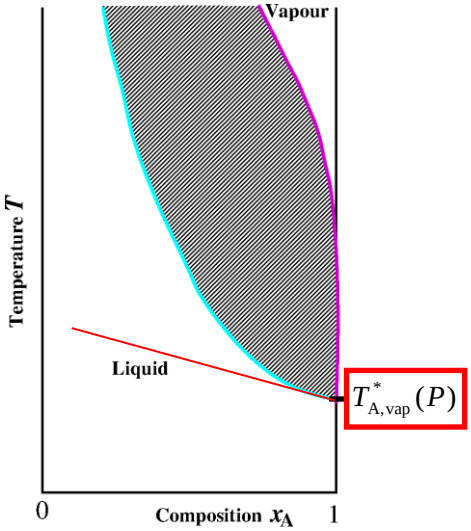
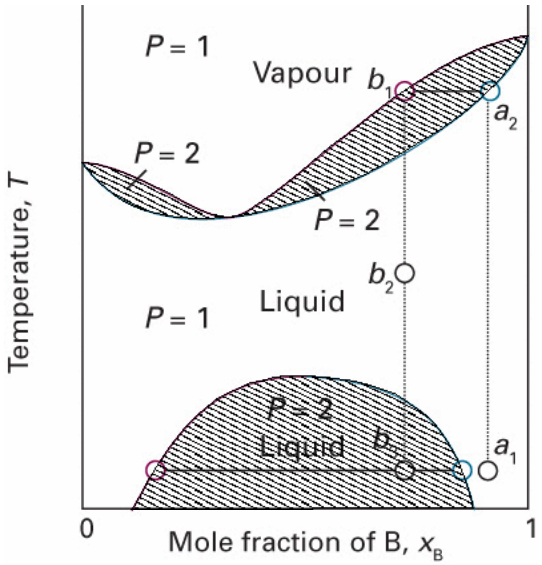
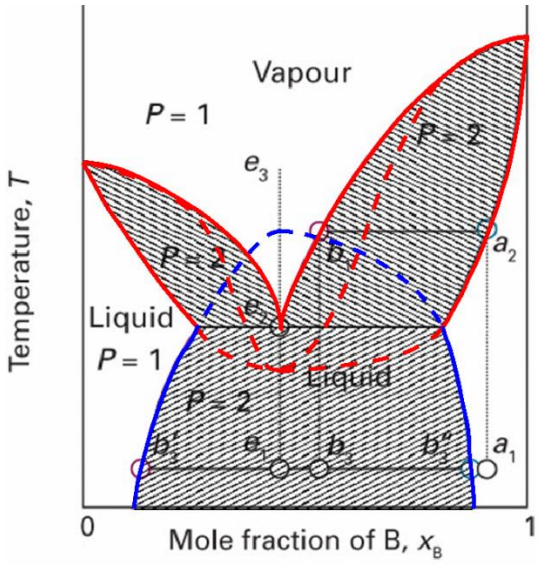
Summary of Lecture 5

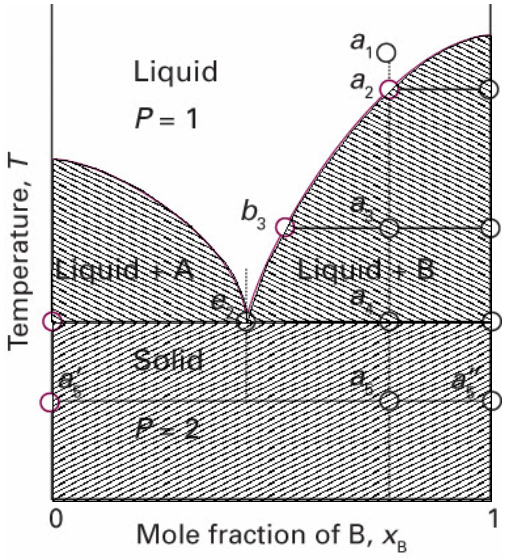
Phase diagrams of multicomponent systems

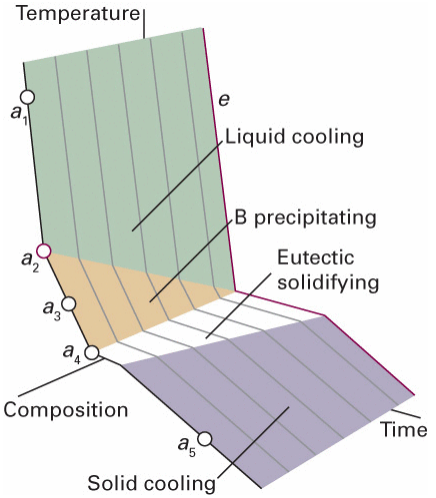


$$\Delta T \approx \frac{RT_A^{*2}}{\Delta_{vap}H_A}x_B$$

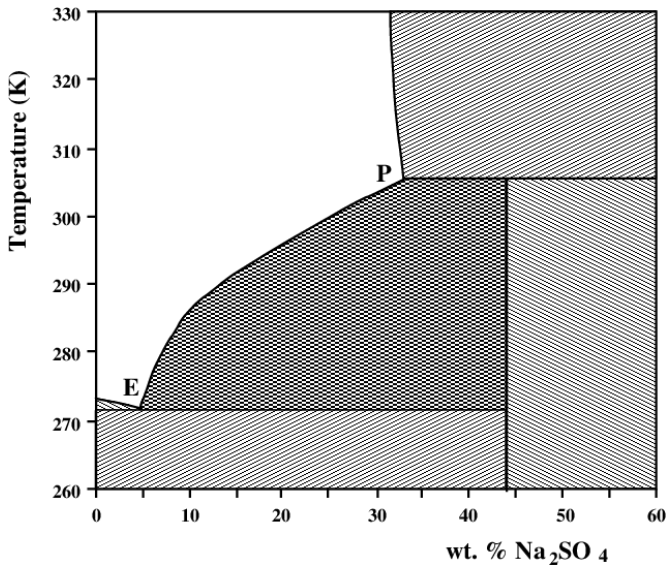


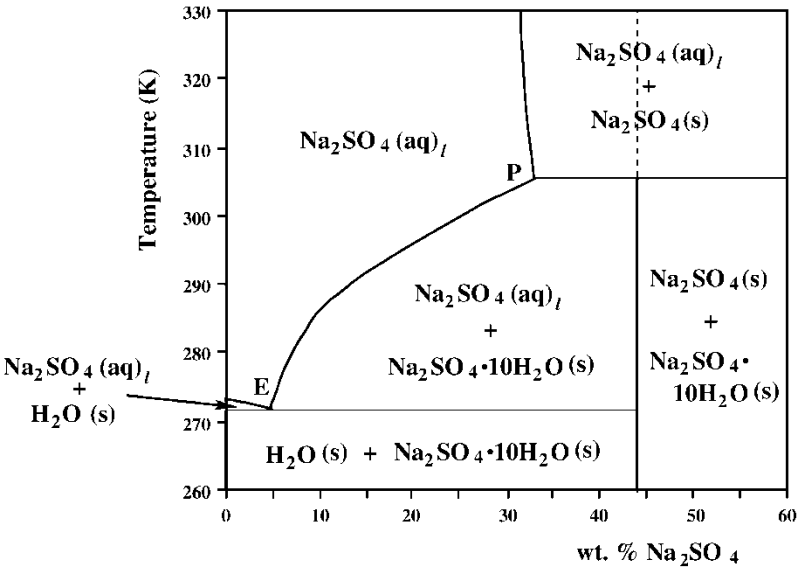


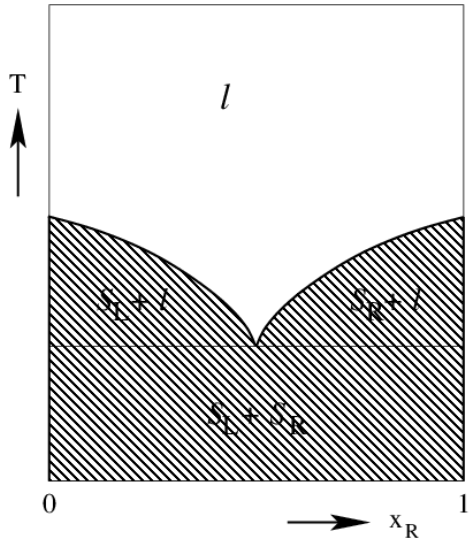


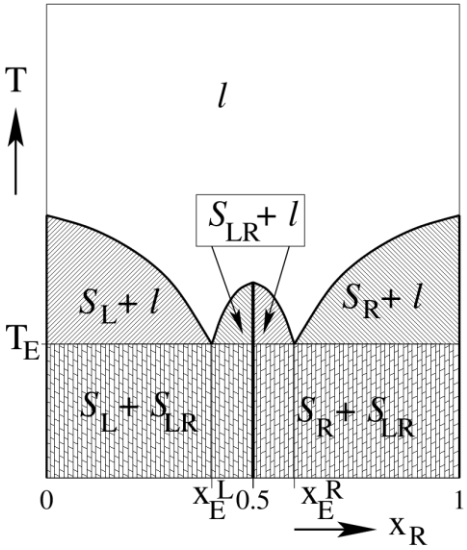


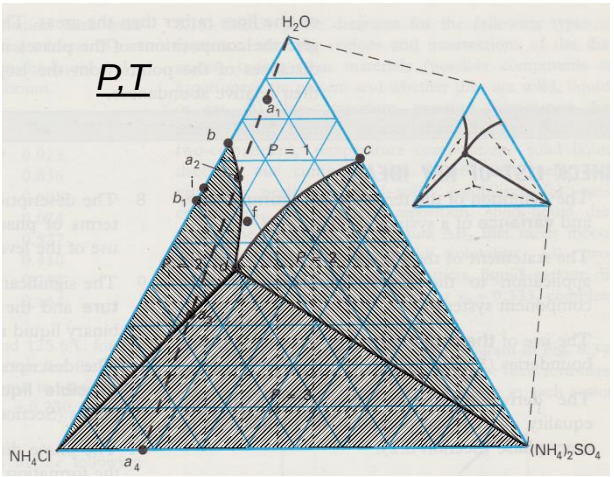
Phase diagrams of multicomponent systems



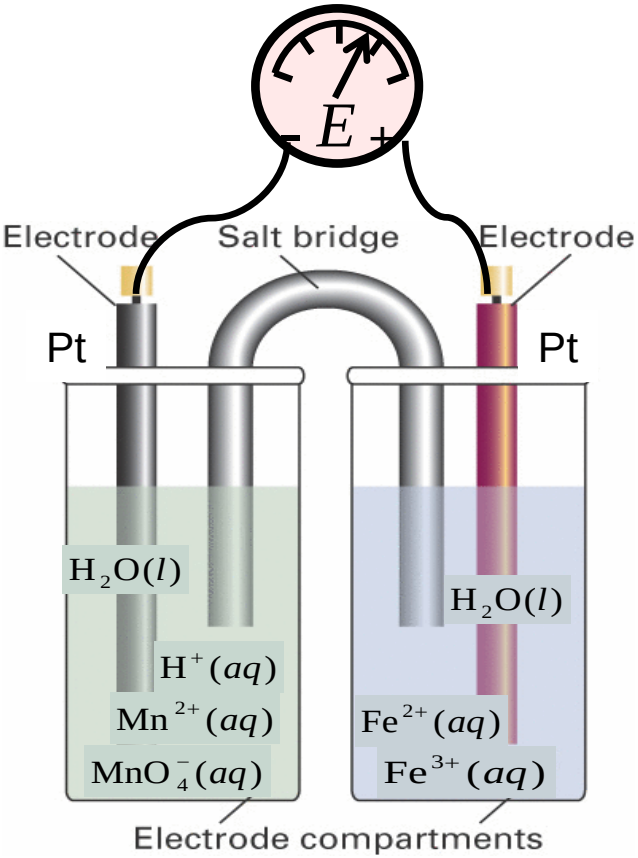








Lecture 6
Electrolytic solutions and Electrochemistry



This is partly a recap from Thermodynamics

(https://dullenslab.com/wp-content/uploads/2022/12/Lecture6_thermo.pdf?action=purge)

Chemical reaction equilibria: general

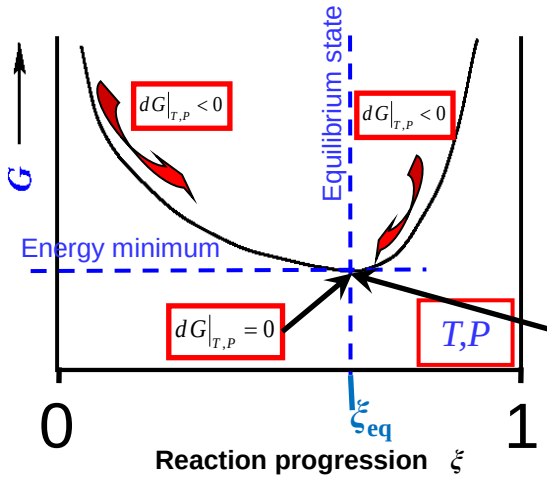
$$N_2(g) + 3H_2(g) \leftrightarrow 2NH_3(g) \quad \Leftrightarrow \quad 0 \leftrightarrow 2NH_3(g) - N_2(g) - 3H_2(g) \quad \Leftrightarrow \quad 0 = \sum_i \nu_i C_i$$

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

$$\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i$$

$$\Delta_r G = \sum_i \nu_i \mu_i^{\Theta} + \sum_i \nu_i RT \ln a_i$$

$$\equiv \Delta_r G^{\Theta} \qquad \equiv RT \ln Q$$



Equilibrium:

$$\Delta_r G = 0$$

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

$$\Delta_r G^{\Theta} = -RT \ln Q_{eq} = -RT \ln \left(\prod_i a_i^{\nu_i}\right)_{eq} \equiv -RT \ln K$$

K is only dependent on T and a_i

Chemical reaction equilibria: general

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

$$K = \left(\prod_i a_i^{\nu_i} \right)_{\text{eq}}$$

$$\Delta_r G^\Theta = \sum_i \nu_i \mu_i^\Theta = \sum_i \nu_i \Delta_f G^\Theta_{i,\text{m}}$$

$P \equiv P^\Theta$
Pure i
$a_i \equiv 1$

reaction components — i

reaction stoichiometry — ν_i

formation — Δ_f

molar — $G^\Theta_{i,\text{m}}$

perfect gas mixtures $a_i = \dfrac{P_i}{P^\Theta}$

pure liquids $a_l \approx 1$

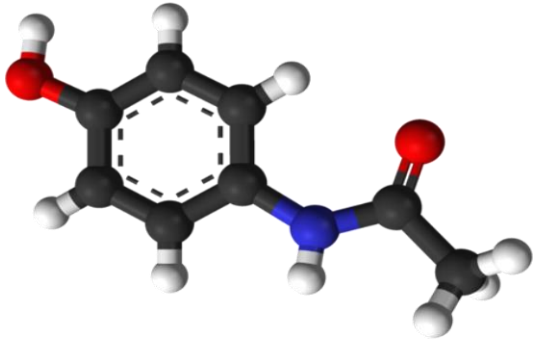
pure solids $a_s \approx 1$

solutions

- **Neutral components(Lecture 3)** $\Rightarrow \Delta_{\text{mix}} G$
- **Electrolytes (ions): Electrochemistry**

Chemical reaction equilibria: dissolution

Aqueous dissolution of paracetamol



$$C_8H_9NO_2(s) \leftrightarrow C_8H_9NO_2(aq)$$

$$0 \leftrightarrow C_8H_9NO_2(aq) - C_8H_9NO_2(s) \Leftrightarrow 0 = \sum_i \nu_i C_i$$

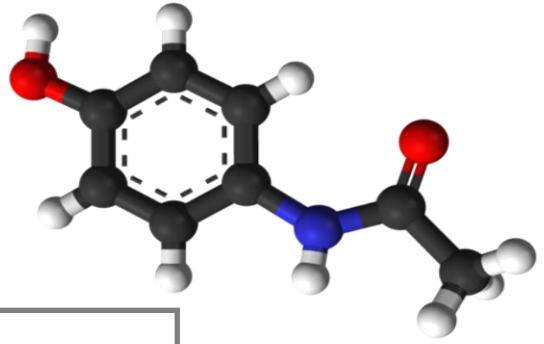
Reaction quotient $Q \equiv \prod_i a_i^{\nu_i}$ $\Rightarrow$ $Q = a^{1}_{C_8H_9NO_2(aq)} \cdot a^{-1}_{C_8H_9NO_2(s)}$

Thermodynamic equilibrium constant

$$K \equiv Q_{eq} = \left(\frac{a_{C_8H_9NO_2(aq)}}{a_{C_8H_9NO_2(s)}} \right)_{eq} \approx \left(a_{C_8H_9NO_2(aq)} \right)_{eq}$$

i.e. **solid in equilibrium with saturated solution '=' solubility**

Chemical reaction equilibria: dissolution



Neutral solutions (Lecture 3) $\Rightarrow \Delta_{\text{mix}} G$

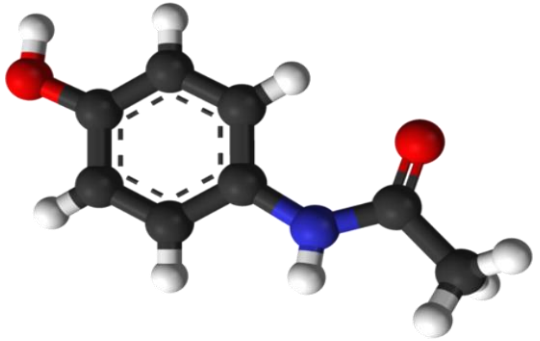
$$\mathrm{C_8H_9NO_2}(s) \leftrightarrow \mathrm{C_8H_9NO_2}(aq)$$

$$K \equiv Q_{\text{eq}} = \left(\frac{a_{\mathrm{C_8H_9NO_2}(aq)}}{a_{\mathrm{C_8H_9NO_2}(s)}} \right)_{\text{eq}} \approx \left(a_{\mathrm{C_8H_9NO_2}(aq)} \right)_{\text{eq}}$$

$$\sum_i \nu_i \mu_i^{\Theta} = \Delta_{\text{r}} G^{\Theta} = -RT \ln K \approx -RT \ln \left(a_{\mathrm{C_8H_9NO_2}(aq)} \right)_{\text{eq}}$$

$$\ln \left(a_{\mathrm{C_8H_9NO_2}(aq)} \right)_{\text{eq}} = -\frac{\Delta_{\text{diss}} \mu^{\Theta}_{\mathrm{C_8H_9NO_2}(s)}}{RT}$$

Chemical reaction equilibria: dissolution



Neutral solutions (Lecture 3) $\Rightarrow \Delta_{\text{mix}} G$

$$\text{C}_8\text{H}_9\text{NO}_2(s) \leftrightarrow \text{C}_8\text{H}_9\text{NO}_2(aq)$$

$$\ln\left(a_{\text{C}_8\text{H}_9\text{NO}_2(aq)}\right)_{\text{eq}} = -\frac{\Delta_{\text{diss}}\mu^{\Theta}_{\text{C}_8\text{H}_9\text{NO}_2(s)}}{RT}$$

Cf. Exercise 16 (where we dropped superscript *):

$$\ln x_B = \frac{\mu^*_{\text{B}}(s) - \mu^*_{\text{B}}(l)}{RT} \approx -\frac{\Delta_{\text{fus}} H_{\text{B}}}{RT} + \frac{\Delta_{\text{fus}} S_{\text{B}}}{R}$$

Assuming ideal solution, so $a_B = x_B$

Assuming $\Delta_{\text{fus}} H_{\text{B}}$ **and** $\Delta_{\text{fus}} S_{\text{B}}$ **are independent of** T

Activity (liquid) mixtures of neutral components

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

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)

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

Real solutions

γ_i : **activity coefficient**

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

Activity (liquid) mixtures of neutral components

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

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Real solutions

γ_i : **activity coefficient**

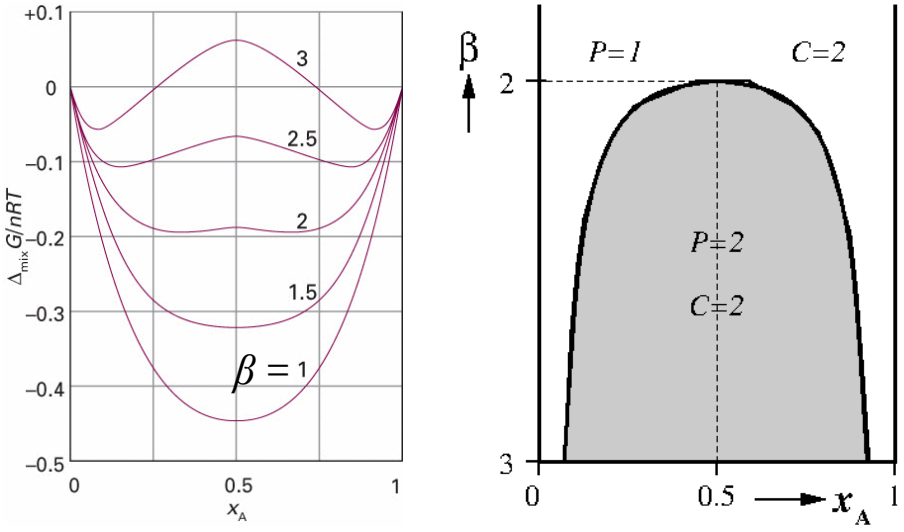
$$a_i^{(l)} = \gamma_i^{(l)} x_i^{(l)} = \frac{P_i^{(g)}}{P_i^*}$$

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

Activity (liquid) mixtures of neutral components

Regular solution example: $G^{\mathrm{E}} = nRT\beta x_{\mathrm{A}} x_{\mathrm{B}}$

(L-L separation exercise 17)



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

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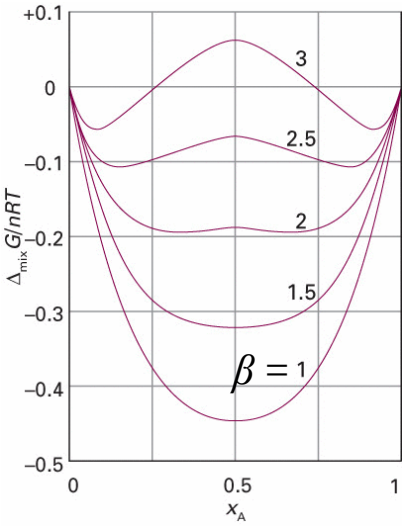
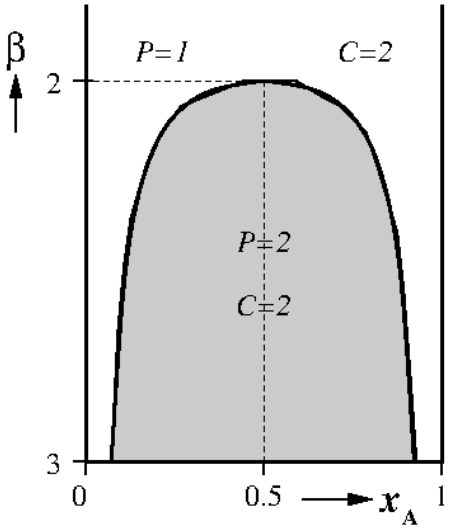
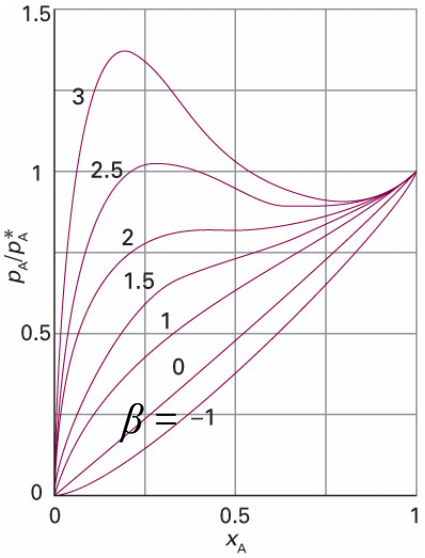






$$\mu_i = \mu_i^* + RT \ln a_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_i = \mu_i^{\text{ideal}} + RT \ln \gamma_i$$

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

(See also Exercise A6d Additional exercises I)

Chemical reaction equilibria: general

Activity as an effective concentration

$$\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i$$

Molarity (mol/L)

$$c_i = \frac{\#\,\text{mol solute } i}{\text{volume } V \text{ solution}} = \frac{n_i}{V}$$

$$a_i = \gamma_i^{(c)} \frac{c_i}{c^{\Theta}}$$

$$c^{\Theta} \equiv 1\,\text{mol/L}$$

Molality (mol/kg)

$$b_i = \frac{\#\,\text{mol solute } i}{\text{mass } m \text{ solvent}} = \frac{n_i}{m}$$

$$a_i = \gamma_i^{(b)} \frac{b_i}{b^{\Theta}}$$

$$b^{\Theta} \equiv 1\,\text{mol/kg}$$

Mole fraction ( )

$$x_i = \frac{\#\,\text{mol solute } i}{\text{total } \#\,\text{mol in solution}} = \frac{n_i}{n}$$

$$a_i = \gamma_i^{(x)} x_i$$

Standard state **Θ**
(still *T* dependent)

$$P = P^{\Theta}$$

$$a_i^{\Theta} = 1$$

and pure

$$c_i^{\Theta} = 1\,\text{mol/L}$$

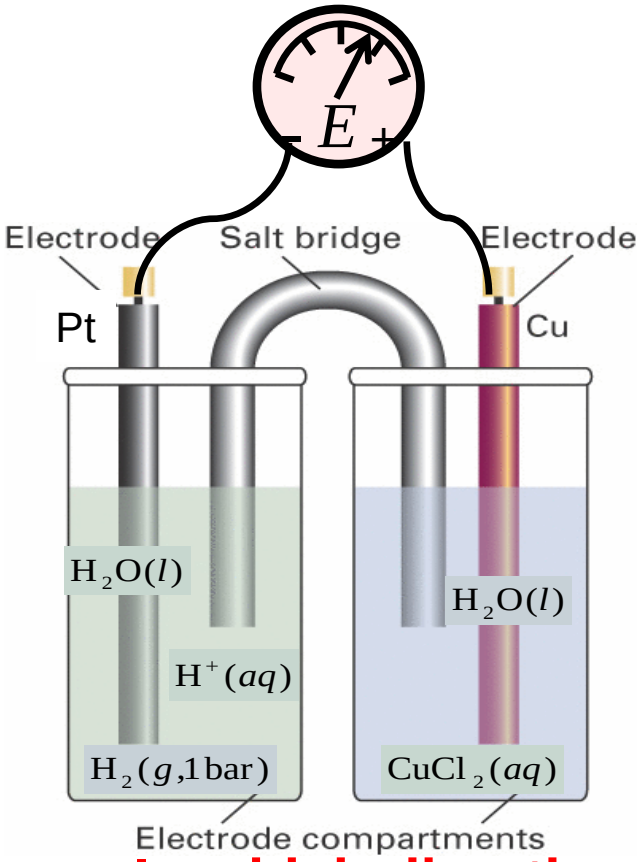
$$b_i^{\Theta} = 1\,\text{mol/kg}$$

$$x_i = 1$$

Chemical reaction equilibria: electrolytes

Chemical reaction equilibria: electrochemistry

Electrochemical cells: basic example



$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

(Reduction halfreaction)

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

(Reduction halfreaction)

$$2H^+(aq) + Cu(s) \rightarrow H_2(g) + Cu^{2+}(aq)$$

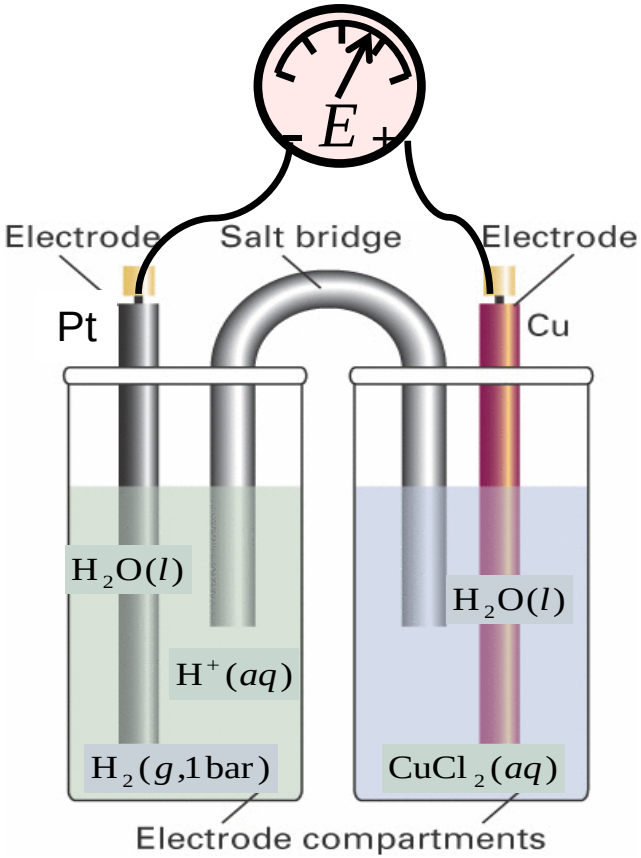
(Total cell reaction)

(Note: the equation is overall charge neutral)

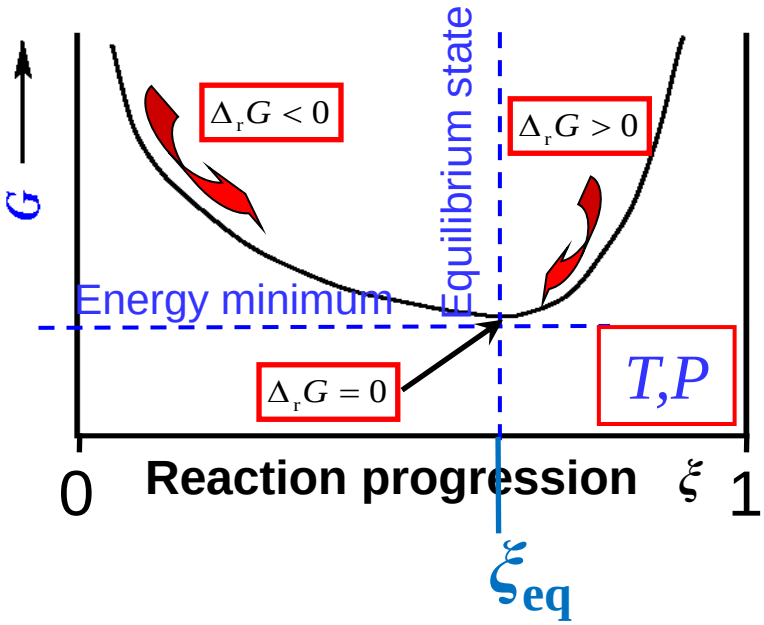
In which direction will the reaction run spontaneously?

→ **Where is the equilibrium?**

Chemical reaction equilibria: electrochemistry



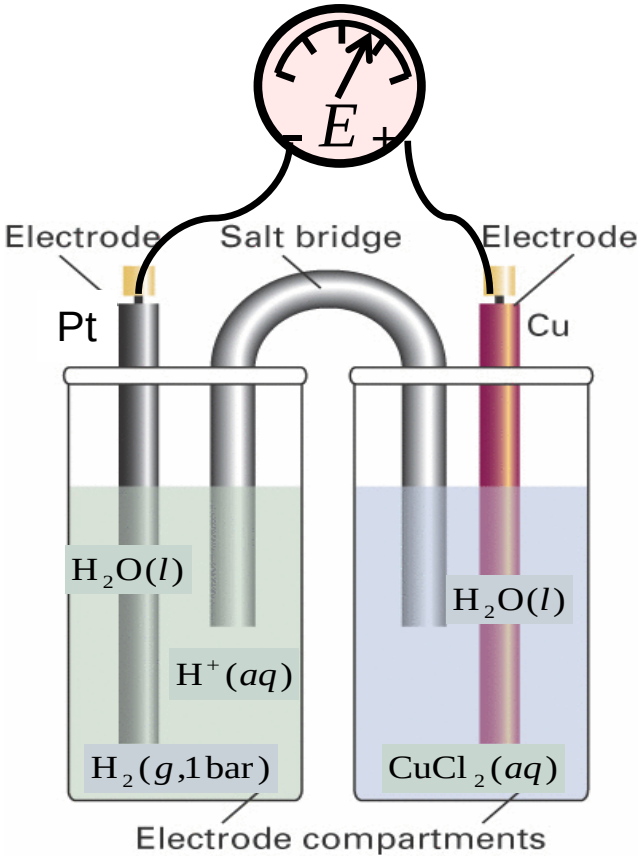
Voltage E represents a 'driving force' like $\Delta_r G$



Ideal volt meter has an infinitely large internal resistance

➔measures E with zero current

Chemical reaction equilibria: electrochemistry



Voltage E represents a 'driving force' like $\Delta_r G$

$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

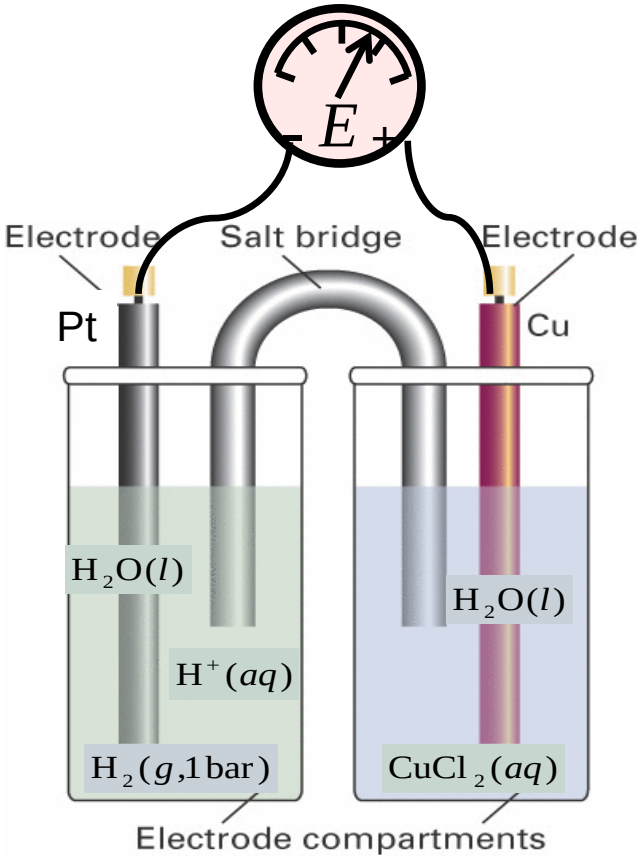
$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G_{m,i}{}^{\Theta}$$

Equilibrium:

$$\Delta_r G^{\Theta} = -RT \ln K$$

Relation between E and $\Delta_r G$

Chemical reaction equilibria: electrochemistry



Voltage E represents a 'driving force' like $\Delta_r G$

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$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G_{m,i}{}^{\Theta}$$

Equilibrium:

$$\Delta_r G^{\Theta} = -RT \ln K$$

Relation between E and $\Delta_r G$

$$\Delta_r G = -\nu F E$$

Chemical reaction equilibria: electrochemistry

$$\Delta_r G = -\nu F E \quad \Rightarrow \quad E = -\frac{\Delta_r G}{\nu F}$$

$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q \quad \Rightarrow \quad E = E^{\Theta} - \frac{RT}{\nu F} \ln Q$$

Equilibrium:

$$\Delta_r G^{\Theta} = -RT \ln K \quad \Rightarrow \quad E^{\Theta} = +\frac{RT}{\nu F} \ln K$$

Standard Gibbs free energy of formation

$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G_{m,i}{}^{\Theta} = -\nu F E^{\Theta}$$

Exercise 22

Number of electrons transferred in chemical equation

Faraday constant (charge of 1 mole of electrons)

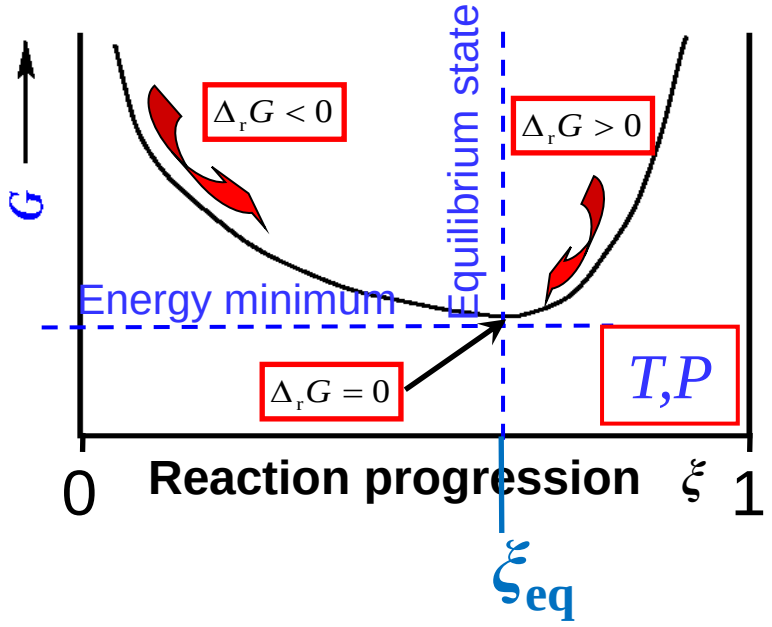
Chemical reaction equilibria: electrochemistry

$$\Delta_r G = \Delta_r G^{\Theta} + RT \ln Q$$

$$\Delta_r G = -\nu F E$$

$$E = E^{\Theta} - \frac{RT}{\nu F} \ln Q$$

Nernst equation



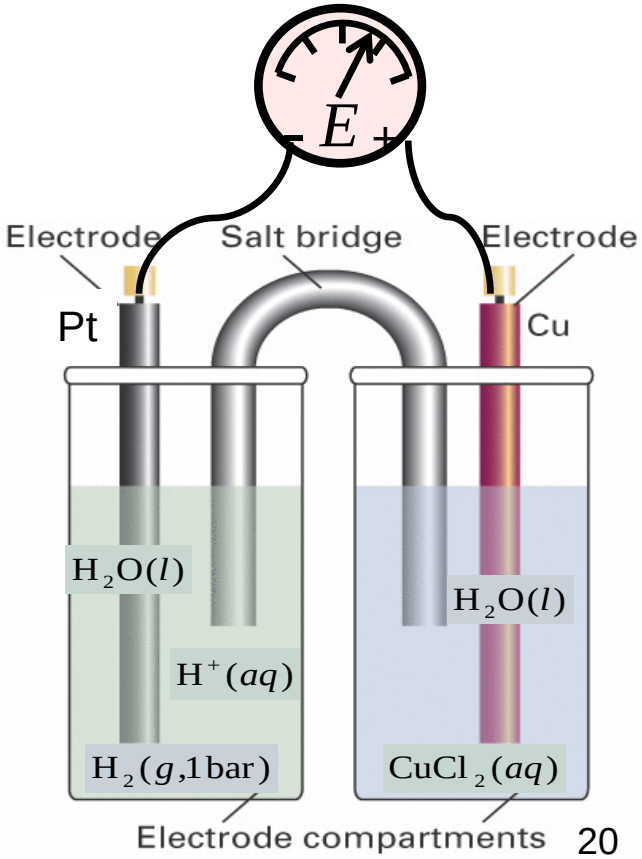
reaction

$\Delta_r G < 0$ $E > 0$ →

$\Delta_r G > 0$ $E < 0$ ←

$\Delta_r G = 0$ $E = 0$ ⟷

(equilibrium)



Chemical reaction equilibria: electrochemistry

Nernst equation $E = E^{\Theta} - \frac{RT}{\nu F} \ln Q$ **with** $Q = \prod_i a_i^{\nu_i}$

Nernst also holds for half reactions:

$$\mathrm{Cu}^{2+}(aq) + 2e^- \rightarrow \mathrm{Cu(s)}$$

$$E_{\mathrm{Cu}^{2+}/\mathrm{Cu}} = E^{\Theta}_{\mathrm{Cu}^{2+}/\mathrm{Cu}} - \frac{RT}{2F} \ln \frac{a_{\mathrm{Cu(s)}}}{a_{\mathrm{Cu}^{2+}(aq)}}$$

$$2\mathrm{H}^+(aq) + 2e^- \rightarrow \mathrm{H}_2(g)$$

Note: reduction half reaction

$$E_{2\mathrm{H}^+/\mathrm{H}_2(\mathrm{g})} = E^{\Theta}_{2\mathrm{H}^+/\mathrm{H}_2(\mathrm{g})} - \frac{RT}{2F} \ln \frac{a_{\mathrm{H}_2(\mathrm{g})}}{a^2_{\mathrm{H}^+(aq)}}$$

Chemical reaction equilibria: electrochemistry

Nernst also holds for half reactions

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

$$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$$

$$2H^+(aq) + Cu(s) \rightarrow H_2(g) + Cu^{2+}(aq)$$

Chemical reaction equilibria: electrochemistry

Nernst also holds for half reactions

$$2H^+(aq) + Cu(s) \rightarrow H_2(g) + Cu^{2+}(aq)$$

$$E_{2H^+/H_2(g)} = E^{\Theta}_{2H^+/H_2(g)} - \frac{RT}{2F} \ln \frac{a_{H_2(g)}}{a^2_{H^+(aq)}}$$

$$E_{Cu^{2+}/Cu} = E^{\Theta}_{Cu^{2+}/Cu} - \frac{RT}{2F} \ln \frac{a_{Cu(s)}}{a_{Cu^{2+}(aq)}}$$

$$E_{\text{total cell}} = E^{\Theta}_{2H^+/H_2} - E^{\Theta}_{Cu^{2+}/Cu} - \frac{RT}{2F}\left[\ln \frac{a_{H_2(g)}}{a^2_{H^+(aq)}} - \ln \frac{a_{Cu(s)}}{a_{Cu^{2+}(aq)}}\right]$$

Reduction half reactions as in the tables

Chemical reaction equilibria: electrochemistry

Nernst also holds for half reactions

$$2H^+(aq) + Cu(s) \rightarrow H_2(g) + Cu^{2+}(aq)$$

$$E_{\text{total cell}} = E^{\Theta}_{2H^+/H_2} - E^{\Theta}_{Cu^{2+}/Cu} - \frac{RT}{2F}\left[\ln \frac{a_{H_2(g)}}{a^2_{H^+(aq)}} - \ln \frac{a_{Cu(s)}}{a_{Cu^{2+}(aq)}}\right]$$

$$E_{\text{total cell}} = E^{\Theta}_{2H^+/H_2} - E^{\Theta}_{Cu^{2+}/Cu} - \frac{RT}{2F}\ln \frac{a_{H_2(g)}a_{Cu^{2+}(aq)}}{a^2_{H^+(aq)}a_{Cu(s)}}$$

$$E_{\text{total cell}} = E^{\Theta}_{2H^+/H_2} - E^{\Theta}_{Cu^{2+}/Cu} - \frac{RT}{2F}\ln \frac{a_{H_2(g)}a_{Cu^{2+}(aq)}}{a^2_{H^+(aq)}}$$

$$a_{Cu(s)} \approx 1$$

Chemical reaction equilibria: electrochemistry

Electrochemical cells: another example

$$MnO_4^-(aq) + 8H^+(aq) + 5Fe^{2+}(aq) \rightarrow Mn^{2+}(aq) + 4H_2O(l) + 5Fe^{3+}(aq)$$

$$E_{\text{total cell}} = E^{\Theta}_{MnO_4^-/Mn^{2+}} - E^{\Theta}_{Fe^{3+}/Fe^{2+}} - \frac{RT}{5F}\left[\ln \frac{a_{Mn^{2+}} a^4_{H_2O} a^5_{Fe^{3+}}}{a_{MnO_4^-} a^8_{H^+} a^5_{Fe^{2+}}}\right]$$

Standard electrochemical potentials of redox couples are in tables as reduction half reactions

$$\nu = 5 \text{ (electrons)}$$

- sign as we need a reduction and an oxidation half reaction

Chemical reaction equilibria: ions in solution

	M/(g mol^{-1})	$\Delta_f H^\ominus$/(kJ mol^{-1})	$\Delta_f G^\ominus$/(kJ mol^{-1})	$S_m^\ominus$/(J K^{-1} mol^{-1})†	$C_{p,m}^\ominus$/(J K^{-1} mol^{-1}
Fluorine					
F_2(g)	38.00	0	0	202.78	31.30
F(g)	19.00	+78.99	+61.91	158.75	22.74
F^-(aq)	19.00	−332.63	−278.79	−13.8	−106.7
HF(g)	20.01	−271.1	−273.2	173.78	29.13
Gold					
Au(s)	196.97	0	0	47.40	25.42
Au(g)	196.97	+366.1	+326.3	180.50	20.79
Helium					
He(g)	4.003	0	0	126.15	20.786
Hydrogen (see also deuterium)					
H_2(g)	2.016	0	0	130.684	28.824
H(g)	1.008	+217.97	+203.25	114.71	20.784
H^+(aq)	1.008	0	0	0	0
H^+(g)	1.008	+1536.20			
H_2O(s)	18.015			37.99	
H_2O(l)	18.015	−285.83	−237.13	69.91	75.291
H_2O(g)	18.015	−241.82	−228.57	188.83	33.58
H_2O_2(l)	34.015	−187.78	−120.35	109.6	89.1
Iodine					
I_2(s)	253.81	0	0	116.135	54.44
I_2(g)	253.81	+62.44	+19.33	260.69	36.90
I(g)	126.90	+106.84	+70.25	180.79	20.786
I^-(aq)	126.90	−55.19	−51.57	+111.3	−142.3
HI(g)	127.91	+26.48	+1.70	206.59	29.158
Iron					
Fe(s)	55.85	0	0	27.28	25.10
Fe(g)	55.85	+416.3	+370.7	180.49	25.68
Fe^{2+}(aq)	55.85	−89.1	−78.90	−137.7	
Fe^{3+}(aq)	55.85	−48.5	−4.7	−315.9	
Fe_3O_4(s) (magnetite)	231.54	−1118.4	−1015.4	146.4	143.43
Fe_2O_3(s) (haematite)	159.69	−824.2	−742.2	87.40	103.85
FeS(s, α)	87.91	−100.0	−100.4	60.29	50.54
FeS_2(s)	119.98	−178.2	−166.9	52.93	62.17
Krypton					
Kr(g)	83.80	0	0	164.08	20.786
Lead					
Pb(s)	207.19	0	0	64.81	26.44
Pb(g)	207.19	+195.0	+161.9	175.37	20.79
Pb^{2+}(aq)	207.19	−1.7	−24.43	+10.5	
PbO(s, yellow)	223.19	−217.32	−187.89	68.70	45.77
PbO(s, red)	223.19	−218.99	−188.93	66.5	45.81
PbO_2(s)	239.19	−277.4	−217.33	68.6	64.64

$$\Delta_r G^\Theta = \sum_i \nu_i \Delta_f G_{m,i}{}^\Theta = -\nu F E^\Theta$$

$$\Delta_f G^\Theta_{m,H^+} \equiv \Delta_f H^\Theta_{m,H^+} \equiv 0 \text{ all } T$$

Standard thermodynamic data

(@ 298K)

(Ed.11: Table 2C.7)

Standard electrochemical potentials $E^{\ominus}$ of redox couples

(@ 298K) alphabetical order (Ed.11: Table 6D.1b)

for all *T*(aq)

Reduction half-reaction	$E^{\ominus}$/V	Reduction half-reaction	$E^{\ominus}$/V
$Ag^+ + e^- \rightarrow Ag$	+0.80	$I_2 + 2e^- \rightarrow 2I^-$	+0.54
$Ag^{2+} + e^- \rightarrow Ag^+$	+1.98	$I_3^- + 2e^- \rightarrow 3I^-$	+0.53
$AgBr + e^- \rightarrow Ag + Br^-$	+0.0713	$In^+ + e^- \rightarrow In$	−0.14
$AgCl + e^- \rightarrow Ag + Cl^-$	+0.22	$In^{2+} + e^- \rightarrow In^+$	−0.40
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	+0.45	$In^{3+} + 2e^- \rightarrow In^+$	−0.44
$AgF + e^- \rightarrow Ag + F^-$	+0.78	$In^{3+} + 3e^- \rightarrow In$	−0.34
$AgI + e^- \rightarrow Ag + I^-$	−0.15	$In^{3+} + e^- \rightarrow In^{2+}$	−0.49
$Al^{3+} + 3e^- \rightarrow Al$	−1.66	$K^+ + e^- \rightarrow K$	−2.93
$Au^+ + e^- \rightarrow Au$	+1.69	$La^{3+} + 3e^- \rightarrow La$	−2.52
$Au^{3+} + 3e^- \rightarrow Au$	+1.40	$Li^+ + e^- \rightarrow Li$	−3.05
$Ba^{2+} + 2e^- \rightarrow Ba$	+2.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.36
$Be^{2+} + 2e^- \rightarrow Be$	−1.85	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$Bi^{3+} + 3e^- \rightarrow Bi$	+0.20	$Mn^{3+} + e^- \rightarrow Mn^{2+}$	+1.51
$Br_2 + 2e^- \rightarrow 2Br^-$	+1.09	$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	+1.23
$BrO^- + H_2O + 2e^- \rightarrow Br^- + 2OH^-$	+0.76	$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.51
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.87	$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	+0.56
$Cd(OH)_2 + 2e^- \rightarrow Cd + 2OH^-$	−0.81	$MnO_4^{2-} + 2H_2O + 2e^- \rightarrow MnO_2 + 4OH^-$	+0.60
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40	$Na^+ + e^- \rightarrow Na$	−2.71
$Ce^{3+} + 3e^- \rightarrow Ce$	−2.48	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61	$NiOOH + H_2O + e^- \rightarrow Ni(OH)_2 + OH^-$	+0.49
$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.36	$NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$	−0.80
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	+0.89	$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	+0.96
$ClO_4^- + 2H^+ + 2e^- \rightarrow ClO_3^- + H_2O$	+1.23	$NO_3^- + H_2O + 2e^- \rightarrow NO_2^- + 2OH^-$	+0.10
$ClO_4^- + H_2O + 2e^- \rightarrow ClO_3^- + 2OH^-$	+0.36	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.40
$Co^{2+} + 2e^- \rightarrow Co$	−0.28	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	+1.23
$Co^{3+} + e^- \rightarrow Co^{2+}$	+1.81	$O_2 + e^- \rightarrow O_2^-$	−0.56
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.91	$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$	−0.08
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	+1.33	$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	+2.07
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.74	$O_3 + H_2O + 2e^- \rightarrow O_2 + 2OH^-$	+1.24
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.41	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Cs^+ + e^- \rightarrow Cs$	−2.92	$Pb^{4+} + 2e^- \rightarrow Pb^{2+}$	+1.67
$Cu^+ + e^- \rightarrow Cu$	+0.52	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.36
$Cu^{2+} + 2e^- \rightarrow Cu$	+0.34	$Pt^{2+} + 2e^- \rightarrow Pt$	+1.20
$Cu^{2+} + e^- \rightarrow Cu^+$	+0.16	$Pu^{4+} + e^- \rightarrow Pu^{3+}$	+0.97
$F_2 + 2e^- \rightarrow 2F^-$	+2.87	$Ra^{2+} + 2e^- \rightarrow Ra$	−2.92
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44	$Rb^+ + e^- \rightarrow Rb$	−2.93
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.04	$S + 2e^- \rightarrow S^{2-}$	−0.48
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.77	$S_2O_8^{2-} + 2e^- \rightarrow 2SO_4^{2-}$	+2.05
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	+0.36	$Sc^{3+} + 3e^- \rightarrow Sc$	−2.09
$2H^+ + 2e^- \rightarrow H_2$	0, by definition	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
$2HBrO + 2H^+ + 2e^- \rightarrow Br_2 + 2H_2O$	+1.60	$Sr^{2+} + 2e^- \rightarrow Sr$	−2.89
$2HClO + 2H^+ + 2e^- \rightarrow Cl_2 + 2H_2O$	+1.63	$Ti^{2+} + 2e^- \rightarrow Ti$	−1.63
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	+1.78	$Ti^{3+} + e^- \rightarrow Ti^{2+}$	−0.37
$H_4XeO_6 + 2H^+ + 2e^- \rightarrow XeO_3 + 3H_2O$	+3.0	$Ti^{4+} + e^- \rightarrow Ti^{3+}$	0.00
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	+0.79	$Tl^+ + e^- \rightarrow Tl$	−0.34
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	+0.27	$U^{3+} + 3e^- \rightarrow U$	−1.79
$Hg^{2+} + 2e^- \rightarrow Hg$	+0.86	$U^{4+} + e^- \rightarrow U^{3+}$	−0.61
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	+0.92	$V^{2+} + 2e^- \rightarrow V$	−1.19
$Hg_2SO_4 + 2e^- \rightarrow 2Hg + SO_4^{2-}$	+0.62	$V^{3+} + e^- \rightarrow V^{2+}$	−0.26
		$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76

Chemical reaction equilibria: electrochemistry

Standard hydrogen electrode

$$\Delta_f G^{\Theta}_{H^+(aq)} \equiv 0 \text{ for all } T$$

$$E^{\Theta}_{2H^+/H_2} \equiv 0 \text{ for all } T$$

Chemical reaction equilibria: electrochemistry

Standard hydrogen electrode:

$$P_{H_2(g)} = P^{\Theta} \text{ and } a_{H^+} = 1$$

$$\Delta_f G^{\Theta}_{H^+(aq)} \equiv 0 \text{ for all } T$$

$$E^{\Theta}_{2H^+/H_2} \equiv 0 \text{ for all } T$$

$$2H^+(aq) + 2e^- \rightarrow H_2(g)$$

$$E_{2H^+/H_2(g)} = E^{\Theta}_{2H^+/H_2(g)} - \frac{RT}{2F} \ln \frac{a_{H_2(g)}}{a^2_{H^+}} = - \frac{RT}{2F} \ln \frac{a_{H_2(g)}}{a^2_{H^+}} = 0$$

$$pH \equiv -^{10}\log a_{H^+} = -^{10}\log \left[H^+\right] - ^{10}\log \gamma^{(c)}_{H^+}$$

Chemical reaction equilibria: general

Activity as an effective concentration

$$\mu_i \equiv \mu_i^{\Theta} + RT \ln a_i$$

Molarity (mol/L)

$$c_i = \frac{\#\,\text{mol solute } i}{\text{volume } V \text{ solution}} = \frac{n_i}{V}$$

$$a_i = \gamma_i^{(c)} \frac{c_i}{c^{\Theta}}$$

$$c^{\Theta} \equiv 1\,\text{mol/L}$$

Molality (mol/kg)

$$b_i = \frac{\#\,\text{mol solute } i}{\text{mass } m \text{ solvent}} = \frac{n_i}{m}$$

$$a_i = \gamma_i^{(b)} \frac{b_i}{b^{\Theta}}$$

$$b^{\Theta} \equiv 1\,\text{mol/kg}$$

Mole fraction ( )

$$x_i = \frac{\#\,\text{mol solute } i}{\text{total } \#\,\text{mol in solution}} = \frac{n_i}{n}$$

$$a_i = \gamma_i^{(x)} x_i$$

Standard state **Θ**
(still *T* dependent)

$$P = P^{\Theta}$$

$$a_i^{\Theta} = 1$$

and pure

$$c_i^{\Theta} = 1\,\text{mol/L}$$

$$b_i^{\Theta} = 1\,\text{mol/kg}$$

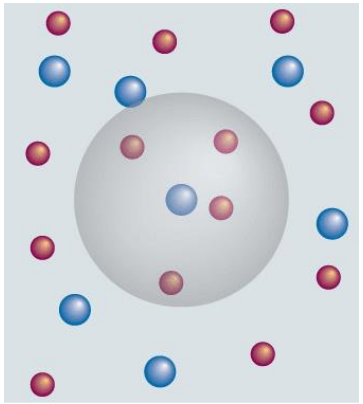
$$x_i = 1$$

even for ions!

Chemical reaction equilibria: electrolytes

Activity coefficients in electrolytic solutions

Activity coefficients solutes electrolytic solutions



$$M_pX_q \leftrightarrow pM^{z+} + qX^{z-}$$

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

chemical potential of the dissolved salt

example

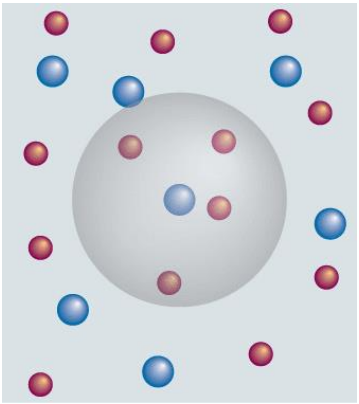
$$FeCl_2(s) \leftrightarrow Fe^{2+}(aq) + 2Cl^-(aq) \rightarrow \begin{cases} p = 1 \\ z+ = +2 \\ q = 2 \\ z- = -1 \end{cases}$$

example

$$Fe_2(SO_4)_3(s) \leftrightarrow 2Fe^{3+}(aq) + 3SO_4^{2-}(aq) \rightarrow \begin{cases} p = 2 \\ z+ = +3 \\ q = 3 \\ z- = -2 \end{cases}$$

→ 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



$$M_pX_q \leftrightarrow pM^{z+} + qX^{z-}$$

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

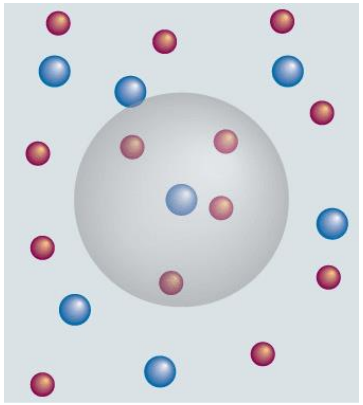
chemical potential of the dissolved salt

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

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

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

Activity coefficients solutes electrolytic solutions



$$M_pX_q \leftrightarrow pM^{z+} + qX^{z-}$$

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

chemical potential of the dissolved salt

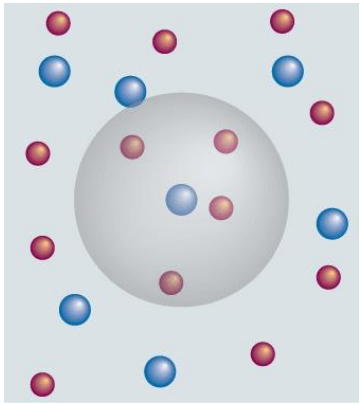
$$\mu_+ = \mu_+^{ideal} + RT \ln \gamma_+ \qquad \mu_- = \mu_-^{ideal} + RT \ln \gamma_-$$

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

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

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

Activity coefficients solutes electrolytic solutions



$$M_pX_q \leftrightarrow pM^{z+} + qX^{z-}$$

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

chemical potential of the dissolved salt

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

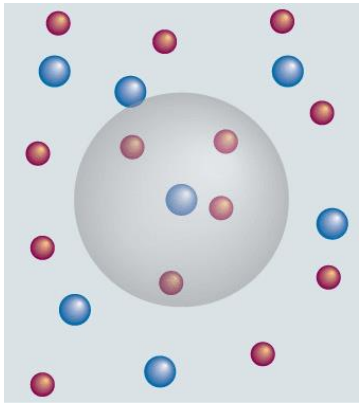
It is impossible to determine (measure) μ_+ and μ_- individually

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

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

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

Activity coefficients solutes electrolytic solutions



$$M_pX_q \leftrightarrow pM^{z+} + qX^{z-}$$

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

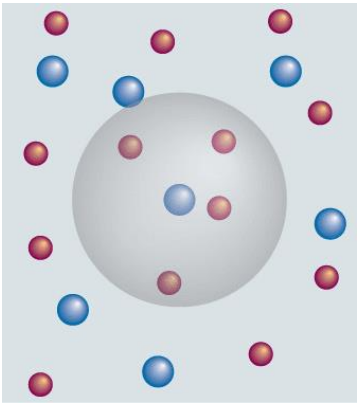
chemical potential of the dissolved salt

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

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

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

Activity coefficients solutes electrolytic solutions



$$M_pX_q \leftrightarrow pM^{z+} + qX^{z-}$$

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

chemical potential of the dissolved salt

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

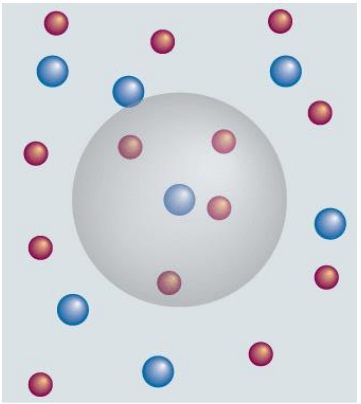
$$\mu^{ideal} = p\mu_+^{ideal} + q\mu_-^{ideal} \Rightarrow \mu = \mu^{ideal} + RT \ln \gamma_+^p \gamma_-^q$$

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

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

(The solution has to be charge neutral)

Activity coefficients solutes electrolytic solutions



$$M_pX_q \leftrightarrow pM^{z+} + qX^{z-}$$

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

chemical potential of the dissolved salt

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

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

average chemical potential per ion

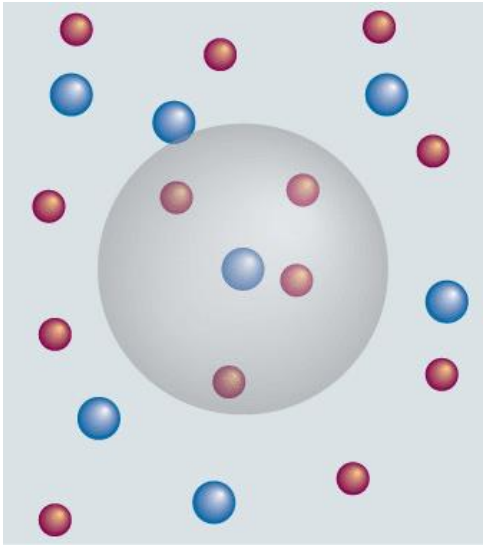
$$\mu_i = \frac{\mu}{p+q} = \frac{\mu^{ideal}}{p+q} + \frac{RT}{p+q} \ln\left(\gamma_+^p \gamma_-^q\right)$$

Mean activity coefficient

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

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

Mean activity coefficient: Debye-Hückel



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

(ions *i* of a dissolved salt)

Mean activity coefficient

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

$$\left(\mathrm{M}_p\mathrm{X}_q \leftrightarrow p\mathrm{M}^{z+} + q\mathrm{X}^{z-}\right)$$

Because of the sensitivity of γ_i of the ions we will use molality b_i

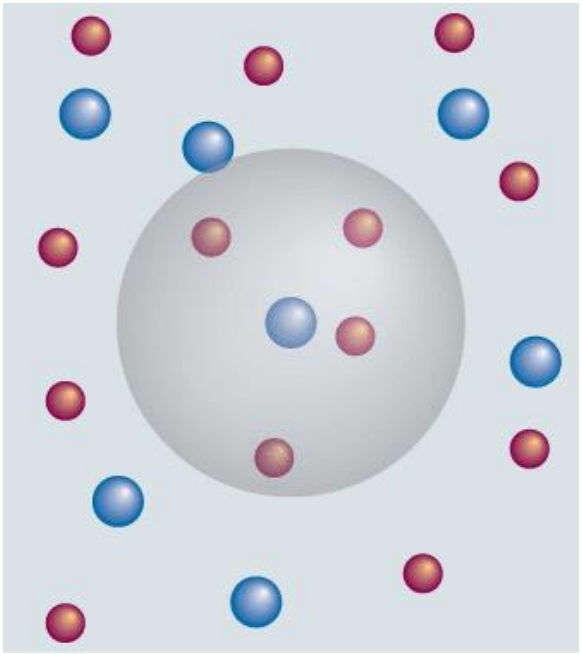
Molality (mol/kg)

$$b_i = \frac{\#\,\text{mol solute } i}{\text{mass } m \text{ solvent}} = \frac{n_i}{m}$$

$$a_i = \gamma_i^{(b)} \frac{b_i}{b^\Theta}$$

$$b^\Theta \equiv 1\,\text{mol/kg}$$

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)

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

Ionic strength

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

(sum over all ions in solution)

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

A = 0.509 for H_2O @ 298 K

Activity coefficients solutes electrolytic solutions

Debye-Hückel:

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

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

Ionic strength

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

Mean activity coefficient

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

Example

$$\mathrm{FeCl_2}(s) + \mathrm{FeCl_3}(s) + \leftrightarrow \mathrm{Fe^{2+}}(aq) + \mathrm{Fe^{3+}}(aq) + 5\mathrm{Cl^-}(aq)$$

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

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

Sum over all ions in the solution

Activity coefficients solutes electrolytic solutions

Debye-Hückel:

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

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

Ionic strength

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

Mean activity coefficient

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

Example

$$\mathrm{FeCl_2}(s) + \mathrm{FeCl_3}(s) + \leftrightarrow \mathrm{Fe^{2+}}(aq) + \mathrm{Fe^{3+}}(aq) + 5\mathrm{Cl^-}(aq)$$

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

relative molality $\dfrac{b_i}{b^{\Theta}} = \dfrac{b_i(\mathrm{mol/kg})}{1(\mathrm{mol/kg})}$

Activity coefficients solutes electrolytic solutions

Debye-Hückel:

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

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

Ionic strength

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

Mean activity coefficient

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

Example

$$\mathrm{FeCl_2}(s) + \mathrm{FeCl_3}(s) + \leftrightarrow \mathrm{Fe^{2+}}(aq) + \mathrm{Fe^{3+}}(aq) + 5\mathrm{Cl^-}(aq)$$

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

$$\log \gamma_{\pm}^{\mathrm{FeCl_2}} = -\left|2 \cdot 1\right| A\sqrt{I} = -2A\sqrt{I}$$

$$\log \gamma_{\pm}^{\mathrm{FeCl_3}} = -3A\sqrt{I}$$

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Exercise 23-25

$$\log \gamma_{\pm}^{\mathrm{FeCl_2}} = -\left|2 \cdot 1\right| A \sqrt{I} = -2A\sqrt{I}$$

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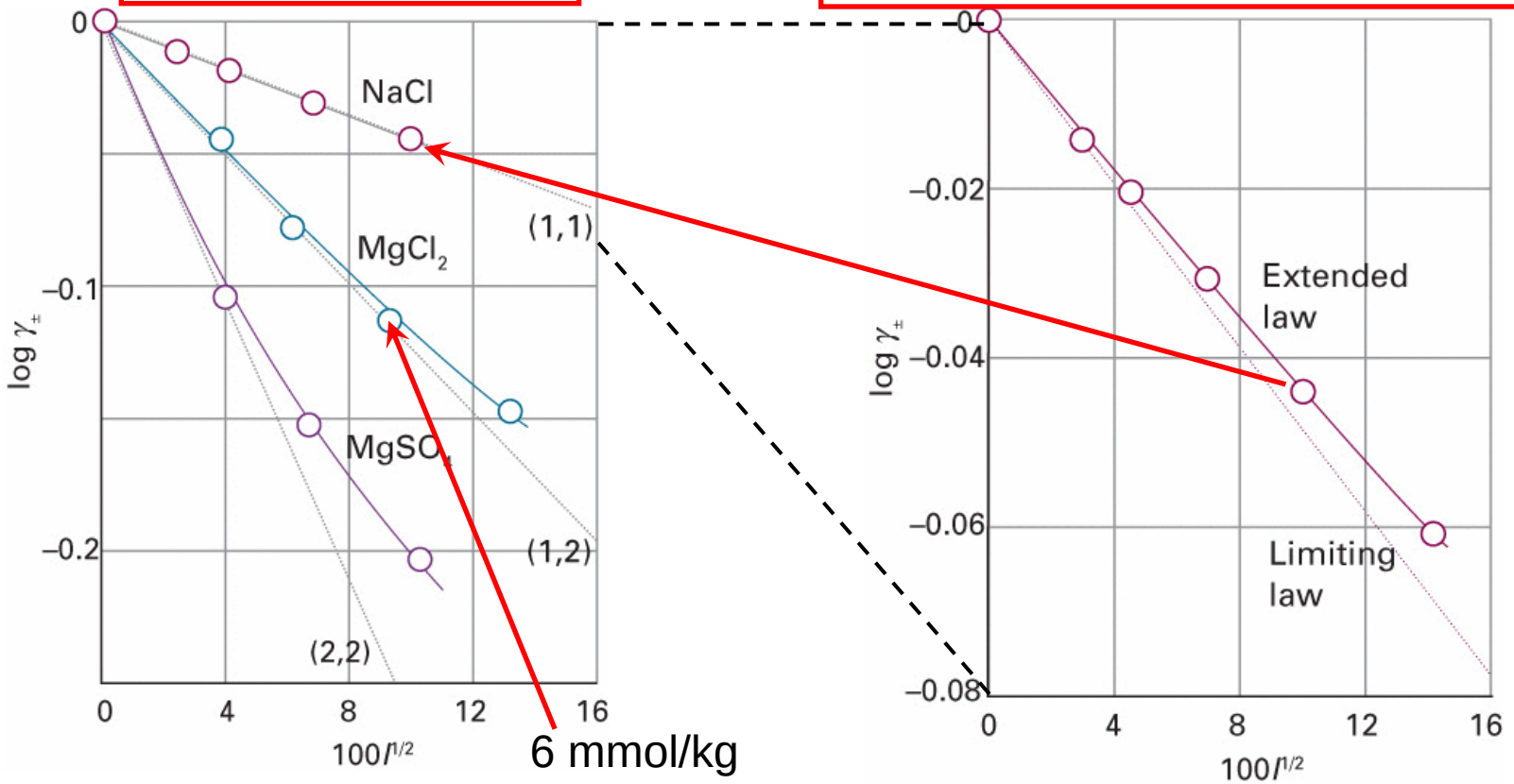
Activity coefficients solutes electrolytic solutions

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

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

extended Debye-Hückel:

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



Activity coefficients solutes electrolytic solutions

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

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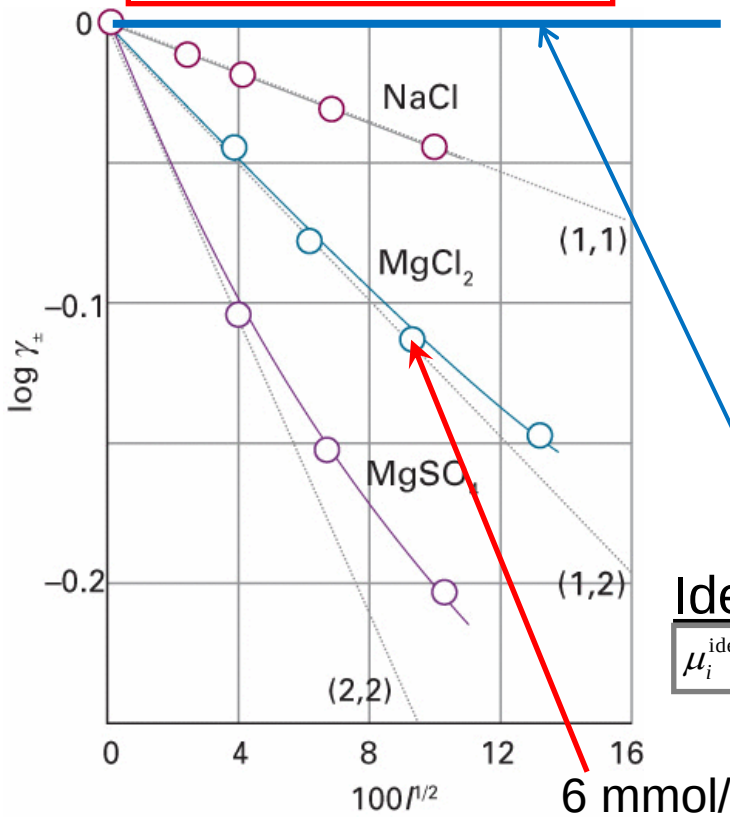
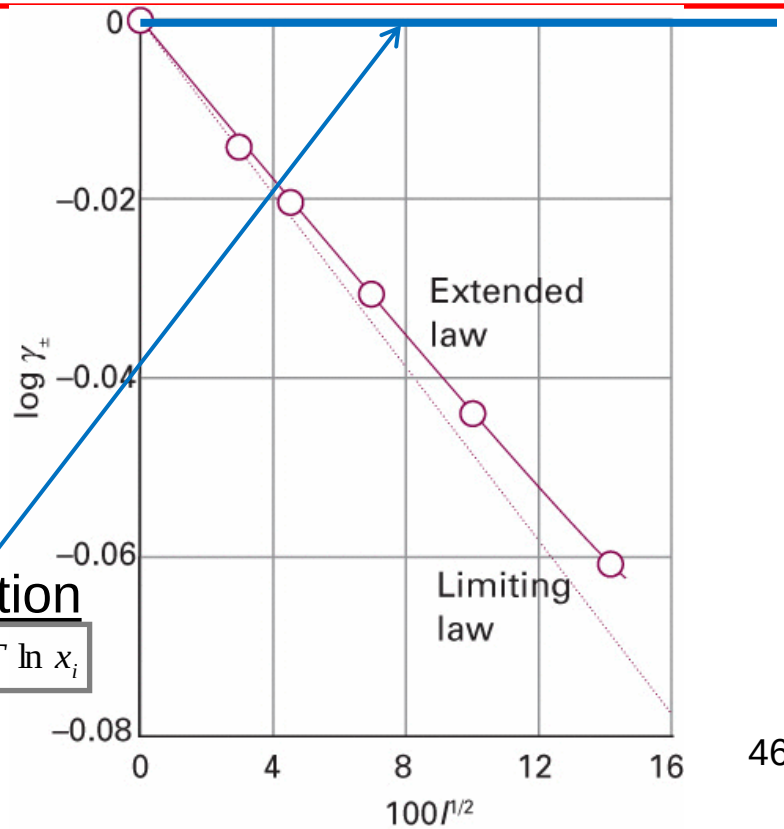


Ideal solution

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

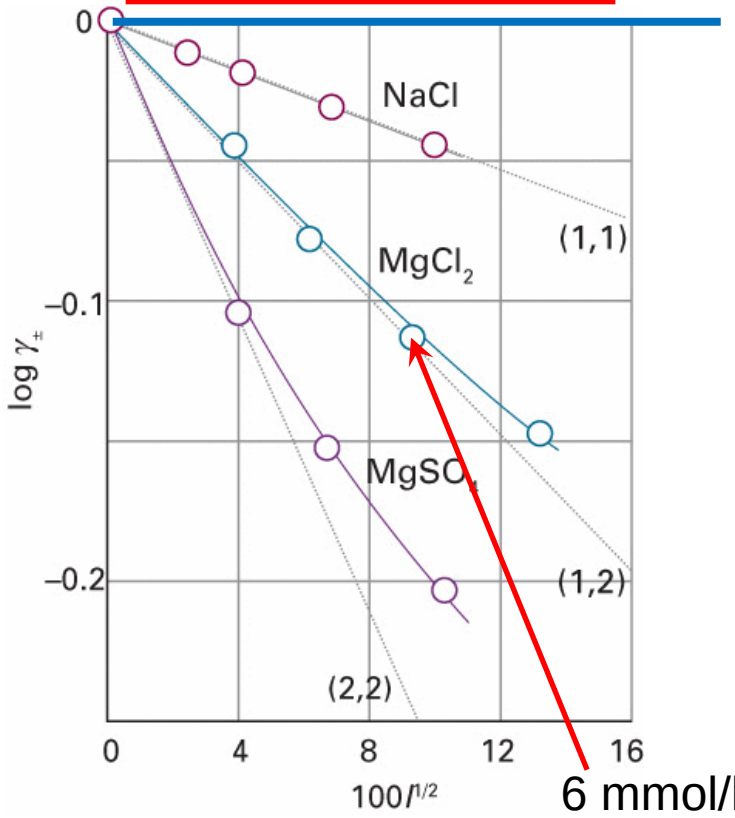
6 mmol/kg



Activity coefficients solutes electrolytic solutions

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

$$I = \frac{1}{2} \sum_{i} z_i^2 \frac{b_i}{b^{\Theta}}$$



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

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

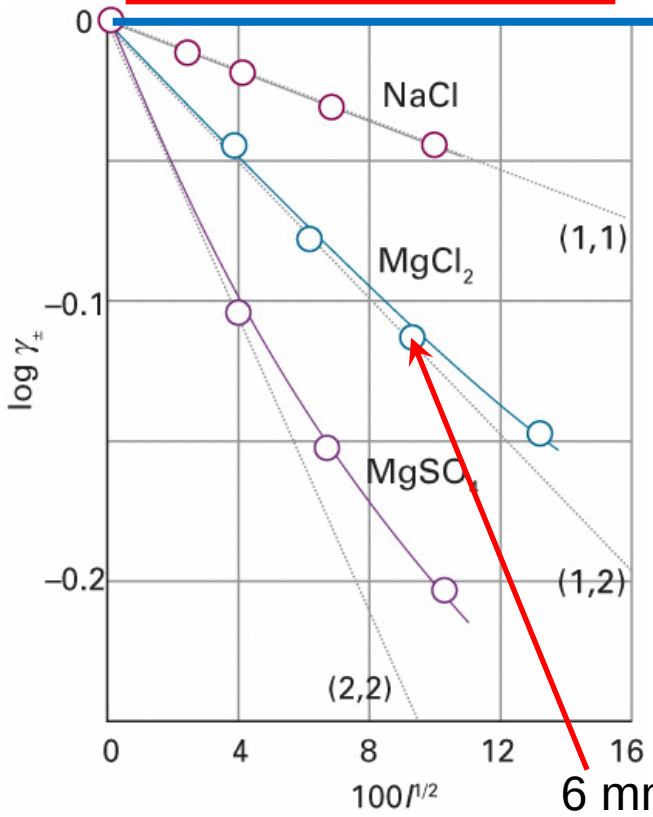
Activity coefficients solutes electrolytic solutions

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

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

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

Ideal mixing entropy term



6 mmol/kg

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

$$\mu_i = \mu_i^* + RT \ln x_i + RT \ln \gamma_{\pm}$$

Lowers μ_i even more due to the electrostatic attraction and repulsion

Chemical reaction equilibria: dissolution

Aqueous dissolution of (sparingly soluble) salts

$$\mathrm{Ca_3(PO_4)_2(s) \leftrightarrow 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$$

(Note: the equation is overall charge neutral)

$$\Delta_r G^\Theta = -RT \ln Q_{eq} = -RT \ln K$$

assume ideal solution: $\gamma_\pm \approx 1$

$$K = \left(\prod_i a_i^{\nu_i} \right)_{eq} = \frac{a^3_{Ca^{2+}(aq)} a^2_{PO_4^{3-}(aq)}}{a_{Ca_3(PO_4)_2}(s)} \approx \frac{\frac{b^3_{Ca^{2+}(aq)}}{(b^\Theta)^3} \cdot \frac{b^2_{PO_4^{3-}(aq)}}{(b^\Theta)^2}}{1} = \frac{b^3_{Ca^{2+}(aq)} b^2_{PO_4^{3-}(aq)}}{(b^\Theta)^5}$$

Solubility s of the salt:
(as a molality)

$$s\left(\frac{\mathrm{mol\ Ca_3(PO_4)_2}(aq)}{\mathrm{kg\ H_2O}(l)} \right) = \frac{b_{Ca^{2+}(aq)}}{3} = \frac{b_{PO_4^{3-}(aq)}}{2}$$

$$K = \frac{(3s)^3 (2s)^2}{(b^\Theta)^5}$$

$$s = \left(\frac{K}{108} \right)^{1/5} b^\Theta (\mathrm{mol/kg})$$

Chemical reaction equilibria: dissolution

Aqueous dissolution of (sparingly soluble) salts

$$\mathrm{Ca_3(PO_4)_2(s) \leftrightarrow 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)}$$

(Note: the equation is overall charge neutral)

$$\Delta_r G^\Theta = -RT \ln Q_{eq} = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^\Theta}{RT}$$

$$s = \frac{K^{1/5}}{108} \text{(mol/kg)}$$

$$\Delta_r G^\Theta = \sum_i \nu_i \Delta_f G^\Theta_{i,m} = 3\Delta_f G^\Theta_{Ca^{2+},m} + 2\Delta_f G^\Theta_{PO_4^{3-},m} - \Delta_f G^\Theta_{Ca_3(PO_4)_2(s),m}$$

$$\Delta_r G^\Theta = 3\cdot(-553.58) + 2\cdot(-1018.7) - (-3884.7) = 186.6$$

kJ/mol @ 298 K

$$K = \exp\left(-\frac{\Delta_r G^\Theta}{RT}\right) = 1.99\cdot10^{-33}$$

$$s = 1.13\cdot10^{-7}$$

mol/kg @ 298 K

No exp. value

Chemical reaction equilibria: dissolution

Aqueous dissolution of (sparingly soluble) salts

Another example

$$\mathrm{AgCl(s)} \leftrightarrow \mathrm{Ag^+(aq) + Cl^-(aq)}$$

(Note: the equation is overall charge neutral)

$$\Delta_r G^\Theta = -RT \ln Q_{eq} = -RT \ln K$$

$$K = \left(\prod_i a_i^{\nu_i} \right)_{eq} = \frac{a_{Ag^+} a_{Cl^-}}{a_{AgCl(s)}} \approx \frac{a_{Ag^+} a_{Cl^-}}{1} = \gamma_\pm^2 \frac{b_{Ag^+} b_{Cl^-}}{(b^\Theta)^2}$$

Solubility s of the salt: (as a molality)

$$s \left(\frac{\text{mol AgCl}(s)}{\text{kg H}_2\text{O}(l)} \right) = b_{Ag^+(aq)} = b_{Cl^+(aq)}$$

$$K = \frac{\gamma_\pm^2 s^2}{(b^\Theta)^2} \quad \Rightarrow \quad s = \frac{K^{1/2}}{\gamma_\pm} b^\Theta \, (\text{mol/kg})$$

Chemical reaction equilibria: dissolution

Aqueous dissolution of (sparingly soluble) salts

$$AgCl(s) \leftrightarrow Ag^{+}(aq) + Cl^{-}(aq)$$

(Note: the equation is overall charge neutral)

assume: $\gamma_{\pm} \approx 1$

$$\Delta_r G^{\Theta} = -RT \ln Q_{eq} = -RT \ln K$$

$$\ln K = -\frac{\Delta_r G^{\Theta}}{RT}$$

$$s = K^{1/2} \text{ (mol/kg)}$$

$$\Delta_r G^{\Theta} = \sum_i \nu_i \Delta_f G^{\Theta}_{i,m} = \Delta_f G^{\Theta}_{Ag^+,m} + \Delta_f G^{\Theta}_{Cl^-,m} - \Delta_f G^{\Theta}_{AgCl(s),m}$$

$$\Delta_r G^{\Theta} = 77.11 + (-131.23) - (-109.8) = 55.68$$

kJ/mol @ 298 K

$$K = \exp\left(-\frac{\Delta_r G^{\Theta}}{RT}\right) = 1.74 \cdot 10^{-10}$$

$$s = 1.3 \cdot 10^{-5}$$

mol/kg @ 298 K

Exercise 24

Chemical reaction equilibria: dissolution

Aqueous dissolution of (sparingly soluble) salts

-Increase in solubility due to ionic strength

Add a well-soluble salt to the sparingly soluble salt solution

$$I \uparrow \Rightarrow \gamma_{\pm} \downarrow \text{ solubility } s \uparrow$$

Exercise 24

-Common ion effect

Add a well-soluble salt with an ion j common to the original salt

$$I \uparrow \Rightarrow \gamma_{\pm} \downarrow, \text{but } b_j \uparrow \Rightarrow \text{solubility } s \downarrow$$

(Le Chatelier's principle)

Exercise 25

Mean activity coefficient: Debye-Hückel

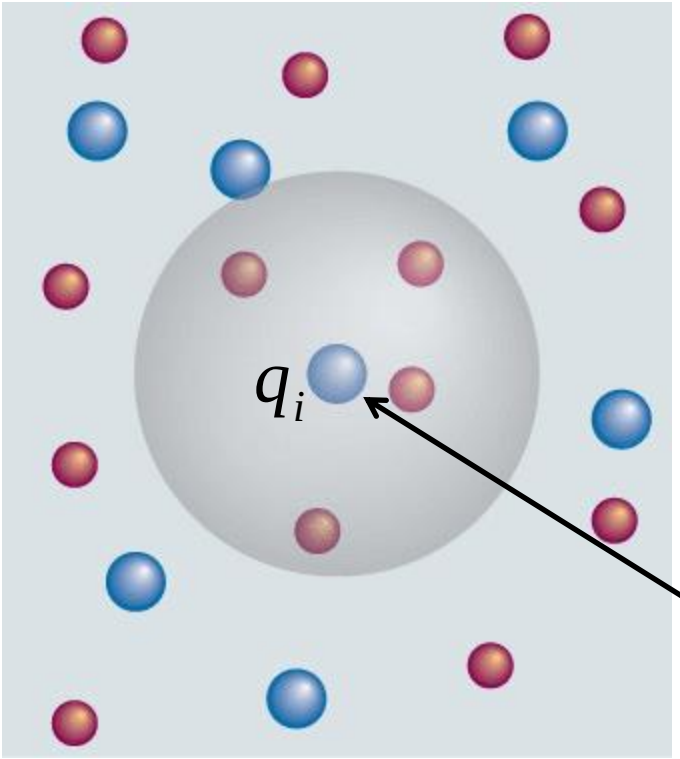
Only in case you are interested in the background of the Debye-Huckel theory (not necessary for the exam)

https://learninglink.oup.com/access/pchem12e-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 :

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



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

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

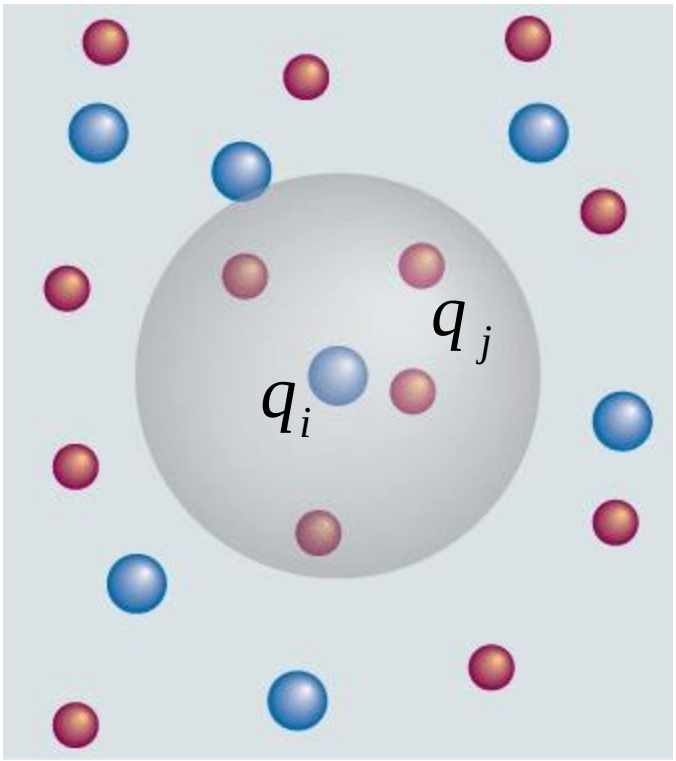
Choose a central ion i with charge q_i in the solution

Mean activity coefficient: Debye-Hückel

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

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

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



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

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

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

Mean activity coefficient: Debye-Hückel

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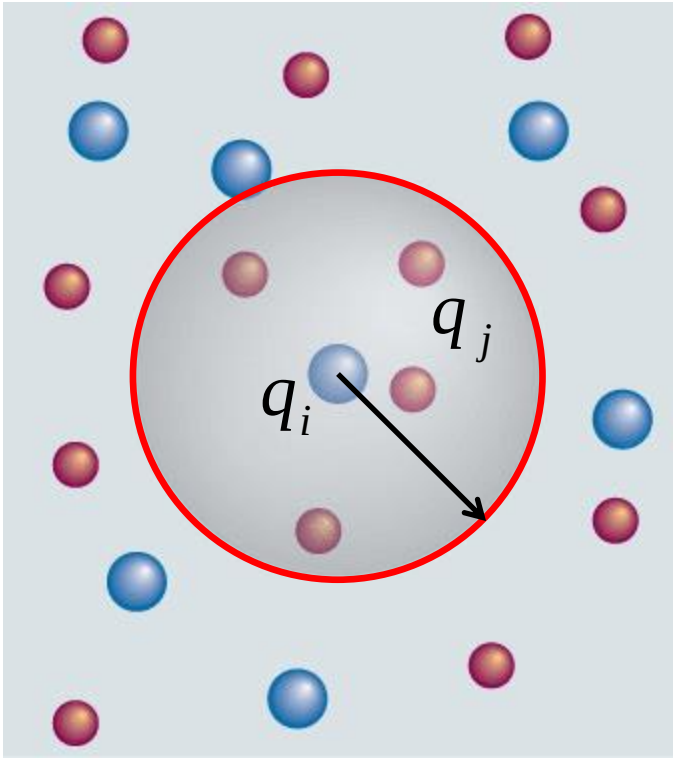


Poisson: $$\nabla^2\Phi(r) = -\frac{\rho(r)}{\varepsilon}$$

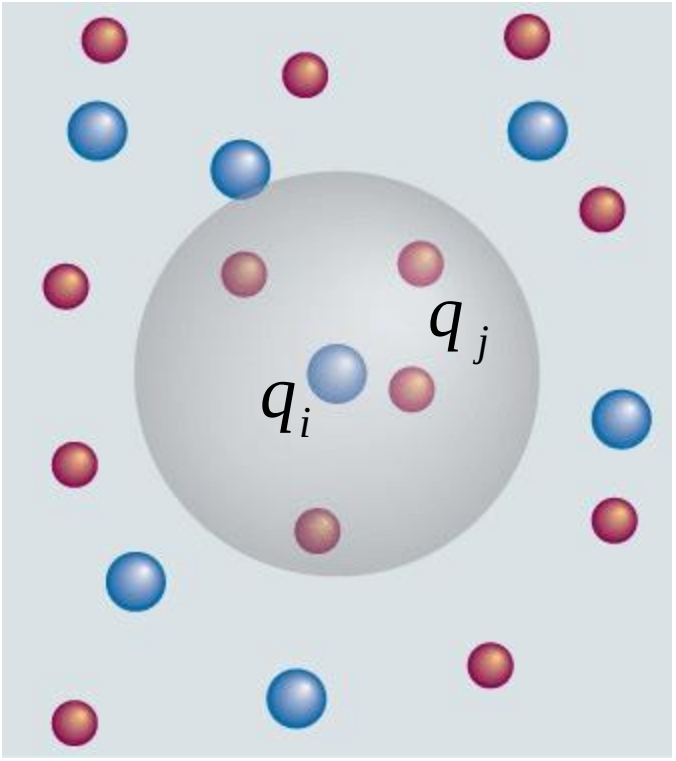
$$\nabla_r^2\Phi(r) = \frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}}{\mathrm{d}r}\right)\Phi(r)$$

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

Mean activity coefficient: Debye-Hückel

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

Energy of ion *j:*



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

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

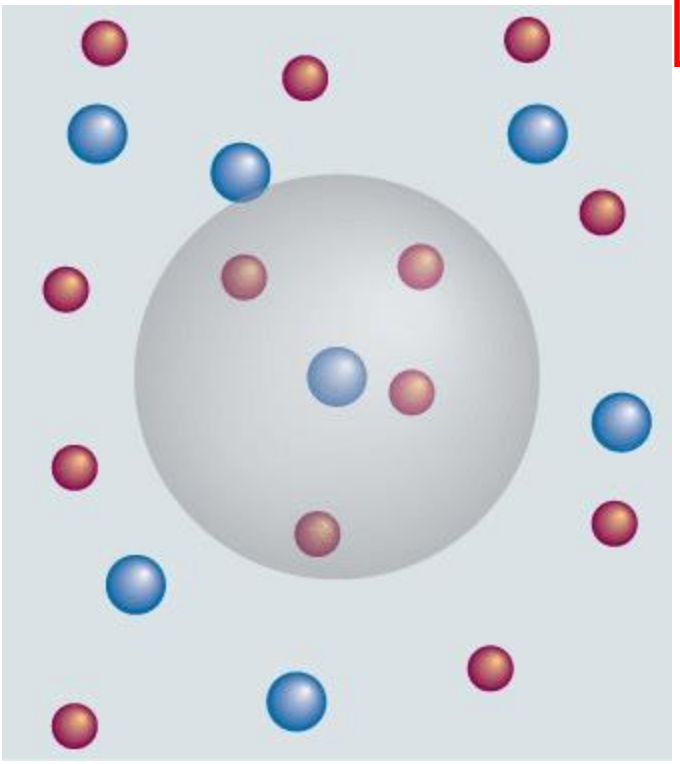
$$\exp\left[-z_j e\Phi_i / kT\right] \approx 1 - \frac{z_j e\Phi_i}{kT}$$

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

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

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

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

Poisson

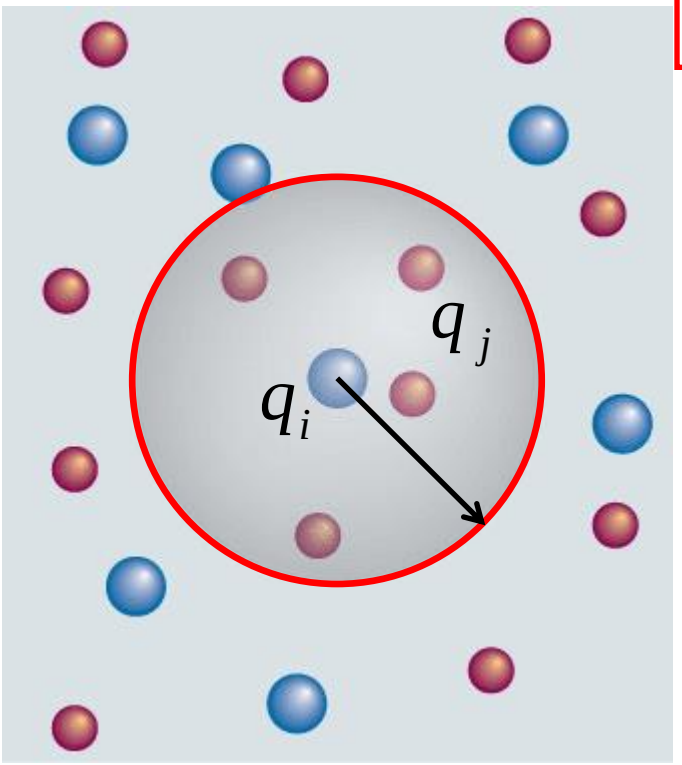
$$r_D^2 = -\frac{\varepsilon \Phi_i(r)}{\rho_j(r)}$$

⇨ Debye screening length

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

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

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Ionic strength

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

Poisson

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

⇒ Debye screening length

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

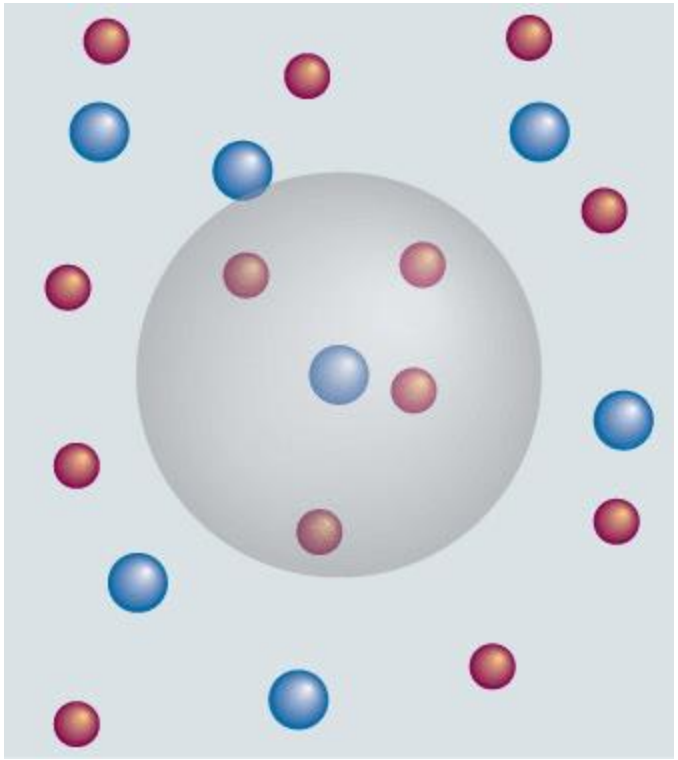
Mean activity coefficient: Debye-Hückel

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

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

$$\mathrm{d}w_e = \Phi_{\text{atm}}(0)\mathrm{d}q$$

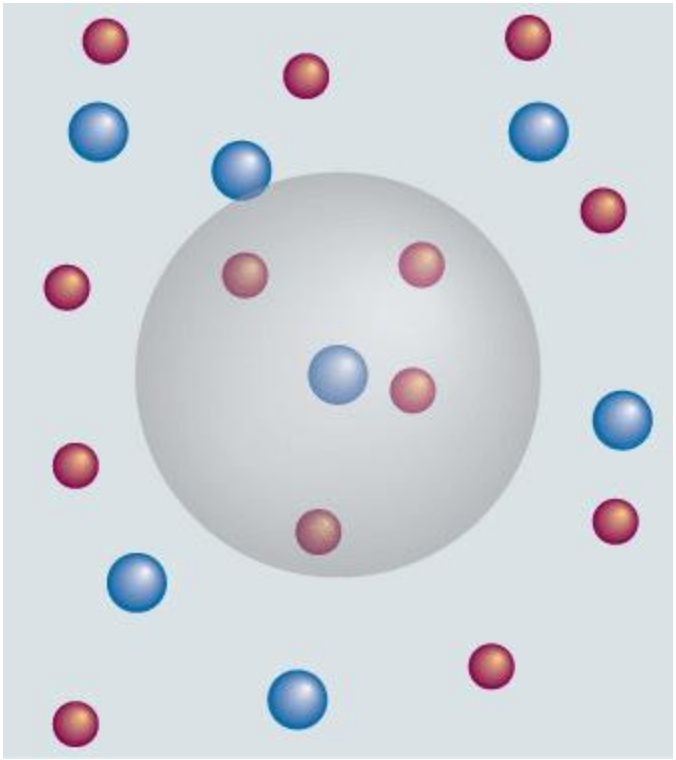
$$\Phi_{\text{atm}}(0) = \frac{q}{4\pi\varepsilon r_{\text{D}}}$$



$$w_{e,i} = \frac{z_i^2 F^2}{8\pi N_{\text{A}} \varepsilon r_{\text{D}}}$$

Mean activity coefficient: Debye-Hückel

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



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

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

$$\ln \gamma_\pm = \frac{p w_{e,+} + q w_{e,-}}{sRT}$$

$$\Rightarrow$$

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

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

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

A = 0.509 for H_2O @ 298 K