§ 7.5 Theories for strong electrolyte

Out-class extensive reading:
Levine, pp.- 300-304
10.8 The Debye-Hückel theory of electrolyte solution
Goals of this class

(1) Be able to make theoretical thinking;
(2) Be able to establish a simplified theoretical model;
(3) Be able to make model improvement;
(4) Be able to think critically.

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Empirical formula for electrolyte solution

Dynamic property
\[ \Lambda_m = \Lambda_m^\infty - A\sqrt{c} \]

Stationary property
\[ \ln \gamma_\pm = -A\sqrt{I} \]
Stationary property

\[ \ln \gamma_\pm = -A\sqrt{I} \]

For ideal solution:

\[ \mu_i = \mu_i^\ominus(T) + RT \ln m_i \]

\[ (\Delta G)_{T,P} = RT \ln \gamma_i = -W_r' \]

For nonideal solution:

\[ \mu_i = \mu_i^\ominus(T) + RT \ln m_i + RT \ln \gamma_i \]

Theoretical evaluation of \( W_r' \)

Before 1894: solution was treated as ideal gas

1918-1920: Ghosh – crystalline structure
1. The Debye-Hückel theory

   (1) Simplified Model

   Germany, Netherlands
   1884/03/24~ 1966/11/02
   Studies on dipole moments and the diffraction of X rays

   Peter J. W. Debye

   Basic assumptions
   1) Point charge
   2) Only Coulombic attraction
   3) Dielectric constant keep unchanged
   4) Boltzmann distribution, Poisson equation

1. The Debye-Hückel theory

(2) Theoretical treatment

**Shielded Coulombic potential**

\[
\Phi = \frac{Z_J e}{4\pi \varepsilon_0 \varepsilon_r r}
\]

**Debye length**

\[
b = \left(\frac{\varepsilon_0 \varepsilon_r kT}{4N_A Ie^2 \rho_0}\right)^{\frac{1}{2}}
\]

\[
\ln \gamma_i = -\frac{W_r'}{RT}
\]

\[
\ln \gamma_i = \frac{-Z_i^2 e^2}{8\pi \varepsilon_0 \varepsilon_r kTb}
\]

\[
\ln \gamma_i = \frac{-e^3 N_A^2 \rho_0^2}{4\pi (\varepsilon_0 \varepsilon_r kT)^2} Z_i^2 \sqrt{I}
\]
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1. The Debye-Hückel theory

(3) Experimental verification

Group exercise:

Deduce

\[
\ln \gamma_{\pm} = -A \left| Z_+ Z_- \right| \sqrt{I}
\]

Lewis’s empirical equation

from

\[
\ln \gamma_i = -A Z_i^2 \sqrt{I}
\]

for aqueous solution at 298 K

\[
\ln \gamma_{\pm} = -1.172 \left| Z_+ Z_- \right| \sqrt{I}
\]

\[
\lg \gamma_{\pm} = -0.509 \left| Z_+ Z_- \right| \sqrt{I}
\]
Debye-Hückel limiting law holds quite well for dilute solutions when \( I < 0.01 \) m, but must be modified to account for the drastic deviations that occur at high concentrations.

\[
\lg \gamma_{\pm} = \frac{-A|Z^+Z^-|\sqrt{I}}{1 + \alpha\beta\sqrt{I}} = \frac{-A|Z^+Z^-|\sqrt{I}}{1 + \sqrt{I}}
\]

Valid for \( c < 0.1 \text{ mol·kg}^{-1} \)

\[
\lg \gamma_{\pm} = \frac{-A|Z^+Z^-|\sqrt{I}}{1 + \alpha\beta\sqrt{I}} + bI
\]

Valid for \( c < 1 \text{ mol·kg}^{-1} \)

Davies equation
1. The Debye-Hückel theory

1. The Debye-Hückel theory

\[ \ln \gamma_\pm = - z_+ z_- \frac{N_A e^2 b}{8 \pi \varepsilon RT} \]

\[ b = \left[ \frac{N_A^2 e^2}{\varepsilon RT} \sum c_i z_i^2 \right]^{1/2} = \left[ \frac{N_A^2 e^2 \rho_0}{\varepsilon RT} \sum m_i z_i^2 \right]^{1/2} = BI^{1/2} \]

\[ \ln \gamma_\pm = - z_+ z_- \frac{N_A e^2}{8 \pi \varepsilon RT} BI^{1/2} \]

\[ \log \gamma_\pm = - A |z_+ z_-| I^{1/2} = -0.509 |z_+ z_-| I^{1/2} \]
1. The Debye-Hückel theory

The Debye–Hückel theory was proposed by Peter Debye and Erich Hückel as a theoretical explanation for departures from ideality in solutions of electrolytes and plasmas. It is a linearized Poisson–Boltzmann model, which assumes an extremely simplified model of the electrolyte solution but nevertheless gave accurate predictions of mean activity coefficients for ions in dilute solution. The Debye–Hückel equation provides a starting point for modern treatments of non-ideality of electrolyte solutions.

Limitations and extensions: hopelessly oversimplified

(1) Complete dissociation; (2) Weak electrolytes; (3) Ions are spherical, point charge and polarized; (4) Role of the solvent
In 1926, Onsager pointed out that as the ion moves across the solution, its ionic atmosphere is repeatedly being destroyed and formed again. The time for formation of a new ionic atmosphere (relaxation time) is \( \text{ca. } 10^{-7} \text{ s} \) in an 0.01 mol·kg\(^{-1}\) solution.

Under normal conditions, the velocity of an ion is sufficiently slow so that the electrostatic force exerted by the atmosphere on the ion tends to retard its motion and hence to decrease the conductance.

2. Debye-Hückel-Onsage theory

\[
\Lambda = \Lambda^\infty - \left[ \frac{2.08 \times 10^6 |Z_+ Z_-| q A^\infty}{(\varepsilon T)^2 (1+\sqrt{q})} + \frac{41.25 (|Z_+| + |Z_-|)}{\eta \sqrt{\varepsilon T}} \right] \sqrt{I}
\]

\[
\Lambda = \Lambda^\infty - (\alpha \Lambda^\infty + \beta) \sqrt{I}
\]

Valid for \(3 \times 10^{-5} \sim 10^{-3} \text{ mol} \cdot \text{kg}^{-1}\)

Fuoss: valid for < 0.1 mol·kg\(^{-1}\)

Falkenhagen: valid for < 5 mol·kg\(^{-1}\), for LiCl: valid until 9 mol·kg\(^{-1}\)

Lars Onsager, 1968 Noble Prize
USA, Norway
1903/11/27~1976/10/05
Studies on the thermodynamics of irreversible processes
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**Process for establishing a theory**

1. Problem-orientation
2. Method-principle
3. Study-data
4. Results-analysis
5. Empirical law

**Empirical law**

1. Propose a simplified Model
2. Theoretical treatment
3. Experimental verification
4. Modification
5. Theory
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Progress of the theories for electrolyte

1800: Nicholson and Carlisle: electrolysis of water—conductivity
1805: Grotthuss: orientation of molecules – molecular wire
1857: Clausius: embryo of dissociation
1886: vant’ Hoff: colligative property – vant’ Hoff factor
1887: Arrhenius: dissociation and ionization – electrolyte, ion
1918: Ghosh: crystalline structure – first structure model
1923: Debye-Hückel: Debye-Hückel theory – activity coefficient
1926: Bjerrum: conjugation theory – ionic pair
1927: Onsager: Debye-Hückel-Onsager theory
1948: Robinson and Stokes: solvation theory – reason for ionization
Question-1:

Compare the solubility of AgCl(s) in NaCl solution, pure water, and concentrated KNO₃ solution using that in pure water as standard.

\[ \text{AgCl(s)} = \text{Ag}^+\text{(aq)} + \text{Cl}^-\text{(aq)} \]

**On solubility equilibrium**

(1) The effect of co-ion;

(2) The effect of additional electrolyte: salt effect