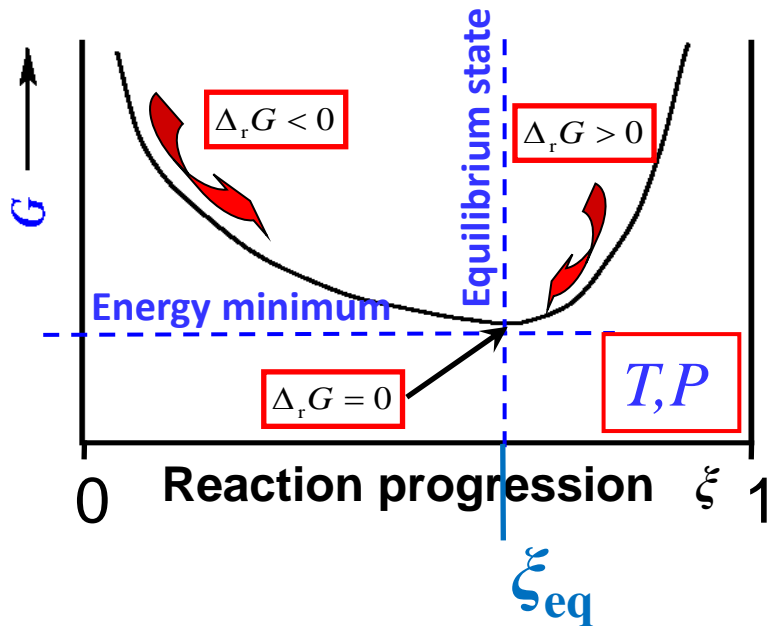


Classical thermodynamics: reaction equilibria: K

Second law →

$$dG|_{P,T} \leq 0$$

$$\Delta_r G \equiv \left(\frac{\partial G}{\partial \xi} \right)_{T,P}$$



$\Delta_r G$ reaction

$$\Delta_r G < 0$$



$$\Delta_r G > 0$$



$$\Delta_r G = 0$$



$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

$$Q = \prod_i a_i^{v_i}$$

Equilibrium constant

$$-RT \ln K = \Delta_r G^\ominus = \sum_i v_i \Delta_f G_{m,i}^\ominus$$

$$P^\ominus \equiv 1 \text{ bar}$$

Classical thermodynamics: reaction equilibria: K

$$\Delta_r G = \Delta_r G^\ominus + RT \ln \prod_i a_i^{\nu_i} = \Delta_r G^\ominus + RT \ln Q$$

Equilibrium: $\Delta_r G = 0 \Rightarrow \Delta_r G^\ominus = -RT \ln Q_{eq} \equiv -RT \ln K$

Electrochemical equilibria: $\Delta_r G = -\nu FE$ $\Delta_r G^\ominus = -\nu FE^\ominus$

$$E = E^\ominus - \frac{RT}{\nu F} \ln \prod_i a_i^{\nu_i} = E^\ominus - \frac{RT}{\nu F} \ln Q$$

Nernst equation

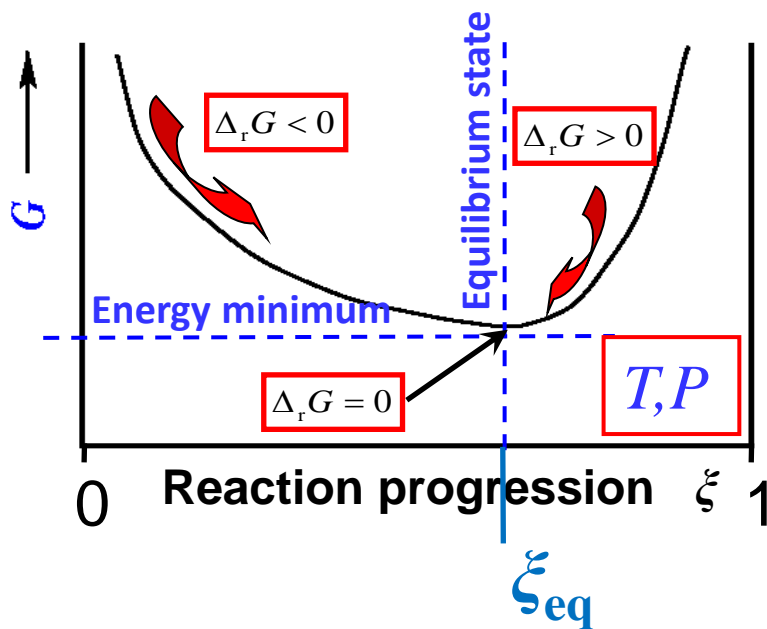
Equilibrium: $E = 0 \Rightarrow E^\ominus = \frac{RT}{\nu F} \ln Q_{eq} \equiv \frac{RT}{\nu F} \ln K$

Classical thermodynamics: reaction equilibria: K

Second law →

$$dG|_{P,T} \leq 0$$

$$\Delta_r G = -vFE$$



$\underline{\Delta_r G}$

reaction

\underline{E}

$$\Delta_r G < 0$$



$$E > 0$$

$$\Delta_r G > 0$$



$$E < 0$$

$$\Delta_r G = 0$$



$$E = 0$$

$$\Delta_r G = \Delta_r G^\ominus + RT \ln Q$$

$$Q = \prod_i a_i^{v_i}$$

Equilibrium constant

$$-RT \ln K = \Delta_r G^\ominus = \sum_i v_i \Delta_f G_{m,i}^\ominus = -vFE^\ominus$$

$$P^\ominus \equiv 1 \text{ bar}$$

Classical thermodynamics: reaction equilibria: K

$$Q = \prod_i a_i^{\nu_i}$$

Activity a_i

$$\mu_i \equiv \mu_i^\ominus + RT \ln a_i$$

Standard state $^\ominus$
(still T dependent)

$$P = P^\ominus$$

pure compound in its **reference** state at T

$$a_i = 1$$

perfect gas

$$a_i = \frac{P_i}{P^\ominus}$$

P_i : partial pressure

real gas

$$a_i = \frac{f_i}{P^\ominus}$$

f_i : fugacity

(pure) solid

$$a_s \approx 1$$

(pure) liquid

$$a_l \approx 1$$

Activity (liquid) mixtures of neutral components

$$Q = \prod_i a_i^{v_i}$$

Activity a_i

$$\mu_i = \mu_i^* + RT \ln a_i$$

Standard state *
(still T dependent)

{

$$P = P_i^*$$

Vapour pressure pure liquid i

Ideal solutions (Raoult)

$$a_i^{(l)} = \frac{P_i^{(g)}}{P_i^*} = x_i^{(l)}$$

Real solutions

γ_i : activity coefficient

$$a_i^{(l)} = \frac{P_i^{(g)}}{P_i^*} = \gamma_i^{(l)} x_i^{(l)}$$

Activity (liquid) mixtures of neutral components

$$Q = \prod_i a_i^{v_i}$$

Activity a_i

$$\mu_i = \mu_i^* + RT \ln a_i$$

Standard state *
(still T dependent)

{

$$P = P_i^*$$

Vapour pressure pure liquid i

Ideal solutions (Raoult)

$$a_i^{(l)} = \frac{P_i^{(g)}}{P_i^*} = x_i^{(l)}$$

Real solutions

γ_i : activity coefficient

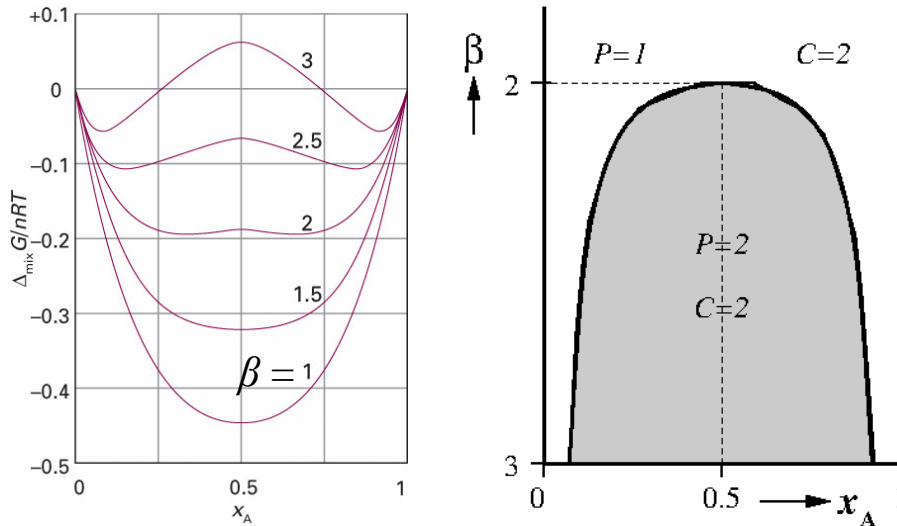
$$a_i^{(l)} = \frac{P_i^{(g)}}{P_i^*} = \gamma_i^{(l)} x_i^{(l)}$$

$$\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i = \mu_i^{\text{ideal}} + RT \ln \gamma_i$$

Activity (liquid) mixtures of neutral components

Regular solution example: $G^E = nRT \beta x_A x_B$

(L-L separation exercise 17)

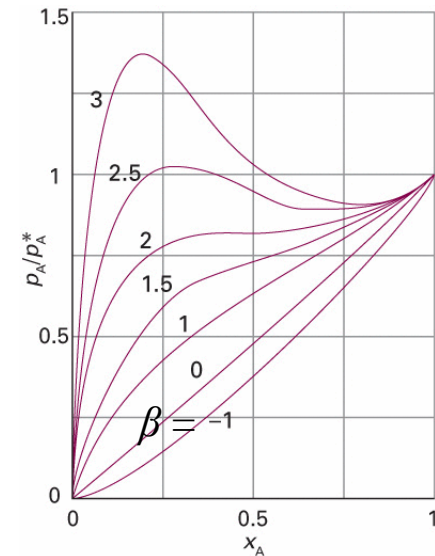
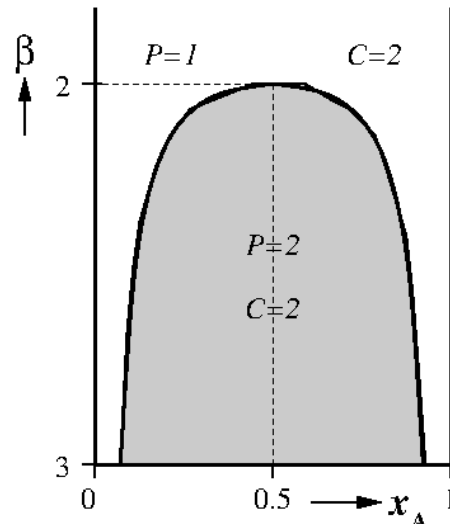
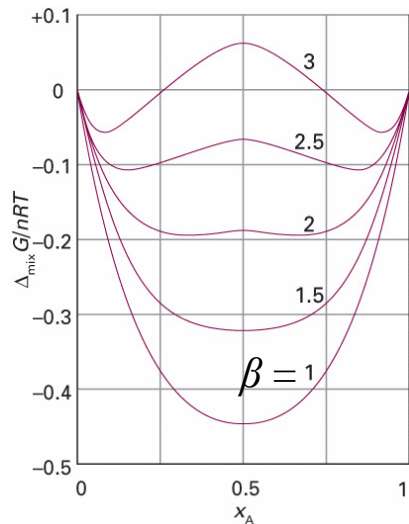


$$\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i = \mu_i^{\text{ideal}} + RT \ln \gamma_i$$

Activity (liquid) mixtures of neutral components

Regular solution example: $G^E = nRT \beta x_A x_B$

(L-L separation exercise 17)



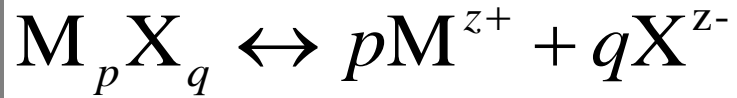
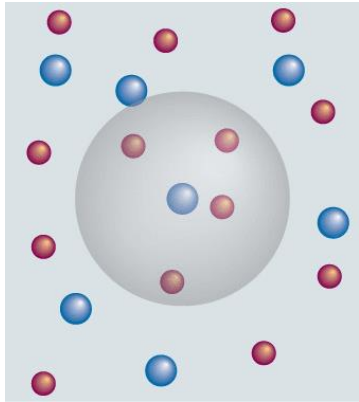
$$\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i = \mu_i^{\text{ideal}} + RT \ln \gamma_i$$

$$a_i^{(l)} = \frac{P_i^{(g)}}{P_i^*} = \gamma_i^{(l)} x_i^{(l)} = x_i^{(l)} \exp \left[\beta (1 - x_i^{(l)})^2 \right]$$

(See also
Additional exercises I
Exercise A4) 8

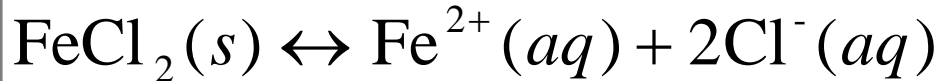
Activity coefficients solutes electrolytic solutions

Activity coefficients solutes electrolytic solutions



$$G_m (M_p X_q) = \mu = p\mu_+ + q\mu_- \quad \text{chemical potential of dissolved salt}$$

example



$$\begin{cases} p = 1 \\ z_+ = +2 \\ q = 2 \\ z_- = -1 \end{cases}$$

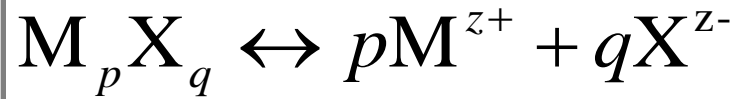
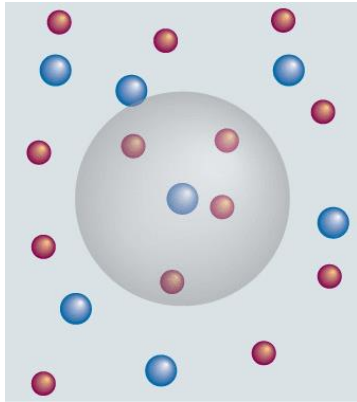
example



$$\begin{cases} p = 2 \\ z_+ = +3 \\ q = 3 \\ z_- = -2 \end{cases}$$

→ If solubility is $s_{Fe_2(SO_4)_3}$ (mol/kg) then $b_{Fe^{3+}} = 2s$ and $b_{SO_4^{2-}} = 3s$

Activity coefficients solutes electrolytic solutions



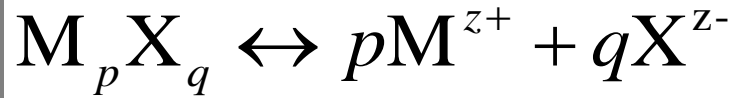
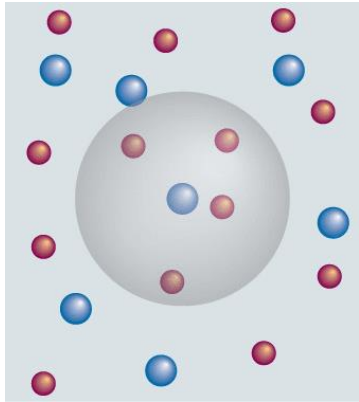
$$G_m (\text{M}_p \text{X}_q) = \mu = p\mu_+ + q\mu_- \quad \text{chemical potential of dissolved salt}$$

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_+$$

$$\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_-$$

$$(\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i = \mu_i^{\text{ideal}} + RT \ln \gamma_i)$$

Activity coefficients solutes electrolytic solutions



$$G_m (M_p X_q) = \mu = p\mu_+ + q\mu_- \quad \text{chemical potential of dissolved salt}$$

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_+$$

$$\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_-$$

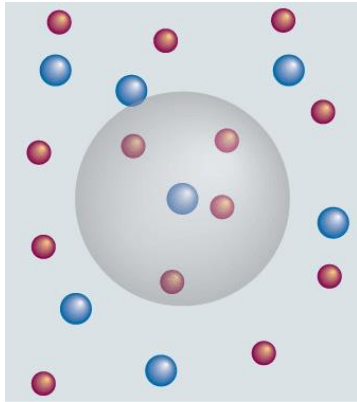
$$(\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i = \mu_i^{\text{ideal}} + RT \ln \gamma_i)$$

It is impossible to determine (measure) μ_+ and μ_- individually

→

$$\left\{ \begin{array}{l} \mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm} \\ \text{Mean activity coefficient} \\ \gamma_{\pm} \equiv (\gamma_+^p \gamma_-^q)^{1/s} ; s \equiv p + q \end{array} \right.$$

Activity coefficients solutes electrolytic solutions



$$G_m (M_p X_q) = \mu = p\mu_+ + q\mu_-$$

chemical potential of dissolved salt

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_+$$

$$\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_-$$

$$(\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln \nu_i + RT \ln \gamma_i = \mu_i^{\text{ideal}} + RT \ln \gamma_i)$$

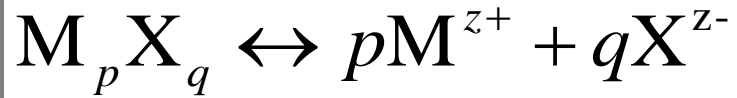
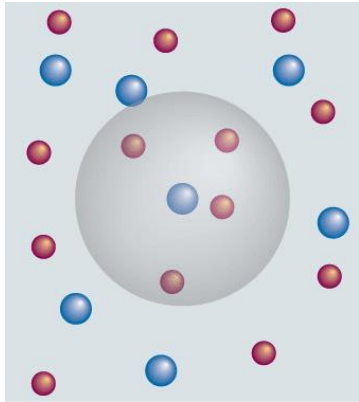
$$\mu_{\pm} = \mu_{\pm}^{\text{ideal}} + RT \ln \gamma_{\pm}$$

Mean activity coefficient

$$\gamma_{\pm} \equiv (\gamma_+^p \gamma_-^q)^{1/s} ; s \equiv p + q$$

Let's work this out in detail

Activity coefficients solutes electrolytic solutions



$$G_m (\text{M}_p \text{X}_q) = \mu = p\mu_+ + q\mu_- \quad \text{chemical potential of dissolved salt}$$

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_+$$

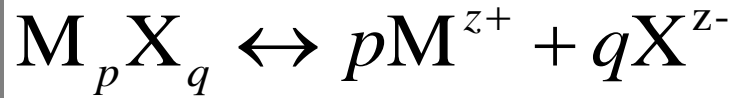
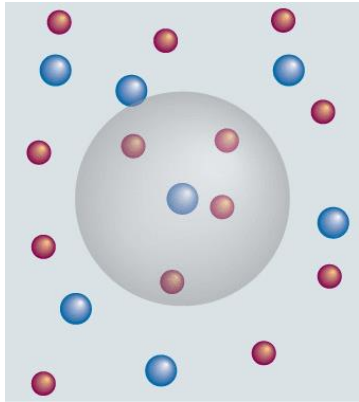
$$\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_-$$

$$(\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i = \mu_i^{\text{ideal}} + RT \ln \gamma_i)$$



$$\mu^{\text{ideal}} = p\mu_+^{\text{ideal}} + q\mu_-^{\text{ideal}}$$

Activity coefficients solutes electrolytic solutions



$$G_m (M_p X_q) = \mu = p\mu_+ + q\mu_- \quad \text{chemical potential of dissolved salt}$$

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_+$$

$$\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_-$$



$$\mu^{\text{ideal}} = p\mu_+^{\text{ideal}} + q\mu_-^{\text{ideal}}$$

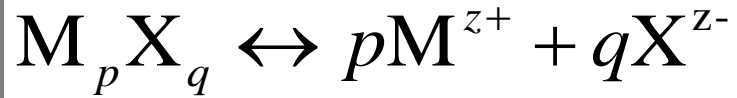
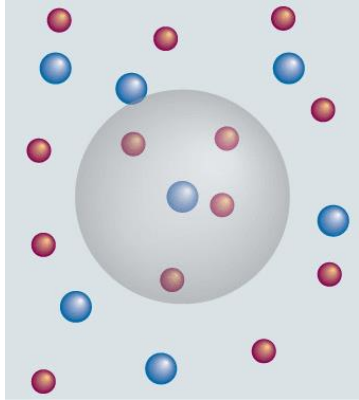
Real solution:

$$\mu = p\mu_+ + q\mu_- = \mu^{\text{ideal}} + pRT \ln \gamma_+ + qRT \ln \gamma_-$$



$$\mu = \mu^{\text{ideal}} + RT \ln \gamma_+^p \gamma_-^q$$

Activity coefficients solutes electrolytic solutions



$$G_m(M_p X_q) = \mu = p\mu_+ + q\mu_- \quad \text{chemical potential of dissolved salt}$$

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_+$$

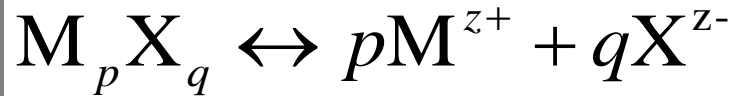
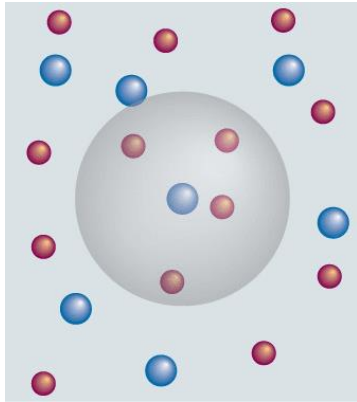
$$\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_-$$

$$\mu^{\text{ideal}} = p\mu_+^{\text{ideal}} + q\mu_-^{\text{ideal}}$$



$$\mu = \mu^{\text{ideal}} + RT \ln \gamma_+^p \gamma_-^q$$

Activity coefficients solutes electrolytic solutions



$$G_m (\text{M}_p \text{X}_q) = \mu = p\mu_+ + q\mu_- \quad \text{chemical potential of dissolved salt}$$

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_+$$

$$\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_-$$

$$\mu^{\text{ideal}} = p\mu_+^{\text{ideal}} + q\mu_-^{\text{ideal}}$$



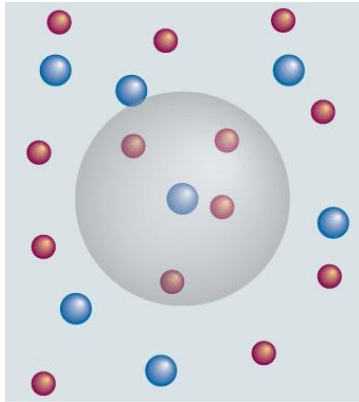
$$\mu = \mu^{\text{ideal}} + RT \ln \gamma_+^p \gamma_-^q$$

average chemical potential per ion
(*i* labels any of the ions)

$$\mu_i = \frac{\mu}{p+q} = \frac{\mu^{\text{ideal}}}{p+q} + \frac{RT}{p+q} \ln (\gamma_+^p \gamma_-^q)$$

(The solution has to be electrically neutral)

Activity coefficients solutes electrolytic solutions



$$G_m (\text{M}_p \text{X}_q) = \mu = p\mu_+ + q\mu_- \quad \text{chemical potential of dissolved salt}$$

$$\mu_+ = \mu_+^{\text{ideal}} + RT \ln \gamma_+$$

$$\mu_- = \mu_-^{\text{ideal}} + RT \ln \gamma_-$$

$$\mu^{\text{ideal}} = p\mu_+^{\text{ideal}} + q\mu_-^{\text{ideal}}$$



$$\mu = \mu^{\text{ideal}} + RT \ln \gamma_+^p \gamma_-^q$$

average chemical potential per ion

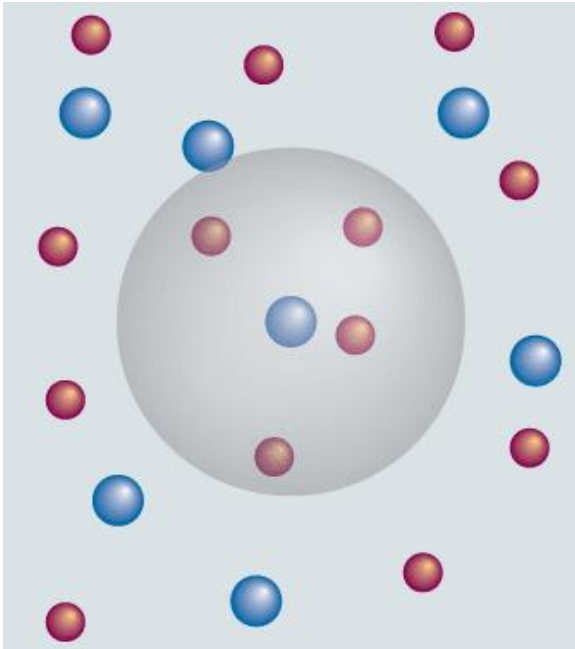
$$\mu_i = \frac{\mu}{p+q} = \frac{\mu^{\text{ideal}}}{p+q} + \frac{RT}{p+q} \ln (\gamma_+^p \gamma_-^q)$$

Mean activity coefficient

$$\gamma_{\pm} \equiv (\gamma_+^p \gamma_-^q)^{1/s} ; s \equiv p + q$$

$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

Mean activity coefficient: Debye-Hückel

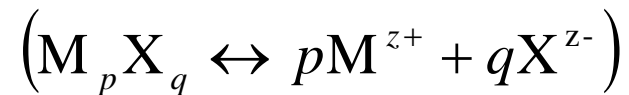


$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

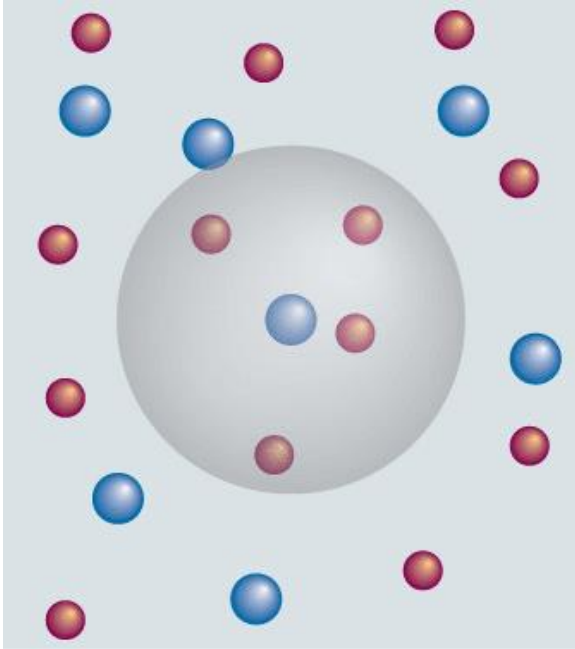
(ions i of a dissolved salt)

Mean activity coefficient

$$\gamma_{\pm} \equiv \left(\gamma_+^p \gamma_-^q \right)^{1/s} ; s \equiv p + q$$



Mean activity coefficient: Debye-Hückel



$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

(ions i of a dissolved salt)

Mean activity coefficient

$$\gamma_{\pm} \equiv \left(\gamma_+^p \gamma_-^q \right)^{1/s} ; s \equiv p + q$$

Debye-Hückel:
(limiting law)

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

Ionic strength

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

$$A = \frac{F^3}{4\pi N_A \ln(10)} \left[\frac{\rho b^{\ominus}}{2\epsilon^3 R^3 T^3} \right]^{1/2}$$

(sum over **all ions** in solution)

$$A = 0.509 \text{ for H}_2\text{O @ 298 K}$$

Activity coefficients solutes electrolytic solutions

Debye-Hückel:

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

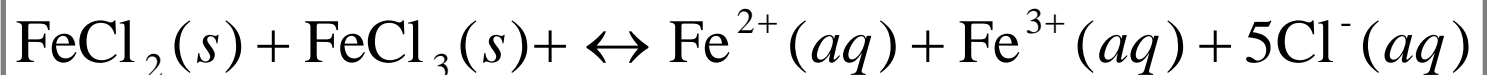
Ionic strength

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

Mean activity coefficient

$$\gamma_{\pm} \equiv (\gamma_+^p \gamma_-^q)^{1/s} ; s \equiv p + q$$

Example



$$\rightarrow I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}} = \frac{1}{2} \left[z_{\text{Fe}^{2+}}^2 \frac{b_{\text{Fe}^{2+}}}{b^{\ominus}} + z_{\text{Fe}^{3+}}^2 \frac{b_{\text{Fe}^{3+}}}{b^{\ominus}} + z_{\text{Cl}^{-}}^2 \frac{b_{\text{Cl}^{-}}}{b^{\ominus}} \right]$$

$$\rightarrow I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}} = \frac{1}{2} \left[4 \frac{b_{\text{Fe}^{2+}}}{b^{\ominus}} + 9 \frac{b_{\text{Fe}^{3+}}}{b^{\ominus}} + 1 \frac{b_{\text{Cl}^{-}}}{b^{\ominus}} \right]$$

Sum over all ions in the solution

Activity coefficients solutes electrolytic solutions

Debye-Hückel:

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

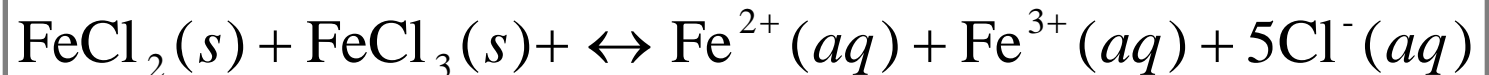
Ionic strength

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

Mean activity coefficient

$$\gamma_{\pm} \equiv (\gamma_+^p \gamma_-^q)^{1/s} ; s \equiv p + q$$

Example



$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}} = \frac{1}{2} \left[4 \frac{b_{\text{Fe}^{2+}}}{b^{\ominus}} + 9 \frac{b_{\text{Fe}^{3+}}}{b^{\ominus}} + 1 \frac{b_{\text{Cl}^{-}}}{b^{\ominus}} \right]$$

relative molality

$$\frac{b_i}{b^{\ominus}} = \frac{b_i(\text{mol/kg})}{1(\text{mol/kg})}$$

Activity coefficients solutes electrolytic solutions

Debye-Hückel:

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

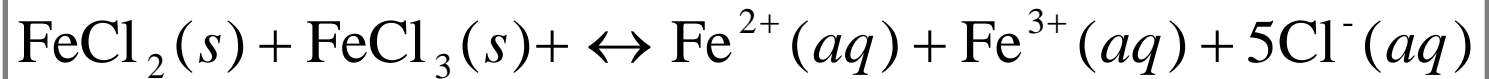
Ionic strength

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

Mean activity coefficient

$$\gamma_{\pm} \equiv (\gamma_+^p \gamma_-^q)^{1/s} ; s \equiv p + q$$

Example



$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}} = \frac{1}{2} \left[4 \frac{b_{\text{Fe}^{2+}}}{b^{\ominus}} + 9 \frac{b_{\text{Fe}^{3+}}}{b^{\ominus}} + 1 \frac{b_{\text{Cl}^{-}}}{b^{\ominus}} \right]$$

$$\log \gamma_{\pm}^{\text{FeCl}_2} = -|2 \cdot 1| A \sqrt{I} = -2A \sqrt{I}$$

$$\log \gamma_{\pm}^{\text{FeCl}_3} = -3A \sqrt{I}$$

Activity coefficients solutes electrolytic solutions

Debye-Hückel:

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

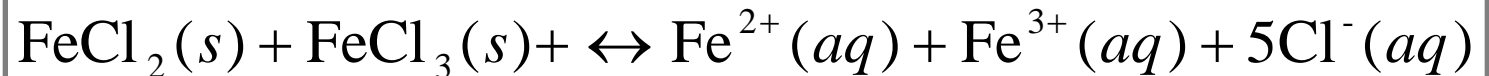
Ionic strength

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

Mean activity coefficient

$$\gamma_{\pm} \equiv (\gamma_+^p \gamma_-^q)^{1/s} ; s \equiv p + q$$

Example



$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}} = \frac{1}{2} \left[4 \frac{b_{\text{Fe}^{2+}}}{b^{\ominus}} + 9 \frac{b_{\text{Fe}^{3+}}}{b^{\ominus}} + 1 \frac{b_{\text{Cl}^{-}}}{b^{\ominus}} \right]$$

Exercise 26-28

$$\log \gamma_{\pm}^{\text{FeCl}_2} = -|2 \cdot 1| A \sqrt{I} = -2A \sqrt{I}$$

$$\log \gamma_{\pm}^{\text{FeCl}_3} = -3A \sqrt{I}$$

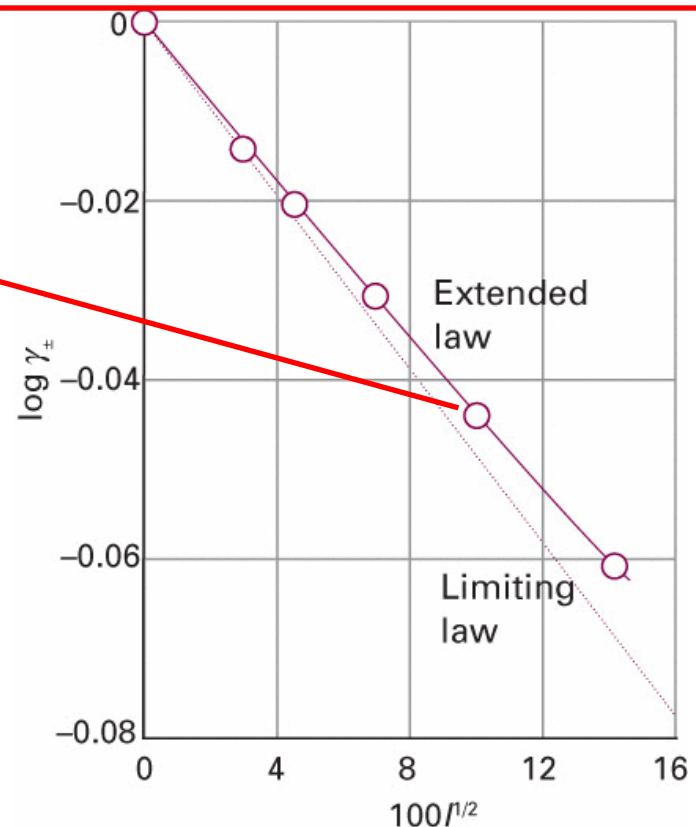
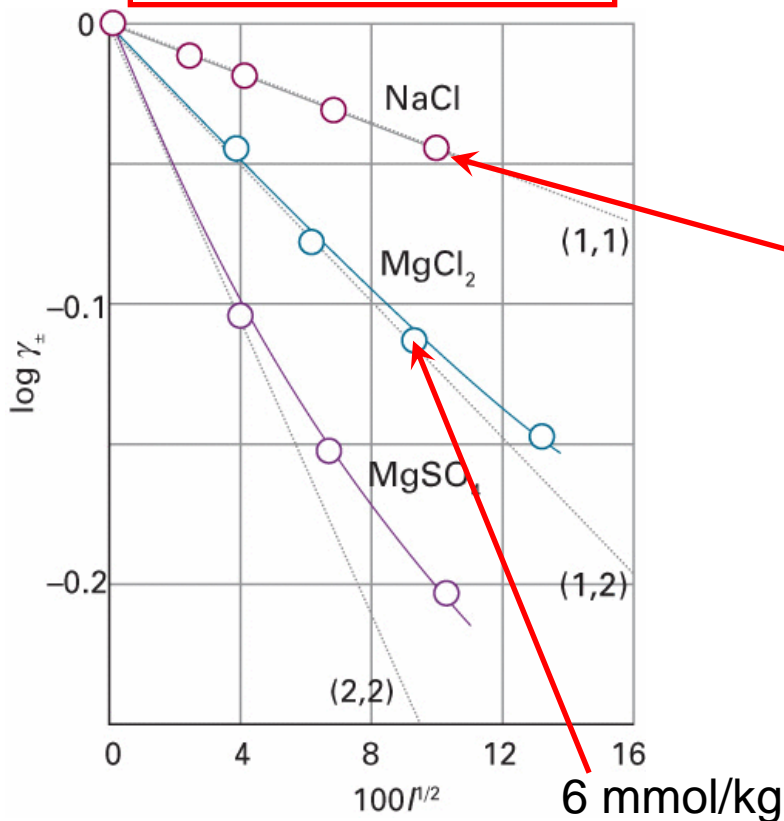
Activity coefficients solutes electrolytic solutions

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

extended Debye-Hückel:

$$\log \gamma_{\pm} = -\frac{A|z_+ z_-| I^{1/2}}{1 + B I^{1/2}} + C I$$



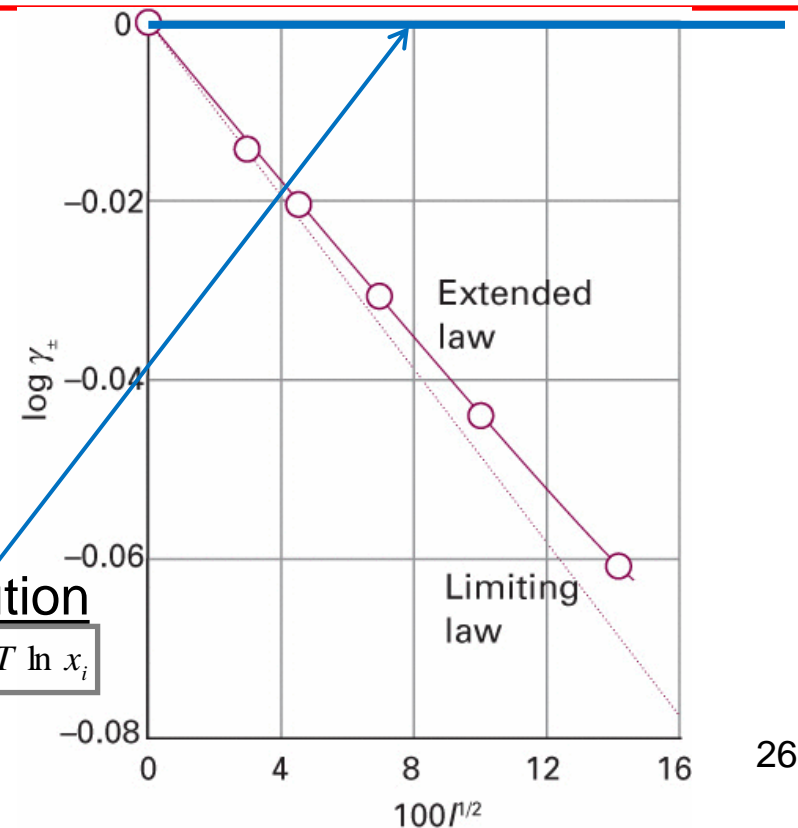
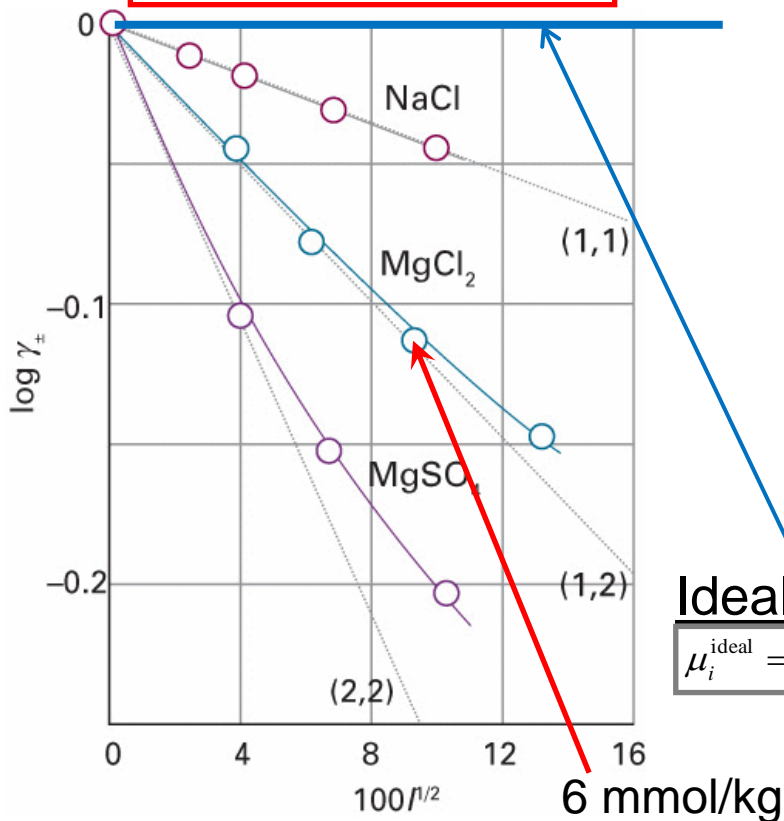
Activity coefficients solutes electrolytic solutions

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

extended Debye-Hückel:

$$\log \gamma_{\pm} = -\frac{A|z_+ z_-| I^{1/2}}{1 + B I^{1/2}} + C I$$



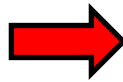
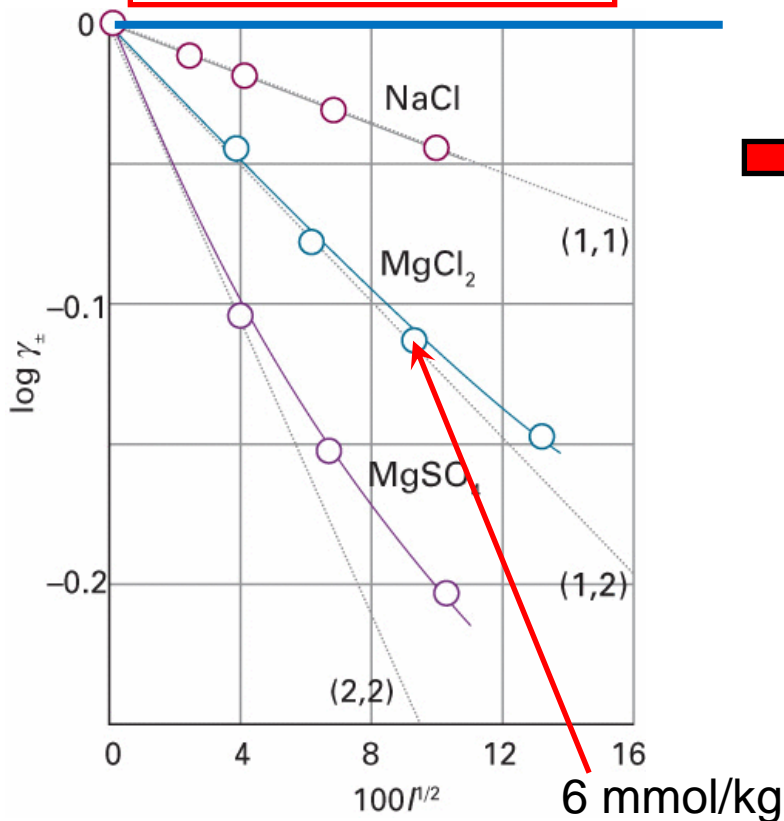
Ideal solution

$$\mu_i^{\text{ideal}} = \mu_i^* + RT \ln x_i$$

Activity coefficients solutes electrolytic solutions

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$



$$\log \gamma_{\pm} < 0 \Rightarrow \gamma_{\pm} < 1$$

$$\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$$

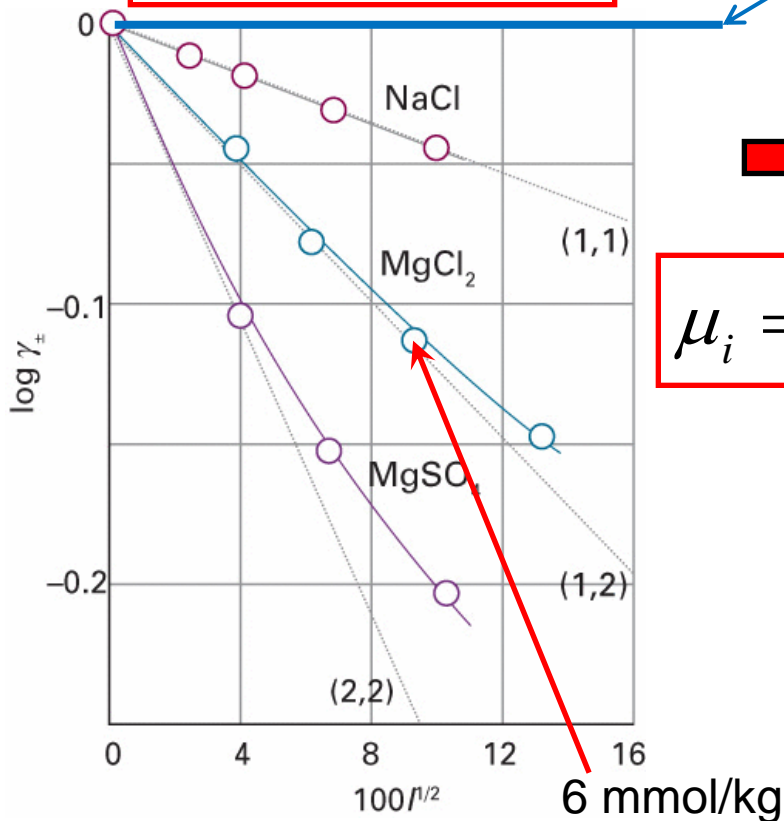
Activity coefficients solutes electrolytic solutions

$$\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^{\ominus}}$$

$$\mu_i^{\text{ideal}} = \underbrace{\mu_i^* + RT \ln x_i}_{\text{Ideal mixing entropy}}$$

Ideal mixing entropy



$$\log \gamma_{\pm} < 0 \Rightarrow \gamma_{\pm} < 1$$

$$\mu_i = \underbrace{\mu_i^* + RT \ln x_i + RT \ln \gamma_{\pm}}_{\text{Reduces mixing entropy due to the electrostatic attraction and repulsion}}$$

Reduces mixing entropy due to the electrostatic attraction and repulsion

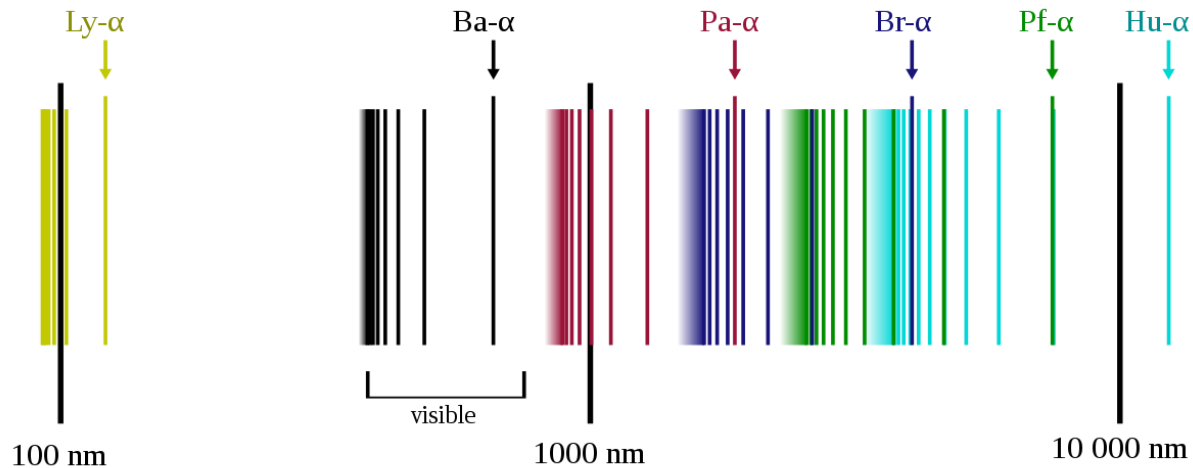
Statistical Thermodynamics: Boltzmann distribution

Statistical Thermodynamics: Boltzmann distribution

Quantum Mechanics: discrete energy levels
(discrete energy spectrum)

$$0 = \varepsilon_0, \varepsilon_1, \varepsilon_2, \dots$$

→ $E(\nu) \rightarrow \varepsilon_i$



The discrete part of the emission spectrum of hydrogen

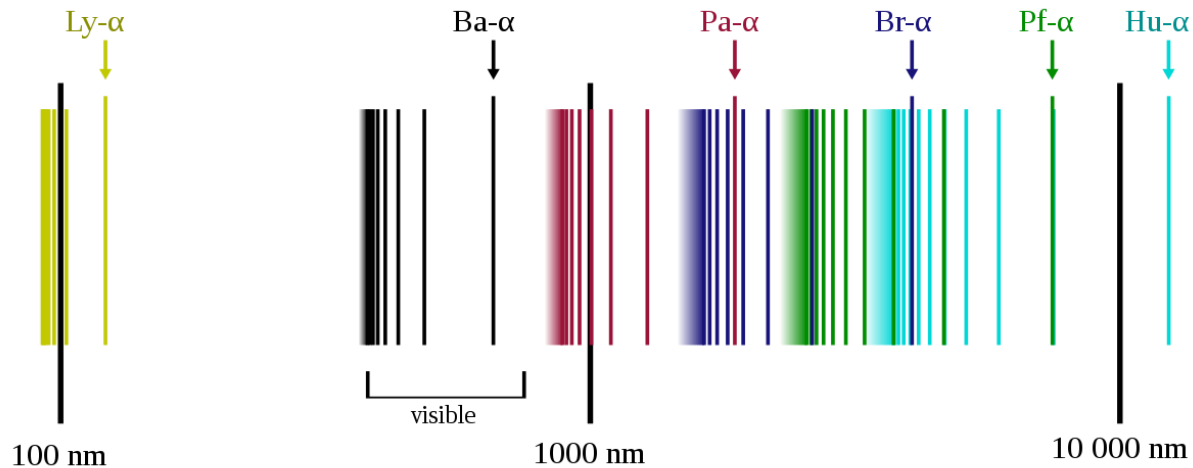
Source: https://en.wikipedia.org/wiki/Discrete_spectrum

Statistical Thermodynamics: Boltzmann distribution

Quantum Mechanics: discrete energy levels
(discrete energy spectrum)

$$0 = \varepsilon_0, \varepsilon_1, \varepsilon_2, \dots$$

→ $E(\nu) \rightarrow \varepsilon_i$



ε_i is the energy of a molecule in quantum state or quantum level i

Statistical Thermodynamics: Boltzmann distribution

Quantum Mechanics: discrete energy levels

$$0 = \varepsilon_0, \varepsilon_1, \varepsilon_2, \dots$$

Boltzmann distribution:

Average number of molecules in quantum state ε_i

$$n_i = N \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{\sum_j \exp\left[-\frac{\varepsilon_j}{kT}\right]}$$

P_i : chance to occupy ε_i

$$P_i = \frac{n_i}{N} = \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{q}$$

$$q = \sum_j \exp\left[-\frac{\varepsilon_j}{kT}\right]$$

Partition function

Total number of molecules

$$k = 1.38 \cdot 10^{-23} \text{ J / K}$$

Statistical Thermodynamics: Boltzmann distribution

Quantum Mechanics: discrete energy levels

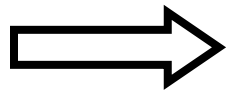
$$0 = \varepsilon_0, \varepsilon_1, \varepsilon_2, \dots$$

Boltzmann distribution

$$P_i = \frac{n_i}{N} = \frac{\exp[-\beta\varepsilon_i]}{q}$$

Partition function

$$q = \sum_j \exp[-\beta\varepsilon_j] \quad \left(\beta \equiv \frac{1}{kT} \right)$$



$$U = N \sum_i \varepsilon_i P_i = \frac{N}{q} \sum_i \varepsilon_i \exp[-\beta\varepsilon_i] = -\frac{N}{q} \left[\frac{\partial q}{\partial \beta} \right]$$

Study Guide page 20

Statistical Thermodynamics: Boltzmann distribution

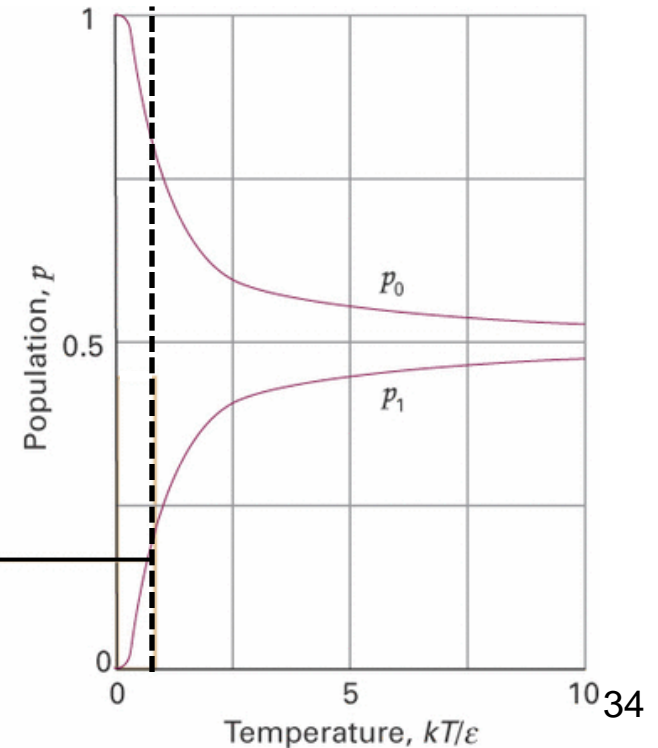
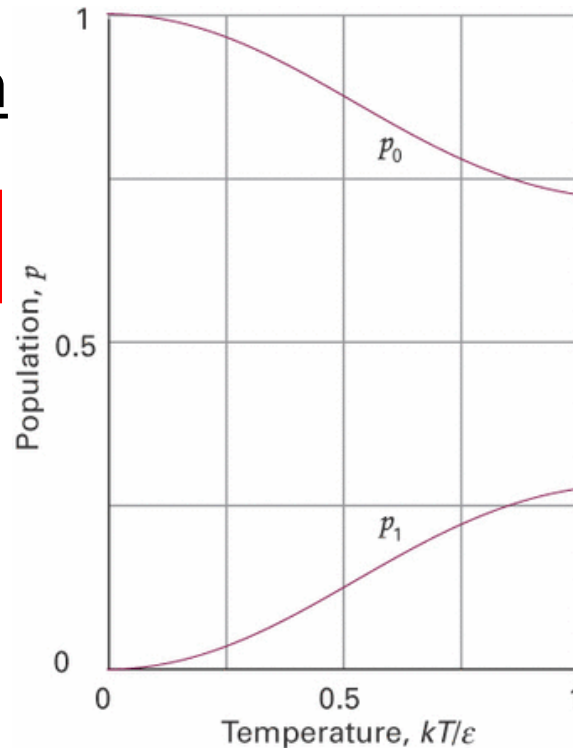
$$P_i = \frac{n_i}{N} = \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{q} = \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{\exp\left[-\frac{\varepsilon_0}{kT}\right] + \exp\left[-\frac{\varepsilon_1}{kT}\right]}$$

Two level system

$$\varepsilon_0 = 0$$

$$\varepsilon_1 = \varepsilon$$

choice



Statistical Thermodynamics: Boltzmann distribution

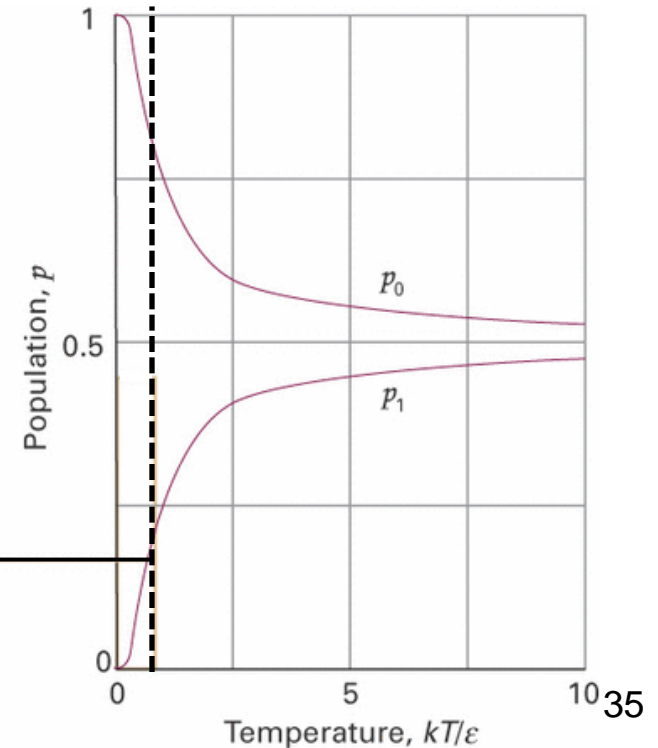
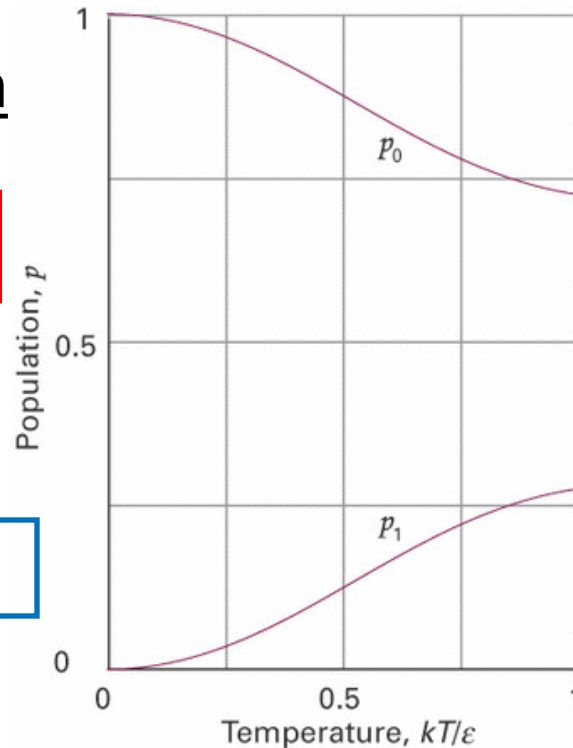
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Two level system

$$\varepsilon_0 = 0$$

$$\varepsilon_1 = \varepsilon$$

Exercise 29-30



Statistical Thermodynamics: Boltzmann distribution

Quantum Mechanics: discrete energy levels

$$0 = \varepsilon_0, \varepsilon_1, \varepsilon_2, \dots$$

Boltzmann distribution

$$P_i = \frac{n_i}{N} = \frac{\exp\left[-\frac{\varepsilon_i}{kT}\right]}{q}$$

Partition function

$$q = \sum_j \exp\left[-\frac{\varepsilon_j}{kT}\right]$$

Boltzmann entropy

$$S = k \ln W$$

Study Guide page 21

<https://dullenslab.com/teaching/> (Lecture 7)

Formulae first year course Thermodynamics

$$PV = nRT = NkT$$

$$U = \frac{3}{2}nRT = \frac{3}{2}NkT$$

$$\Delta U = W + Q$$

$$dW = -P_{ext}dV + dW' \quad \text{and} \quad dW'_{max} = (dG)_{P,T}$$

$$dQ|_P = C_P dT \quad \text{and} \quad dQ|_V = C_V dT$$

$$\frac{Q_1}{Q_2} = -\frac{T_1}{T_2}$$

$$dS = \frac{dQ^{rev}}{T} \geq \frac{dQ}{T}$$

$$dS_{tot} = dS + dS_{env} \geq 0$$

$$dU = -PdV + TdS + \sum_i \mu_i dn_i$$

$$H = U + PV$$

$$dH = VdP + TdS + \sum_i \mu_i dn_i$$

$$A = U - TS$$

$$dA = -PdV - SdT + \sum_i \mu_i dn_i$$

$$G = H - TS$$

$$dG = VdP - SdT + \sum_i \mu_i dn_i$$

$$\Delta_r G = \left(\frac{\partial G}{\partial \xi} \right)_{P,T} = \Delta_r G^\ominus + RT \ln Q \quad \text{with} \quad Q = \prod_i a_i^{\nu_i}$$

$$RT \ln K = -\Delta_r G^\ominus$$

$$E = E^\ominus - \frac{RT}{\nu F} \ln Q \quad \text{and} \quad dW' = Edq \quad \text{furthermore} \quad E = IR \quad \text{and} \quad P = EI$$

$$\mu_i = \mu_i^\ominus + RT \ln a_i = \mu_i^\ominus + RT \ln \frac{P_i}{P^\ominus}$$

$$G_{P,T} = \sum_i \mu_i n_i$$

$$\sum_j n_j d\mu_j = 0$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{trs} H} \right) x_B$$

$$\Delta S = -nR(x_A \ln x_A + x_B \ln x_B)$$

$$\Pi = [B]RT = \frac{n_B}{V} RT$$

$$S = k \ln W$$

$$\frac{n_i}{N} = \frac{\exp \frac{-\epsilon_i}{kT}}{q} \quad \text{with} \quad q = \sum_i \exp \frac{-\epsilon_i}{kT} \quad \text{and} \quad \langle X \rangle = N \langle x \rangle = N \sum_i x_i \frac{n_i}{N}$$

Formulae Thermodynamics 2

$$\left(\frac{\partial V}{\partial T}\right)_{P,W',n_i} = -\left(\frac{\partial S}{\partial P}\right)_{T,W',n_i}$$

$$X_i = \left(\frac{\partial X}{\partial n_i}\right)_{P,T,n_{j \neq i}}$$

$$\sum_j n_j d\mu_j = 0$$

$$P_j = x_j P_j^*$$

$$P_j = y_j P$$

$$P_B = x_B K_B$$

$$\left(\frac{\partial \mu_\beta}{\partial P}\right)_T - \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T = \Delta_{\text{trs}} V$$

$$\left(\frac{\partial \mu_\beta}{\partial T}\right)_P - \left(\frac{\partial \mu_\alpha}{\partial T}\right)_P = -\Delta_{\text{trs}} S$$

$$P = P^* \exp\left(\frac{V_m \Delta P}{RT}\right)$$

$$\frac{dP}{dT} = \frac{\Delta_{\text{trs}} S}{\Delta_{\text{trs}} V} = \frac{\Delta_{\text{trs}} H}{T \Delta_{\text{trs}} V}$$

$$\frac{d \ln P}{dT} \approx \frac{\Delta_{\text{trs}} H}{RT^2}$$

$$\Delta T = \left(\frac{RT^{*2}}{\Delta_{\text{trs}} H}\right) x_B \quad \ln x_B = \frac{\Delta_{\text{fus}} H}{R} \left[\frac{1}{T_{\text{fus}}} - \frac{1}{T}\right]$$

$$\mu = \mu^\ominus + RT \ln a = \mu^\ominus + RT \ln x + RT \ln \gamma$$

$$\mu = \mu^\ominus + RT \ln a = \mu^\ominus + RT \ln \frac{b}{b^\ominus} + RT \ln \gamma$$

$$F = C - P + 2$$

$$n_\alpha l_\alpha = n_\beta l_\beta$$

$$\Delta_{\text{solv}} G^\ominus = -\frac{z_i^2 e^2 N_A}{8\pi \epsilon_0 r_i} \left(1 - \frac{1}{\epsilon_r}\right)$$

$$\gamma_\pm = (\gamma_+^p \gamma_-^q)^{\frac{1}{p+q}}$$

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

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^\ominus}$$

$$A = \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^\ominus}{2\epsilon^3 R^3 T^3}\right)^{\frac{1}{2}}$$

$$P_{in} = P_{out} + \frac{2\gamma}{r} \quad P = \rho g h \quad w_{ad} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \quad \gamma_{sg} = \gamma_{sl} + \gamma_{lg} \cos \Theta_c$$

Mean activity coefficient: Debye-Hückel

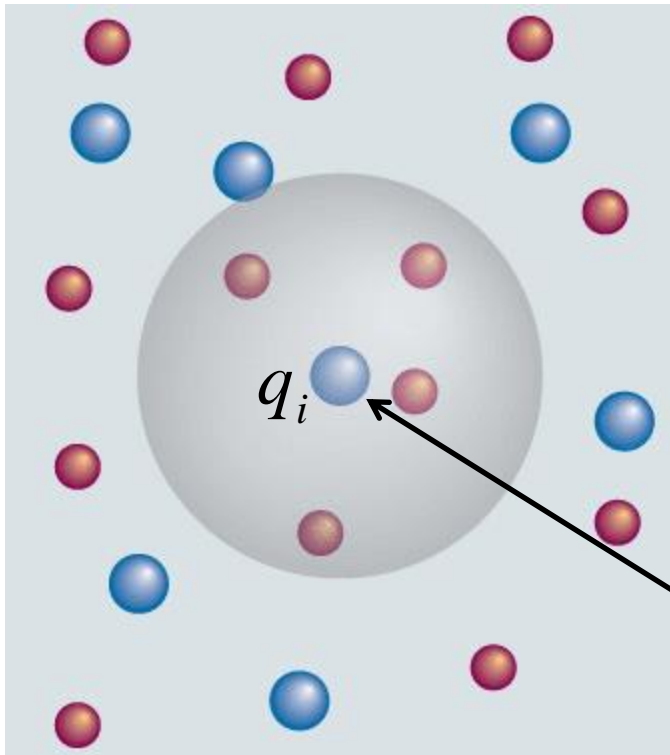
Only in case you are interested in the background of the Debye-Huckel theory (not necessary for the exam)

https://learninglink.oup.com/access/pchem11e-student-resources#tag_a-deeper-look

Mean activity coefficient: Debye-Hückel

1) Work to charge all ions starting from an ideal solution with all (uncharged) ions already in their ideal solution positions is :

$$w_e = \mu - \mu^{\text{ideal}} = pRT \ln \gamma_+ + qRT \ln \gamma_- = sRT \ln \gamma_{\pm}$$



$$\gamma_{\pm} = \left(\gamma_+^p \gamma_-^q \right)^{1/s} \quad s = p + q$$

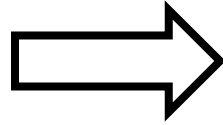
$$\ln \gamma_{\pm} = \frac{w_e}{sRT}$$

Choose a central ion i with charge q_i in the solution

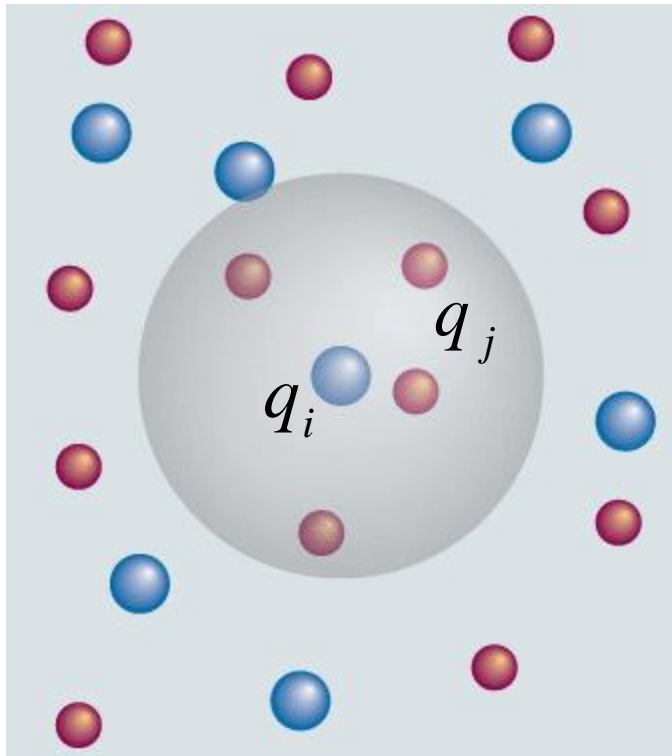
Mean activity coefficient: Debye-Hückel

2) Ionic atmosphere (all other charges q_j) will screen the charge of the central ion :

$$\Phi_i(r) = \frac{q_i}{4\pi\epsilon} \frac{1}{r}$$

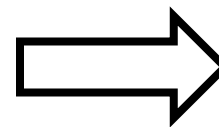


$$\Phi_i(r) = \frac{q_i}{4\pi\epsilon} \frac{1}{r} \exp\left[-\frac{r}{r_D}\right]$$



Poisson: $\nabla^2 \Phi(r) = -\frac{\rho(r)}{\epsilon}$

$$\nabla_r^2 \Phi(r) = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \Phi(r)$$

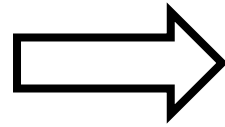


$$r_D^2 = \frac{\epsilon \Phi_i(r)}{\rho_j(r)}$$

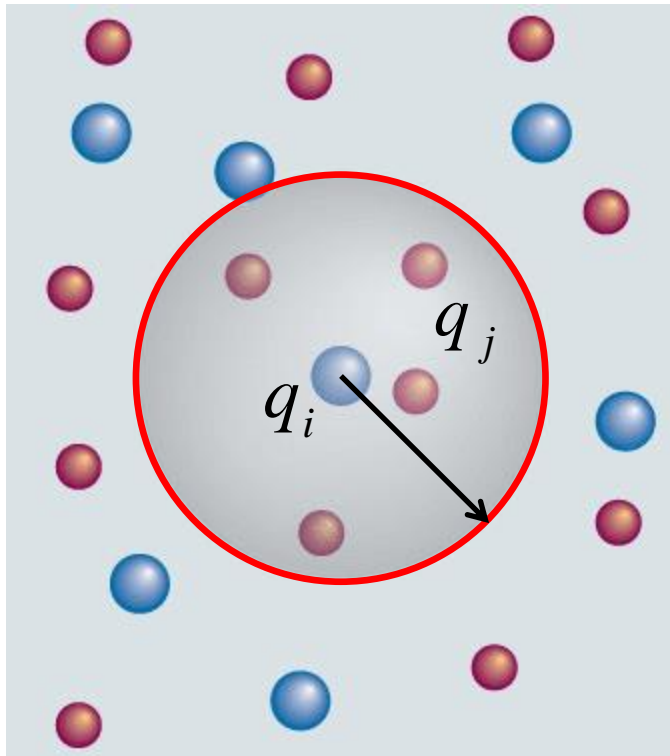
Mean activity coefficient: Debye-Hückel

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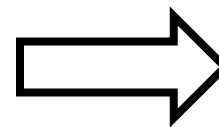


$$\Phi_i(r) = \frac{q_i}{4\pi\epsilon} \frac{1}{r} \exp\left[-\frac{r}{r_D}\right]$$



Poisson: $\nabla^2 \Phi(r) = -\frac{\rho(r)}{\epsilon}$

$$\nabla_r^2 \Phi(r) = \frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d}{dr} \right) \Phi(r)$$



$$r_D^2 = \frac{\epsilon \Phi_i(r)}{\rho_j(r)}$$

Mean activity coefficient: Debye-Hückel

3) Use Boltzmann distribution to determine ion distribution in the bulk solution:

Energy of ion j :

$$E_j = z_j e \Phi_i = \frac{z_i z_j e^2}{4\pi\epsilon} \frac{1}{r} \exp\left[-\frac{r}{r_D}\right]$$

Boltzmann:

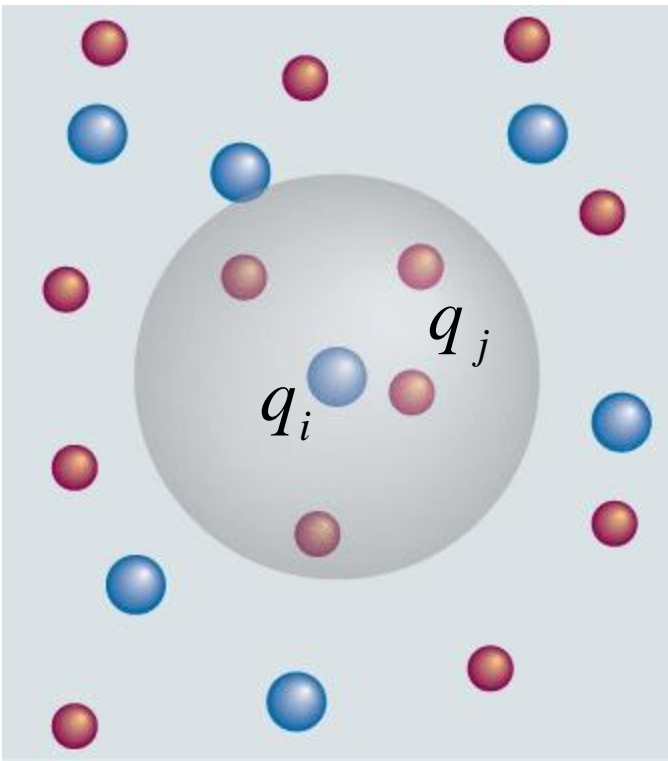
$$\frac{c_j}{c_\infty} = \exp\left[-z_j e \Phi_i / kT\right]$$

$$\exp\left[-z_j e \Phi_i / kT\right] \approx 1 - \frac{z_j e \Phi_i}{kT}$$

$$\rho_{e,j} = c_j z_j e N_A = c_j z_j F$$

Charge density ion j :

$$\rho_{e,j}(r) \approx -\left[c_{+,\infty} z_+^2 + c_{-,\infty} z_-^2\right] \frac{F^2 \Phi_i(r)}{RT^3}$$



Mean activity coefficient: Debye-Hückel

3) Use ion distribution to find Debye screening length:

$$\rho_{e,j}(r) \approx -\left[c_{+, \infty} z_+^2 + c_{-, \infty} z_-^2 \right] \frac{F^2 \Phi_i(r)}{RT}$$

ρ_s : Mass density solvent

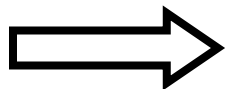
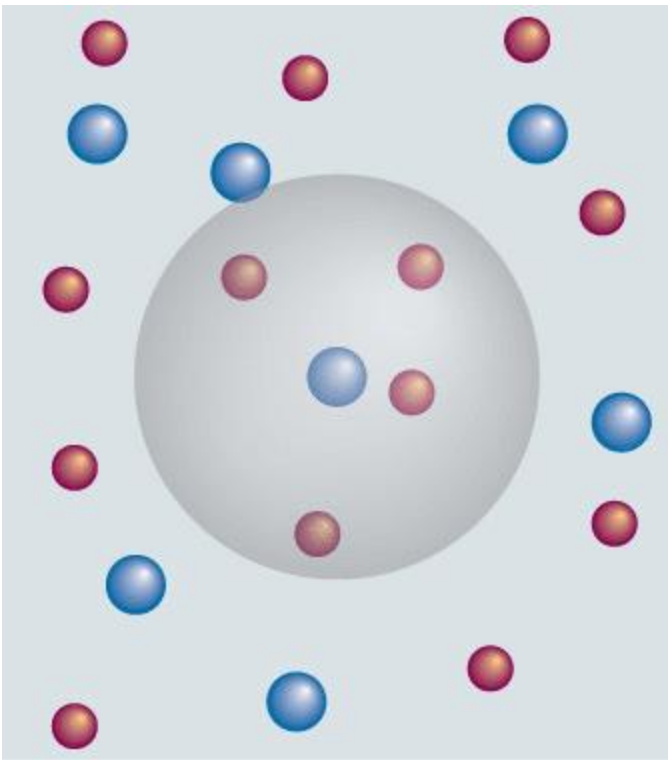
$$c_j \approx b_j \rho_s$$

Ionic strength

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^\ominus}$$

Poisson

$$r_D^2 = -\frac{\epsilon \Phi_i(r)}{\rho_j(r)}$$



Debye screening length

$$r_D = \left(\frac{\epsilon RT}{2 \rho_s F^2 I b^\ominus} \right)^{1/2}$$

Mean activity coefficient: Debye-Hückel

3) Use ion distribution to find Debye screening length:

$$\rho_{e,j}(r) \approx -\left[c_{+,\infty} z_+^2 + c_{-,\infty} z_-^2\right] \frac{F^2 \Phi_i(r)}{RT}$$

ρ_s : Mass density solvent

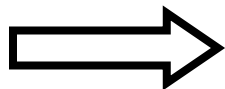
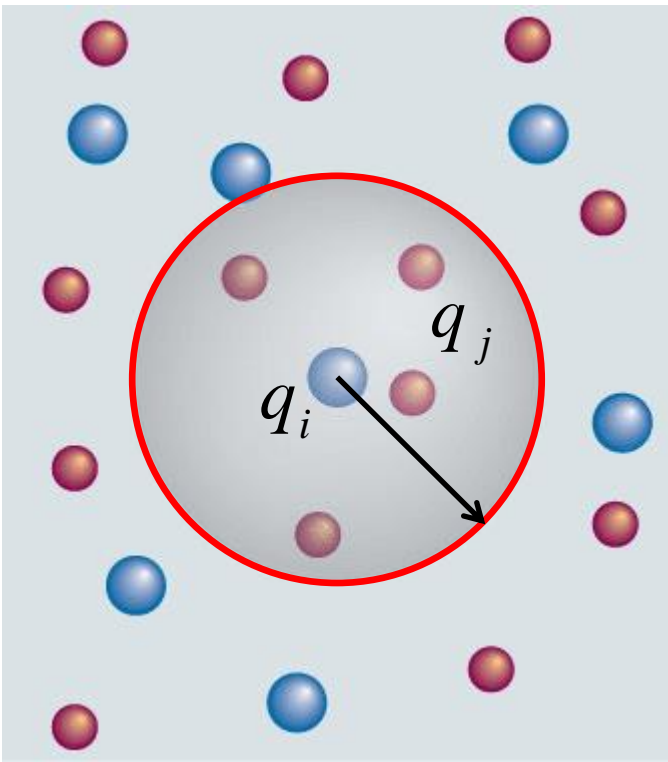
$$c_j \approx b_j \rho_s$$

Ionic strength

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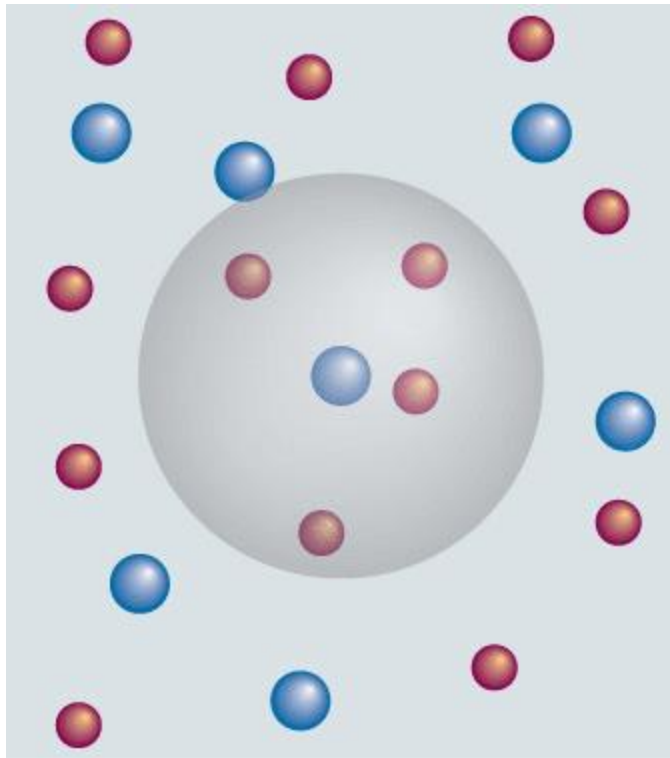
Debye screening length

$$r_D = \left(\frac{\epsilon RT}{2 \rho_s F^2 I b^\ominus} \right)^{1/2}$$

Mean activity coefficient: Debye-Hückel

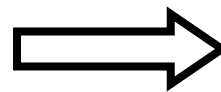
4) Determine work to charge central ion in presence of the ionic atmosphere potential:

$$\Phi_{\text{atm}}(r) = \Phi(r) - \Phi_i(r) = \frac{z_i e}{4\pi\epsilon} \left[\frac{\exp[-r/r_D]}{r} - \frac{1}{r} \right]$$



$$dw_e = \Phi_{\text{atm}}(0) dq$$

$$\Phi_{\text{atm}}(0) = \frac{q}{4\pi\epsilon r_D}$$



$$w_{e,i} = \frac{z_i^2 F^2}{8\pi N_A \epsilon r_D}$$

Mean activity coefficient: Debye-Hückel

5) Collect all results and include charging of all ions in w_e :

$$w_{e,i} = \frac{z_i^2 F^2}{8\pi N_A \epsilon r_D}$$

$$r_D = \left(\frac{\epsilon RT}{2\rho_s F^2 I b^\ominus} \right)^{1/2}$$

$$\ln \gamma_{\pm} = \frac{pw_{e,+} + qw_{e,-}}{sRT}$$

$$\log \gamma_{\pm} = -|z_+ z_-| AI^{1/2}$$

$$I = \frac{1}{2} \sum_i z_i^2 \frac{b_i}{b^\ominus}$$

$$A = \frac{F^3}{4\pi N_A \ln(10)} \left[\frac{\rho b^\ominus}{2\epsilon^3 R^3 T^3} \right]^{1/2}$$

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 $A = 0.509$ for H_2O @ 298 K

