

A DEEPER LOOK 1 The Debye–Hückel theory

The strategy for the development of the Debye–Hückel theory of electrolyte solutions is to establish the relation between the work needed to charge an ion and its chemical potential. Then that work is related to the ion's interaction with the atmosphere of counter ions that has assembled around it as a result of the competition of the attraction between oppositely charged ions, the repulsion of like-charged ions, and the distributing effect of thermal motion.

Step 1 Calculate the work of charging an ion

Imagine a solution in which all the ions have their actual positions, but in which their Coulombic interactions have been turned off and so are behaving 'ideally'. The difference in molar Gibbs energy between the ideal and real solutions is equal to w_e , the electrical work of charging the system in this arrangement. For a salt M_pX_q ,

$$w_e = \overbrace{(p\mu_+ + q\mu_-)}^{G_m, \text{ charged}} - \overbrace{(p\mu_+^{\text{ideal}} + q\mu_-^{\text{ideal}})}^{G_m^{\text{ideal}}, \text{ uncharged}} \quad (1)$$

$$= p(\mu_+ - \mu_+^{\text{ideal}}) + q(\mu_- - \mu_-^{\text{ideal}})$$

From eqn 5F.26 ($\mu_i = \mu_i^{\text{ideal}} + RT \ln \gamma_{\pm}$) the terms in parentheses are written as

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

so it follows that

$$w_e = p \overbrace{RT \ln \gamma_{\pm}}^{\mu_+ - \mu_+^{\text{ideal}}} + q \overbrace{RT \ln \gamma_{\pm}}^{\mu_- - \mu_-^{\text{ideal}}} = (p+q)RT \ln \gamma_{\pm}$$

and therefore

$$\ln \gamma_{\pm} = \frac{w_e}{sRT} \quad s = p+q \quad (2)$$

This equation implies that the final distribution of the ions and then the work of charging them in that distribution must be found.

Step 2 Calculate the Coulomb potential experienced by an ion

The Coulomb potential at a distance r from an isolated ion of charge $z_i e$ in a medium of permittivity ϵ is

$$\phi_i = \frac{Z_i}{r} \quad Z_i = \frac{z_i e}{4\pi\epsilon} \quad (3a)$$

However, the ionic atmosphere causes the potential to decay with distance more sharply than this expression implies. Such shielding is a familiar problem in electrostatics, and its effect is taken into account by replacing the

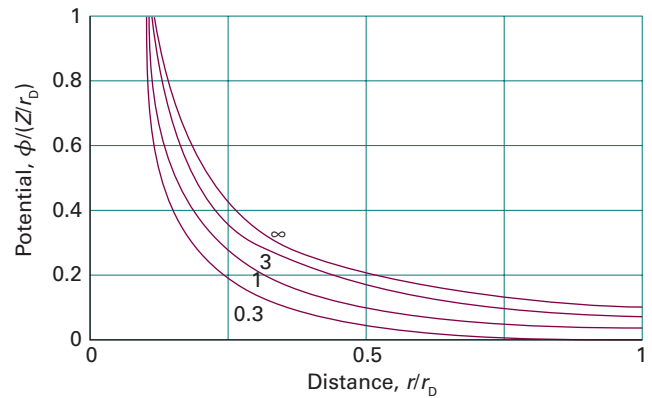


Figure 1 The variation of the shielded Coulomb potential with distance for different values of the Debye length, r_D/a . The smaller the Debye length, the more sharply the potential decays to zero. In each case, a is an arbitrary unit of length.

Coulomb potential by the **shielded Coulomb potential**, an expression of the form

$$\phi_i = \frac{Z_i}{r} e^{-r/r_D} \quad \text{Shielded Coulomb potential} \quad (3b)$$

where r_D is called the **Debye length**. When r_D is large, the shielded potential is virtually the same as the unshielded potential. When r_D is small, the shielded potential is much smaller than the unshielded potential, even for short distances (Fig. 1).

To calculate r_D , it is necessary to know how the **charge density**, ρ , of the ionic atmosphere, the charge in a small region divided by the volume of the region, varies with distance from the ion. This step draws on another standard result of electrostatics, in which charge density and potential are related by **Poisson's equation**:

$$\nabla^2 \phi = -\frac{\rho}{\epsilon} \quad \text{Poisson's equation} \quad (4a)$$

where $\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2$. Because the ionic atmosphere is spherically symmetric the charge density varies only with distance from the central ion and eqn 4a becomes

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{d\phi_i}{dr} \right) = -\frac{\rho_i}{\epsilon} \quad (4b)$$

Substitution of the expression for the shielded potential (eqn 3b) results in

$$r_D^2 = -\frac{\epsilon \phi_i}{\rho_i} \quad (5)$$

Step 3 Calculate the Debye length

To solve eqn 5 for r_D , ρ_i must be related to ϕ_i . For this step, note that the energy of an ion depends on its closeness to the central ion, and then use the Boltzmann distribution

to evaluate the probability that an ion will be found at each distance.

The energy of an ion j of charge $z_j e$ at a distance where it experiences the potential ϕ_i of the central ion i relative to its energy when it is far away in the bulk solution is its charge $z_j e$ times the potential ϕ_i . Therefore, according to the Boltzmann distribution, the ratio of the molar concentration, c_j , of ions at a distance r where their electrostatic energy is $z_j e \phi_i$ and the molar concentration in the bulk, c_j° , where their electrostatic energy is zero, is

$$\frac{c_j}{c_j^\circ} = e^{-z_j e \phi_i / kT} \quad (6)$$

The charge density, ρ_i , at a distance r from the ion i is the molar concentration of each type of ion multiplied by the charge per mole of ions, $z_i e N_A = z_i F$ (F is Faraday's constant, $F = e N_A$). It follows that

$$\rho_i = c_{+z_+} F + c_{-z_-} F = c_{+z_+}^\circ F e^{-z_+ e \phi_i / kT} + c_{-z_-}^\circ F e^{-z_- e \phi_i / kT} \quad (7)$$

Because the average electrostatic interaction energy is small compared with kT it is permissible to use $e^x = 1 + x + \dots$ and to write the charge density as

$$\begin{aligned} \rho_i &= c_{+z_+}^\circ F \left(1 - \frac{z_+ e \phi_i}{kT} + \dots \right) + c_{-z_-}^\circ F \left(1 - \frac{z_- e \phi_i}{kT} + \dots \right) \\ &= \overbrace{(c_{+z_+}^\circ + c_{-z_-}^\circ)}^0 F - (c_{+z_+}^\circ z_+ + c_{-z_-}^\circ z_-) \frac{F e \phi_i}{kT} + \dots \end{aligned}$$

The term in blue is zero because it is the charge density in the bulk, uniform solution, and the solution is electrically neutral. The replacement of e by F/N_A and $N_A k$ by R results in the following expression:

$$\rho_i = -(c_{+z_+}^\circ z_+ + c_{-z_-}^\circ z_-) \frac{F^2 \phi_i}{RT} \quad (8)$$

The higher-order unwritten terms are assumed to be too small to be significant. This equation can be expressed in terms of the ionic strength by noting that in the dilute aqueous solutions being considered $c \approx b\rho$, where ρ is the mass density of the solvent. Therefore

$$c_{+z_+}^\circ z_+^2 + c_{-z_-}^\circ z_-^2 \approx \overbrace{(b_{+z_+}^\circ z_+^2 + b_{-z_-}^\circ z_-^2)}^{2Ib^\circ} \rho = 2Ib^\circ \rho$$

With these approximations, eqn 8 becomes

$$\rho_i = -\frac{2Ib^\circ \rho F^2 \phi_i}{RT} \quad (9)$$

When this expression is substituted into $r_D^2 = -\epsilon \phi_i / \rho_i$, the ϕ_i cancel and the result is

$$r_D = \left(\frac{\epsilon RT}{2\rho F^2 I b^\circ} \right)^{1/2} \quad \text{Debye length} \quad (10)$$

Step 4 Calculate the work of charging the ion in the presence of the ionic atmosphere

To calculate the work of charging the central ion it is necessary to know the potential at the ion due to its atmosphere, ϕ_{atmos} . This potential is the difference between the total potential, given by eqn 3b, and the potential due to the central ion itself:

$$\phi_{\text{atmosphere}} = \phi - \phi_{\text{central ion}} = Z_i \left(\frac{e^{-r/r_D}}{r} - \frac{1}{r} \right) \quad (11a)$$

The potential at the central ion (at $r=0$) is obtained by taking the limit of this expression as $r \rightarrow 0$ and is

$$\phi_{\text{atmosphere}}(0) = Z_i \lim_{r \rightarrow 0} \left(\frac{1-r/r_D + \dots}{r} - \frac{1}{r} \right) = -\frac{Z_i}{r_D} \quad (11b)$$

This expression shows that the potential due to the ionic atmosphere is equivalent to the potential arising from a single charge of equal magnitude but opposite sign to that of the central ion and located at a distance r_D from the ion. Therefore, if the charge of the central ion were Q and not $z_i e$, then the potential due to its atmosphere would be

$$\phi_{\text{atmosphere}}(0) = -\frac{Q}{4\pi\epsilon r_D} \quad (11c)$$

The work of adding a charge dQ to a region where the electrical potential is $\phi_{\text{atmosphere}}(0)$ (from $dw = \phi dQ$), is

$$dw_e = \phi_{\text{atmosphere}}(0) dQ \quad (12)$$

It follows that the total molar work of fully charging the ion i in the presence of its atmosphere is

$$\begin{aligned} w_{e,i} &= N_A \int_0^{z_i e} \phi_{\text{atmosphere}}(0) dQ = -\frac{N_A}{4\pi\epsilon r_D} \int_0^{z_i e} Q dQ \\ &= -\frac{N_A z_i^2 e^2}{8\pi\epsilon r_D} = -\frac{z_i^2 F^2}{8\pi N_A \epsilon r_D} \quad (13) \end{aligned}$$

Step 5 Evaluate the activity coefficient

The total work of charging p cations and q anions in the presence of their atmospheres is $w_e = pw_{e,+} + qw_{e,-}$, and therefore the mean activity coefficient of the ions is

$$\ln \gamma_{\pm} = \frac{pw_{e,+} + qw_{e,-}}{sRT} = -\frac{(pz_+^2 + qz_-^2)F^2}{8\pi N_A sRT \epsilon r_D} \quad (14a)$$

However, for neutrality $pz_+ + qz_- = 0$; therefore

$$pz_+^2 + qz_-^2 = \overbrace{pz_+}^{-qz_-} z_+ + \overbrace{qz_-}^{-pz_+} z_- = -(p+q)z_+ z_- = s|z_+ z_-|$$

It then follows that

$$\ln \gamma_{\pm} = -\frac{|z_+ z_-| F^2}{8\pi N_A RT \epsilon r_D} \quad (14b)$$

The replacement of r_D with the expression in eqn 10 gives

$$\begin{aligned} \ln \gamma_{\pm} &= -\frac{|z_+ z_-| F^2}{8\pi N_A RT \epsilon} \left(\frac{2\rho F^2 I b^{\ominus}}{\epsilon RT} \right)^{1/2} \\ &= -|z_+ z_-| \left\{ \frac{F^3}{4\pi N_A} \left(\frac{\rho b^{\ominus}}{2\epsilon^3 R^3 T^3} \right)^{1/2} \right\} I^{1/2} \end{aligned} \quad (15)$$

where terms have been grouped to show that this expression is beginning to take the form of the limiting law

($\log \gamma_{\pm} = -|z_+ z_-| A I^{1/2}$). Indeed, conversion to common logarithms (by using $\ln x = \ln 10 \times \log x$) gives

$$\log \gamma_{\pm} = -|z_+ z_-| \overbrace{\left\{ \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^{\ominus}}{2\epsilon^3 R^3 T^3} \right)^{1/2} \right\}}^A I^{1/2} \quad (16a)$$

which is the Debye-Hückel limiting law (eqn 5F.27) with

$$A = \frac{F^3}{4\pi N_A \ln 10} \left(\frac{\rho b^{\ominus}}{2\epsilon^3 R^3 T^3} \right)^{1/2} \quad (16b)$$