Physical & Interfacial Electrochemistry 2013

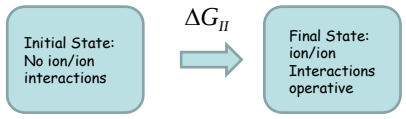
Lecture 3.

Ion-ion interactions in electrolyte solutions.

Module JS CH3304 MolecularThermodynamics and Kinetics

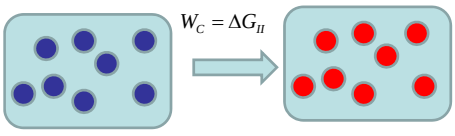
Ion-Ion Interactions

The thermodynamic properties of electrolyte solutions exhibit marked deviations from ideal behaviour. This is because strong electrolytes are completely dissociated into ions and the deviation from ideal behaviour is due to the *operation of electrical interactions between the ions*: they are long range (they vary with distance as 1/r) and are essentially Coulombic.
One should also consider short range (r^{-6}) effects arising either from incomplete dissociation or ion association. The latter factor becomes important in non-aqueous solutions where the dielectric constant is low. Also in more concentrated ionic solutions ion/solvent interactions become important.
Any theory attempting to predict the equilibrium thermodynamic properties of ionic solutions must concentrate on interionic forces and be able to calculate the free energy change arising from such interactions.



ΔG_{II} = Gibbs energy of ion/ion interactions

We model the initial state of non interacting ions as an assembly of discharged spheres, whereas the final state where ion/ion interactions operate is modelled as an assembly of interacting charged spheres.



Initial State: Assembly of discharged Non-interacting spheres

Final State: Assembly of charged interacting spheres

Both cations and anions are charged up using this protocol.
We wish to isolate the Gibbs energy for ion/ion interactions due to one specific ion which we label j.
Hence we work in terms of chemical potentials and introduce $\Delta\mu_{j,I}$ which defines the change in chemical potential arising from the interaction between a specific ion j and the assembly of all of the ions I.
How do we calculate this chemical potential change? We assume that the reference ion j is uncharged in an assembly of charged ions. We then calculate the electrostatic work required to charge up this reference ion j.

This analysis is similar to that used in deriving the Born equation.

$$\Delta\mu_{j,I} = N_A W_C = N_A \int_{q=0}^{q=z_j e} \psi\left(r_j\right) dq$$

$$= N_A \int_{q=0}^{q=z_j e} \frac{z_j e}{4\pi\varepsilon_0\varepsilon_r} dq = \frac{N_A}{4\pi\varepsilon_0\varepsilon_r r_j} \int_{q=0}^{q=z_j e} q dq$$

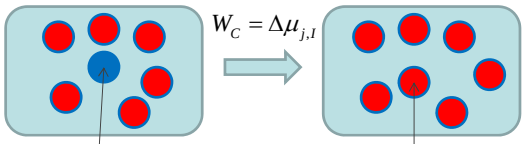
$$= \frac{N_A}{4\pi\varepsilon_0\varepsilon_r r_j}\left[\frac{q^2}{2}\right]_{q=0}^{q=z_j e} = \frac{N_A}{4\pi\varepsilon_0}\left\{\frac{\left(z_j e\right)^2}{2\varepsilon_r r_j}\right\}$$

We can simplify the latter expression by noting The following expression for the electrostatic potential $\psi(r_j)$.

$$\psi\left(r_j\right) = \frac{z_j e}{4\pi\varepsilon_0\varepsilon_r r_j}$$

Hence the change in chemical potential is given by the following fundamental expression.

$$\Delta\mu_{j,I} = \frac{z_j e N_A}{2}\psi\left(r_j\right)$$



Initial state

Discharged reference ion j

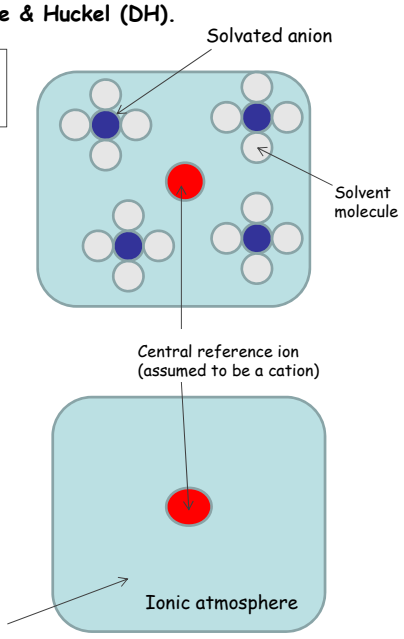
Final State

Charged reference ion j of radius r_j.

The problem in essence : The approach of Debye & Huckel (DH).

Real System:
Assembly of solvent Molecules & ions

We note therefore that the problem in essence boils down to theoretically evaluating the electrostatic potential $\psi(r_j)$ at the surface of the reference ion j using the methods of classical electrostatics.
Hence the chemical potential change due to the interaction between a specific reference ion j and its ionic environment essentially depends on the electrostatic potential produced at the surface of the reference ion j by the rest of the ionic ensemble (assembly).
We now discuss the way in which this quantity is evaluated.
The most simple approach is due to that developed many years ago by Debye and Huckel (DH) (1923).
The main problem is to quantify the time averaged spatial distribution of ions around the central reference ion.
The central idea in the DH approach is to replace the structured solvent by a dielectric continuum as was done when we discussed the Born model.
The net charge density ρ (r) due to all other ions is represented by an ion cloud or ionic atmosphere.

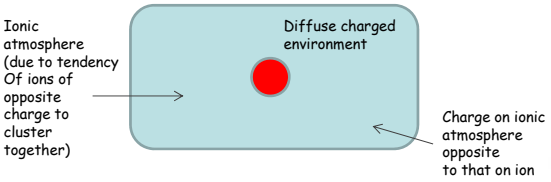


We draw from two disciplines to quantify the model. The first is classical electrostatics, and the second is statistical mechanics.
We also have a choice with respect to ion dimensions.

(i) Point charge model: most simple approach, valid for very dilute solutions (slightly polluted water!!), results in the formulation of the Debye-Huckel (DH) Limiting Law.

(ii) Finite ion size model: more realistic, ion size is quantified by a size parameter a.

(iii) The ion distribution about the central reference ion is treated in terms of the Poisson equation of classical electrostatics in terms of a continuous charge density $\rho_j(r)$. This is only an approximation since in reality one has a discrete distribution of counterions about the central reference ion. Hence there is a local excess of ions of opposite charge about a central reference ion: this is the ionic atmosphere.



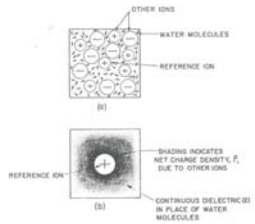


Fig. 3.6. A schematic comparison of (a) the assembly of ions and solvent molecules which constitute a real electrolytic solution and (b) the Debye–Hückel picture in which a reference ion is surrounded by net charge density σ due to the surrounding ions and a dielectric continuum of the same dielectric constant ϵ as the bulk solvent.

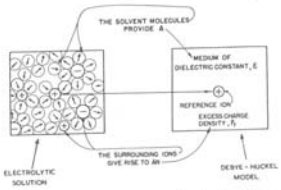


Fig. 3.7. The Debye-Hückel model is based upon selecting one ion as a reference ion, replacing the solvent molecules by a continuous medium of dielectric constant ϵ and the remaining ions by an excess charge density σ_i (the shading used in this book to represent the charge density is not indicated in this figure).

Main assumptions of the DH Theory

1. We assume that strong electrolytes are completely ionized at all concentrations for which the theory is valid. Ion association proceses are therefore ignored in the model.
2. Ions are regarded as point charges to a first approximation. This assumption will be valid for very dilute solutions. For more concentrated solutions the ions are of finite size (regarded as spheres of radius a) which are not subject to distortion and which possess a symmetric Coulomb field.
3. Interionic forces are assumed to be Coulombic in form: other forces such as short range dispersion interactions are neglected.
4. The electrical potential energy of an ion is much smaller than its thermal energy so we can state that

$$\left|q_j\psi_j\right| = \left|z_j e\psi_j\right| << k_B T$$

5. The dielectric constant of the solvent is unchanged by the presence of the ion. Hence dielectric saturation effects are neglected. Hence the macroscopic dielectric constant of the bulk solvent is used. This is a poor approximation since due to the effect of dielectric saturation effects, the effective local dielectric constant near an ion may be much less than its bulk value.

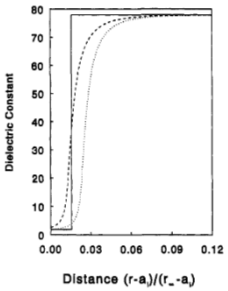
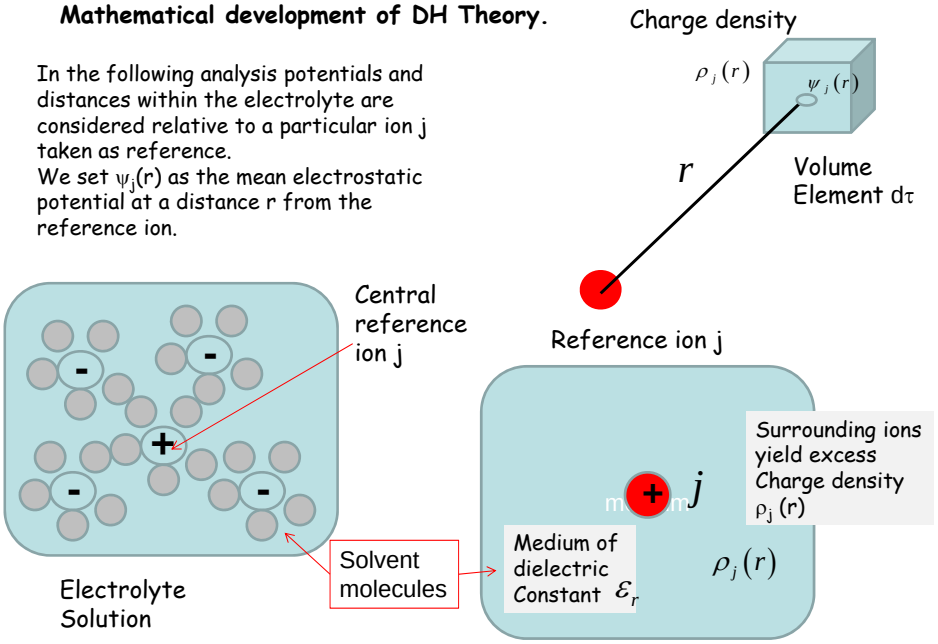


Figure 5. Radial variation in the predicted solvent dielectric profile for univalent cations in water at 298 K: (—) Li^+; (- -) Cs^+; (—) one-layer profile of Abraham and Lizzi.[8]

Mathematical development of DH Theory.

In the following analysis potentials and distances within the electrolyte are considered relative to a particular ion j taken as reference.
We set $\psi_j(r)$ as the mean electrostatic potential at a distance r from the reference ion.



We use classical electrostatics to obtain
An expression termed the Poisson equation
Which serves to relate the electrostatic potential $\psi_j(r)$ and the excess charge density $\rho_j(r)$ both evaluated at a point distant r from a central reference ion j as follows.

$$\varepsilon = \varepsilon_0 \varepsilon_r$$
$$\varepsilon_0 = 8.854x10^{-12} C^2 N^{-1} m^{-2}$$
$$\varepsilon_r = 78.5\,(\text{water})$$

$$\nabla^2 \psi_j(r) = -\frac{\rho_j(r)}{\varepsilon}$$

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2 \frac{\partial}{\partial r}\right\}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}\left\{r^2 \frac{\partial \psi_j(r)}{\partial r}\right\} = -\frac{\rho_j(r)}{\varepsilon}$$

We note that the charge distribution about the central reference ion is spherically symmetric and so the potential is also spherically symmetric.

We now note that the excess charge density is defined as the charge per unit volume and we can readily define it in the following manner.

$$\rho_j(r) = \sum_i z_i e n_i(r)$$

In this latter expression $n_i(r)$ represents the number density (concentration) of ion labelled i in the ionic atmosphere distant r from the central ion j.

Now is where Statistical (Sadistical??) Mechanics rears its head and enters stage left.
We can relate the number density of ion i in the ionic atmosphere to the bulk concentration of the ion i which we label n_i^∞ via the well known **Boltzmann Equation**.

$$n_i(r) = n_i^\infty \exp\left[-\frac{U_{ij}(r)}{k_B T}\right]$$

In the latter expression the quantity $U_{ij}(r)$ represents the Potential of mean force. Now if the central reference ion j is a cation, we can state that we have a local deficit of cations and a local excess of anions in the ionic atmosphere. Mathematically this can be stated by:

$$n_+(r) < n_+^\infty \qquad n_-(r) > n_-^\infty$$

The opposite pertains if the reference ion is an anion.
We also assume that the potential of mean force is given by The following simple expression:

$$U_{ij}(r) = z_i e \psi_j(r)$$

This assumption is termed the central approximation. Now U_{ij} relates to the time Average forces between the ions. If ion/ion interactions are absent then $U_{ij} = 0$. Hence $n_j(r) = n_j^\infty$. If the interaction force is attractive then $U_{ij} < 0$ and $n_j(r) > n_j^\infty$, And there is a local accumulation of ions in excess of bulk values. In contrast, if the interaction force is repulsive with $U_{ij} > 0$ then $n_j(r) < n_j^\infty$, and there is a local depletion of ions.

If the central ion has a finite size a then we can write the following.

$$U_{ij} = \infty \quad r < a$$

$$U_{ij} = \frac{z_i z_j e^2}{4\pi\varepsilon r} \quad r \geq a$$

Furthermore, as r → ∞ then $\rho_j(r) \to 0 \quad \psi_j(r) \to 0$

This condition implies that electroneutrality pertains the bulk solution and that the excess charge density is defined only on a local scale.

Now comes the important bit. We substitute the Boltzmann equation from Statistical Thermodynamics into the Poisson Equation from claiiical electrostatics, and obtain The famous (or infamous depending on your viewpoint) **Poisson-Boltzmann (PB) Equation**.

$$\nabla^2 \psi_j(r) = \frac{1}{r^2}\frac{d}{dr}\left\{r^2 \frac{d\psi_j(r)}{dr}\right\} = -\frac{1}{\varepsilon}\sum_i z_i e n_i^\infty \exp\left[-\frac{z_i e \psi_j(r)}{k_B T}\right]$$

This non-linear differential PB equation must be solved to obtain an expression for the electrostatic potential $\psi_j(r)$.

The PB equation is found in a great many physical situations pertinent to electrochemical systems, most notably when one is discussing the interface between a planar electrode and an electrolyte solution and when one considers the interface between a colloidal particle and its surrounding environment. In these important situations one will often have to attempt to solve the full non linear equation which can be quite challenging. However under the present circumstances we do not need to do this and we can simplify matters considerably by making the important assumption that **the solution is so dilute that the ions will rarely be close together**. Under such circumstances, the interionic potential energy will be much less than the average thermal energy. This assumption means that we can state the following.

$$\frac{z_i e\psi_j}{k_B T} << 1$$

Now we can make the following assumption. When x is small we can assume that exp[-x] ≈ 1-x .

$$\exp\left[-\frac{z_i e\psi_j(r)}{k_B T}\right] \cong 1-\frac{z_i e\psi_j(r)}{k_B T}$$

We now substitute this approximation into the PB equation to obtain the following.

$$\frac{1}{r^2}\frac{d}{dr}\left\{r^2\frac{d\psi_j(r)}{dr}\right\} = -\frac{1}{\varepsilon}\sum_i z_i e n_i^{\infty}\left\{1-\frac{z_i e\psi_j(r)}{k_B T}\right\}$$

$$= -\frac{1}{\varepsilon}\sum_i z_i e n_i^{\infty} + \frac{1}{\varepsilon}\sum_i \frac{z_i^2 e^2 n_i^{\infty}\psi_j(r)}{k_B T} \cong \frac{1}{\varepsilon}\sum_i \frac{z_i^2 e^2 n_i^{\infty}\psi_j(r)}{k_B T} = \kappa^2\psi_j(r)$$

In the latter we have introduced the electroneutrlity Condition which states that

$$\sum_i z_i e n_i^{\infty} = 0$$

We also have introduced the DH parameter κ such that

$$\kappa^2 = \frac{e^2}{\varepsilon k_B T}\sum_i z_i^2 n_i^{\infty} = \frac{1}{L_D^2}$$

We will show that the inverse kappa $\kappa^{-1} = L_D$ is an effective **measure of the ionic atmosphere**. We see that κ depends on the number density of ions in the atmosphere and also note the following quantitative relationship:

$$n_i^{\infty} = \frac{N_A c_i}{10^3} = N_A \rho_o m_i$$

Where c_i denotes the molar concentration of ion i and ρ_0 denotes the density of the solvent.

We recall the definition of ionic strength I as $\mathrm{I} = \frac{1}{2}\sum_i c_i z_i^2 = \frac{1}{2}\sum_i m_i z_i^2$

Hence the DH parameter k is related to the ionic strength I as follows $\kappa^2 = \frac{2N_A e^2 \rho_0}{\varepsilon k_B T} I$

We now introduce the Debye Length L_D as $1/\kappa$ and write that

$$L_D = \frac{1}{\kappa} = \sqrt{\frac{\varepsilon k_B T}{2\rho_0 N_A e^2}}\, I^{-\frac{1}{2}}$$

Hence the Debye Length is a measure of the thickness of the ionic atmosphere And we note that it decreases with increasing ionic strength I. For an aqueous medium we note that $\rho_0 = 0.997 \times 10^{-3}$ kgm^{-3}, $\varepsilon_r = 78.5$, and assuming That T = 298 K, $k_B = 1.38 \times 10^{-23}$ JK^{-1}, e = 1.60×10^{-19}C, $N_A = 6.023 \times 10^{23}$ mol^{-1} and $E_0 = 8.854 \times 10^{-12}$ C^{2}N^{-1}m^{-2} we can calculate that the Debye Length can we written in the following useful format.

$$L_D = \left(3.05\times10^{-10}\,\mathrm{mol^{1/2}kg^{-1/2}m}\right)\times\left(\mathrm{I/\,molkg^{-1}}\right)$$

The following results are obtained for a 1,1 electrolyte at 298 K.

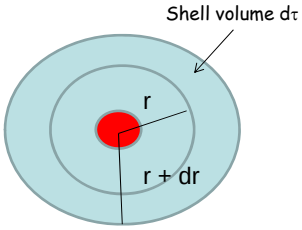
m/mol kg^{-1}	0.0001	0.001	0.01	0.10	1.0
L_D/nm	30.5	9.64	3.05	0.96	0.30

Hence as m → 0, the ionic atmosphere spreads out and becomes more diffuse.

We can calculate the total excess charge contained in the ionic atmosphere which surrounds the central ion as follows.

$$-\frac{\rho_j(r)}{\varepsilon} = \kappa^2 \psi_j(r) = \kappa^2 \frac{z_j e}{4\pi\varepsilon r}\exp[-\kappa r]$$

$$\rho_j(r) = -\frac{z_j e}{4\pi r}\kappa^2 \exp[-\kappa r]$$



We consider a spherical shell of thickness dr located At a distance r from the central reference ion.

Charge in shell volume

$$dq = \rho_j(r)d\tau$$

The charge in spherical shell is given by

$$dq = \rho_j(r)d\tau = \rho_j(r)4\pi r^2 dr$$

Hence the total charge of the ionic atmosphere is got by Integrating over all the spherical shells of value dq as follows.

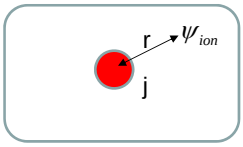
$$q_{cloud} = \int_{r=0}^{r=\infty} dq = \int_{r=0}^{r=\infty} 4\pi r^2 \rho_j(r)dr = -\int_0^\infty 4\pi r^2 \left\{\frac{z_j e}{4\pi}\right\}\frac{\kappa^2}{r}\exp[-\kappa r]dr = -\int_0^\infty z_j e\kappa^2 r \exp[-\kappa r]dr$$

The last integral may be solved via integration by parts to obtain the final significant result.

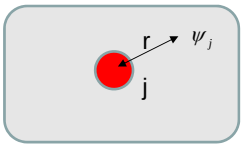
$$q_{cloud} = -z_j e = -q_{ion}$$

Hence we have shown that the total charge on the surrounding ion cloud is equal and opposite to that on the central reference ion. Electroneutrality is therefore satisfied.

We now determine the contribution of the ionic atmosphere to the electrostatic potential at a point distant r in the atmosphere from the central reference ion j.



Atmosphere absent



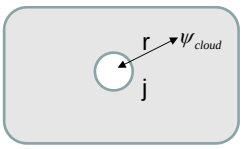
$$\psi_j(r) = \psi_{ion}(r) + \psi_{cloud}(r)$$

$$\psi_{cloud}(r) = \psi_j(r) - \psi_{ion}(r)$$

$$\psi_{ion}(r) = \frac{z_j e}{4\pi\varepsilon r}$$

$$\psi_j(r) = \frac{z_j e}{4\pi\varepsilon r}\exp[-\kappa r]$$

Ion plus atmosphere present



Ion absent

Now from the principle of superposition of potentials, the total potential at a distance r from the central reference ion is given by the sum of the potential due to The central ion and that due to the ion atmosphere. Hence we can make the following analysis.

In the limit of very dilute solutions we can make the following approximations.

$$\kappa r << 1, \quad r << \kappa^{-1} = L_D$$

$$\exp[-\kappa r] \cong 1 - \kappa r$$

$$\{\exp[-\kappa r] - 1\} \cong -\kappa r$$

Hence the electrostatic potential due to the ionic cloud is given by the following expression.

$$\psi_{cloud}(r) = \frac{z_j e}{4\pi\varepsilon r}\{\exp[-\kappa r] - 1\}$$

Electrostatic potential of Cloud in very dilute solution limit.

$$\psi_{cloud}(r) \cong -\frac{z_j e\kappa}{4\pi\varepsilon} = -\frac{z_j e}{4\pi\varepsilon\kappa^{-1}} = -\frac{z_j e}{4\pi\varepsilon L_D}$$

We now wish to evaluate the total potential at the surface of the reference ion (assumed to be a point charge).

$$\psi_j(r) = \frac{z_j e}{4\pi\varepsilon}\left\{\frac{1}{r} - \frac{1}{L_D}\right\}$$

$$\psi_j(r=0) = \psi_{j,0} = -\frac{z_j r}{4\pi\varepsilon L_D}$$

Now we finally recall that the change in chemical potential due to ion/ion interactions is given by The following expression.

$$\Delta\mu_{j,I} = \frac{N_A z_j e}{2}\psi_{j,0} = -\frac{N_A (z_j e)^2}{8\pi\varepsilon L_D} \quad \textbf{(1)}$$

This is the fundamental theoretical result which we require. We now relate this result to the Thermodynamics of electrolyte solutions.

For an ideal solution containing <u>non-interacting solute</u> we can write the following expression for the Chemical potential.

$$\mu_j(ideal) = \mu_j^0 + RT\ln m_j$$

In contrast for a real solution containing <u>interacting solute particles</u> we introduce activities rather than molalities where we note that $a_j = \gamma_j m_j$.

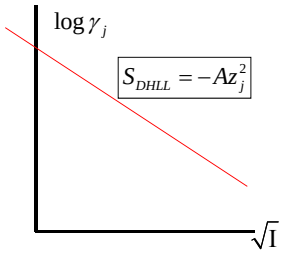
$$\mu_j(real) = \mu_j^0 + RT\ln a_j = \mu_j^0 + RT\ln \gamma_j m_j$$

Now we note that $\Delta\mu_{j,I} = \mu_j(real) - \mu_j(ideal)$

Hence $\Delta\mu_{j,I} = RT\ln\gamma_j$ **(2)**

We can now of course get a handle on the meaning of the ionic activity coefficient as it relates to the change in activity of ionic solvation from comparing eqn.1 and eqn.2.

$$\ln\gamma_j = -\frac{N_A (z_j e)^2}{8\pi\varepsilon_0\varepsilon_r RT} L_D^{-1} = -\frac{(z_j e)^2}{8\pi\varepsilon_0\varepsilon_r k_B T} L_D^{-1} \quad \textbf{(3)}$$



We now recall that the inverse Debye Length is related
To the Ionic strength I of the solution according to the following relationship.

$$L_D^{-1} = \sqrt{\frac{2\rho_0 N_A e^2}{\varepsilon_0\varepsilon_r k_B T}} I^{1/2} \quad \textbf{(4)}$$

From eqn.3 and eqn.4 we derive the relationship between the ionic activity coefficient abd the square root of the Ionic Strength which is the fundamental result of the Debye-Huckel Theory valid for very dilute electrolyte solutions, and is termed the <u>DH Limiting Law</u>.

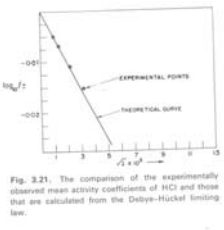


Fig. 3.21. The comparison of the experimentally observed mean activity coefficients of HCl and those that are calculated from the Debye-Hückel limiting law.

$$\log\gamma_j = -Az_j^2 I^{1/2} \quad \textbf{(5)}$$

$$A = \frac{\sqrt{2\rho_0 N_A}e^3}{2.303\times 8\pi(\varepsilon_0\varepsilon_r k_B T)^{3/2}} = \frac{1.82\times 10^6}{(\varepsilon_r T)^{3/2}}$$

For an aqueous solution (ε_r=78.5) at T = 298 K the DH constant A = 0.51 $mol^{-1/2}kg^{1/2}$.

The DH limiting law expressed in eqn.5 will be valid only for very dilute solutions where m < 10^{-3} mol kg^{-1}.
One rapidly observes marked deviations from this law as the solution becomes more complicated.

Now we have derived an expression for the activity of a single ion j. Such a quantity cannot be measured experimentally. Instead we can measure the <u>mean ionic activity coefficient</u>, and one can show that the following holds.

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

The valence factor $F_V = |z_+|\,|z_-|$ can be evaluated as follows for different electrolyte types.

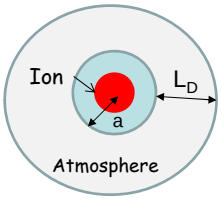
Electrolyte Type	Example	Ionic valence	F_V
(1,1)	NaCl	$z_+ = 1, z_- = -1$	1
(1,2)	$MgCl_2$	$z_+ = 2, z_- = -1$	2
(1,3)	$LaCl_3$	$z_+ = 3, z_- = -1$	3
(2,2)	$MgSO_4$	$z_+ = 2, z_- = -2$	4
(2,3)	$Fe_2(SO_4)_3$	$z_+ = 3, z_- = -2$	6

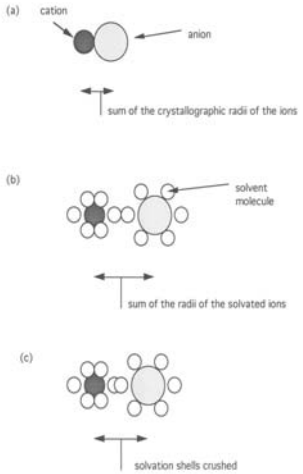
The DH limiting Law holds only for the most dilute solutions (slightly polluted water. The model must be modified in a number of respects if agreement between theory And experiment is to be obtained at higher concentrations.

Extension to basic DH Model

The most simple extension is that of finite ion size. The point charge picture of a reference ion is only valid for very dilute solutions. If we wish to describe more concentrated solutions, then we must assume that the reference ion is of a finite size.
We therefore introduce a finite ion size parameter a.
The ion size parameter cannot :

(i) Be less than the sum of the crystallographic radii of the ions
(ii) More than the sum of the hydrated radii of the ions
(iii) Is most probably less than the sum of the solvated radii because the solvation shells may be crushed.
Hence the parameter a should be termed the mean distance of closest approach.
Hence for a finite size ion, the ionic atmosphere starts at a distance a from the centre of the reference ion.





As previously noted the point charge picture is valid only for very dilute solutions but becomes less so as concentration is increased. We therefore introduce the ion size parameter a the mean distance of closest approach.
We again may write the following expressions.
In the latter A is a constant of integration
Which must be evaluated from the boundary conditions.
Again, the charge carried by an infinitesimally thin shell of solution located at a distance r from the central ion is given by the following expression.

$$\psi_j(r) = \frac{A}{r}\exp[-\kappa r]$$
$$\rho_j(r) = -\frac{\varepsilon\kappa A}{r}\exp[-\kappa r]$$

$$dq = 4\pi r^2 \rho_j(r)\, dr$$

Now for an ion of finite size, the ionic atmosphere begins at a distance a from the centre of the reference ion j. Also the total charge carried by all the spherical shells between r = a and r = ∞ is obtained by summation over all spherical shells. This charge is balanced by the equal and opposite charge of the central reference ion (the electroneutrality condition). Hence mathematically we can make the following assertion.

$$\int_{r=a}^{r=\infty} 4\pi\rho_j(r) r^2 dr = -z_j e$$
$$4\pi\varepsilon\kappa^2 A \int_a^{\infty} r\exp[-\kappa r]\, dr = z_j e$$

This expression may be solved via integration by part to obtain the following result.

$$z_j e == 4\pi\varepsilon\kappa^2 A\left\{\frac{1+\kappa a}{\kappa^2}\exp[-\kappa a]\right\}$$
$$A = \frac{z_j e}{4\pi\varepsilon}\left\{\frac{\exp[\kappa a]}{(1+\kappa a)}\right\}$$

Hence the electrostatic potential at a distance r
From the reference ion j is given by the following expression.

$$\psi_j(r) = \frac{z_j e}{4\pi\varepsilon}\left\{\frac{\exp[\kappa a]}{(1+\kappa a)}\right\}\left(\frac{\exp[-\kappa r]}{r}\right)$$

We again use the superposition principle to obtain an expression for ψ_{cloud} as follows.

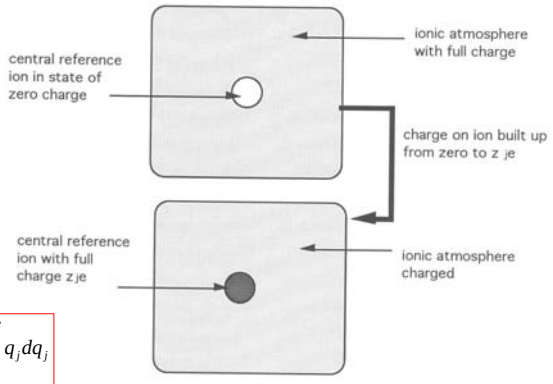
$$\psi_{cloud}(r) = \psi_j(r) - \psi_{ion}(r)$$
$$\psi_{ion}(r) = \frac{z_j e}{4\pi\varepsilon r}$$
$$\psi_{cloud}(r) = \frac{z_j e}{4\pi\varepsilon r}\left\{\frac{\exp[\kappa a]\exp[-\kappa r]}{1+\kappa a} - 1\right\}$$

Since no ions from the atmosphere can approach the central ion more closely than r = a, then the potential that exists at the site of the central reference ion due to the ionic atmosphere is obtained by setting r = a in th expression just derived above to obtain the following result.

$$\psi_j(r=a) = \frac{z_j e}{4\pi\varepsilon a}\left\{\frac{1}{1+\kappa a} - 1\right\} = -\frac{z_j e}{4\pi\varepsilon}\left\{\frac{1}{\kappa^{-1}+a}\right\} = -\frac{z_j e}{4\pi\varepsilon\kappa^{-1}}\left\{\frac{1}{1+\kappa a}\right\}$$

Now for dilute dolutions κa <<1 and the expression just derived decomposes to that altrady Obtained for the point charge model as indeed it should.

We now consider the Guntelberg-Mu charging process. The reference ion introduced into the solution in an uncharged state. One then increases charge gradually to its final value given by $z_j e$. The work done in this process is now evaluated.
The electrostatic work required per W_c to increase the charge on ion j fr $q_j = 0$ to $q_j = z_j e$ can be calculated via the following procedure.



$$W_C = \int_{q_j=0}^{q_j=z_j e} \psi_j(r=a)dq = -\frac{1}{4\pi\varepsilon}\left\{\frac{\kappa}{1+\kappa a}\right\}\int_0^{z_j e} q_j dq_j$$

$$= --\frac{1}{4\pi\varepsilon}\left\{\frac{\kappa}{1+\kappa a}\right\}\left|\frac{q_j^2}{2}\right|_0^{z_j e}$$

$$W_C = -\frac{z_j^2 e^2}{8\pi\varepsilon}\left\{\frac{\kappa}{1+\kappa a}\right\}$$

Hence the change in chemical potential due to the interaction between the central reference ion and the associated ionic atmosphere is given by the following expression below.

$$\Delta\mu_{j,I} = N_A W_C = -\frac{z_j^2 e^2 N_A}{8\pi\varepsilon}\left\{\frac{\kappa}{1+\kappa a}\right\}$$

This is the fundamental theoretical result for finite size ions. As before we can state the following relationships.

$$\Delta\mu_{j,I} = RT\ln\gamma_j$$

$$\ln\gamma_j = -\frac{z_j^2 e^2 N_A}{8\pi\varepsilon RT}\left\{\frac{\kappa}{1+\kappa a}\right\} = -\frac{z_j^2 e^2}{8\pi\varepsilon k_B T}\left\{\frac{\kappa}{1+\kappa a}\right\}$$

Hence we may obtain the extended DH equation for finite size ions as follows.

$$\log\gamma_j = -\frac{Az_j^2\sqrt{\mathrm{I}}}{1+Ba\sqrt{\mathrm{I}}}$$

Where we have noted the following

$$\kappa = \sqrt{\frac{2N_A e^2\rho_0}{\varepsilon_0\varepsilon_r k_B T}}\sqrt{\mathrm{I}}$$

$$A = \frac{\sqrt{2\rho_0 N_A}e^3}{2.303\times 8\pi(\varepsilon_0 k_B)^{3/2}}\left\{\frac{1}{(\varepsilon_r T)^{3/2}}\right\} = \frac{1.82\times 10^6}{(\varepsilon_r T)^{3/2}}$$

$$B = \sqrt{\frac{2N_A e^2\rho_0}{\varepsilon_0\varepsilon_r k_B T}} = \frac{5.02\times 10^{11}}{(\varepsilon_r T)^{1/2}}$$

For water where ε_r = 78.5 at T = 298 K we note that A = 0.51 $kg^{1/2}mol^{-1/2}$
And B = 3.28 x 10^9 $mol^{-1/2}kg^{1/2}m^{-1}$

Relationship between Ionic Strength I and molality m, I = km

	X^-	X^{2-}	X^{3-}	X^{4-}
M^+	1	3	6	10
M^{2+}	3	4	15	12
M^{3+}	6	15	9	42
M^{4+}	10	12	42	16

Relationship between activity coefficients on various scales.

$f_\pm$ = mole fraction scale (x_j)
$\gamma_\pm$ = molal scale (m_j)
$y_\pm$ = molar scale (c_j)

$$f_\pm = \gamma_\pm (1 + 0.001 \upsilon M_S m)$$
$$f_\pm = y_\pm (\rho + 0.001 c(\upsilon M_S - M_\pm))/\rho_0$$
$$\gamma_\pm = \frac{\rho - 0.001 c M_\pm}{\rho_0} y_\pm = \frac{c}{m\rho_0} y_\pm$$
$$y_\pm = (1 + 0.001 m M_\pm)\left(\frac{\rho_0}{\rho}\right)\gamma_\pm = \frac{m\rho_0}{c}\gamma_\pm$$

$M_\pm$ = molar mass of salt
M_S = molar mass of solvent
ρ = desnity of solution
ρ_0 = density of solvent
$\upsilon = \upsilon_+ + \upsilon_-$ = stoichiometric ionization factor

Finally the extended DH equation may be written in terms of the mean ionic activity coefficient in the following manner.

$$\log \gamma_\pm = -\frac{A|z_+||z_-|\sqrt{I}}{1 + Ba\sqrt{I}} = -\frac{AF_V\sqrt{I}}{1 + Ba\sqrt{I}}$$

A reasonable fit for the ion size parameter is 0.4 nm. The a factor is best treated as an adjustable parameter used to obtain a best fit between experimentally obtained and theoretically calculated activity coefficients. Note that for high concentrations of some electrolytes the parameter a attains negative values which of course are not physically reasonable for concentrated ionic solutions.
The extended DH equation is generally valid up to I ≈ 0.05 mol kg^{-1}.

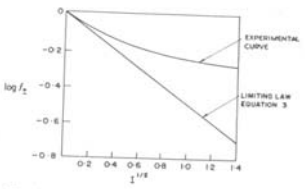
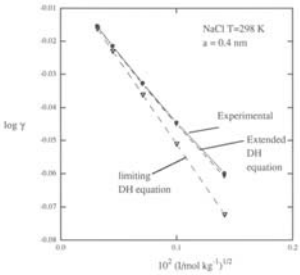


Fig. 3.25. The experimental log $f_\pm$ versus $I^{\frac{1}{2}}$ curve is a straight line only at extremely low concentrations.



One gets even more complex behaviour as the electrolyte solution Becomes more concentrated. This points out that the extended DH model is still too simplistic an approach.
A better fit follows the expression presented below, Where C is an adjustable parameter.

$$\log \gamma_\pm = -\frac{A|z_+||z_-|\sqrt{I}}{1 + Ba\sqrt{I}} + CI$$

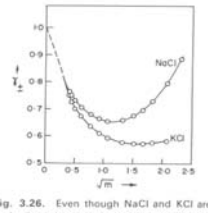


Fig. 3.26. Even though NaCl and KCl are 1 : 1 electrolytes, their activity coefficients vary in different ways with concentration directly one examines to higher concentrations.

Hydration effects by Robinson and Stokes have proven to be useful. We quickly enter realm of current research when concentrated solutions are considered.