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Conductance of solutions : anions and cations containing solutions

Colligative property measurements } van't Hoff factor, $i > 1$
Osmotic pressure " } $\Rightarrow$ dissociation takes place

aq. solutions of electrolytes are electrically neutral, although ions are present

$$B \equiv M^{z+}_{n_+} X^{z-}_{n_-} \;\downarrow\; n_+ M^{z+} + n_- X^{z-}$$

$Al_2(SO_4)_3$: $n_+ = 2$, $n_- = 3$
$z_+ = +3$, $z_- = -2$

$$n_+ z_+ + n_- z_- = 0$$

$\mu = \mu^0 + RT \ln(p/p^0)$: provided our solution/system is ideal.

$\mu = \mu^0 + RT \ln a_B$, $a_B = m_B \gamma_B$

m_B = molality of B
γ_B = activity coeff. of B.
m^0 = standard molality

or, $\mu = \mu^0 + RT \ln \frac{m_B}{m^0} + RT \ln \gamma_B$

$\gamma_B = 1$ provided the soln. is ideal.

$$\mu_B = \mu^0_B + RT \ln(m_B/m^0) + RT \ln \gamma_B$$

μ_+, μ_- the chem. pot. of the cations and anions

$$\mu_B = n_+\mu_+ + n_-\mu_-$$

$$\left.\begin{aligned}\mu_+ &= \mu^0_+ + RT \ln \frac{m_+}{m^0} + RT \ln \gamma_+\\ \mu_- &= \mu^0_- + RT \ln \frac{m_-}{m^0} + RT \ln \gamma_-\end{aligned}\right\}$$

$$\mu_B = n_+\mu^0_+ + RT \ln\left(\frac{m_+}{m^0}\right)^{n_+} + RT \ln(\gamma_+)^{n_+} + n_-\mu^0_- + RT \ln\left(\frac{m_-}{m^0}\right)^{n_-} + RT \ln(\gamma_-)^{n_-}$$

or, $$\mu_B = (n_+\mu^0_+ + n_-\mu^0_-) + RT \ln \frac{m_+^{n_+} m_-^{n_-}}{(m^0)^{n_+ + n_-}} + RT \ln\left(\gamma_+^{n_+}\gamma_-^{n_-}\right)$$

γ_+ and γ_- may be determined experimentally.

Define: $m_\pm^n = m_+^{n_+} m_-^{n_-}$, $n = n_+ + n_-$

or, $m_\pm = \left(m_+^{n_+} m_-^{n_-}\right)^{1/n}$: mean ionic molality

$\gamma_\pm^n = \left(\gamma_+^{n_+}\gamma_-^{n_-}\right)$

or, $\gamma_\pm = \left(\gamma_+^{n_+}\gamma_-^{n_-}\right)^{1/n}$: mean ionic activity coeff.

$$\therefore \mu_B = (n_+\mu^0_+ + n_-\mu^0_-) + RT\ln\frac{m_\pm^n}{(m^0)^n} + RT\ln\gamma_\pm^n$$

$$\text{or, } \mu_B = \mu^0_B + RT\ln\left(\frac{m_\pm\gamma_\pm}{m^0}\right)^n = \mu^0_B + nRT\ln\frac{m_\pm\gamma_\pm}{m^0}$$

$$\left.\begin{aligned}\mu_B &= \mu^0_B + \cancel{n}RT\ln\left(\frac{m_\pm\gamma_\pm}{m^0}\right)^n\\ \mu_B &= \mu^0_B + RT\ln a_B\end{aligned}\right\} \quad a_B = \left(\frac{m_\pm\gamma_\pm}{m^0}\right)^n = a_+^{n_+}a_-^{n_-}$$

NaCl; $a_{NaCl} = a_{Na^+}a_{Cl^-} = \gamma_\pm^2(m_{NaCl}/m^0)^2$

$S \equiv Fe(ClO_4)_3$: $a_S = a_{Fe^{3+}}a^3_{ClO_4^-} = 27\gamma_\pm^4(m_S/m^0)^4$

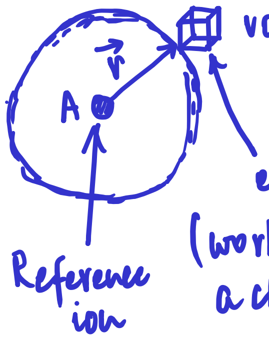
Debye-Hückel theory helps to calculate $\gamma_\pm$.

$\boxed{\text{DH theory}}$

DH theory of ion-ion interactions

postulate: every ion may be considered to be surrounded by an ionic atmosphere of opposite sign.

ρ = charge density (electrical) in dv.
(net charge per unit vol.)



$|\vec{r}| \sim 100 \times$ ionic diameter

electrostatic potential, ψ
(work needed/involved to bring a charge from ∞ to dv)

work needed to bring a +ve charge from ∞ to the centre of dv $= z_+e\psi$
" " " " -ve " " " " " " " " $= -z_-e\psi$

z_+, z_- = valences (magnitude only) of cations and anions.
e = fundamental charge
n_+, n_- = total no. of positive and negative ions, respectively

$$\left.\begin{aligned}&\text{No. of +ve ions present in dv, } dn_+ = n_+e^{-z_+e\psi/kT}dv\\ &\text{No. of -ve ions present in dv, } dn_- = n_-e^{-(-z_-e\psi/kT)}dv\end{aligned}\right\} \text{time-averaged numbers}$$

$$\rho = \frac{e(z_+dn_+ + (-z_-)dn_-)}{dv} = e\left(n_+z_+e^{-z_+e\psi/kT} - n_-z_-e^{z_-e\psi/kT}\right)$$

For a uni-univalent (NaCl) electrolyte, $z_+ = z_- = 1$, $n_+ = n_- = n$

$NaCl \rightarrow Na^+ + Cl^-$

$CaSO_4 \rightarrow Ca^{2+} + SO_4^{2-}$

$$\therefore \rho(1:1) = ne\left(e^{-e\psi/kT} - e^{e\psi/kT}\right) = ne\left(e^{-x} - e^{x}\right), \quad x = e\psi/kT$$

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \frac{x^4}{4!} - \frac{x^5}{5!} + \cdots$$

$$e^{x} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \frac{x^4}{4!} + \frac{x^5}{5!} + \cdots$$

$$e^{-x} - e^{x} = -2x - 2\frac{x^3}{3!} - 2\frac{x^5}{5!} - \cdots = -2x\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right)$$

$$\therefore \rho(1:1) = ne\left(e^{-x} - e^{x}\right) = -2xne\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right)$$

$$\text{or, } \rho(1:1) = -\frac{e^2\psi}{kT}2n\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right)$$

If we assume that, $x = e\psi/kT \ll 1$, $\rho(1:1) = -\left(e^2\psi/kT\right)2n$

Chemical potential and activity of ionic solutions/salts

There is an important point to consider in the context of salt solutions. For a dilute aqueous solution containing say sodium chloride, osmotic and colligative properties confirm that for each mole of sodium chloride the aqueous solution contains (almost exactly) two moles of solutes. These observations result in an added complexity in that chemists describe the solute, sodium chloride in two ways. In one description there is one solute – 'sodium chloride'. In another description there are two solutes sodium ions and chloride ions. The latter description is certainly attractive because we can ring the changes through a series of solutes: $\mathrm{NaCl} \rightarrow \mathrm{NaBr} \rightarrow \mathrm{KCl} \rightarrow \mathrm{KBr} \rightarrow \cdots$. Here we change in stepwise fashion one chemical substance in the salt to produce a new solute. There is, however, one crucial condition. Aqueous solutions are electrically neutral although the solutions contain ions. Therefore, the total charge on all cations equals in magnitude the total charge on all anions in the same solution. There is, therefore, a major problem. In fact, a common procedure involves estimating the properties of single ions but then in the last stage of the analysis we pull the derived single ion properties together to describe the properties of a given salt solution. In the following we will discuss ionic solutions containing the species B that yields the ions

$$B \equiv M_{\nu_+}^{z_+} X_{\nu_-}^{z_-}$$

Here z_+ and z_- are the charges, and ν_+ and ν_- are the number of cations and anions, respectively, for each formula unit of B. Such solutions differ strongly from regular solutions because even at very small concentration no ideal behavior is found. Again, deviation from the ideal case as described by

$$\mu = \mu^0 + RT\ln\frac{p}{p^0}$$

are incorporated by

$$\mu_B = \mu_B^0 + RT\ln\frac{m_B}{m^0} + RT\ln\gamma_B \equiv \nu_+\mu_+ + \nu_-\mu_-.$$

Here γ is the activity coefficient and m^0 is the standard molality (i.e., 1 mol/kg). Thus, $\gamma = 1$ represents the ideal case. Using the activity,

$$a = (m/m^0)\gamma$$

the chemical potentials for both components are

$$\mu_+ = \mu_+^0 + RT\ln\frac{m_+}{m^0} + RT\ln\gamma_+ \quad \text{and} \quad \mu_- = \mu_-^0 + RT\ln\frac{m_-}{m^0} + RT\ln\gamma_-$$

leading to

$$\mu_B = \nu_+\mu_+ + \nu_-\mu_- = \nu_+\mu_+^0 + \nu_-\mu_-^0 + RT\ln\left(\frac{m_+}{m^0}\right)^{\nu_+}\left(\frac{m_-}{m^0}\right)^{\nu_-} + RT\ln\gamma_+^{\nu_+}\gamma_-^{\nu_-}.$$

We will see later that all parameters but γ_+ and γ_- can be extracted from experiments. Defining the geometric mean of molality, $m_\pm = \left(m_+^{\nu_+}m_-^{\nu_-}\right)^{1/\nu}$ and the geometric mean for the activity coefficient $\gamma_\pm = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/\nu}$, with $\nu = \nu_+ + \nu_-$, we get,

$$\mu_B = \nu_+\mu_+^0 + \nu_-\mu_-^0 + RT\ln\gamma_\pm\left(\frac{m_\pm}{m^0}\right)^{\nu} = \mu_B^0 + \nu RT\ln\gamma_\pm\frac{m_\pm}{m^0}$$

Only $\gamma_\pm$ can be extracted from experiments. According to the definition, $a = (m/m^0)\gamma$, we find for the activity

$$a_B = a_+^{\nu_+}a_-^{\nu_-} = \left(\gamma_\pm\frac{m_\pm}{m^0}\right)^{\nu} = \gamma_\pm^{\nu}\frac{m_+^{\nu_+}m_-^{\nu_-}}{(m^0)^{\nu}}$$

With $m_+ = \nu_+m_B$ and $m_- = \nu_-m_B$, we get from the last equation,

$$a_B = \left(\gamma_\pm\frac{m_\pm}{m^0}\right)^{\nu} = \gamma_\pm^{\nu}\frac{(\nu_+m_B)^{\nu_+}(\nu_-m_B)^{\nu_-}}{(m^0)^{\nu}}$$

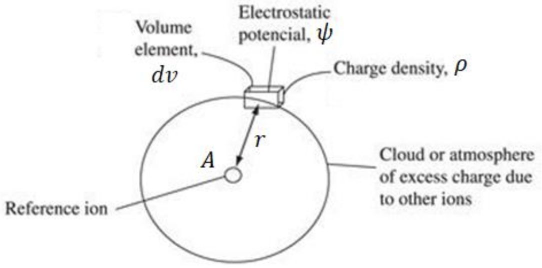
Thus, for NaCl, $a_{NaCl} = a_{\mathrm{Na}^+}a_{\mathrm{Cl}^-} = \gamma_\pm^2(m_{\mathrm{NaCl}}/m^0)^2$. Similarly, for $\mathrm{Fe(ClO_4)_3}$, $a_{\mathrm{Fe(ClO_4)_3}} = a_{Fe^{3+}}a_{ClO_4^-}^3 = 27\gamma_\pm^4\left(m_{\mathrm{Fe(ClO_4)_3}}/m^0\right)^4$, where we have used,

$$m_{\mathrm{Fe^{3+}}} = m_{\mathrm{Fe(ClO_4)_3}};\, m_{\mathrm{ClO_4^-}} = 3m_{\mathrm{Fe(ClO_4)_3}}$$

Thus, the key-point is always how to calculate (or measure) $\gamma_\pm$. One such method to evaluate $\gamma_\pm$, theoretically, is to use the Debye-Hückel theory.

Debye-Hückel theory for strong electrolytes: The electrical potential of ions in solution

Postulate: Every ion may be considered as being surrounded by an ionic atmosphere of opposite sign.



Imagine a positive ion situated at the point A. Consider a small volume element dv at the end of the radius vector $\vec{r}$. The distance r is supposed to be of the order of $1/100$ of the ion diameter. Due to the thermal motion of the ions, there will sometimes be an excess of positive and sometimes an excess of negative ions in the volume element dv. Time-average will show, dv to have a negative charge density (positive ion at A). Net charge of the atmosphere is equal in magnitude but opposite in sign to that of the ion at A. Charge density greater in the immediate vicinity of the ion at A; falls off as $r \uparrow$.

Say, $\psi =$ the electrical potential in the centre of dv. The work involved to bring a positive ion from ∞ to the centre of $dv = z_+e\psi$. The work involved to bring a negative ion from ∞ to the centre of $dv = -z_-e\psi$.

$z_+ =$ numerical value (magnitude only) of the valences of the positive ions.

$z_- =$ numerical value (magnitude only) of the valences of the negative ions.

$e =$ the electronic charge

Say, the Boltzmann law is applicable for the distribution of particles in a field of varying potential energy.

$dn_+ =$ time-average numbers of positive ions present in the volume element dv,

$$dn_+ = n_+e^{-(z_+e\psi/kT)}dv = n_+e^{-z_+e\psi/kT}dv$$

$dn_- =$ time-average numbers of negative ions present in the volume element dv,

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$$dn_- = n_- e^{-(-z_- e\psi/kT)} dv = n_- e^{z_- e\psi/kT} dv$$

$n_+ =$ total number of positive ions per unit volume of the solution

$n_- =$ total number of negative ions per unit volume of the solution

If $\rho =$ (electrical) charge density, that is, the net charge per unit volume, then in the given volume element dv, it is

$$\rho = \frac{e(z_+ dn_+ - z_- dn_-)}{dv} = e\left(n_+ z_+ e^{-z_+ e\psi/kT} - n_- z_- e^{z_- e\psi/kT}\right)$$

For a uni-univalent $(1:1)$ electrolyte, $z_+ = z_- = 1$ and to maintain electrical neutrality, $n_+ = n_- = n$, so that, for the $1:1$ electrolytes,

$$\rho_{1:1} = ne\left(e^{-e\psi/kT} - e^{e\psi/kT}\right) = ne(e^{-x} - e^{x}), \text{ with } x = e\psi/kT$$

Note that,

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \cdots; e^{x} = 1 + x + \frac{x^2}{2!} + \frac{x^3}{3!} + \cdots$$

Therefore,

$$e^{-x} - e^{x} = -2x - 2\frac{x^3}{3!} - 2\frac{x^5}{5!} - \cdots = -2x\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right)$$

Hence,

$$\rho_{1:1} = ne(e^{-x} - e^{x}) = -2xne\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right) = -\frac{e^2\psi}{kT}2n\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right)$$

If it is assumed that $x = e\psi/kT \ll 1$, then,

$$\rho_{1:1} = -\frac{e^2\psi}{kT}2n\left(1 + \frac{x^2}{3!} + \frac{x^4}{5!} + \cdots\right) \approx -\frac{e^2\psi}{kT}2n$$

However, the situation is not so simple for a general $x:y$ electrolyte. For the general electrolyte, we have seen that,

$$\rho = e\left(n_+ z_+ e^{-z_+ e\psi/kT} - n_- z_- e^{z_- e\psi/kT}\right) = e(n_+ z_+ e^{-z_+ x} - n_- z_- e^{z_- x}),$$

with $x = e\psi/kT$. Now, expanding the two exponential terms separately in Taylor's series, we get,

$$\rho = e\left[n_+ z_+\left(1 - z_+ x + \frac{z_+^2 x^2}{2!} - \cdots\right) - n_- z_-\left(1 + z_- x + \frac{z_-^2 x^2}{2!} + \cdots\right)\right]$$

Therefore, from,

$$\rho = e\left[n_+ z_+\left(1 - z_+ x + \frac{z_+^2 x^2}{2!} - \cdots\right) - n_- z_-\left(1 + z_- x + \frac{z_-^2 x^2}{2!} + \cdots\right)\right]$$

upon neglecting the terms of higher powers (and retaining the linear terms only),

$$\rho \approx e[n_+ z_+(1 - z_+ x) - n_- z_-(1 + z_- x)]$$

Hence,

$$\rho \approx e[n_+ z_+ - n_+ z_+^2 x - n_- z_- - n_- z_-^2 x] = e[(n_+ z_+ - n_- z_-) - (n_+ z_+^2 + n_- z_-^2)x]$$

The electrolyte solution is homogeneous (and electrically neutral, as well), so that $(n_+ z_+ - n_- z_-) = 0$.

$$\therefore \rho = -ex(n_+ z_+^2 + n_- z_-^2) = -\frac{e^2\psi}{kT}(n_+ z_+^2 + n_- z_-^2)$$

Thus, for the most general case, where one may have multiple electrolytes, and so many different kinds of ions,

$$\rho = -\frac{e^2\psi}{kT}\sum_i n_i z_i^2$$

where, n_i and z_i represent the number density and valence of the ions of ith kind.

For a uni-univalent electrolyte, $\rho = (-e^2\psi/kT)\,2n$

For the general electrolyte,

$$\rho = e\left(n_+z_+e^{-z_+e\psi/kT} - n_-z_-e^{z_-e\psi/kT}\right) = e\left(n_+z_+e^{-z_+x} - n_-z_-e^{z_-x}\right)$$

where $x = e\psi/kT$.

$$\therefore \rho = e\left[n_+z_+\left(1 - z_+x + \frac{z_+^2x^2}{2!} - \cdots\right) - n_-z_-\left(1 + z_-x + \frac{z_-^2x^2}{2!} + \cdots\right)\right]$$

Since $x = e\psi/kT \ll 1$, upon neglecting terms of higher order

$$\rho \simeq e\left[n_+z_+(1 - z_+x) - n_-z_-(1 + z_-x)\right]$$

$$= e\left[n_+z_+ - n_+z_+^2x - n_-z_- - n_-z_-^2x\right] = e\left[(n_+z_+ - n_-z_-) - (n_+z_+^2 + n_-z_-^2)x\right]$$

$= -e(n_+z_+^2 + n_-z_-^2)x$, since $n_+z_+ - n_-z_- = 0$ due to electrical neutrality

$$= -ex\sum_i n_iz_i^2 \qquad \text{or,}\ \boxed{\rho = -\frac{e^2\psi}{kT}\sum_i n_iz_i^2} \text{ ——— ①}$$

$\vec{\nabla}\cdot\vec{E} = \dfrac{4\pi\rho}{D}$: Maxwell's first equation → One of the fundamental laws of electrostatics.

$\vec{E}$ = electric field vector.

ρ = 〃 charge density.

D = dielectric constant of the medium

$\vec{\nabla}$ = gradient vector

$$\vec{\nabla} = \hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

$$\vec{A} = \hat{i}A_x + \hat{j}A_y + \hat{k}A_z$$

$$\vec{q} = -\vec{\nabla}A$$

Electric field associated with a system of charges is the –ve gradient of the electrostatic potential, ψ

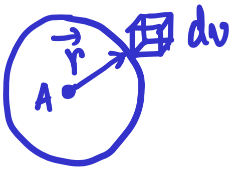
$$\therefore \vec{E} = -\vec{\nabla}\psi \qquad \therefore\ \vec{\nabla}\cdot(-\vec{\nabla}\psi) = \frac{4\pi\rho}{D}$$

$$\text{or,}\ (\vec{\nabla}\cdot\vec{\nabla})\psi = -\frac{4\pi\rho}{D}$$

$$\vec{\nabla}\cdot\vec{\nabla} = \left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)\cdot\left(\hat{i}\frac{\partial}{\partial x} + \hat{j}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)$$

$$= \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2 \text{ (Laplacian function)}$$

$$\therefore \boxed{\nabla^2\psi = -\frac{4\pi\rho}{D}} \text{ ——— ②}$$



$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

for a spherically sym. situation,

$$\nabla^2 = \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right) \quad \therefore \quad \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = -\frac{4\pi\rho}{D}$$

$\psi(r)$ is to be determined by solving the above eqn.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \frac{4\pi e^2}{DkT}\psi\sum_i n_i z_i^2 \qquad \text{or,} \quad \boxed{\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \kappa^2\psi} \text{ — ③}$$

where, $\kappa = \left(\frac{4\pi e^2}{DkT}\sum_i n_i z_i^2\right)^{1/2}$ → has the dimension of length. (relate to the thickness of the ionic atmosphere)

Say, $\psi(r) = \frac{\beta(r)}{r} \Rightarrow \frac{d\psi}{dr} = \frac{d}{dr}\frac{\beta}{r} = -\frac{\beta}{r^2} + \frac{1}{r}\frac{d\beta}{dr}$

or, $r^2\frac{d\psi}{dr} = -\beta + r\frac{d\beta}{dr}$ or, $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \frac{1}{r^2}\frac{d}{dr}\left(-\beta + r\frac{d\beta}{dr}\right)$

or, $\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \frac{1}{r^2}\left(-\cancel{\frac{d\beta}{dr}} + r\frac{d^2\beta}{dr^2} + \cancel{\frac{d\beta}{dr}}\right) = \frac{1}{r}\frac{d^2\beta}{dr^2}$

∴ From ③ : $\frac{1}{r}\frac{d^2\beta}{dr^2} = \kappa^2\frac{\beta}{r} \Rightarrow \frac{d^2\beta}{dr^2} = \kappa^2\beta$

Say, $f(x) = e^{\pm\alpha x} \Rightarrow \frac{d^2 f(x)}{dx^2} = \alpha^2 e^{\pm\alpha x}$ or, $\frac{d^2 f}{dx^2} = \alpha^2 f$

If $\underline{\beta(r) = e^{\pm\kappa r}}$, then $\frac{d^2\beta}{dr^2} = \kappa^2 e^{\pm\kappa r}$

∴ $\beta(r) = Ae^{-\kappa r} + Be^{\kappa r}$ or, $\frac{\beta(r)}{r} = \frac{Ae^{-\kappa r}}{r} + \frac{Be^{\kappa r}}{r}$

$\psi(r) = \frac{Ae^{-\kappa r}}{r} + \frac{Be^{\kappa r}}{r}$ → general solution

General solution $\xrightarrow[\text{condition}]{\text{Boundary}}$ particular solution ↗ How to find the value of A?

When $r\to\infty$, $\psi(r)\to 0 \Rightarrow B = 0$ $\quad \boxed{\psi(r) = \frac{Ae^{-\kappa r}}{r}}$

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However, the situation is not so simple for a general $x\!:\!y$ electrolyte. For the general electrolyte, we have seen that,

$$\rho = e\left(n_+z_+e^{-z_+e\psi/kT} - n_-z_-e^{z_-e\psi/kT}\right) = e\left(n_+z_+e^{-z_+x} - n_-z_-e^{z_-x}\right),$$

with $x = e\psi/kT$. Now, expanding the two exponential terms separately in Taylor's series, we get,

$$\rho = e\left[n_+z_+\left(1 - z_+x + \frac{z_+^2x^2}{2!} - \cdots\right) - n_-z_-\left(1 + z_-x + \frac{z_-^2x^2}{2!} + \cdots\right)\right]$$

Therefore, with the assumption that $x = e\psi/kT \ll 1$, upon neglecting the terms of higher powers (and retaining the linear terms only),

$$\rho \approx e[n_+z_+(1 - z_+x) - n_-z_-(1 + z_-x)]$$

Hence,

$$\rho \approx e[n_+z_+ - n_+z_+^2x - n_-z_- - n_-z_-^2x] = e[(n_+z_+ - n_-z_-) - (n_+z_+^2 + n_-z_-^2)x]$$

The electrolyte solution is homogeneous (and electrically neutral, as well), so that $(n_+z_+ - n_-z_-) = 0$.

$$\therefore\ \rho = -ex(n_+z_+^2 + n_-z_-^2) = -\frac{e^2\psi}{kT}(n_+z_+^2 + n_-z_-^2)$$

Thus, for the most general case, where one may have multiple electrolytes, and so many different kinds of ions,

$$\rho = -\frac{e^2\psi}{kT}\sum_i n_iz_i^2$$

where, n_i and z_i represent the number density and valence of the ions of ith kind. Both ρ and ψ are unknowns, and to know any one of them, another relation between them is needed. One of the fundamental laws of electrostatics (often called Maxwell's first equation) says that,

$$\vec{\nabla}\cdot\vec{E} = \frac{4\pi\rho}{D}$$

where $\vec{E}$ is the electric field vector, ρ the charge density (measured per unit volume) as before, and D is the dielectric constant of the medium. The vector, $\vec{\nabla}$ is the gradient vector, and is defined as,

$$\vec{\nabla} = \hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}$$

Now, $\vec{E}$ is just $-\vec{\nabla}\psi$ (just like the force being the gradient of the potential energy), and therefore,

$$\vec{\nabla}\cdot\vec{E} = \frac{4\pi\rho}{D} \Rightarrow \vec{\nabla}\cdot\vec{\nabla}\psi = -\frac{4\pi\rho}{D}$$

Now,

$$\vec{\nabla}\cdot\vec{\nabla} = \left(\hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right)\cdot\left(\hat{\imath}\frac{\partial}{\partial x} + \hat{\jmath}\frac{\partial}{\partial y} + \hat{k}\frac{\partial}{\partial z}\right) = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} = \nabla^2$$

where, ∇^2 is the Laplacian function. Thus, we have,

$$\nabla^2\psi = -\frac{4\pi\rho}{D}$$

This equation is known as the Poisson equation (in electrostatics). Thus, for the most general case, where one may have multiple electrolytes, and so many kinds of ions,

$$\rho = -\frac{e^2\psi}{kT}\sum_i n_iz_i^2$$

where, n_i and z_i represent the number density and valence of the ions of ith kind. From the Poisson equation (in electrostatics), we have,

$$\nabla^2\psi = -\frac{4\pi\rho}{D}$$

The Poisson equation is a partial differential equation (PDE) in three variables. We realize that the ion and its atmosphere, in the absence of any external electric field, is overall a spherically symmetric entity. Therefore, it will be mathematically easier to deal with the Poisson equation if we express it in the spherical polar coordinates.

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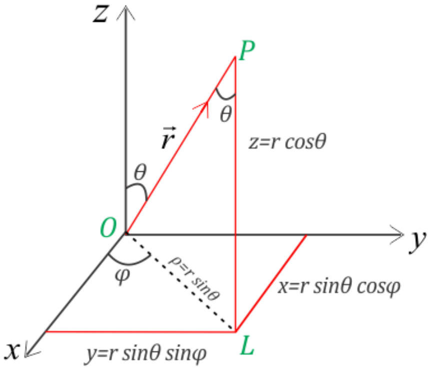


$$x = r\sin\theta\cos\phi\,; y = r\sin\theta\sin\phi\,;\; z = r\cos\theta$$

The Laplacian function in Cartesian coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

becomes,

$$\nabla^2 = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\phi^2}$$

Since the distribution of potential about any point in the electrolyte must be spherically symmetric, the terms having dependence on the angular coordinates, θ and ϕ are all zero. Therefore, under spherical symmetry,

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

so that the Poisson equation becomes,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)\psi = -\frac{4\pi\rho}{D}$$

We have already seen that,

$$\rho = -\frac{e^2\psi}{kT}\sum_i n_i z_i^2$$

so that,

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d}{dr}\right)\psi = \frac{4\pi e^2}{DkT}\psi\sum_i n_i z_i^2 = \kappa^2\psi,$$

where the quantity κ is defined as,

$$\kappa = \left(\frac{4\pi e^2}{DkT}\sum_i n_i z_i^2\right)^{1/2}$$

Thus, the Poisson-Boltzmann equation is

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

How do we solve the Poisson-Boltzmann equation? Let us define a new variable $\beta(r)$, as $\psi(r) = \beta(r)/r$.

$$\therefore \frac{d\psi}{dr} = \frac{d}{dr}\frac{\beta}{r} = -\frac{\beta}{r^2} + \frac{1}{r}\frac{d\beta}{dr} \Rightarrow r^2\frac{d\psi}{dr} = -\beta + r\frac{d\beta}{dr}$$

$$\therefore \frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi}{dr}\right) = \frac{1}{r^2}\frac{d}{dr}\left(-\beta + r\frac{d\beta}{dr}\right) = \frac{1}{r^2}\left(-\frac{d\beta}{dr} + r\frac{d^2\beta}{dr^2} + \frac{d\beta}{dr}\right) = \frac{1}{r}\frac{d^2\beta}{dr^2}$$

Hence, the Poisson-Boltzmann equation becomes,

$$\frac{1}{r}\frac{d^2\beta}{dr^2} = \kappa^2\frac{\beta}{r} \Rightarrow \frac{d^2\beta}{dr^2} = \kappa^2\beta$$

To solve the Poisson-Boltzmann equation,

$$\frac{d^2\beta}{dr^2} = \kappa^2\beta$$

it is recalled that the differentiation of an exponential function results in the multiplication of that function by the constant in the exponent. Thus, if $\beta(r) = e^{\pm\kappa r}$,

$$\therefore \frac{d}{dr}e^{\pm\kappa r} = \pm\kappa e^{\pm\kappa r} \quad \text{and} \quad \frac{d^2}{dr^2}e^{\pm\kappa r} = \kappa^2 e^{\pm\kappa r}$$

If β is an exponential function of r, one will obtain a differential equation of the form $d^2\beta/dr^2 = \kappa^2\beta$. Two possible exponential functions, $e^{-\kappa r}$ and $e^{+\kappa r}$, will lead to the same final differential equation.

$$\therefore \beta(r) = Ae^{-\kappa r} + Be^{+\kappa r} \Rightarrow \frac{\beta(r)}{r} = \psi(r) = \frac{Ae^{-\kappa r}}{r} + \frac{Be^{+\kappa r}}{r}$$

$$\therefore \psi(r) = \frac{Ae^{-\kappa r}}{r} + \frac{Be^{+\kappa r}}{r}$$

Applying a suitable boundary condition ($r \to \infty$, $\psi \to 0$), we obtained $B = 0$.

$$\therefore \psi(r) = \frac{Ae^{-\kappa r}}{r}$$

Applying appropriate boundary conditions, the electrostatic potential at any location $\vec{r}$ is given by,

$$\boxed{\psi(r) = A e^{-\kappa r}/r}$$

κ^{-1} has the dimension of length (we will prove this)

where A is an unknown constant.

$\boxed{\text{How to determine A?}}$

Solution of the electrolyte is extremely dilute ⇒ interionic interactions are min.

$n_i \to 0;$

$$\kappa = \left(\frac{4\pi e^2}{DkT}\sum_i n_i z_i^2\right)^{1/2} \to 0$$

Central ion → point charge

Coulomb's law: $\psi(r) = \frac{z_i e}{Dr}$

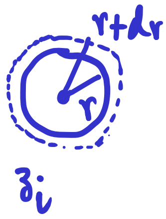
∴ $e^{-\kappa r}$ in $\psi(r) = A e^{-\kappa r}/r$, $\psi(r) = A/r$ when $\kappa \to 0$ $(n_i \to 0)$

for an extremely dil. solution:

$$\psi(r) = \frac{z_i e}{Dr}, \quad \psi(r) = \frac{A}{r} \quad \Rightarrow A = z_i e/D$$

$$\boxed{\psi(r) = \frac{z_i e}{D}\,\frac{e^{-\kappa r}}{r}}$$

How do we calculate the total charge associated with the ionic atmosphere?



dq = is the infinitesimal charge contained in the shell of thickness dr.

$$\frac{4}{3}\pi(r+dr)^3 - \frac{4}{3}\pi r^3 = \frac{4}{3}\pi\left[r^3 + 3r^2 dr + 3r(dr)^2 + (dr)^3\right] - \frac{4}{3}\pi r^3$$

$$\cong 4\pi r^2 dr$$

$$dq = \rho \times 4\pi r^2 dr$$

$$q_{cloud} = \int_{r=0}^{r\to\infty} dq = \int_{r=0}^{r\to\infty} \rho\, 4\pi r^2 dr = -\int_{r=0}^{r\to\infty} \frac{z_i e}{4\pi}\kappa^2 \frac{e^{-\kappa r}}{r}\, 4\pi r^2 dr$$

$$\text{or, } q_{cloud} = -z_i e \int_{r=0}^{r\to\infty} e^{-\kappa r}(\kappa r)\, d(\kappa r)$$

$$\boxed{\int v\,du = uv - \int u\,dv}$$

$$\int_{r=0}^{r\to\infty} (\kappa r)\, e^{-\kappa r}\, d(\kappa r) = \left[-\kappa r e^{-\kappa r} - \int \frac{e^{-\kappa r}}{(-1)}\, d(\kappa r)\right]_{r=0}^{r\to\infty}$$

$$= \left[-\kappa r e^{-\kappa r} - e^{-\kappa r}\right]_{r=0}^{r\to\infty} = \left[-e^{-\kappa r}(\kappa r + 1)\right]_{r=0}^{r\to\infty} = 1$$

$$\therefore \boxed{q_{cloud} = -z_i e}$$

$\therefore$ the ionic atmosphere has a total charge of $-z_i e$, which is equal in magnitude, but opposite in sign to that of the central ion.

electroneutrality

How is the charge of the ionic atmosphere distributed in space?

$$\rho = -\frac{z_i e}{4\pi}\kappa^2 \frac{e^{-\kappa r}}{r}, \quad \text{and} \quad dq = \rho\, 4\pi r^2 dr$$

$$q = f(r)$$

$$\therefore \boxed{dq = -z_i e \kappa^2 e^{-\kappa r} r\, dr}$$

for which value of r, q is a max.? $\frac{dq}{dr} = 0$

$$0 = \frac{dq}{dr} = \frac{d}{dr}\left[-z_i e \kappa^2 (e^{-\kappa r} r)\right] = -z_i e \kappa^2 \frac{d}{dr}(r e^{-\kappa r}) = -z_i e \kappa^2 (e^{-\kappa r} - \kappa r e^{-\kappa r})$$

$$\therefore -z_i e \kappa^2 (e^{-\kappa r} - \kappa r e^{-\kappa r}) = 0$$

$$\Rightarrow e^{-\kappa r} - \kappa r e^{-\kappa r} = 0 \quad \Rightarrow \boxed{r = \kappa^{-1}}$$

κ^{-1} is the radius of the ionic atmosphere.
thickness of the ionic atmosphere

$$\kappa^{-1} = \left(\frac{DkT}{4\pi}\frac{1}{e^2 \sum_i n_i z_i^2}\right)^{1/2}$$

DH length

for an extremely dil. sol.
$n_i \to 0$
$\sum_i n_i z_i^2 \to 0$, $\kappa r \ll 1$

$$e^{-\kappa r} - 1 \cong 1 - \kappa r + \frac{(\kappa r)^2}{2!} - \dots - 1$$

$$\cong 1 - \kappa r - 1 = -\kappa r$$

$$\psi_{cloud} = -\frac{z_i e}{D \cancel{r}} \kappa \cancel{r}$$

$$\boxed{\psi_{cloud} = -\frac{z_i e}{D \kappa^{-1}}}$$

$$\boxed{\psi_{ion} = \frac{z_i e}{D r}}$$

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

$$\psi_{cloud} = \psi(r) - \psi_{ion} = \frac{z_i e}{D}\frac{e^{-\kappa r}}{r} - \frac{z_i e}{D r} = \frac{z_i e}{D r}\left(e^{-\kappa r} - 1\right)$$

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The Debye-Hückel theory is in general valid for appreciably dilute solutions only. To evaluate the integration constant A, a hypothetical condition is considered in which the solution is so dilute and on the average the ions are so far apart that there is a negligible interionic field. Further, the central ion is assumed to be a point charge → having a radius negligible compared with the distances otherwise to be considered. Hence, the potential near the central ion is, in this special case, is simply that due to an isolated point charge of value $z_i e$. This is given directly from Coulomb's law as

$$\psi(r) = \frac{z_i e}{Dr}$$

At the same time, for this hypothetical solution in which the concentration tends to zero, that is, $n_i \to 0$, so that,

$$\kappa = \left(\frac{4\pi e^2}{DkT}\sum_i n_i z_i^2\right)^{1/2} \to 0$$

Therefore, the term $e^{-\kappa r}$ in $\psi(r) = Ae^{-\kappa r}/r$ goes to unity as $\kappa \to 0$.

$$\therefore \psi(r) = A/r$$

Thus, from

$$\psi(r) = \frac{z_i e}{Dr} \quad \text{and} \quad \psi(r) = A/r$$

we obtain, $A = z_i e/D$

Therefore, using $A = z_i e/D$, in $\psi(r) = Ae^{-\kappa r}/r$, we get,

$$\psi(r) = \frac{z_i e}{D}\frac{e^{-\kappa r}}{r}$$

This is the solution of the Poisson-Boltzmann equation valid for dilute solutions.

How do we calculate the total charge associated with the atmosphere/cloud? Consider a spherical shell of thickness dr, at a distance r from the centre of the reference ion. Hence, the charge contained in this thin shell, dq, is given by, $dq = \rho \times 4\pi r^2 dr$, where $4\pi r^2 dr$ is the volume of this shell. The total charge, q_{cloud}, contained in the ion atmosphere is the sum of the charges dq contained in all the infinitesimally thick spherical shells. Therefore, the total excess charge surrounding the reference ion is computed by integrating dq (which is a function of the distance r from the central ion) from a lower limit corresponding to the distance from the central ion at which the cloud is taken to commence to the point where the cloud ends. Now, the ion atmosphere begins at the surface of the ion, so the lower limit depends upon the model of the ion. The first model (Debye and Hückel): point-charge ions; lower limit is $r = 0$. The upper limit is $r \to \infty$, because the charge of the ionic cloud decays exponentially into the solution and becomes zero only in the limit $r \to \infty$. Thus,

$$q_{cloud} = \int_{r=0}^{r\to\infty} dq = \int_{r=0}^{r\to\infty} \rho \times 4\pi r^2 dr = -\int_{r=0}^{r\to\infty} \frac{z_i e}{4\pi}\kappa^2 \frac{e^{-\kappa r}}{r} 4\pi r^2 dr$$

Therefore,

$$q_{cloud} = -z_i e \int_{r=0}^{r\to\infty} e^{-\kappa r}\,(\kappa r) d(\kappa r)$$

Using the method of integration by parts, $\int v\,du = uv - \int u\,dv$, we get

$$\int_{r=0}^{r\to\infty} (\kappa r)e^{-\kappa r}\,d(\kappa r) = \left[-\kappa r e^{-\kappa r} - \int \frac{e^{-\kappa r}}{(-1)} d(\kappa r)\right]_{r=0}^{r\to\infty} = [-\kappa r e^{-\kappa r} - e^{-\kappa r}]_{r=0}^{r\to\infty} = [-e^{-\kappa r}(\kappa r + 1)]_{r=0}^{r\to\infty}$$

$$= 1$$

$$\therefore q_{cloud} = -z_i e$$

That is, a central ion of charge $+z_i e$ is enveloped by a cloud containing a total charge of $-z_i e$ → Electroneutrality. How is this equal and opposite charge of the ion atmosphere distributed in the space around the central ion? From,

$$\rho = -\frac{z_i e}{4\pi}\kappa^2 \frac{e^{-\kappa r}}{r} \text{ and } dq = \rho \times 4\pi r^2 dr$$

it is seen that the net charge in a spherical shell of thickness dr and at a distance r from the origin is

$$dq = -z_i e\kappa^2 e^{-\kappa r} r dr$$

Thus, the excess charge on a spherical shell varies with r and has a maximum value for a value of r given by

$$0 = \frac{dq}{dr} = \frac{d}{dr}[-z_i e\kappa^2 (e^{-\kappa r} r)] = -z_i e\kappa^2 \frac{d}{dr}(e^{-\kappa r} r) = -z_i e\kappa^2 (e^{-\kappa r} - r\kappa e^{-\kappa r})$$

Since, $z_i e\kappa^2$ is finite, the above equality can only be true, if,

$$0 = e^{-\kappa r} - r\kappa e^{-\kappa r} \Rightarrow r = \kappa^{-1}$$

Hence, the maximum value of the charge contained in a spherical shell (of infinitesimal thickness dr) is attained when the spherical shell is at a distance $r = \kappa^{-1}$ from the reference ion. For this reason, κ^{-1} is known as the thickness, or radius, of the ionic atmosphere / cloud that surrounds a reference ion. An elementary dimensional analysis of κ^{-1}, using, say,

$$\kappa^{-1} = \left(\frac{DkT}{4\pi} \frac{1}{e^2 \sum_i n_i z_i^2}\right)^{1/2}$$

will indeed reveal that κ^{-1} has the dimensions of length. Consequently, κ^{-1} is sometimes referred to as the Debye-Hückel length. As the concentration tends toward zero, the cloud tends to spread out increasingly. To get a better feel of these effects, let us perform a thought experiment. Say the charge on the ionic cloud does not exist. There is only one charge now, that on the central ion. What is the potential at distance r from the central ion? It is simply,

$$\psi_{ion} = \frac{z_i e}{Dr}$$

Let the charge on the cloud be now switched on. The potential $\psi(r)$ at the distance r from the central ion is no longer given by the central ion only. It is given by the law of superposition of potentials, i.e., $\psi(r)$ is the sum of the potential due to the central ion and that due to the ionic cloud $\psi(r) = \psi_{ion} + \psi_{cloud}$. The contribution ψ_{cloud} can thus be easily found.

$$\psi_{cloud} = \psi(r) - \psi_{ion} = \frac{z_i e}{D}\frac{e^{-\kappa r}}{r} - \frac{z_i e}{Dr} = \frac{z_i e}{Dr}(e^{-\kappa r} - 1)$$

We know, that κ depends on $\sum_i n_i z_i^2$.

For sufficiently dilute solutions, $\sum_i n_i z_i^2$ can be taken as sufficiently small so that, $\kappa r \ll 1$.

$$\therefore e^{-\kappa r} - 1 = 1 - \kappa r - 1 = -\kappa r,$$

and based on this approximation,

$$\psi_{cloud} = \frac{z_i e}{Dr}(e^{-\kappa r} - 1) = -\frac{z_i e}{Dr}\kappa r = -\frac{z_i e}{D\kappa^{-1}}$$

Therefore, using

$$\psi_{ion} = \frac{z_i e}{Dr} \text{ and } \psi_{cloud} = -\frac{z_i e}{D\kappa^{-1}}$$

in

$$\psi(r) = \psi_{ion} + \psi_{cloud} = \frac{z_i e}{Dr} - \frac{z_i e}{D\kappa^{-1}}$$

The second term, which arises from the cloud, reduces the value of the potential to a value less than that if there were no cloud.

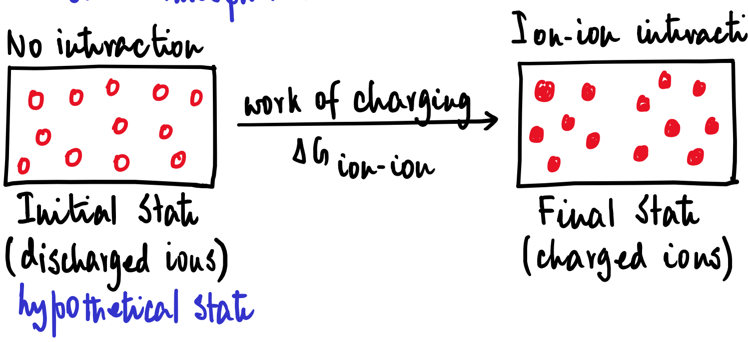
This is consistent with the model; the cloud has a charge opposite to that on the central ion and must therefore alter the potential in a sense opposite to that due to the central ion.

Thermodynamics of ion-ion interactions:

from previous classes, we know, the expressions for electrostatic potentials due to the ion and the ionic atmosphere. $\boxed{\psi_{ion} \text{ and } \psi_{cloud} \text{ have opposite signs!}}$

$\boxed{\psi_{ion} = \frac{z_i e}{Dr}}$ and $\boxed{\psi_{cloud} = -\frac{z_i e}{D\kappa^{-1}}}$, where $\kappa = \left(\frac{4\pi e^2}{DkT}\sum_i n_i z_i^2\right)^{1/2}$ postulate made by DH theory.

κ^{-1} has the dimension of length (Debye-Hückel length) and represents the thickness of the ionic atmosphere.



$\Delta G_{ion-ion}$ = Gibbs free energy change due to the ion-ion interactions.

For an ionic species i: this reference ion is charged from a state of zero charge to its final state of charge $z_i e = W$ (say)

Partial molar free energy change arising from the interactions of one ionic species with the other ions in the collection $= \Delta\mu^{(i)}_{ion-ion} = N_A W$

Now, $W = \frac{1}{2} \times$ charge on the conductor (reference ion) $\times$ electrostatic potential of the conductor

$$\therefore \Delta\mu^{(i)}_{ion-ion} = N_A W = N_A \cdot \frac{1}{2} z_i e \cdot \psi$$

Now, ψ = electrostatic pot. of the ref. ion due to the influence on it by the interactions of the surrounding field.

$\therefore \psi = \psi_{cloud}$ $\quad \therefore \Delta\mu^{(i)}_{ion-ion} = \frac{1}{2} N_A z_i e \psi_{cloud}$, where $\psi_{cloud} = -\frac{z_i e}{D\kappa^{-1}}$

$$\therefore \Delta\mu^{(i)}_{ion-ion} = -\frac{N_A (z_i e)^2}{2D\kappa^{-1}} \text{ —— ①}$$

$\mu_i = \mu_i^0 + RT\ln x_i$ (ideal) : initial state of the system

$\mu_i = \mu_i^0 + RT\ln a_i$ (real) : final state of the system

$= \mu_i^0 + RT\ln x_i + RT\ln \gamma_i$

$\Delta\mu^{(i)}_{ion-ion} = \mu_i(\text{real}) - \mu_i(\text{ideal})$

$\Delta\mu^{(i)}_{ion-ion} = RT\ln\gamma_i$ —— ②

$\therefore$ From ① and ②: $RT\ln\gamma_i = -\frac{N_A (z_i e)^2}{2D\kappa^{-1}}$ or, $\boxed{\ln\gamma_i = -\frac{N_A e^2}{2DRT}\kappa z_i^2}$ —— ③

for the general electrolyte, $B \equiv M^{z+}_{n_+} X^{z-}_{n_-}$

$$\mu_B = (n_+\mu_+^0 + n_-\mu_-^0) + RT\ln \gamma_\pm (m_\pm/m^0)^n = \mu_B^0 + nRT\ln\gamma_\pm(m_\pm/m^0)$$

$m_\pm = (m_+^{n_+} m_-^{n_-})^{1/n}$, $\gamma_\pm = (\gamma_+^{n_+}\gamma_-^{n_-})^{1/n}$, $n = n_+ + n_-$, $m^0 = 1 \text{ mol kg}^{-1}$ (standard molality)

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$$\therefore \ln\gamma_\pm = \frac{1}{n}\left(n_+\ln\gamma_+ + n_-\ln\gamma_-\right)$$

$$\therefore \ln\gamma_\pm = -\frac{1}{n}\left[n_+\frac{N_Ae^2}{2DRT}\kappa z_+^2 + n_-\frac{N_Ae^2}{2DRT}\kappa z_-^2\right] = -\frac{1}{n}\left[\frac{N_Ae^2}{2DRT}\kappa\left(n_+z_+^2+n_-z_-^2\right)\right]$$

Since the electrolyte is as a whole electrically neutral,

$$n_+z_+ = n_-z_-$$

$$\therefore n_+z_+^2+n_-z_-^2 = n_+z_+z_+ + n_-z_-z_- = n_-z_-z_+ + n_+z_+z_-$$

$$= z_+z_-(n_++n_-) = nz_+z_-$$

$$\therefore \ln\gamma_\pm = -\frac{1}{n}\left[\frac{N_Ae^2}{2DRT}\kappa n z_+z_-\right] = -\frac{N_A(z_+z_-)e^2}{2DRT}\kappa$$

Concentration, c_i of any species i = $\frac{\text{no. of moles of } i}{\text{unit vol.}}$

$$c_i = \frac{n_i/N_A}{1.0\ \text{ml}}\times 1000\ \text{ml} \Rightarrow n_i = \frac{c_iN_A}{1000}$$

$$\kappa = \left(\frac{4\pi e^2}{DkT}\sum_i n_iz_i^2\right)^{1/2} = \left(\frac{4\pi}{DkT}\frac{N_Ae^2}{1000}\sum_i c_iz_i^2\right)^{1/2} = \left(\frac{8\pi N_Ae^2}{1000DkT}\right)^{1/2}\sqrt{I} = B\sqrt{I}$$

$\uparrow$ a constant at a const. T for a definite electrolyte solution (solvent is fixed, D is fixed)

ionic strength of the solution, $I = \frac{1}{2}\sum_i c_iz_i^2$

$$\therefore \ln\gamma_\pm = -\frac{N_A(z_+z_-)e^2}{2DRT}B\sqrt{I}$$

or, $$\log_{10}\gamma_\pm = -\frac{N_A(z_+z_-)e^2}{2.303\times 2DRT}B\sqrt{I} = -A(z_+z_-)\sqrt{I}$$

$$A = \frac{N_Ae^2B}{2.303\times 2DRT} \qquad \boxed{\log_{10}\gamma_\pm = -A(z_+z_-)\sqrt{I}}$$

Thermodynamics of ion-ion interactions

Aim: To develop a quantitative measure of the ion-ion interactions.

Consider, an initial state in which ion-ion interactions do not exist (are "switched off"), and in which ion-ion interactions do not exist. The free-energy change in going from the initial state to the final state can be considered the free energy of ion-ion interactions, $\Delta G_{ion-ion}$. The final state is obvious; it is ions in solution. The initial state is not so straightforward; one cannot take ions in vacuum, because then there will be ion-solvent interactions when these ions enter the solvent. One conceives of a hypothetical situation in which the ions are there in solution but are nevertheless not interacting. Now, if ion-ion interactions are assumed to be electrostatic in origin, then the imaginary initial state of noninteracting ions implies an assembly of discharged ions.

∴ The initial state of noninteracting ions → final state of ion-ion interactions is equivalent to taking an assembly of discharged ions → charging them up and setting the electrostatic charging work equal to the free energy $\Delta G_{ion-ion}$ of ion-ion interactions. Since, in the charging process, both the positively charged and negatively charged ionic species are charged up, one obtains a free-energy change that involves all the ionic species constituting the electrolyte.

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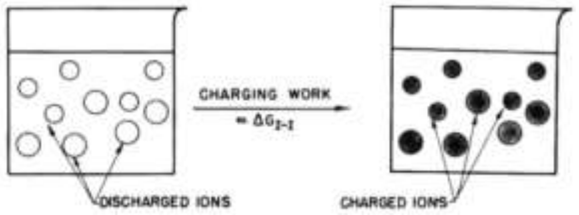

This partial free-energy change is the chemical-potential change, $\Delta\mu_{ion-ion}^{(i)}$, arising from the interactions of one ionic species with the ionic assembly. To calculate $\Delta\mu_{ion-ion}^{(i)}$, let us imagine an ion of species i and consider that this reference ion alone of all the ions in solution is in a state of zero charge. If one computes the work of charging up the reference ion (of radius r_i) from a state of zero charge to its final charge of $z_i e$, then, the work of charging is W (say). Then, the partial molar free energy of ion-ion interactions, i.e., to the chemical potential of ion-ion interactions is

$$\Delta\mu_{ion-ion}^{(i)} = N_A W$$

From electrostatics, the work of charging a conductor,

$$W = \frac{1}{2}[(\text{charge on the conductor}) \times (\text{conductor's electrostatic potential})]$$

$$\therefore \Delta\mu_{ion-ion}^{(i)} = N_A W = N_A \frac{1}{2} z_i e\psi$$

Note that, ψ is the electrostatic potential of the ion due to the influence on it by the electrostatic interactions of the surrounding field. Thus, ψ must be ψ_{cloud}, so that, $\Delta\mu_{ion-ion}^{(i)} = N_A z_i e\psi_{cloud}/2$.

Thus,

$$\Delta\mu_{ion-ion}^{(i)} = \frac{1}{2} N_A z_i e\psi_{cloud}$$

We know,

$$\psi_{cloud} = -\frac{z_i e}{D\kappa^{-1}} \Rightarrow \Delta\mu_{ion-ion}^{(i)} = -\frac{N_A (z_i e)^2}{2D\kappa^{-1}}$$

The Debye-Hückel ionic-cloud model for the distribution of ions in an electrolytic solution has permitted the theoretical calculation of the chemical-potential change arising from ion-ion interactions. How is this theoretical expression to be checked? For a hypothetical system of ideal (non-interacting) particles, the chemical potential is given by

$$\mu_i(\text{ideal}) = \mu_i^0 + RT\ln x_i.$$

For a real system of interacting particles, the chemical potential has been expressed in the form

$$\mu_i(\text{real}) = \mu_i^0 + RT\ln x_i + RT\ln\gamma_i.$$

Therefore,

$$\mu_i(\text{real}) - \mu_i(\text{ideal}) = \Delta\mu_{ion-ion}^{(i)},$$

so that,

$$\Delta\mu_{ion-ion}^{(i)} = RT\ln\gamma_i$$

Thus, the activity coefficient is a measure of the chemical potential change arising from ion-ion interactions.

$$\therefore RT\ln\gamma_i = -\frac{N_A (z_i e)^2}{2D\kappa^{-1}} \Rightarrow \ln\gamma_i = -\frac{N_A (z_i e)^2}{2DRT}\kappa = -\frac{N_A e^2}{2DRT}\kappa z_i^2$$

Thus, the Debye-Hückel ionic-cloud model for ion-ion interactions has permitted a theoretical calculation of activity coefficients. In one of our earlier classes (Electrochemistry 1), for a (general) electrolyte $B \equiv M_{\nu_+}^{z_+} X_{\nu_-}^{z_-}$,

$$\mu_B = \nu_+\mu_+^0 + \nu_-\mu_-^0 + RT\ln\gamma_\pm\left(\frac{m_\pm}{m^0}\right)^\nu = \mu_B^0 + \nu RT\ln\gamma_\pm\frac{m_\pm}{m^0}$$

where, the geometric mean of molality, $m_\pm = \left(m_+^{\nu_+} m_-^{\nu_-}\right)^{1/\nu}$ and the geometric mean for the activity coefficient $\gamma_\pm = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/\nu}$, with $\nu = \nu_+ + \nu_-$, and and m^0 is the standard molality (i.e., 1 mol/kg).

Thus,

$$\mu_B = \mu_B^0 + \nu RT\ln\frac{m_\pm}{m^0} + \nu RT\ln\gamma_\pm$$

GOOGLE MEET LINK: https://meet.google.com/beq-bejw-vqz (CLASS-16, 02/06/2024)

Now, from $\gamma_\pm = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/\nu}$,

$$\ln\gamma_\pm = \frac{1}{\nu}(\nu_+\ln\gamma_+ + \nu_-\ln\gamma_-)$$

From,

$$\ln\gamma_i = -\frac{N_A e^2}{2DRT}\kappa z_i^2$$

we write,

$$\ln\gamma_\pm = -\frac{1}{\nu}\left[\nu_+\frac{N_A e^2}{2DRT}\kappa z_+^2 + \nu_-\frac{N_A e^2}{2DRT}\kappa z_-^2\right] = -\frac{1}{\nu}\left[\frac{N_A e^2}{2DRT}\kappa(\nu_+ z_+^2 + \nu_- z_-^2)\right]$$

Thus,

$$\ln\gamma_\pm = -\frac{1}{\nu}\left[\frac{N_A e^2}{2DRT}\kappa(\nu_+ z_+^2 + \nu_- z_-^2)\right]$$

Since the solution as a whole is electroneutral, $\nu_+ z_+ = \nu_- z_-$ and therefore,

$$\nu_+ z_+^2 + \nu_- z_-^2 = \nu_+ z_+ z_+ + \nu_- z_- z_- = \nu_- z_- z_+ + \nu_+ z_+ z_- = z_+ z_-(\nu_+ + \nu_-) = z_+ z_- \nu$$

Therefore,

$$\ln\gamma_\pm = -\frac{1}{\nu}\left[\frac{N_A e^2}{2DRT}\kappa z_+ z_- \nu\right] = -\frac{N_A (z_+ z_-) e^2}{2DRT}\kappa$$

We know,

$$\kappa = \left(\frac{4\pi e^2}{DkT}\sum_i n_i z_i^2\right)^{1/2} = \left(\frac{4\pi}{DkT}\sum_i n_i z_i^2\, e^2\right)^{1/2}$$

Since,

$$n_i = \frac{c_i N_A}{1000} \Rightarrow \sum_i n_i z_i^2\, e^2 = \frac{N_A e^2}{1000}\sum_i c_i z_i^2$$

Thus,

$$\ln\gamma_\pm = -\frac{N_A (z_+ z_-) e^2}{2DRT}\kappa \quad \text{and} \quad \kappa = \left(\frac{4\pi}{DkT}\frac{N_A e^2}{1000}\sum_i c_i z_i^2\right)^{1/2}$$

Prior to the development of the Debye-Hückel theory, Lewis introduced the idea of ionic strength, I, and defined it as,

$$I = \frac{1}{2}\sum_i c_i z_i^2$$

$$\therefore \kappa = \left(\frac{8\pi}{DkT}\frac{N_A e^2}{1000}\frac{1}{2}\sum_i c_i z_i^2\right)^{1/2} = \left(\frac{8\pi N_A e^2}{1000DkT}\right)^{1/2}\sqrt{I} = B\sqrt{I}$$

Hence,

$$\ln\gamma_\pm = -\frac{N_A (z_+ z_-) e^2}{2DRT}B\sqrt{I}$$

In a slightly different way,

$$\log\gamma_\pm = -\frac{1}{2.303}\frac{N_A e^2}{2DRT}B(z_+ z_-)\sqrt{I} = -A(z_+ z_-)\sqrt{I}\,,\ \text{with } A = \frac{1}{2.303}\frac{N_A e^2}{2DRT}B$$

For uni-univalent $(1:1)$ electrolytes, $z_+ = z_- = 1$ and $I = c$, and hence,

$$\log\gamma_\pm = -A\sqrt{c}$$