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Review

Gibbs Duhem – says any constant can be added to μ

– must state new reference state

Eg: $\mu_{A\text{"Fred"}} = \mu_A^\circ + RT\ln x_A + \text{"Fred"} = \mu^\circ_{A\text{"Fred"}} + RT\ln x_A$

$\mu_{B\text{"Ginger"}} = \mu_B^\circ + RT\ln x_B + \text{"Ginger"} = \mu^\circ_{B\text{ginger}} + RT\ln x_B$

Then

$$\mu_{A\text{"F"}} - \mu_{B\text{"g"}} = \mu^\circ_{A_{\text{"F"}}} - \mu^\circ_{B_{\text{"g"}}} + RT\ln x_A/x_B = \Delta G^\circ_{\substack{\text{ballroom}\\ \text{dancing}}} + RT\ln \frac{x_A}{x_B}$$

For dilute

$c \sim$ constant $\Rightarrow \mu_A = \mu_A^\circ + RT\ln x_A + RT\ln c$

usually $\rightarrow$ $\mu = \mu_A^\circ + RT\ln c_A$

no notation is made of new std state!

For nonideal $\mu_A = \mu_A^\circ + RT\ln \gamma_A c_A$

if $\gamma \simeq$ const, define new μ_A° so

$$\mu_A = \underbrace{\mu_A^\circ}_{\text{contains } \ln\gamma \text{ term}} + RT\ln c_A$$

Eg. For dissociation of H_2O in an ionic solution

see Silbey page 229-230 and p.257

$$\log \gamma_{H^+} = \frac{A z_1 z_2 I^{1/2}}{1 + 1.6 I^{1/2}} \qquad A = 0.509\ \text{kg}^{1/2}\,\text{mol}^{-1/2} @ 25^\circ C$$

Say 0.1 M $CuSO_4$ then $I \sim \frac{1}{2}(0.1(2^2) + 0.1(2^2))$

$= 0.4$

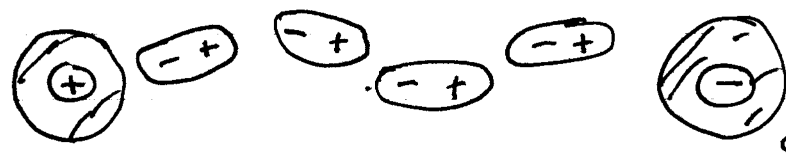
$\log \gamma_{H^+} = -0.5$

$$pH_a = -\log \gamma_{H^+}[H^+] = -\log[H^+] - \log\gamma_{H^+}$$

$$= -\log[H^+] + 0.5$$

Electrochemical Potential

1st consider 2 fixed charges



q_1 solvent molecules polarize q_2 — hept 1.9

$\epsilon = \epsilon(T)$ dielectric const — H_2O 79

Entropy lost due to organization

$$U(r) = \frac{q_1 q_2}{4\pi \epsilon_0 \epsilon r} = q_2 \psi$$

ϵ_0: permittivity of vaccuum

ψ: electric potential

~~Potent~~ Field: $E = -\nabla \psi$

Just Add electrochemical energy to other energy terms!

$$dU = TdS - PdV + \sum_{j=1}^{t} \mu_j dN_j + \sum_{i=1}^{M} \psi \, dq_i$$

Sub into dG (skip algebra)

$$dG = -SdT + VdP + \sum_{j=1}^{t} \mu_j dN_j + \sum_{i=1}^{M} \psi \, dq_i$$

q_i = total charge on i = $z_i \, e \, N_i$

z_i: valency; e: electron charge; N_i: total # i

If all particles have the same charge:

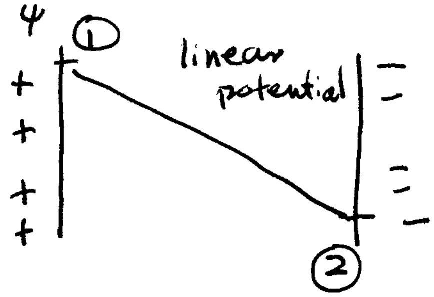
$$dG = -SdT + VdP + \sum_{i=1}^{M} (\mu_i + z_i e \psi) dN_i$$

lets us define a new electrochem potential

$$\mu_i' = \mu_i + z_i e \psi$$

6
2

How will ionic species align



Electroneutral fluid overall
ions are mobile - will have the same electrochemical potential everywhere

Single species at eq^m must have

$$\mu'(x_1) = \mu'(x_2)$$

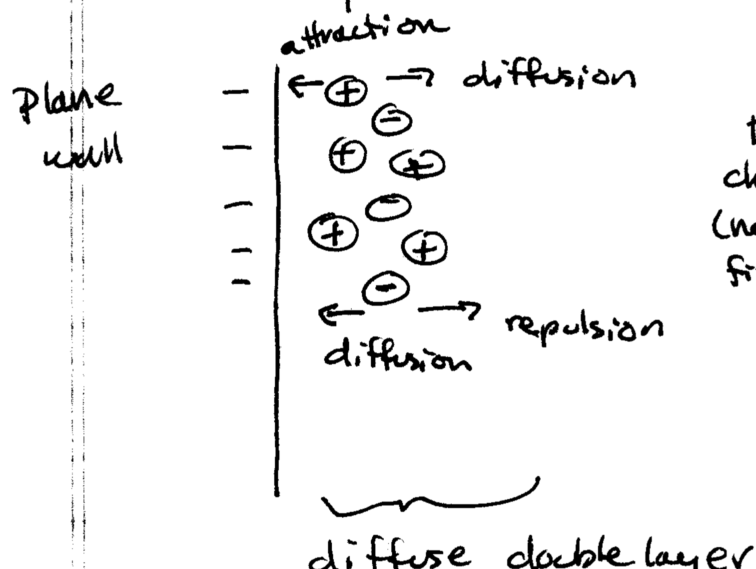
$$\mu'(x) = \mu^\circ + RT \ln c(x) + N_A z e \psi(x)$$

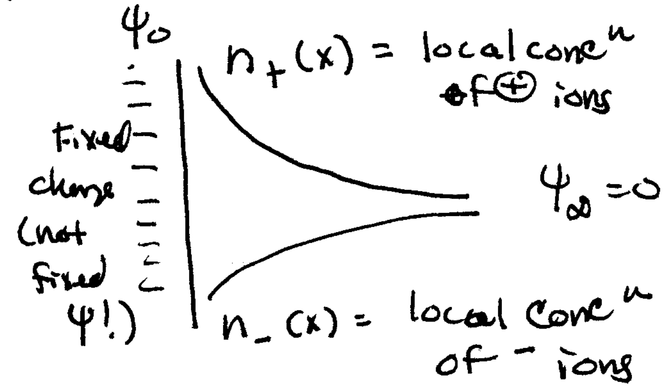
$\uparrow$ independent of x

$$RT \ln c_1 + N_A z e \psi_1 = RT \ln c_2 + N_A z e \psi_2$$

$$c_2 = c_1 e^{-N_A z e(\psi_2 - \psi_1)/RT}$$

Now - we go through some analysis to get to an important result





electroneutral @ $x = \infty$

ions hothe experience & create field.
Know: surface charge
don't know ψ_0 or $\psi(x)$

Simple derivation

Local Excess charge (above that @ ∞)

$$\rho(x) = \sum z_i e n_i(x) = z e[n_+(x) - n_-(x)]$$

Poisson eq^n relates potential to local charge density

$$\nabla \cdot E = \nabla^2 \psi = -\frac{\rho x}{\epsilon \epsilon_0} \qquad \text{Poisson Eq}^n$$

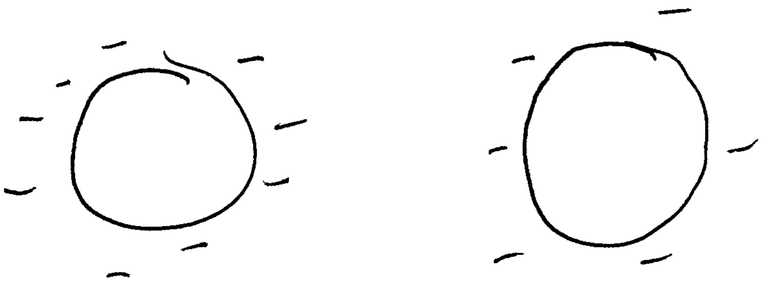
For 1-D $$\frac{d^2\psi}{dx^2} = \underbrace{\frac{z e n_0}{\epsilon\epsilon_0}\left(e^{z e\psi(x)/kT} - e^{-z e\psi(x)/kT}\right)}_{\text{Poisson-Boltzman eq}^n}$$

will not solve here (non linear 2nd order)
For small $\psi \rightarrow$ linearize

$$\nabla^2 \psi = K^2 \psi \qquad K^2 = \frac{2 z^2 e^2 n_0}{\epsilon \epsilon_0 kT}$$

Then for a plane $\psi(x) = \psi_0 e^{-Kx}$
potential decays as $\frac{1}{K}$.

TAKE HOME $\frac{1}{\kappa}$ = Debye length = effective distance charges are shielded

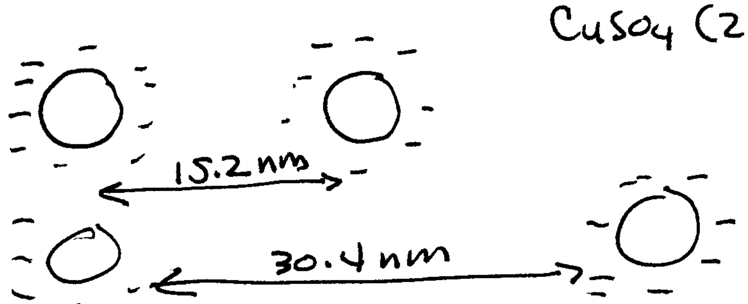


see notes for how to write κ in terms of ionic strength - messy units.

$$\kappa \sim \frac{I^{1/2}}{T^{1/2}} \qquad I = \text{ionic strength}$$

0.001 molal

$CuSO_4$ (2:2)



NaCl

0.1

$CuSO_4$

NaCl

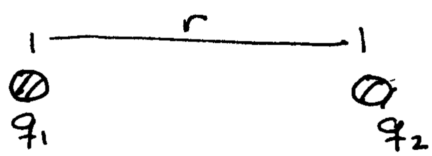
.94

Electrolyte Solution Basics

11/23

Readings: Dill & Bromberg: Chap 21 through p 398 (review of electrostatics)
Chap 22 through p 412
Chap 23 through p 440
SAB 7.1-7.2

1. Basic Electrostatics Review



two charges

Force between charges in a vacuum

$$F = \frac{q_1 q_2}{4\pi\epsilon_0 r^2}$$ (Charge in Coulomb units) SI units

ϵ_0 = permittivity of vacuum $= 8.854 \times 10^{-12}\ C^2/J\text{-}m$

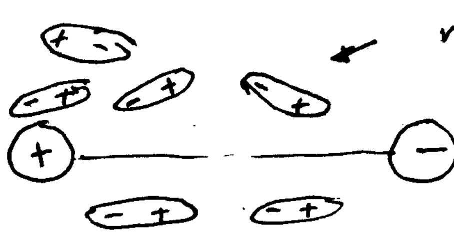
Force is repulsive for like charges

Energy of interaction:

$$U = -\int_\infty^r F\,dr = \frac{q_1 q_2}{4\pi\epsilon_0 r}$$

Forces & interaction energies change outside a vacuum

in a liquid now



molecules can polarize

$\epsilon = \epsilon(T)$

entropy lost due to organization

$$U(r) = \frac{q_1 q_2}{4\pi\epsilon_0 \epsilon r}$$

ϵ ← dielectric constant

"Non polar" liquids have low ϵ and polar have high ϵ

heptane (30°C) = 1.9

methanol (30) = 33

water ~~(0)~~ (0°C) = 88

water (25°C) = 78.5

HCN (0°C) = 158

HCN (20°C) = 114

The electric field & potential are defined per charge

$$\underset{\text{field}}{E} = \frac{F}{q_2} \qquad \underset{\text{potential}}{\psi} = U/q_2$$

$$E = -\nabla \psi$$

Since Electrostatic energy is $q_i \psi$ for charge i, the fundamental energy equation can be altered to include charge effects

$$dU = T\,dS - P\,dV + \sum_{j=1}^{t} \mu_j\, dN_j + \sum_{i=1}^{M} \psi\, dq_i$$

Sub into dG equation (skipping the algebra)

$$dG = -S\,dT + V\,dP + \sum_{j=1}^{t} \mu_j\, dN_j + \sum_{i=1}^{M} \psi\, dq_i$$

Note that the total charge on a species i = $q_i = z_i e N_i$

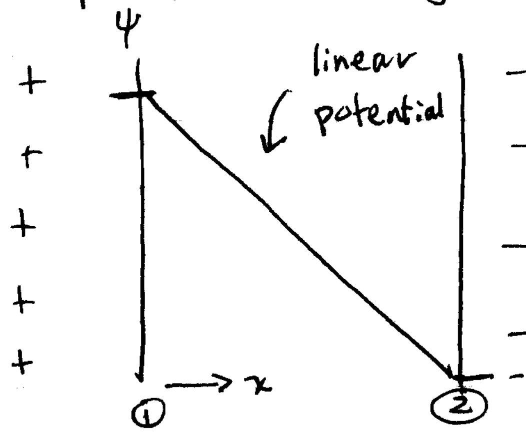
valency, electron charge, total # of ion i

If all particles have the same charge

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{M} (\mu_i + z_i e \psi)\, dN_i$$

We can define a new <u>electrochemical</u> potential: $\mu_i' = \mu_i + z_i e \psi$

Simple problem using electrochemical potential



- Linear potential is maintained between points 1 & 2 $\psi =$
- Fluid contains mobile ions
- Electroneutral overall!!

Consider 1st a single ionic species

At eq^m, must have

$$\mu'(x_1) \doteq \mu'(x_2)$$

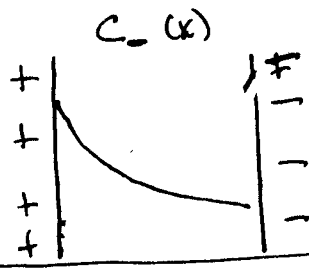
$$\mu'(x) = \mu^\circ + RT \ln c(x) + N_A z e \psi(x)$$

μ° ↑ independent of x

$$RT \ln c_1 + N_A z e \psi_1 = RT \ln c_2 + N_A z e \psi_2$$

$$c_2 = c_1 e^{-N_A z e (\psi_2 - \psi_1)/RT} \qquad \text{Nernst eq}^n$$

distribution of ions is exponential



$$c(x) = c_1 e^{-N_A z e (\psi_2 - \psi_1)\frac{x}{L}/RT}$$

$\boxed{\text{Poisson-Boltzmann Model} \Rightarrow \text{Debye Length}}$

Now consider the more general case – Not setting $\psi(x)$

plane wall, ⊖ charge

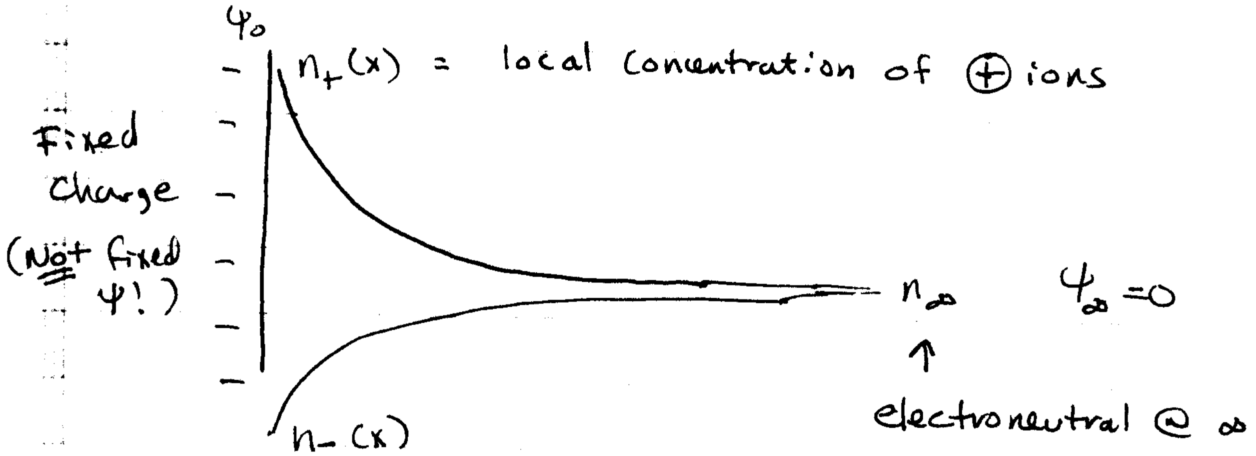
← ⊕ Coulomb attraction

→ ⊕ diffusion

⊖ → coulomb repulsion

← ⊖ Diffusion

Surface charge sets up potential $\psi(x)$ in adjacent fluid
as $x \to \infty$ $\psi \to \psi_\infty = 0$



ions both experience & create field
We may know surface charge but not ψ_0 or $\psi(x)$
How to get? Too difficult to show here all detail!
Outline general approach & focus on results.
Local charge density (excess charge)

$$\rho(x) = \sum z_i e n_i(x) = z e [n_+(x) - n_-(x)]$$

Poisson eq^n relates potential to local charge density

$$\nabla \cdot E = \nabla^2 \psi = -\frac{\rho(x)}{\epsilon \epsilon_0} \quad \leftarrow \text{Poisson Equation}$$

For 1-D $$\frac{d^2\psi}{dx^2} = \frac{z e n_\infty}{\epsilon \epsilon_0}\left(e^{z e \psi(x)/kT} - e^{-z e \psi(x)/kT}\right)$$

Poisson-Boltzmann Eq^n

Non linear 2nd order $\Rightarrow$ will not solve here.

For small ψ the equation can be linearized

Linearized PB

$$\nabla^2 \psi = \kappa^2 \psi \qquad \kappa^2 = \frac{2 z^2 e^2 n_\infty}{\epsilon \epsilon_0 kT}$$

For a plane

$$\psi(x) = \psi_0 \, e^{-\kappa x} \Rightarrow \text{Potential decays as } \tfrac{1}{\kappa}$$

DEBYE LENGTH

Important take-home lesson:

$\frac{1}{\kappa}$ = Debye length = effective distance charges are shielded.

More useful to write κ in terms of ion concentrations cast as ionic strength

$$\boxed{\kappa = \left(\frac{8\pi N_A e^2 \rho_A}{1000 \, \epsilon k_B T} \right)^{1/2} I^{1/2} \qquad \rho_A = \text{solvent density}}$$

I = ionic strength = $\frac{1}{2} \sum m_i z_i^2$ $\qquad$ m_i = molal concn of i, z_i = ion charge

Eg. 0.1 m NaCl

$$I = \tfrac{1}{2} \sum 0.1(1)^2 + 0.1(1)^2 = 0.1$$

$$I = m$$

0.1m $Cu(SO_4)$ $\qquad I = \frac{1}{2}\left(0.1(2)^2 + 0.1(2)^2\right)$

Cu^{++} $SO_4^{=}$ $\qquad = 4$

$$I = 4m$$

Debye Length in Aqueous Solution @ 25°C UNITS = nm

Salt Molal Concn	NaCl (1:1)	$CuCl_2$ (1:2)	$CuSO_4$ (2:2)
0.0001	30.4 nm	17.6 nm	15.2 nm
0.001	9.6	5.55	4.8
0.01	3.04	1.76	1.52
0.1	0.96	0.55	0.48