Lectures: UTR ~~$8-8^{50}$~~ 10-11 ①-1

Office: UTR ~~$10-11^{50}$~~ 9-10, 11-12

After each Chapter Quiz about homework

→ no homework submission

<u>1. Major Exam</u> ~~March 2~~ October 20, 7-9 pm no change!

1. Major: Electrochemistry Chap. 34/10, 10, 11

2. Major: Kinetics: Chap. 35, 36

Final: Transport properties: Chap. 34

~~Transport hap~~ Today: electric, charge conduction = transport

Transport happens ~~when~~ after distribution of eg. mass or energy is shifted away from equilibrium by an external perturbation

perturbation off: transport for return to equilibrium distribution

flux: transport of a quantity ~~thoa~~ through an Area A in time t:

<u>flux</u> $J_x = -\alpha \dfrac{d(\text{quantity})}{dx}$.

linear relation if only small displacement from equilibrium

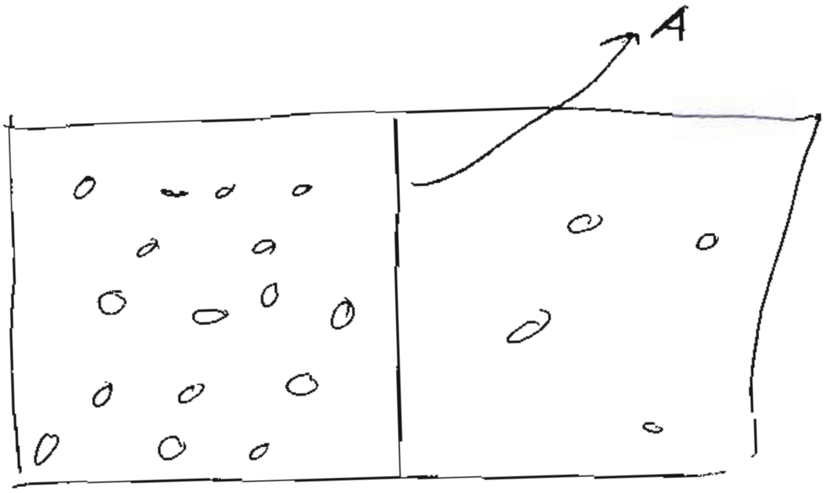
$[\text{flux}] = \dfrac{\text{quantity units}}{\text{area} \cdot \text{time}}$ $\underline{\alpha}$: transport coefficient

- sign: flux in opposite direction of the gradient

→ flux makes gradient smaller

if gradient kept = const. ⇒ flux = const. in time

e.g. $\tilde{N}$ particle number density



⟵ increase of $\tilde{N}$

⟶ flux direction

<u>electric conduction</u>

transport of electric charge as electrons (metals) or ions (solutions) in an electric potential field

current: charge transported in time t

$$I = \frac{dQ}{dt}$$

$$[I] = 1A = 1\frac{C}{s} = 1\frac{As}{s} = 1A$$

electronic charge: $e = 1.60 \cdot 10^{-19}$ C (As)

1A ≙ flow of $6.25 \cdot 10^{18}$ electrons in 1s current = const. in time $\Rightarrow$ $Q = I \cdot t$ ①-2a

current density : j = amount of current flowing through a conductor with crosssection area A

$$j = I/A$$

<u>transp</u>

Unfortunately, by convention thermal conductivity and electrical conductivity are both denoted by the symbol κ. Therefore, we will use the terms *thermal* or *electrical* when discussing conductivity to avoid confusion. Electrical conductivity has units of siemens per meter, or S m^{-1}, where 1 S equals $1\Omega^{-1}$ (ohm^{-1}). Finally, the **resistivity** ρ of a material is the inverse of the electrical conductivity:

$$\rho = \frac{1}{\kappa} = \frac{E}{j} \tag{34.65}$$

Resistivity is expressed in units of Ω m. Consider Figure 34.19 in which an electric field E is applied to a cylindrical conductor with a cross-sectional area and length l. If the cylinder is homogeneous in composition, the electric field and current density will be equivalent throughout the conductor, allowing us to write:

$$E = \frac{V}{l} \tag{34.66}$$

$$j = \frac{I}{Area} \tag{34.67}$$

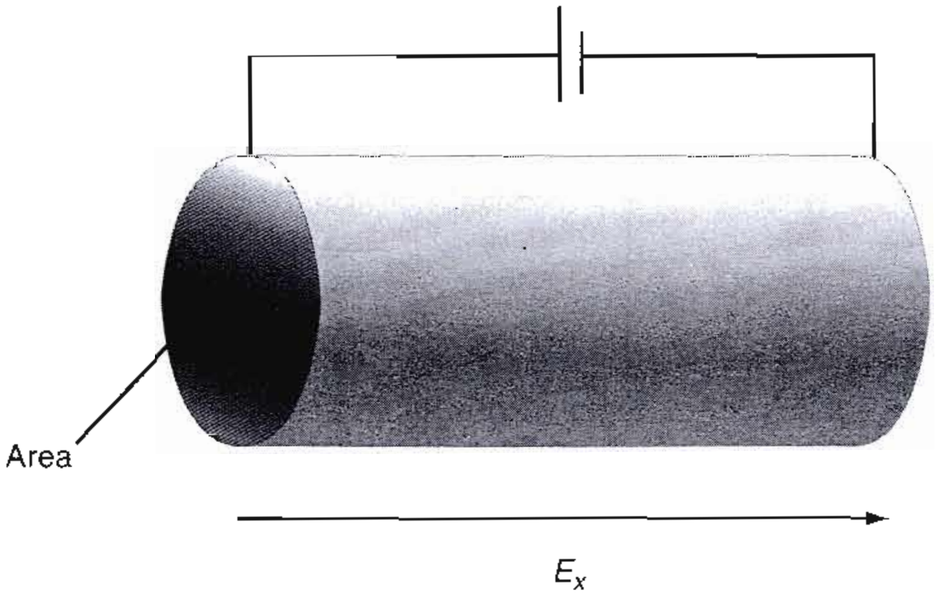


FIGURE 34.19
Cross section of a current-carrying conductor. The conductor cross-sectional area is indicated by the shaded area. The direction of the applied electric field E_x created by the battery is also shown.

transport of charge by electric force ①-3
from an electric field E which is created
by a battery : $j \sim E$ el. field strength
electric conductivity κ = proportionality constant

$$\rightarrow j = \kappa E$$

$$[\kappa] = 1 \frac{S}{m} \quad , \quad 1 S = 1 \Omega^{-1} \quad 1 \Omega = 1 \frac{V}{A}$$

Ω : ohm from $R = \frac{V}{I}$

homogeneous cylinder as conductor :

resistivity $\rho = \frac{1}{\kappa} = \frac{E}{j}$ $\quad [\rho] = 1 \frac{m}{S} = 1 \Omega m$

$E = \frac{V}{l}$ l : length of conductor , E = const.

$j = \frac{I}{A}$ A : cross section aerea

$V = \Delta\phi$ electric potential difference between ends of conductor

V : voltage , unit 1V

$$\rho = \frac{1}{\kappa} = \frac{E}{j} = \frac{V}{l} \cdot \frac{A}{I} \quad E = \frac{V}{l} \ , \ j = \frac{I}{A} \ , \text{A area}$$

$$= \frac{V}{I} \cdot \frac{A}{l} = R \frac{A}{l}$$

$\frac{A}{l}$: cell constant in electrolysis

$R = \frac{V}{I}$ ohm's law , $\rho \sim R$

proportionality constant : $\frac{A}{l}$

battery produces an electric field in the conductor . field direction called x $\Rightarrow E_x$

$$E_x = - \frac{d\phi}{dx}$$ electric potential gradiend

$$j = \kappa E_x = \frac{I}{A} = \frac{1}{A}\frac{dQ}{dt}$$

$$\rightarrow \frac{1}{A}\frac{dQ}{dt} = -\kappa \frac{d\phi}{dx}$$

transport equation

$\frac{1}{A}\frac{dQ}{dt}$ flux of charge th~~ro~~rough conductor originated by potential gradient

similar to all transport phenomena

κ: proportionality constant between flux and ~~con~~ potential gradient (transport coefficient)

in solutions: measure $\kappa = f(c)$

done ~~by~~ with conductivity cells:

container + electrolyte solution + electrodes with known aera and distance (ℓ)

alternating (ac) current $\Rightarrow$ no electrolysis products are build up at electrodes

Wheatstone bridge:

if 2 arm~~e~~s have same resistance → 0 current between A and B

R_1, R_2 = const., R_3 is changed until $I = 0$

$$I = 0: \frac{R_3}{R_1} = \frac{R_{cell}}{R_2} \Rightarrow R_{cell} = \frac{R_2 R_3}{R_1}$$

→ conductivity: $\frac{1}{\kappa} = R_{cell}\frac{A}{\ell}$ A: aerea

$$\Rightarrow \kappa = \frac{1}{R_{cell}} \cdot \frac{\ell}{A}$$

using a conductivity cell, which is simply a container in which two electrodes of well-defined area and spacing are placed, and into which a solution of electrolyte is added (Figure 34.20). The resistance of the conductivity cell is generally measured using alternating currents to limit the buildup of electrolysis products at the electrodes. The resistance of the cell is measured using a Wheatstone bridge as illustrated in Figure 34.20. The operating principle behind this circuit is that when the two "arms" of

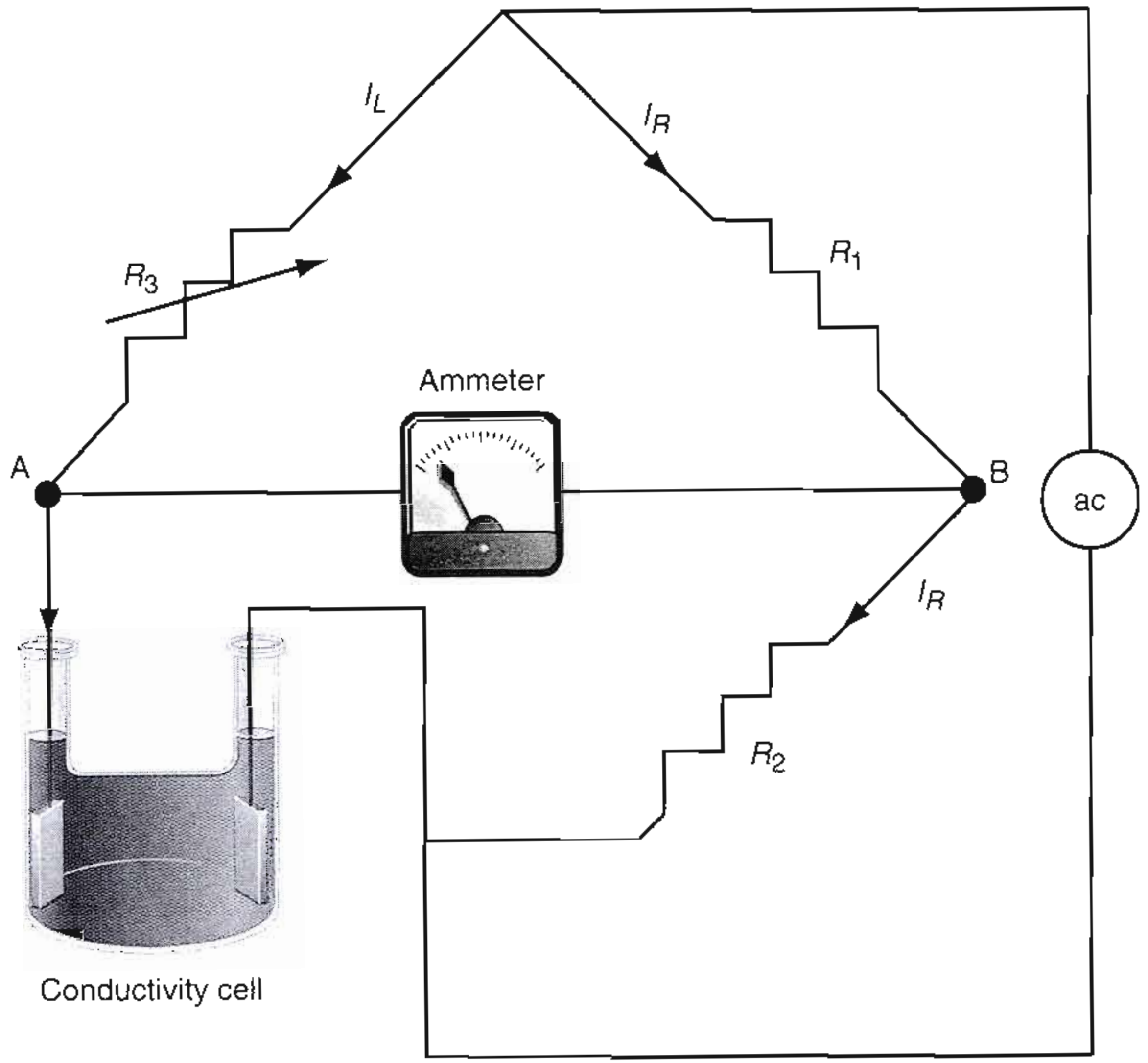


FIGURE 34.20
Schematic of the electrical circuit used to perform electrical conductivity measurements. The solution of interest is placed in the conductivity cell, which is placed in one arm of a Wheatstone bridge circuit, which includes R_3 and the cell. Resistor R_3 is adjusted until no current flows between points A and B. Under these conditions, the resistance of the cell can be determined.

molar conductivity: $\Lambda_m = \frac{\kappa}{c}$

c: molarity of the electrolyte solution

$[\Lambda_m] = 1 \frac{Sm^2}{mol}$ $(1\,S = 1\,\Omega^{-1})$

if $\kappa \sim c \Rightarrow \Lambda_m$ does not change with c

transp. Λ_m vs c

HCl(aq), KCl(aq), NaCl(aq) strong electrolytes

only small dependence of Λ_m on c especially when $c \to 0$

H_3CCOOH (aq) weak electrolyte

Λ_m similar to strong ones at small c

Λ_m decrease when c increases faster than for strong electrolytes

$CuSO_4$ (aq) in between

Cu^{2+}, SO_4^{2-} → strong bonding when the ions meet

→ $Cu^{2+}SO_4^{2-}$ move together, no charge

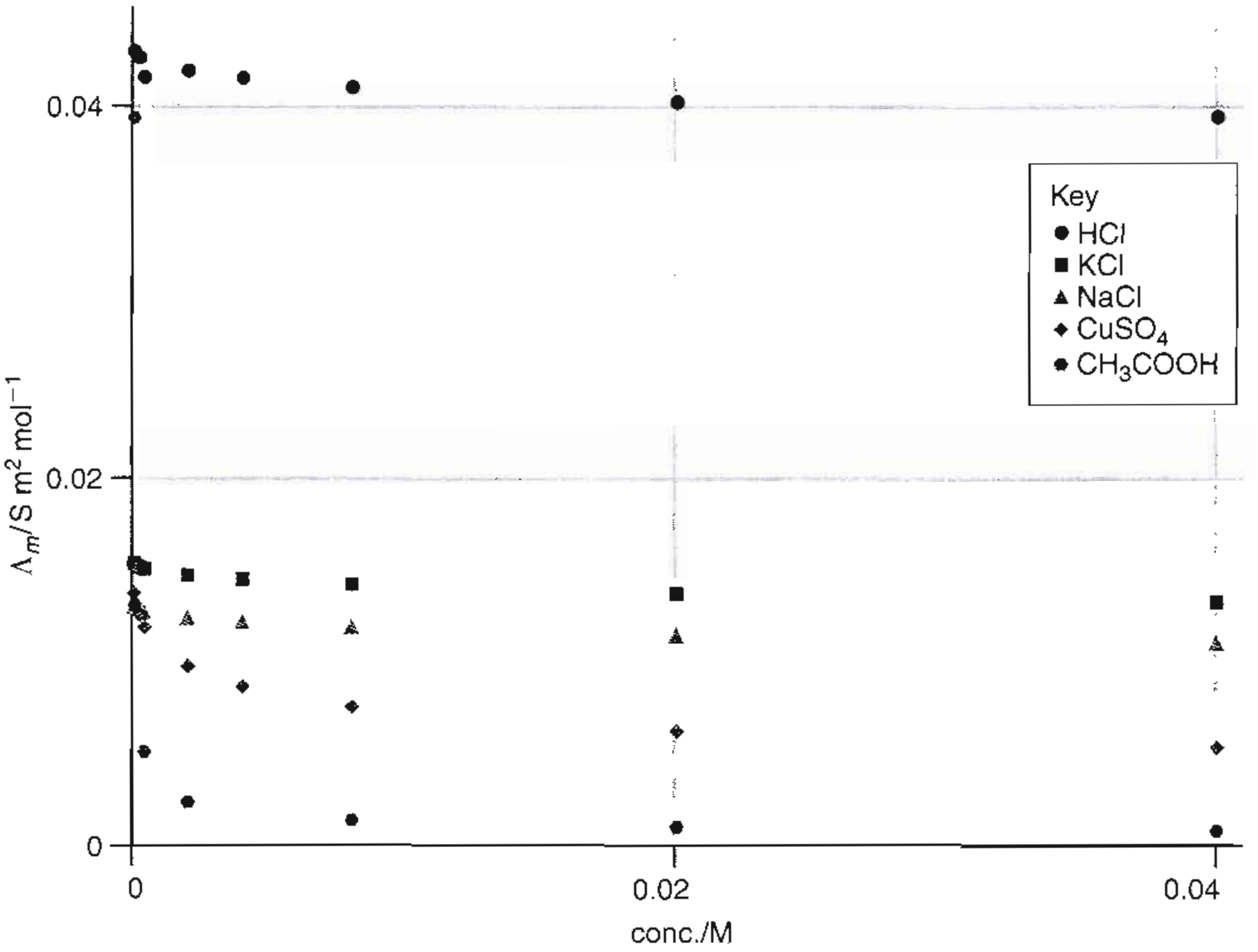


FIGURE 34.21
Molar conductivity Λ_m of various compounds as a function of concentration c. Measurements were performed in water at 25°C. Notice the mild reduction in Λ_m as a function of concentration for HCl, KCl, NaCl, and CuSO$_4$. This behavior is characteristic of a strong electrolyte. In contrast, CH$_3$COOH demonstrates a substantial reduction in Λ_m with increased concentration, characteristic of a weak electrolyte.

the bridge have equal resistance, no current will flow between points A and B. In the experiment, the resistance of R_3 is varied until this occurs. Under these conditions, the resistance of the cell is given by

$$R_{cell} = \frac{R_2 R_3}{R_1} \tag{34.71}$$

different solvents:
same electrolyte can be weak in one solvent, strong in the other

Strong Electrolytes

ionic solids, strong acids and bases:
completely dissociated into ions in solution
(100%) ⇒ c(ions) ~ c(electrolyte):

$$Na_2SO_4(s) \xrightarrow{H_2O} 2Na^+(aq) + SO_4^{2-}(aq)$$

no equilibrium, no Na_2SO_4 molecules in solution

$BaSO_4$: insoluble <u>but</u> strong.
all dissolved $BaSO_4$ in form of $Ba^{2+}(aq) + SO_4^{2-}(aq)$
~~no mo~~ not dissolved: in solid, no $BaSO_4(aq)$ molecules

$\Rightarrow [Na^+] = 2[Na_2SO_4] \quad [SO_4^{2-}] = [Na_2SO_4]$

if A_aB_b $[A^{\nu+}] = a[A_aB_b]$, $[B^{\nu-}] = b[A_aB_b]$

$[Na_2SO_4]$ total amount of dissolved electrolyte

Experiment → Kohlrausch's law:

$$\Lambda_m = \Lambda_m^\circ - K\sqrt{\frac{c}{c_0}} \text{ only for strong electrolytes}$$

c_0: standard concentration (~~1N~~ 1M)

~~1N(NaCl) = 1M(NaCl) 1N[Na_2SO_4] = $\frac{1}{2}$M(Na_2SO_4)~~

~~1N(Na_3PO_4) = $\frac{1}{3}$M(Na_3PO_4) 1N($\overset{Mg}{\cancel{Ba}}SO_4$) = $\frac{1}{2}$M($\overset{Mg}{\cancel{Ba}}SO_4$)~~

①-6a

molar conductivity of strong electrolyte solutions decreases with $\sqrt{c/c_0}$

transp. Λ_m vs $\sqrt{c/c_0}$ for strong electrolytes

→ straight lines if strong

slope = - K

slope depends mostly on stoichiometry not on the ion type

strong A_aB_b

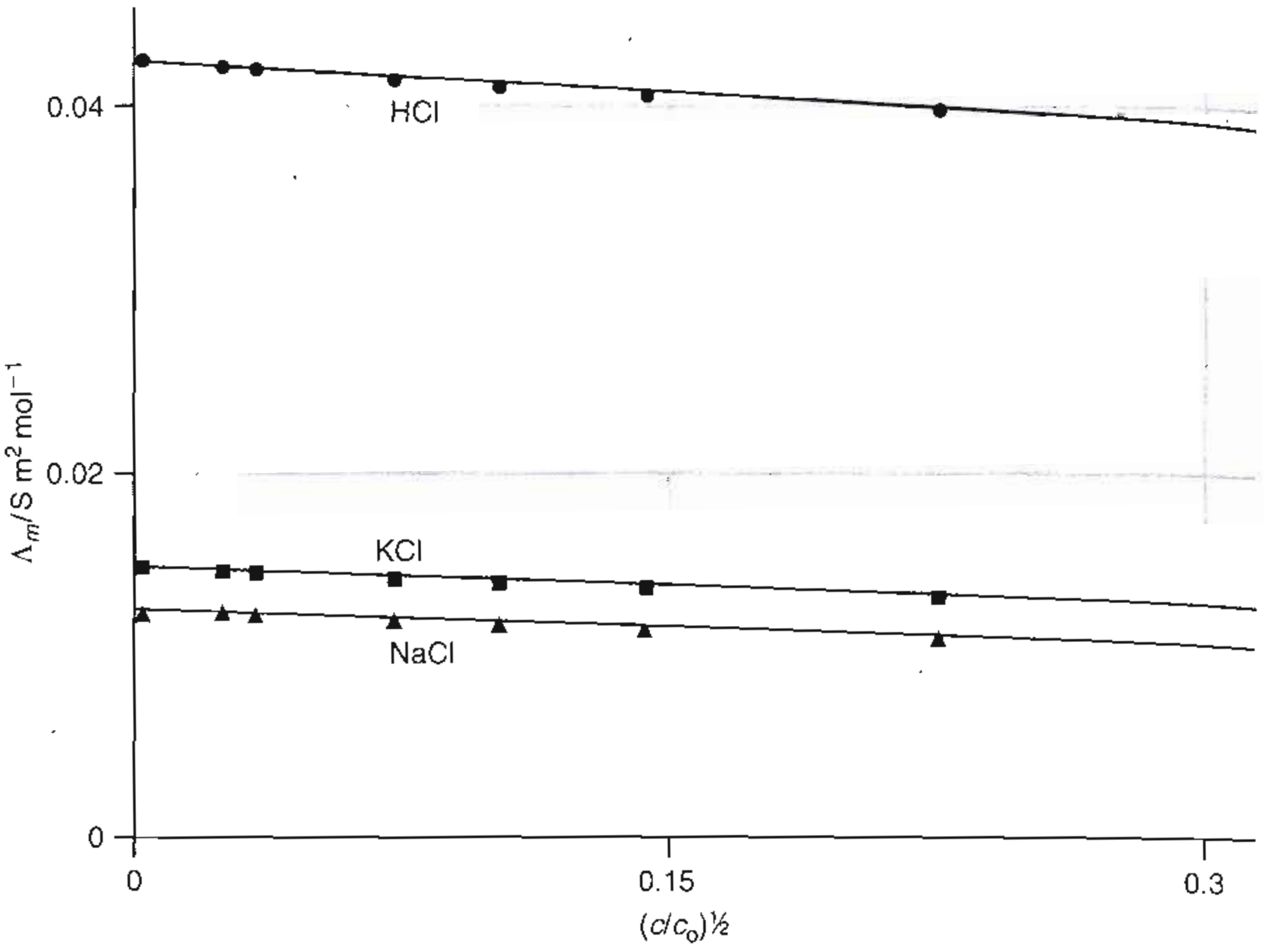
$[A^{z+}] = a[A_aB_b]$

$[B^{z-}] = b[A_aB_b]$

Obj. finish of strong electrolytes
ionic conduction for weak electrolytes

FIGURE 34.22

Molar conductivity Λ_m versus the square root of concentration for three strong electrolytes: HCl, KCl, and NaCl. The solid lines are fits to Kohlrausch's law [Equation (34.73)].



In 1900, Kohlrausch demonstrated that the concentration dependence of the molar conductivity for strong electrolytes is well described by the following equation:

$$\Lambda_m = \Lambda_m^0 - K\sqrt{\frac{c}{c_0}} \tag{34.73}$$

This equation, known as **Kohlrausch's law,** states that the molar conductivity for strong electrolytes decreases as the square root of concentration, with slope given

slope depends on # of ions → on ①-7
stoichiometry (same in all 3 lines), not on the kind of ions

→ ~~pralle~~ parallel lines

intercept : Λ_m^0 molar conductivity at infinite dilution

cannot be directly measured ($\kappa = 0$ at $c = 0$)

Λ_m^0 different for different kinds of ions

can be obtained for strong electrolytes as intercept of a Λ_m vs $\sqrt{c/c_0}$ plot

Λ_m^0 = molar conductivity without interactions between the ions

no interactions → infinite distance

→ infinite dilution

Repetition

2 charges, Q_1, Q_2, distance r, vacuum

force $F = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r^2}$

medium: $\varepsilon\varepsilon_0$ instead of ε_0

electric field r away from charge Q

$$E = \frac{Q}{4\pi\varepsilon_0 r^2}$$

$$E = -\frac{d\phi}{dr}$$

$\Rightarrow$ $\phi = -\int E\,dr$ electric potential

$= \frac{Q}{4\pi\varepsilon_0 r}$ in distance r from a charge Q

②-1

Obj. Ionic conduction
Weak Electrolytes

Kohlrausch could show experimentally that Λ_m° can be obtained from contributions of individual ions, which are the same, no matter in which electrolyte they are

e.g. he found: $\lambda_{Na^+}^\circ - \lambda_{K^+}^\circ$

$$= \Lambda_m^\circ(NaCl) - \Lambda_m^\circ(KCl)$$
$$= \Lambda_m^\circ(NaBr) - \Lambda_m^\circ(KBr)$$
$$= \Lambda_m^\circ(NaI) - \Lambda_m^\circ(KI)$$

The equal anion contributions cancel out and all 3 differences are equal

$$\Rightarrow \Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

λ_+ : ionic molar conductivity of the cation
λ_- : " " " " " anion
ν_+, ν_- : stoichiometric numbers of cation ~~at~~ and anion in the electrolyte formula unit

NaCl: $\nu_+ = \nu_- = 1$ Na_2SO_4: $\nu_+ = 2, \nu_- = 1$, Al_2S_3 $\nu_+ = 2, \nu_- = 3$

$\Rightarrow$ Law of Independent Migration of Ions:

Under infinite dilution conditions the molar conductivity of an electrolyte solution is equal to the sum of the ~~inic~~ ionic molar conductivities of cations &

anion (or sum of all ions involved) weighted ②-1a by their stoichiometric numbers in the formula unit of the electrolyte

transp. examples of $\lambda_{\pm}$ values (all λ° values)

calculate $\Lambda_m^{\circ}(MgCl_2)$!

$$\Lambda_m^{\circ}(MgCl_2) = 1 \cdot \lambda(Mg^{2+}) + 2 \cdot \lambda(Cl^-)$$

$$= 0.0106 \frac{Sm^2}{mol} + 2 \cdot 0.0076 \frac{Sm^2}{mol}$$

$$= 0.0258 \frac{Sm^2}{mol}$$

~~always λ means λ°~~

similar result from the intercept of $\Lambda_m(MgCl_2)$ vs $\sqrt{c/c_0}$ plot. Namely from plot

$$\Lambda_m^{\circ}(MgCl_2) = 0.0212 \frac{Sm^2}{mol}$$

$MgCl_2$ has some $Mg^{2+}2Cl^-$ "molecules" in the solution (ion association)

TABLE 34.2 Ionic Equivalent Conductance Values for Representative Ions

Ion	λ (S m^2 mol^{-1})	Ion	λ (S m^2 mol^{-1})
H^+	0.0350	OH^-	0.0199
Na^+	0.0050	Cl^-	0.0076
K^+	0.0074	Br^-	0.0078
Mg^{2+}	0.0106	F^-	0.0054
Cu^{2+}	0.0107	NO_3^-	0.0071
Ca^{2+}	0.0119	CO_3^{2-}	0.0139

EXAMPLE PROBLEM 34.11

What is the expected molar conductivity at infinite dilution for $MgCl_2$?

Solution

Using Equation (34.74) and the data provided in Table 34.2,

$$\begin{aligned} \Lambda_m^0(MgCl_2) &= 1\lambda(Mg^{2+}) + 2\lambda(Cl^-) \\ &= (0.0106\ \text{S m}^2\ \text{mol}^{-1}) + 2(0.0076\ \text{S m}^2\ \text{mol}^{-1}) \\ &= 0.0258\ \text{S m}^2\ \text{mol}^{-1} \end{aligned}$$

As determined by a plot of conductivity versus $(c/c_0)^{1/2}$, Λ_m^0 for $MgCl_2$ is equal to 0.0212 S m^2 mol^{-1}. Comparison of this value to the expected molar conductivity cal-from where the $c^{1/2}$ dependence of Λ_m°?

When concentrations of ions are involved in an equation, they should be replaced by activities

We will see in Chapter 10 that the dependence of activity on concentration is related to dielectric screening through the Debye-Hückel Limiting Law (DHLL):

$$\ln(\text{ion activity } \overset{a}{\gamma}) \sim \sqrt{\text{ionic strength } I}$$

ionic strength: $I = \frac{1}{2} \sum_i c_i z_i^2$

$\sum_i$ over all ion types in a solution

c_i : concentration of ion i

z_i : charge number of ion i

reason: properties of an ion in solution are not only determined by the ion ~~ist~~ itself, but also by the ionic atmosphere of other ions around it.

<u>transp.</u> (a) spherical ionic atmosphere of a few cations around an anion without electric field.

(b) distorted ionic atmosphere when the central anion moves under an electric field t infinite dilution for $MgCl_2$?

ded in Table 34.2,

$2\lambda(Cl^-)$

$\text{mol}^{-1}) + 2(0.0076\ \text{S m}^2\ \text{mol}^{-1})$

nol^{-1}

ersus $(c/c_0)^{1/2}$, Λ_m^0 for $MgCl_2$ is equal to lue to the expected molar conductivity cal- ehaves as a strong electrolyte in aqueous

ce stated in Kohlrausch's law? In Chapter 10 olytes demonstrates a similar concentration lated to dielectric screening as expressed by states that the natural log of the ion activity is tion ionic strength, or ion concentration. An y the ion itself, but also by the ionic atmos- Chapter 10, and depicted in Figure 34.23. In y a few close-lying positive ions comprising n electric field, the ionic atmosphere will be positive and negative charge will be identical. in ion motion, and this motion will create two the negative ion in Figure 34.23 migrates and or. The ionic atmosphere is not capable of ion instantaneously, and the lag in response f positive and negative charge. This displace- field in opposition to the applied field. e ion, and subsequently the conductivity, will **ation effect,** and this term implies that a time menon. In this case, it is the time it takes the of the negative ion.

or ionic atmosphere relaxation can be gained ic field to study ionic conductivity. A second f the ion is the **electrophoretic effect.** The ll migrate in opposite directions such that the ease. The reduction in ion mobility accompa- crease the conductivity.

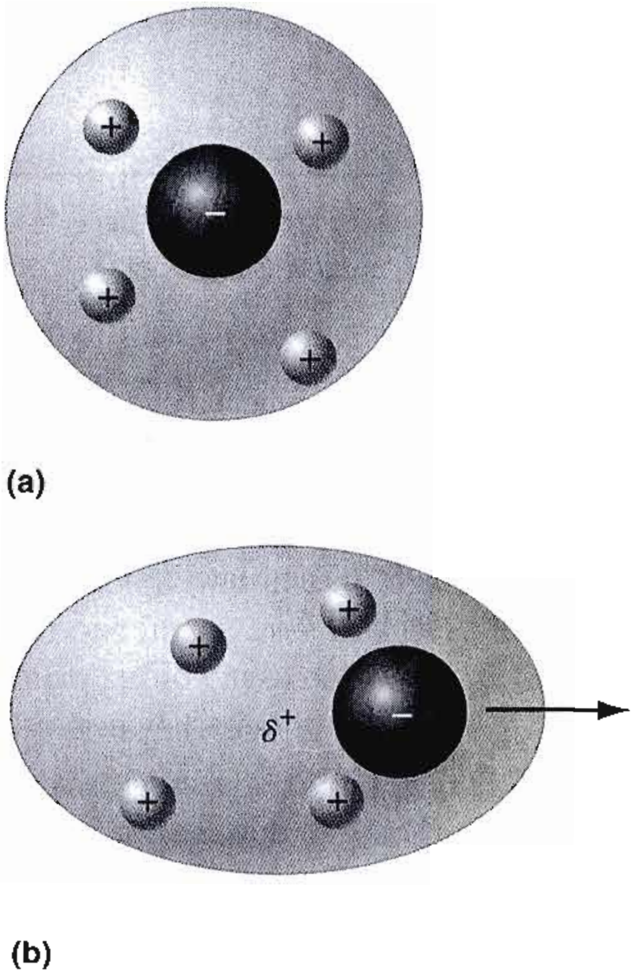


FIGURE 34.23
Negative ion in solution and associated ionic atmosphere. **(a)** In the absence of an electric field, the center of the positive and negative charge is identical. **(b)** However, when an electric field is present, the motion of the negative ion results in displacement of the center of the positive and negative charge. This local electric field is in opposition to the applied electric field such that the rate of ion migration is reduced.

The ionic atmosphere cannot follow the moving ion immediately

⇒ centers of + and - charges are displaced (different locations) for some time

⇒ a local electric field is created which is in opposite direction of the applied one.

⇒ speed of moving ion is slowed

⇒ ionic conductivity is reduced

relaxation effect: relaxation time = time needed by the ionic atmosphere to follow the moving ion

electrophoretic effect: also reduces the ionic conductivity:

under a field cations and anions move in ~~different~~ opposite directions

each ion will experience a viscous drag from the flow of the oppositely charged ions

⇒ slows ions down   ion swims upstream

Weak Electrolytes

only fractional, not full dissociation happens in solution ⇒ undissociated molecules also in solution:

$$AB(aq) \overset{H_2O}{\rightleftharpoons} A^+(aq) + B^-(aq)$$

equilibrium ⇒ also molecules in solution $AB(aq)$

weak acids: incomplete dissociation into $H_3O^+(aq)$ and the conjugate base

α = extent of ionization: fraction of dissociated electrolyte molecules ~~to~~ of the total initial amount

weak acid: $HA(aq) \overset{H_2O}{\rightleftharpoons} H_3O^+(aq) + \underset{\text{conjugate base}}{A^-(aq)}$

$$\Rightarrow [H_3O^+] = [A^-] = \alpha \cdot c$$

$$[HA] = (1-\alpha)\cdot c$$

c: initial molarity of HA before dissociation

α: degree of ionization, $0 \le \alpha \le 1$

$$K_a = \left(\frac{[H_3O^+][A^-]}{[HA]}\right)_{eq} = \frac{\alpha c\, \alpha c}{(1-\alpha)c} = \frac{\alpha^2 c}{\boxed{1-\alpha}}$$

$$\rightarrow \boxed{\alpha^2 c}\boxed{-K_a(1-\alpha)} = 0 \Rightarrow \alpha^2 + \frac{K_a}{c}\alpha - \frac{K_a}{c} = 0$$

$$\alpha = \frac{1}{2}\left[-\frac{K_a}{c} \overset{+}{(-)} \sqrt{\frac{K_a^2}{c^2} + \frac{4K_a}{c}}\right]$$

$$= \frac{K_a}{2c}\left[\sqrt{\frac{4c}{K_a}+1} - 1\right]$$

to take $\frac{K_a}{c}$ out of $\sqrt{}$

$$\sqrt{\frac{K_a^2}{c^2} + \frac{4K_a}{c}} = \sqrt{\frac{K_a^2}{c^2}\left(1 + \frac{4c}{K_a}\right)} = \frac{K_a}{c}\sqrt{\frac{4c}{K_a}+1}$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^{\circ}} \text{ definition} \Rightarrow \Lambda_m = \alpha \Lambda_m^{\circ}$$

② – 5

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

$$\Rightarrow K_a = \frac{\Lambda_m^2 c}{\Lambda_m^{\circ 2}\,\frac{\Lambda_m^{\circ} - \Lambda_m}{\Lambda_m^{\circ}}} = \frac{\Lambda_m^2 c}{\Lambda_m^{\circ}(\Lambda_m^{\circ} - \Lambda_m)}$$

$$K_a (\Lambda_m^{\circ})^2 - K_a \Lambda_m^{\circ} \Lambda_m = \Lambda_m^2 c \quad \Big| \cdot \frac{1}{(\Lambda_m^{\circ})^2}$$

$$K_a - K_a \frac{\Lambda_m}{\Lambda_m^{\circ}} = \frac{\Lambda_m^2 c}{(\Lambda_m^{\circ})^2} \quad \Big| \cdot \frac{1}{K_a \Lambda_m}$$

$$\frac{1}{\Lambda_m} - \frac{1}{\Lambda_m^{\circ}} = \frac{\Lambda_m c}{(\Lambda_m^{\circ})^2 K_a}$$

$$\rightarrow \quad \frac{1}{\Lambda_m} = \frac{1}{\Lambda_m^{\circ}} + \frac{\Lambda_m c}{(\Lambda_m^{\circ})^2 K_a}$$

Ostwald's dilution law

plot of $\frac{1}{\Lambda_m}$ vs $\Lambda_m c = \kappa$ must give a straight line for weak electrolytes (not for strong ones!)

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

slope $= \frac{1}{K_a (\Lambda_m^{\circ})^2}$

strong

Λ_m vs $\sqrt{c} \rightarrow$ straight line

no good values ~~f~~ of Λ_m° in this way for weak electrolytes while plot for strong ones gives good Λ_m° values!

$$[\mathrm{HA}]$$

In Equations (34.75) and (34.76), α is the
to 1), and c is the initial concentration
and (34.76) into the expression for the e
Equation (34.77):

$$K_a =$$

Solving Equation (34.77) for α yields

$$\alpha = \frac{K_a}{2c}((1$$

The molar conductivity of a weak electro
will be related to the molar conductivity a

$$\Lambda_m$$

Using Equations (34.78) and (34.79), the
ductivity can be determined and compared
and c for a weak electrolyte is described b

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

The comparison of the predicted behavior
acetic acid ($K_a = 1.8 \times 10^{-5}$, $\Lambda_m^0 = 0.03$
and excellent agreement is observed. The C
the molar conductivity at infinite dilution fo

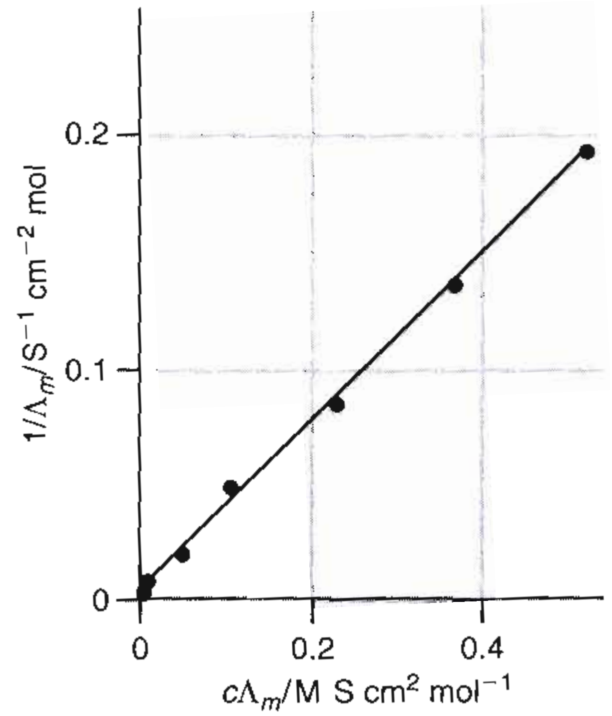


FIGURE 34.24
Comparison of experimental and predicted conductivity of acetic acid (CH_3COOH) as a function of concentration using the Ostwald dilution law of Equation (34.80). The y intercept on the graph is equal to $1/\Lambda_m^0$.

Vocabulary

- boundary layer
- Brownian motion
- centrifuge
- diffusion
- diffusion coefficient
- diffusion equation
- Einstein–Smoluchowski equation
- electrical conductivity
- electrophoretic effect
- Fick's first law
- Fick's second law of diffusion
- ionic equivalent conductance
- Kohlrausch's law
- laminar flow
- law of independent migration of ions
- mass transport
- molar conductivity
- Ostwald dilution law
- Ostwald viscometer
- Poiseuille's law
- random walk
- relaxation effect

③-00

HAc

$\lambda^\circ(H_3O^+) = 349.65 \frac{S\,cm^2}{mol}$

$\lambda^\circ(Ac^-) = 40.9 \frac{S\,cm^2}{mol}$

$\Lambda_m^\circ(HAc) = \lambda_{H^+}^\circ + \lambda_{Ac^-}^\circ$

$= (349.65 + 40.9) \frac{S\,cm^2}{mol}$

$= 390.6 \frac{S\,cm^2}{mol}$

book: from $\frac{1}{\Lambda_m}$ vs $\Lambda_m c = \kappa$ plot

$\Lambda_m^\circ(HAc) = \frac{1}{\text{intercept}}$

$= 395.7 \frac{S\,cm^2}{mol}$

1.3% error

strong

$\Lambda_m = \Lambda_m^\circ - K\sqrt{c/c^\circ}$

$c^\circ = 1M$ not $1N$

obj. ionic enthalpy, Gibb's energy, and entropy of formation in solution

conventional and absalute values

↓

relative to a standard

an electrolyte dissociates in solution into solvated ions

e.g. $H^+(aq)$, better $H_3O^+(aq)$ solvated ion in solution

aq for water as solvent

if there is complete (100%) dissociation in solution: strong electrolyte, no molecules in soln.

incomplete dissociation: weak electrolyte

ions and molecules in solution

equilibrium!

dissolved, undissociated molecules with dipole moment (sugar): non-electrolyte

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq)$$

$$\Delta H_R^\circ = -167.2 \text{ kJ/mol} \quad \text{exothermic}$$

but

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow H^+(g) + Cl^-(g) \quad \text{endothermic}$$

$$H^+(g) + \cancel{\tfrac{1}{2}}\,Cl^-(g) \rightarrow H^+(aq) + Cl^-(aq)$$

⇒ ordering and binding of H_2O around the ions makes overall reaction exothermic!

$$\Delta H_R^\circ = \Delta H_f^\circ(H^+, aq) + \Delta H_f^\circ(Cl^-, aq)$$

ΔH_f° of an element in the standard and most stable state is 0

a solution is always uncharged

→ $\Delta H_f^\circ(H^+, aq)$ cannot be measured alone, because that would require a charged solution

a thermodynamic quantity relative to a chosen 0-point is a <u>conventional</u> one

<u>conventions</u> (for all tabulated conv. values):

$$\Delta G_f^\circ\,(H^+, aq) = 0 \quad \text{for all } T$$

$$S_m^\circ\,(H^+, qaq) = \Delta S_f^\circ\,(H^+, aq) = -\left[\frac{\partial \Delta G_f^\circ\,(H^+, aq)}{\partial T}\right]_p = 0$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Rightarrow \Delta H_f^\circ(H^+, aq) = \Delta G_f^\circ(H^+, aq) + T S_m^\circ(H^+, aq) = 0$$

<u>measurable</u>!

ΔH_R° of $\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq)$

<u>then</u> $\Delta G_R^\circ = -RT\ln K$

from conductivity measurements

<u>and</u> $\Delta S_R^\circ = \frac{1}{T}(\Delta H_R^\circ - \Delta G_R^\circ)$

$$\Delta G_R^\circ = \Delta G_f^\circ(Cl^-, aq)$$

$\Delta G_f^\circ(H^+, aq) = 0$ due to convention

$$\Delta H_R^\circ = \Delta H_f^\circ(Cl^-, aq)$$

$$\Delta S_R^\circ = S_m^\circ(Cl^-, aq) - \frac{1}{2} S_m^\circ(H_2, g) - \frac{1}{2} S_m^\circ(Cl_2, g)$$

standard: all involved concentration 1m

other ions:

$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$ $\Delta H_R^\circ = 3.90 \frac{kJ}{mol}$

<u>and</u> $$\Delta H_R^\circ = \underbrace{\Delta H_f^\circ(Cl^-, aq)}_{\text{known from above discussion}} + \Delta H_f^\circ(Na^+, aq) - \Delta H_f^\circ(NaCl, s)$$

$\Rightarrow$ Na^+ value from ΔH_R° and so on for others

ΔH_f°, ΔG_f°, S_m° for other ions in solution is similar, when 1 ion is known!

<u>Transp.</u> Conv. values (examples)

ΔH_f° for multiply charged ions is more negative than that of singly charged ions, and ΔH_f° for a given charge is more negative for smaller ions because of the stronger electrostatic attraction between the multiply charged or smaller ion and the water in the solvation shell.

Recall from Section 5.8 that the entropy of an atom or molecule was shown to be always positive. This is not the case for solvated ions because the entropy is measured relative to $H^+(aq)$. The entropy decreases as the hydration shell is formed because liquid water molecules are converted to relatively immobile molecules. Ions with a negative value for the conventional standard entropy such as $Mg^{2+}(aq)$, $Zn^{2+}(aq)$, and $PO_4^{3-}(aq)$ have a larger charge-to-size ratio than $H^+(aq)$. For this reason, the solvation shell is more tightly bound. Conversely, ions with a positive value for the standard entropy such as $Na^+(aq)$, $Cs^+(aq)$, and $NO_3^-(aq)$ have a smaller charge-to-size ratio than $H^+(aq)$ and a less tightly bound solvation shell.

TABLE 10.1 Conventional Formation Enthalpies, Gibbs Energies, and Entropies of Selected Aqueous Anions and Cations

Ion	ΔH_f° (kJ mol^{-1})	ΔG_f° (kJ mol^{-1})	S_m° (J K^{-1} mol^{-1})
$Ag^+(aq)$	105.6	77.1	72.7
$Br^-(aq)$	−121.6	−104.0	82.4
$Ca^{2+}(aq)$	−542.8	−553.6	−53.1
$Cl^-(aq)$	−167.2	−131.2	56.5
$Cs^+(aq)$	−258.3	−292.0	133.1
$Cu^+(aq)$	71.7	50.0	40.6
$Cu^{2+}(aq)$	64.8	65.5	−99.6
$F^-(aq)$	−332.6	−278.8	−13.8
$H^+(aq)$	0	0	0
$I^-(aq)$	−55.2	−51.6	111.3
$K^+(aq)$	−252.4	−283.3	102.5
$Li^+(aq)$	−278.5	−293.3	13.4
$Mg^{2+}(aq)$	−466.9	−454.8	−138.1
$NO_3^-(aq)$	−207.4	−111.3	146.4
$Na^+(aq)$	−240.1	−261.9	59.0
$OH^-(aq)$	−230.0	−157.2	−10.9
$PO_4^{3-}(aq)$	−1277.4	−1018.7	−220.5
$SO_4^{2-}(aq)$	−909.3	−744.5	20.1
$Zn^{2+}(aq)$	−153.9	−147.1	−112.1

Source: Lide, D. R., ed. *Handbook of Chemistry and Physics*. 83rd ed. Boca Raton, FL: CRC Press 2002.

note: all conv. quantities are relative to $H^+(aq)$

$\Delta H_f^\circ(A^{n+})$ is more negative than $\Delta H_f^\circ(A^+)$

also ΔH_f° is more negative for small ions which bind H_2O dipoles more strong than big ions

for Mg^{2+}, Zn^{2+}, PO_4^{3-} $\frac{Q}{size}$ larger than for H^+

→ solvation shell more tightly bound

Q = ~~Quantity~~ Charge   negative S relative to H^+

for the larger ions Na^+, Cs^+, NO_3^- $\frac{Q}{size}$ is smaller than for H^+

→ less tightly bound solvation shell

⇒ positive S relative to H^+

absolute values can be calculated

G is a state function

⇒ ΔG is the same for the direct path and for the ways around

10.2 Understanding the Thermodynamics of Ion Formation and Solvation

As discussed in the preceding section, ΔH_f°, ΔG_f°, and S_m° can be determined for a formula unit but not for an individual ion in a calorimetric experiment. However, as seen next, values for thermodynamic functions associated with individual ions can be calculated with a reasonable level of confidence using a thermodynamic model. This result allows the conventional values of ΔH_f°, ΔG_f°, and S_m° to be converted to absolute values for individual ions. In the following discussion, the focus is on ΔG_f°.

We first discuss the individual contributions to ΔG_f°, and do so by analyzing the following sequence of steps that describe the formation of $H^+(aq)$ and $Cl^-(aq)$:

$$\begin{array}{ll}
1/2\, H_2(g) \rightarrow H(g) & \Delta G^\circ = 203.3 \text{ kJ mol}^{-1} \\
1/2\, Cl_2(g) \rightarrow Cl(g) & \Delta G^\circ = 105.7 \text{ kJ mol}^{-1} \\
H(g) \rightarrow H^+(g) + e^- & \Delta G^\circ = 1312 \text{ kJ mol}^{-1} \\
Cl(g) + e^- \rightarrow Cl^-(g) & \Delta G^\circ = -349 \text{ kJ mol}^{-1} \\
Cl^-(g) \rightarrow Cl^-(aq) & \Delta G^\circ = \Delta G^\circ_{solvation}(Cl^-, aq) \\
H^+(g) \rightarrow H^+(aq) & \Delta G^\circ = \Delta G^\circ_{solvation}(H^+, aq) \\
\hline
1/2\, H_2(g) + 1/2\, Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq) & \Delta G_R^\circ = -131.2 \text{ kJ mol}^{-1}
\end{array}$$

This pathway is shown pictorially in Figure 10.1. Because G is a state function, both the black and red paths must have the same ΔG value. The first two reactions in this sequence are the dissociation of the molecules in the gas phase, and the second two reactions are the formation of gas phase ions from the neutral gas phase atoms. ΔG° can be determined experimentally for these four reactions. Substituting the known values for ΔG° for these four reactions in ΔG° for the overall process,

$$\Delta G_R^\circ = \Delta G^\circ_{solvation}(Cl^-, aq) + \Delta G^\circ_{solvation}(H^+, aq) + 1272 \text{ kJ mol}^{-1} \quad \textbf{(10.7)}$$

Equation 10.7 allows us to relate the $\Delta G^\circ_{solvation}$ of the H^+ and Cl^- ions with ΔG_R° for the overall reaction.

As Equation (10.7) shows, $\Delta G^\circ_{solvation}$ plays a critical role in the determination of the Gibbs energies of ion formation. Although $\Delta G^\circ_{solvation}$ of an individual cation or anion cannot be determined experimentally, it can be estimated using a model developed by Max Born. In this model, the solvent is treated as a uniform fluid with the appropriate dielectric constant, and the ion is treated as a charged sphere. How can $\Delta G^\circ_{solvation}$ be calculated with these assumptions? At constant T and P, the nonexpansion work for a reversible process equals ΔG for the process. Therefore, if the reversible work associated with solvation can be calculated, ΔG for the process is known. Imagine a process in which a neutral atom A gains the charge Q, first in a vacuum and secondly in a uniform dielectric medium. The value of $\Delta G^\circ_{solvation}$ of an ion with a charge q is the reversible work for the process $(A(g) \rightarrow A^Q(aq))_{solvation}$ minus that for the reversible process $(A(g) \rightarrow A^Q(g))_{vacuum}$.

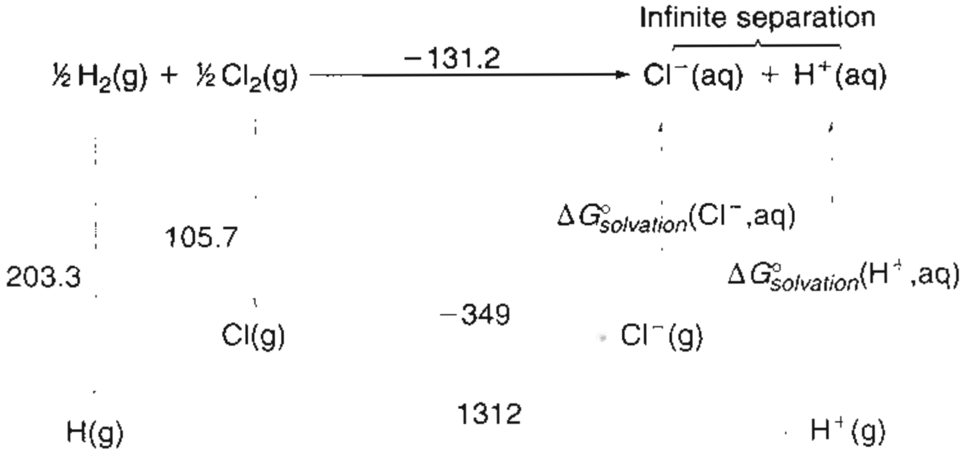
$$
\begin{array}{ll}
1/2\ \mathrm{H_2}(g) \rightarrow \mathrm{H}(g) & \Delta G^\circ = 203.3\ \mathrm{kJ\ mol^{-1}} \\
1/2\ \mathrm{Cl_2}(g) \rightarrow \mathrm{Cl}(g) & \Delta G^\circ = 105.7\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{H}(g) \rightarrow \mathrm{H^+}(g) + e^- & \Delta G^\circ = 1312\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{Cl}(g) + e^- \rightarrow \mathrm{Cl^-}(g) & \Delta G^\circ = -349\ \mathrm{kJ\ mol^{-1}} \\
\mathrm{Cl^-}(g) \rightarrow \mathrm{Cl^-}(aq) & \Delta G^\circ = \Delta G^\circ_{solvation}(\mathrm{Cl^-}, aq) \\
\mathrm{H^+}(g) \rightarrow \mathrm{H^+}(aq) & \Delta G^\circ = \Delta G^\circ_{solvation}(\mathrm{H^+}, aq) \\
\hline
1/2\ \mathrm{H_2}(g) + 1/2\ \mathrm{Cl_2}(g) \rightarrow \mathrm{H^+}(aq) + \mathrm{Cl^-}(aq) & \Delta G^\circ_R = -131.2\ \mathrm{kJ\ mol^{-1}}
\end{array}
$$

This pathway is shown pictorially in Figure 10.1. Because G is a state function, both the black and red paths must have the same ΔG value. The first two reactions in this sequence are the dissociation of the molecules in the gas phase, and the second two reactions are the formation of gas phase ions from the neutral gas phase atoms. ΔG° can be determined experimentally for these four reactions. Substituting the known values for ΔG° for these four reactions in ΔG° for the overall process,

$$\Delta G^\circ_R = \Delta G^\circ_{solvation}(\mathrm{Cl^-}, aq) + \Delta G^\circ_{solvation}(\mathrm{H^+}, aq) + 1272\,\mathrm{kJ\ mol^{-1}} \quad \textbf{(10.7)}$$

Equation 10.7 allows us to relate the $\Delta G^\circ_{solvation}$ of the $\mathrm{H^+}$ and $\mathrm{Cl^-}$ ions with ΔG°_R for the overall reaction.

As Equation (10.7) shows, $\Delta G^\circ_{solvation}$ plays a critical role in the determination of the Gibbs energies of ion formation. Although $\Delta G^\circ_{solvation}$ of an individual cation or anion cannot be determined experimentally, it can be estimated using a model developed by Max Born. In this model, the solvent is treated as a uniform fluid with the appropriate dielectric constant, and the ion is treated as a charged sphere. How can $\Delta G^\circ_{solvation}$ be calculated with these assumptions? At constant T and P, the nonexpansion work for a reversible process equals ΔG for the process. Therefore, if the reversible work associated with solvation can be calculated, ΔG for the process is known. Imagine a process in which a neutral atom A gains the charge Q, first in a vacuum and secondly in a uniform dielectric medium. The value of $\Delta G^\circ_{solvation}$ of an ion with a charge q is the reversible work for the process $(\mathrm{A}(g) \rightarrow \mathrm{A^Q}(aq))_{solvation}$ minus that for the reversible process $(\mathrm{A}(g) \rightarrow \mathrm{A^Q}(g))_{vacuum}$.



$R: \frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq)$ ③ - 5

can be measured: $\Delta G_R^\circ = -131.2 \frac{kJ}{mol}$

paths around: atomization and ionization in gas phase can be measured

$$\Rightarrow \Delta G_R^\circ = \Delta G^\circ_{solvation}(Cl^-, aq) + \Delta G^\circ_{solvation}(H^+, aq)$$

$$+ 1272 \frac{kJ}{mol}$$ (from all measurable steps)

$\Delta G^\circ_{solvation}$ is the reversible work for the process

$$\left[A(g) \xrightarrow{rev.} A^Q(aq)\right]_{\underline{solvation}} - \left[A(g) \xrightarrow{rev.} A^Q(g)\right]_{vacuum}$$

potential ~~for~~ around, ~~outside~~ solvent a sphere with radius r and charge Q':

$$\phi = \frac{Q'}{4\pi\varepsilon_0 r}$$

work needed to charge the sphere with additional charge dQ: $\phi \, dQ$

work to charge a ~~sh~~ sphere in vacuum, beginning with 0 charge to charge Q:

$$W = \int_0^Q \frac{Q' dQ'}{4\pi\varepsilon_0 r} = \frac{1}{4\pi\varepsilon_0 r} \int_0^Q Q' dQ'$$

$$= \frac{Q^2}{8\pi\varepsilon_0 r}$$

in solvent: not ε_0 but $\varepsilon_0 \varepsilon_r$

ε_r relative permittivity of the solvent

ionic charge is $ze = Q$, ~~Total $N_A ze$~~

to be done for N_A ions

$$\Delta G^0_{solvation} = \frac{z^2 e^2 N_A}{8\pi\varepsilon_0 r}\left(\frac{1}{\varepsilon_r} - 1\right)$$ Born model

vacuum value ($\varepsilon_r = 1$) subtrated

to compare ~~Born~~ Born model with experiment values for H^+ are needed.

theoretical calculations:

$$\Delta H^0_{solvation}(H^+, aq) = -1090 \frac{kJ}{mol}$$

$$\Delta G^0_{solvation}(H^+, aq) = -1050 \frac{kJ}{mol}$$

$$S^0_{solvation}(H^+, aq) = -130 \frac{J}{K\,mol}$$

with those absolute values can be calculated from conventional ones (relative to H^+) b.w.

$\Delta G^0_{solvation}$ vs $\frac{z^2}{r}$: straight line if the model is ok

transp. not very good

because r is taken from crystal structures

better: r_{eff}

ng that solvation is a spontaneous process.
nts are listed in Table 10.2 (see Appendix B,

compare absolute values of $\Delta G^\circ_{solvation}$ for ions
orm proposed in Equation (10.9). However, this
$\Delta G^\circ_{solvation}(H^+, aq)$ to convert experimentally
enced to $H^+(aq)$ to absolute values. It turns out
$_{ion}(H^+, aq)$, and $S^\circ_{solvation}(H^+, aq)$ can be calcu-
ved, the results are simply stated here.

$$aq) \approx -1090\,\text{kJ mol}^{-1}$$

$$aq) \approx -1050\,\text{kJ mol}^{-1}$$

$$aq) \approx -130\,\text{J mol}^{-1}\,\text{K}^{-1} \qquad \textbf{(10.10)}$$

) can be used to calculate absolute values of
or other ions from the conventional values refer-
lute values can be used to test the validity of the
$\Delta G^\circ_{solvation}$ versus z^2/r will give a straight
the data points for individual ions should lie on
10.2, where r is the ionic radius obtained from

points in Figure 10.2 are for singly and doubly
are compared with the result predicted by
be seen from the figure, the trends are repro-
reement. The agreement can be considerably
or the solvated ion rather than the ionic radius
The effective radius is defined as the distance
charge in the dipolar water molecule in the sol-
[*J. Chemical Physics*, 7 (1939) 109] found the
y adding 0.085 nm to the crystal radius of posi-
ius for negative ions to account for the fact that
This difference is explained by the fact that the
s closer to positive ions than to negative ions.
obtained between the predictions of Equation
od if this correction to the ionic radii is made.
ween the predictions of the Born model and cal-
fies the approach used to calculate absolute
r solvated ions. However, because of uncertain-
nic radii and for the dielectric constant of the
an ion, the uncertainty is ±50 kJ mol^{-1} for the
gy and ±10 J K^{-1} mol^{-1} for the absolute sol-
s are large compared to the uncertainty of the
ation described in Equations (10.3) and (10.4),

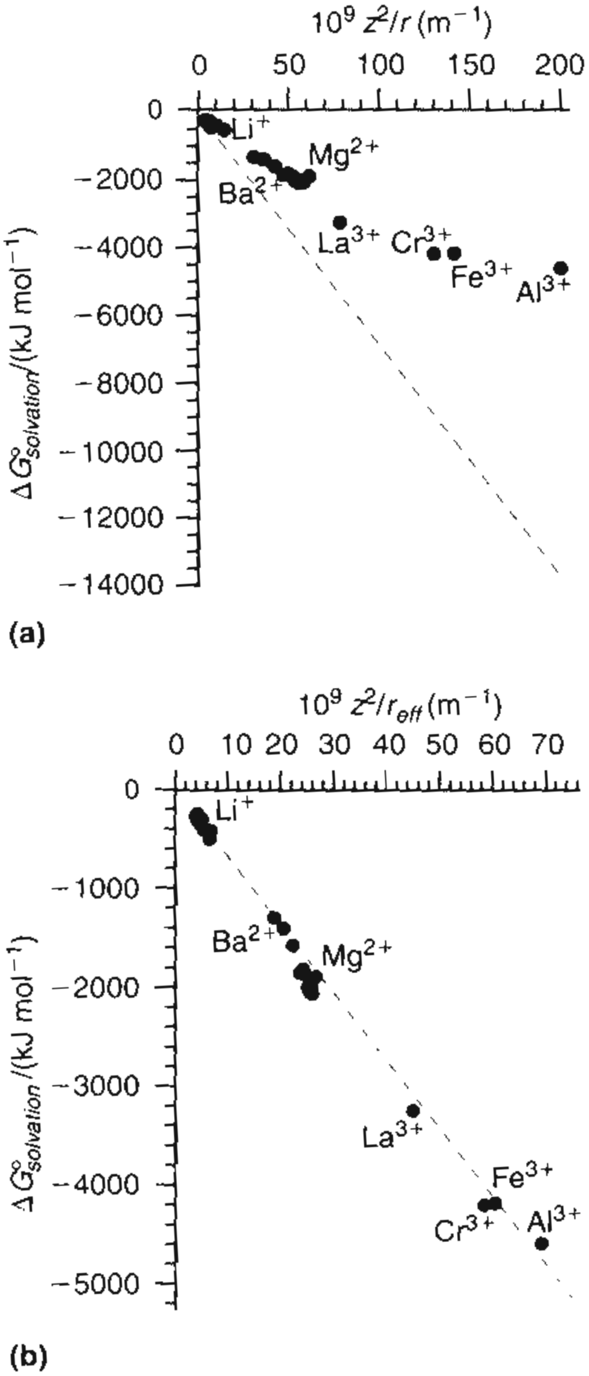
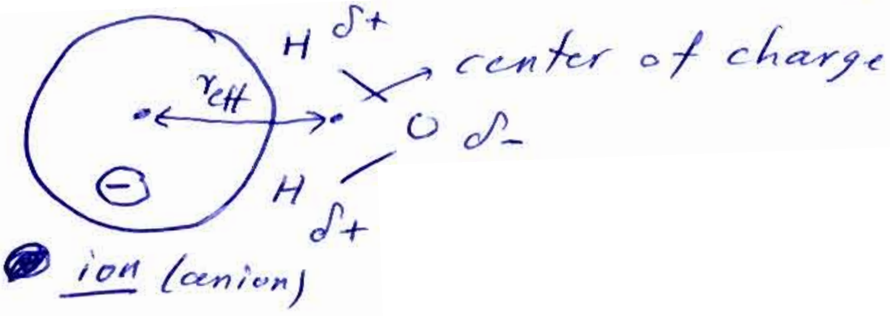


FIGURE 10.2
(a) The solvation energy calculated using the Born model is shown as a function of z^2/r. **(b)** The same results are shown as a function of z^2/r_{eff}. (See text.) The dashed line shows the behavior predicted by Equation (10.9).



$r_{eff} = r + 0{,}085$ nm for cations

$r_{eff} = r + 0.100$ nm for anions

the center of charge in H_2O is closer to cations than to anions

transp. $\Delta G^0_{solvation}$ vs $\frac{z^2}{r_{eff}}$

much better ~~at~~ agreement

however, uncertainty is relatively ~~larg~~ large in absolute values: (because of uncertain radius etc.,

± 50 $\frac{kJ}{mol}$ in absolute $\Delta H^0_{solvation}$, $\Delta G^0_{solvation}$

± 10 $\frac{J}{K\,mol}$ in absolute $S^0_{solvation}$

⇒ larger errors in absolute than in conventional values

⇒ mostly conv. values are used!

Qbj. Activity and Activity Coefficients ④-1

$NaCl(s) + H_2O(l) \rightarrow Na^+(aq) + Cl^-(aq)$

in dilute solutions: strong electrolyte
100% dissociated

higher conc.: ion association!

dilute solution: all solute - solute interactions are electrostatic

$$G = n_{solvent}\mu_{solvent} + n_{solute}\mu_{solute}$$

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{P,T}$$

if $A_{\nu_+}B_{\nu_-}$ completely dissociated:

$$G = n_{solvent}\mu_{solvent} + n_+\mu_+ + n_-\mu_-$$

$$= n_{solvent}\mu_{solvent} + n_{solute}(\nu_+\mu_+ + \nu_-\mu_-)$$

ν_+, ν_-: stoichiometric coefficients in formula

1-1 electrolyte ($\nu_+ = \nu_- = 1$, e.g. NaCl)

2-3 electrolyte ($\nu_+ = 2$, $\nu_- = 3$, e.g. Al_2S_3)

$$\Rightarrow \mu_{solute} = \nu_+\mu_+ + \nu_-\mu_-$$

μ_+, μ_- cannot be measured (always counter-ions in solutions)

$\Rightarrow$ mean ionic chemical potential $\mu_\pm$ for solute:

$$\mu_\pm = \frac{1}{\nu}\mu_{solute} = \frac{1}{\nu}(\nu_+\mu_+ + \nu_-\mu_-) \quad \nu = \nu_+ + \nu_-$$

$\mu_\pm$ <u>can</u> be measured

$$\mu_+ = \mu_+^\circ + RT \ln a_+$$

$$\mu_- = \mu_-^\circ + RT \ln a_-$$

standard: Henry's law standard state
(will be discussed later)

$$\rightarrow \mu_\pm = \mu_\pm^\circ + RT \ln a_\pm$$

$$a_\pm^\nu = a_+^{\nu_+} a_-^{\nu_-} \rightarrow a_\pm = \left(a_+^{\nu_+} a_-^{\nu_-}\right)^{1/\nu}$$

activity a: no unit!

$$a_{NaCl}^2 = a_{Na^+} a_{Cl^-} , \quad a_{NaCl} = \sqrt{a_{Na^+} a_{Cl^-}}$$

$$a_{K_2SO_4}^3 = a_{K^+}^2 a_{SO_4^{2-}} , \quad a_{K_2SO_4} = \sqrt[3]{a_{K^+}^2 a_{SO_4^{2-}}}$$

$$a_{H_3PO_4}^4 = a_{H^+}^3 a_{PO_4^{3-}} , \quad a_{H_3PO_4} = \sqrt[4]{a_{H^+}^3 a_{SO_4^{2-}}}$$

m: molality of the electrolyte

$$\rightarrow m_+ = \nu_+ m , \quad m_- = \nu_- m$$

activity unitless ⇒ reference of molalities to a standard molality m_0

$$m_0 = 1 \, \frac{mol\,(solute)}{kg\,(solvent)}$$

$$\rightarrow a_+ = \frac{m_+}{m_0} \gamma_+ , \quad a_- = \frac{m_-}{m_0} \gamma_-$$

γ: activity coefficients

$$a_\pm^\nu = a_+^{\nu_+} a_-^{\nu_-} = \left(\frac{m_+}{m_0}\right)^{\nu_+} \left(\frac{m_-}{m_0}\right)^{\nu_-} \gamma_+^{\nu_+} \gamma_-^{\nu_-}$$

$m_\pm$ mean ionic molality

$\gamma_\pm$ mean activity coefficient

$$m_\pm^{\nu} = m_+^{\nu_+} m_-^{\nu_-} \qquad m_+ = \nu_+ m, \; m_- = \nu_- m$$

$$\rightarrow m_\pm = \left(\nu_+^{\nu_+} \nu_-^{\nu_-}\right)^{1/\nu} m$$

$$\gamma_\pm^{\nu} = \gamma_+^{\nu_+} \gamma_-^{\nu_-}, \quad \gamma_\pm = \left(\gamma_+^{\nu_+} \gamma_-^{\nu_-}\right)^{1/\nu}$$

$$a_\pm^{\nu} = \left(\frac{m_\pm}{m_0}\right)^{\nu} \gamma_\pm^{\nu} \rightarrow a_\pm = \frac{m_\pm}{m_0} \gamma_\pm$$

mean quantities: measurable

$$\rightarrow \mu_{solute} = \mu_{solute}^{0} + RT \ln a_\pm^{\nu} = \mu_\pm$$

$$\mu_\pm = \left[\nu \mu_\pm^{0} + RT \ln \left(\nu_+^{\nu_+} \nu_-^{\nu_-}\right)\right] + \nu RT \ln \left(\frac{m}{m_0}\right) + \nu RT \ln \gamma_\pm$$

↑ "normal" standard state: based on Henry's law

$$\mu_\pm = \mu_\pm^{00} + \nu RT \ln \left(\frac{m}{m_0}\right) + \nu RT \ln \gamma_\pm$$

$$\Rightarrow \mu_\pm^{00} = \nu \mu_\pm^{0} + RT \ln \left(\nu_+^{\nu_+} \nu_-^{\nu_-}\right)$$

↗ from formula

$\mu_\pm^{00} + \nu RT \ln \left(\frac{m}{m_0}\right)$: ideal ionic solution ($\gamma_\pm = 1$)

$\nu RT \ln \gamma_\pm$: deviations from ideal ionic solution

$a_{solvent}$ from boiling point elevation
freezing point depression
vapor pressure lowering over solution

$a_{solvent}$ + Gibbs-Duhem equation

$\rightarrow a_{solute}$:

$$d\mu_A = \frac{n_B}{n_A} d\mu_B \quad \text{or} \quad d\mu_B = \frac{x_A}{x_A - 1} d\mu_A$$

$$\nearrow \quad d\mu_B = \frac{n_A}{n_B} d\mu_A = \frac{x_A}{x_B} d\mu_A$$

$$= \frac{x_A}{x_A - 1} d\mu_A$$

$$x_A = \frac{n_A}{n_A + n_B}$$

$$x_B = \frac{n_B}{n_A + n_B}$$

a also from <u>osmotic pressure of solutions</u>:

$\Pi V = -RT \ln a_A$ ~~A = solvent~~

$\rightarrow \Pi V = \phi RT \ln [B]$

$\Pi = \gamma c_{solute} RT$

$\Delta T_b = K_b \gamma m_{solute}$

$\Delta T_f = -K_f \gamma m_{solute}$

~~$\phi = -\frac{x_A}{x_B} \ln a_A$ osmotic coefficient~~

if one knows a_A

$$\rightarrow \ln \frac{a_B}{r} = \phi - \phi(0) + \int_0^r \frac{\phi - 1}{r} dr$$

$$r = \frac{x_B}{x_A}, \quad \phi(0) = \phi(r=0)$$

$l \rightleftharpoons g$ equilibrium $\Rightarrow \mu_i(g) = \mu_i(l)$ in equilibrium

for ideal gas:

$$\mu_i(g) = \mu_i^\circ(g) + RT \ln \frac{P_i}{P_0} \qquad P_0 = 1 \text{ bar}$$

$$\mu_i(l) = \mu_i^\circ(l) + RT \ln a_i$$

$\rightarrow$ in equilibrium

$$\mu_i^\circ(g) + RT \ln \frac{P_i}{P_0} = \mu_i^\circ(l) + RT \ln a_i$$

pure liquid: $a_i = 1$

$$\rightarrow \mu_i^\circ(l) = \mu_i^\circ(g) + RT \ln \frac{P_i}{P_0}$$ ④-5

Henry's law: $m_B = K_B P_B$ $B =$ solute

P_B partial pressure of solute

K_B Henry's law constant

or $P_B = K_B' x_B$ or $P_B = K_B'' c_B$

for dilute solutions: $x_B \sim c_B$

$$\mu_i(l) = \mu_i^\circ(g) + RT \ln \frac{K_i x_i}{P_0} \quad , \quad P_i = K_i x_i$$

$$= \mu_i^\circ(g) + RT \ln \frac{K_i}{P_0} + RT \ln x_i$$

$$= \mu_i^*(l) + RT \ln x_i$$

$$\mu_i^*(l) = \mu_i^\circ(g) + RT \ln \frac{K_i}{P_0} \qquad \underline{x_i = 1}$$

(Hypothetical) Henry's law standard state:

At $x_i = 1$ the solute has the same properties as in very dilute solutions: each solute molecule is <u>only</u> surrounded by solvent molecule shells

$$\mu^{\circ H}_{solute} = \mu^\circ_{solute} + RT \ln \frac{K^H_{solute}}{p^*_{solute}}$$

P_{vap} of pure solute is the Henry's law constant hypothetical instead of P^*_{solut} in Henry's law standard state

Henry's law

names "solvent", "solute" given such that

$$x_{solvent} > x_{solute}$$

$$P_{solute} = x_{solute} \, k_H^{solute} \quad \text{in limit } x_{solute} \to 0$$

P_{solute} ↓ vapor pressure of solute over solution

x_{solute} ↑ mole fraction of solute in solution

k_H^{solute} ↓ Henry's law constant for solute

binary mixture: $x_{solute} = \frac{n_{solute}}{n_{solute} + n_{solvent}}$

chemical potential of solute in solution:

$$\mu_{solute}^{solution} = \mu_{solute}^{*} + RT \ln \frac{k_H^{solute} \, x_{solute}}{p_{solute}^{*}}$$

because for component i:

$$\mu_i^{solution} = \mu_i^{*} + RT \ln \frac{p_i}{p_i^{*}}$$

and for $x_{solute} \to 0$ $P_{solute}(x_{solute} \to 0) = k_H^{solute} \, x_{solute}$

p^* vapor pressure of the pure substance

μ^* chemical potential of the pure substance

$$\Rightarrow \mu_{solute}^{solution} = \mu_{solute}^{\ominus H} + RT \ln x_{solute}$$

⇒ Henry's law standard state chemical potentials

$$\mu_{solute}^{\ominus H} = \mu_{solute}^{*} + RT \ln \frac{k_H^{solute}}{p_{solute}^{*}}$$

$$\neq \mu_{solute}^{0}$$

~~activity based on Henry's law:~~

~~$a_i = \frac{P_i^{real}}{K_i^H}$, $\gamma_i = \frac{a_i}{x_i}$~~

activity based on Henry's law

$$a_i = \frac{P_i(\text{real})}{k_i^H}$$

$$\gamma_i = \frac{a_i}{x_i}$$

⇒ Henry's law standard state is a ~~st~~ non-existing state in which the solute (at $x_{solute} = 1$) has a vapor pressure of k^H_{solute} not its real value, P^*_{solute}

In this way:

When $x_{solute} \to 0$, then $a_{solute} \to x_{solute}$, $\gamma_{solute} \to 1$

Debye-Hückel Theory

for activities

neutral solutes: no general model

because ~~for~~ deviations in A-A, B-B, - A-B interactions depend on the nature of A and B

in electrolyte solutions: no neglect possible ~~ever~~ of long-range Coulomb interactions even not in dilute solutions

However, Coulomb interactions depend only on charge and distance not on detailed nature of ion!

ery dilute electrolyte solutions: ~~ln~~ $\lim_{m \to 0} \gamma_\pm = 1$

$\gamma_\pm < 1$: μ of ions in dilute solutions is lower than that of neutral molecules

there are attractive ~~is~~ interactions of a freely chosen central ion with surrounding ~~ions~~ counterions

solute ions in a solvent: electrostatic potential:

if the distribution of ions in space is known,

~~ϕ~~ · $\phi(r)$ can be calculated

energy change of an ion ~~±~~ze when ϕ is turned on is small compared to thermal energy:

$$|\cancel{\pm} ze\phi| \ll k_BT$$

z pos. or negative

↳ Boltzmann's constant

isolated ion in dielectric medium (ε_r relative permittivity of the medium):

$$\phi_{\substack{\text{isolated}\\ \text{ion}}}(r) = \frac{ze}{4\pi\varepsilon_r\varepsilon_0 r}$$

in a dilute electrolyte solution

$$\phi^{\text{ion in}}_{\text{solution}}(r) = \frac{ze}{4\pi\varepsilon_r\varepsilon_0 r}\, e^{-\kappa r}$$

ϕ_{solution} decrease exponentially (much faster) than $\phi_{\substack{\text{isolated}\\ \text{ion}}}$ with r

because is in a screening (shielding) potential of the other ions

Transp $\dfrac{\phi_{\text{solution}}}{\phi_{\text{isolated ion}}}$ vs r (in meter m) for different concentrations

Debye - Hückel ~~limiting Law (DHLL)~~ Theory:

$$\kappa^2 = e^2 N_A \left(10^3 \frac{\overset{\nearrow dm^3}{L}}{m^3}\right) m \left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\varepsilon_0\varepsilon_r k_B T}\right) \overset{\text{density}\,\swarrow}{\rho_{\text{solvent}}}$$

$\Rightarrow$ increasing molality: more effective screening also when charges (z_+; z_-) and stoichiometric coefficients (ν_+, ν_-) increase

further: $\dfrac{\phi_{\text{solution}}}{\phi_{\text{isolated}}} = e^{-\kappa r}$

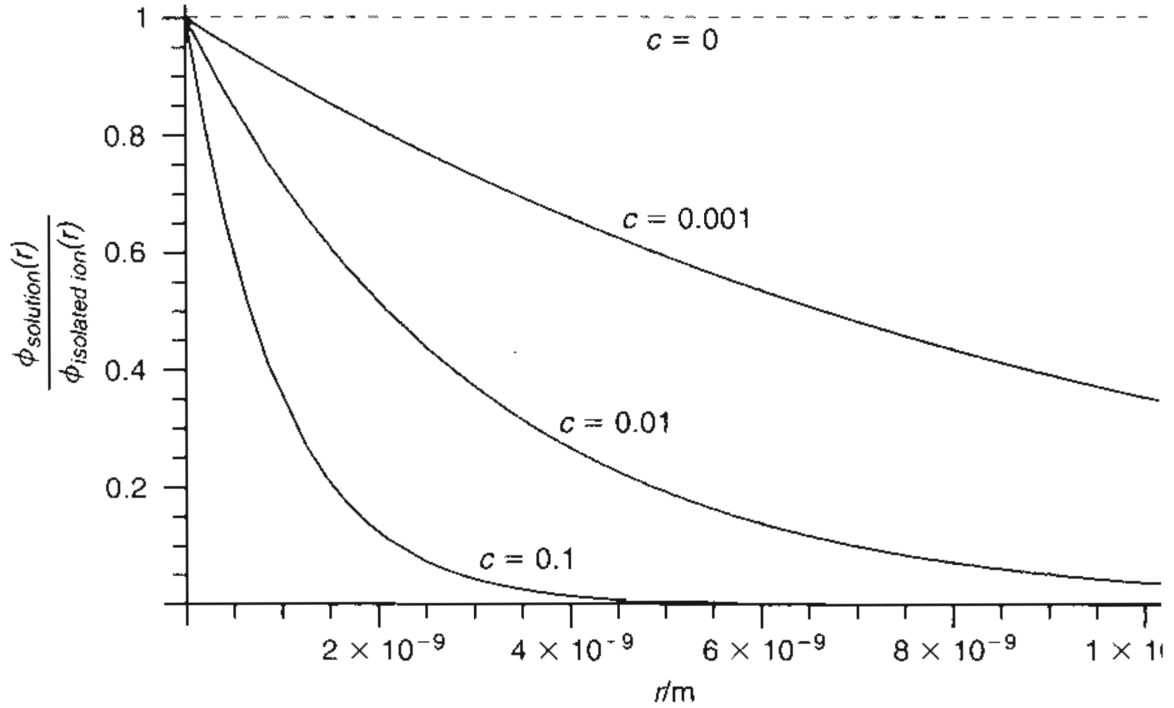


FIGURE 10.3
The ratio of the falloff in the electrostatic potential in the electrolyte solution to that for a lated ion is shown as a function of the radial distance for three different molarities of a 1– trolyte such as NaCl.

In Equations (10.27) and (10.28), ε_0 and ε_r are the permittivity of free space a relative permittivity (dielectric constant) of the dielectric medium or solvent, r tively. Because of the exponential term, $\phi_{solution}(r)$ falls off much more rapidly than $\phi_{isolated\ ion}(r)$. We say that an individual ion experiences a **screened po** from the other ions.

The Debye–Hückel theory shows that κ is related to the individual charges ions and to the solute molality m by

$$\kappa^2 = e^2 N_A \,(1000\ \mathrm{L\ m^{-3}})\, m \left(\frac{\nu_+ z_+^2 + \nu_- z_-^2}{\varepsilon_0 \varepsilon_r k_B T}\right) \rho_{solvent} \qquad ($$

From this formula, we can see that screening becomes more effective as the conc tion of the ionic species increases. Screening is also more effective for multiply c ions and for larger values of ν_+ and ν_-.

The ratio

$$\frac{\phi_{solution}(r)}{\phi_{isolated\ ion}(r)} = e^{-\kappa r}$$

is plotted in Figure 10.3 for different values of m for an aqueous solution of a 1– trolyte. Note that the potential falls off much more rapidly with the radial distan the electrolyte solution than in the uniform dielectric medium. Note also that the tial falls off more rapidly with increasing concentration of the electrolyte. The ori this effect is that ions of sign opposite to the central ion are more likely to be found

Transp: ions of opposite sign are more likely to be found around a central ion

if ~~sh~~ sphere, center = central ion

→ net charge in sphere can be calculated

it decreases fast with distance

net charge → 0 at $\kappa r \approx 8$

$\kappa r > 8$: central ion completely screened

⇒ net charge in sphere = 0

sphere: actually a diffuse ion cloud

$\frac{1}{\kappa}$: Debye-Hückel screening length

the central ion is screened from rest of solution

ionic strength: ~~$I = \frac{1}{2} m \sum_i (\nu_{i+} z_{i+}^2 + \nu_{i-}$~~

$$I = \frac{1}{2} \underset{\downarrow}{m} \sum_i (\nu_i z_i^2) = \frac{1}{2} \sum_i (m_i z_i^2)$$

electrolyte

only for 1 electrolyte

for all electrolytes

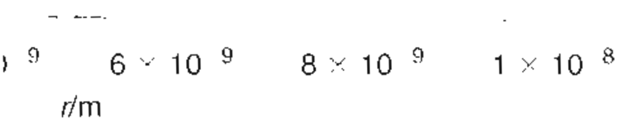
i: all types of ion in solution

1 term for each ion

0.05 m solution of e.g. KCl:

$$I_{KCl} = \frac{m}{2}(\nu_+ z_+^2 + \nu_- z_-^2) = \frac{1}{2} \cdot 0.05\, m\, (1+1)$$

$$= 0.05\, m$$



tial in the electrolyte solution to that for an iso-
tance for three different molarities of a 1–1 elec-

ε_r are the permittivity of free space and the
of the dielectric medium or solvent, respec-
$_{olution}(r)$ falls off much more rapidly with r
idual ion experiences a **screened potential**

κ is related to the individual charges on the

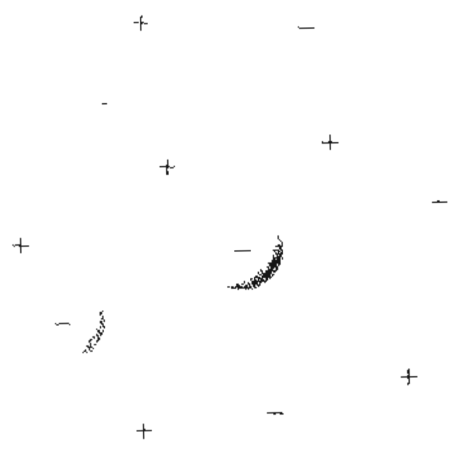
(10.29)

ng becomes more effective as the concentra-
g is also more effective for multiply charged

$$\frac{\quad r)}{\quad(r)} = e^{\kappa r}$$

s of m for an aqueous solution of a 1–1 elec-
ch more rapidly with the radial distance r in
dielectric medium. Note also that the poten-
ntration of the electrolyte. The origin of
central ion are more likely to be found close
form a diffuse ion cloud around the central
a spherical surface is drawn centered at the
can be calculated. The results show that the
charge, falls off rapidly with distance, and is
of κr, the central ion is completely screened
t charge in the sphere around the central ion
d is to screen the central ion from the rest of
n as the **Debye–Hückel screening length.**
iffuse cloud, and a more effective screening.
ration-dependent terms that contribute to κ

(10.30)



Pictorial rendering of the arrangement of ions about an arbitrary ion in an electrolyte solution. The central ion is more likely to have oppositely charged ions as neighbors. The large circle represents a sphere of radius $r \sim 8/\kappa$. From a point outside of this sphere, the charge on the central ion is essentially totally screened.

Using the

The first f
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$\kappa = 3.29 \times 1$
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This equation
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Figure 10.6 s
$AgNO_3$ and C
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Figure 10.7 is

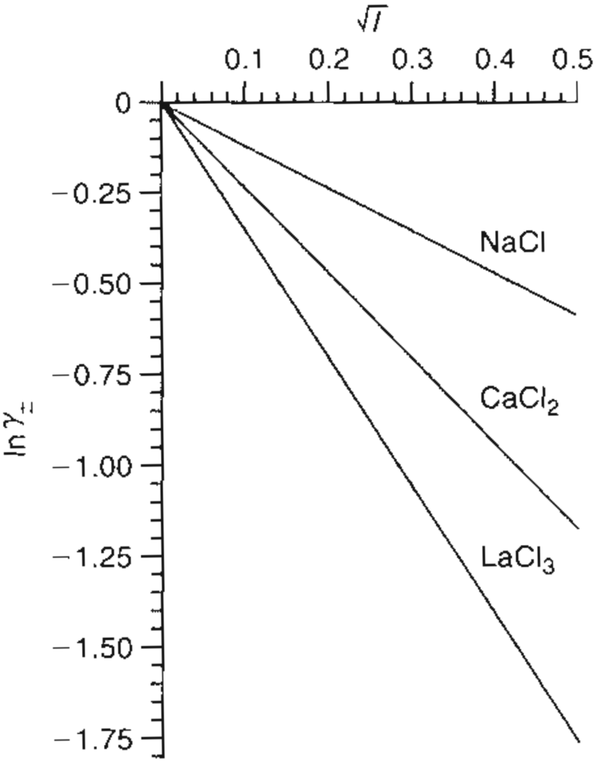


FIGURE 10.5
The decrease in the Debye–Hückel mean activity coefficient with the square root of the ionic strength is shown for a 1–1, a 1–2, and a 1–3 electrolyte, all of the same molality in the solute.

ɔr high values of I, $\gamma_\pm > 1$. Experimental values ɛrent concentrations in aqueous solution are listed Tables).

y the experimental values of $\gamma_\pm$ differ at high ionic e Debye–Hückel limiting law. They mainly involve t has been assumed that the ions can be treated as ːas ions and their associated solvation shells occupy increase in the repulsive interaction among ions in oint charges, which becomes more important as the ɛractions raise the energy of the solution and, there- model also assumes that the solvent can be treated . However, the ion is surrounded by a relatively ɛll as by more loosely bound water molecules. The n shell is not adequately represented by using the other factor that has not been taken into account is ne ion pairing occurs such that the concentration of cu[illegible]ed assuming complete dissociation.

at [illegible]e water molecules in the solvation shell have ent. For example, in an aqueous solution of H_2SO_4, e tightly bound per dissolved H_2SO_4 formula unit. O as solvent in 1 L of a one molar H_2SO_4 solution 46 in the solution. Consequently, the actual solute by assuming that all the H_2O is in the form of sol- nearly with the actual molarity, $\gamma_\pm$ increases as the e were no change in the enthalpy of solvation with would be removed from the solvent at a concentra- assumption is unreasonable. What actually happens ally less favorable as the H_2SO_4 concentration s negative value of ln $\gamma_\pm$, or equivalently to an cto[illegible] explain why the Debye–Hückel limiting law is ecause of the complexity of these different factors, theory that can replace the Debye–Hückel limiting ed in Figures 10.6 and 10.7 are reproduced in more olutions.

dels are valid at high concentrations, empirical e–Hückel model by predicting an increase in $\gamma_\pm$ lespread use. An empirical modification of the the form

$$z_-\left|\left[\frac{\left(\frac{I}{m^\circ}\right)^{1/2}}{1+\left(\frac{I}{m^\circ}\right)^{1/2}} - 0.30\left(\frac{I}{m^\circ}\right)\right]\right. \qquad \textbf{(10.34)}$$

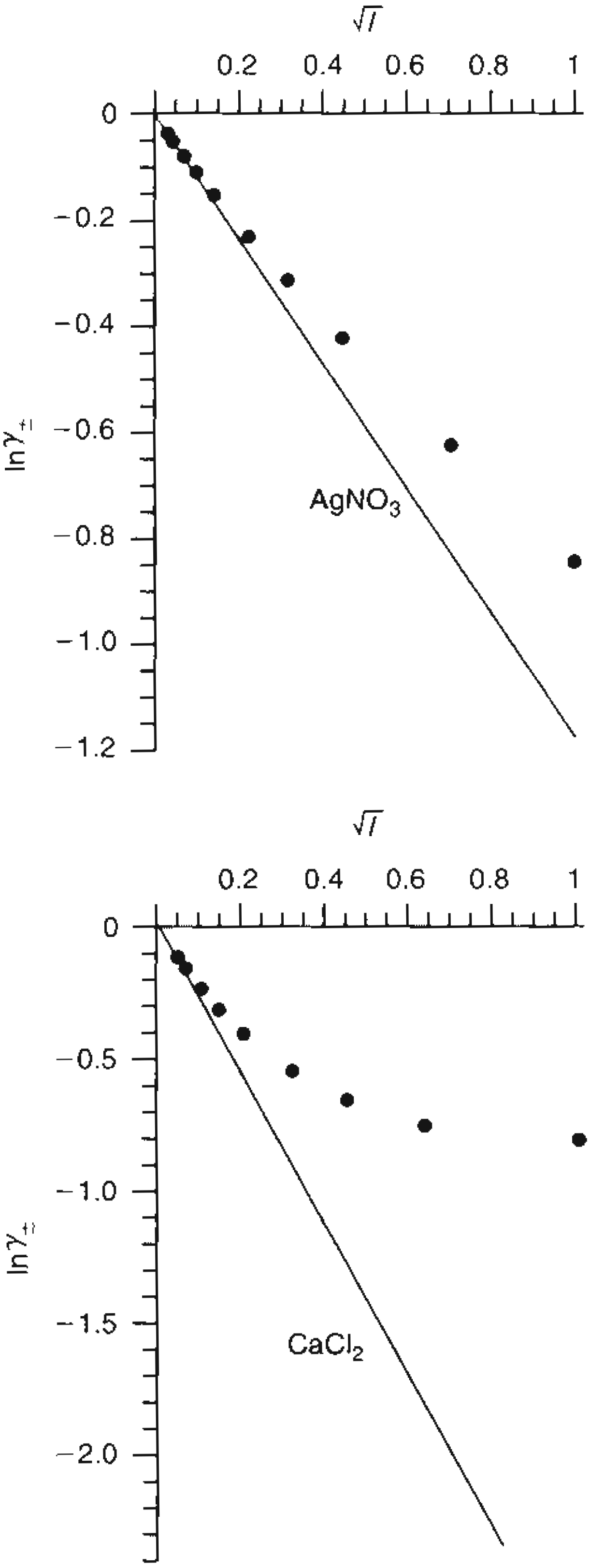


FIGURE 10.6
The experimentally determined activity coefficients for $AgNO_3$ and $CaCl_2$ are shown as a function of the square root of the ionic strength. The solid lines are the prediction of the Debye–Hückel theory.

0,05 m Na_2SO_4 solution:

$$I_{Na_2SO_4} = \frac{1}{2}\, 0.05m\,(2\cdot 1^2 + 1\cdot(-2)^2) = \frac{1}{2}\, 0.05m\,(2+4) = 0.15m$$

$$\kappa = \sqrt{\frac{2e^2 N_A}{\varepsilon_0 k_B T}\left(10^3 \frac{L}{m^3}\right)}\ \sqrt{\frac{I}{\varepsilon_r}\, \rho_{solvent}}$$

$$= 2{,}91\cdot 10^8 \sqrt{I/\left(\frac{mol}{kg}\right) \frac{\rho_{solvent}}{kg/L}}\ m^{-1} \quad \text{at } 298\ K$$

unit: $\frac{mol}{L}$ $\quad \kappa = 3{,}29\cdot 10^9 \sqrt{I/_M}\ m^{-1}$ at 298 K, H_2O

unitless here!

Debye-Hückel Limiting Law (DHLL)

$$\ln \gamma_\pm = - \frac{e^2 \kappa}{8\pi\varepsilon_0\varepsilon_r k_B T} |z_+ z_-|$$

limiting: only correct for very small I

$-$ sign $\Rightarrow \gamma_\pm < 1$

aqueous (water) solutions at 298,15K:

$$\log_{10} \gamma_\pm = - \underbrace{0{,}5092}_{B} |z_+ z_-| \sqrt{I/M}$$

$$\ln \gamma_\pm = -1{,}173\, |z_+ z_-| \sqrt{I/m}$$

Transp. 1) $\ln \gamma_\pm$ vs $\sqrt{I}$ plot straight line

2) $AgNO_3$ (aq) ($m = 0{,}01m$)

3) $CaCl_2$ (aq) ($m = 0{,}004m$)

only for $I \to 0$ DHLL correct!

Transp. $ZnBr_2$, Davies equation (empirical) ⑤-5

$m = 10\, m$

1. part: $I \to 0$: DHLL ok

2. part: $\ln \gamma_I$ decreases more slow DHLL

reaches minimum

3. part: $\ln \gamma_I$ increases up to $\gamma_\pm = 2.32$

$\ln \gamma_I$ even becomes positive $\Rightarrow \gamma_\pm > 1$

same trend for all ionic solutes

reasons for failure of DHLL

- assumption of ions as point charges

not good for ion + solvation shell

$\Rightarrow$ increased repulsion between ions than for point charges for larger I

→ increase of energy of solution → $\gamma_\pm$ increase

the higher I, the closer the ions come together

- assumption of solvent as a structureless dielectric medium

ion + relatively ordered (= tightly bound) primary solvation shell

+ loosely bound H_2O further away

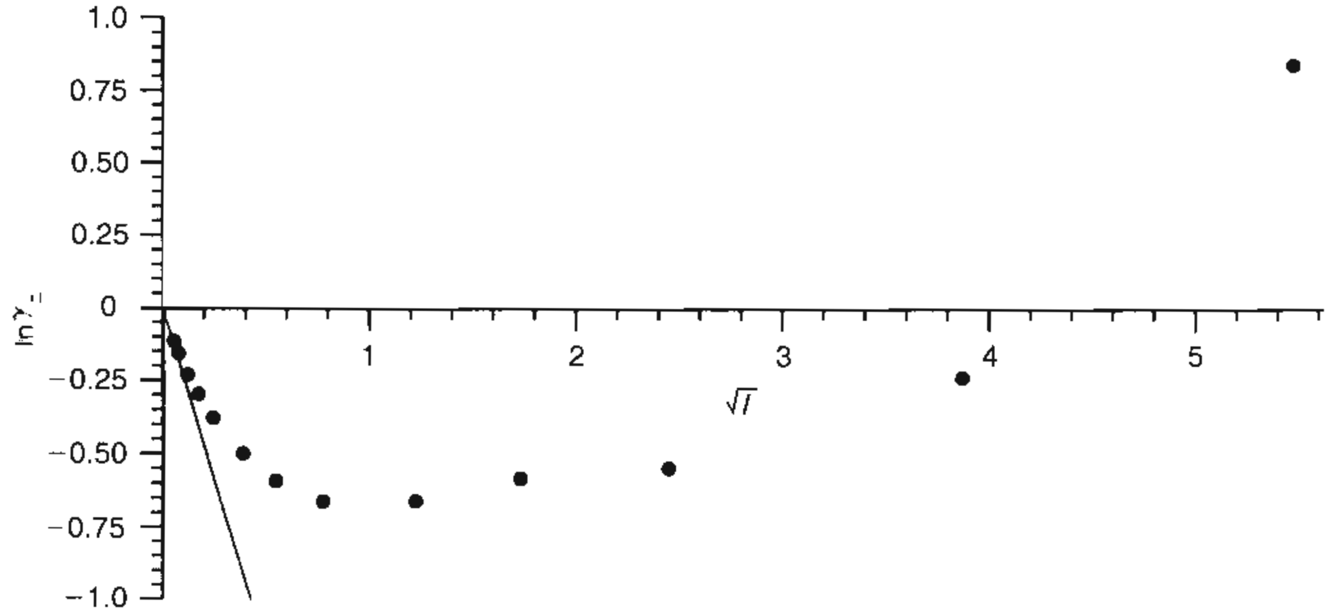
$\Rightarrow$ structureless solvent (described just by ε_r) not enough but molecular level structure of H_2O ~~mst~~ must be used!

ordered primary solvation shell, as well as by more loosely bound water molecules. The atomic level structure of the solvation shell is not adequately represented by using the dielectric strength of bulk solvent. Another factor that has not been taken into account is that as the concentration increases, some ion pairing occurs such that the concentration of ionic species is less than would be calculated assuming complete dissociation.

Additionally, consider the fact that the water molecules in the solvation shell have effectively been removed from the solvent. For example, in an aqueous solution of H_2SO_4, approximately nine H_2O molecules are tightly bound per dissolved H_2SO_4 formula unit. Therefore, the number of moles of H_2O as solvent in 1 L of a one molar H_2SO_4 solution is reduced from 55 for pure H_2O to 46 in the solution. Consequently, the actual solute molarity is larger than that calculated by assuming that all the H_2O is in the form of solvent. Because the activity increases linearly with the actual molarity, $\gamma_\pm$ increases as the solute concentration increases. If there were no change in the enthalpy of solvation with concentration, all the H_2O molecules would be removed from the solvent at a concentration of six molar H_2SO_4. Clearly, this assumption is unreasonable. What actually happens is that solvation becomes energetically less favorable as the H_2SO_4 concentration increases. This corresponds to a less negative value of $\ln \gamma_\pm$, or equivalently to an increase in $\gamma_\pm$. Summing up, many factors explain why the Debye–Hückel limiting law is only valid for small concentrations. Because of the complexity of these different factors, there is no simple formula based on theory that can replace the Debye–Hückel limiting law. However, the main trends exhibited in Figures 10.6 and 10.7 are reproduced in more sophisticated theories of electrolyte solutions.

Because none of the usual models are valid at high concentrations, empirical models that "improve" on the Debye–Hückel model by predicting an increase in $\gamma_\pm$ for high concentrations are in widespread use. An empirical modification of the Debye–Hückel limiting law that has the form

$$\log_{10}\gamma_\pm = -0.51\left|z_+z_-\right|\left[\frac{\left(\dfrac{I}{m^\circ}\right)^{1/2}}{1+\left(\dfrac{I}{m^\circ}\right)^{1/2}} - 0.30\left(\frac{I}{m^\circ}\right)\right] \qquad \textbf{(10.34)}$$



H_2O in solvation shell are effectively removed from free solvent

e.g. H_2SO_4 solution: 9 H_2O tightly bound to H_2SO_4

$\Rightarrow$ in 1L 1M H_2SO_4 solution: 46 mol H_2O in free solvent

in pure water: 55 mol H_2O

$\Rightarrow$ $M_{H_2SO_4}$ ~~lower~~ different than calculated assuming that all water is free solvent

a: linear increase with solute molarity

$\rightarrow$ $\gamma_\pm$ increase

solvation gets energetically less favorable when H_2SO_4 amount increases

$\rightarrow$ less negative $\ln \gamma_\pm$ $\rightarrow$ increase of $\gamma_\pm$

no closed formula or theory exists which can include all these effects

$\rightarrow$ no theory which can explain high I behavior of $\gamma_\pm$

$\rightarrow$ empirical models (fit to experiment) without theoretical reason are needed like the Davies formula

transp. plot of Davies formula

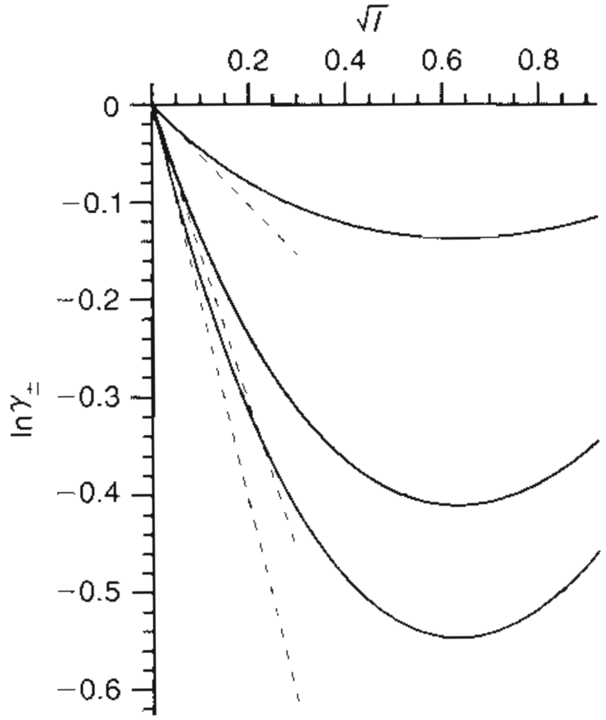


FIGURE 10.8
Comparison between the predictions of the Debye–Hückel limiting law (dashed lines) and the Davies equation (solid curves) for 1–1 (red), 1–2 (purple), and 1–3 (blue) electrolytes.

is known as the **Davies equation.** As seen in the correct limiting behavior for low I values, better agreement with the experimental res However, unlike the Debye–Hückel limiting Davies equation.

10.5 Chemical Equilib Solutions

As discussed in Section 9.13, the equilibrium Equation (9.66):

$$K = \prod_i ($$

It is convenient to define the activity of a speci

$$a_i = \gamma_i$$

where γ_i is the activity coefficient of species cal equilibrium in electrolyte solutions, illust trations must be taken into account to accura We first restrict our considerations to the Debye–Hückel limiting law is valid. As an ex ciation of MgF_2 in water. The equilibrium c salts is usually given the symbol K_{sp}, where th uct. The equilibrium constant K_{sp} is unitless reaction shown in Equation (10.37). Value reduced concentration units of molarity (c/c° ues for selected substances are listed in Table is 0.998 kg, the numerical value of the conce dilute solutions.

We next consider dissociation of MgF_2 in

$$MgF_2(s) \rightarrow Mg^{2+}(a$$

Because the activity of the pure solid can be se

$$K_{sp} = a_{Mg^{2+}} a_{F^-}^2 = \left(\frac{c_{Mg^{2+}}}{c^{\circ}}\right)($$

From the stoichiometry of the overall equat Equation (10.38) still contains two unknowns, as shown in Example Problem 10.3.

Chemical Equilibrium in Electrolyte Solutions

equilibrium constant in terms of activities:

$K = \prod_i (a_i^{eq})^{\nu_i}$ ν_i : stoichiometric factors in reaction equation

reactants: ν_i negative, products ν_i positive

activity in terms of molarity: $a_i = \gamma_i \frac{c_i}{c_0}$

$c_0 = 1M$

assume that a_i small enough for DHLL to work

solubility product: K_{sp}, no unit!

e.g. MgF_2 in H_2O: $K_{sp} = 6.4 \cdot 10^{-9}$

$MgF_2(s) \xrightarrow{H_2O} Mg^{2+}(aq) + 2F^-(aq)$

Tables are usually in molarities $\frac{c}{c_0}$ not molalities $\frac{m}{m_0}$

1 L H_2O: 0.998 kg $\frac{c}{c_0}$, $\frac{m}{m_0}$ same in dilute solutions

MgF_2: $K_{sp} = a_{Mg^{2+}} a_{F^-}^2 = \left(\frac{c_{Mg^{2+}}}{c_0}\right)\left(\frac{c_{F^-}}{c_0}\right)^2 \gamma_\pm^3 = 6.4 \cdot 10^{-9}$

$c_{F^-} = 2c_{Mg^{2+}}$ $\gamma_\pm$ unknown, also $c \Rightarrow$ iteration

<u>0. Iteration</u> assume $\gamma_\pm = 1$, $c_{F^-} = 2c_{Mg^{2+}}$

$\frac{c_{\cancel{F}\,Mg^{2+}}}{c_0} = x$; $K_{sp} = \frac{c_{Mg^{2+}}}{c_0}\left(\frac{c_{F^-}}{c_0}\right)^2 \underset{\nearrow}{\gamma_\pm^3} = x(2x)^2 = 6.4 \cdot 10^{-9}$

1 in 1. iteration

$\Rightarrow 4x^3 = 6.4 \cdot 10^{-9}$

$x = \frac{c_{Mg^{2+}}}{c_0} = 1.17 \cdot 10^{-3}$ (in $\frac{mol}{L}$ and in $\frac{mol}{kg}$)

<u>1. Iter.</u> ionic strength:

$$I = \frac{1}{2} m \left(\nu_+ z_+^{+} + \nu_- z_-^{2}\right) = \frac{1}{2} \cdot 1.17 \cdot 10^{-3} \frac{mol}{kg} \left(\underset{Mg^{2+}}{\underset{\nearrow}{2^2}} + \underset{F^-}{\underset{\nearrow}{2}}\right)$$

$$= 3.51 \cdot 10^{-3} \frac{mol}{kg}$$

DHLL:

$$\ln \gamma_\pm = -1.173 \cdot \overset{z_{Mg^{2+}}}{\overset{\nearrow}{2}} \cdot \overset{c_{F^-}}{\overset{\nearrow}{|-1|}} \cdot \sqrt{3.51 \cdot 10^{-3}} = -0.1390$$

$$\gamma_\pm = \exp(-0.1390) = 0.870$$

~~$x = c_{Mg^{2+}}$~~

$$4x^3 \gamma_\pm^3 = 6.4 \cdot 10^{-9} \rightarrow 4x^3 = \frac{6.4 \cdot 10^{-9}}{(0.870)^3}$$

$$\rightarrow x = \frac{c_{Mg^{2+}}}{c_0} = 1.34 \cdot 10^{-3} \text{ in } \frac{mol}{l} \text{ and } \frac{mol}{kg}$$

<u>2. iteration</u>: $\gamma_\pm = 0.862$, $c_{Mg^{2+}} = 1.36 \cdot 10^{-3} \frac{mol}{l}$

<u>3. iteration</u>: $\gamma_\pm = 0.861$, $c_{Mg^{2+}} = 1.36 \cdot 10^{-3} \frac{mol}{l}$

converged! 14% error when $\gamma_\pm = 1$ is used

$$K_{sp} = \frac{c_{Mg^{2+}}}{c_0} \left(\frac{c_{F^-}}{c_0}\right)^2 \gamma_\pm^3 = \text{const. when } T = \text{const.}$$

<u>small I</u>: $\gamma_\pm < 1 \Rightarrow \gamma_\pm$ decrease → solubility increase

→ adding inert (non-reacting) electrolyte

→ I increase → $\gamma_\pm$ decrease

→ solubility increase when K_{sp} = const.

→ <u>saltingin</u> region of I

I larger than minimum in $\ln \gamma_\pm$ vs $\sqrt{I}$ curve

then $\gamma_\pm > 1$ and solubility decreases as $\gamma_\pm$ increases

→ ~~in~~ electrolyte addition

→ I increase → $\gamma_\pm$ increases

→ solubility decreases

<u>salting out</u> region of I

can be used for protein purification

e.g. the blood clotting proten fibrinogen is precipitating in 0.8 M $(NH_4)_2SO_4$ solution while to precipitate the protein albumin 2.4 M is needed

~~if~~ <u>I is large</u>

⇒ DHLL not valid

⇒ $\gamma_\pm$ must be estimated, e.g. with Davies equation

<u>example</u>: a buffer is made of a weak acid and its conjugate base:

0.1 M CH_3COOH (HAc) + 0.1 M CH_3COONa (NaAc)

What is the pH value?

dissociation constant of HAc based on molality

$K_a(HAc) = 1.75\cdot10^{-5}$

$$K_a = \frac{m(H_3O^+)\,\gamma_\pm\; m(Ac^-)\,\gamma_\pm}{m(HAc)}$$

↳ neutral molecules, so $\gamma \approx 1$ for them (not exact because of the dipole moment)

$m(Ac^-) = 0.1 + x$

because 0.1 M NaAc : +0.1

x : $m(Ac^-)$ from HAc dissociation

x: amount of HAc that dissociated

$\Rightarrow m(HAc) = 0.1$ (initial) $- x$ (dissociated)

$m(H_3O^+) = x$

since $K_a = 1.75 \cdot 10^{-5}$ is very small

$\Rightarrow x \ll 0.1$ and can be neglected compared to 0.1

$$K_a = \frac{x \cdot (0.1 + x)}{0.1 - x} \gamma_\pm^2 \approx \frac{x \cdot 0.1}{0.1} \gamma_\pm^2 = \gamma_\pm^2 \cdot x$$

$$x = \frac{K_a}{\gamma_\pm^2} = m(H_3O^+)$$

because K_a is small, the degree of dissociation of HAc is small

$\Rightarrow$ ionic strength can be calculate from NaAc which is a strong electrolyte

$$I = \frac{1}{2} m (\nu_+ z_+^2 + \nu_- z_-^2) = \frac{1}{2} \cdot 0.1 \frac{mol}{kg} (1 \cdot (+1)^2 + 1 \cdot (-1)^2)$$

$$= \frac{1}{2} \cdot 0.1 \frac{mol}{kg} \cdot 2 = 0.1 \frac{mol}{kg}$$

Davies equation:

$$\log_{10} \gamma_\pm = -0.51 |z_+ z_-| \left[\frac{\sqrt{I/m_0}}{1 + \sqrt{I/m_0}} - 0.30\, I/m_0 \right]$$

$$= -0.51 \left| \underset{\overset{\nearrow}{z_+}}{(+1)} \underset{\overset{\uparrow}{z_-}}{(-1)} \right| \left[\frac{\sqrt{0.1}}{1+\sqrt{0.1}} - 0.30 \cdot 0.1 \right]$$

$$= -0.1270$$

$$\gamma_\pm = 10^{-0.1270} = 0.746$$

$$\Rightarrow m(H_3O^+) = x = \frac{K_a}{\gamma_\pm^2} = \frac{1.75 \cdot 10^{-5}}{(0.746)^2}$$

$$= 3.14 \cdot 10^{-5} \ \frac{mol}{kg}$$

$$pH = -\log_{10}(3.14 \cdot 10^{-5}) = 4.5$$

if $\gamma_\pm = 1$ is assumed, then

$m(H_3O^+) = 1.57 \cdot 10^{-5}$

and $pH = 4.76$

larger than correct $pH = 4.5$

Lec. ⑦ is Quiz