The chemical potential of salt \( j \) in an aqueous solution at temperature \( T \) and pressure \( p \) (which is close to the standard pressure \( p^0 \)) is related to the molality of salt \( m_j \) using equation (a).

\[
\mu_j(\text{aq}) = \mu_j^0(\text{aq}) + \nu \cdot R \cdot T \cdot \ln(Q \cdot m_j \cdot \gamma_{\pm} / m^0) \quad (a)
\]

Here \( Q^\nu = \nu_+^\nu \cdot \nu_-^\nu \quad (b) \)

In equation (b), \( \nu_+ \) and \( \nu_- \) are the number of moles of cations and anions respectively produced on complete dissociation by one mole of salt; \( \nu = \nu_+ + \nu_- \). Here \( \gamma_{\pm} \) is the mean ionic activity coefficient where by definition, at all \( T \) and \( p \),

\[
\lim_{m_j \to 0} \gamma_{\pm} = 1 \quad (c)
\]

If the thermodynamic properties of the solution are ideal than \( \gamma_{\pm} \) is unity. However the thermodynamic properties of salt solutions, even quite dilute solutions, are not ideal as a consequence of strong long-range charge-charge interactions between ions in solution. The challenge is therefore to come up with an equation for \( \gamma_{\pm} \) granted that the temperature, pressure and properties of the solvent and salt are known together with the composition of the solution.

The first successful attempt to meet this challenge was published by Debye and Huckel in 1923 and 1924 [1,2].

In most published accounts, the CGS system of units is used. However here we use the SI system and trace the units through the treatment. The solvent is a dielectric (structureless) continuum characterised by its relative permittivity, \( \varepsilon_r \).

The solute (salt) comprises ions characterised by their charge and radius; e.g. for ion-j, charge \( z_j \cdot e \) and radius \( r_j \) such that for cations \( z_j \geq 1 \) and for anions \( z_j \leq -1 \) where \( z_j \) is an integer.

The analysis combines two important physical chemical relationships; Boltzmann’s Law and Poisson’s Equation.

We consider an aqueous salt solution containing i-ionic substances, each substance having molality \( m_i \). The solution contains cations and anions. A KEY condition requires that the electric charge on the solution is zero.
Thus, $\sum_{j=i}^{j=i} m_j \cdot z_j = 0$ \hspace{1cm} (d)

Published accounts of the Debye-Huckel equation almost always use the concentration scale because the analysis concentrates on the distances between ions in solution rather than their mass. The concentration of $j$ ions in a solution, volume $V$, is given by equation (e)

Thus, $\sum_{j=i}^{j=i} c_j \cdot z_j = 0$ \hspace{1cm} (e)

\[ c_j = \frac{n_j}{V} \hspace{1cm} (f) \]

Here $n_j$ is the amount of solute $j$ (expressed using the unit, mole) and $V$ is the volume of solution.

These equations describe the solution as seen from the standpoint of a chemist interested in the properties of a given solution. However the ‘view’ from the standpoint of, for example, a cation in the solution is quite different. The neutrality condition in equation (d) requires that the electric charge on the solution surrounding the cation $j$ with charge $+|z_j \cdot e|$ equals $-|z_j \cdot e|$; i.e. equal in magnitude but opposite in sign. This is the electric charge on the rest of the solution and constitutes the ‘ion atmosphere’ of the $j$ ion. Every ion in the solution has its own atmosphere having a charge equal in magnitude but opposite in sign. Moreover interaction between a $j$ ion and its atmosphere stabilises the $j$ ion in solution. The task of the theory is to obtain an equation for this stabilisation of the salt (i.e. the lowering of its chemical potential in solution). Intuitively we might conclude that this stabilisation is a function of the ionic strength of the salt solution and the dielectric properties of the solvent.

We consider a reference $j$ ion, radius $r_j$, in solution together with a small volume element, $dV$, a distance not more than say $(50 \times r_j)$ from the $j$ ion. In terms of probabilities, if the $j$ ion is a cation the probability of finding an anion in the reference volume is greater than finding a cation. Again with the $j$ ion as reference, we identify a time averaged electric potential $\psi_j$ at the volume element. The distribution of ions about the cation $j$ is assumed to follow the Boltzmann distribution law. The time average number of cations $d n_+$ and anions $d n_-$ in the volume element is given by equation (g) where ion $i$ is, in turn, taken as a cation and then as an anion.
\[
dn_i = p_i \cdot \exp\left(-\frac{Z_i \cdot e \cdot \psi_j}{k \cdot T}\right) \cdot dV \quad (g)
\]

Here \(p_i\) is the number of \(i\) ions in unit volume of the solution [3]. Each \(i\) ion has electric charge \(Z_i \cdot e\). Hence the electric charge on the volume \(dV\) is obtained by summing over the charge on the time average number of all ions. The charge density \(\rho_j\) is given by equation (h), where the subscript \(j\) on \(\rho_j\) stresses that the charge is described with respect to the charge on the \(j\) ion [4].

\[
\rho_j = \sum p_i \cdot Z_i \cdot e \cdot \exp\left(-\frac{Z_i \cdot e \cdot \psi_j}{k \cdot T}\right) \quad (h)
\]

The subscript \(j\) on \(\rho_j\) and \(\psi_j\) identifies the impact of ion \(j\) on the composition and electric potential of the reference volume \(dV\) distance \(r\) from the \(j\) ion. At this point some simplification is welcomed. We expand the exponential in equation (h) [5].

Hence,

\[
\rho_j = \sum p_i \cdot Z_i \cdot e - \sum p_i \cdot Z_i \cdot e \cdot \left(\frac{Z_i \cdot e \cdot \psi_j}{k \cdot T}\right) + \sum p_i \cdot Z_i \cdot e \cdot (1/2) \cdot \left(\frac{Z_i \cdot e \cdot \psi_j}{k \cdot T}\right)^2 - \ldots \quad (i)
\]

The solution as a whole has zero electric charge.

Hence \(\sum p_i \cdot Z_i \cdot e = 0\) \quad (j)

Also for dilute solutions, \(\left(\frac{Z_i \cdot e \cdot \psi_j}{k \cdot T}\right) << 1\) \quad (k)

Hence the third and all subsequent terms in equation (i) are negligibly small.

Therefore \(\rho_j = -\sum p_i \cdot Z_i \cdot e^2 \cdot \psi_j \quad \frac{1}{k \cdot T}\) \quad (\ell)

The approximation leading to equation (\ell) is welcome for an important reason. Equation (\ell) satisfies a key condition which requires a linear interdependence between \(\rho_j\) and \(\psi_j\).

Equation (\ell) relates charge density \(\rho_j\) and electric potential \(\psi_j\). These two properties are also related by Poisson’s theorem [6]:

\[
\nabla^2 \psi_j = -\frac{\rho_j}{\varepsilon_0 \cdot \varepsilon_r} \quad (m)
\]
Here $\varepsilon_0$ is the permittivity of free space; $\varepsilon_r$ is the relative permittivity of the solvent [6]; $\rho_j$ is the charge density per unit volume.

In the case considered here, the electric charges (ions) are spherically distributed about the reference $j$ ion. Then Poisson’s equation takes the following form [7].

$$\left[ \frac{1}{r^2} \right] \frac{d}{dr} \left( r^2 \cdot \frac{d\psi_j}{dr} \right) = -\frac{\rho_j}{\varepsilon_0 \cdot \varepsilon_r} \quad (n)$$

Combination of equations (ℓ) and (n) yields the key equation (o).

$$\left[ \frac{1}{r^2} \right] \frac{d}{dr} \left( r^2 \cdot \frac{d\psi_j}{dr} \right) = \frac{e^2}{\varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T} \sum p_i \cdot z_i^2 \cdot \psi_j \quad (o)$$

Or,

$$\left[ \frac{1}{r^2} \right] \frac{d}{dr} \left( r^2 \cdot \frac{d\psi_j}{dr} \right) = \kappa^2 \cdot \psi_j \quad (p)$$

where [8] $\kappa^2 = \frac{e^2}{\varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T} \sum p_i \cdot z_i^2 \quad (q)$

Property $\kappa$ has the unit ‘reciprocal distance’. Equation (p) is a second order differential equation [9] having the general solution given by equation (p).

$$\psi_j = A_1 \cdot \exp(-\kappa \cdot r)/r + A_2 \cdot \exp(\kappa \cdot r)/r \quad (r)$$

However, $\lim_{r \to \infty} \exp(\kappa \cdot r)/r$ is very large where $\psi_j$ is zero. Hence $A_2$ must be zero.

Therefore [10], $\psi_j = A_1 \cdot \exp(-\kappa \cdot r)/r \quad (s)$

We combine equations (ℓ) and (s) [11].

$$\rho_j = -A_1 \cdot \exp(-\kappa \cdot r) \cdot \sum p_i \cdot (z_i \cdot e)^2 \cdot \frac{k \cdot T}{r} \quad (t)$$

Using the definition of $\kappa^2$ in equation (q) [12],

$$\rho_j = -A_1 \cdot \varepsilon_0 \cdot \varepsilon_r \cdot \kappa^2 \cdot \frac{\exp(-\kappa \cdot r)}{r} \quad (u)$$

At this point, a geometric condition is taken into account. Charge density $\rho_j$ describes the electrical properties of the solution ‘outside’ the $j$ ion. No other ions can approach the $j$ ion closer than a ‘distance of closest approach’ $a_j$. The total charge on the solution ‘outside’ the $j$ ion equals in magnitude but opposite in sign that on the $j$ ion. Hence,
\[
4 \cdot \pi \cdot \int_{a(j)}^{\infty} \rho_j \cdot r^2 \cdot dr = -z_j \cdot e \quad (v)
\]

Or,
\[
4 \cdot \pi \cdot \int_{a(j)}^{\infty} [-A_1 \cdot \varepsilon_0 \cdot \varepsilon_r \cdot \kappa^2 \cdot \frac{\exp(-\kappa \cdot r)}{r}] \cdot r^2 \cdot dr = -z_j \cdot e \quad (w)
\]

This integration yields an equation for \( A_1 \).
\[
A_1 = \frac{(z_j \cdot e) \cdot \exp(\kappa \cdot a_j)}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot (1 + \kappa \cdot a_j)} \quad (x)
\]

Hence
\[
\psi_j = \frac{(z_j \cdot e) \cdot \exp(\kappa \cdot a_j)}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot (1 + \kappa \cdot a_j)} \cdot \frac{\exp(-\kappa \cdot r)}{r} \quad (y)
\]

We recall that \( \psi_j \) is the electric potential at distance \( r \) from the \( j \) ion. In the event that the solution contains just the \( j \) ion (i.e. an isolated \( j \) ion) with charge \( z_j \cdot e \), the electric potential \( \psi(\text{iso}) \), distance \( r \) from the \( j \) ion, is given by equation (z) [13].
\[
\psi_j(\text{iso}) = \frac{z_j \cdot e}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot r} \quad (z)
\]

The electric potential \( \psi_j \) given by equation (y) is the sum of \( \psi(\text{iso}) \) and the electric potential produced by all other ions in solution \( \psi(\text{rest}) \).

Then
\[
\psi_j = \psi_j(\text{iso}) + \psi_j(\text{rest}) \quad (za)
\]

Hence,
\[
\psi_j(\text{rest}) = \frac{z_j \cdot e}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot r} \left[ \frac{\exp(\kappa \cdot a_j) \cdot \exp(-\kappa \cdot r)}{1 + \kappa \cdot a_j} - 1 \right] \quad (zb)
\]

Equation (zb) is valid for all values of \( r \), including for \( r = a_j \). Then from equation (zb), \( \psi_j(\text{rest}) \) at \( r = a_j \) is given by equation (zc).
\[
\psi_j(\text{rest}) = -\frac{z_j \cdot e}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r} \cdot \frac{\kappa}{1 + \kappa \cdot a_j} \quad (zc)
\]

We imagine that the \( j \) ion is isolated in solution and that the electrical interaction with all other \( i \) ions is then switched on at fixed \( T \) and \( p \). The change in chemical potential of single \( j \) ion is given by equation (zd),
\[
\Delta \mu_j(\text{elec}) = -\frac{z_j^2 \cdot e^2}{4 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r} \cdot \frac{\kappa}{1 + \kappa \cdot a_j} \quad (zd)
\]
For one mole of $j$ ions, $\Delta \mu_{j, \text{elec}}$ is given by equation (ze) where an additional factor of ‘2’ is introduced into the denominator. Otherwise each ion would be counted twice; i.e. once as the $j$ ion and once in solution around the $j$ ion \cite{14}.

$$\Delta \mu_{j, \text{elec; one mole}} = -\frac{z_j^2 \cdot e^2 \cdot N_A}{8 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r} \cdot \frac{\kappa}{1 + \kappa \cdot a_j} \quad (ze)$$

The chemical potential of single ion $j$ in an aqueous solution, $\mu_j(aq)$ is related to molality $m_j$ and single ion activity coefficient $\gamma_j$ using equation (zf).

$$\mu_j(aq) = \mu_j^0(aq) + R \cdot T \cdot \ln(m_j / m_j^0) + R \cdot T \cdot \ln(\gamma_j) \quad (zf)$$

Comparison of equations (ze) and (zf) yields equation (zg).

$$\ln(\gamma_j) = -\frac{z_j^2 \cdot e^2}{8 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T} \cdot \frac{\kappa}{1 + \kappa \cdot a_j} \quad (zg)$$

The mean ionic activity coefficient $\gamma_z$ for the salt in solution is given by equation (zh); i.e. for a simple salt where each mole of salt contains $\nu_+$ moles of cations and $\nu_-$ moles of anions.

$$\gamma_z = (\gamma_{z+}^{\nu_+} \cdot \gamma_{z-}^{\nu_-})^{1/\nu} \quad (zh)$$

Or, \( (\nu_+ + \nu_-) \cdot \ln(\gamma_z) = \nu_+ \cdot \ln(\gamma_+) + \nu_- \cdot \ln(\gamma_-) \) \quad (zi)

We envisage closest approaches only between differently charged ions. Then for a given salt, $a_+ = a_- = a_j$. Hence from equation (zg),

$$\ln(\gamma_z) = -\frac{e^2}{8 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T} \left(\frac{\kappa}{1 + \kappa \cdot a_j}\right) \left(\frac{\nu_+ \cdot z_+^2 + \nu_- \cdot z_-^2}{\nu_+ + \nu_-}\right) \quad (zj)$$

But the salt is overall electrically neutral.

$$\nu_+ \cdot z_+ = -\nu_- \cdot z_- \quad (zk)$$

Whence, \( \nu_+ = -\nu_- \cdot z_- / z_+ \) \quad (z\ell)

So \cite{15}, \( \frac{\nu_+ \cdot z_+^2 + \nu_- \cdot z_-^2}{\nu_+ + \nu_-} = -z_+ \cdot z_- \) \quad (zm)

Hence we arrive at an equation for the mean ionic activity coefficient, $\gamma_z$ \cite{16}.

$$\ln(\gamma_z) = -\frac{z_+ \cdot z_- \cdot e^2}{8 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T} \left(\frac{\kappa}{1 + \kappa \cdot a_j}\right) \quad (zn)$$
At this point we return to equation (q) and recall that \( p_i \) is the number of ions in unit volume of solution. If the concentration of \( i \) ions equals \( c_i \), (with \( N_A \) = the Avogadro constant),

then [17] \( p_i = N_A \cdot c_i \)  

\[ (zo) \]

Therefore [18],  

\[ \kappa^2 = \frac{e^2 \cdot (N_A)^2}{\varepsilon_0 \cdot \varepsilon_r \cdot R \cdot T} \cdot \sum c_i \cdot z_i^2 \]  

\[ (zp) \]

The convention is to express concentrations using the unit, mol dm\(^{-3}\) for which we use the symbol, \( c' \).

Hence \( \kappa^2 = \frac{e^2 \cdot (N_A)^2}{10^5 \cdot \varepsilon_0 \cdot \varepsilon_r \cdot R \cdot T} \cdot \sum c_i \cdot z_i^2 \)  

\[ (zq) \]

For dilute solutions, the following approximation is valid where

ionic strength \( I = (1/2) \cdot \sum m_i \cdot z_i^2 \)  

\[ (zr) \]

\[ \kappa^2 = \frac{2 \cdot e^2 \cdot (N_A)^2 \cdot \rho_1^* (\ell)}{\varepsilon_0 \cdot \varepsilon_r \cdot R \cdot T} \cdot I \]  

\[ (zs) \]

From equations (zn) and (zs) [19],

\[ \ln(\gamma_z) = \frac{Z_+ \cdot Z_- \cdot e^2}{8 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T} \cdot \left[ \frac{2 \cdot e^2 (N_A)^2 \cdot \rho_1^* (\ell)}{\varepsilon_0 \cdot \varepsilon_r \cdot R \cdot T} \right]^{1/2} \cdot \frac{(I)^{1/2}}{1 + \kappa \cdot a_j} \]  

\[ (zt) \]

For very dilute solutions, the Debye-Hückel Limiting Law (DHLL) is used where it is assumed that \( 1 + \kappa \cdot a_j = 1.0 \). Hence,

\[ \ln(\gamma_z) = \frac{e^3 \cdot [2 \cdot N_A \cdot \rho_1^* (\ell)]^{1/2}}{8 \cdot \pi \cdot [\varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T]^{1/2}} \cdot \left[ \frac{N_A}{\varepsilon_0 \cdot \varepsilon_r \cdot R \cdot T} \right]^{1/2} \cdot Z_+ \cdot Z_- \cdot (I)^{1/2} \]  

\[ (zu) \]

Equation (zu) may be written in the following form.

\[ \ln(\gamma_z) = \frac{e^3 \cdot [2 \cdot N_A \cdot \rho_1^* (\ell)]^{1/2}}{8 \cdot \pi \cdot [\varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T]^{1/2}} \cdot Z_+ \cdot Z_- \cdot (I)^{1/2} \]  

\[ (zv) \]

For aqueous solutions at ambient pressure and 298.15 K, \( \rho_1^* (\ell) = 997.047 \text{ kg m}^{-3} \) and \( \varepsilon_r = 78.36 \).

Hence [20] \( \ln(\gamma_z) = (1.1749) \cdot Z_+ \cdot Z_- \cdot (I/\text{mol kg}^{-1})^{1/2} \)  

\[ (zw) \]

We note that with \( Z_+ \cdot Z_- = -|Z_+ \cdot Z_-| \), \( \ln(\gamma_z) < 0 \).

In other words \( \ln(\gamma_z) \) is a linear function of the square root of the ionic strength I. Most authors choose to write equation (zx) using logarithms to base 10.

Then \( \log(\gamma_z) = |Z_+ \cdot Z_-| \cdot A_T \cdot (I/\text{mol kg}^{-1})^{1/2} \)  

\[ (zx) \]
Here[22] \( A_\gamma = 0.510 \). Certainly the latter constant is readily remembered as ‘one-half’. Slight disagreements between published estimates of \( A_\gamma \) are a result of different estimates of \( \varepsilon_\gamma \) and \( \rho_\gamma^{\epsilon}(\ell) \). Harned and Owen [1d] published a useful Table for \( A_\gamma \) as a function of temperature for aqueous solutions.

The full equation for \( \ln(\gamma_\pm) \) following on from equation (zt) takes the following form [22].

\[
\ln(\gamma_\pm) = \frac{-[z_+ \cdot z_-] \cdot S_{\gamma} \cdot (I/\text{mol kg}^{-1})^{1/2}}{1 + \beta \cdot a_j \cdot (I/\text{mol kg}^{-1})^{1/2}} \quad (zy)
\]

For aqueous solutions at ambient pressure and 298.15 K [5], \( S_\gamma = 1.175 \) and \( \beta = 3.285 \text{ nm}^{-1} \). Adam [23] suggests that \( a_j \) can be treated as a variable in fitting the measured dependence of \( \ln(\gamma_\pm) \) on ionic strength for a given salt.

Footnotes
[2] For accounts of the theory see--
(b) S. Glasstone, An Introduction to Electrochemistry, D Van Nostrand, New York, 1942, chapter III.
For comments on the role of water-water and water-ion interactions in aqueous salt solutions see H. S. Frank, Z. fur physik. Chemie, 1965, 228, 364.

[3] In equation (g), $dn_i$ describes the number of ions in volume $dV$; $p_i$ describes the number of ions in unit volume of solution. [In other words the units used to express $p_i$ and $dn_i$ differ.]

\[
\frac{z_i \cdot e \cdot \psi_j}{k \cdot T} = \frac{[1] \cdot [C] \cdot [V]}{[J K^{-1}] \cdot [K]} = \frac{[1] \cdot [A s] \cdot [J A^{-1} s^{-1}]}{[J K^{-1}] \cdot [K]} = [I]
\]

\[
p_i \cdot \exp \left( - \frac{z_i \cdot e \cdot \psi_j}{k \cdot T} \right) \cdot dV = \left[ \frac{1}{m^3} \right] \cdot [I] \cdot [m^3] = [I]
\]

\[
dn_i = [I] \quad \quad \text{[m}^3\text{]}
\]

\[
\frac{z_i \cdot e \cdot \psi}{k \cdot T} = \frac{[1] \cdot [C] \cdot [V]}{[J K^{-1}] \cdot [K]} = \frac{[A s] \cdot [J A^{-1} s^{-1}]}{[J]} = [I]
\]

Then $\rho_j = \left[ \frac{1}{m^3} \right] \cdot [I] \cdot [C] = \left[ \frac{C}{m^3} \right]$; i.e. charge per unit volume

\[
\exp(x) = 1 + \frac{x}{1!} + \frac{x^2}{2!} + \frac{x^3}{3!} + \ldots
\]

\[
\rho_j = \frac{[m^{-3}] \cdot [I]^2 \cdot [C] \cdot [V]}{[J K^{-1}] \cdot [K]} = \frac{[m^{-3}] \cdot [A s]^2 \cdot [J A^{-1} s^{-1}]}{[J]} = [C m^{-3}]
\]

i.e. charge per unit volume

\[
\nabla^2 \psi_j = \frac{1}{[m^3]} \cdot [V] = \left[ \frac{V}{m^2} \right]
\]

\[
\rho_j / \varepsilon_0 \cdot \epsilon_r = \frac{[C m^{-3}]}{[F m^{-3}] \cdot [I]} = \frac{[A s m^{-3}]}{[A s V^{-3} m^3]} = \left[ \frac{V}{m^2} \right]
\]

\[
\frac{1}{r^2} \cdot \frac{d}{dr} \left( r^2 \cdot \frac{d \psi_j}{dr} \right) = \frac{1}{[m^3]} \cdot \frac{1}{[m]} \cdot [m^3] = \frac{[J A^{-1} s^{-1}]}{[m^2]}
\]

\[
\rho / \varepsilon_0 \cdot \epsilon_r = \frac{[C m^{-3}]}{[F m^{-3}] \cdot [I]} = \frac{[A s m^{-3}]}{[A s V^{-3} m^3]} = \left[ \frac{V}{m^2} \right] = \frac{[J A^{-1} s^{-1}]}{m^2}
\]

[8]
\[ \kappa^2 = \frac{[C]^2}{[F \text{ m}^{-1}] \cdot [I] \cdot [J \text{ K}^{-1}] \cdot [K]} \left[ \frac{1}{\text{m}^3} \right] \cdot [I]^2 \]

\[ = \frac{[A s]^2}{[A s \text{ V}^{-1} \text{ m}^{-1}] \cdot [J]} \left[ \frac{1}{\text{m}^3} \right] = \frac{[A s]^2}{[A s J^{-1} \text{ A s}^{-1} \text{ m}^{-1}] \cdot [J]} \left[ \frac{1}{\text{m}^3} \right] = [\text{m}^{-2}] \]

\[ \kappa = [\text{m}^{-1}] \]

[9]

\[ \frac{d}{dr} \left( r^2 \cdot \frac{d\psi_j}{dr} \right) = 2 \cdot r \cdot \frac{d\psi_j}{dr} + r^2 \cdot \frac{d^2\psi_j}{dr^2} = \kappa^2 \cdot \psi_j \]

Then, \[ r^2 \cdot \frac{d^2\psi_j}{dr^2} + 2 \cdot r \cdot \frac{d\psi_j}{dr} - \kappa^2 \cdot \psi_j = 0 \]

[10] \[ \psi_j = [V] \]

and \[ \psi_j = A_i \cdot \exp((m)^{-1} \cdot [m]) / [m] \]

\[ A_i = [\text{V m}] \]

[11] \[ \rho_j = \left[ \frac{C}{\text{m}^3} \right] \]

[12]

\[ A_i \cdot \varepsilon_0 \cdot \varepsilon_r \cdot \kappa^2 \cdot \frac{\exp(-\kappa \cdot r)}{r} = [V \text{ m}] \cdot [F \text{ m}^{-1}] \cdot [I] \cdot [m]^{-2} \cdot \frac{[I]}{[m]} \]

\[ = [V \text{ m}] \cdot [A s \text{ V}^{-1} \text{ m}^{-1}] \cdot [I] \cdot [m]^{-2} \cdot \frac{[I]}{[m]} = [C] \left[ \frac{1}{\text{m}^2} \right] \]

[13] \[ \psi_j(\text{iso}) = \frac{[I] \cdot [C]}{[I] \cdot [F \text{ m}^{-1}] \cdot [I] \cdot [m]} = \frac{[A s]}{[A s \text{ V}^{-3}]} = [V] \]

[14]

\[ \Delta \mu_j (\text{elec; one mole}) = \frac{[I]^2 \cdot [C]^2 \cdot [\text{mol}]^{-1}}{[I] \cdot [F \text{ m}^{-1}] \cdot [I]} \left[ \frac{[m]^{-1}}{1 + [m]^{-1} \cdot [m]} \right] \]

\[ = \frac{[A s]^2 \cdot [\text{mol}]^{-1} \cdot [m]^{-1}}{[A s \text{ V}^{-1} \text{ m}^{-1}]} = \frac{[A s] \cdot [\text{mol}]^{1}}{[J \cdot A s]} = [J \text{ mol}^{-1}] \]

[15] \[ \frac{\nu_+ \cdot z_+^2 + \nu_- \cdot z_-^2}{\nu_+ + \nu_-} = -\left( \frac{\nu_- \cdot z_- \cdot z_+}{\nu_+ + \nu_-} \right) + \left( \frac{\nu_- \cdot z_-^2}{\nu_+ + \nu_-} \right) = -z_+ \cdot z_- \left( \frac{\nu_- - (\nu_- \cdot z_- / z_+)}{-(\nu_- \cdot z_- / z_+) + \nu_-} \right) \]

\[ = -z_+ \cdot z_- \]
\[ \ln(\gamma_z) = \frac{[1] \cdot [C]^2}{[1] \cdot [F \text{ m}^{-1}] \cdot [I] \cdot [J K^{-1}] \cdot [K]} \cdot \left[ \frac{[m]^{-1}}{1 + [m]^{-1} \cdot [m]} \right] \]

\[ = \frac{[A \text{ s}]^2}{[A \text{ s V}^{-1}] \cdot [J] \cdot [J^{-1} A \text{ s}] \cdot [J]} = [I] \]

\[ N_A \cdot c_i = [\text{mol}^{-1}] \cdot [\text{mol m}^{-3}] = [m^{-3}] \]

\[ \kappa^2 = \frac{[C]^2 \cdot [\text{mol}^{-1}]^2}{[F \text{ m}^{-1}] \cdot [1] \cdot [J \text{ mol}^{-1} K^{-1}] \cdot [K]} \]

\[ = \frac{[A \text{ s}]^2 \cdot [m]^{-2}}{[A \text{ s V}^{-1}] \cdot [J] \cdot [J^{-1} A \text{ s}] \cdot [J]} = [m^{-2}] \]

\[ \frac{z_e \cdot z_- \cdot e^2}{8 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T} = \frac{[1] \cdot [C]^2}{[1] \cdot [1] \cdot [F \text{ m}^{-1}] \cdot [J K^{-1}] \cdot [K]} \]

\[ = \frac{[A \text{ s}^2 \text{ m}^{-3}]}{[A \text{ s } J^{-1} A \text{ s m}^{-1}] \cdot [J]} = [m] \]

\[ = \left[ \frac{2 \cdot e^2 \cdot (N_A)^2 \cdot \rho_1^*(\ell)}{\varepsilon_0 \cdot \varepsilon_r \cdot R \cdot T} \right]^{1/2} = \left[ \frac{[1] \cdot [C]^2 \cdot [\text{mol}^{-1}]^2 \cdot [\text{kg m}^{-3}]}{[F \text{ m}^{-1}] \cdot [1] \cdot [J \text{ mol}^{-1} K^{-1}] \cdot [K]} \right]^{1/2} \]

\[ = \left[ \frac{[A \text{ s}^2 \text{ m}^{-3}]}{[A \text{ s } J^{-1} A \text{ s m}^{-1}] \cdot [J \text{ mol}^{-1}]} \right]^{1/2} = [\text{mol}^{-1}] \cdot [\text{kg}] \cdot [m^{-2}]^{1/2} \]

\[ = \frac{[m]}{[\text{mol kg}^{-1}]}^{1/2} = [m^{-1}] \cdot [m] = [I] \]

\[ \kappa \cdot a_j = [m^{-1}] \cdot [m] = [I] \]

\[ \frac{z_e \cdot z_- \cdot e^2}{8 \cdot \pi \cdot \varepsilon_0 \cdot \varepsilon_r \cdot k \cdot T} \left[ \frac{2 \cdot e^2 \cdot (N_A)^2 \cdot \rho_1^*(\ell)}{\varepsilon_0 \cdot \varepsilon_r \cdot R \cdot T} \right]^{1/2} \cdot \frac{(I)^{1/2}}{1 + \kappa \cdot a_j} \]

\[ = [m] \cdot \frac{[m^{-1}]}{[\text{mol kg}^{-1}]}^{1/2} = [I] \]

As required \( \ln(\gamma_z) = [I] \)


[22] Using

(a) $p^*_1(H_2O; \ell; 2981.5K) = 997.0474$;

(b) $\varepsilon_1(H_2O; \ell; 2981.5K) = 78.36 \pm 0.05$

(c) CODATA 1986 fundamental constants