Chapter 10. Electrolyte Solutions

Summary

- ***A whole chapter on just one kind of solution ?***
- ***What’s so special about electrolyte solutions ?***
- Enthalpy, entropy, and Gibbs energy of ions in solutions
- Ion solvation
- Activities of ions in solution
- Debye-Huckel theory for dilute electrolyte solutions
- Ionic reaction equilibrium

What is an “electrolyte solution” ?

- a solution of **ionic species** of positive and negative electrical charge **dissolved in a solvent**
- the ions are mobile and conduct electric current in an applied electric field (ionic conductivity)
- usually (but not always) liquid solutions
- important examples:
  - ♦ <u>all</u> biological and physiological solutions
  - ♦ strong acids and strong bases
  - ♦ buffer solutions for pH control
  - ♦ seawater, brines, and groundwater
  - ♦ battery electrolytes
  - ♦ molten salts

What's Special About Electrolyte Solutions ?

- thermodynamic properties of nonelectrolyte solution components are functions of T, p, and composition
- the properties of ions also depend on the **electric potential** ϕ
- applied electric potential ϕ changes the chemical potential of an ion of charge z by

$$\Delta\mu_{\text{electrical}} = zF\phi$$

Example A **1.5 volt applied electric potential** (from a common AA battery) increases the chemical potential of Na^+ ions by

$$\Delta\mu_{\text{electrical}} = zF\phi = (+1)\,(96{,}485\ \text{C mol}^{-1})\,(1.5\ \text{V})$$

$$= \mathbf{145{,}000\ J\ mol^{-1}} \quad \text{(significant!!!)}$$

- application: electrochemical synthesis of sodium metal

Section 10.1 Enthalpy, Entropy, and Gibbs Energy of Ions in Solution

- electrolyte solutions are **electrically neutral**

- impossible to study solutions containing only cations or anions
- impossible to independently vary cation and anion concentrations

example aqueous $MgCl_2$ solutions

$$2c_{\mathrm{Mg2+}} = c_{\mathrm{Cl-}}$$

- **important result:** the internal energy, enthalpy, entropy, Gibbs energy, volume, … of individual ions cannot be measured

But Many Important Processes Involve Ion Formation

Dissolution

$$\mathrm{CaCO_3(s) \rightarrow Ca^{2+}(aq) + CO_3^{2-}(aq)}$$

Dissociation

$$\mathrm{H_2O(}l\mathrm{) \rightarrow H^{+}(aq) + OH^{-}(aq)}$$

pH Control (Buffers)

$$\mathrm{H^{+}(aq) + CH_3COO^{-}(aq) \rightarrow CH_3COOH(aq)}$$

Molten Salts

$$\mathrm{NaCl(s) \rightarrow Na^{+}(}l\mathrm{) + Cl^{-}(}l\mathrm{)}$$

Billion-Dollar Electrochemical Industries

Chlor-Alkali Production (Cl$_2$, H$_2$, and NaOH from saltwater)

$$\mathrm{Na^+(aq) + Cl^-(aq) + H_2O}(l) \rightarrow \mathrm{Na^+(aq) + OH^-(aq) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g)}$$

Aluminum Production (from molten cryolite)

$$\mathrm{2Al^{3+}}(l) + \mathrm{3O_2^-}(l) + \mathrm{3C(s)} \rightarrow \mathrm{2Al}(l) + \mathrm{3CO_2(g)}$$

Corrosion

$$\mathrm{Fe(s)} + \mathrm{H_2O}(l) \rightarrow \mathrm{Fe^{2+}(aq)} + \mathrm{H_2(g)}$$

Batteries

$$\mathrm{PbO_2(s)} + \mathrm{Pb(s)} + \mathrm{2H_2SO_4(aq)} \rightarrow \mathrm{2PbSO_4(s)} + \mathrm{H_2O}(l)$$

Thermodynamic Convention for Ion Formation

$\Delta H_{\mathrm{fm}}{}^{\mathrm{o}}$, $\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}$, and $S_{\mathrm{m}}{}^{\mathrm{o}}$ values are useful for many ionic reactions.

But these quantities **cannot be measured** for individual ions.

For convenient tabulation purposes, the standard enthalpy, Gibbs energy, and entropy of formation of aqueous H^+ ions are defined as zero at all temperatures.

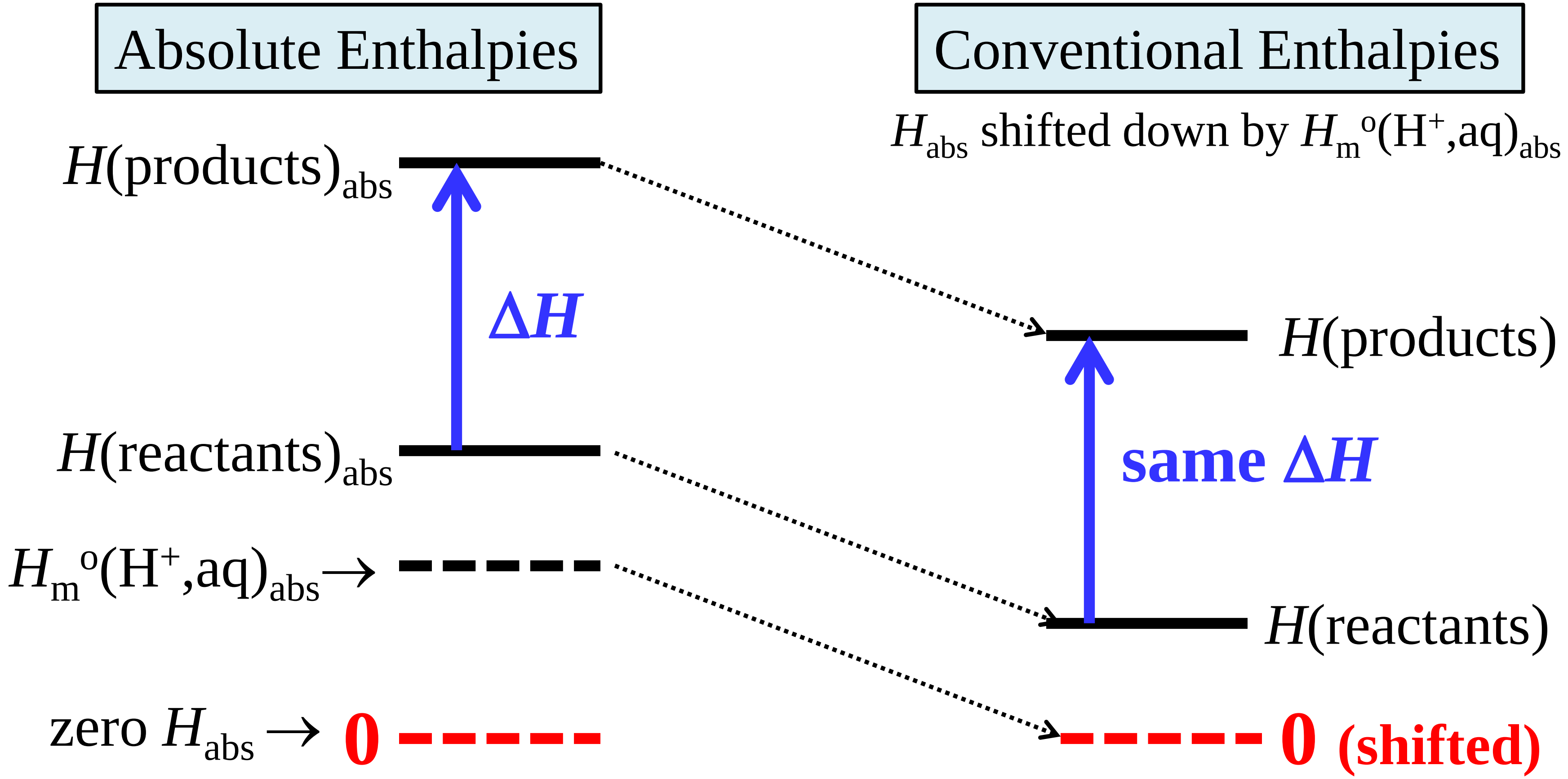
$$\boldsymbol{\Delta H_{\mathrm{f,m}}{}^{\mathrm{o}}(\mathrm{H}^+, \mathrm{aq}) = 0 \qquad \Delta G_{\mathrm{f,m}}{}^{\mathrm{o}}(\mathrm{H}^+, \mathrm{aq}) = 0 \qquad \Delta S_{\mathrm{f,m}}{}^{\mathrm{o}}(\mathrm{H}^+, \mathrm{aq}) = 0}$$

Why does this work?

Thermodynamic Convention for Ion Formation

<u>Example</u> $\Delta H_{fm}^{o}(H^{+}, aq) = 0$ Why is this convention valid?

The zero-point for enthalpy can be chosen arbitrarily to calculate ΔH.



Absolute Enthalpies

$H(\text{products})_{abs}$

ΔH

$H(\text{reactants})_{abs}$

$H_m^{o}(H^{+},aq)_{abs} \rightarrow$

zero $H_{abs} \rightarrow$ 0

Conventional Enthalpies

H_{abs} shifted down by $H_m^{o}(H^{+},aq)_{abs}$

$H(\text{products})$

same ΔH

$H(\text{reactants})$

0 (shifted)

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

Example Calculate ΔH^o and ΔG^o at 25 ^{o}C for the reaction

$$\mathbf{Cl^-(aq) + H_2O(\mathit{l}) \rightarrow OH^-(aq) + \tfrac{1}{2}H_2(g) + \tfrac{1}{2}Cl_2(g)}$$

Data: Tables 4.1 and 10.2

$$\Delta H^o = \Delta H_f^o(\text{products}) - \Delta H_f^o(\text{reactants})$$

$$= \Delta H_{fm}^o(OH^-,aq) + \tfrac{1}{2}\,\Delta H_{fm}^o(H_2,g) + \tfrac{1}{2}\,\Delta H_{fm}^o(Cl_2,g)$$

$$- \Delta H_{fm}^o(Cl^-,aq) - \Delta H_{fm}^o(H_2O,l)$$

$$= -230.0 + \tfrac{1}{2}\,(0) + \tfrac{1}{2}\,(0) - (-167.2) - (-285.8) = \mathbf{223.0\ kJ}$$

$$\Delta G^o = \Delta G_{fm}^o(OH^-,aq) + \tfrac{1}{2}\,\Delta G_{fm}^o(H_2,g) + \tfrac{1}{2}\,\Delta G_{fm}^o(Cl_2,g)$$

$$- \Delta G_{fm}^o(Cl^-,aq) - \Delta G_{fm}^o(H_2O,l)$$

$$= -157.2 + \tfrac{1}{2}\,(0) + \tfrac{1}{2}\,(0) - (-131.2) - (-237.1) = \mathbf{211.1\ kJ}$$

(not spontaneous)

Section 10.2 Ion Solvation

Why are electrolyte solutions "special" ?

For years, many scientists believed solutions of ions couldn't exist under ambient conditions ($T \approx 300$ K). *Why*?

Consider the **formation of gas-phase H^+ and Cl^- ions** at 25 °C.

$$\tfrac{1}{2}\,H_2(g) \rightarrow H(g) \qquad \Delta G^o = +203\ \text{kJ}$$

$$\tfrac{1}{2}\,Cl_2(g) \rightarrow Cl(g) \qquad \Delta G^o = +106\ \text{kJ}$$

$$H(g) \rightarrow H^+(g) + e^- \qquad \Delta G^o = +1312\ \text{kJ}$$

$$Cl(g) + e^- \rightarrow Cl^-(g) \qquad \Delta G^o = -349\ \text{kJ}$$

Overall:

$$\tfrac{1}{2}\,H_2(g) + \tfrac{1}{2}\,Cl_2(g) \rightarrow H^+(g) + Cl^-(g) \qquad \boldsymbol{\Delta G^o = +1272\ \text{kJ}}$$

extremely unfavorable

Ion Solvation

For comparison, the **formation of aqueous H^+ and Cl^- ions** at 25 °C:

$\frac{1}{2} H_2(g) \rightarrow H(g)$ $\Delta G^o = +203$ kJ

$\frac{1}{2} Cl_2(g) \rightarrow Cl(g)$ $\Delta G^o = +106$ kJ

$H(g) \rightarrow H^+(g) + e^-$ $\Delta G^o = +1312$ kJ

$Cl(g) + e^- \rightarrow Cl^-(g)$ $\Delta G^o = -349$ kJ

$H^+(g) + Cl^-(g) \xrightarrow{\text{solvation}} H^+(aq) + Cl^-(aq)$ $\Delta G^o = -1403$ kJ

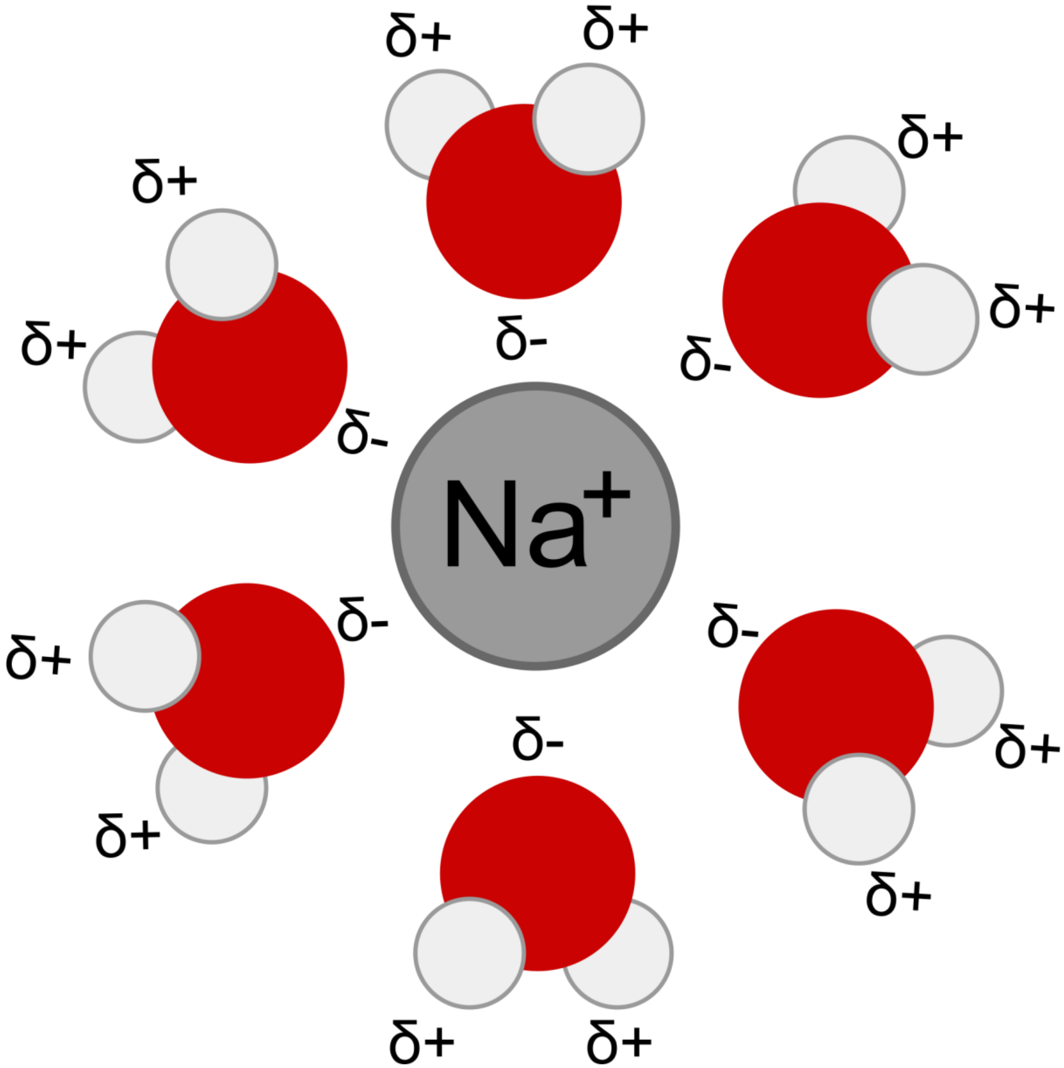
Overall:

$\frac{1}{2} H_2(g) + \frac{1}{2} Cl_2(g) \rightarrow H^+(aq) + Cl^-(aq)$ **$\Delta G^o = -131$ kJ**

favorable

Interaction with water molecules stabilizes the aqueous ions. ***Why?***

Hydration of a Sodium Ion



Section 10.3 Activities of Electrolytes

Why are electrolyte solutions “special” ?

- ions in solution interact by long-range electrostatic forces
- electrolyte solutions can be strongly nonideal, even if dilute
- nonelectrolyte (Chap. 9) and electrolyte activity expressions are very different

Examples Activities of Aqueous NaCl, $LaCl_3$, and $Al_2(SO_4)_3$

$$a_{\mathrm{NaCl}} = a_{\mathrm{Na+}}a_{\mathrm{Cl-}}$$

$$a_{\mathrm{LaCl3}} = a_{\mathrm{La+++}}(a_{\mathrm{Cl-}})^3$$

$$a_{\mathrm{Al2(SO4)3}} = (a_{\mathrm{Al+++}})^2(a_{\mathrm{SO4--}})^3$$

Chemical Potential (Molar Gibbs Energy) of Aqueous Sodium Chloride

$$\mu_{\mathrm{NaCl}} = \mu_{\mathrm{Na+}} + \mu_{\mathrm{Cl-}}$$

$$= \overset{\text{(chemical)}}{\mu_{\mathrm{Na+}}{}^{o} + RT\ln a_{\mathrm{Na+}}} + \overset{\text{(electrical)}}{\cancel{z_{\mathrm{Na+}}F\phi}}$$

$$+ \overset{\text{(chemical)}}{\mu_{\mathrm{Cl-}}{}^{o} + RT\ln a_{\mathrm{Cl-}}} + \overset{\text{(electrical)}}{\cancel{z_{\mathrm{Cl-}}F\phi}}$$

$$= \mu_{\mathrm{Na+}}{}^{o} + \mu_{\mathrm{Cl-}}{}^{o} + RT\ln(a_{\mathrm{Na+}}a_{\mathrm{Cl-}})$$

$$\mu_{\mathrm{NaCl}} = \mu_{\mathrm{NaCl}}{}^{o} + RT\ln a_{\mathrm{NaCl}}$$

$$a_{\mathrm{NaCl}} = a_{\mathrm{Na+}}a_{\mathrm{Cl-}}$$

Why is there no electric potential ϕ in the expression for the chemical potential of aqueous NaCl?

Chemical Potential of Electrolyte $A_{v+}C_{v-}$

$$\mu_{Cv+Av-} = v_+\mu_C + v_-\mu_A$$

$$= v_+(\mu_C^o + RT\ln a_C + \cancel{z_C F\phi})$$

$$+ v_-(\mu_A^o + RT\ln a_A + \cancel{z_A F\phi})$$

$$= v_+\mu_C^o + v_-\mu_A^o + RT\ln(a_C^{v+}a_A^{v-})$$

$$\mu_{Cv+Av-} = \mu_{Cv+Av-}^o + RT\ln a_{Cv+Av-}$$

$$a_{Cv+Av-} = a_C^{v+}a_A^{v-}$$

Mean (Average) Activity of Electrolyte $A_{v+}C_{v-}$

$$\mu_{Cv+Av-} = \mu_{C}^{o} + \mu_{A}^{o} + RT\ln(a_{C}^{v+}a_{A}^{v-})$$

Useful, but cation and anion activities a_C and a_A can’t be measured.

For practical calculations, the **measurable mean ionic activity** $a_\pm$ is used, a weighted-average of the cation and ion activities

$$\boxed{a_\pm = (a_{C}^{v+}a_{A}^{v-})^{1/v}} \qquad \boxed{v = v_+ + v_-}$$

which gives the **mean ionic chemical potential** $\mu_\pm$

$$\mu_\pm = \frac{v_+\mu_C + v_-\mu_A}{v} = \mu_\pm^{o} + RT\ln a_\pm$$

$$\boxed{\mu_{Cv+Av-} = v\mu_\pm^{o} + RT\ln(a_\pm^{v})}$$

Practical (Rational) Electrolyte Activities

Electrolyte activities are defined on the **molality** concentration scale

$$m \;=\; \text{moles of electrolyte per kilogram of solvent}$$

using **Henry's law** (*why ?*)

$$\gamma_C \to 1 \qquad \text{and} \qquad \gamma_A \to 1 \qquad \text{as} \quad m \to 0$$

for the cation and anion activity coefficients.

Why molalities? Why not molarities (moles of electrolyte per liter of solution)?

- Molalities can be calculated accurately and precisely from measured masses of electrolyte and solvent. Volumetric flasks (relatively low 0.2 % accuracy, *at best*) are not required
- Molalities (but not molarities) are independent of temperature

Practical (Rational) Electrolyte Activities

$a_{\mathrm{C}} = a_+ = \gamma_+ m_+ = v_+ \gamma_+ m$ cation activity

$a_{\mathrm{A}} = a_- = \gamma_- m_- = v_- \gamma_- m$ anion activity

$\boxed{m_\pm = (m_+^{v+} m_-^{v-})^{1/v}}$ mean ionic molality

$\boxed{\gamma_\pm = (\gamma_+^{v+} \gamma_-^{v-})^{1/v}}$ mean ionic activity coefficient

$\boxed{a_\pm = (a_+^{v+} a_-^{v-})^{1/v} = \gamma_\pm m_\pm}$ mean ionic activity

$\boxed{a = (a_\pm)^v = (\gamma_\pm m_\pm)^v}$ electrolyte activity

$\boxed{\mu_{\mathrm{C}v+\mathrm{A}v-} = v\mu_\pm^{\mathrm{o}} + RT \ln(a_\pm^{v})}$ electrolyte chemical potential

Example Aqueous NaCl at molality m

$v_+ = 1$ $\qquad$ $v_- = 1$ $\qquad$ $v = 2$

$m_\pm = (m_+^{v+} m_-^{v-})^{1/v} = (m^1 m^1)^{1/2} = m$

$\gamma_\pm = (\gamma_+^{v+} \gamma_-^{v-})^{1/v} = (\gamma_+ \gamma_-)^{1/2}$

$a_{\mathrm{NaCl}} = (\gamma_\pm m_\pm)^v = \gamma_\pm^2 m^2$

Example Aqueous $\mathbf{CaCl_2}$ at molality m

$v_+ = 1$ $\qquad$ $v_- = 2$ $\qquad$ $v = 3$

$m_\pm = [m_+^{v+} m_-^{v-}]^{1/v} = [m^1 (2m)^2]^{1/3} = (4m^3)^{1/3} = 4^{1/3} m$

$\gamma_\pm = (\gamma_+^{v+} \gamma_-^{v-})^{1/v} = (\gamma_+ \gamma_-^2)^{1/3}$

$a_{\mathrm{CaCl2}} = (\gamma_\pm m_\pm)^3 = 4\gamma_\pm^3 m^3$

What is the mean ionic activity coefficient $\gamma_\pm$?

Example **Chemical Potential of Aqueous NaCl at molality *m***

$$\mu_{\mathrm{NaCl}} = \mu_{\mathrm{NaCl}}{}^{\mathrm{o}} + RT \ln a_{\mathrm{NaCl}}$$

$$= \mu_{\mathrm{NaCl}}{}^{\mathrm{o}} + RT \ln(\gamma_\pm m)^2$$

$$= \mu_{\mathrm{NaCl}}{}^{\mathrm{o}} + RT \ln(\gamma_\pm m)^2$$

$$= \mu_{\mathrm{NaCl}}{}^{\mathrm{o}} + RT \ln(m)^2 + RT \ln(\gamma_\pm)^2$$

(ideal chemical potential) **(nonideal part)**

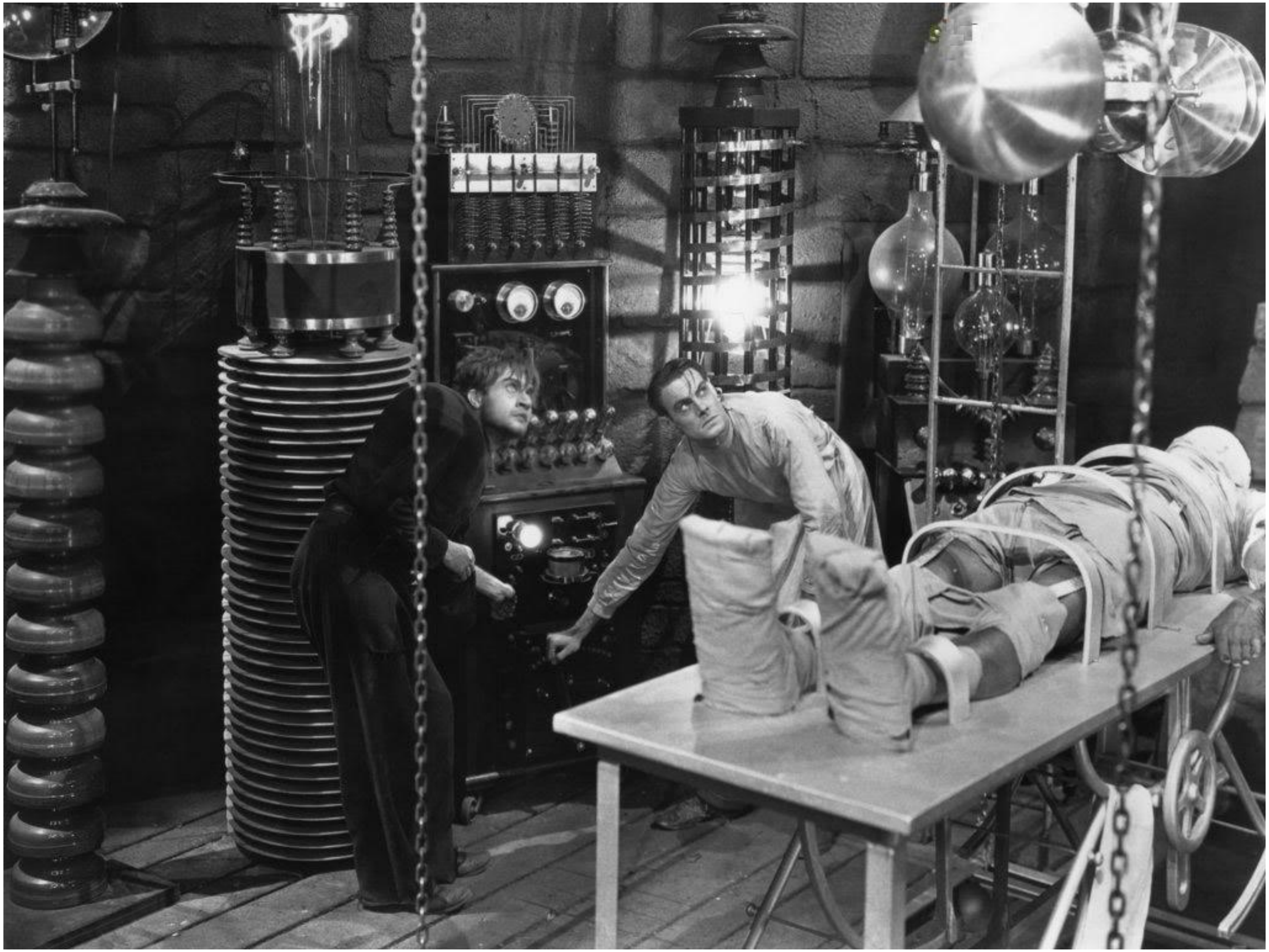
Interpretation:

$2RT \ln\gamma_\pm$ is the nonideal Gibbs energy per mole of NaCl

Gibbs-Donnan Equilibrium

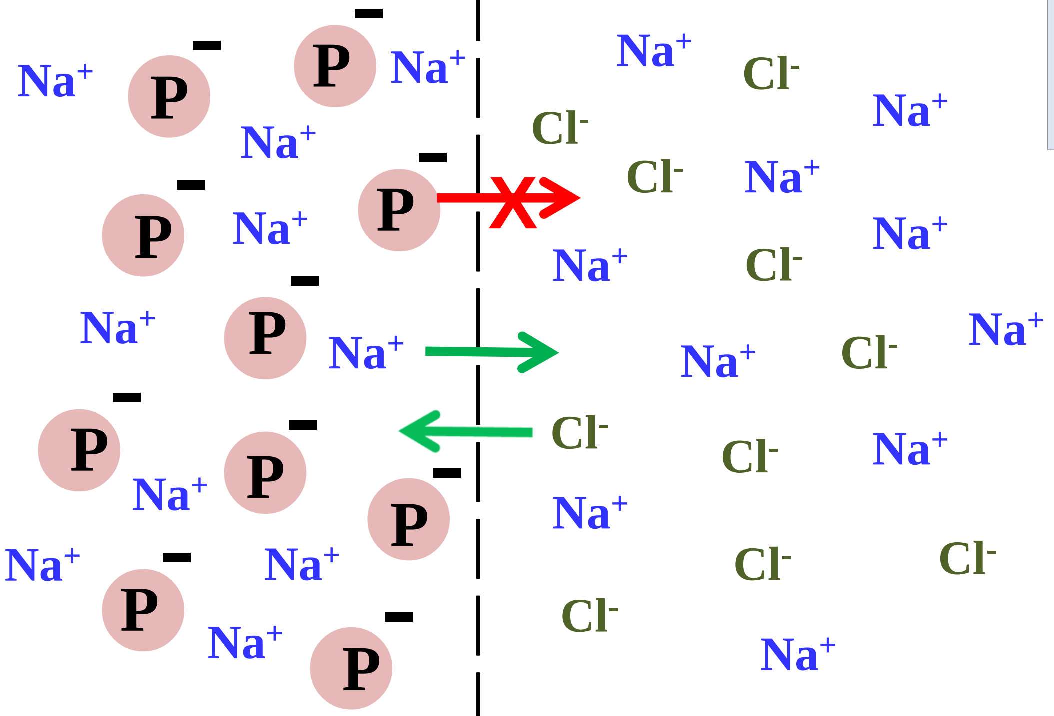
- unequal distribution of ions across semipermeable membranes
- **voltage differences generated *without electrodes or batteries!***
- illustrates an important application of electrolyte activities
- pH and other ion measurements using concentration cells
- electrical effects in charged colloid systems (*e.g.*, proteins)
- transmission of nerve impulses
- **origin of brain waves and *consciousness* ???**

Igor and Dr. Frankenstein throw the electrical switch



Gibbs-Donnan Equilibrium

Left Side **Right Side**



The membrane is permeable for small Na^+ and Cl^- ions, but not permeable for large P^- ions.

$$m_{\mathrm{NaP}} = 0.100 \text{ mol kg}^{-1} \qquad m_{\mathrm{NaP}} = 0.000 \text{ mol kg}^{-1}$$

$$m_{\mathrm{NaCl}} = 0.000 \text{ mol kg}^{-1} \qquad m_{\mathrm{NaCl}} = 0.100 \text{ mol kg}^{-1}$$

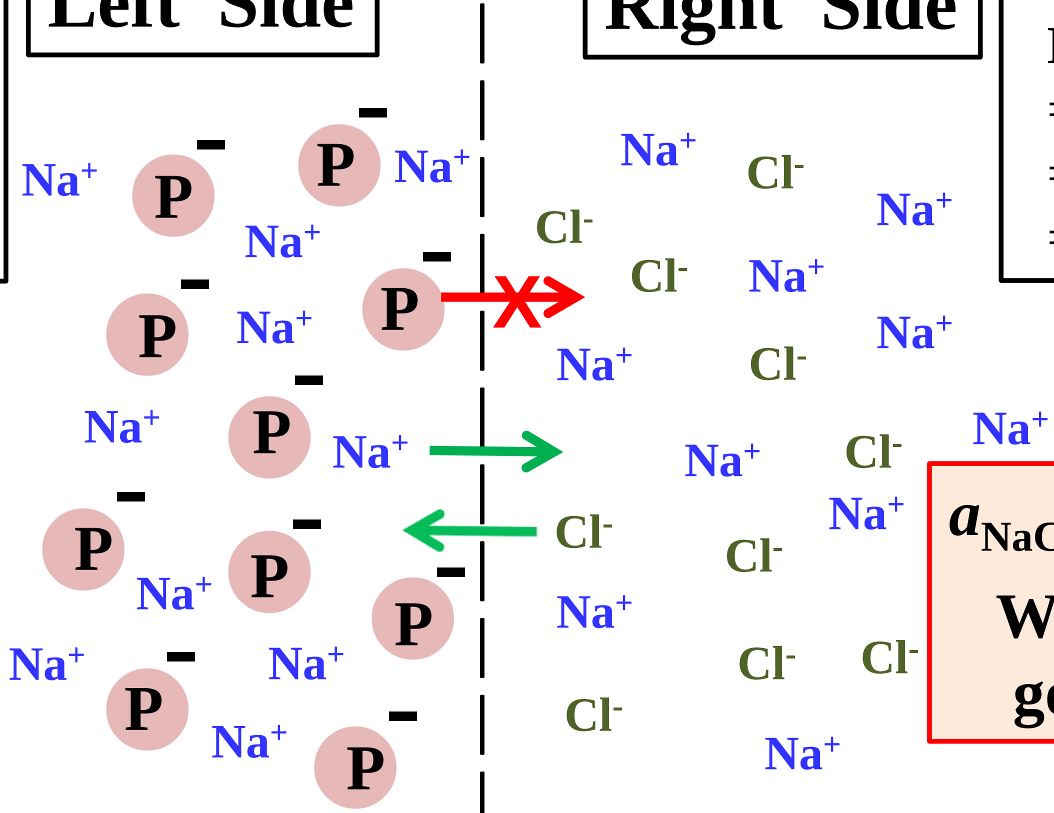
Gibbs-Donnan Equilibrium

Left-Side NaCl activity
$= m_{Na+}m_{Cl-}$
$= (0.100)(0)$
$= 0$

Left Side

Right Side

Right-Side NaCl activity
$= m_{Na+}m_{Cl-}$
$= (0.100)(0.100)$
$= 0.0100\ \mathrm{mol^2\ kg^{-2}}$



$a_{NaCl(right)} > a_{NaCl(left)}$

What is NaCl going to do?

$m_{NaP} = 0.100\ \mathrm{mol\ kg^{-1}}$

$m_{NaCl} = 0.000\ \mathrm{mol\ kg^{-1}}$

$m_{NaP} = 0.000\ \mathrm{mol\ kg^{-1}}$

$m_{NaCl} = 0.100\ \mathrm{mol\ kg^{-1}}$

Gibbs-Donnan Equilibrium

To reach equilibrium, NaCl diffuses from the right side (higher activity) to the left side (lower activity) across the semipermeable membrane until the left and right NaCl activities are equal.

$$m_{\mathrm{NaP}} = 0.100$$

$$m_{\mathrm{NaP}} = 0.000$$

$\leftarrow$ **x mol kg^{-1} NaCl**

$$m_{\mathrm{NaCl}} = 0.000 + x$$

$$m_{\mathrm{NaCl}} = 0.100 - x$$

$$a_{\mathrm{NaCl}}(\mathrm{Left}) = a_{\mathrm{Na+}}(\mathrm{Left})\, a_{\mathrm{Cl-}}(\mathrm{Left})$$

$$= \mathbf{(0.100 + \mathit{x})\, \mathit{x}}$$

$$a_{\mathrm{NaCl}}(\mathrm{Right}) = a_{\mathrm{Na+}}(\mathrm{Right})\, a_{\mathrm{Cl-}}(\mathrm{Right})$$

$$= \mathbf{(0.100 - \mathit{x})\, (0.100 - \mathit{x})}$$

at equilibrium:

$$\mathbf{(0.100 + \mathit{x})\, \mathit{x} = (0.100 - \mathit{x})\, (0.100 - \mathit{x})}$$

solve for
$x = 0.0333$

Gibbs-Donnan Equilibrium

NaCl is free to diffuse across the membrane: the left-side and right-side NaCl activities are equal at equilibrium:

Left:

$\boldsymbol{m_{\mathrm{NaP}} = 0.1000}$

$\boldsymbol{m_{\mathrm{NaCl}} = 0.0333}$

$m_{\mathrm{Na+}} = 0.1333$

$m_{\mathrm{Cl-}} = 0.0333$

$$\begin{aligned} a_{\mathrm{NaCl}} &= m_{\mathrm{Na+}}\, m_{\mathrm{Cl-}} \\ &= (0.1333)(0.0333) \\ &= \mathbf{0.00445} \end{aligned}$$

Right:

$\boldsymbol{m_{\mathrm{NaP}} = 0.0000}$

$\boldsymbol{m_{\mathrm{NaCl}} = 0.0667}$

$m_{\mathrm{Na+}} = 0.0667$

$m_{\mathrm{Cl-}} = 0.0667$

$$\begin{aligned} a_{\mathrm{NaCl}} &= m_{\mathrm{Na+}}\, m_{\mathrm{Cl-}} \\ &= (0.0667)(0.0667) \\ &= \mathbf{0.00445} \end{aligned}$$

Gibbs-Donnan Equilibrium

Equilibrium is reached. ***Zzzzzz*** **….**

$m_{\mathrm{Na+}} = 0.1333$	$m_{\mathrm{Na+}} = 0.0667$
$m_{\mathrm{Cl-}} = 0.0333$	$m_{\mathrm{Cl-}} = 0.0667$
Left: Na^+ more concentrated	Right: Cl^- more concentrated

But wait!

$m_{\mathrm{Na+}}(\mathrm{Left}) > m_{\mathrm{Na+}}(\mathrm{Right})$ **Why doesn't Na^+ diffuse to the right?**

$m_{\mathrm{Cl-}}(\mathrm{Left}) < m_{\mathrm{Cl-}}(\mathrm{Right})$ **Why doesn't Cl^- diffuse to the left?**

Gibbs-Donnan Equilibrium

$z_{Na+} = 1$
$F = 96485\ \text{C mol}^{-1}$

The left and right solutions are at **different electric potentials.**

$m_{Na+} = 0.1333$ | $m_{Na+} = 0.0667$
$m_{Cl-} = 0.0333$ | $m_{Cl-} = 0.0667$

$\phi_{\mathbf{Left}}$ | $\phi_{\mathbf{Right}}$

$$\mu_{Na+(total)}(\text{Left}) = \mu_{Na+(total)}(\text{Right})$$

$$\mu_{Na+(chem)}(\text{Left}) + \mu_{Na+(elec)}(\text{Left}) = \mu_{Na+(chem)}(\text{Right}) + \mu_{Na+(elec)}(\text{Right})$$

$$(\cancel{\mu_{Na+}{}^{o}} + RT\ln m_{Na+} + z_{Na+}F\phi)_{Left} = (\cancel{\mu_{Na+}{}^{o}} + RT\ln m_{Na+} + z_{Na+}F\phi)_{Right}$$

$$\boxed{\Delta\phi = \phi_{Right} - \phi_{Left} = \frac{RT}{z_{Na+}F}\ln\frac{m_{Na+Left}}{m_{Na+Right}} = 0.0178 \text{ volt at } 25\ {}^{o}\text{C}}$$

Gibbs-Donnan Equilibrium

$z_{\mathrm{Cl}^-} = -1$
$F = 96485\ \mathrm{C\ mol^{-1}}$

The left and right solutions are at **different electric potentials.**

$m_{\mathrm{Na}^+} = 0.1333$

$m_{\mathrm{Cl}^-} = 0.0333$

$\phi_{\mathbf{Left}}$ | $\phi_{\mathbf{Right}}$

$m_{\mathrm{Na}^+} = 0.0667$

$m_{\mathrm{Cl}^-} = 0.0667$

$$\mu_{\mathrm{Cl}^-(\mathrm{total})}(\mathrm{Left}) = \mu_{\mathrm{Cl}^-(\mathrm{total})}(\mathrm{Right})$$

$$\mu_{\mathrm{Cl}^-(\mathrm{chem})}(\mathrm{Left}) + \mu_{\mathrm{Cl}^-(\mathrm{elec})}(\mathrm{Left}) = \mu_{\mathrm{Cl}^-(\mathrm{chem})}(\mathrm{Right}) + \mu_{\mathrm{Cl}^-(\mathrm{elec})}(\mathrm{Right})$$

$$(\cancel{\mu_{\mathrm{Cl}^-}{}^{o}} + RT\ln m_{\mathrm{Cl}^-} + z_{\mathrm{Cl}^-}F\phi)_{\mathrm{Left}} = (\cancel{\mu_{\mathrm{Cl}^-}{}^{o}} + RT\ln m_{\mathrm{Cl}^-} + z_{\mathrm{Cl}^-}F\phi)_{\mathrm{Right}}$$

$$\boxed{\Delta\phi = \phi_{\mathrm{Right}} - \phi_{\mathrm{Left}} = \frac{RT}{z_{\mathrm{Cl\text{-}}}F}\ln\frac{m_{\mathrm{Cl\text{-}Left}}}{m_{\mathrm{Cl\text{-}Right}}} = 0.0178\ \text{volt at } 25\ {}^{o}\mathrm{C}}$$

Gibbs-Donnan Equilibrium

$$\phi_{\text{Right}} - \phi_{\text{Left}} = \mathbf{0.0178\ volt}$$

$m_{\text{Na+}} = 0.1333$	$m_{\text{Na+}} = 0.0667$
$m_{\text{Cl–}} = 0.0333$	$m_{\text{Cl–}} = 0.0667$

The Na^+ ions on the right are more dilute and therefore have a lower chemical potential than on the left.

But the Na^+ ions on the right are at a higher voltage and therefore have a higher electric potential than on the left.

Vice versa for Cl^- ions.

Electrolyte solutions can be very strongly nonideal !

Ion Association **Mean ionic activity coefficients < 0.01** have been reported for aqueous CdI_2 and other associating electrolytes.

In aqueous CdI_2 solutions, for example, the formation of CdI^+, CdI_2, CdI_3^-, and CdI_4^{2-} ion complexes sharply reduces the molalities of free Cd^{2+} and free I^- ions below m and $2m$, which in turn sharply reduces both the CdI_2 activity and $\gamma_\pm$:

$$a_{\mathrm{CdI2}} = \gamma_{\mathrm{Cd2+}} m_{\mathrm{Cd2+}} (\gamma_{\mathrm{I-}} m_{\mathrm{I-}})^2 = 4\gamma_\pm^3 m^3$$

Ion Hydration **Mean ionic activity coefficients > 1000** have been reported for concentrated solutions of strongly hydrated electrolytes, such as aqueous $U(NO_3)_2$.

Hydrating water molecules bound to ions reduce the amount of “free” water molecules acting as the solvent, making the solutions effectively much more concentrated (gels in some cases).

Section 10.4 Experimental Electrolyte Activities

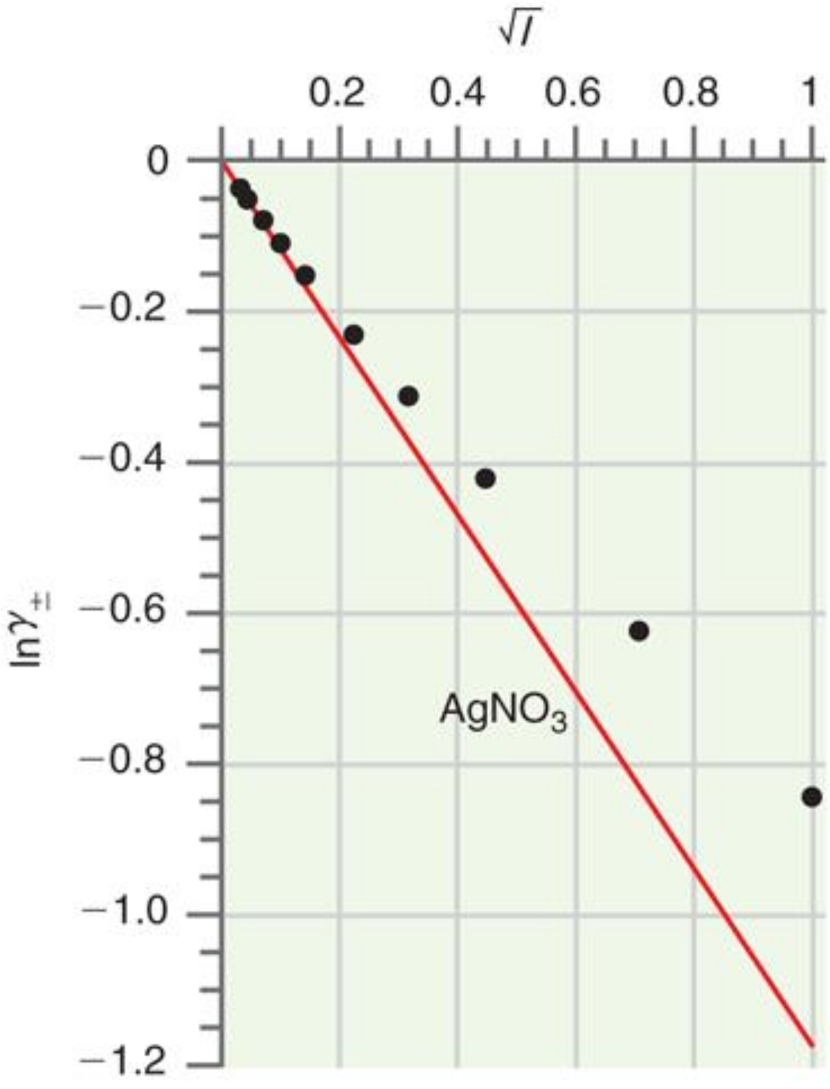
Debye-Huckel Limiting Law

In **dilute** solutions, the logarithm of the mean ionic activity coefficient is proportional to z_+z_- and the square root of the ionic strength I.

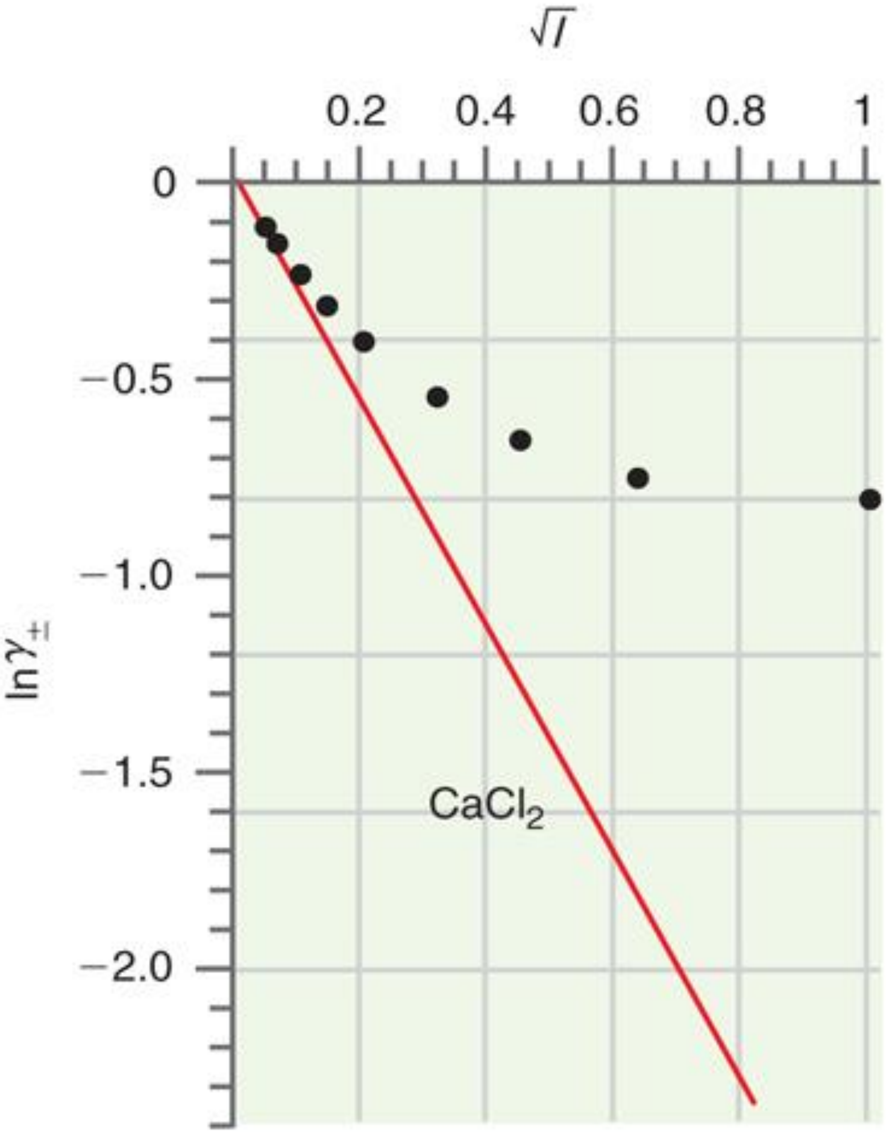
$$I = \frac{z_+^2 m_+ + z_-^2 m_-}{2}$$

$$\ln \gamma_\pm \propto z_+ z_- \sqrt{I}$$

Aqueous $AgNO_3$ at 25 ºC



Aqueous $CaCl_2$ at 25 ºC



limiting slope for
$CaCl_2$ solutions
two times larger
than the slope
for NaCl solutions

Debye-Huckel Theory

- cations and anions in solutions are not randomly distributed

- cations are slightly more likely to be near anions, and *vice versa*

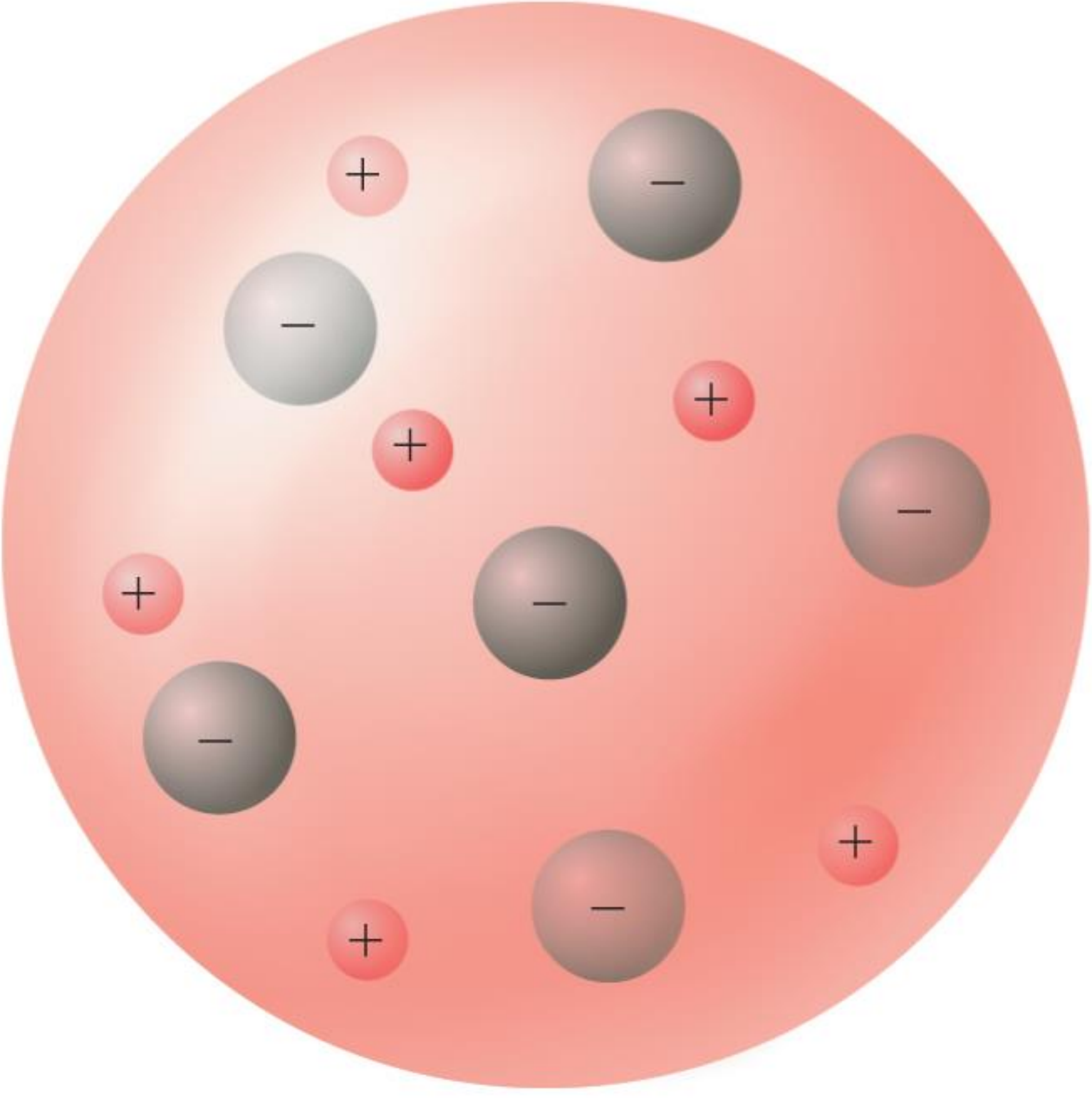
- averaging over time, each ion is surrounded by an "atmosphere" of opposite electric charge

- electrical stabilization (negative charge next to positive charge) reduces the Gibbs energy relative to an ideal solution:

$$\ln\gamma_\pm < 1$$

$$\mu^{\text{nonideal}} = vRT\ln\gamma_\pm < 0$$

Non-Random Distribution of Ions in Solution



Debye-Huckel Theory

Using statistical mechanics to calculate the charge distribution in dilute electrolyte solutions, Debye Huckel derived the **limiting law**:

$$\boxed{\ln \gamma_{\pm} \; = \; -\left| z_{+} z_{-} \right| \frac{e^{2}\kappa}{8\pi\varepsilon_{0}\varepsilon_{\mathrm{r}}k_{\mathrm{B}}T}}$$

$1/\kappa$ is the **Debye-Huckel screening length** (≈ ion atmosphere radius)

$$\kappa \; = \; \sqrt{\frac{2e^{2}N_{\mathrm{A}}\rho_{\mathrm{solvent}}}{\varepsilon_{0}\varepsilon_{\mathrm{r}}k_{\mathrm{B}}T} \; \frac{1000\ \mathrm{L}}{\mathrm{m}^{3}}} \; \sqrt{I}$$

Can you explain why deviations from ideal behavior increase with z_+, z_- and the ionic strength, but decrease if T or the dielectric constant are raised?

e = proton charge
ε_0 = vacuum permittivity
ε_r = dielectric constant

N_A = Avogadro number
ρ_{solvent} = solvent density
k_B = Boltzmann constant

Debye-Huckel Theory

for aqueous electrolyte solutions at 25 °C

solvent density $\rho_{\text{solvent}} = 997.1 \text{ kg m}^{-1}$

solvent dielectric constant $\varepsilon_r = 78.5$

mean ionic activity coefficient:

$$\boxed{\ln \gamma_{\pm} = -1.17 \left| z_+ z_- \right| \sqrt{I}}$$

Debye-Huckel screening length:

$$\kappa = 3.29 \times 10^9 \sqrt{I / (\text{mol kg}^{-1})} \text{ m}^{-1}$$

Debye-Huckel Theory

DH theory is very useful for dilute solutions and for establishing Henry’s law standard states for electrolytes, *but* ...

!!! Warning !!!

DH predictions are accurate only for very dilute solutions.

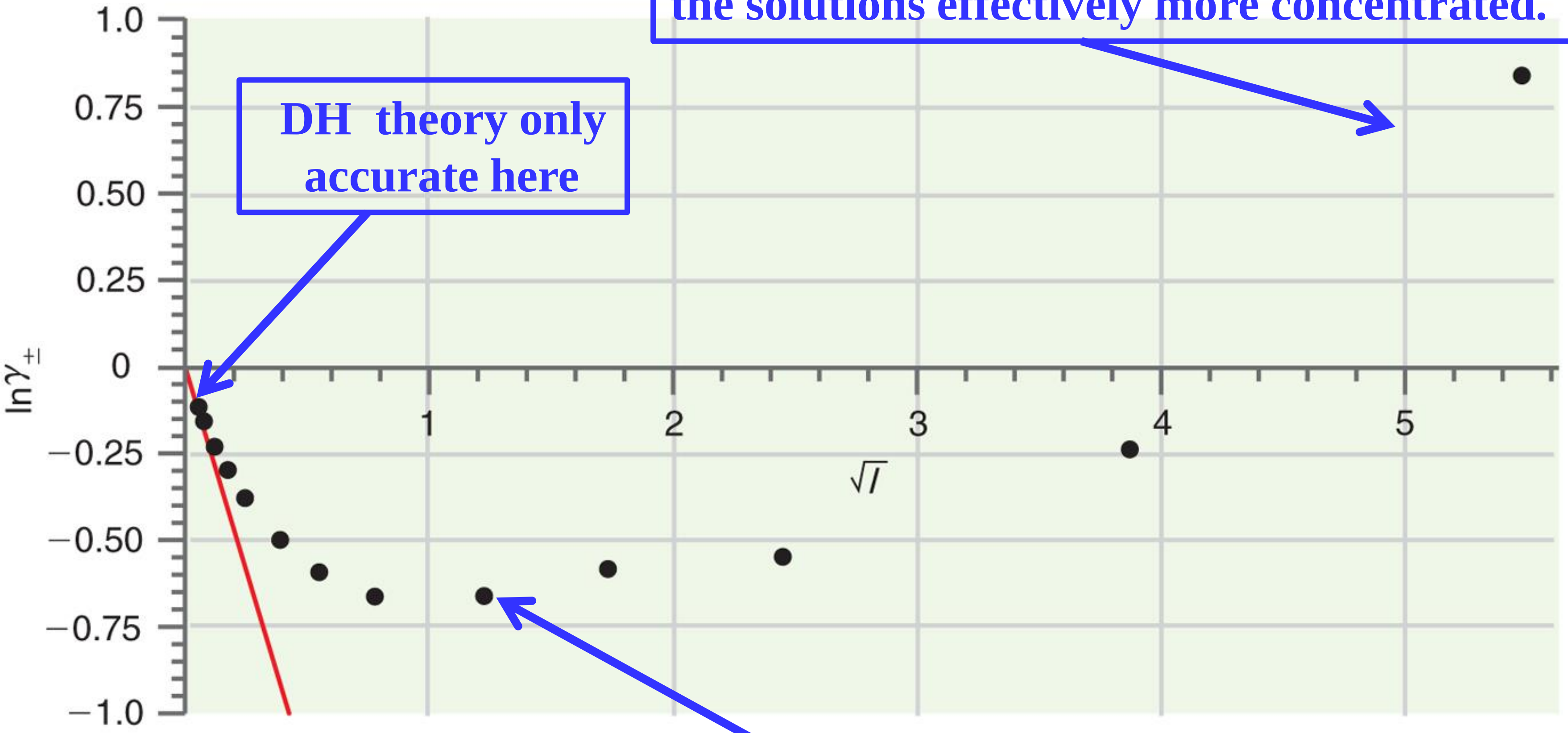
$$I < 0.005 \text{ mol kg}^{-1}$$

Why ?

DH theory does not include:

- specific ion interactions (such as ion binding)
- ion hydration (reduces free-water solvent molecules)

Aqueous $ZnBr_2$ at 25 °C



Ion hydration reduces the amount of free water available to dissolve ions, making the solutions effectively more concentrated.

DH theory only accurate here

$ZnBr^+$, $ZnBr_2$, and $ZnBr_3^-$ complex-ion formation reduces the free Zn^{2+} the free Br^- molalities, reducing the $a_{ZnBr2} = a_{Zn2+}a_{Br-}{}^2$ activity

Section 10.5 Chemical Reaction Equilibrium in Electrolyte Solutions

Tabulated enthalpies, entropies, and Gibbs energies of formation use **Henry's law standard states on the molality scale**.

Example Calculate the equilibrium constant at 25 °C for:

$$\mathbf{MgF_2(s) \rightarrow Mg^{2+}(aq) + 2F^{-}(aq)}$$

$$K = a_{\mathrm{MgF2}} = a_{\mathrm{Mg++}}a_{\mathrm{F-}}{}^{2} = 4\gamma_{\pm}{}^{3}m^{3}$$

$$\Delta G^{\mathrm{o}} = \Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{Mg^{2+},aq}) + 2\Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{F^{-},aq}) - \Delta G_{\mathrm{fm}}{}^{\mathrm{o}}(\mathrm{MgF_2,s})$$

$$= -454.8 + 2(-278.8) - (-965.63) = -46.8\ \mathrm{kJ\ mol^{-1}}$$

$$K = \exp(-\Delta G^{\mathrm{o}}/RT) = \exp[-46800/(8.314 \times 298.15)] = 6.4 \times 10^{-9}$$

Example Calculate the solubility of aqueous MgF_2 at 25 °C.

$$\mathbf{MgF_2(s) \rightarrow Mg^{2+}(aq) + 2F^{-}(aq)}$$

$$K = K_{sp} = a_{MgF2} = a_{Mg++}a_{F-}{}^2 = 4\gamma_\pm{}^3 m^3 = 6.4 \times 10^{-9}$$

1st Approximation

$\gamma_\pm = 1$ $K \approx 4m^3 = 6.4 \times 10^{-9}$ $m = 0.00117 \text{ mol kg}^{-1}$

2nd Approximation

$\ln\gamma_\pm = -1.17|z_+z_-|\,I^{1/2} = -1.17|2|(3m)^{1/2} = -1.17|2|(3 \times 0.00117)^{1/2}$

$\gamma_\pm = 0.870$ $K = 4\,\gamma_\pm{}^3 m^3 = 6.4 \times 10^{-9} \approx 4\,(0.870)^3 m^3$

solve for $0.00134 \text{ mol kg}^{-1}$ (15 % larger than 1st approximation)

$$\mathbf{MgF_2(s) \rightarrow Mg^{2+}(aq) + 2F^{-}(aq)}$$

$$K = K_{\text{sp}} = a_{\text{MgF2}} = a_{\text{Mg++}}a_{\text{F–}}{}^2 = 4\gamma_{\pm}{}^3m^3 = 6.4 \times 10^{-9}$$

3rd Approximation

$\ln\gamma_{\pm} = -1.17|\,z_+z_-|\,I^{\,1/2} = -1.17|\,2|\,(3m)^{\,1/2} = -1.17|\,2\,|\,(3 \times 0.00134)^{\,1/2}$

$\gamma_{\pm} = 0.861$ $\qquad K = 4\,\gamma_{\pm}{}^3m^3 = 6.4 \times 10^{-9} \approx 4\,(0.861)^3m^3$

solve for 0.00136 mol kg^{-1} (16 % larger than 1st approximation)

Etc.

4th Approximation

0.00136 mol kg^{-1} calculation converged