

Advanced Electrochemistry

CHEM1001C

(Physical Chemistry Special)

The Syllabus

Course No. CHEM 1001C (FM = 50; C = 4)
Physical Special - I

Unit 4 Advanced Electrochemistry (M = 15)

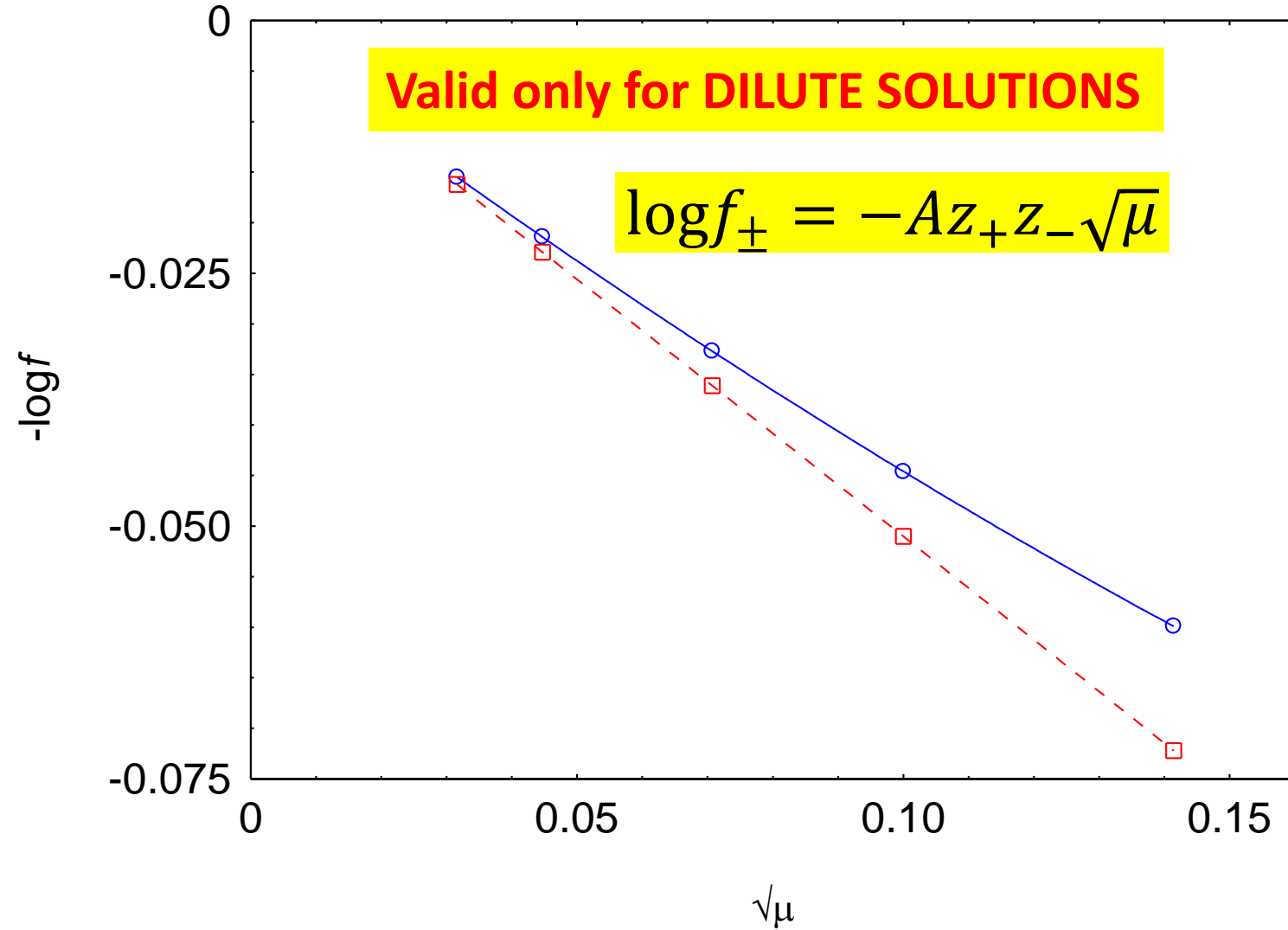
Limitation of Debye-Hückel limiting law and its extension; Pitzer ion-interaction approach. Debye-Hückel-Onsager (DHO) theory of electrical conduction of electrolytes, electrophoretic and relaxation effects, Wien effect, Debye-Falkenhagen effect, application of DHO theory. Limitation of DHO equation and Shedlovsky approach.

Double layer studies: nature of the double layer across electrode-solution interface, polarizable and non-polarizable electrodes, electrocapilarity (EC) – nature of EC curves, its thermodynamics, Lipmann equation, Helmholtz, Guoy-Chapman and Stern double layer models. Electron transfer reactions; fuel cells.

References

- 1. Modern Electrochemistry 1: Ionics by J.O'M. Bockris & A.K.N. Reddy**
- 2. Modern Electrochemistry 2A: Fundamentals of Electrodeics by J.O'M. Bockris & A.K.N. Reddy**
- 3. Modern Electrochemistry 2B: Electrodeics in Chemistry, Engineering, Biology and Environmental Sciences by J.O'M. Bockris & A.K.N. Reddy**
- 4. An Introduction to Electrochemistry by S. Glasstone**
- 5. Textbook of Physical Chemistry by S. Glasstone**
- 6. Chemical Kinetics by K.J. Laidler**

Limitation of Debye-Hückel Theory



Reason: Assumptions do not hold true for concentrated solutions

Extension of DH Theory to Concentrated Solutions

Conc. of a 1:1 Electrolyte Solution in H ₂ O at 298.15 K (mol.L ⁻¹)	Thickness of Ionic Atmosphere (κ^{-1}) (Angstrom)
0.0001	304
0.001	96
0.01	30.4
0.1	9.6

$$\begin{aligned}\kappa^2 &= \frac{4\pi e_0^2}{\epsilon kT} \sum n_0^2 z_i^2 \\ &= \frac{4\pi N_A e_0^2}{1000\epsilon kT} \sum c_i z_i^2 \\ &= \frac{8\pi N_A e_0^2}{1000\epsilon kT} \mu\end{aligned}$$

Crystallographic Radius of Na⁺ = 0.95 Å

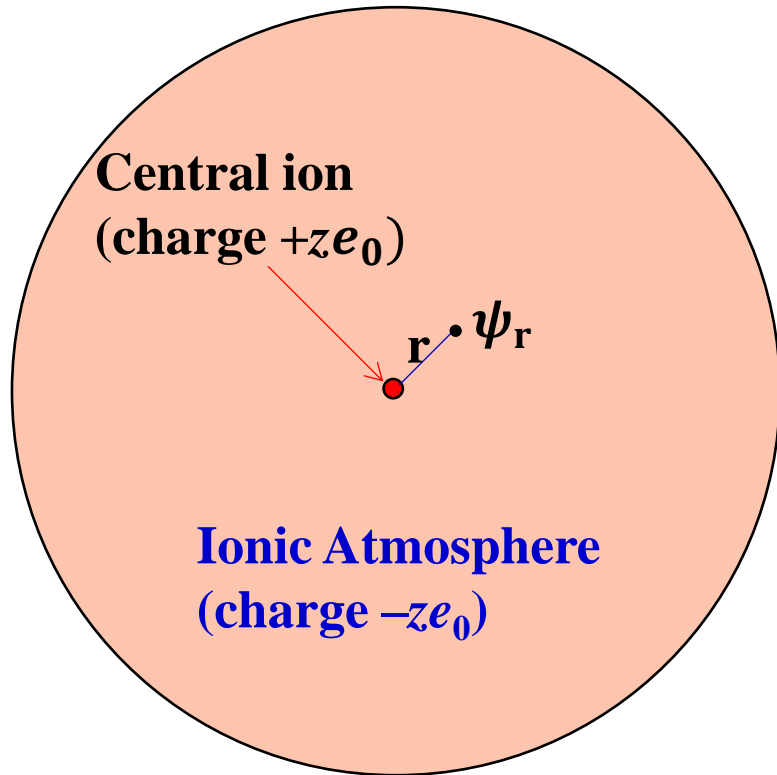
Crystallographic Radius of K⁺ = 1.33 Å

Crystallographic Radius of Cl⁻ = 1.81 Å

Crystallographic Radius of Br⁺ = 0.95 Å

**Ions cannot be considered
as point charges in
concentrated solutions**

Where did we Use this Assumption?



$$\nabla^2 \psi_r = \kappa^2 \psi_r$$

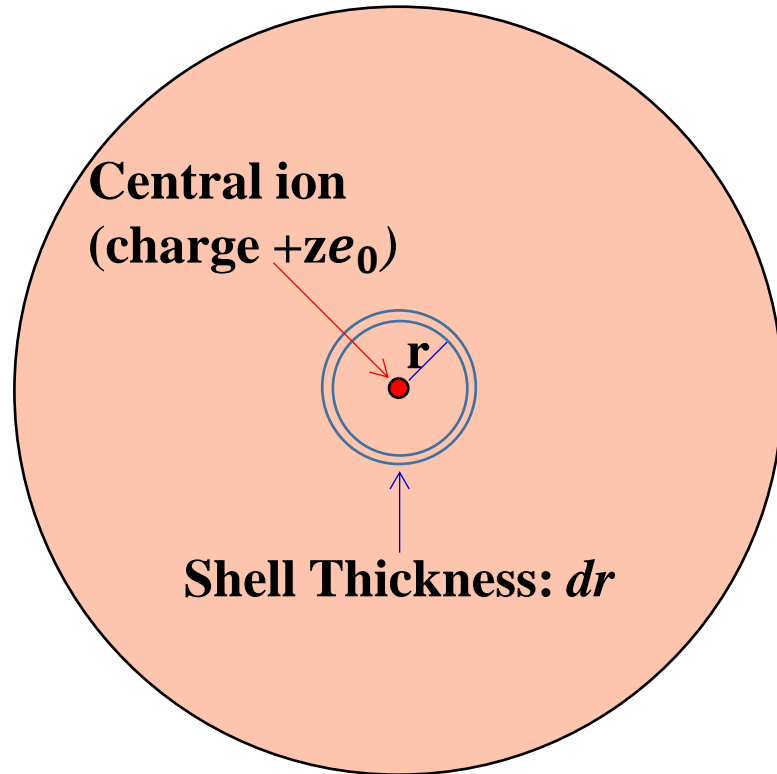
Or,
$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\psi_r}{dr} \right) = \kappa^2 \psi_r$$

Solution:
$$\psi_r = \frac{A}{r} e^{-\kappa r} + \frac{B}{r} e^{+\kappa r}$$

B was found to be 0:
$$\psi_r = \frac{A}{r} e^{-\kappa r}$$

A was then evaluated assuming the ion to be a point charge.
$$A = \frac{ze_0}{\epsilon}$$

Re-evaluation of A considering Ions of Finite Size



$$\text{Volume of Spherical Shell} = 4\pi r^2 dr$$

$$\text{Volume of Ionic Atmosphere} = \int_a^\infty 4\pi r^2 dr$$

[a = distance of closest approach of the central ion and an oppositely charged ion]

$$\begin{aligned} \text{Total Charge of the Ionic Atmosphere} \\ = \int_a^\infty 4\pi r^2 dr \cdot \rho_r \end{aligned}$$

[ρ_r : Charge density at a distance or r from the central ion]

$$= -ze_0 \quad (\text{since the soln is electroneutral})$$

Re-evaluation of A considering Ions of Finite Size

Charge density: $\rho_r = \sum n_i^0 z_i e_0 e^{-z_i e_0 \psi_r / kT}$

If $z_i e_0 \psi_r / kT \ll 1$: $\rho_r = \sum n_i^0 z_i e_0 \left(1 - \frac{z_i e_0 \psi_r}{kT} \right)$

$$= - \sum \frac{n_i^0 z_i^2 e_0^2}{kT} \psi_r$$

[$\sum n_i^0 z_i e_0 = 0$ (electroneutrality)]

$$= - A \frac{e^{-\kappa r}}{r} \sum \frac{n_i^0 z_i^2 e_0^2}{kT} \psi_r$$

[Since, $\psi_r = \frac{A}{r} e^{-\kappa r}$]

$$= - A \frac{e^{-\kappa r}}{r} \left[\frac{4\pi e_0^2}{\epsilon kT} \sum n_i^0 z_i^2 \right] \frac{\epsilon}{4\pi}$$

$$= - A \frac{e^{-\kappa r}}{r} \cdot \frac{\kappa^2 \epsilon}{4\pi}$$

Re-evaluation of A considering Ions of Finite Size

$$\int_a^{\infty} 4\pi r^2 dr \rho_r = -ze_0 \quad \rho_r = -A \frac{e^{-\kappa r}}{r} \cdot \frac{\kappa^2 \epsilon}{4\pi}$$

Combining the above equations:

$$-\int_a^{\infty} 4\pi r^2 dr A \frac{e^{-\kappa r}}{r} \cdot \frac{\kappa^2 \epsilon}{4\pi} = -ze_0$$

$$\text{Or, } A\kappa^2 \epsilon \int_a^{\infty} r e^{-\kappa r} dr = ze_0$$

Re-evaluation of A considering Ions of Finite Size

$$A\kappa^2 \varepsilon \int_a^\infty r e^{-\kappa r} dr = z e_0$$

Let, $y = \kappa r$; so $r = \frac{y}{\kappa}$, and $dr = \frac{dy}{\kappa}$

When $r = a$, $y = \kappa a$, and when $r = \infty$, $y = \infty$

Therefore, $A\kappa^2 \varepsilon \int_{\kappa a}^\infty \frac{y}{\kappa a} e^{-y} \frac{dy}{\kappa} = z e_0$

Or, $A\varepsilon \int_{\kappa a}^\infty y e^{-y} dy = z e_0$

Potential (ψ_r) at Appreciable Concentrations

$$A\varepsilon \int_{\kappa a}^{\infty} ye^{-y} dy = ze_0$$

$$\text{Or, } A\varepsilon \left[y \cdot (-e^{-y}) - \int 1 \cdot (-e^{-y}) dy \right]_{\kappa a}^{\infty} = ze_0$$

$$\text{Or, } A\varepsilon \left[-ye^{-y} + \int e^{-y} dy \right]_{\kappa a}^{\infty} = ze_0$$

$$\text{Or, } A\varepsilon [-ye^{-y} - e^{-y}]_{\kappa a}^{\infty} = ze_0$$

$$\text{Or, } A\varepsilon [e^{-y}(1 + y)]_{\infty}^{\kappa a} = ze_0$$

$$\text{Or, } A\varepsilon \cdot e^{-\kappa a}(1 + \kappa a) = ze_0$$

$$A = \frac{ze_0}{\varepsilon} \frac{e^{\kappa a}}{1 + \kappa a}$$

$$\text{Since, } \psi_r = \frac{A}{r} e^{-\kappa r}$$

Potential at r from the central ion:

$$\psi_r = \frac{ze_0}{\varepsilon r} e^{-\kappa r} \frac{e^{\kappa a}}{1 + \kappa a}$$

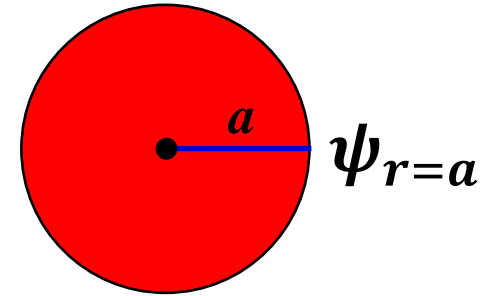
[Applicable for concentrated solutions]

Work of Charging the Reference (Central) Ion

Potential at the surface (i.e., when $r = a$) of the central ion:

$$\psi_{r=a} = \frac{ze_0}{\epsilon a} e^{-\kappa a} \frac{e^{\kappa a}}{1 + \kappa a} = \frac{ze_0}{\epsilon a} \cdot \frac{1}{1 + \kappa a} = \frac{e}{\epsilon a} \cdot \frac{1}{1 + \kappa a}$$

(replacing ze_0 by e)



Work of charging the central ion:

$$W = \int_0^e \psi_{r=a} de$$

$$W = \int_0^e \frac{e}{\epsilon a} \cdot \frac{1}{1 + \kappa a} de$$

This is the work of charging the Central ion in a solution of given concentration *in presence of ionic atmosphere.*

Work of Charging in an Infinitely Dilute Solution

$$W = \int_0^e \frac{e}{\epsilon a} \cdot \frac{1}{1+\kappa a} de \quad [\text{in presence of ionic atmosphere}]$$

In an Infinitely dilute solution: $\kappa = 0$

$$\text{Note: } \kappa^2 = \frac{8\pi N_A e_0^2}{1000 \epsilon k T} \mu$$

$$\text{Work of charging in infinitely dilute solution: } W_{\text{id}} = \int_0^e \frac{e}{\epsilon a} = \frac{e^2}{2\epsilon a} = \frac{z^2 e_0^2}{2\epsilon a}$$

[In absence of ionic atmosphere]

Free Energy due to Electrical Interactions

$$W = \int_0^e \frac{e}{\epsilon a} \cdot \frac{1}{1+\kappa a} de \quad (\text{In presence of ionic atmosphere})$$

$$W_{id} = \int_0^e \frac{e}{\epsilon a} = \frac{e^2}{2\epsilon a} = \frac{z^2 e_0^2}{2\epsilon a} \quad (\text{In absence of ionic atmosphere})$$

$W - W_{id}$ = Free energy due to electrical interaction

$$= \frac{z^2 e_0^2}{2\epsilon a} \left[\frac{1}{1+\kappa a} - 1 \right] = - \frac{z^2 e_0^2}{2\epsilon a} \frac{\kappa}{1+\kappa a} \quad \text{per ion}$$

$$= - N_A \frac{z^2 e_0^2}{2\epsilon a} \frac{\kappa}{1+\kappa a} \quad \text{per g. ion}$$

Free Energy due to Electrical Interactions

The Free Energy per g. ion in an Ideal Solution:

$$\mu = \mu^0 + RT \ln x$$

The Free Energy per g. ion in a Non-ideal Solution:

$$\mu = \mu^0 + RT \ln a = \mu^0 + RT \ln x + RT \ln f$$

The Free Energy per g. ion due to electrical interactions: $RT \ln f$

Single-Ion Activity Coefficient = $f(\mu)$

$$RT \ln f = - \frac{N_A z^2 e_0^2 \kappa}{2 \epsilon} \cdot \frac{1}{1 + \kappa a}$$

$$\text{Or, } \ln f = - \frac{N_A z^2 e_0^2 \kappa}{2 \epsilon RT} \cdot \frac{1}{1 + \kappa a}$$

$$\text{Or, } \log f = - \frac{N_A z^2 e_0^2 \kappa}{2 \times 2.303 \epsilon RT} \cdot \frac{1}{1 + \kappa a}$$

Note: $\kappa^2 = \frac{8\pi N_A e_0^2}{1000 \epsilon k T} \mu = B^2 \cdot \mu$

$$\text{Or, } \log f = - \frac{N_A z^2 e_0^2}{2 \times 2.303 \epsilon RT} B \sqrt{\mu} \cdot \frac{1}{1 + B \sqrt{\mu} a}$$

$$\text{Or, } \log f = - \frac{A' z^2 \sqrt{\mu}}{1 + a B \sqrt{\mu}}$$

Mean Ionic Activity Coefficient of Electrolyte = $f(\mu)$



$$f_{\pm}^{\nu_+ + \nu_-} = f_{\pm}^{\nu} = f_+^{\nu_+} \cdot f_-^{\nu_-}$$

$$\nu \log f_{\pm} = \nu_+ \log f_+ + \nu_- \log f_-$$

$$\log f = - \frac{A' z^2 \sqrt{\mu}}{1 + aB\sqrt{\mu}}$$

$$= - \nu_+ \frac{A' z_+^2 \sqrt{\mu}}{1 + aB\sqrt{\mu}} - \nu_- \frac{A' z_-^2 \sqrt{\mu}}{1 + aB\sqrt{\mu}}$$

$$= - \frac{A' \sqrt{\mu}}{1 + aB\sqrt{\mu}} (\nu_+ z_+^2 + \nu_- z_-^2) = - \frac{A' \sqrt{\mu}}{1 + aB\sqrt{\mu}} (\nu_+ z_+ z_+ + \nu_- z_- z_-)$$

$$= - \frac{A' \sqrt{\mu}}{1 + aB\sqrt{\mu}} (\nu_- z_- z_+ + \nu_+ z_+ z_-) = \frac{A' \sqrt{\mu}}{1 + aB\sqrt{\mu}} z_+ z_- (\nu_+ + \nu_-)$$

$$\log f_{\pm} = - \frac{A' z_+ z_- \sqrt{\mu}}{1 + aB\sqrt{\mu}}$$

- Extended DH Equation
- Applicable for appreciable concentration

Pitzer Ion-Interaction Approach

The mean ionic activity coefficient of an electrolyte in solution is given by:

$$\ln \gamma = |z_M z_X| f^\gamma + \frac{2\nu_M \nu_X}{\nu} m B^\gamma + \frac{2(\nu_M \nu_X)^{3/2}}{\nu} m^2 C^\gamma \quad [\text{Applied up to saturation}]$$

$[\nu_M, \nu_X$: no. of ions in the formula; z_M, z_X : charges on ions; $\nu = \nu_M + \nu_X$; m = molality]

$$f^\gamma = f^\phi + (2/b) A_\phi \ln(1 + bI^{1/2}) \quad [b = 1.2]$$

$$B^\gamma = 2\beta^{(0)} + \frac{2\beta^{(1)}}{x^2} [1 - e^{-x}(1 + x - 0.5x^2)]$$

$$x = \alpha I^{1/2} \quad [I = \text{Ionic strength and } \alpha = 2]$$

$$A_\phi = \frac{1}{3} \left(\frac{2\pi N_0 d_w}{1000} \right)^{1/2} \left(\frac{e^2}{\epsilon k T} \right)^{3/2} \quad [d_w = \text{Density of H}_2\text{O}]$$

[Ref: KS Pitzer, J. Phys. Chem., 77, 268 (1973)]

Till 13-04-21