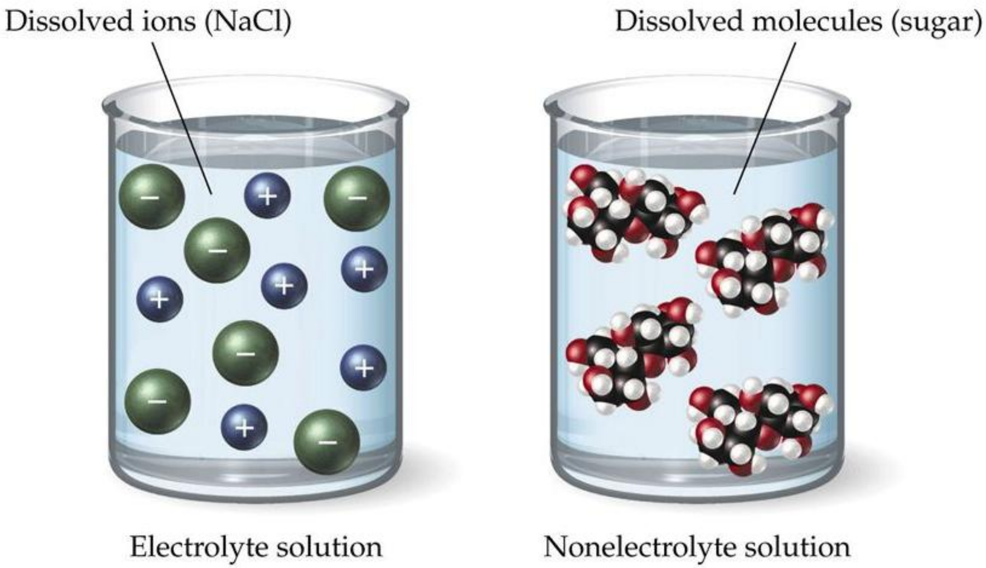
Chapter (6-B)



ELECTROCHEMISTRY:

Properties of Electrolyte Solutions

Feb. 2nd , 2018

Electrical Conductivity

- In metallic conductors, the electricity carriers are the free electrons migrating through the 3D lattice of the metal. The formula below describes Ohm's law (Ω=Ohm).
- The conductivity (κ) of a conductor (e.g. metal wire) characterizes its ability to conduct electricity.
- By definition it is inversely proportional to its resistivity.

$$\text{Electric current}(I) = \frac{\text{Voltage}(U)}{\text{Resistance}(R)}, \quad \text{Units}: I(\text{Ampere}), R(\text{Ohm}), U(\text{Volts})$$

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

l – Length

R – Resistance

A – cross-sectional area

$$\kappa = \frac{1}{\rho} \quad \text{– conductivity}, \quad \text{units}: \Omega^{-1}.m^{-1}$$

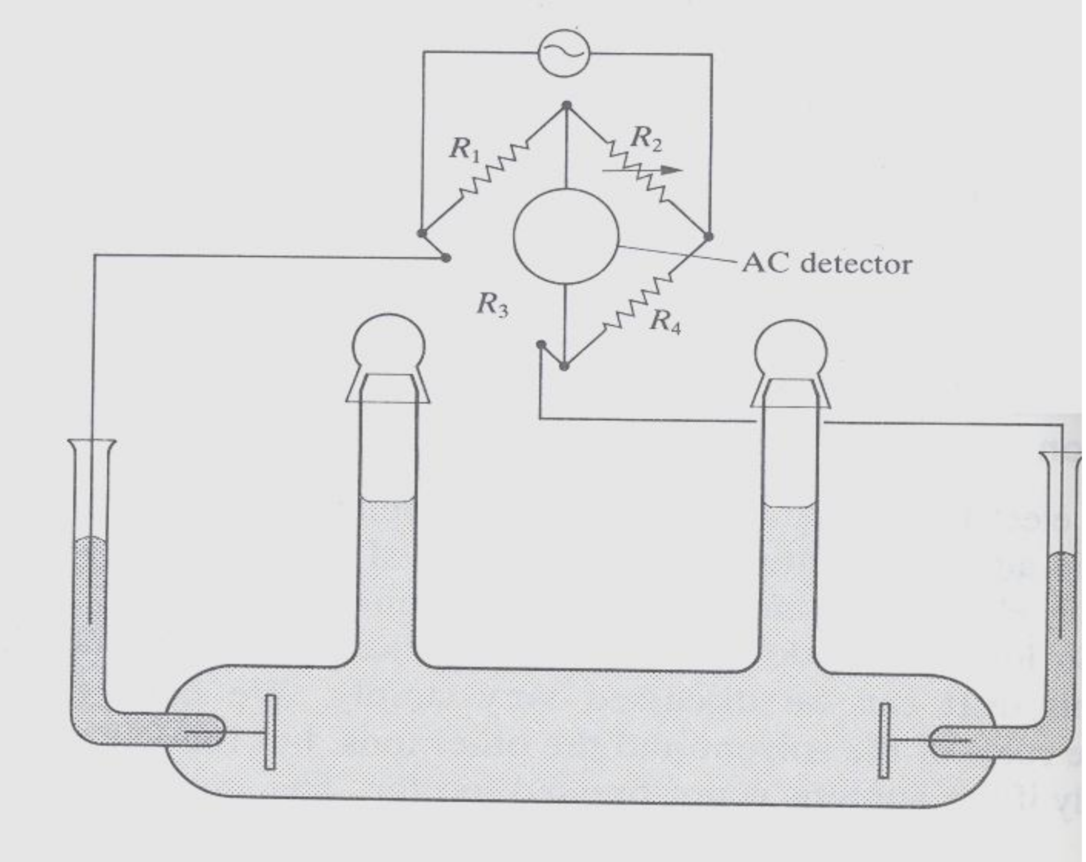
$$\rho \text{ – resistivity}, \quad \text{units}: \Omega.m$$

Conductivity of Electrolytes

- Solutions of ionic salts (electrolytes) and some polar compounds that can dissociate upon dissolution also conduct electricity.
- In this case the electricity carriers are two types: cations (+) and anions (-).
- Examples of electrolytes: *Aqueous solutions of*

  NaCl, K2SO4, NH4Cl, HCl, KOH, CH3COOH
- When a potential difference is applied across two electrodes immersed in ionic solution the net motion of the ions is towards one or other electrodes and electric current is conducted through the solution.
- In solution, the cations migrate towards a negatively charged electrode and the anions move towards a positively charged electrode.

Measuring Conductivity of Electrolytes



$$\frac{R_1}{R_2} = \frac{R_3}{R_4}$$

$$R_3 = R_4 \frac{R_1}{R_2}$$

R_3 – *resistance of the electrolyte*

The conductivity of a solution is determined by measuring its electrical resistance and the standard method is to incorporate a conductivity cell into one arm of a **Wheatstone bridge** and to search for the balance point (zero current). AC current is used to avoid electrolysis.

Measuring Conductivity of Electrolytes

How to determine κ from R_3 ?

- Calculating the conductivity from the resistance of the sample is unreliable because the current distribution is complicated.

$$\boxed{\kappa = \frac{1}{\rho} = \frac{l}{AR} = \frac{C}{R} \qquad C - cell \;\; constant}$$

- In practice, the cell is calibrated using a solution of known conductivity κ* (typically an aqueous solution of KCl). R* is the observed resistance

$$\boxed{\kappa^* = \frac{C}{R^*}, \qquad hence \quad C = \kappa^* R^*}$$

- Then if the measured sample has a resistance R, κ=C/R

Examples

Example: The molar conductivity of 0.100M KCl(aq) at 298K is 129 Ω^{-1} cm^2 mol^{-1}. The measured resistance of the cell is 28.44 Ω. When the same cell contained 0.050M NaOH (aq) the resistance was 31.6 Ω. Calculate the molar conductivity of NaOH(aq) at that temperature and concentration.

Solution: Establish the cell constant using $C=\kappa^*R^*$. Then use C and R to find κ of the test solution. For 0.100M KCl (aq):

$$\boxed{\kappa^* = c_m\Lambda_m = 0.100 mol.dm^{-3} \times 129\Omega^{-1}cm^2mol^{-1} = 1.29\times10^{-2}\Omega^{-1}cm^{-1}}$$

$$\boxed{C = (1.29\times10^{-2}\Omega^{-1}cm^{-1})\times(28.44\Omega) = 0.367 cm^{-1}}$$ cell const.

Hence for NaOH(aq) we have

$$\boxed{\kappa = C/R = (0.367cm^{-1})/(31.6\Omega) = 0.0116\Omega^{-1}cm^{-1}}$$

$$\boxed{\Lambda_m = \frac{\kappa}{c_m} = \frac{0.0116\Omega^{-1}cm^{-1}}{0.050mol\ dm^{-3}} = 232\Omega^{-1}cm^2mol^{-1}}$$

Conductivities of electrolyte solutions

- Conductance, G, of a solution ≡ the inverse of its resistance:

$G = 1/R$ in units of Ω^{-1}

- Since G decreases with length, ℓ, we can write:

$$\mathbf{G = \frac{\kappa A}{\ell}}$$

where κ ≡ conductivity and A ≡ cross-sectional area

- Conductivity depends on number of ions, so
molar conductivity ≡ $\Lambda_m = \kappa/c$ with c in molarity units.

Molar Conductivity

- The conductivity of a solution is due to contributions from both cations and anions and depends on the number of ions present (very sensitive to concentration).
- Practically, we work with the molar conductivity Λm, defined as:

$$\Lambda_m = \frac{\kappa}{c_m}, \qquad c_m - \textit{molar electrolyte concentration.}$$

Λ_m is expressed in $\mathrm{Ohm^{-1}\ cm^{2}\ mol^{-1}}$.

- Note that electrolyte ions of different valency transport different amount of electricity.
- For example: in NaCl solution each ion carries out unit charge in each direction, while in CuSO4, each ion transports 2 units of charge in each direction.

Conductivity of Strong and Weak Electrolytes

- Measurement of the concentration dependence of the molar conductivities shows that there are two classes of electrolytes:

  1. Strong electrolytes: Λ_m depends slightly on the electrolyte concentration, c_m , ($NaCl$, K_2SO_4)

  2. Weak electrolytes: Λ_m is normal at low concentrations but drops sharply when, c_m , is increased (CH_3COOH).

Conductivity of Strong and Weak Electrolytes

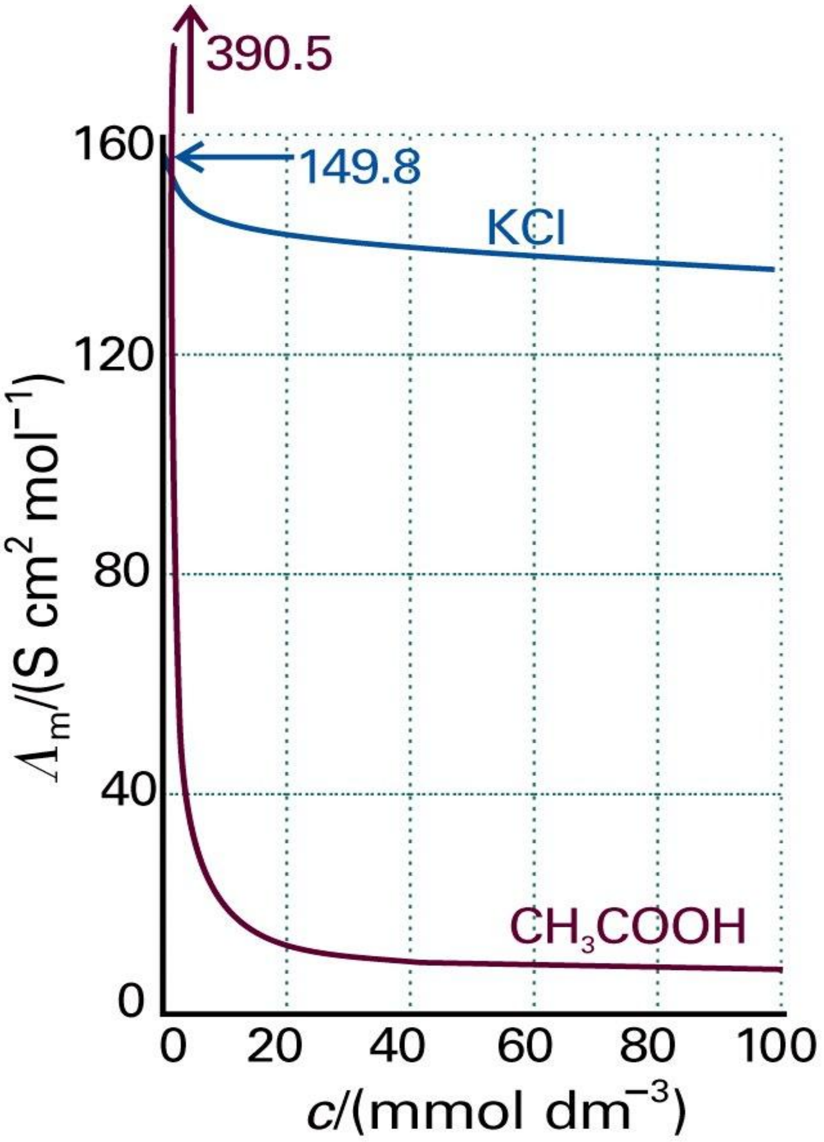


Figure 21-14
Atkins Physical Chemistry, Eighth Edition

- **Strong electrolyte** – molar conductivity depends only slightly on concentration

- **Weak electrolyte** – molar conductivity is normal at very low concentrations but falls sharply to low values at high concentrations

Fig 21.14 The concentration dependence of the molar conductivities of:

(a) a strong, and

(b) a weak electrolyte

Arrhenius Theory

1. Arrhenius proposed the now "*classic theory of dissociation*": When electrolytes are dissolved in solution, the solute exists in the form of ions in the solution:

$$\mathbf{NaCl + H_2O \rightarrow Na^+ + Cl^- + H_2O}$$

$$\mathbf{HCl + H_2O \rightarrow H_3O^+ + Cl^-}$$

$$\mathbf{CH_3COOH + H_2O \leftrightarrow CH_3COO^- + H_3O^+}$$

2. The differentiated between strong and weak electrolytes by the fraction of the molecules ionized: *the degree of dissociation* α. The degree of dissociation, according to Arrhenius theory, does not account for behavior of strong electrolyte.

3. A strong electrolytes is one that dissociated into ions to a high degree and a weak electrolyte is one that dissociated into ions to a low degree.

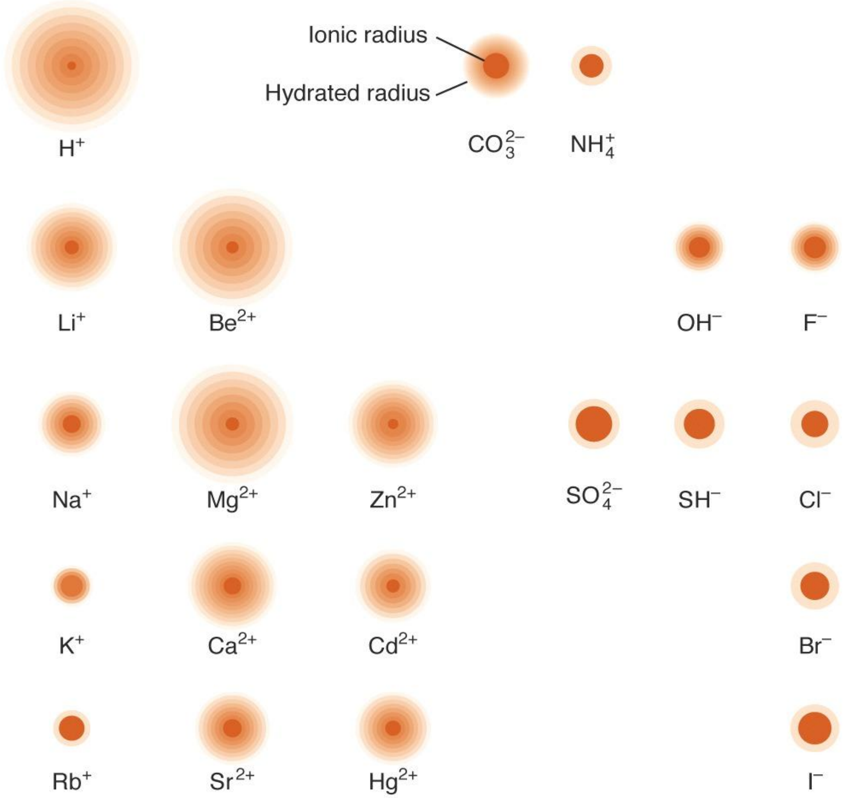
Arrhenius Theory

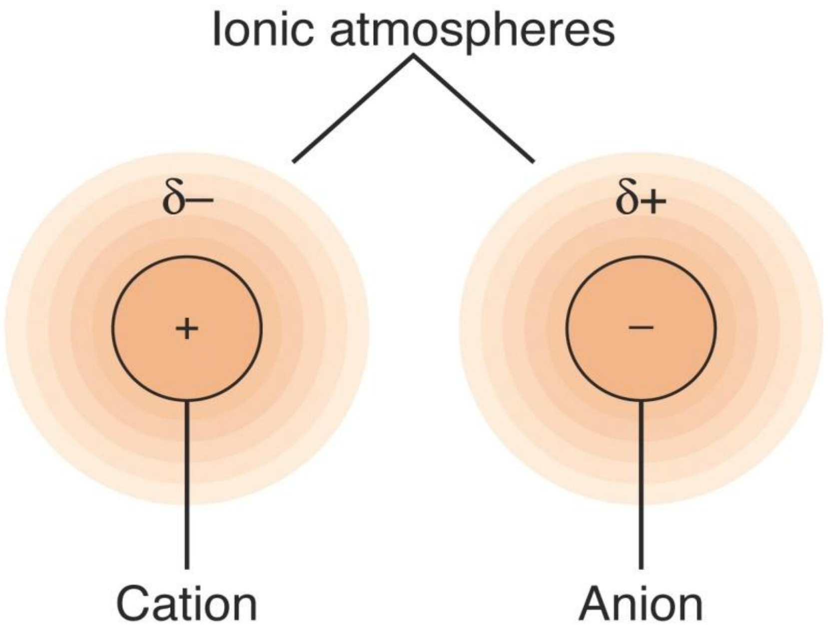
- The degree of dissociation can be determined from conductance measurements.
- Equivalent conductance at infinite dilution Λ_o was a measure of the complete dissociation of the solute into its ions, and that Λm represented the number of solute particles present as ions at concentration “cm”.
- Hence the fraction of solute molecules ionized, or the degree of dissociation, can be expressed by the equation, in which $\Lambda_{m/}\Lambda_o$ is known as the conductance ratio:

$$\alpha = \Lambda m_/ \Lambda^o m$$

1. Strong Electrolytes

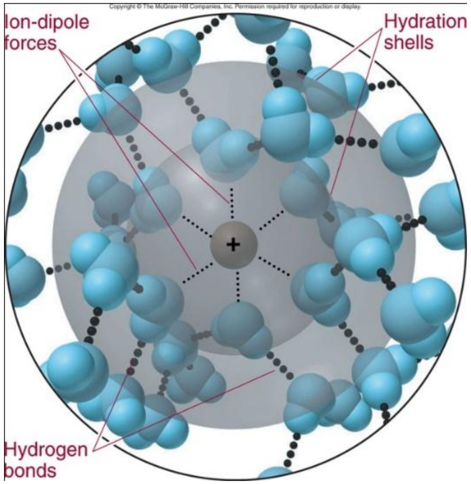
- The decrease of conductivity of strong electrolytes with concentration can be explained based on Coulomb’s law of opposite charge attraction, ionic hydration and solvation, *ionic atmosphere* formation and *electrophoresis*.

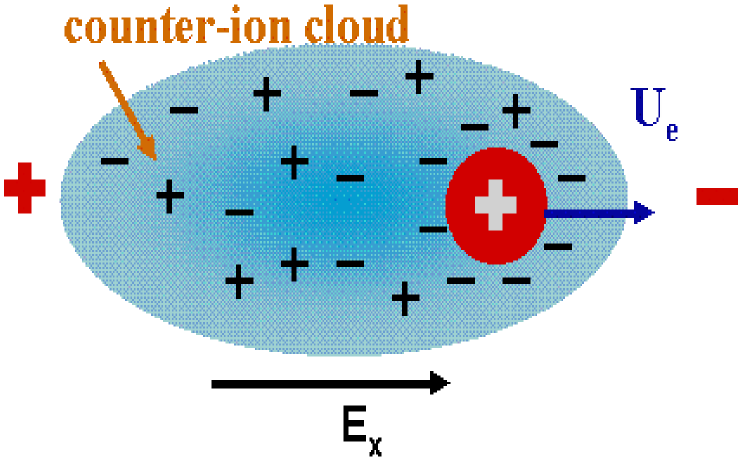




Strong Electrolytes

- **Electrophoresis** is the movement of charged particles (or large ions) under the influence of electric field.
- The above phenomena will synergistically drive towards forming a non-ideal solution that retards and may impede the transport of cations attracted by the cell anode and anions attracted by the cell anode. This retardation is associated by forming large charged particle of ionic and water layers around the original single ion.





Example

- Calculate the limiting molar conductivity of $BaCl_2$ in water at 298 K.

BaCl2 = Ba ++ + 2 Cl- $\nu_+ = 1, \nu_- = 2$

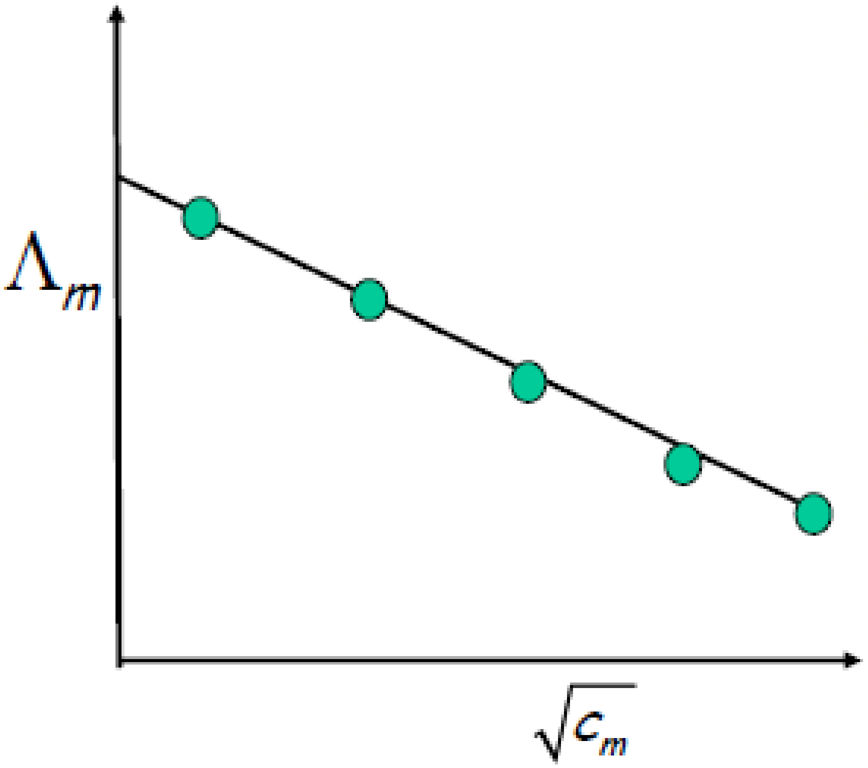
$$\lambda_+ = 12.72\,\mathrm{mS\,m^2\,mol^{-1}}, \lambda_- = 7.63\,\mathrm{mS\,m^2\,mol^{-1}}$$

$$\Lambda_m^0 = \nu_+\lambda_+ + \nu_-\lambda_-$$

$$= (12.72 + 2 \times 7.63)\,\mathrm{mS\,m^2\,mol^{-1}}$$

$$= 27.98\,\mathrm{mS\,m^2\,mol^{-1}}$$

Onsager Equation for Strong Electrolytes



Strong electrolytes are substances that are fully ionised in solution (ionic solids, strong acids)

$$\boxed{\Lambda_m = \Lambda_m^0 - K\sqrt{c_m}}$$

Kohlrausch law for strong electrolytes:

Λ_m^0 - limiting molar conductivity (at infinite dilution)
c_m - molar concentration of electrolyte
K- coefficient depending on the nature of electrolyte MA, or M_2A, etc.

Low of Independent Migration of Ions

- **Kohlrausch** also confirmed that Λºm for any electrolyte can be expressed as the sum of contributions from its individual ions:

$$\boxed{\Lambda_m^0 = \nu_+\lambda_+ + \nu_-\lambda_-}$$

- ν+ and ν- are the numbers of cations and anions per formula unit of the electrolyte

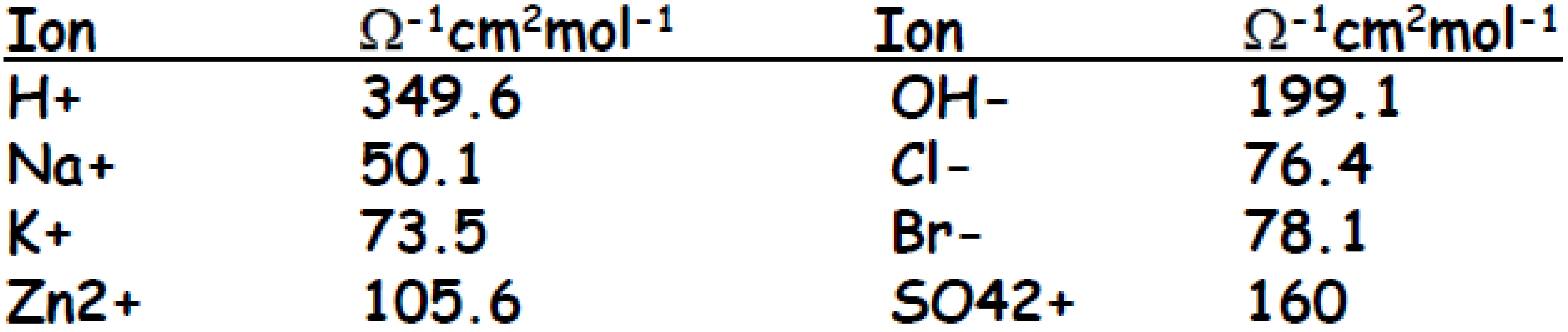
ν+=ν-=1 for NaCl, HCl, CuSO4

ν+=1, ν-=2 for MgCl2

- λ+ and λ- - limiting molar conductivities of the individual ions (*Tabulated for many ions, see nest slide*).
- Implications: ions behave independently when the solution is infinitely diluted, i.e. we can predict the conductivity of any strong electrolyte.

Low of Independent Migration of Ions

Limiting ionic conductivities in water at 298K

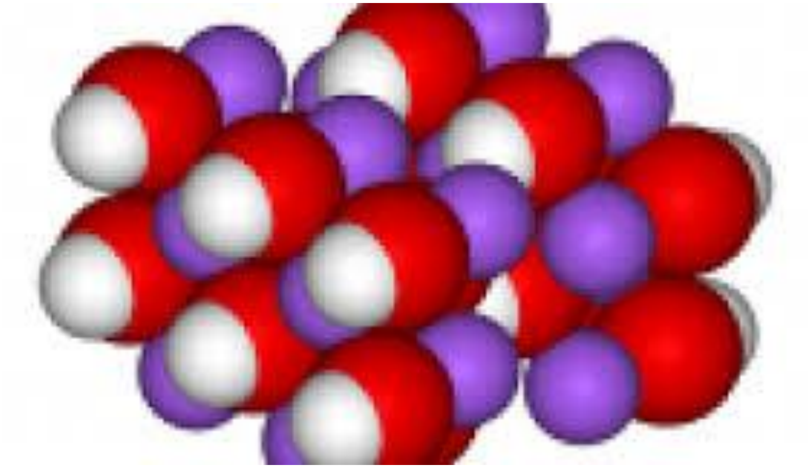


Ion	$\Omega^{-1}cm^{2}mol^{-1}$	Ion	$\Omega^{-1}cm^{2}mol^{-1}$
H+	349.6	OH-	199.1
Na+	50.1	Cl-	76.4
K+	73.5	Br-	78.1
Zn2+	105.6	SO42+	160

Low of Independent Migration of Ions

Example: Predict the limiting molar conductivities of the aqueous solutions of LiBr and $BaCl_2$ at 298K.

Ion	$\lambda / \Omega^{-1}cm^2mol^{-1}$
Li^+	38.7
Br^-	78.1
Ba^{2+}	127.2
Cl^-	76.3



Solution:

for LiBr:

$$\boxed{\Lambda_m^0 = (38.7 + 78.1)\,\Omega^{-1}cm^2mol^{-1} = 116.8\,\Omega^{-1}cm^2mol^{-1}}$$

for $BaCl_2$:

$$\boxed{\Lambda_m^0 = (127.2 + 2 \times 76.3)\,\Omega^{-1}cm^2mol^{-1} = 279.8\,\Omega^{-1}cm^2mol^{-1}}$$

2. Weak Electrolytes

- Weak electrolytes are substances that are not fully ionized in solution (weak acids and bases).

- Marked dependence of Λm on cm due to the shifting of the dissociation equilibrium upon dilution.

$$\boxed{\alpha = \frac{number\ of\ disscoiated\ MA}{total\ number\ of\ MA}}$$ **- degree of dissociation**

$$MA(aq) \rightleftharpoons M^{+}(aq) + A^{-}(aq)$$

$$(1-\alpha)c_m \qquad \alpha c_m \qquad \alpha c_m$$

$$K = \frac{[M^{+}(aq)][A^{-}(aq)]}{[MA(aq)]} = \frac{\alpha c_m . \alpha c_m}{(1-\alpha)c_m} = \frac{\alpha^2 c_m}{1-\alpha}$$ **- dissociation equilibrium constant**

How to connect α with Λ_m for weak electrolytes?

EXAMPLE

The Λ value of HAc solution at 25°C is 5.201×10^{-4} $S\cdot m^2\cdot mol^{-1}$, what is the degree of dissociation α and the equilibrium constant K_c of HAc. (*From Tables: Λ^o = 0.039071 S.m2.mol-1 for HAc at infinite dilution)*

$$Solution: \because \Lambda^o{}_{(HAc,25^\circ C)} = 0.039071 S\cdot m^2\cdot mol^{-1},$$

$$So:\ \alpha = \Lambda \big/ \Lambda^o = 5.201\times10^{-4} \big/ 0.039071 = 0.01331$$

$$K_C = \frac{c\alpha}{1-\alpha} = \frac{0.1000\times(0.01331)^2}{1-0.01331} = 1.795\times10^{-5} mol\cdot dm^{-3}$$

Weak Electrolytes

$$\boxed{\alpha \approx \frac{\Lambda_m}{\Lambda_m^0}}$$

This expression gives the connection between Λm and α

$$\boxed{K = \frac{\alpha^2 c_m}{1-\alpha}}$$

This expression gives the connection of the dissociation equilibrium constant K and α

If we eliminate α from this expression we obtain

$$K = c_m \frac{(\Lambda_m / \Lambda_m^0)^2}{1 - \Lambda_m / \Lambda_m^0}$$

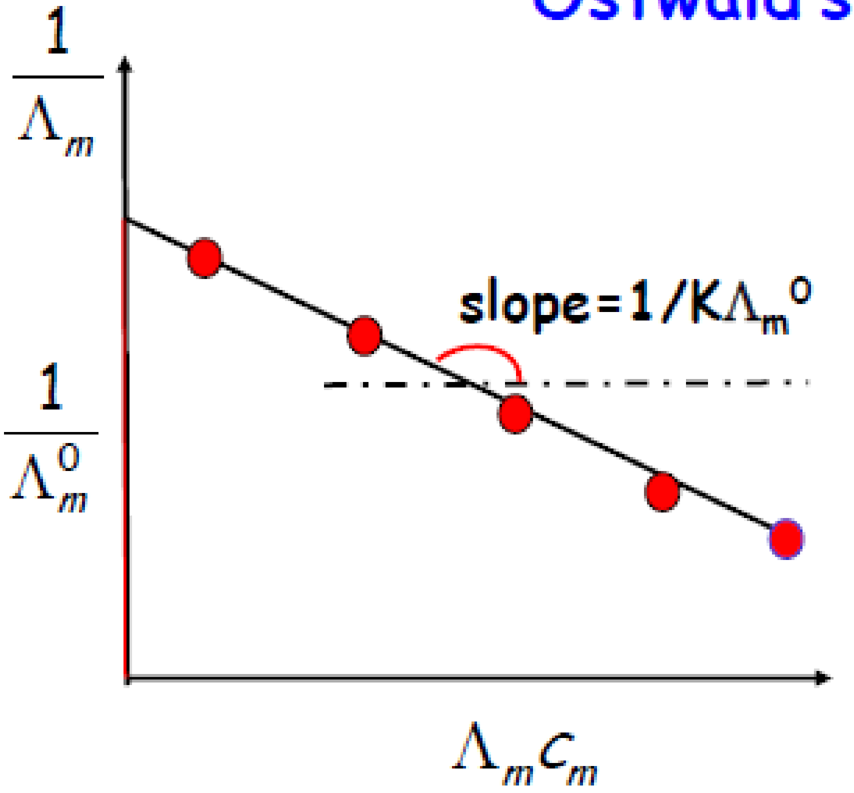
which can also be represented in linearised form

$$\boxed{\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{1}{K\Lambda_m^0}(\Lambda_m c_m)}$$

This is called *Ostwald Dilution Law*

Weak Electrolytes

Ostwald's Dilution Law



$$\boxed{\frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^0} + \frac{1}{K\Lambda_m^0}(\Lambda_m c_m)}$$

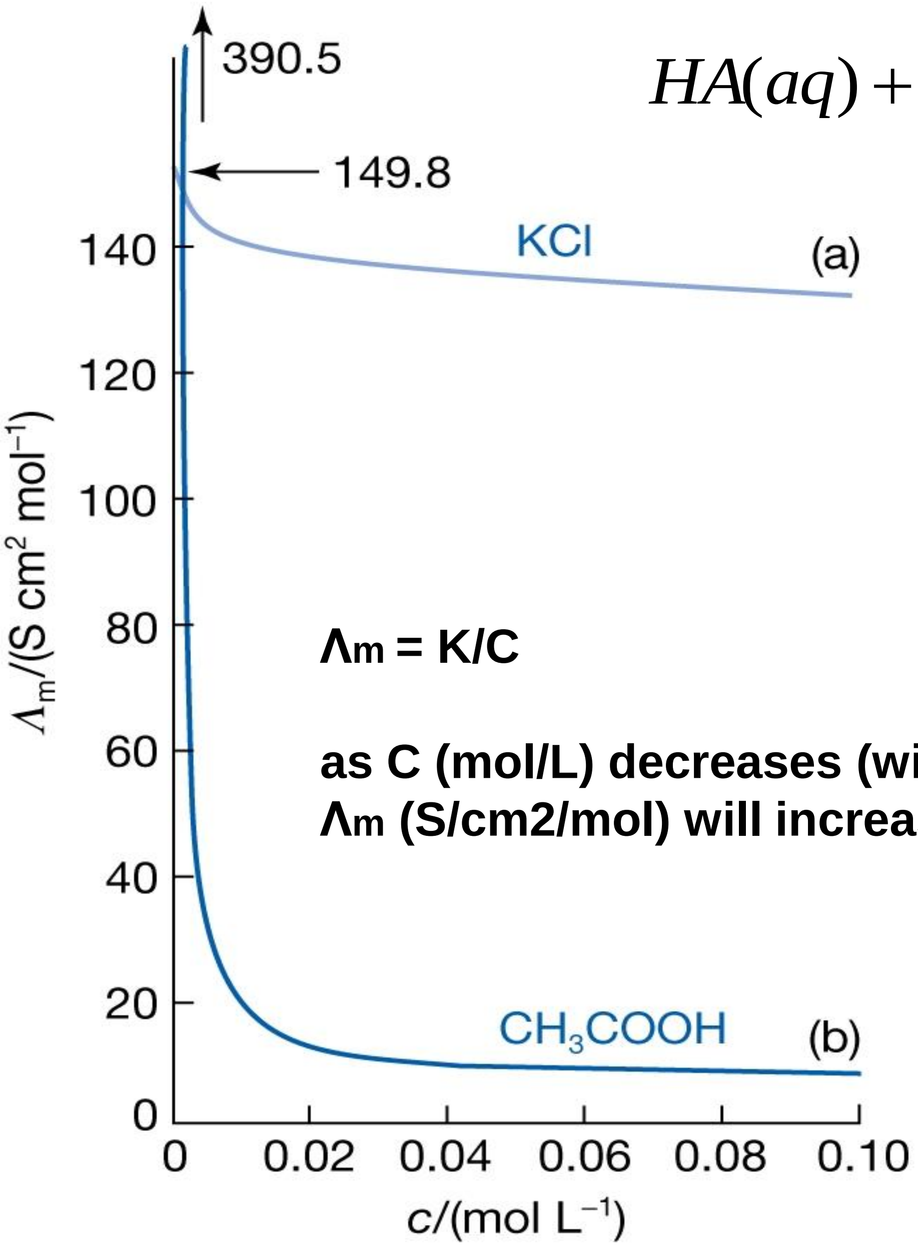
$$intercept = \frac{1}{\Lambda_m^0}$$

$$slope = \frac{1}{K\Lambda_m^0}$$

From the slope and the intercept we can determine the dissociation constant K of a weak electrolyte and the limiting molar conductivity Λ_m° of its ions:

$$\Lambda_m^0 = 1/\,intercept, \quad K = intercept\,/\,slope$$

Weak electrolytes



Λm = K/C

as C (mol/L) decreases (with dilution), Λm (S/cm2/mol) will increase

$$HA(aq) + H_2O(l) \Leftrightarrow H_3O^+(aq) + A^-(aq)$$

$$K_a = \frac{a_{H_3O^+} a_{A^-}}{a_{HA}} = \frac{[H_3O^+][A^-]}{[HA]}$$

$$K_a = \frac{\alpha^2 c}{1-\alpha}$$

$$\Lambda_m = \alpha \Lambda_m^0$$

Example

The molar conductivity of 0.0100 M CH_3COOH (aq) is Λ_m= 1.65 $mS.m^2.mol^{-1}$. Calculate the degree of dissociation α and acid dissociation constant *Ka*.

$$\Lambda_m = \alpha \Lambda_m^0$$

λ of CH_3COO^-

$$\Lambda_m^0 = 34.96 \times 1 + 4.09 \times 1$$

$$= 39.05\ \mathrm{mSm}^2\mathrm{mol}^{-1}$$

$$\mathrm{Ka} = ?$$

$$\alpha = \Lambda_m / \Lambda_m^0 = 0.0423$$

$$K_a = \frac{\alpha^2 c}{1-\alpha} \qquad K_a = \frac{(0.0423)^2 \times 0.01}{1-0.0423} = 1.9 \times 10^{-5}$$

Weak Electrolytes

Example: The resistance of an 0.010 M CH_3COOH (aq) solution was measured to be 2220 Ω. Find the dissociation constant K_a, the value of pK_a, the degree of dissociation of the acid and the pH of the solution. Assume the same cell constant C=0.367 cm^{-1}.

Ion	λ/ $\Omega^{-1}cm^2mol^{-1}$
H^+	349.6
CH_3COO^-	40.9

Solution:

$$\Lambda_m^0 = (349.6 + 40.9)\Omega^{-1}cm^2mol^{-1} = 390.5\Omega^{-1}cm^2mol^{-1}$$

$$\Lambda_m = \kappa / C_m = C / Rc_m = \underline{16.5\ \Omega^{-1}cm^2mol}^{-1}$$

$$\alpha = \Lambda_m / \Lambda_m^0 = 16.5/390.5 = \underline{0.0423} \quad (4.23\%)$$

$$K = \frac{\alpha^2 c_m}{1-\alpha} = \frac{0.0423^2 \times 0.010}{1-0.423} = \underline{1.9 \times 10^{-5}}, \quad \underline{pK_a = -\log K_a = 4.72}$$

$$[H^+] = \alpha c_m = 0.0423 \times 0.010 = \underline{4.23 \times 10^{-4} M}, \qquad pH = -\log[H^+] = \underline{3.37}$$

Ion mobility

Qualitatively: Large ions in viscous liquids can be expected to be drifting slowly and have low conductivities

electric field strength

Quantitatively: drift velocity $s = uE$

ion mobility

Two forces are acting on the ion: $F_{field} = zeE$

elementary charge

number of ion charges

Stokes' law $F_{retardation} = 6\pi\eta r s$

drift velocity

ion radius

viscosity

Field Strength,
E: V.m-1

When the ion has reached its drift velocity, both forces are equal!

$$\Rightarrow \quad ezE = 6\pi\eta r s \quad \Rightarrow \quad s = \frac{ezE}{6\pi\eta r}$$

u

$$\boxed{u = \frac{s}{E} = \frac{ez}{6\pi\eta r} \quad [m^2 s^{-1} V^{-1}]}$$

ionic conductivities:

$$\lambda_+ = z_+ F u_+ \qquad \lambda_- = z_- F u_-$$

Faraday constant

Measured ion mobilities

$$\boxed{u = \frac{ez}{6\pi\eta r}}$$

⇒ u is high for an ion that is:

- highly charged
- in a solution of low viscosity
- of small radius r

BUT: r = hydrodynamic radius
(including water ligands)

Illustration

- The Cs^+ cations with z=1 and hydrodynamic radius (taken as the ion radius plus the first hydration sphere) a=170 pm move in a solution with viscosity of 1.0 cP (1.0x 10^{-3}kg $m^{-1}s^{-1}$).
- Estimate the mobility of the cation.

$$u = ze/6\pi\eta a \sim 5\times 10^{-8}\ m^2V^{-1}s^{-1}$$

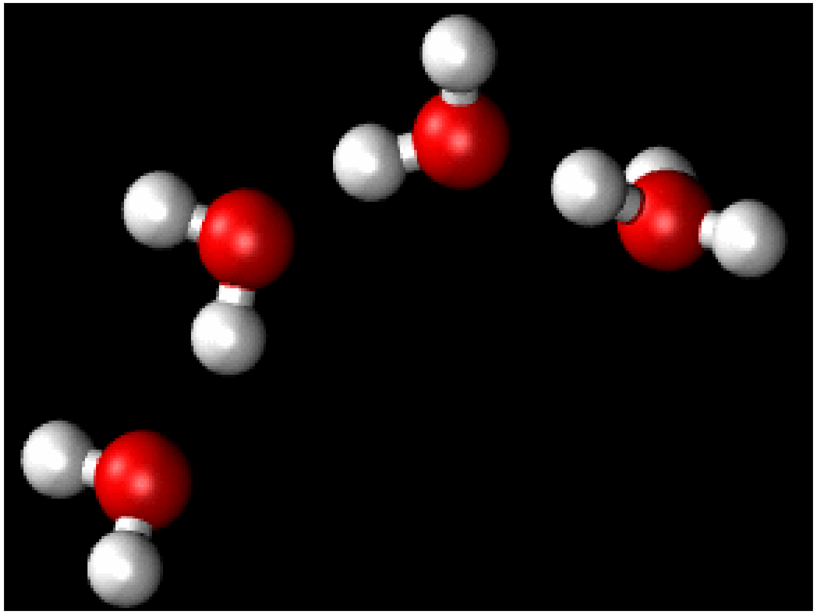
- A 1.0 *V* battery is connected to the two terminals of the solution across a length of 1 *cm*. Calculate the drift speed of Cs^+ cations.

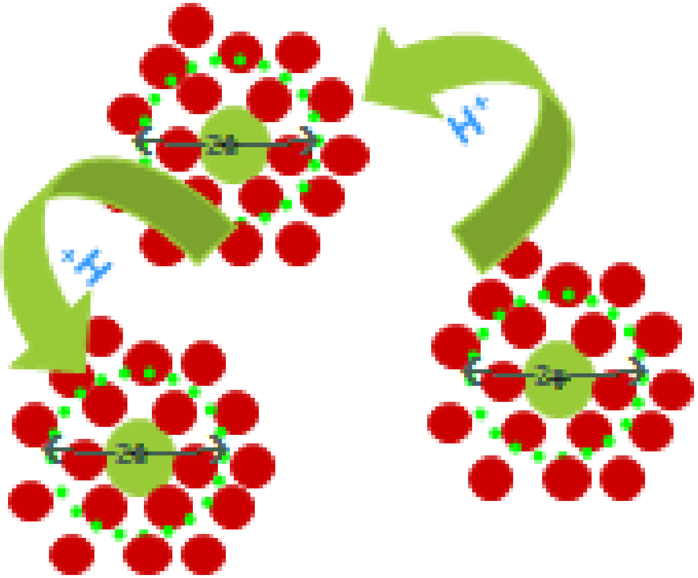
The electric field E=1 V/0.01 m = 100 V/m

$$s=uE \sim 5 \times 10^{-6}\ \text{m s-1} = 5\ \mu m s^{-1}$$

The cation passes about 10000 solvent molecules per second.

Grotthuss mechanism for proton conduction





Proton hopping involves rearrangement of the hydrogen bonds of a group of water molecules.

Transport Numbers of Ions

- The transport number (or the migration number) is the fraction of the total current carried by each ion present in solution:

$$t_+ = \frac{I_+}{I} = \frac{I_+}{I_+ + I_-} \qquad t_- = \frac{I_-}{I} = \frac{I_-}{I_+ + I_-}$$

$$t_+ + t_- = 1$$

$$t_+ = \frac{\nu_+ \lambda_+}{\Lambda_m} \qquad t_- = \frac{\nu_- \lambda_-}{\Lambda_m}$$

t_+ = fraction of charge carried by cations.

t_- = fraction of charge carried by anions.

- Transport numbers can also be determined from the ionic mobilities.

$$t_+ = \frac{u_+}{u_+ + u_-} \qquad t_- = \frac{u_-}{u_+ + u_-}$$

u_+ = cation mobility.

u_- = anion mobility.

Since ionic Conductivity is directly proportional to ionic mobility:

$$\lambda = zuF$$

Where

$$\text{Faraday constant}: F = N_A e$$

$$= 9.64853 \times 10^4 \text{ Coulomb.mol}^{-1}$$

Hittorf Method

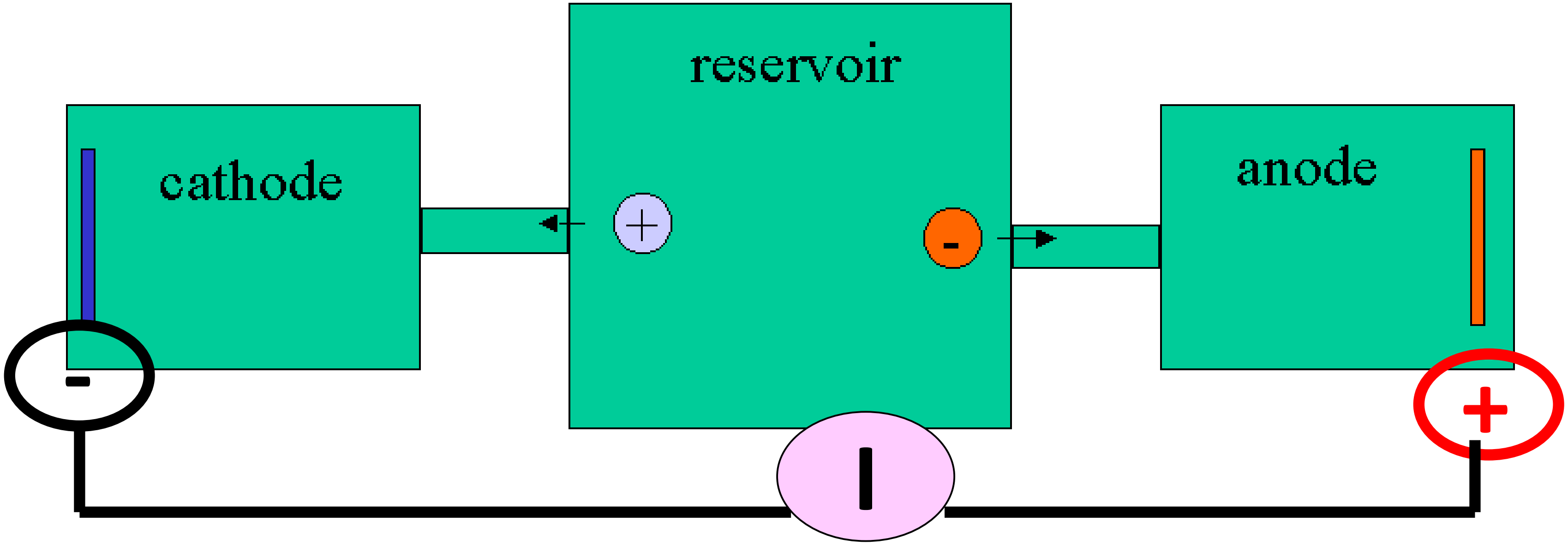
number of cations discharged at cathode is $$discharge = \frac{I\Delta t}{z_+F}$$

migration of cations to cathode is $$migration = \frac{t_+ I\Delta t}{z_+F}$$

change cation conc. at cathode

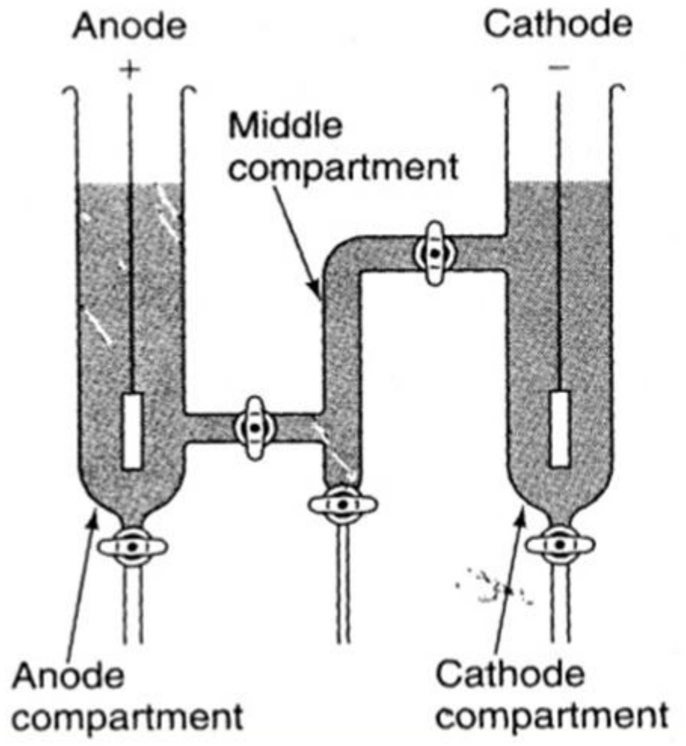
$$change = (t_+ - 1)\frac{I\Delta t}{z_+F} = -t_- \frac{I\Delta t}{z_+F}$$

gives anion transport no.



Hittorf Method

- The most common method for determination of transport numbers of ions.
- It is based on determination of changes in the composition (concentrations of ions) of an electrolytic solution around its cathode and anode.



number of cations discharged at cathode is $discharge = \frac{I\Delta t}{z_+ F}$

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change cation conc. at cathode

$$change = (t_+ - 1)\frac{I\Delta t}{z_+ F} = -t_- \frac{I\Delta t}{z_+ F}$$

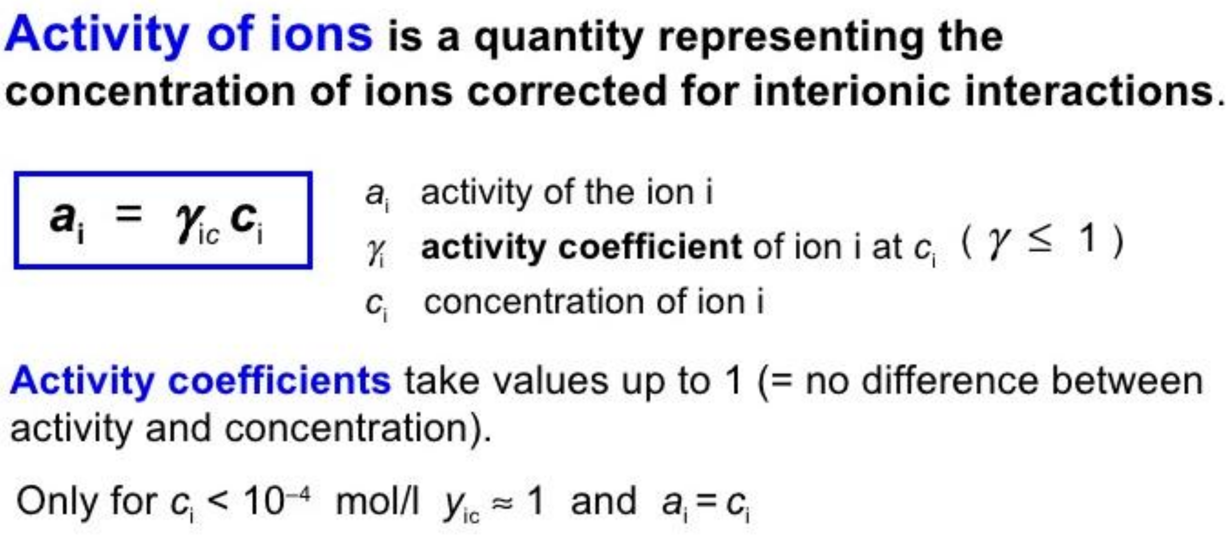
gives anion transport no.

Activity Coefficients of Ions

- The electrostatic interactions between ions, besides having an important effect on the conductivities of solutions of strong electrolytes, have an effect on the thermodynamic properties of ions.
- This matter is most conveniently dealt with in terms of **activity coefficients, where s**everal experimental methods are now available for determining these activity coefficients.

Debye-Huckel Limiting Law

- There are various reasons why a solution shows deviations from ideality and the matter is quite complicated.
- We are here concerned with a relatively simple reason for non-ideality in an ionic solution, namely the *electrostatic interactions* between ions, as interpreted by the Debye-Huckel theory.



Activity of ions is a quantity representing the concentration of ions corrected for interionic interactions.

$$\boxed{a_i = \gamma_{ic} c_i}$$

a_i activity of the ion i

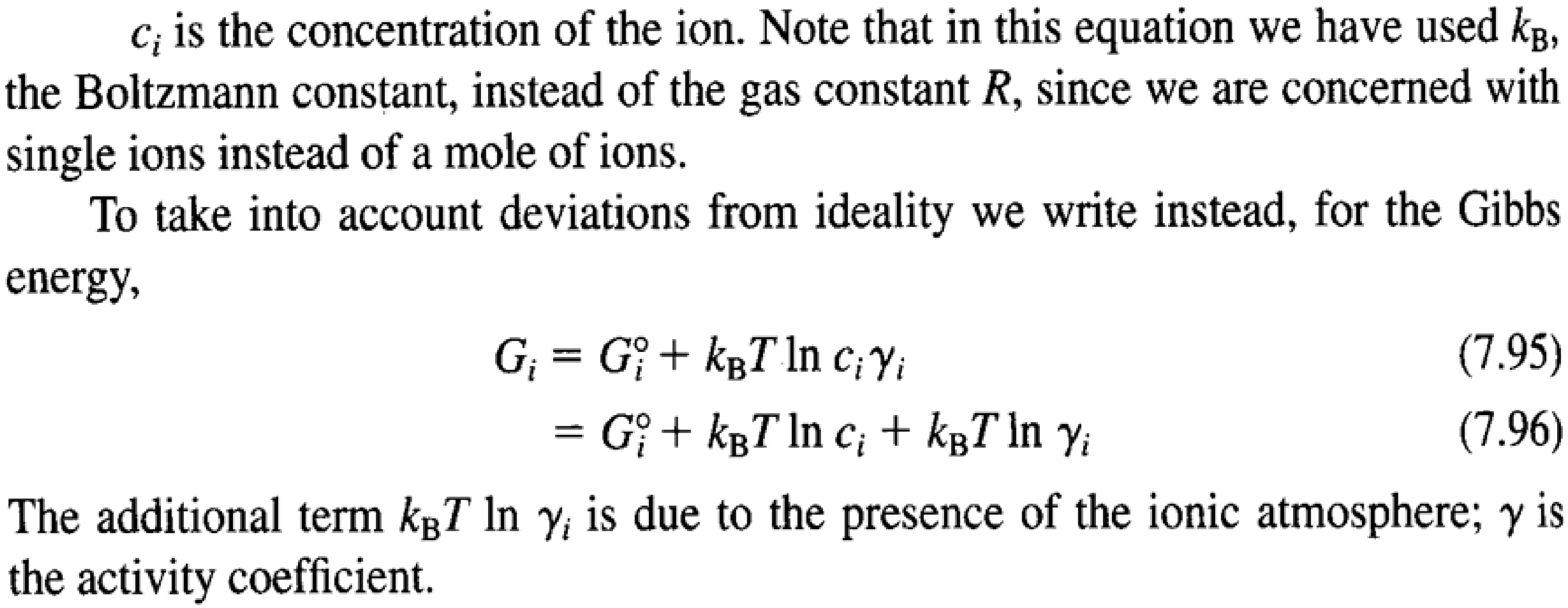
γ_i **activity coefficient** of ion i at c_i ($\gamma \leq 1$)

c_i concentration of ion i

Activity coefficients take values up to 1 (= no difference between activity and concentration).

Only for $c_i < 10^{-4}$ mol/l $y_{ic} \approx 1$ and $a_i = c_i$

Activity Coefficients of Ions



c_i is the concentration of the ion. Note that in this equation we have used k_B, the Boltzmann constant, instead of the gas constant R, since we are concerned with single ions instead of a mole of ions.

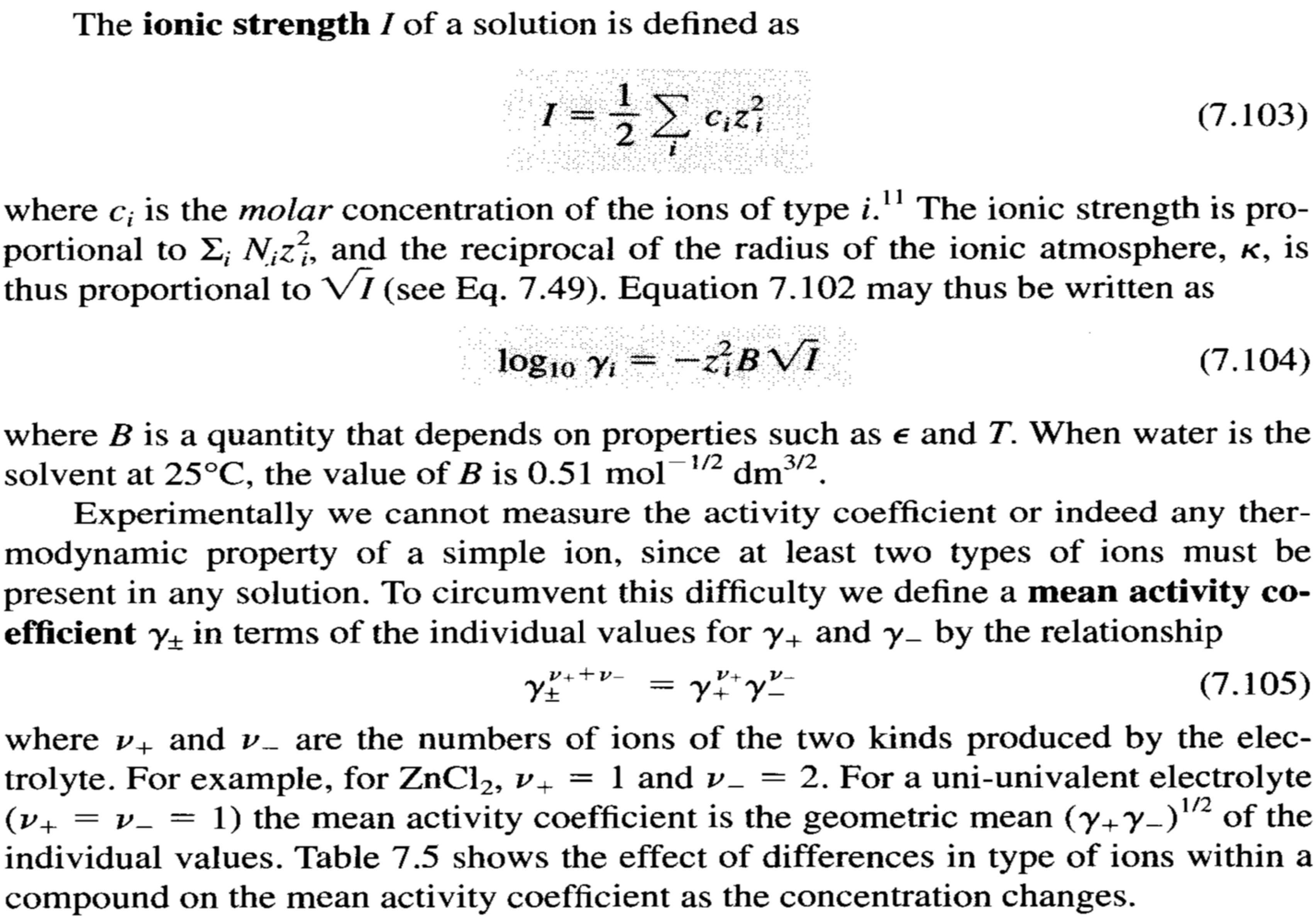
To take into account deviations from ideality we write instead, for the Gibbs energy,

$$G_i = G_i^\circ + k_B T \ln c_i \gamma_i \tag{7.95}$$

$$= G_i^\circ + k_B T \ln c_i + k_B T \ln \gamma_i \tag{7.96}$$

The additional term $k_B T \ln \gamma_i$ is due to the presence of the ionic atmosphere; γ is the activity coefficient.

Ionic Strength



The **ionic strength** I of a solution is defined as

$$I = \frac{1}{2}\sum_i c_i z_i^2 \tag{7.103}$$

where c_i is the *molar* concentration of the ions of type i.[11] The ionic strength is proportional to $\Sigma_i N_i z_i^2$, and the reciprocal of the radius of the ionic atmosphere, κ, is thus proportional to $\sqrt{I}$ (see Eq. 7.49). Equation 7.102 may thus be written as

$$\log_{10} \gamma_i = -z_i^2 B \sqrt{I} \tag{7.104}$$

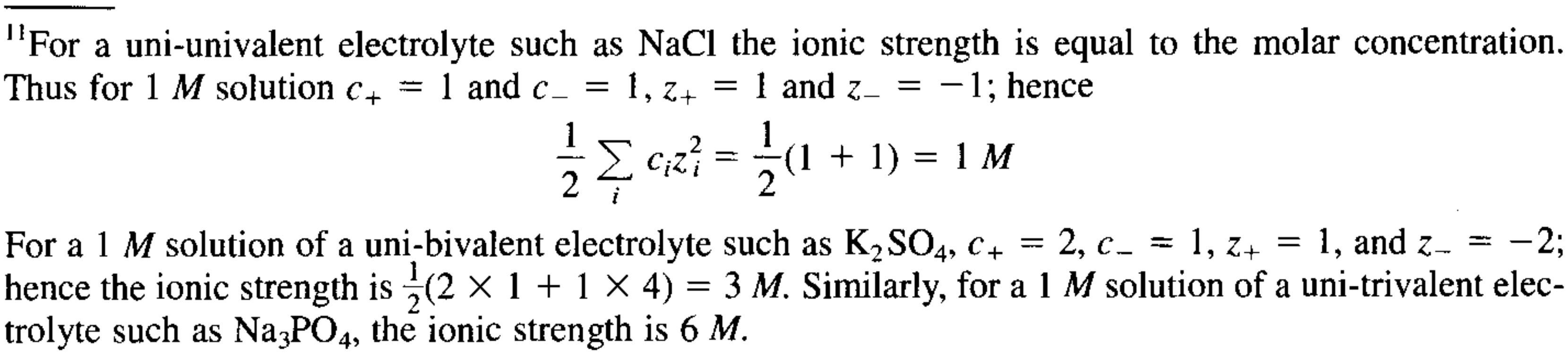
where B is a quantity that depends on properties such as ϵ and T. When water is the solvent at 25°C, the value of B is 0.51 $\text{mol}^{-1/2}\ \text{dm}^{3/2}$.

Experimentally we cannot measure the activity coefficient or indeed any thermodynamic property of a simple ion, since at least two types of ions must be present in any solution. To circumvent this difficulty we define a **mean activity coefficient** $\gamma_\pm$ in terms of the individual values for γ_+ and γ_- by the relationship

$$\gamma_\pm^{\nu_+ + \nu_-} = \gamma_+^{\nu_+} \gamma_-^{\nu_-} \tag{7.105}$$

where ν_+ and ν_- are the numbers of ions of the two kinds produced by the electrolyte. For example, for $ZnCl_2$, $\nu_+ = 1$ and $\nu_- = 2$. For a uni-univalent electrolyte ($\nu_+ = \nu_- = 1$) the mean activity coefficient is the geometric mean $(\gamma_+\gamma_-)^{1/2}$ of the individual values. Table 7.5 shows the effect of differences in type of ions within a compound on the mean activity coefficient as the concentration changes.

Ionic Strength and Activity Coefficients



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[11] For a uni-univalent electrolyte such as NaCl the ionic strength is equal to the molar concentration. Thus for 1 *M* solution $c_+ = 1$ and $c_- = 1$, $z_+ = 1$ and $z_- = -1$; hence

$$\frac{1}{2}\sum_i c_i z_i^2 = \frac{1}{2}(1 + 1) = 1\ M$$

For a 1 *M* solution of a uni-bivalent electrolyte such as K_2SO_4, $c_+ = 2$, $c_- = 1$, $z_+ = 1$, and $z_- = -2$; hence the ionic strength is $\frac{1}{2}(2 \times 1 + 1 \times 4) = 3\ M$. Similarly, for a 1 *M* solution of a uni-trivalent electrolyte such as Na_3PO_4, the ionic strength is 6 *M*.

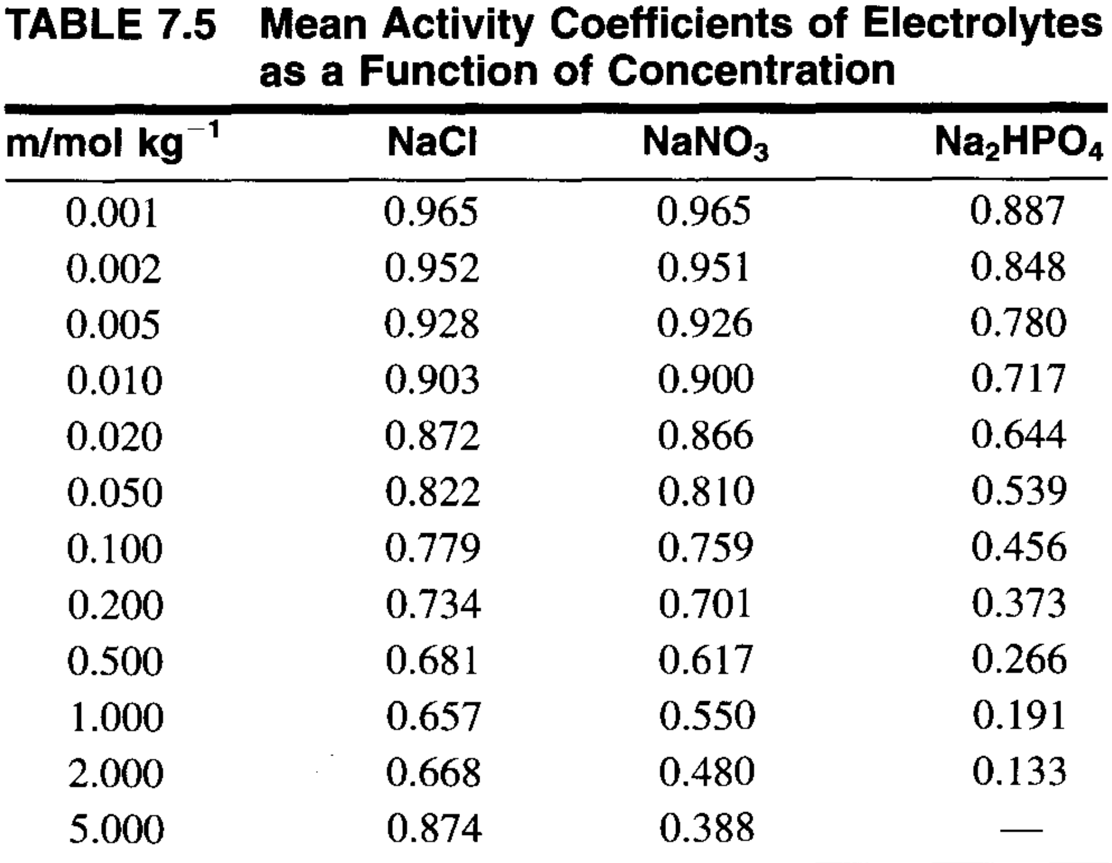
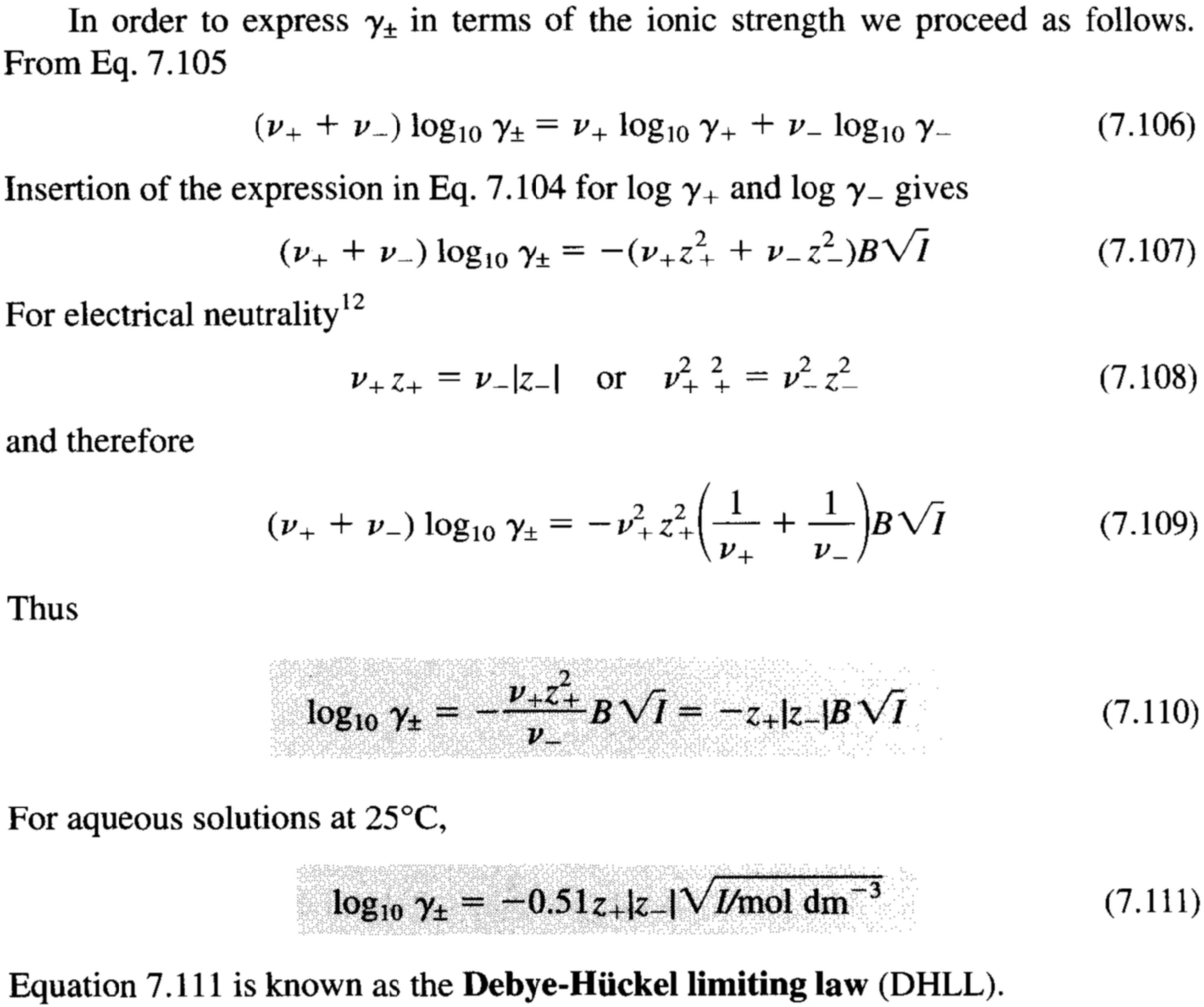


TABLE 7.5 Mean Activity Coefficients of Electrolytes as a Function of Concentration

m/mol kg^{-1}	NaCl	$NaNO_3$	Na_2HPO_4
0.001	0.965	0.965	0.887
0.002	0.952	0.951	0.848
0.005	0.928	0.926	0.780
0.010	0.903	0.900	0.717
0.020	0.872	0.866	0.644
0.050	0.822	0.810	0.539
0.100	0.779	0.759	0.456
0.200	0.734	0.701	0.373
0.500	0.681	0.617	0.266
1.000	0.657	0.550	0.191
2.000	0.668	0.480	0.133
5.000	0.874	0.388	—

Activity Coefficients



In order to express $\gamma_\pm$ in terms of the ionic strength we proceed as follows. From Eq. 7.105

$$(\nu_+ + \nu_-)\log_{10}\gamma_\pm = \nu_+\log_{10}\gamma_+ + \nu_-\log_{10}\gamma_- \tag{7.106}$$

Insertion of the expression in Eq. 7.104 for log γ_+ and log γ_- gives

$$(\nu_+ + \nu_-)\log_{10}\gamma_\pm = -(\nu_+ z_+^2 + \nu_- z_-^2)B\sqrt{I} \tag{7.107}$$

For electrical neutrality[12]

$$\nu_+ z_+ = \nu_-|z_-| \quad \text{or} \quad \nu_+^2\,{}_+^2 = \nu_-^2 z_-^2 \tag{7.108}$$

and therefore

$$(\nu_+ + \nu_-)\log_{10}\gamma_\pm = -\nu_+^2 z_+^2\left(\frac{1}{\nu_+} + \frac{1}{\nu_-}\right)B\sqrt{I} \tag{7.109}$$

Thus

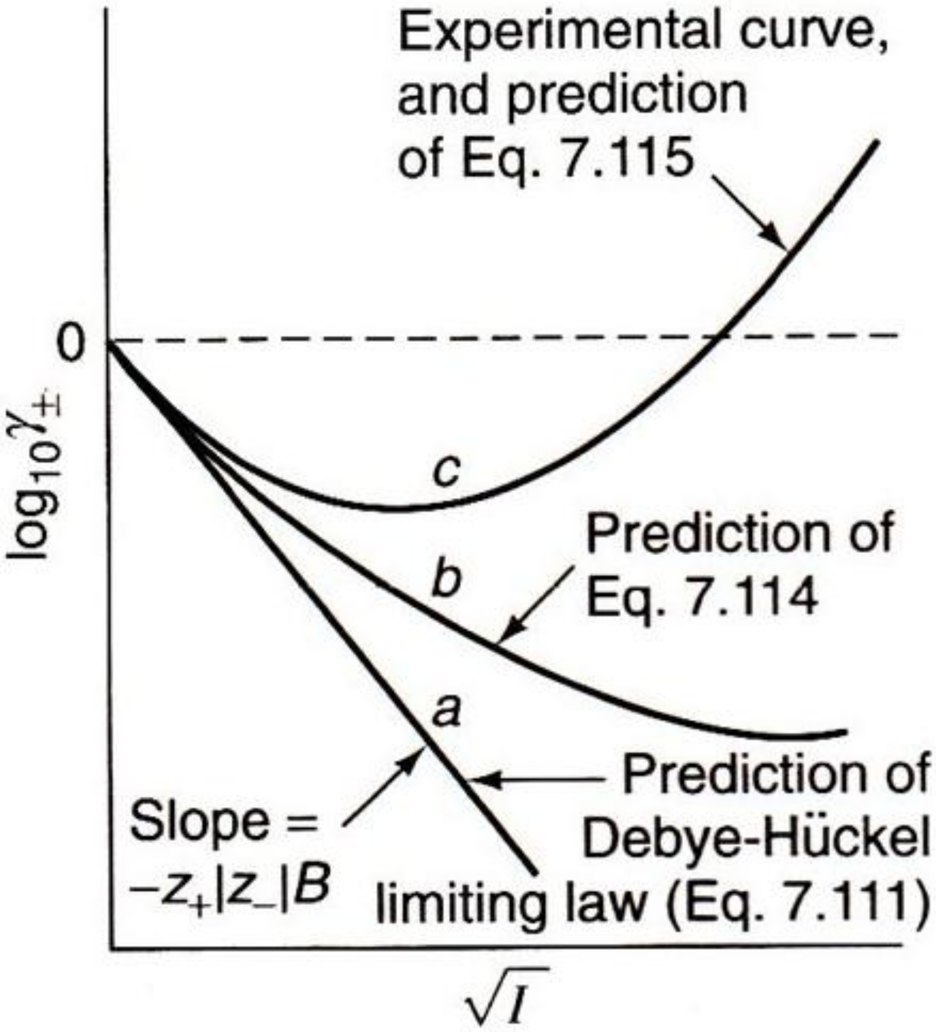
$$\log_{10}\gamma_\pm = -\frac{\nu_+ z_+^2}{\nu_-}B\sqrt{I} = -z_+|z_-|B\sqrt{I} \tag{7.110}$$

For aqueous solutions at 25°C,

$$\log_{10}\gamma_\pm = -0.51 z_+|z_-|\sqrt{I/\text{mol dm}^{-3}} \tag{7.111}$$

Equation 7.111 is known as the **Debye-Hückel limiting law** (DHLL).

Activity Coefficients



Debye-Huckel Limiting Law

$$\log \gamma_\pm = -0.510\,|z_+ z_-|(I_c)^{\frac{1}{2}}$$

Z_+ = charge of cation; z_- = charge of anion

Ionic Equilibria

Activity Coefficients from Equilibrium Constant Measurements

Equilibrium constant determinations can provide values of activity coefficients. The procedure may be illustrated with reference to the dissociation of acetic acid,

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

The practical equilibrium constant is

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \cdot \frac{\gamma_+ \gamma_-}{\gamma_u} \qquad (7.116)$$

where γ_+ and γ_- are the activity coefficients of the ions and γ_u is that of the undissociated acid. In reasonably dilute solution the undissociated acid will behave ideally ($\gamma_u = 1$), but γ_+ and γ_- may be significantly different from unity because of the electrostatic interactions. Replacement of $\gamma_+\gamma_-$ by $\gamma_\pm^2$ and taking logarithms of Eq. 7.116 leads to[14]

$$\log_{10}\left(\frac{[H^+][CH_3COO^-]}{[CH_3COOH]}\right)^u = \log_{10} K^\circ - 2\log_{10}\gamma_\pm \qquad (7.117)$$

Ionic Equilibria

The left-hand side can be written as

$$\log_{10}\left(\frac{c\alpha^2}{1-\alpha}\right)^u = \log_{10} K^\circ - 2\log_{10}\gamma_\pm \tag{7.118}$$

where c is the concentration and α is the degree of dissociation, which can be determined from conductivity measurements. (See Eq. 7.11.) Values of the left-hand side of this equation can therefore be calculated for a variety of concentrations, and these values are equal to $\log_{10} K^\circ - 2\log_{10}\gamma_\pm$.

If the Debye-Hückel limiting law applies, $\log_{10}\gamma_\pm$ is given by Eq. 7.111. If the solution contains only acetic acid, the ionic strength I is given by

$$I = \tfrac{1}{2}[(c\alpha)(1)^2 + (c\alpha)(-1)^2] = c\alpha \tag{7.119}$$

Ionic Equilibria

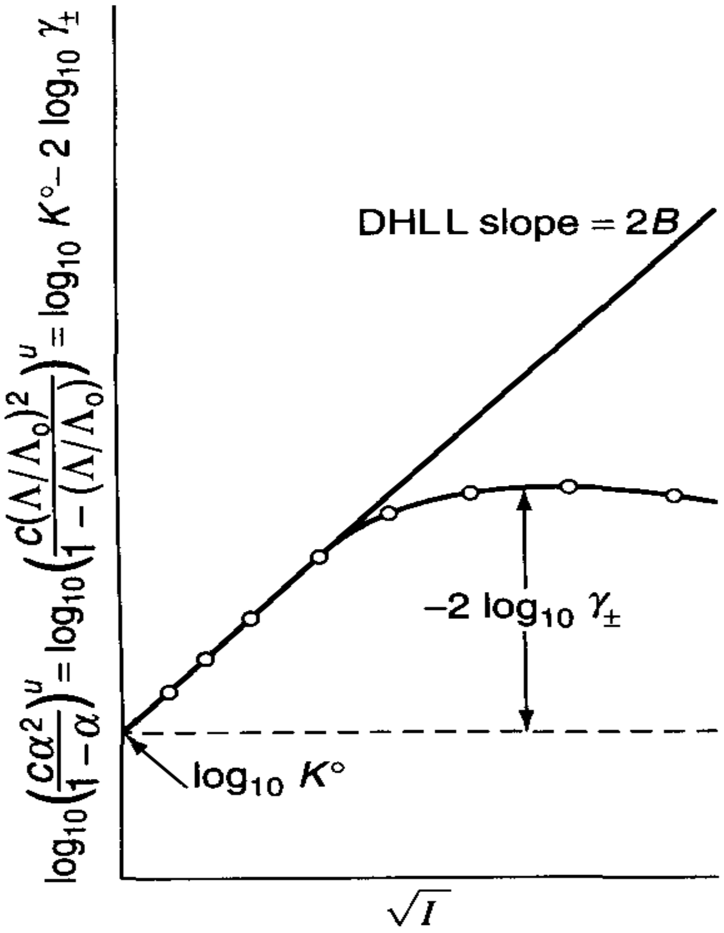
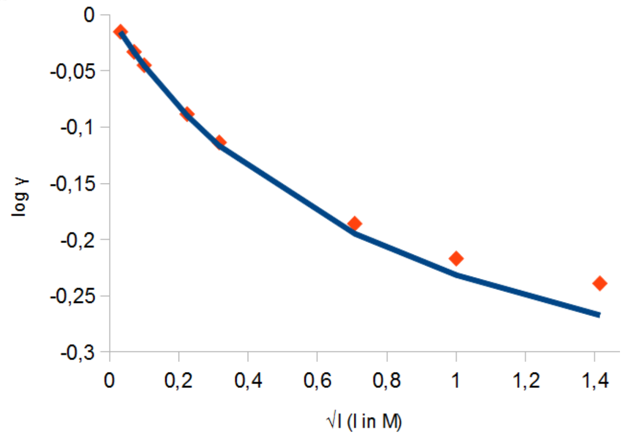


FIGURE 7.23
A schematic plot against $\sqrt{I}$ of $\log_{10}[c\alpha^2/(1-\alpha)]^u$, where α, the degree of dissociation, may be obtained from conductivity measurements.

Accuracy of the Debye-Hückel limiting law

Example: The mean activity coefficient in a 0.100 mol kg^{-1} $MnCl_2$(aq) solution is 0.47 at 25°C. What is the percentage error in the value predicted by the Debye-Huckel limiting law?



Solution: First, calculate the ionic strength

$$I = \tfrac{1}{2}(2^2*0.1 + 1^2*(2*0.1)) = 0.3$$

to calculate the mean activity coefficient.

$$\log(\gamma) = -|2*1|A*(0.3)^{1/2};$$

$$= -\ 2*0.509*0.5477$$

$$= -\ 0.5576$$

so $\gamma = 0.277$

Error = (0.47-0.277)/0.47 * 100%

= 41%

Solubility Products

IUPAC: solubility product

The product of the ion activities raised to appropriate powers of an ionic solute in its saturated solution expressed with due reference to the dissociation equilibria involved and the ions present.

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

$$K = \frac{[A^+]\cdot[B^-]}{[AB]}$$

$$K_{Sol} = [A^+]\cdot[B^-]$$

$$AB_2 \rightleftharpoons A^+ + B^-$$

$$K_{Sol} = [A^{2+}]\cdot[B^-]^2$$

Solubility Products

When we write solubility products (Section 4.4), we often ignore activity coefficients; the solubility products are expressed as products of concentrations instead of activities. The solubility product for silver chloride should more accurately be written as

$$K_s = [\mathrm{Ag}^+][\mathrm{Cl}^-]\gamma_+\gamma_- \tag{7.120}$$

where γ_+ and γ_- are the activity coefficients of Ag^+ and Cl^-, respectively. The product $\gamma_+\gamma_-$ is equal to $\gamma_\pm^2$, where $\gamma_\pm$ is the mean activity coefficient, and therefore

$$K_s = [\mathrm{Ag}^+][\mathrm{Cl}^-]\gamma_\pm^2 \tag{7.121}$$

One matter of interest that can be understood in terms of this equation is the effect of inert electrolytes on solubilities. An inert electrolyte is one that does not contain a common ion (Ag^+ or Cl^- in this instance) and also does not contain any ion that will complicate the situation by forming a precipitate with either the Ag^+ or the Cl^- ions. In other words, the added inert electrolyte does not bring about a chemical effect; its influence arises only because of its ionic strength.

Solubility Products

The influence of ionic strength I on the activity coefficient of an ion is given according to the DHLL by the equation

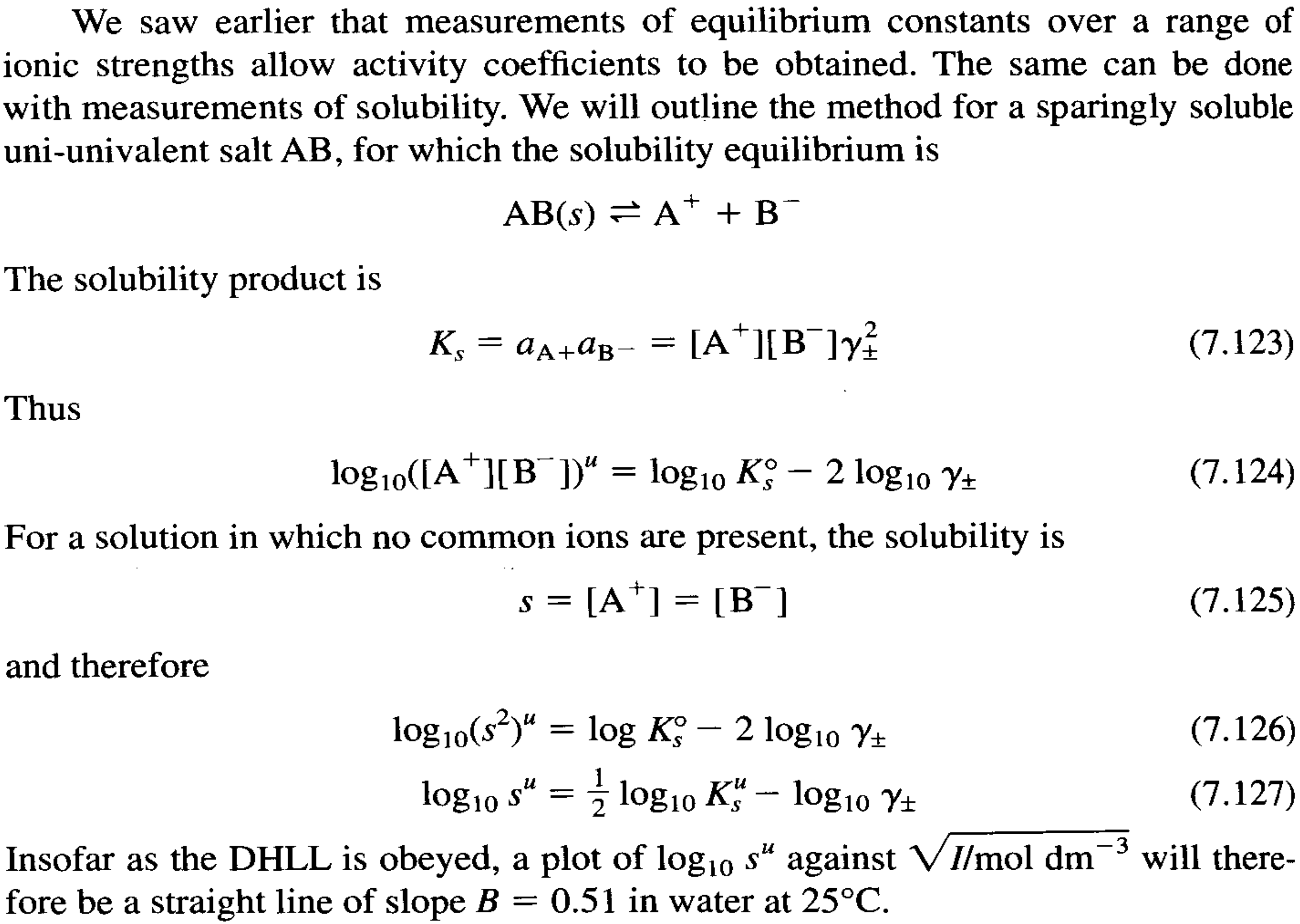
$$\log_{10} \gamma_\pm = -z_+|z_-|B\sqrt{I} \tag{7.122}$$

Figure 7.22 shows that this equation satisfactorily accounts for the drop in $\gamma_\pm$ that occurs at very low ionic strengths but that considerable deviations occur at higher ones; the value of $\log_{10} \gamma_\pm$ becomes positive (i.e., $\gamma_\pm$ is greater than unity) at sufficiently high values of I.

It follows as a result of this behavior that there are two qualitatively different ionic-strength effects on solubilities, one arising at low I values when the $\gamma_\pm$ falls with increasing I and the other being found when $\gamma_\pm$ increases with increasing I. Thus, at low ionic strengths the product $[Ag^+][Cl^-]$ will increase with increasing I, because the product $[Ag^+][Cl^-]\gamma_\pm^2$ remains constant and $\gamma_\pm$ decreases. Under these conditions, added salt increases solubility, and we speak of *salting in.*

At higher ionic strengths, however, $\gamma_\pm$ rises as I increases, and $[Ag^+][Cl^-]$ therefore diminishes. Thus there is a decrease in solubility, and we speak of *salting out.* Of particular interest are the salting-in and salting-out effects found with protein molecules, a matter of considerable practical importance since proteins are conveniently classified in terms of their solubility behavior.

Solubility Products



We saw earlier that measurements of equilibrium constants over a range of ionic strengths allow activity coefficients to be obtained. The same can be done with measurements of solubility. We will outline the method for a sparingly soluble uni-univalent salt AB, for which the solubility equilibrium is

$$AB(s) \rightleftharpoons A^+ + B^-$$

The solubility product is

$$K_s = a_{A^+}a_{B^-} = [A^+][B^-]\gamma_\pm^2 \qquad (7.123)$$

Thus

$$\log_{10}([A^+][B^-])^u = \log_{10} K_s^\circ - 2\log_{10}\gamma_\pm \qquad (7.124)$$

For a solution in which no common ions are present, the solubility is

$$s = [A^+] = [B^-] \qquad (7.125)$$

and therefore

$$\log_{10}(s^2)^u = \log K_s^\circ - 2\log_{10}\gamma_\pm \qquad (7.126)$$

$$\log_{10} s^u = \frac{1}{2}\log_{10} K_s^u - \log_{10}\gamma_\pm \qquad (7.127)$$

Insofar as the DHLL is obeyed, a plot of $\log_{10} s^u$ against $\sqrt{I/\text{mol dm}^{-3}}$ will therefore be a straight line of slope $B = 0.51$ in water at 25°C.

Solubility Products

Figure 7.24 shows the type of plot that is obtained in this way. At sufficiently low ionic strengths the points lie on a line of slope B. Extrapolation to zero ionic strength, where $\log_{10} \gamma_\pm = 0$, therefore gives $\frac{1}{2} \log_{10} K_s^\circ$, from which the true thermodynamic solubility product K_s is obtained. The value of $\log \gamma_\pm$ is then given by the difference between $\frac{1}{2} \log_{10} K_s^\circ$ and $\log_{10} s^u$ at that ionic strength, as shown in the figure.

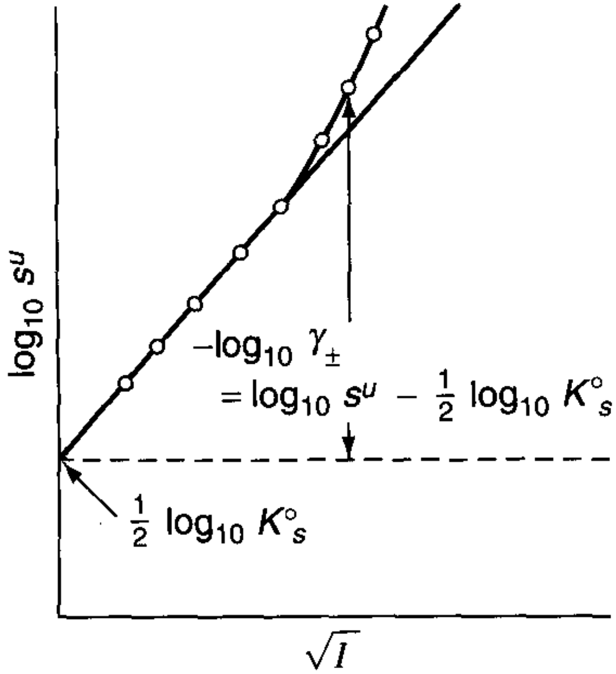


FIGURE 7.24
A schematic plot of $\log_{10} s^u$ against the square root of the ionic strength, showing how K_s° and $\gamma_\pm$ are obtained.

$AgCl(s) \rightarrow Ag^{+}(aq) + Cl^{-}(aq)$ ∴ calculate $[Ag+]$ or $[Cl^{-}]$

Solubility of AgCl(s) in water at 25°C is 1.274×10^{-5} mol kg^{-1}.

Calculate the solubility of AgCl(s) in 0.010 mol kg^{-1} $Na_2SO_4(aq)$.

In the presence of Na_2SO_4 the solution is no longer ideal → calculate activity coeff's

$$I = \frac{1}{2}\sum_i m_i z_i^{\,2} = \frac{1}{2}\left[(0.020)(+1)^2 + (0.010)(-2)^2\right] = 0.030$$

$I < 0.05$ ⇒ Use Debye-Hückel law

$$\log \gamma_{\pm} = -A|z_{+}z_{-}|\sqrt{I}$$

$$\log \gamma_{\pm} = -(0.509)|(+1)(-2)|\sqrt{0.030} = -0.176$$

$$\gamma_{\pm} = 0.666$$

Calculate K_{sp} for the ideal soln and assume it be the same for the non-ideal soln

$K_{sp} = a_{Ag+}\,a_{Cl-}$ ⟶ For AgCl dissolving in H_2O assume $\gamma = 1$ since $m \cong 0$

$K_{sp} = (1.274\times10^{-5})^2 = 1.623\times10^{-10}$

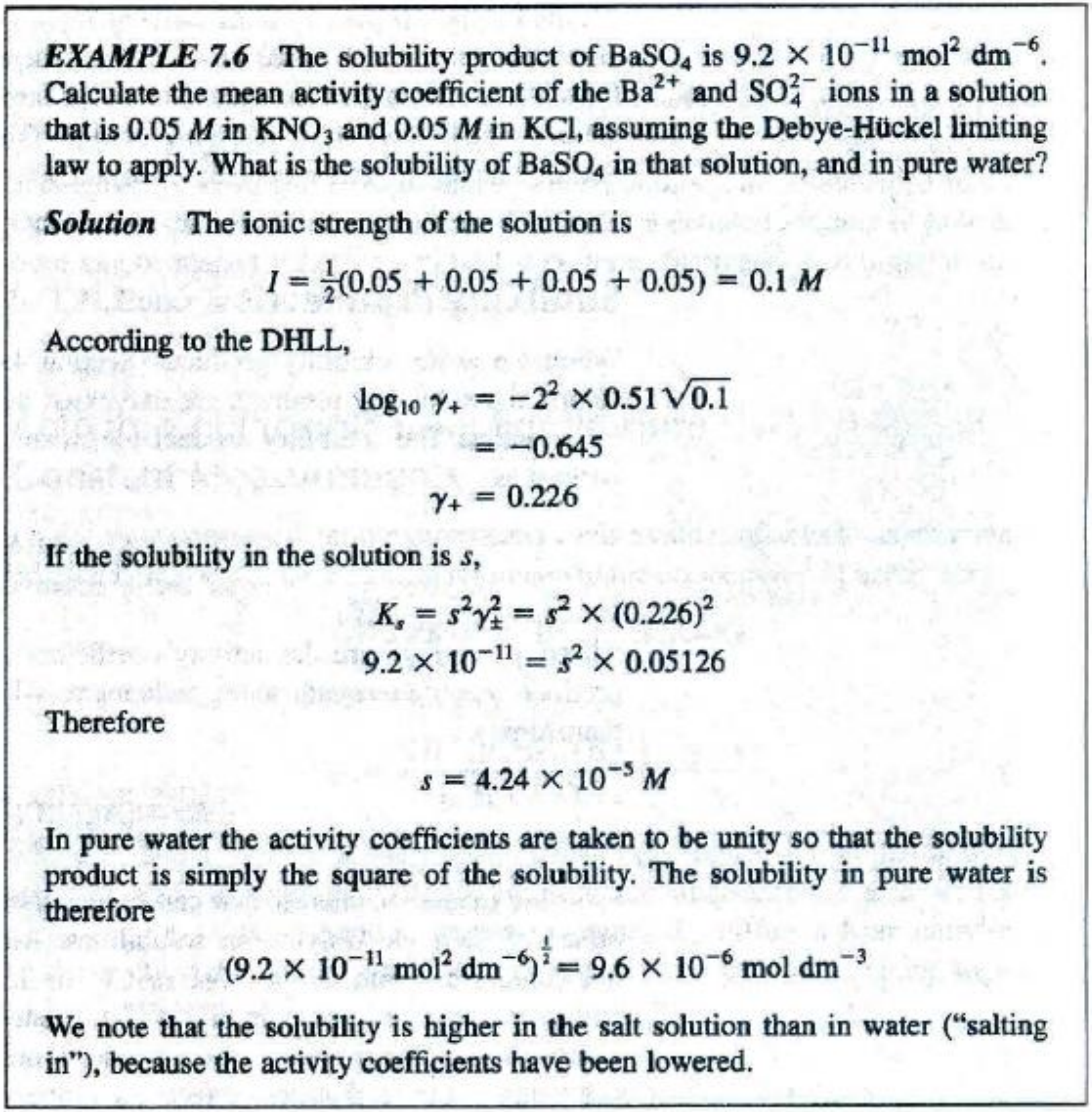
For $I = 0.030$ mol kg^{-1} ⟶ Ignore Ag^{+} and Cl^{-} in solution as conc's v. low

$$K_{sp} = a_{Ag+}\,a_{Cl-} = \gamma_{\pm} m_{Ag+}\,\gamma_{\pm} m_{Cl-}$$

$$1.623\times10^{-10} = (0.666)^2\, m^2$$

$$m = 1.91\times10^{-5} \text{ mol kg}^{-1} = \text{solubility}$$

Solubility Products Example



EXAMPLE 7.6 The solubility product of $BaSO_4$ is 9.2×10^{-11} mol^2 dm^{-6}. Calculate the mean activity coefficient of the Ba^{2+} and SO_4^{2-} ions in a solution that is 0.05 *M* in KNO_3 and 0.05 *M* in KCl, assuming the Debye-Hückel limiting law to apply. What is the solubility of $BaSO_4$ in that solution, and in pure water?

Solution The ionic strength of the solution is

$$I = \tfrac{1}{2}(0.05 + 0.05 + 0.05 + 0.05) = 0.1\ M$$

According to the DHLL,

$$\begin{aligned} \log_{10} \gamma_+ &= -2^2 \times 0.51\sqrt{0.1} \\ &= -0.645 \\ \gamma_+ &= 0.226 \end{aligned}$$

If the solubility in the solution is *s*,

$$K_s = s^2\gamma_\pm^2 = s^2 \times (0.226)^2$$

$$9.2 \times 10^{-11} = s^2 \times 0.05126$$

Therefore

$$s = 4.24 \times 10^{-5}\ M$$

In pure water the activity coefficients are taken to be unity so that the solubility product is simply the square of the solubility. The solubility in pure water is therefore

$$(9.2 \times 10^{-11}\ \text{mol}^2\ \text{dm}^{-6})^{\frac{1}{2}} = 9.6 \times 10^{-6}\ \text{mol dm}^{-3}$$

We note that the solubility is higher in the salt solution than in water ("salting in"), because the activity coefficients have been lowered.