** fraction of current.
- The velocities of the ions in turn depend on
  - hydration
  - as well as ion **size** and **charge**.
  - **For example,**
  - the transference number of the sodium ion in **a 0.10 M** solution of NaCl is 0.385. **Because** it is greatly hydrated
  - the lithium ion in **a 0.10 M** solution of LiCl moves **more slowly** than the sodium ion and hence has a lower transference number(t+), 0.317 because it is less **hydrated**

- Explain why? the speed and the transference numbers are not necessarily the same for positive and negative ions. Prove your answer with example

Faraday's Laws (1838,1839)

- Faraday's laws: In 1833 and 1834, Michael Faraday announced his famous laws of electricity, which may be summarized in the statement; the passage of **96,500 coulombs** of electricity through a conductivity cell produces a chemical change **of 1 g equivalent weight** of any substance
- 96500 of coulombs = 1 g of substance.
- Each 1g of ions carries Avogadro's number (6.02 x 10^{23}) of + or - charges.
- From Faraday's laws, the passage of 96,500 coulombs of electricity results in the transport of 6.02 x 10^{23} electrons in the cell.
- One faraday is an Avogadro's number of electrons.

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Faraday's Laws (1838,1839)

Faraday's laws can be used to compute the charge on an electron in the following way. Because 6.02×10^{23} electrons are associated with 96,500 coulombs of electricity, each electron has a charge e of

$$e = \frac{96{,}500 \text{ coulombs}}{6.02 \times 10^{23}}$$

$$= 1.6 \times 10^{-19} \text{ coulomb} \qquad \textbf{(6-11)}$$

and because 1 coulomb $= 3 \times 10^9$ esu,

$$e = 4.8 \times 10^{-10} \text{ electrostatic unit of charge} \qquad \textbf{(6-12)}$$

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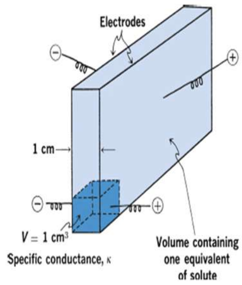
Electrolytic Conductance

- The resistance, R. in ohms of any uniform metallic or electrolytic conductor is
  - ***directly*** proportional to length(*l*) (cm)
  - and **inversely** proportional to its cross-sectional area, A, in cm2
- The conductance, C is reciprocal of R.



› between specific conductance and equivalent con

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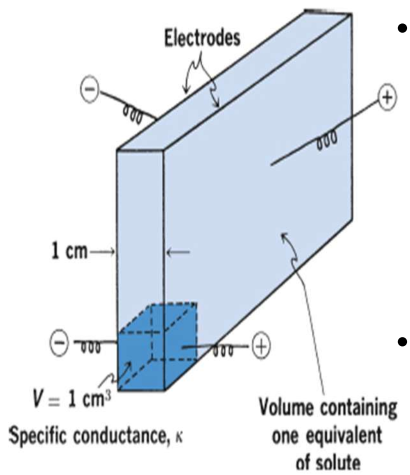
- <u>**Specific conductance**</u>, measures the current-carrying capacity of **all ions** in **a unit** volume of solution <u>**and accordingly**</u> varies with concentration.



› between specific conductance and equivalent con

- <u>**Equivalent conductance**</u> is used to study the dissociation of molecules into ions, **independent** of the concentration of the electrolyte.
- **Where** it measures the current- carrying capacity of all ions after complete dissociation.

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Equivalent Conductance of Strong and Weak Electrolytes

- As the solution of a **strong electrolyte** is diluted, the **specific conductance** decreases, because the number of ions per unit volume of solution is reduced.
- Conversely, the equivalent conductance of a solution of a strong electrolyte steadily increases on dilution.
- **This is because:**
  - the quantity of electrolyte remains constant
  - and the ions are hindered less by their neighbors in the more dilute solution and so can move faster. **(ensure complete dissociation of ions)**
- The equivalent conductance of a ***weak electrolyte*** also increases on dilution, **but not as rapidly at first**.

- Equivalent conductance was found to be a linear function of the square root of the concentration for strong electrolytes in dilute solutions.
- The **steeply** rising curve for acetic acid **results** from the fact that the dissociation of weak electrolytes increases in dilution, with a large increase in the number of ions capable of carrying the current.

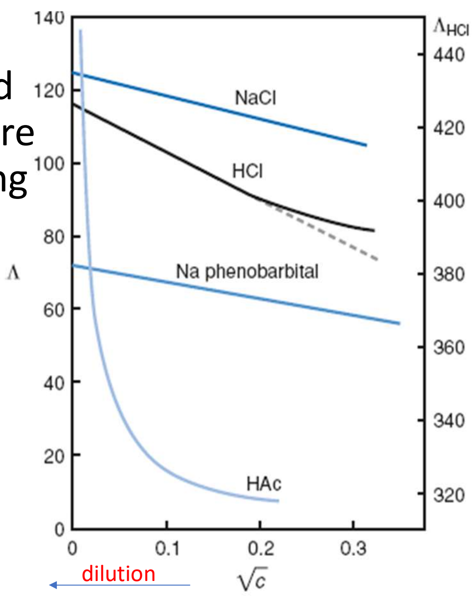


FIG. 6-4 Equivalent conductance of strong and weak electrolytes.

Colligative properties of electrolytic and non electrolytic solutions

- **osmotic pressure (π) = RTc** …….. For nonelectrolyte
  - Where;
  - R is the gas constant,
  - T is the absolute temperature,
  - and c is the concentration in moles/liter.

colligative properties *are those properties of solutions that depend on the ratio of the number of solute particles to the number of solvent particles in a solution, and not on the nature of the chemical species present*

  - It has been found that solutions of **electrolytes** gave osmotic pressures approximately two, three, and more times **larger** than expected from this equation,
  - Thus, a correction **factor *i*** to account for the **irrational** behavior of ionic solutions, has been introduced.

$$\pi = iRTc$$

- The i factor is plotted against the molal concentration of both electrolytes and nonelectrolytes in Figure 6-5.
- **For nonelectrolytes**, it is seen to approach unity,
- **and for strong electrolytes**, it tends toward a value **equal to** the number of ions formed upon dissociation.
- For example, i approaches the value of
  - 2 for solutes such as NaCl and CaSO4,
  - 3 for K2SO4 and CaCl2,
  - and 4 for K3Fe(C)$_6$ and FeCl3.

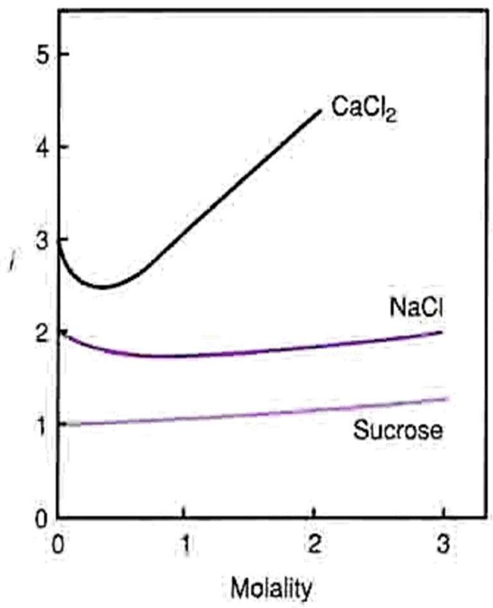


Fig. 6–5. van't Hoff *i* factor of representative compounds.

EXAMPLE 6-5

Osmotic Pressure of Sodium Chloride

What is the osmotic pressure of a 2.0 *m* solution of sodium chloride at 20°C?

The *i* factor for a 2.0 *m* solution of sodium chloride as observed in Figure 6-5 is about 1.9. Thus, $\pi = iRTc$

$$\pi = 1.9 \times 0.082 \times 293 \times 2.0 = 91.3 \text{ atm}$$

- All other colligative properties like vapor pressure, freezing temperature and boiling temperature for non electrolytes are increased by a correction factor (i) in electrolytes. As follows:

$$\Delta p = 0.018 i p_1{}^{\circ} m \qquad (6\text{–}25)$$

$$\pi = iRTm \qquad (6\text{–}26)$$

$$\Delta T_f = iK_f m \qquad (6\text{–}27)$$

$$\Delta T_b = iK_b m \qquad (6\text{–}28)$$

THEORY OF ELECTROLYTIC DISSOCIATION

- When electrolytes are dissolved in water, the solute exists in the form of ions in the solution, as seen in the following equations:

The solid form of sodium chloride is marked with plus and minus signs in reaction (6-29) to indicate that sodium chloride exists as ions even in the crystalline state.

Hydrogen chloride exists essentially as neutral molecules rather than as ions in the pure form and does not conduct electricity. When it reacts with water, however, it ionizes according to reaction (equation (6-30)).

$$H_2O + \underset{\text{[Ionic compound]}}{Na^+Cl^-} \rightarrow \underset{\text{[Strong electrolyte]}}{Na^+ + Cl^- + H_2O} \quad (6\text{-}29)$$

$$H_2O + \underset{\text{[Covalent compound]}}{HCl} \rightarrow \underset{\text{[Strong electrolyte]}}{H_3O^+ + Cl^-} \quad (6\text{-}30)$$

$$H_2O + \underset{\text{[Covalent compound]}}{CH_3COOH} \rightleftharpoons \underset{\text{[Weak electrolyte]}}{H_3O^+ + CH_3COO^-} \quad (6\text{-}31)$$

Strong Electrolytes	Weak electrolytes
HCl, HNO_3, H_2SO_4 $NaOH$, KOH $Ba(OH)_2$, $Ca(OH)_2$	H_3BO_3, H_2CO_3, NH_4OH $HgCl_2$, HgI, lead actate, HBr $Hg(NH_3)^{2-,}$ $Cu(NH_3)_4^{2+}$, $Fe(CN)_6^{3-}$

Drugs and Ionization

- Some drugs, such as anionic and cationic antibacterial and antiprotozoal agents, are **more active** when found in the ionic state.
- While compounds, such as the hydroxy benzoate esters (parabens) and many general anesthetics, have action as **non electrolytes (non ionic).**
- Others act by both forms like the sulfonamides.

Degree of Dissociation

- Arrhenius determined the degree of dissociation directly from conductance measurements.
- He recognized that the equivalent conductance at infinite dilution Λ_0 **(was a measure of the complete dissociation of the solute into its ions)** and that Λc (**represented the number of solute particles present as ions at a concentration c**). Hence, the fraction of solute molecules ionized, or the degree of dissociation, was expressed by the equation.

the degree of dissociation $$\alpha = \frac{\Lambda c}{\Lambda_0}$$

where Λc/Λ0 is known as the conductance ratio.

- Arrhenius differentiated between **strong** and **weak** electrolytes by the **fraction** of the molecules ionized (the degree of dissociation, α). So there are:
  - a high degree of dissociation (strong)
  - and low degree of dissociation (weak).

EXAMPLE 6-6 :
Degree of Dissociation of Acetic Acid

- The equivalent conductance of acetic acid at 25°C and at infinite dilution is 390.7 ohm cm2/Eq. The equivalent conductance of a 5.9 × 10−3 M solution of acetic acid is 14.4 ohm cm2/Eq. What is the degree of dissociation of acetic acid at this concentration? We write

$$\alpha = \frac{14.4}{390.7} = 0.037 \text{ or } 3.7\%$$

- The van't Ho factor, *i*, can be connected with the degree of dissociation, α, in the following way.

$$i = 1 + \alpha(\nu - 1) \quad \rightarrow \quad \alpha = \frac{i - 1}{\nu - 1}$$

V= no. of dissociated ions ($CaCl_2$)=3

- The cryoscopic method is used to determine i from the expression

$$\Delta T_f = iK_f m \quad \rightarrow \quad i = \frac{\Delta T_f}{K_f m}$$

- i: The van 't Hoff factor, indicating the number of particles a compound dissociates into in solution.
- ΔTf: The freezing point depression, which is the difference between the freezing point of the pure solvent and the solution.
- Kf: The cryoscopic constant (freezing point depression constant) for the solvent, specific to each solvent.
- m: The molality of the solution, defined as moles of solute per kilogram of solvent.

EXAMPLE 6-7 Degree of Ionization of Acetic Acid

- The freezing point of a 0.10 m solution of acetic acid is –0.188°C. Calculate the degree of ionization of acetic acid at this concentration. Acetic acid dissociates into two ions, that is, v = 2. We write

$$i = \frac{\Delta T_f}{K_f m}$$

$$i = \frac{0.188}{1.86 \times 0.10} = 1.011$$

$$\alpha = \frac{i-1}{v-1} = \frac{1.011-1}{2-1} = 0.011$$

In other words, according to the result of Example 6-7, the fraction of acetic acid present as free ions in a 0.10 m solution is 0.011. Stated in percentage terms, acetic acid in 0.1 m concentration is ionized to the extent of about 1%

THEORY OF STRONG ELECTROLYTES

- Arrhenius used **α** to express the degree of dissociation of both strong and weak electrolytes,

A. and van't Ho introduced the factor ***i*** to account for the **deviation of** strong and weak electrolytes and nonelectrolytes from the ideal laws of the colligative properties, regardless of the nature of these discrepancies.

EXAMPLE 6-8
Degree of Dissociation

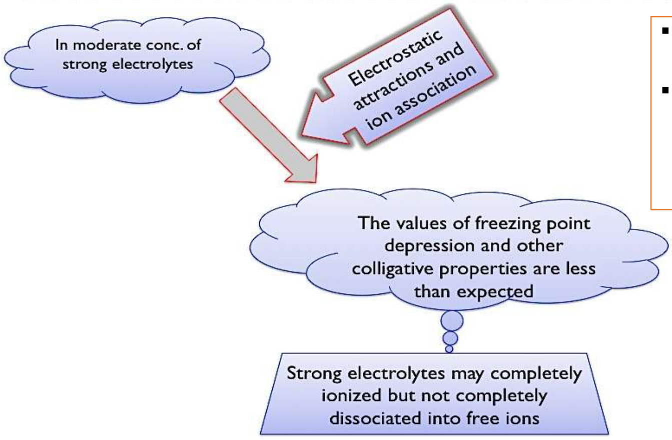
- The freezing point depression for a 0.01 m solution of ammonium chloride is 0.0367°C. Calculate the "degree of dissociation" of this electrolyte. We write

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.0367°\text{C}}{1.86 \times 0.010} = 1.97$$

$$\alpha = \frac{i-1}{v-1} \qquad \alpha = \frac{1.97-1}{2-1} = 0.97$$

Activity and Activity Coefficients

The theory of electrolyte dissociation is applicable to dilute and moderate concentrations (less than 0.5 M) of strong electrolytes



- the behavior of strong electrolytes **ascribes** to *an electrostatic attraction between the ions.*
- At high concentration of some strong electrolytes, groups of ions (not free ions) may be formed called ion pair (Na+Cl-) or ion triplet (Na+Cl-Na+) specially in solvents of low dielectric constant, in which the force of attraction of oppositely charged ions is large.

Because of the electrostatic attraction and ion association in **moderately** concentrated solutions of strong electrolytes, the values of the freezing point depression and the other colligative properties are than expected for solutions of **unhindered ions**. Consequently, a strong electrolyte may be ***completely ionized, yet*** incompletely dissociated into free ions.

- The activity, in general, is less than the actual or stoichiometric concentration of the solute, because
- the strong electrolyte is partly ionized,
- some of the ions are effectively “taken out of play” by the electrostatic forces of interaction.
- **At infinite dilution**, in which the ions are so **widely** separated that they do not interact with one another, the activity a of an ion is **equal** to its concentration, expressed as molality or molarity. It is written on a molal basis at infinite dilution as
- a =m➔ a/m=1
- As the concentration of the solution is increased, the ratio becomes less than unity because the effective concentration or activity of the ions becomes less than the stoichiometric or molal concentration. This ratio is known as the practical activity coeffcient, γ_m,

$$\frac{a}{m} = \gamma_m$$

$$\frac{a}{m} = \gamma_m \qquad (6\text{-}40)$$

or

$$a = \gamma_m m \qquad (6\text{-}41)$$

On the molarity scale, another *practical activity coefficient,* γ_c, is defined as

$$a = \gamma_c c \qquad (6\text{-}42)$$

and on the mole fraction scale, a *rational activity coefficient* is defined as

$$a = \gamma_x X \qquad (6\text{-}43)$$

- The activity of an electrolyte is defined by its mean ionic activity, which is given by the relation

$$a_\pm = (a_+{}^m a_-{}^n)^{1/(m+n)}$$

- where the exponents m and n give the stoichiometric numbers of given ions that are in solution.
  - Thus, an NaCl solution has a mean ionic activity of

$$a_\pm = (a_{Na^+} a_{Cl^-})^{1/2}$$

whereas an $FeCl_3$ solution has a mean ionic activity of

$$a_\pm = (a_{Fe^{+3}} a_{Cl^-} 3)^{1/4}$$

  - The ionic activities of equation (6-44) can be expressed in terms of concentrations

$$a_\pm = \gamma_\pm (c_+{}^m c_-{}^n)^{1/(m+n)}$$

a=ionic activity m=molarity or molality
ɣ= practical activity coefficient
a± = mean of ionic activity(the activity of an electrolyte)

EXAMPLE 6-9 Mean Ionic Activity of FeCl3

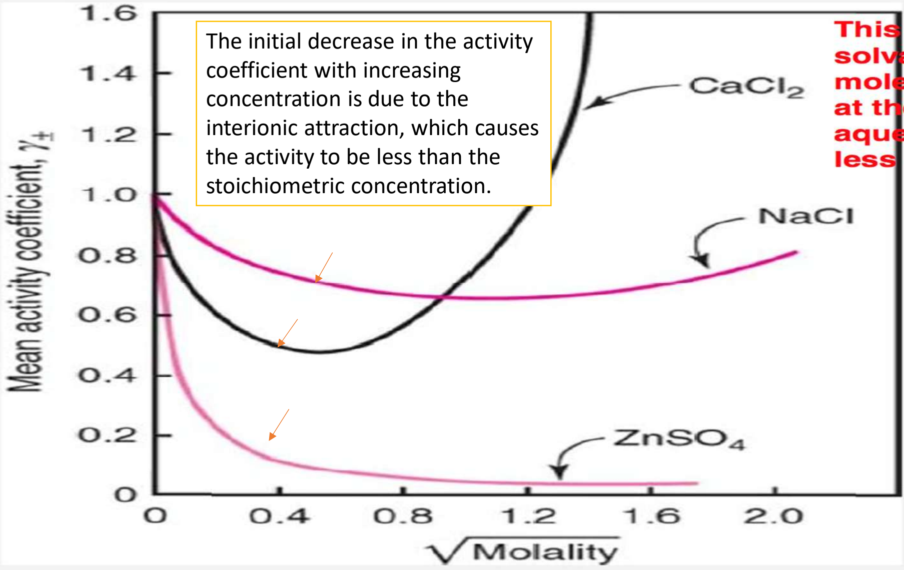
- What is the mean ionic activity of a 0.01 M solution of FeCl3? We write

$$a_{\pm} = \gamma_{\pm}(c_{+}c_{-}^{\,3})^{1/4} = \gamma_{\pm}[(0.01)(3\times 0.01)^{3}]^{1/4}$$
$$= 2.3\times 10^{-2}\gamma_{+}$$

TABLE 6-1

MEAN IONIC ACTIVITY COEFFICIENTS OF SOME STRONG ELECTROLYTES AT 25°C ON THE MOLAL SCALE

Molality (m)	HCl	NaCl	KCl	NaOH	$CaCl_2$	H_2SO_2	Na_2SO_2	$CuSO_2$	$ZnSO_2$
0.000	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0.005	0.93	0.93	0.93	–	0.79	0.64	0.78	0.53	0.48
0.01	0.91	0.90	0.90	0.90	0.72	0.55	0.72	0.40	0.39
0.05	0.83	0.82	0.82	0.81	0.58	0.34	0.51	0.21	0.20
0.10	0.80	0.79	0.77	0.76	0.52	0.27	0.44	0.15	0.15
0.50	0.77	0.68	0.65	0.68	0.51	0.16	0.27	0.067	0.063
1.00	0.81	0.66	0.61	0.67	0.73	0.13	0.21	0.042	0.044
2.00	1.01	0.67	0.58	0.69	1.55	0.13	0.15	–	0.035
4.00	1.74	0.79	0.58	0.90	2.93	0.17	0.14	–	–



This rise may be due to solvation effect (water molecules attract the ions at the concentrated aqueous solution, causing less interionic attractions

Fig. 6-6. Mean ionic activity coefficients of representative electrolytes plotted against the square root of concentration.

HW

- Explain why:
- Arrhenius theory and the concept of the degree of dissociation are valid for solutions of weak electrolytes but not for strong electrolytes.

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Ionic strength

- For weak electrolytes solutions and non-electrolytes the ionic concentration terms and activities are usually identical.
- For strong electrolytes and for solutions of weak electrolytes together with salts and other electrolytes (as in buffers), it is important to use activities instead of concentrations.
- **Ionic strength (μ)** is used to relate interionic attractions and activity coefficients.
- It represents the contribution to the **electrostatic** forces of the ions of all types, depend on the **total** number of ionic charges.

Cations: Na^+ Ca^{2+} Mg^{2+} K^+
Anions: Cl^- $HCO3^-$ $CO3^{2-}$ $SO4^{2-}$

$$\mu = \frac{1}{2}\sum_{1}^{j} CiZi^2$$

The term ci is the concentration in moles/liter of any of the ions and zi is its valence.

$$\mu = \frac{1}{2}(c_1 z_1^2 + c_2 z_2^2 + c_3 z_3^2 + \cdots + c_j z_j^2)$$

EXAMPLE

Calculating Ionic Strength

What is the ionic strength of (*a*) 0.010 M KCl, (*b*) 0.010 M $BaSO_4$, and (*c*) 0.010 M Na_2SO_4, and (*d*) what is the ionic strength of a solution containing all three electrolytes together with salicylic acid in 0.010 M concentration in aqueous solution?

(*a*) KCl:

$$\mu = \frac{1}{2}[(0.01 \times 1^2) + (0.01 \times 1^2)] = 0.010$$

(*b*) $BaSO_4$:

$$\mu = \frac{1}{2}[(0.01 \times 2^2) + (0.01 \times 2^2)] = 0.040$$

(*c*) $Na_2\,SO_4$:

$$\mu = \frac{1}{2}[(0.02 \times 1^2) + (0.01 \times 2^2)]$$
$$= 0.030$$

(*d*) The ionic strength of a 0.010 M solution of salicylic acid is 0.003 as calculated from a knowledge of the ionization of the acid at this concentration (using the equation $[H_3O^+] = \sqrt{K_a c}$). Unionized salicylic acid does not contribute to the ionic strength. The ionic strength of the mixture of electrolytes is the sum of the ionic strength of the individual salts. Thus,

$$\mu_{total} = \mu_{KCl} + \mu_{BaSO_4} + \mu_{Na_2SO_4} + \mu_{HSal}$$
$$= 0.010 + 0.040 + 0.030 + 0.003$$
$$= 0.083$$

EXAMPLE 6-12

Ionic Strength of a Solution

A buffer contains 0.3 mole of K_2HPO_4 and 0.1 mole of KH_2PO_4 per liter of solution. Calculate the ionic strength of the solution.

The concentrations of the ions of K_2HPO_4 are $[K^+] = 0.3 \times 2$ and $[HPO_4^{2-}] = 0.3$. The values for KH_2PO_4 are $[K^+] = 0.1$ and $[H_2PO_4^-] = 0.1$. Any contributions to μ by further dissociation of $[HPO_4^{2-}]$ and $[H_2PO_4^-]$ are neglected. Thus,

$$\mu = \frac{1}{2}[(0.3 \times 2 \times 1^2) + (0.3 \times 2^2) + (0.1 \times 1^2) + (0.1 \times 1^2)]$$
$$\mu = 1.0$$

The Debye–Hückel Theory

Based on three assumptions of how ions act in solution:
1. Strong electrolytes completely dissociate into ions in solution.
2. Solutions of Electrolytes are very dilute, on the order of 0.01 M.
3. Each ion is surrounded by ions of the opposite charge, on average.

$$\log \gamma_i = -Az_i^2\sqrt{\mu}$$

- (γ_i)the activity coefficient,,
- A= for water at 25°C, is a factor that depends only on:
  - the temperature
  - and the dielectric constant of the medium, is approximately 0.51

- The values of A for various solvents of pharmaceutical importance are found in Table 6-2

TABLE 6-2 Values of *A* for Solvents at 25°C[a]

Solvent	Dielectric Constant, α	A_{calc}
Acetone	20.70	3.76
Ethanol	24.30	2.96
Water	78.54	0.509

COEFFICIENTS FOR EXPRESSING COLLIGATIVE PROPERTIES

- From van't Hoff equation, $\Delta Tf = iKf\ m$, in dilute solutions, by substituting molar concentration c and by writing iKf as L, so that: $\Delta Tf = L\ c$
- ➢L is computed experimentally for a number of drugs.
- ➢It varies with the concentration of the solution, at a concentration of drug that is isotonic with body fluids, L= iKf is designated as Liso .
- L_{iso}. for nonelectrolytes=1.9 (actually 1.86),
- for weak electrolytes= 2.0,
- for uni- univalent electrolytes= 3.4,
- and larger values for electrolytes of high valences.

A plot of iKf against the concentration of some drugs is presented in Figure 6-7, where each curve is represented as a band to show the variability of the L values within each ionic class. The approximate Liso for each of the ionic classes can be obtained from the dashed line running through the figure

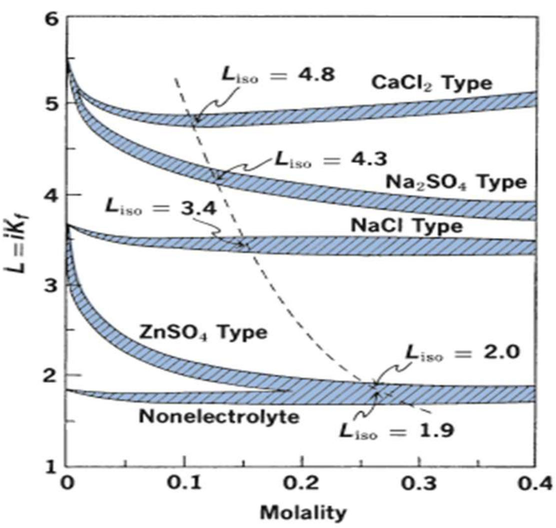

FIG. 6-7 Liso values of various ionic classes.

Osmotic Coefficient

- As the solution becomes more dilute, i approaches v (= valence), the number of ion into which an electrolyte dissociate, and at infinite dilution, i = v or i/v =1.
- The ratio i/v is designated as **g** and is known as the practical osmotic coefficient when expressed on a molal basis.
- In case of weak electrolyte, it provides a measure of the degree of dissociation.

$$\Delta T_f = g v K_f m$$

EXAMPLE 6-15 Molality and Molarity

- The osmotic coefficient of LiBr at 0.2 m is 0.944 and the Liso value is 3.4. Compute ΔTf for this compound using g and Liso. Disregard the difference between molality and molarity. We have

$$\Delta T_f = gvK_f m = 0.944 \times 2 \times 1.86 \times 0.2$$
$$= 0.70°$$
$$\Delta T_f = L_{iso} c = 3.4 \times 0.2 = 0.68°$$

Osmolality

Osmotic coefficient and osmolarity

- Osmotic pressure unit is atmospheres and in clinical practice is expressed by Osmols or milliosmols (mOsm)
- 1Osmol= 1mole of substance in1kg water
- Osmolality = total no. of particles in 1 kg of water
- Osmolarity = total no. of particles I 1L of water
- It is effected by the interionic interactions.

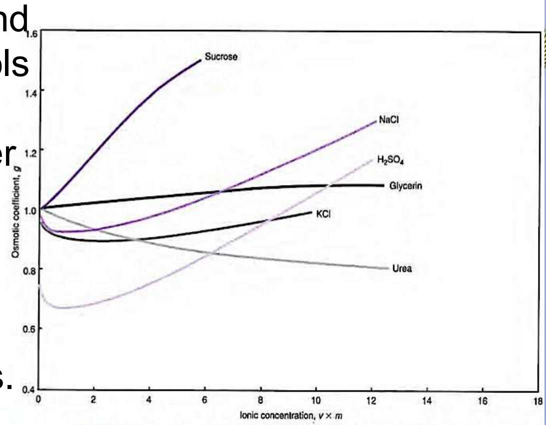

Fig. 6-8. Osmotic coefficient, *g*, for some common solutes. (From G. Scatchard, W. Hamer, and S. Wood, J. Am. Chem. Soc. 60, 3061, 1938. With permission.)

$$\text{Milliosmolality (mOsm/kg)} = i \cdot mm$$

where i is approximately the number of ions formed per molecule and mm is the millimolal concentration.

EXAMPLE 6–16

Calculating Milliosmolality

What is the milliosmolality of a 0.120 m solution of potassium bromide? What is its osmotic pressure in atmospheres?

For a 120 millimolal solution of KBr:

$$\text{Milliosmolality} = 1.86 \times 120 = 223 \text{ mOsm/kg}$$

A 1-osmolal solution raises the boiling point 0.52°C, lowers the freezing point 1.86°C, and produces an osmotic pressure of 24.4 atm at 25°C. Therefore, a 0.223-Osm/kg solution yields an osmotic pressure of $24.4 \times 0.223 = 5.44$ atm.

Examples 6-17, 6-18 and 6-19 are important

$$\text{Osmolarity} = (\text{Measured osmolality}) \times (\text{Solution density in g/mL} - \text{Anhydrous solute concentration in g/mL})$$

Thanks for your attention