CHAPTER 4

Electrochemistry – I: Ion-Ion Interactions

❖ The Debye-Huckel Theory of Ion-Ion Interactions

When an ion goes into the solution, it interacts not only with the solvent molecules but also with other ions that are produced as a result of electrolytic dissociation. The interaction of this ion with its solvent-surrounding is quite important as it helps the ion to get stabilized in that medium. Nevertheless, the other types of interactions, i.e., the ion-ion interactions, are also of very much significant value to the overall understanding of the system because these interactions affect a number of properties of these solutions such as partial molar free energy change or the electrolytic conductance. Now, since the phenomenon of ion-ion interactions is a function of interionic separations, which in turn depends upon the population density of these ions; the first step to know this phenomenon must be the rationalization of ionic population density.

In the case of weak electrolytes, the degree of dissociation is very small at high concentrations yielding a very low population density of charge carriers. This would result in almost zero ion-ion interactions at high concentrations. Now, although the degree of dissociation increases with dilution, which in turn also increases the total number of charge carriers, the population density remains almost unchanged since the extra water has also been added for these extra ions. Thus, we can conclude that there are no ion-ion interactions in weak electrolytes, neither at higher nor at the lower concentrations. On the other hand, in the case of strong electrolytes, the degree of dissociation is a hundred percent even at high concentrations yielding a very high population density of charge carriers. This would result in very strong ion-ion interactions at high concentrations. Now, when more and more solvent is added, the total number of charge carriers remains the same but the population density decreases continuously, creating large interionic separations. This would result in a decrease in the magnitude of ion-ion interaction with increasing dilution.

In 1913, a British physicist Samuel Milner proposed the first quantitative explanation of ion-ion interactions in a statistical framework. After that, in 1918, an Indian Chemist, Sir Jnan Chandra Ghosh proposed a model to compute the energy of Coulombic interaction of the ions with an assumption that the ions in the solution are fixed just like in the crystals. The Milner's model was quite complicated mathematically, while Ghosh's model did not consider the distorting effect of thermal motion on the ionic distribution in the solution phase of electrolyte under consideration.

In 1923, Peter Debye and Erich Huckel proposed an extremely important idea to quantify the ion-ion interactions in the solutions of strong electrolytes. In this model, the solute, i.e., the strong electrolyte, is assumed to dissociate completely. They considered the ions as perfect spheres that cannot be polarized by the surrounding electric field while the solvation of ions was ignored. The solvent plays no role other than providing a medium of the constant relative permittivity (dielectric constant). A reference ion was thought to be suspended in solvent-continuum of dielectric constant ε with zero electrostriction, and this ion is surrounded by oppositely charged ionic cloud.

➢ *Fundamental Concept*

It is quite interesting to recall the fact that like many other coupling effects, the phenomena of ion-ion interaction can also be quantified in terms of free energy change. In this case, it can be achieved by assuming an initial state with no ion-ion interaction and a final state in which the ion-ion interactions do exist; and then calculating the free energy change in going from initial to the final state.

The initial state, i.e., the state with no ion-ion interaction, can be created hypothetically by taking ions in the vacuum. However, since the final state possesses ions in solution, the initial state should also have ions in solution and not in the vacuum, otherwise, two states would differ not only by ion-ion interaction but also in respect of ion-solvent interaction. Conversely, if we imagine some discharged ions in the solution (discharged ions mean no ion-ion interaction) and then charge them up fully, free energy change of ion-ion interaction would be the amount of work done in doing so.

Figure 1. The pictorial representation of the fundamental idea for calculating the free energy of ion-ion in the Debye-Huckel model of ionic interactions.

It should also be noted that the procedure depicted in 'Figure 1' gives the work of charging (i.e., the free energy of ion-ion interaction) for all the ions present in the solution whether they are positive or negative. However, the scientific analysis of electrolytic solutions typically needs the free energy of ionic interactions for individual species. This partial free energy change is called as chemical potential change and is typically denoted as $\Delta\mu_{i-I}$. The value of $\Delta\mu_{i-I}$ for *i*th species of radius r_i can be obtained by computing the work of charging this sphere from a neutral state to its full charge of Z_ie_0. The work of charging (w) a spherical conductor can be given by the following relation (from electrostatics):

$$w = \frac{1}{2}[Charge\ on\ the\ conductor \times Electrostatic\ Potential\ of\ conductor] \tag{1}$$

Since the Debye-Huckel model also considers the ions as spherical conductors, the work of charging an ion of radius r will be

$$w = \frac{1}{2}[Z_i e_0 \times \psi] \tag{2}$$

Where ψ represents the electrostatic potential of the reference ion due to the influence on it by the Coulombic forces of the neighboring ions. Multiplying equation (2) by Avogadro number, we can obtain the amount of work done required to charge one mole of such ions i.e. the partial molar free energy change.

$$\Delta\mu_{i-I} = N_A w = \frac{N_A}{2}[Z_i e_0 \times \psi] \tag{3}$$

The only thing that is unknown in the above expression is ψ. Therefore, the partial molar free energy change due to the interaction of ith species with the rest of the solution requires the determination of electrostatic potential exerted at the reference ion by its ionic-surrounding. Now, from the law of superposition of potentials, we know that the potential at any point due to an assembly of charges is just the sum of the individual potentials exerted at that point by the individual charges. Since the electrostatic potentials depend upon the distances between the charges under consideration, the time-averaged distribution of all ions around must be known (distances from the reference ion are the function of the population distribution of other ions).

Although we know that the total electrostatic potential at the reference ion can be obtained by knowing the distance of each surrounding ion from the reference ion, the number of ions is extremely large making it almost impossible to follow the conventional route to do so. So, instead of dealing with individual ions, Debye and Huckel proposed the revolutionary idea of considering all the surrounding ions as a continuous ionic cloud that surrounds the reference ions. They assigned the discrete charge only to the reference ion which is situated in the solvent's continuum of dielectric constant ε, i.e., water in this case.

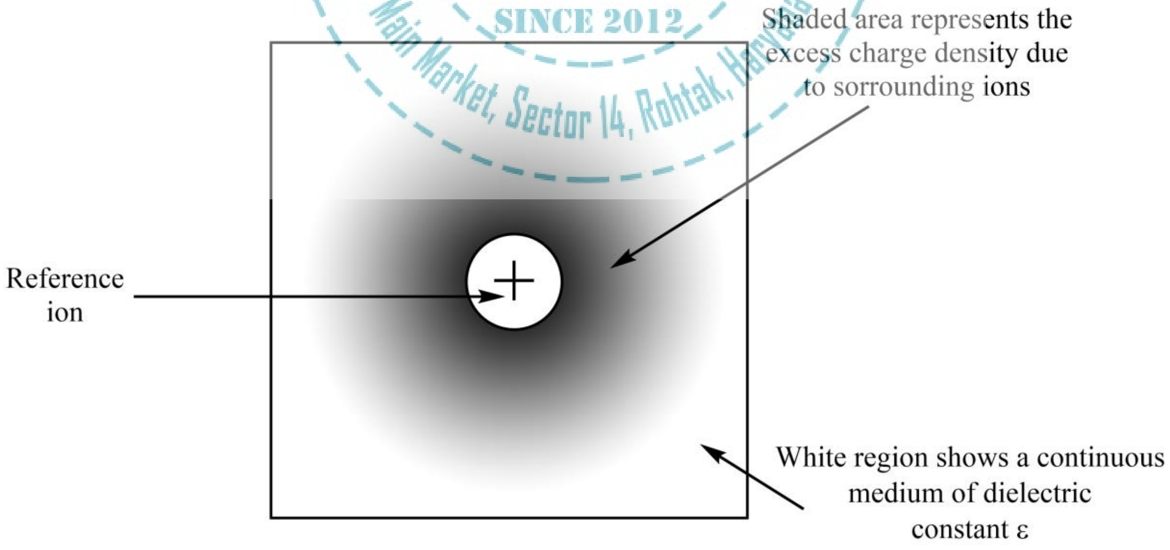


Figure 2. The pictorial representation of reference ion in its ionic cloud.

Hence, the Debye-Huckel's idea transformed the complex problem of computing the population density around the reference to the determination of excess charge density (ρ). At this point, one might think why the excess charge density is not zero everywhere because the solution as a whole is actually electroneutral. The reason for this behavior lies in the fact that positive centers attract negative density while a negative center tries to accumulate a positive cloud around it. Therefore, in a volume element near positive ion, there should be a more negative charge, i.e., excess negative charge density and vice-versa. This excess negative charge density near a positive center is counterbalanced by excess positive charge density near a negative center, keeping the overall electroneutrality maintained. It should also be mentioned here that since the thermal forces in the solution are always trying to randomize the ionic distribution, the excess charge density diminishes in moving away from the center.

- ***Mathematical Development***

So far we have discussed the fundamentals aspects of how we can determine the partial molar free energy change generated by the ionic interactions of *i*th species. All we need is the electrostatic potential (ψ) of the reference ion due to the influence on it by the Coulombic forces of the surrounding. Since ψ, at a distance r from the reference ion, depends upon the excess charge density at r, the first thing we need to develop it mathematically is the correlation between these two parameters, i.e., ψ_r and ρ_r. One such relation for spherically symmetric charge distribution is the Poisson's equation in electrostatics that can be given as:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)=-\frac{4\pi}{\varepsilon}\rho_r \tag{4}$$

Where ψ_r and ρ_r are electrostatic potential and excess charge density in a very small volume element dV situated at distance r from the reference ion.

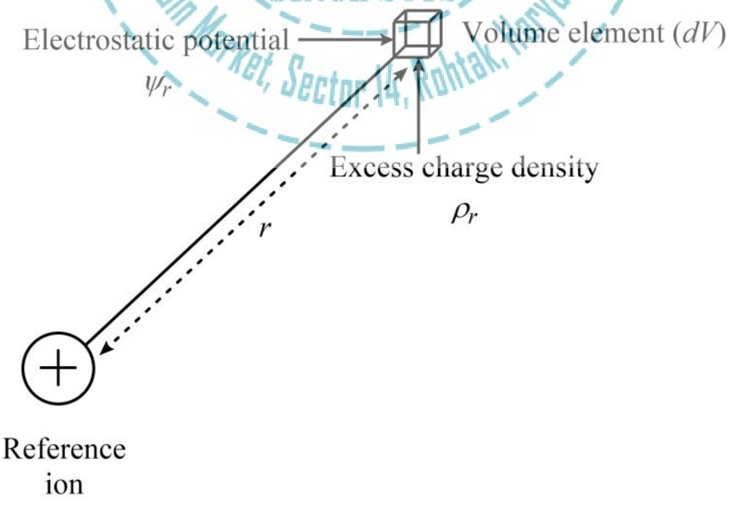


Figure 3. The depiction of electrostatic potential and excess charge density in dV volume element at a distance r from the reference ion.

Rearranging the Poisson’s equation for excess charge density, we get

$$\rho_r = -\frac{\varepsilon}{4\pi}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)\right] \tag{5}$$

Also, the “linearized Boltzmann distribution” can be used to prove that

$$\rho_r = -\sum_i \frac{n_i^0 Z_i^2 e_0^2 \psi_r}{kT} \tag{6}$$

Where n_i^0 is the bulk concentration of the ith species and k is simply the Boltzmann constant. Equating the Poisson’s expression with the Boltzmann Formula, i.e., from equation (5) and (6), we get the linearized Poisson Boltzmann equation as:

$$-\frac{\varepsilon}{4\pi}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)\right] = -\sum_i \frac{n_i^0 Z_i^2 e_0^2 \psi_r}{kT} \tag{7}$$

or

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = \left(\frac{4\pi}{\varepsilon kT}\sum_i n_i^0 Z_i^2 e_0^2\right)\psi_r \tag{8}$$

Now assume a constant κ^2 with value

$$\kappa^2 = \frac{4\pi}{\varepsilon kT}\sum_i n_i^0 Z_i^2 e_0^2 \tag{9}$$

Using the value of equation (9) in equation (8), we get

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = \kappa^2\psi_r \tag{10}$$

The above differential equation is the popular form of linearized Poisson-Boltzmann expression and its solution gives

$$\psi_r = \frac{Z_i e_0}{\varepsilon}\frac{e^{-\kappa r}}{r} \tag{11}$$

Now comparing equation (4) and equation (10), we get

$$\kappa^2\psi_r = -\frac{4\pi}{\varepsilon}\rho_r \tag{12}$$

or

$$\rho_r = -\frac{\varepsilon\kappa^2\psi_r}{4\pi} \tag{13}$$

Now putting the value of electrostatic potential from equation (11) in equation (13), we get the expression for excess charge density as a function of *r*.

$$\rho_r = -\frac{\varepsilon\kappa^2}{4\pi} \times \frac{Z_i e_0}{\varepsilon} \frac{e^{-\kappa r}}{r} \tag{14}$$

$$\rho_r = -\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r} \tag{15}$$

Now because the magnitude of ρ_r is a consequence of the unequal distribution of anions and cations, the above expression also defines the ionic-population-distribution around the reference ion.

Figure 4. The variation of electrostatic potential and excess charge density as a function of the distance *r* from the reference ion.

After knowing that the excess charge density decreases exponentially with *r*, we can determine the total excess charge (*dq*) at the same distance just by the following relation.

$$dq = \rho_r 4\pi r^2 dr \tag{16}$$

Where $4\pi r^2 dr$ is the volume element of a hollow spherical shell of thickness *dr* with the inner and outer radius as *r* and *r*+*dr*, respectively. After putting the value of ρ_r from equation (15) in equation (16), we have

$$dq = \left(-\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r}\right) 4\pi r^2 dr \tag{17}$$

or

$$dq = -Z_i e_0 e^{-\kappa r} \kappa^2 r dr \tag{18}$$

Thus, the exponential part decreases with increasing *r* while the non-exponential part shows a continuous increase as we move away from the reference ion.

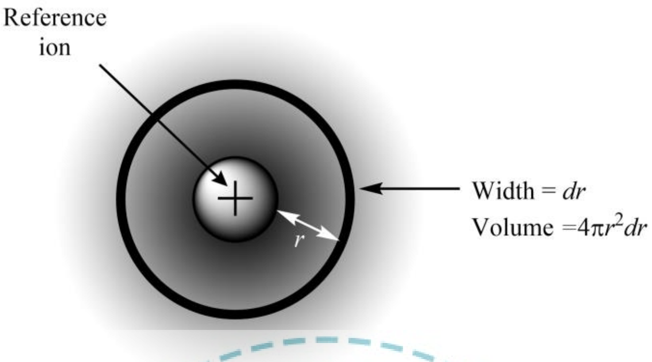


Figure 5. The depiction of excess charge density in a volume element of thickness '*dr*' as a function of the distance *r* from the reference ion.

In order to find the distance of maximum "excess charge", we need to differentiate the equation (18) with respect to *r*, and then derivative needs to be put equal to zero i.e.

$$\frac{dq}{dr} = -Z_i e_0 \kappa^2 (e^{-\kappa r} - \kappa r e^{-\kappa r}) = 0 \tag{19}$$

Since $-Z_i e_0 \kappa^2$ is non zero for sure, the above equation holds true only if

$$e^{-\kappa r} - \kappa r e^{-\kappa r} = 0 \tag{20}$$

Which implies

$$r = \kappa^{-1} \tag{21}$$

Also from equation (9), we have

$$\kappa = \left(\frac{4\pi}{\varepsilon kT} \sum_i n_i^0 Z_i^2 e_0^2\right)^{1/2} \tag{22}$$

Hence, the radius of maximum excess charge from the center of the reference ion can be obtained by putting the value of *κ* from equation (22) in equation (21), we get r_{max} or the "Debye-Huckel length" as

$$r_{max} = \left(\frac{\varepsilon kT}{4\pi} \frac{1}{\sum_i n_i^0 Z_i^2 e_0^2}\right)^{1/2} \tag{23}$$

At this point, we have understood most of the ideas of Debye-Huckel's theory of ion-ion interaction, and the question we raised initially is near to its end, i.e., to calculate the molar chemical potential change of ion-ion interaction. Now, although we have calculated the electrostatic potential, we cannot use the same in equation (3) because what we have obtained contains the contributions from the ionic cloud as well as from the reference ion itself. Therefore, before we calculate the partial molar free energy of ion-ion interaction, we need to separate potential from the ionic cloud and from the central ion first. The total electrostatic potential at a distance *r* can be fragmented as given below.

$$\psi_r = \psi_{ion} + \psi_{cloud} \tag{24}$$

$$\psi_{cloud} = \psi_r - \psi_{ion} \tag{25}$$

From the formulation of potential due to a single charge at a distance *r*, we know that

$$\psi_{ion} = \frac{Z_i e_0}{\varepsilon r} \tag{26}$$

Now using the value of ψ_r from equation (11) and of ψ_{ion} from equation (26) into equation (25), we get

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon}\frac{e^{-\kappa r}}{r} - \frac{Z_i e_0}{\varepsilon r} \tag{27}$$

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon r}(e^{-\kappa r} - 1) \tag{28}$$

Now because the value of κ is proportional to $\sum_i n_i^0 Z_i^2 e_0^2$, at very large dilution κ becomes very small and $e^{-\kappa r}$ and can be expended as $1 - \kappa r$ ($e^x = 1 + x$). Therefore, equation (28) takes the form

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon r}(1 - \kappa r - 1) \tag{29}$$

$$\psi_{cloud} = -\frac{Z_i e_0 \kappa}{\varepsilon} \tag{30}$$

Hence, potential due to ionic cloud is independent of the distance *r* in this case. Now putting the value of ψ_{cloud} from equation (30) into equation (3), we get

$$\Delta\mu_{i-I} = N_A w = \frac{N_A}{2}\left[Z_i e_0 \times \left(-\frac{Z_i e_0 \kappa}{\varepsilon}\right)\right] \tag{31}$$

$$\Delta\mu_{i-I} = -\frac{N_A Z_i^2 e_0^2 \kappa}{2\varepsilon} \tag{32}$$

Hence, the Debye-Huckel's model gives the theoretical value of $\Delta\mu_{i-I}$ arising from ion-ion interactions. Now before we check the validity of the Debye-Huckel model, we will discuss the many aspects of mathematical treatment Debye-Huckel model in more detail in forthcoming sections.

❖ Potential and Excess Charge Density as a Function of Distance from the Central Ion

In order to determine the potential and excess charge density as a function of radial distance *r*, consider a very small volume element *dV*, situated at distance *r* from the reference ion, in which ψ_r and ρ_r are electrostatic potential and excess charge density, respectively.

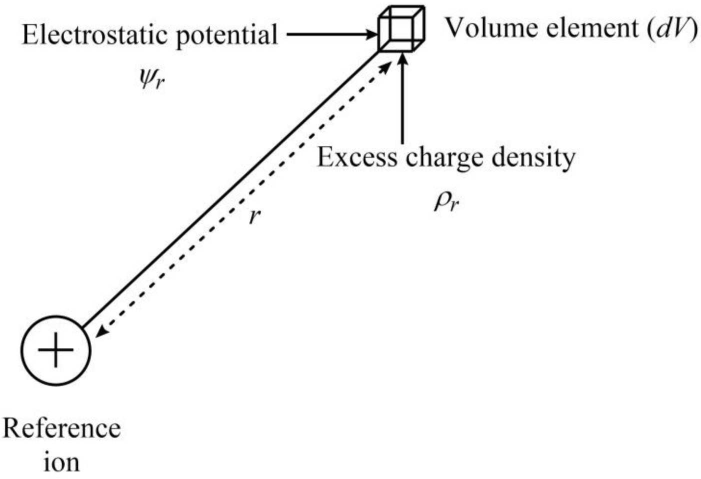


Figure 6. The depiction of electrostatic potential and excess charge density in *dV* volume element at distance *r* from the reference ion.

Since we want to study how electrostatic potential and excess charge density depend upon the distance from the reference ion, the first thing we need to develop it mathematically is a correlation of these two parameters i.e. ψ_r and ρ_r. One such relation for spherically symmetric charge distribution is the Poisson's equation in electrostatics which can be given as:

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = -\frac{4\pi}{\varepsilon}\rho_r \tag{33}$$

Now the excess charge density in the volume element *dV* can be obtained by multiplying the total number of ions per unit volume with their corresponding charges i.e.

$$\rho_r = n_1Z_1e_0 + n_2Z_2e_0 + n_3Z_3e_0 \ldots\ldots n_iZ_ie_0 \tag{34}$$

or

$$\rho_r = \sum n_iZ_ie_0 \tag{35}$$

Where n_1 is the number of first kind ions with Z_1e_0 charge, n_2 is the number of second kind ions with Z_2e_0 charge and so on up to *i*th type.

Now, from the Boltzmann distribution law of classical statistical mechanics, we know that

$$n_i = n_i^0 e^{-U/kT} \tag{36}$$

Where U represents the total change in the potential energy of the ith particle in going from the bulk concentration n_i^0 to the actual concentration of the ith particle i.e. n_i. At this stage, three cases arise, the magnitude of U can be zero, positive or negative. If $U = 0$ i.e. there are no ion-ion interaction, $n_i = n_i^0$, which implies that concentration near the reference ion will be equal to the bulk concentration. If $U = -$, i.e., there are attractive ion-ion interaction, $n_i > n_i^0$, which implies that concentration near the reference ion will be higher to the bulk concentration. In the third scenario, if $U = +$, i.e., there are repulsive ion-ion interaction, $n_i < n_i^0$, which implies that concentration near the reference ion will be less to the bulk concentration. Now according to the Debye-Huckel model, only simple Coulombic forces need to be considered for very dilute solutions. Therefore, excluding all other short-range interactions like dispersion ones, the potential of average force U simply can be written as given below.

$$U = Z_i e_0 \psi_r \tag{37}$$

After using the value of U from equation (37) in equation (36), we get

$$n_i = n_i^0 e^{-Z_i e_0 \psi_r/kT} \tag{38}$$

Putting the value of n_i from equation (38) in equation (35), we have

$$\rho_r = \sum n_i^0 Z_i e_0 \, e^{-Z_i e_0 \psi_r/kT} \tag{39}$$

Now because the Debye-Huckel model considers the solutions in which ψ_r is much less than kT, we can conclude that $Z_i e_0 \psi_r \ll kT$. Therefore, $e^{-Z_i e_0 \psi_r/kT}$ can be expended as

$$\rho_r = \sum n_i^0 Z_i e_0 \left(1 - \frac{Z_i e_0 \psi_r}{kT}\right) \tag{40}$$

or

$$\rho_r = \sum n_i^0 Z_i e_0 - \sum \frac{n_i^0 Z_i^2 e_0^2 \psi_r}{kT} \tag{41}$$

The first term of the above equation gives the net charge on the whole of the solution, and it must be zero since the overall electrical neutrality is maintained. Therefore, the above equation takes the form

$$\rho_r = -\sum \frac{n_i^0 Z_i^2 e_0^2 \psi_r}{kT} \tag{42}$$

The above equation is the "linearized Boltzmann distribution".

Rearranging the Poisson's equation for excess charge density i.e. equation (33), we get

$$\rho_r = -\frac{\varepsilon}{4\pi}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)\right] \tag{43}$$

Where n_i^0 is the bulk concentration of the ith species and k is simply the Boltzmann constant. Equating the Poisson's expression with the Boltzmann Formula i.e. from equation (43) and (42), we get the linearized Poisson Boltzmann equation as:

$$-\frac{\varepsilon}{4\pi}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)\right] = -\sum_i \frac{n_i^0 Z_i^2 e_0^2 \psi_r}{kT} \tag{44}$$

or

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = \left(\frac{4\pi}{\varepsilon kT}\sum_i n_i^0 Z_i^2 e_0^2\right)\psi_r \tag{45}$$

Now assume a constant κ^2 with value

$$\kappa^2 = \frac{4\pi}{\varepsilon kT}\sum_i n_i^0 Z_i^2 e_0^2 \tag{46}$$

Using the value of equation (46) in equation (45), we get

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = \kappa^2\psi_r \tag{47}$$

To solve the above differential equation, assume that ψ_r is a function of a new variable, called μ, as

$$\psi_r = \frac{\mu}{r} \tag{48}$$

Differentiating equation (48), we get

$$\frac{d\psi_r}{dr} = -\frac{\mu}{r^2} + \frac{1}{r}\frac{d\mu}{dr} \tag{49}$$

Multiplying both sides by r^2

$$r^2\frac{d\psi_r}{dr} = -\mu + r\frac{d\mu}{dr} \tag{50}$$

Now first multiplying both sides by d/dr and then by $1/r^2$, we get

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right) = \frac{1}{r^2}\frac{d}{dr}\left(-\mu + r\frac{d\mu}{dr}\right) \tag{51}$$

or

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)=\frac{1}{r^2}\left(-\frac{d\mu}{dr}+r\frac{d^2\mu}{dr^2}+\frac{d\mu}{dr}\right) \tag{52}$$

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)=\frac{1}{r}\frac{d^2\mu}{dr^2} \tag{53}$$

Using the value of equation (48) and (53) into equation (47), we have

$$\frac{1}{r}\frac{d^2\mu}{dr^2}=\kappa^2\frac{\mu}{r} \tag{54}$$

or

$$\frac{d^2\mu}{dr^2}=\kappa^2\mu \tag{55}$$

The general solution of such an equation may be written as

$$\mu=Ae^{-\kappa r}+Be^{+\kappa r} \tag{56}$$

Where A and B are two unknown constants. Now using the value of μ from equation (56) into equation (48), we get

$$\psi_r=A\frac{e^{-\kappa r}}{r}+B\frac{e^{+\kappa r}}{r} \tag{57}$$

Since the potential at $r=\infty$ must vanish, this boundary condition is satisfied only if $B=0$. Therefore, the acceptable form of the equation (57) should be like this

$$\psi_r=A\frac{e^{-\kappa r}}{r} \tag{58}$$

To evaluate the value of constant, imagine a situation in which ions are so apart from each other that there are no ion-ion interactions. Such a situation can be created by diluting the solution to a very large extent. In this state, potential around the reference ion will simply be due to the reference ion itself i.e.

$$\psi_r=\frac{Z_ie_0}{\varepsilon r} \tag{59}$$

Furthermore, at such large dilution, the bulk concentration will almost be zero ($n_i^0=0$) which in turn would make $\kappa=0$. Thus, the equation (58) in such a scenario will be

$$\psi_r=\frac{A}{r} \tag{60}$$

Equating the results of equation (59) and (60), we have

$$\frac{Z_i e_0}{\varepsilon r} = \frac{A}{r} \tag{61}$$

or

$$A = \frac{Z_i e_0 r}{\varepsilon r} \tag{62}$$

After putting the value of *A* from equation (62) in equation (58), the final result for electrostatic potential is

$$\psi_r = \frac{Z_i e_0}{\varepsilon} \frac{e^{-\kappa r}}{r} \tag{63}$$

The expression is the solution of the linearized Poisson-Boltzmann equation.

Figure 7. The variation of electrostatic potential as a function of the distance *r* from the reference ion.

Now, in order to evaluate the excess charge density as a function of distance from the reference ion, compare equation (33) and equation (47) i.e.

$$\kappa^2 \psi_r = -\frac{4\pi}{\varepsilon} \rho_r \tag{64}$$

or

$$\rho_r = -\frac{\varepsilon \kappa^2 \psi_r}{4\pi} \tag{65}$$

Now putting the value of electrostatic potential from equation (63) in equation (65), we get the expression for excess charge density as a function of *r*.

$$\rho_r = -\frac{\varepsilon\kappa^2}{4\pi} \times \frac{Z_i e_0}{\varepsilon} \frac{e^{-\kappa r}}{r} \tag{66}$$

$$\rho_r = -\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r} \tag{67}$$

Now because the magnitude of ρ_r is a consequence of the unequal distribution of anions and cations, the above also defines the ionic population distribution around the reference ion.

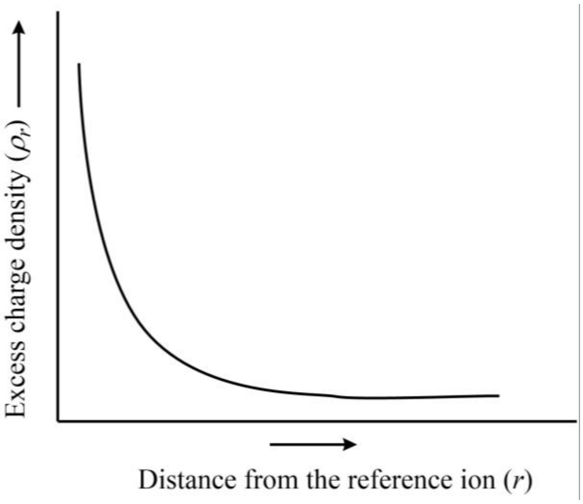


Figure 8. The variation of excess charge density as a function of the distance r from the reference ion.

Hence, the magnitude of excess charge density declines exponentially as the distance from the reference increases. It is also worthy to note that the sign of excess charge around the reference ion is always opposite to the reference ion. A negatively charged reference ion has a positively charged surrounding atmosphere and vice-versa.

❖ Debye-Huckel Reciprocal Length

The concept of Debye-Huckel length can be understood in a better way only after knowing how much charge actually surrounds the reference ion. For this, assume that the total space around the reference ion is divided into the infinite number of hollow spherical shells of thickness *dr* with the inner and outer radii as *r* and *r*+*dr*, respectively. The volume of each such shell will be $4\pi r^2 dr$, and the total excess charge (*dq*) in the same can be obtained by multiplying this volume element with the excess charge density, i.e.,

$$dq = \rho_r 4\pi r^2 dr \tag{68}$$

Now, as we know that the excess charge density at distance *r* from the reference ion is

$$\rho_r = -\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r} \tag{69}$$

Putting the value of equation (69) in equation (68), we get

$$dq = \left(-\frac{Z_i e_0 \kappa^2}{4\pi r} e^{-\kappa r}\right) 4\pi r^2 dr \tag{70}$$

or

$$dq = -Z_i e_0 e^{-\kappa r} \kappa^2 r dr \tag{71}$$

Since the exponential part becomes zero only at $r = \infty$, the total charge around the reference ion can be obtained by integrating the equation (71) from $r = 0$ to $r = \infty$.

$$q_{cloud} = \int_{r=0}^{r=\infty} dq = \int_{r=0}^{r=\infty} -Z_i e_0 e^{-\kappa r} \kappa^2 r dr \tag{72}$$

or

$$q_{cloud} = -Z_i e_0 \tag{73}$$

This is an important result which proves that a reference ion, with the charge $+Z_i e_0$, is surrounded by an exactly equal but oppositely charged cloud i.e. $-Z_i e_0$.

Now, since the exponential part decreases with increasing r while the non-exponential part shows a continuous increase as we move away from the reference ion, there should be a distance of maximum charge.

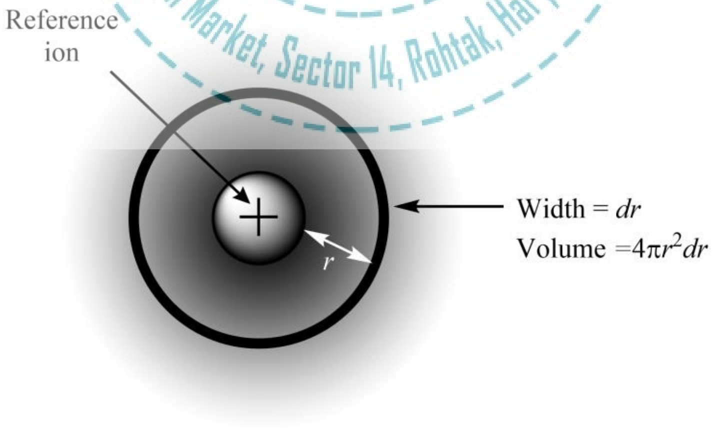


Figure 9. The depiction of excess charge density in a volume element of thickness ‘dr’ as a function of the distance r from the reference ion.

In order to find the distance of maximum "excess charge", we need to differentiate the equation (71) with respect to *r*, and then derivative needs to be put equal to zero i.e.

$$\frac{dq}{dr} = -Z_i e_0 \kappa^2 (e^{-\kappa r} - \kappa r e^{-\kappa r}) = 0 \tag{74}$$

Since $-Z_i e_0 \kappa^2$ is non zero for sure, the above equation holds true only if

$$e^{-\kappa r} - \kappa r e^{-\kappa r} = 0 \tag{75}$$

Which implies

$$r = \kappa^{-1} \tag{76}$$

Also as we know that

$$\kappa = \left(\frac{4\pi}{\varepsilon kT} \sum_i n_i^0 Z_i^2 e_0^2\right)^{1/2} \tag{77}$$

Hence, the radius of maximum excess charge from the center of the reference ion can be obtained by putting the value of *κ* from equation (77) in equation (76), we get *r*

Hence, the radius of maximum excess charge from the center of the reference ion can be obtained by putting the value of κ from equation (77) in equation (76), we get r_{max} or the "Debye-Huckel length" as

$$r_{max} = \left(\frac{\varepsilon kT}{4\pi} \frac{1}{\sum_i n_i^0 Z_i^2 e_0^2}\right)^{1/2} \tag{78}$$

It is also worthy to note that the cloud will tend to fade out ever more with the decreasing concentration.

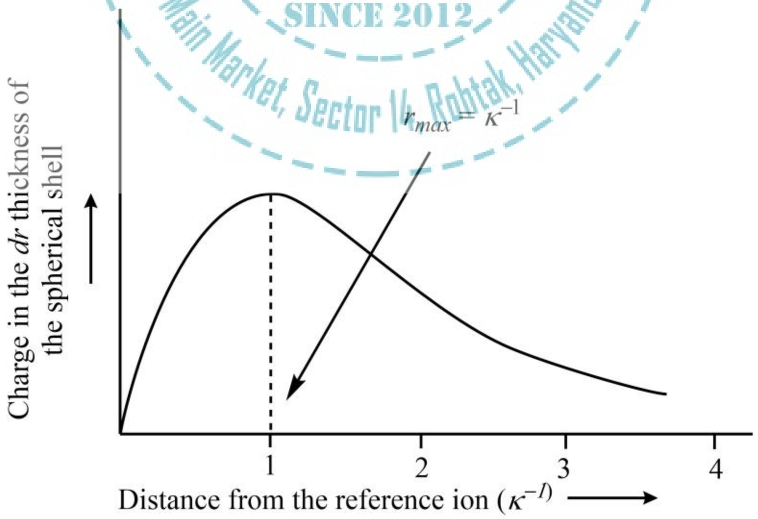


Figure 10. The variation of total charge enclosed in the *dr* thickness of the spherical shell as a function of the distance *r* from the reference ion.

❖ Ionic Cloud and Its Contribution to the Total Potential

According to the Debye-Huckel theory of ion-ion interaction, the molar chemical potential change ($\Delta\mu_{i-I}$) of ion-ion interaction can be calculated from the following relation.

$$\Delta\mu_{i-I} = \frac{N_A}{2}[Z_i e_0 \times \psi] \tag{79}$$

Where N_A is the Avogadro number and ψ the electrostatic potential at distance r due to ionic cloud. The symbol $Z_i e_0$ is the charge on the ith species. The value of ψ_r is

$$\psi_r = \frac{Z_i e_0}{\varepsilon} \frac{e^{-\kappa r}}{r} \tag{80}$$

Where ε is the dielectric constant of the surrounding medium and κ is a constant defined by

$$\kappa = \left(\frac{4\pi}{\varepsilon kT} \sum_i n_i^0 Z_i^2 e_0^2\right)^{1/2} \tag{81}$$

The value of electrostatic potential given by equation (80) cannot be used in equation (79) because contains the contribution form the ionic cloud as well as from the reference ion itself. Therefore, before we calculate the partial molar free energy of ion-ion interaction, we need to separate potential from the ionic cloud and from the central ion first.

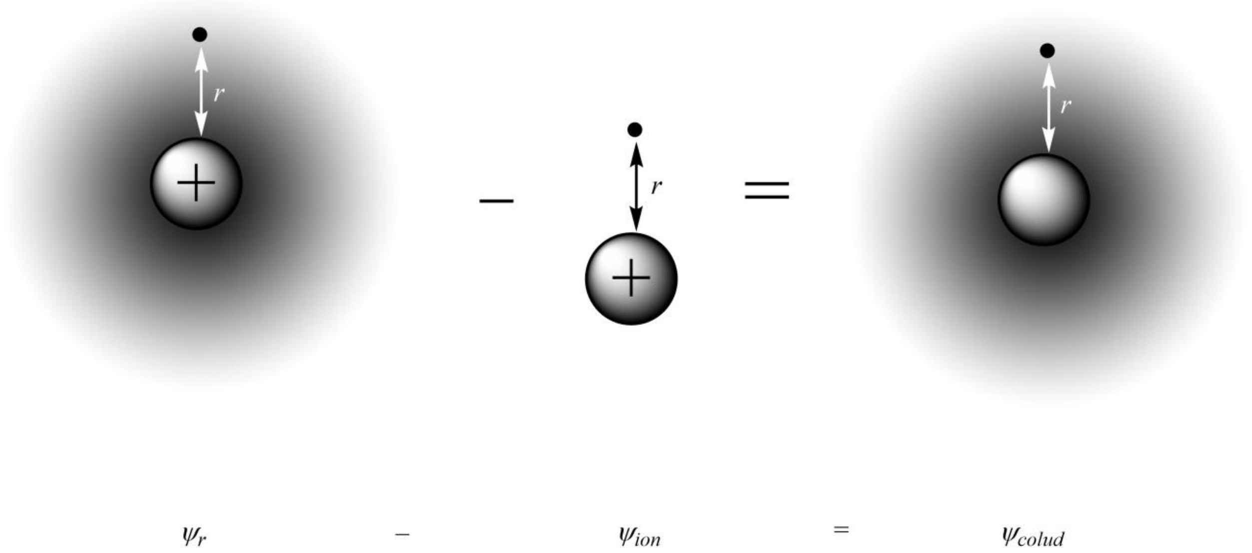


Figure 11. The pictorial representation of the superposition of the potentials at distance r from the reference ion due to the ionic cloud ion and the potential due to the central ion itself.

The total electrostatic potential at a distance *r* can be fragmented as given below.

$$\psi_r = \psi_{ion} + \psi_{cloud} \tag{82}$$

or

$$\psi_{cloud} = \psi_r - \psi_{ion} \tag{83}$$

From the formulation of potential due to a single charge at a distance *r*, we know that

$$\psi_{ion} = \frac{Z_i e_0}{\varepsilon r} \tag{84}$$

Now using the value of ψ_r from equation (80) and ψ_{ion} from equation (84) into equation (83), we get

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon}\frac{e^{-\kappa r}}{r} - \frac{Z_i e_0}{\varepsilon r} \tag{85}$$

or

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon r}(e^{-\kappa r} - 1) \tag{86}$$

Now because the value of κ is proportional to $\sum_i n_i^0 Z_i^2 e_0^2$, at very large dilution κ becomes very small and $e^{-\kappa r}$ and can be expended as $1 - \kappa r$ ($e^x = 1 + x$). Therefore, equation (86) takes the form

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon r}(1 - \kappa r - 1) \tag{87}$$

or

$$\psi_{cloud} = -\frac{Z_i e_0 \kappa}{\varepsilon} \tag{88}$$

Hence, potential due to ionic cloud is independent of the distance *r* in this case. Hence, potential due to ionic cloud is independent of the distance *r* in this case. Now putting the value of ψ_{cloud} from equation (88) into equation (79), we get

$$\Delta\mu_{i-I} = N_A w = \frac{N_A}{2}\left[Z_i e_0 \times \left(-\frac{Z_i e_0 \kappa}{\varepsilon}\right)\right] \tag{89}$$

or

$$\Delta\mu_{i-I} = -\frac{N_A Z_i^2 e_0^2 \kappa}{2\varepsilon} \tag{90}$$

Hence, Debye-Hückel model gives the theoretical value of $\Delta\mu_{i-I}$ arising from ion-ion interactions.

❖ Debye-Huckel Limiting Law of Activity Coefficients and Its Limitations

So far in this chapter, the idea of ions in electrolytic solutions and their mutual interactions was taken for granted. However, the conceptual understanding of these electrolytic solutions thrived via a different route. Initially, the scientific community thought that the electrolytic solutions are the same as the non-electrolytic ones. In other words, they did not pay any special attention to the charged species, and therefore, treated them just like the non-electrolytes.

➢ *Derivation of Debye-Huckel Limiting Law*

Classically, the partial molar free energy (μ_i) of the *i*th species in a non-electrolyte is given by the following relation.

$$\mu_i = \mu_i^0 + RT \ln x_i \tag{91}$$

Where μ_i^0 is the partial molar free energy when the concentration (x_i) is unity (standard state). Mathematically, we can say that is if $x_i = 1$, $\mu_i = \mu_i^0$.

At this point, it worthy to point out that the Coulombic interactions (long-range) can be neglected in the case of non-electrolytic solutions, which is obviously due to the uncharged or neutral nature of the solute particles. However, some short-range electrostatic interactions like the London dispersion forces or the dipole-dipole may play a significant role if the average inter-particle distance is small enough. This means that if the dilution is large enough, the ion-ion interactions (long-range Coulombic effects) can simply be ignored in a non-electrolytic solution. Thus, the equation (91) is valid only for those solutions in which no long-range electrostatic interactions occur, and such solutions are called as ideal solutions. However, when the equation (91) was applied to the electrolytic solutions, it was found that

$$\mu_i - \mu_i^0 \neq RT \ln x_i \tag{92}$$

Such solutions which show deviation from equation (91) are called as non-ideal solutions. This means that unlike non-electrolytes, the ion-ion interactions must be considered before any theoretical treatment for the chemical potential of ionic solutions is carried out.

Therefore, to rationalize this deviation, the scientific community developed a unique approach even before the Debye-Huckel's ionic-cloud theory. They tried to quantify the deviation from "idealistic behavior" by incorporating an empirical parameter f_i in the equation (92) as

$$\mu_i - \mu_i^0 = RT \ln x_i f_i \tag{93}$$

Where μ_i^0 is the partial molar free energy when the concentration (x_i) and correction factor (f_i) both are unity. Mathematically, we can say that if $x_i = 1$ and $f_i = 1$, $\mu_i = \mu_i^0$; which is obviously a hypothetical situation in which standard state behaves ideally. Moreover, it should also be noted that term x_i represents the actual concentration of the ions of *i*th type which may or may not be equal to expected concentration because weak electrolytes do not dissociate completely like the strong one. After that, it was assumed that it is not the actual concentration (x_i) but the effective concentration ($x_i f_i$) that dictates the chemical potential change. For simplicity, the effective concentration if ith species was simply labeled as the activity (a_i). Mathematically, we can say that

$$a_i = x_i f_i \tag{94}$$

The correction factor f_i is also called as the "activity coefficient" and has a value of unity for ideal solutions i.e. when $f_i = 1$, $a_i = x_i$.

Consequently, the partial molar free energy change in going from the ideal state to the real state in ionic solutions can be written as

$$\mu_i - \mu_i^0 = RT \ln x_i + RT \ln f_i \tag{95}$$

The above equation is an empirical formulation of the behavior of ionic solutions and cannot give any theoretical result for f_i. Therefore, in order to find out the physical significance of the activity coefficient, we need to assume an ionic solution that can be switched from ideal (no ion-ion interaction) to the real situation (with ion-ion interaction). For ideal solutions, we have

$$\mu_i(\text{ideal}) = \mu_i^0 + RT \ln x_i \tag{96}$$

For real solutions,

$$\mu_i(\text{real}) = \mu_i^0 + RT \ln x_i + RT \ln f_i \tag{97}$$

The chemical potential change from ion-ion interaction can be obtained by subtracting equation (96) from equation (97) i.e.

$$\mu_i(\text{real}) - \mu_i(\text{ideal}) = \Delta\mu_{i-I} = \mu_i^0 + RT \ln x_i + RT \ln f_i - \mu_i^0 - RT \ln x_i \tag{98}$$

$$\Delta\mu_{i-I} = RT \ln f_i \tag{99}$$

Hence, the activity coefficient is a measure of chemical potential change due to the interaction of ith types with the rest of the ionic species. Now, according to the Debye-Huckel theory of ion-ion interaction, the partial molar free energy change due to ion-ion interaction is

$$\Delta\mu_{i-I} = -\frac{N_A Z_i^2 e_0^2 \kappa}{2\varepsilon} \tag{100}$$

Where Z_i is the charge number on the ith type of ion while e_0 is the electronic charge. N_A is the Avogadro number and ε is the dielectric constant of the surrounding medium, i.e., solvent. The symbol κ with n_i^0 as the bulk concentration is

$$\kappa = \left(\frac{4\pi}{\varepsilon kT}\sum_i n_i^0 Z_i^2 e_0^2\right)^{1/2} \tag{101}$$

Now, from equation (99) and equation (100), we have

$$RT \ln f_i = -\frac{N_A Z_i^2 e_0^2 \kappa}{2\varepsilon} \tag{102}$$

The above result implies that the Debye-Huckel's ionic cloud theory enables us to determine the activity coefficient in a theoretical framework.

Furthermore, if the actual concentration of the ith type of ion is represented in terms of molarity (c_i) or the molality (m_i), the equation (96) takes the form

$$\mu_i = \mu_i^0(c) + RT \ln c_i \tag{103}$$

and

$$\mu_i = \mu_i^0(m) + RT \ln m_i \tag{104}$$

Similarly, for real solutions, equation (97) takes the forms

$$\mu_i = \mu_i^0(c) + RT \ln c_i + RT \ln f_c \tag{105}$$

and

$$\mu_i = \mu_i^0(m) + RT \ln m_i + RT \ln f_m \tag{106}$$

Where $\mu_i^0(c)$ and $\mu_i^0(m)$ are corresponding standard chemical potential at a molarity c_i and molality m_i, respectively.

At this point, some experimental limitations must be discussed before any comparative analysis of the activity coefficient is carried out. It is a quite well-known fact that we cannot measure the hydration energy, i.e., ion-solvent interaction of individual ionic species because the addition of only cations or the anions is not possible practically. Even if it was possible, it would result in a negatively or positively charged solution depending upon the nature of the ions added, which eventually, would cause undesired interactions. Owing to similar arguments, it is also practically impossible to measure the activity coefficient f_i which is also a function chemical potential change arising from ion-ion interaction. The only way to avoid the situation is to add the electroneutral electrolytes to the solvent which would eventually produce the positive and negative ions simultaneously irrespective of whether it is strong or weak. Therefore, one can determine the activity of a net electrolyte consisted of minimum two ionic species, and we need something that can connect activity coefficient of electrolyte with the individual ionic species. In other words, the activity coefficient of a single ionic species can be determined only via a theoretical route. All this resulted in the idea of "mean ionic activity coefficient". To illustrate mathematically, consider a NaCl-type univalent electrolyte MA. The chemical potential of cations (M^+) and anions (A^-) can be written as

$$\mu_{M^+} = \mu_{M^+}^0 + RT \ln x_{M^+} + RT \ln f_{M^+} \tag{107}$$

and

$$\mu_{A^-} = \mu^0_{A^-} + RT\ln x_{A^-} + RT\ln f_{A^-} \tag{108}$$

Combining the equation (107) with equation (108), we get

$$\mu_{M^+} + \mu_{A^-} = (\mu^0_{M^+} + \mu^0_{A^-}) + RT\ln(x_{M^+}x_{A^-}) + RT\ln(f_{M^+}f_{A^-}) \tag{109}$$

The above equation gives the free energy of the system due to two moles of ions i.e. one mole of M^+ and mole of A^-; or due to one mole of electroneutral electrolyte. Since we are interested in the average input to the total free energy due to one mole of ions only, therefore, we must divide the equation (109) by 2, i.e.,

$$\frac{\mu_{M^+} + \mu_{A^-}}{2} = \frac{\mu^0_{M^+} + \mu^0_{A^-}}{2} + RT\ln(x_{M^+}x_{A^-})^{1/2} + RT\ln(f_{M^+}f_{A^-})^{1/2} \tag{110}$$

If we consider

$$\mu_\pm = \frac{\mu_{M^+} + \mu_{A^-}}{2} \tag{111}$$

$$\mu^0_\pm = \frac{\mu^0_{M^+} + \mu^0_{A^-}}{2} \tag{112}$$

and

$$x_\pm = (x_{M^+}x_{A^-})^{1/2} \tag{113}$$

$$f_\pm = (f_{M^+}f_{A^-})^{1/2} \tag{114}$$

Where $\mu_\pm$ and $\mu^0_\pm$ are the mean chemical potential and standard mean chemical potential, respectively. The symbol $x_\pm$ and $f_\pm$ represent the mean ionic mole fraction and mean ionic activity coefficient, respectively. Here, it is also worthy to note that $\mu_\pm$ and $\mu^0_\pm$ are simply the arithmetic means whereas $x_\pm$ and $f_\pm$ are the geometric mean quantities. Now using values from equations (111−114) into equation (110), we get

$$\mu_\pm = \mu^0_\pm + RT\ln x_\pm + RT\ln f_\pm \tag{115}$$

Since it is for one mole instead two, we can write

$$\frac{1}{2}\mu_{MA} = \mu_\pm = \mu^0_\pm + RT\ln x_\pm + RT\ln f_\pm \tag{116}$$

Hence, the experimental value of $f_\pm$ can be obtained just by knowing the free energy of one mole of electrolytic solution at a particular concentration. Once the value of $f_\pm$ is known, the product of individual activity coefficients can be obtained using equation (114). The individual values of activity coefficients obtained from equation (102) can be put into equation (114) to compare with experimentally observed value so that the Debye-Huckel model can be tested.

Furthermore, if one mole of electroneutral electrolyte generates ν_+ and ν_- moles of cations and anions, then equation (107) and equation (108) will become

$$\nu_+\mu_+ = \nu_+\mu_+^0 + \nu_+RT\ln x_+ + \nu_+RT\ln f_+ \tag{117}$$

and

$$\nu_-\mu_- = \nu_-\mu_-^0 + \nu_-RT\ln x_- + \nu_-RT\ln f_- \tag{118}$$

To find the free energy change due to per mole of cation and anion, add equation (117) to equation (118) and then divide by $\nu = \nu_+ + \nu_-$.

$$\frac{\nu_+\mu_+ + \nu_-\mu_-}{\nu} = \frac{\nu_+\mu_+^0 + \nu_-\mu_-^0}{\nu} + RT\ln\left(x_+^{\nu_+}x_-^{\nu_-}\right)^{1/\nu} + RT\ln\left(f_+^{\nu_+}f_-^{\nu_-}\right)^{1/\nu} \tag{119}$$

If we consider

$$\mu_\pm = \frac{\nu_+\mu_+ + \nu_-\mu_-}{\nu} \tag{120}$$

$$\mu_\pm^0 = \frac{\nu_+\mu_+^0 + \nu_-\mu_-^0}{\nu} \tag{121}$$

and

$$x_\pm = \left(x_+^{\nu_+}x_-^{\nu_-}\right)^{1/\nu} \tag{122}$$

$$f_\pm = \left(f_+^{\nu_+}f_-^{\nu_-}\right)^{1/\nu} \tag{123}$$

Now using values from equations (120–123) into equation (119), we get

$$\mu_\pm = \mu_\pm^0 + RT\ln x_\pm + RT\ln f_\pm \tag{124}$$

Taking logarithm both side of equation (123), we have

$$\ln f_\pm = \frac{1}{\nu}(\nu_+\ln f_+ + \nu_-\ln f_-) \tag{125}$$

Now putting the value of $\ln f_+$ and $\ln f_-$ using equation (102), we get

$$\ln f_\pm = -\frac{1}{\nu}\left[\frac{N_A e_0^2\kappa}{2\varepsilon RT}(\nu_+Z_+^2 + \nu_-Z_-^2)\right] \tag{126}$$

Now owing to the electroneutrality of the solution, ν_+Z_+ must be equal to ν_-Z_-, i.e.,

$$\nu_+Z_+^2 + \nu_-Z_-^2 = \nu_+Z_+Z_- + \nu_-Z_-Z_+ \tag{127}$$

$$\nu_+Z_+^2 + \nu_-Z_-^2 = Z_+Z_-(\nu_+ + \nu_-) \tag{128}$$

$$\nu_+Z_+^2+\nu_-Z_-^2=Z_+Z_-\nu \tag{129}$$

After putting the value of equation (129) into equation (126), we have

$$\ln f_\pm=-\frac{N_Ae_0^2\kappa}{2\varepsilon RT}Z_+Z_- \tag{130}$$

Furthermore, using the value of κ using equation (101), the above equation takes the form

$$\ln f_\pm=-\frac{N_Ae_0^2Z_+Z_-}{2\varepsilon RT}\left(\frac{4\pi}{\varepsilon kT}\sum_i n_i^0Z_i^2e_0^2\right)^{1/2} \tag{131}$$

Since $n_i^0=c_iN_A/1000$, the equation (131) becomes

$$\ln f_\pm=-\frac{N_Ae_0^2Z_+Z_-}{2\varepsilon RT}\left(\frac{4\pi}{\varepsilon kT}\sum_i\frac{c_iN_AZ_i^2e_0^2}{1000}\right)^{1/2} \tag{132}$$

Multiply and divide the equation (132) by 2, and then put $c_iZ_i^2/2=I$, i.e., ionic strength, we get

$$\ln f_\pm=-\frac{N_Ae_0^2Z_+Z_-}{2\varepsilon RT}\left(\frac{8\pi N_Ae_0^2}{1000\varepsilon kT}\right)^{1/2}\sqrt{I} \tag{133}$$

$$\ln f_\pm=-\frac{N_Ae_0^2Z_+Z_-}{2\varepsilon RT}B\sqrt{I} \tag{134}$$

Where the constant B is defined as

$$B=\left(\frac{8\pi N_Ae_0^2}{1000\varepsilon kT}\right)^{1/2} \tag{135}$$

Converting the natural logarithm to the common logarithm, the equation (134) becomes

$$\log f_\pm=-\frac{1}{2.303}\frac{N_Ae_0^2Z_+Z_-}{2\varepsilon RT}B\sqrt{I} \tag{136}$$

After a new constant A as

$$A=\frac{1}{2.303}\frac{N_Ae_0^2}{2\varepsilon RT}B \tag{137}$$

The equation (136) can be further simplified as given below.

$$\log f_\pm=-A(Z_+Z_-)\sqrt{I} \tag{138}$$

Which is the Debye-Huckel limiting law of activity coefficients.

➢ *Limitations of Debye-Huckel Limiting Law*

The negative sign in the Debye-Huckel limiting law implies the fact that the activity coefficient is always less than unity. In order to discuss the limitations of this law, recall the popular relationship, i.e.,

$$\log f_{\pm} = -A(Z_{+}Z_{-})\sqrt{I} \tag{139}$$

Since A is constant and the product $Z_{+}Z_{-}$ is also constant for a particular electrolyte, the logarithm of activity coefficient must decrease linearly with the square root of ionic strength. In other words, the slope $\log f_{\pm}$ and $\sqrt{I}$ can be determined simply by knowing the valences of the ions involved and by the knowledge of some physical constants. Furthermore, it should also be noted that the slope is independent of the very nature of the electrolyte and is a function of valences of cations and anions only. For instance, since the value of A for the water as solvent is 0.509, the slope of for NaCl as well as for KCl must be equal to 1×0.509 only. For uni-bivalent and the bi-bivalent electrolyte is should be 2×0.509 and 4×0.509. The logarithmic variation of mean ionic activity coefficient ($f_{\pm}$) with the square root of the ionic strength ($\sqrt{I}$) for electrolytes of different valences follows the equation (139) pretty strictly.

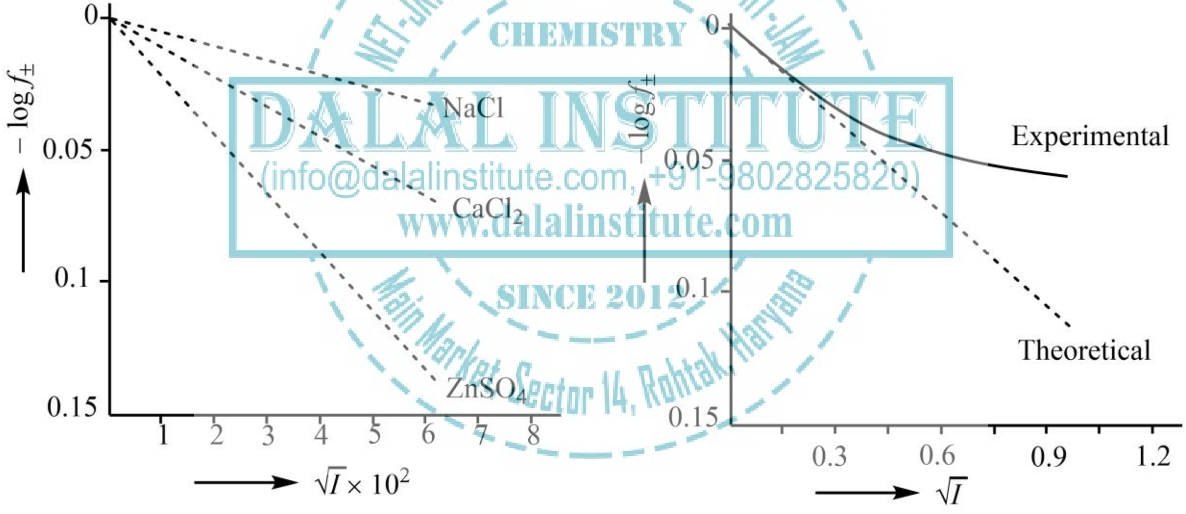


Figure 12. The logarithmic variation of $f_{\pm}$ with the square root of the ionic strength ($\sqrt{I}$) for electrolytes of different valences in very dilute (left) and in solutions up to large concentration (right).

It is obvious from both the graphs that $\log f_{\pm}$ becomes zero when the dilution is very large indicating that the activity coefficient is unity, which is according to the Debye-Huckel limiting law. However, it should also be remembered that any theory is always a simplification of the real problem, and therefore, some deviations are expected. The same has been observed when the ionic strength is increased. It can be clearly seen that the deviation of the experimental result increases with the rise in the square root of the ionic strength.

❖ Ion-Size Effect on Potential

In the Debye-Huckel theory of ion-ion interaction, the central ion was simply treated as a point charge instead of its actual size. The scientific community realized that it might be one of the reasons behind the deviations observed from Debye-Huckel limiting law of activity coefficients. In order to understand the effect of ion size on the potential, recall the expression for the Debye-Huckel length (r_{max}) or κ^{-1}, i.e.,

$$r_{max} = \left(\frac{\varepsilon kT}{4\pi}\frac{1}{\sum_i n_i^0 Z_i^2 e_0^2}\right)^{1/2} \tag{140}$$

Where n_i^0 is the bulk concentration of the *i*th species and *k* is simply the Boltzmann constant. The symbol ε represents the dielectric constant of the surrounding medium. The symbol Z_i shows the charge number of the ion whereas e_0 represents the electronic charge. It is obvious from the equation (140) that the mean thickness of the ionic cloud (κ^{-1}) is actually inversely proportional to the concentration. This means that at higher concentrations, the mean thickness of the ionic cloud will be small and cannot outrank the size of the central ion anymore. In other words, at higher concentration, the size of the reference ion cannot be neglected at all, and therefore, the point charge approximation is no longer valid. For instance, At a concentration of 0.1*N*, the mean thickness of the ionic cloud is only ten times the radius of the reference ion.

Consider $4\pi r^2 dr$ as the volume element of a hollow spherical shell of thickness *dr* with the inner and outer radius as *r* and *r*+*dr*, respectively, with the size of the ion represented by the parameter *a*.

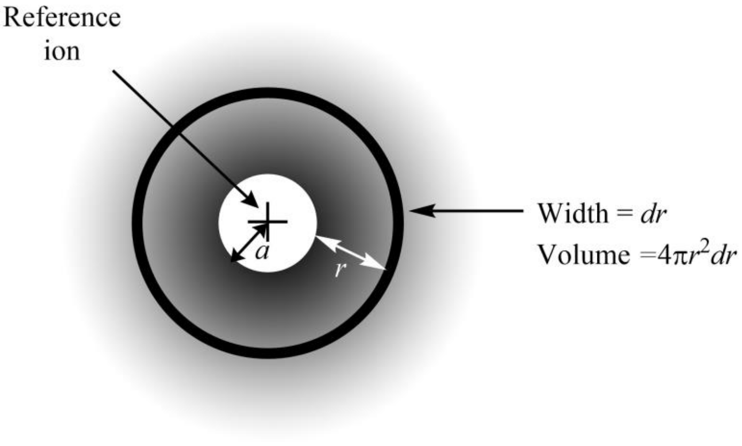


Figure 13. The depiction of excess charge density as a function of the distance *r* from the reference ion of finite size *a*.

Therefore, the ion-size must be considered for a more realistic picture of the actual situation. To do so, consider the linearized Poisson-Boltzmann equation which is free from both approximations, i.e., ion-size matters and the point charge consideration.

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)=\kappa^2\psi_r \tag{141}$$

Where ψ_r is the potential at a distance r from the reference ion. The symbol κ is defined as

$$\kappa=\left(\frac{4\pi}{\varepsilon kT}\sum_i n_i^0 Z_i^2 e_0^2\right)^{1/2} \tag{142}$$

The general solution of the above equation is

$$\psi_r = A\frac{e^{-\kappa r}}{r}+B\frac{e^{+\kappa r}}{r} \tag{143}$$

Since the potential at $r = \infty$ must vanish, this boundary condition is satisfied only if $B = 0$. Therefore, the acceptable form of the equation (143) should be like this

$$\psi_r = A\frac{e^{-\kappa r}}{r} \tag{144}$$

To evaluate the value of constant A in this scenario, a slightly different route is followed. As we know that the total charge in the dr thickness of a spherical shell at distance r is

$$dq = \rho_r 4\pi r^2 dr \tag{145}$$

Now, the excess charge density at distance r from the reference ion will be

$$\rho_r = -\frac{\varepsilon}{4\pi}\left[\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{d\psi_r}{dr}\right)\right]=-\frac{\varepsilon\kappa^2\psi_r}{4\pi} \tag{146}$$

Using the value of ψ_r from equation (144) into equation (146), we get

$$\rho_r = -\frac{\varepsilon\kappa^2}{4\pi}A\frac{e^{-\kappa r}}{r} \tag{147}$$

After putting the value of equation (147) into equation (145), we have

$$dq = -\frac{\varepsilon\kappa^2}{4\pi}A\frac{e^{-\kappa r}}{r}4\pi r^2 dr \tag{148}$$

or

$$dq = -\varepsilon\kappa^2 A e^{-\kappa r} r dr \tag{149}$$

Since the exponential part becomes zero only at $r = \infty$, the total charge around the reference ion can be obtained by integrating the equation (149) from an unknown parameter $r = a$ to $r = \infty$.

$$q_{cloud} = \int_{r=a}^{r=\infty} dq\, dr = \int_{r=a}^{r=\infty} -\varepsilon\kappa^2 A e^{-\kappa r} r dr \tag{150}$$

or

$$q_{cloud} = \int_{r=a}^{r=\infty} dq\, dr = -A\varepsilon e^{-\kappa a}(1+\kappa a) \tag{151}$$

Also as we know that the total charge on the ionic cloud must be equal and opposite to the charge on the reference ion i.e.

$$q_{cloud} = -Z_i e_0 \tag{152}$$

Equating the results of equation (151) and equation (152), we have

$$-A\varepsilon e^{-\kappa a}(1+\kappa a) = -Z_i e_0 \tag{153}$$

or

$$A = \frac{Z_i e_0}{\varepsilon}\frac{e^{\kappa a}}{(1+\kappa a)} \tag{154}$$

Using the value of *A* from equation (154) in equation (144), we get

$$\psi_r = \frac{Z_i e_0}{\varepsilon}\frac{e^{\kappa a}}{(1+\kappa a)}\frac{e^{-\kappa r}}{r} \tag{155}$$

❖ Ion-Size Parameter and the Theoretical Mean - Activity Coefficient in the Case of Ionic Clouds with Finite-Sized Ions

As we know that the total electrostatic potential at a distance *r* can simply be fragmented as given below.

$$\psi_r = \psi_{ion} + \psi_{cloud} \tag{156}$$

or

$$\psi_{cloud} = \psi_r - \psi_{ion} \tag{157}$$

The electrostatic potential at a distance *r* from an ion of finite size is

$$\psi_r = \frac{Z_i e_0}{\varepsilon}\frac{e^{\kappa a}}{(1+\kappa a)}\frac{e^{-\kappa r}}{r} \tag{158}$$

Also, from the formulation of potential due to a single charge at a distance *r*, we know that

$$\psi_{ion} = \frac{Z_i e_0}{\varepsilon r} \tag{159}$$

After putting the values of ψ_r and ψ_{ion} from equation (158) and equation (159) into equation (157), we have

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon} \frac{e^{\kappa a}}{(1+\kappa a)} \frac{e^{-\kappa r}}{r} - \frac{Z_i e_0}{\varepsilon r} \tag{160}$$

or

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon r}\left[\frac{e^{\kappa(a-r)}}{(1+\kappa a)} - 1\right] \tag{161}$$

At this point, we must recall the relationship of mean activity coefficient and chemical potential change of the ion-ion interaction, i.e.,

$$RT \ln f_i = \Delta\mu_{i-I} \tag{162}$$

also

$$\Delta\mu_{i-I} = \frac{N_A Z_i e_0}{2}\psi \tag{163}$$

From equation (162) and (163), we have

$$RT \ln f_i = \frac{N_A Z_i e_0}{2}\psi \tag{164}$$

$$\ln f_i = \frac{N_A Z_i e_0}{2RT}\psi \tag{165}$$

Moreover, as the potential at the surface ($r = a$) of the ion must be

$$\psi = \psi_{cloud} \tag{166}$$

Which implies that ψ_{cloud} in equation (161) at $r = a$ should become

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon a}\left[\frac{1}{(1+\kappa a)} - 1\right] \tag{167}$$

or

$$\psi_{cloud} = \frac{Z_i e_0}{\varepsilon a}\left[\frac{1 - 1 - \kappa a}{(1+\kappa a)}\right] \tag{168}$$

$$\psi_{cloud} = -\frac{Z_i e_0}{\varepsilon \kappa^{-}} \frac{1}{(1+\kappa a)} \tag{169}$$

After using the value of equation (169) in equation (165), we get

$$\ln f_i = -\frac{N_A Z_i^2 e_0^2}{2RT\varepsilon\kappa^{-1}} \frac{1}{(1+\kappa a)} \tag{170}$$

The mean ionic activity coefficient, in this case, will be

$$\log f_\pm = -\frac{AZ_+Z_-}{(1+\kappa a)} I^{1/2} \tag{171}$$

Where I is the ionic strength and A is Debye-Huckel constant. Now since the thickness of the ionic cloud is defined as

$$\kappa = BI^{1/2} \tag{172}$$

After putting the value of κ from equation (172) into equation (171), we have

$$\log f_\pm = -\frac{AZ_+Z_- I^{1/2}}{1 + a\, BI^{1/2}} \tag{173}$$

Which is the equation for the mean ionic activity coefficient when the central ion has a finite size. Now recall the equation for mean ionic activity coefficient when the central ion was considered as point charge i.e.

$$\log f_\pm = -AZ_+Z_- I^{1/2} \tag{174}$$

Hence, the two equations differ only in respect of denominator $1 + \kappa a$. The rearranged form of the equation (171) is

$$\log f_\pm = -\frac{AZ_+Z_-}{(1 + a/\kappa^{-1})} I^{1/2} \tag{175}$$

At large dilution, $a \ll \kappa^{-1}$, and the denominator tends to approach unity. Therefore, at very large dilution, the equation (175) becomes equal to equation (174), proving the correspondence principle.

The most obvious approach to estimate the ion size parameter is the sum of the crystallographic radii of the cation and anions present in the electrolytic-solution. This is because the two ions cannot come closer than the sum of their individual ionic radii. However, since ions are hydrated in aqueous solutions, one might think the ion size parameter as the sum of the hydrated radii instead. Nevertheless, the hydrated radii would face some compression during the course of the collision of ion. All this suggests that the magnitude of 'a' must be greater than the sum of the individual crystallographic radii and should be less than the sum of their individual hydrated radii. Therefore, the "mean distance of closest approach" should be more appropriate for this situation. The best way to estimate the ion-size parameter is to calibrated equation (175) to match the experimental value of mean ionic activity coefficient. After knowing the ion size parameter at one concentration, the value of mean ionic activity coefficient can easily be determined at other concentrations.

❖ Debye-Huckel-Onsager Treatment for Aqueous Solutions and Its Limitations

It is a well-known fact that the conductance of weak electrolytic solutions increases with the increase in dilution. This can be easily explained on the basis of Arrhenius's theory of electrolytic dissociation which says that the magnitude of dissociated electrolyte, and hence the number of charge carriers, increases with the increase in dilution. However, the problem arises when the strong or true electrolytes show the same trend but at a much lower scale. We used the word "problem" because even at the higher concentration, the electrolyte dissociates completely inferring that there is no possibility of further dissociation with dilution. This means that there should be no increase in the conductance of strong electrolytes with the addition of water.

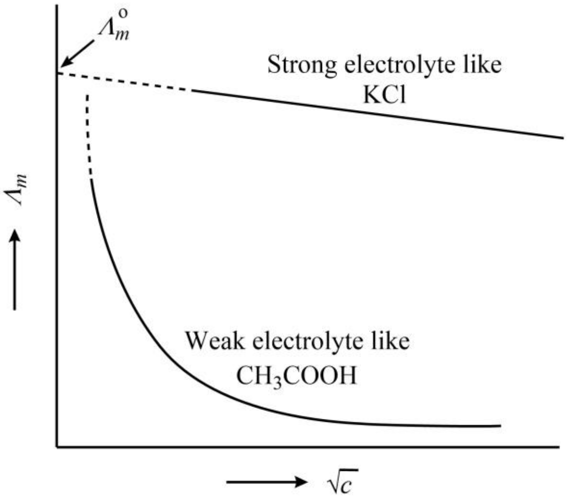


Figure 14. The typical variation of molar conductance (Λ_m) with the square root of the concentration ($\sqrt{c}$) for strong and weak electrolytes.

The primary reason behind this weird behavior of strong electrolyte is that the conductance of any electrolytic solution depends not only upon the number of charge carriers but also upon the speed of these charge carriers. Therefore, if the dilution does not affect the number of charge carriers in strong electrolytes, it must be affecting the speed of ions to change its conductance. The main factor that is responsible for governing the ionic mobility is ion-ion interactions. Now since these ion-ion interactions are dependent upon the interionic distances, they eventually vary with the population density of charge carriers. Higher population density means smaller interionic distances and therefore stronger ion-ion interactions. On the other hand, the lesser population density of ions would result in larger interionic separations and hence weaker ion-ion interactions.

In the case of weak electrolytes, the degree of dissociation is very small at high concentrations yielding a very low population density of charge carriers. This would result in almost zero ion-ion interactions at high concentrations. Now although the degree of dissociation increases with dilution which in turn also increases the total number of charge carriers, the population density remains almost unchanged since extra water has been added for these extra ions. Thus, we can conclude that there are no ion-ion interactions in weak electrolytes neither at high nor at the low concentration; and hence the rise in conductance with dilution almost a function dissociation only.

In the case of strong electrolytes, the degree of dissociation is a hundred percent even at high concentrations yielding a very high population density of charge carriers. This would result in very strong ion-ion interactions at high concentrations, hindering the speed of various charge carriers. Now when more and more solvent is added, the total number of charge carriers remains the same but the population density decreases continuously creating large interionic separations. This would result in a decrease in ion-ion interaction with increasing dilution, and therefore, the charge carriers would be freer to move in the solution. Thus, we can conclude that though there is no rise in the number of charge carriers with dilution, the declining magnitude of ion-ion interaction creates faster ions and larger conductance.

- ***Factor Affecting the Conductance of Strong Electrolytic Solutions***

In 1923, Peter Debye and Erich Huckel proposed an extremely important idea to quantify the conductance of strong electrolytes in terms of these interionic interactions. In this model, a reference ion is thought to be suspended in solvent-continuum of dielectric constant ε and is surrounded by oppositely charged ions. Besides the ion-ion interaction, the viscosity of the solvent also affects the overall speed of the moving ion. The primary effects which are responsible for controlling the ionic mobility are discussed below.

1. Asymmetry effect or the relaxation effect: In the absence of applied electric field, the ionic atmosphere of the reference ion remains spherically symmetrical. This means that the electrostatic force of attraction on the reference ion from all the directions would be the same. However, when the electric field is applied, the ion starts to move towards the oppositely charged electrode. This, in turn, would destroy the spherical symmetry of the cloud, and more ions would be left behind creating a net backward pull to the reference ion. This effect, therefore, would slow down the moving ions and the conductance would be decreased.

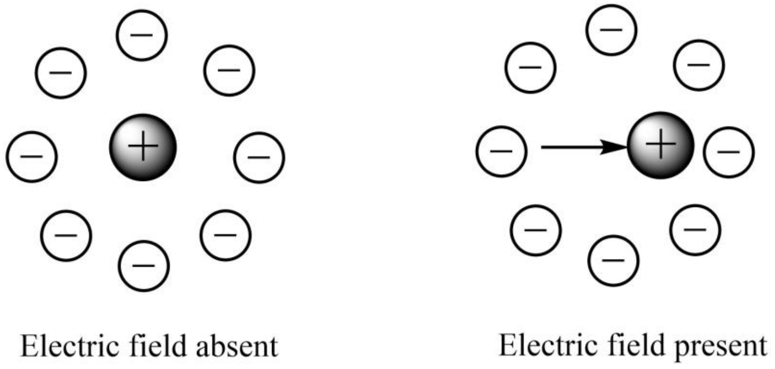


Figure 15. The asymmetric or relaxation effect in the conductance of strong electrolytes.

Alternatively, this can also be visualized in terms of cloud-destruction and cloud-building around the reference ion. In other words, during the movement of ion, the ionic cloud around the reference ion must rebuild itself to keep things natural. Since this rebuilding is not instantaneous and takes some time called as relaxation time, the old cloud exerts a backward pull on the reference ion opposing oppressing its speed. All this results in a diminished magnitude of the conductance.

2. Electrophoretic effect: After the application of the external electric field, the reference ion and ionic could move in opposite directions. During the course of this movement, the solvent associated with the surrounding ions also moves in a direction opposite to the central ion. In other words, we can say that the reference ion has to move against a solvent stream, which makes it somewhat slower than usual. This phenomenon is called as the electrophoretic effect.

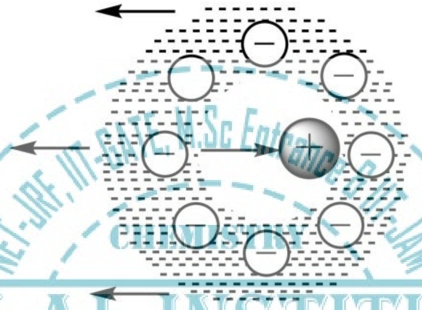


Figure 16. The asymmetric or relaxation effect in the conductance of strong electrolytes.

Since the electrophoretic effect reduces the speed of the ion, the conductance of the electrolytic solution is also affected considerably.

3. Viscous Effect: In addition to the asymmetric and electrophoretic effects, another type of resistance also exists which affects the conductance of electrolytic solutions, the "viscous effect". This is simply the frictional resistance created by the viscosity of the solvent used. For an ion of given charge and size, the ionic mobility as well the conductance decrease with the increase in the magnitude of the viscosity of the solvent used. In other words, less viscous solvents yield higher conductance and vice-versa.

➢ *Mathematical Development of Debye-Huckel-Onsager theory of Strong Electrolytes*

It is a well-known fact that the equivalent conductivity (Λ) of an electrolytic solution is correlated to the ionic mobilities (u) ions involved as

$$\Lambda = F(u_+ + u_-) \tag{176}$$

Where F is the Faraday constant. Now, recall the ionic mobilities of the cation and anion i.e.

$$u_+ = u_+^0 - \kappa\left(\frac{Z_+e_0}{6\pi\eta} + \frac{e_0^2\omega}{6\varepsilon kT}u_+^0\right) \tag{177}$$

$$u_- = u_-^0 - \kappa\left(\frac{Z_- e_0}{6\pi\eta} + \frac{e_0^2\omega}{6\varepsilon kT}u_-^0\right) \tag{178}$$

Where u_+^0 and u_-^0 are the ionic mobilities of the cation and anions at infinite dilution, respectively. The symbol ε represents the dielectric constant of the medium whereas η is the coefficient of viscosity. Z_+ and Z_- are charge numbers of the cation and anion, respectively. The symbol e_0 simply shows the electronic charge. The symbol κ represents (n_i^0 is the bulk concentration)

$$\kappa = \left(\frac{4\pi}{\varepsilon kT}\sum_i n_i^0 Z_i^2 e_0^2\right)^{1/2} = \left(\frac{4\pi Z^2 e_0^2 c}{\varepsilon kT}\right)^{\frac{1}{2}}\left(\frac{N_A}{1000}\right)^{1/2} \tag{179}$$

The quantity ω is defined as

$$\omega = \frac{Z_+Z_-2q}{1+\sqrt{q}} \quad where \quad q = \frac{Z_+Z_-}{Z_+ + Z_-}\frac{\lambda_+ + \lambda_-}{Z_+\lambda_+ + Z_-\lambda_-} \tag{180}$$

After putting the values of u_+ and u_- from equation (177) and (178) in equation (176), we get

$$\Lambda = F\left[u_+^0 - \kappa\left(\frac{Z_+e_0}{6\pi\eta} + \frac{e_0^2\omega}{6\varepsilon kT}u_+^0\right)\right] + F\left[u_-^0 - \kappa\left(\frac{Z_-e_0}{6\pi\eta} + \frac{e_0^2\omega}{6\varepsilon kT}u_-^0\right)\right] \tag{181}$$

In the case of symmetrical electrolytes, we can put $Z_+ = Z_- = Z$, and therefore $Z_+ + Z_- = 2Z$. Thus, the above equation for such cases takes the form

$$\Lambda = F(u_+^0 + u_-^0) - \left[\frac{FZ\kappa e_0}{3\pi\eta} + \frac{e_0^2\omega k}{6\varepsilon kT}F(u_+^0 + u_-^0)\right] \tag{182}$$

Since $F(u_+^0 + u_-^0) = \Lambda^0$, the equation (182) becomes

$$\Lambda = \Lambda^0 - \left[\frac{FZ\kappa e_0}{3\pi\eta} + \frac{e_0^2\omega k}{6\varepsilon kT}\Lambda^0\right] \tag{183}$$

Now expending above equation further by putting the value of κ from equation (179), we get

$$\Lambda = \Lambda^0 - \left[\frac{FZe_0}{3\pi\eta}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} + \frac{e_0^2\omega}{6\varepsilon kT}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}}\Lambda^0\right]\sqrt{c} \tag{184}$$

Define two constant A and B as

$$A = \frac{FZe_0}{3\pi\eta}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} \quad and \quad B = \frac{e_0^2\omega}{6\varepsilon kT}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} \tag{185}$$

Therefore, the equation (184) can be simplified as

$$\Lambda = \Lambda^0 - (A + B\Lambda^0)\sqrt{c} \tag{186}$$

or

$$\Lambda = \Lambda^0 - constant\sqrt{c} \tag{187}$$

The equation (184) and equation (186) are the popular forms famous Debye-Huckel-Onsager equation for electrolyte solutions. The constants *A* and *B* can easily be determined from the knowledge of temperature T, valence type of the electrolyte z, the viscosity of the medium, the dielectric constant and other universal constants like Avogadro number. From Equation (187), it is obviously a straight line equation which means the for symmetrical electrolytic solutions, we can plot the conductance vs square root of the concentration for which the slope will be negative. The intercept after extrapolation gives the value of conductance of such solutions at infinite dilution.

- ***Limitations of Debye-Huckel-Onsager Equation***

Since the plot of conductance vs square root of the concentration is linear with negative slope and positive intercept, it seems quite straightforward to study the strong electrolytes. However, it has been observed that the equation (187) is followed only up low and moderate concentrations.

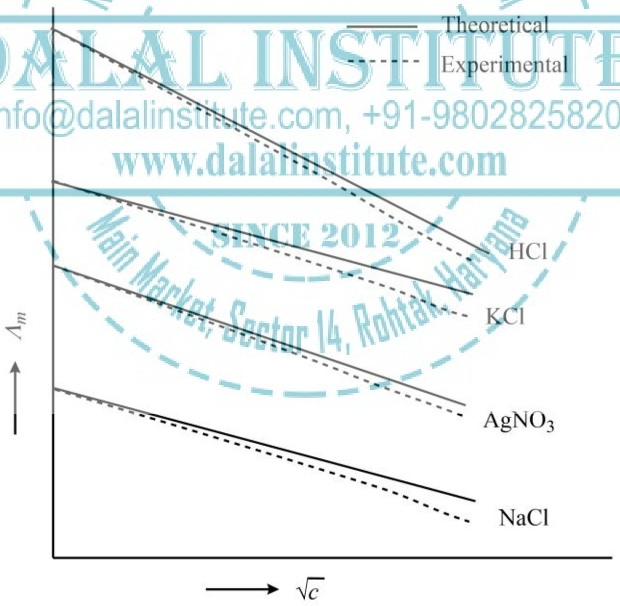


Figure 17. The comparison of theoretical and experimental conductance as a function of concentration for some symmetric electrolytes.

It can be clearly seen that the theory and experiment move apart as the concentration increases. This is simply because some approximation used to derive are Debye-Huckel-Onsager equation are not valid.

❖ Debye-Huckel-Onsager Theory for Non-Aqueous Solutions

Before we discuss the Debye-Huckel-Onsager theory for non-aqueous solutions, recall the same for aqueous solutions i.e.

$$\Lambda = \Lambda^0 - constant\sqrt{c} \tag{187}$$

or

$$\Lambda = \Lambda^0 - (A + B\Lambda^0)\sqrt{c} \tag{188}$$

Where the two constants, *A* and *B*, are defined as

$$A = \frac{FZe_0}{3\pi\eta}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} \tag{189}$$

and

$$B = \frac{e_0^2\omega}{6\varepsilon kT}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} \tag{190}$$

Where F is the Faraday constant and N_A is the Avogadro number. The symbol ε represents the dielectric constant of the medium whereas η is the coefficient of viscosity. Z is charge numbers of the cation and anion. The symbol e_0 simply shows the electronic charge. The quantity ω is defined as

$$\omega = \frac{Z_+Z_-2q}{1+\sqrt{q}}$$

Where q is defined as

$$q = \frac{Z_+Z_-}{Z_+ + Z_-}\frac{\lambda_+ + \lambda_-}{Z_+\lambda_+ + Z_-\lambda_-}$$

it is obvious from the Debye-Huckel-Onsager equation that the plot of conductance vs square root of the concentration will be a straight line with a negative slope and positive intercept. The intercept after extrapolation gives the value of conductance of such solutions at infinite dilution.

Now, it has been observed that the Debye-Huckel-Onsager equation can also be applied to non-aqueous solutions up to the fairly good agreement. For instance, consider the variation of equivalent conductivity as a function of the square root of the concentration for different alkali sulfocyanates in methanol as the solvent. The theoretical predictions show that the results of the Debye-Hückel-Onsager equation are in good agreement with the experiment up to 0.002 mol dm^{-3}.

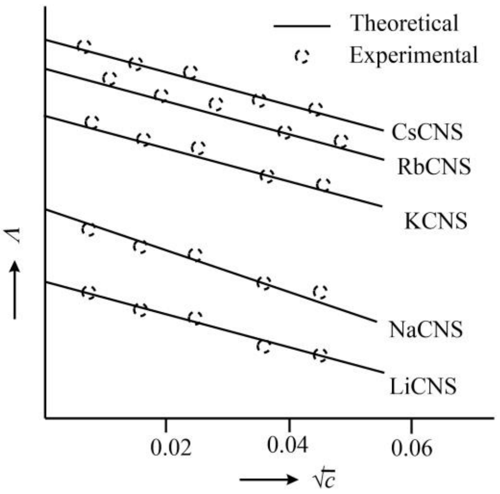


Figure 18. The variation of equivalent conductivity of alkali sulfocyanates vs $c^{1/2}$ in CH_3OH.

In going from water to nonaqueous solvent, a significant variation in the quantities like dielectric constant of the medium, the distance of the closest approach, or viscosity is observed. Now since the Debye-Hückel-Onsager equation does have these quantities, the slope and intercept of the Λ vs $c^{1/2}$ may also vary drastically.

❖ The Solvent Effect on the Mobility at Infinite Dilution

As we know that the asymmetry and electrophoretic effects are not active at infinite dilution because of their dependence on the size of ionic-cloud, the mobility of ions in such cases can be formulated simply from the Stokes law, i.e.,

$$u_{con}^{0} = \frac{Ze_0}{6\pi\eta r} \tag{191}$$

Where r represents the radius of the solvated ion and η is the coefficient of viscosity. Z is charge numbers of the cation and anion. The symbol e_0 simply shows the electronic charge. Now, if we imagine the same electrolyte in different electrolytic solutions, we can say

$$u_{con}^{0}\eta r = constant \tag{192}$$

Assuming further that the r is also independent of solvent type, we have

$$u_{con}^{0}\eta = constant \tag{193}$$

Thus, it is obvious from the equation (193) that ionic mobility is inversely proportional to the coefficient of viscosity. More viscous solvents would result in a slow drift of ions and vice-versa. It has also been found that the equation (193) is more valid for solvents other than water.

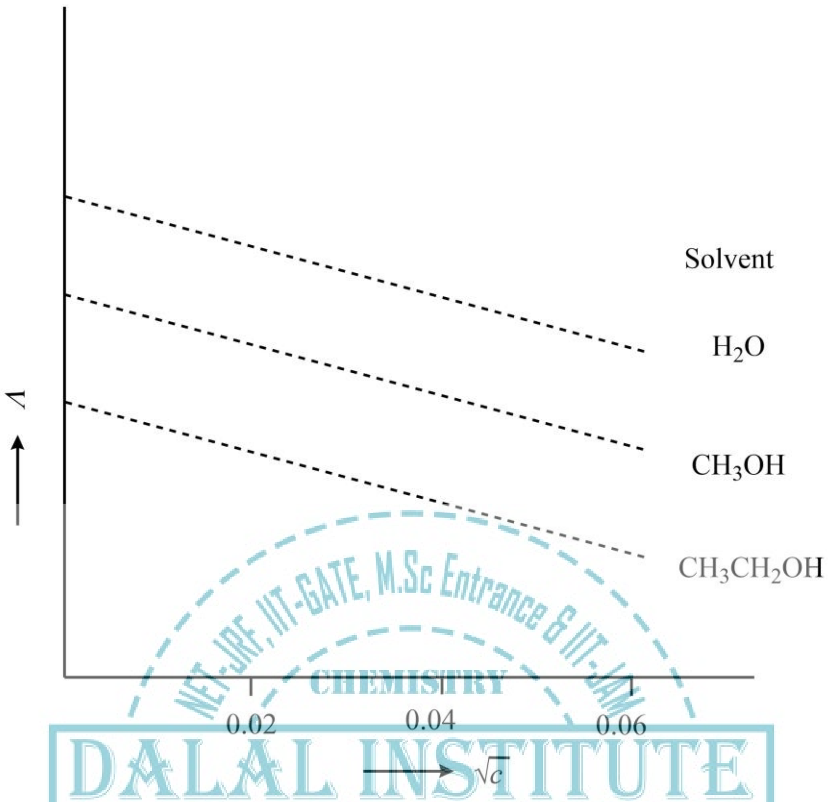


Figure 19. The variation of equivalent conductivity vs $c^{1/2}$ in different solvents.

Moreover, the radius of solvated ion may vary drastically in going from one solvent to another (in some cases it gets even double), the result of equation (193) does not find a very large application domain. This variation in the solvated radius is primarily due to the difference in the size of solvent molecules. For instance, the size of the solvated ion is larger in ethanol than in methanol, which in turn, is larger than what is observed in water. All this results in an opposite trend in the ionic mobilities, and therefore, in the equivalent conductivities as well. Recalling the simple Walden's rule i.e.

$$\Lambda\eta = constant \tag{194}$$

Where Λ is the equivalent conductivity of the electrolytic solution at concentration c. This simply means that equivalent conductivity and the viscosity of the solvent are inversely proportional to each other. However, the effect of the solvated radius must be considered for more accurate results. Therefore, we must more acceptable form of Walden's rule, i.e.,

$$u^0\eta r = constant \tag{195}$$

The symbol r represents the radius of the ionic species considered in the solvent under examination.

❖ Equivalent Conductivity (Λ) vs Concentration $C^{1/2}$ as a Function of the Solvent

In order to understand the variation of equivalent conductivity with the square root of concentration for different solvents, recall the generalized Walden's rule, i.e.,

$$u^0\eta r = constant \tag{196}$$

The u^0 is the ionic mobility at infinite dilution and symbol r represents the radius of the ionic species considered in the solvent under examination. The symbol η represents the coefficient of viscosity of the solvent used. Also, as we know that the equivalent conductivity at infinite dilution can be obtained from the relation given below.

$$\Lambda^0 = Fu^0 \tag{197}$$

Now, if the ionic mobility obtained using equation (196) is used in equation (197) for different nonaqueous solutions, it has been found that predicted values of equivalent conductivity are quite large and sometimes even outnumber the equivalent conductivity in water as the solvent. All this suggests that there should be no problem in using non-aqueous solutions in electrochemical systems. However, the quantity that is more important for practical applications is the specific conductivity (σ) at a finite concentration rather than the equivalent conductivity at infinite dilution. In other words, the conjugative relationship of electrode geometry and specific conductivity dictates the overall electrolytic resistance of the system under consideration. At this point, one might ask why the electrolytic resistance is important. The answer lies in the fact that the magnitude of useful power wasted as heat in the electrolytic solution is I^2R (I is the current passed); and therefore, it is the electrolytic resistance that R must possess a lower value for feasibility. The lower value of R implies a higher value of specific conductivity, and the relation of specific conductivity with equivalent conductivity at a certain concentration 'c' is

$$\sigma = \Lambda Zc \tag{198}$$

Now since the equivalent conductance Λ also depends on concentration, we cannot use equivalent conductance at infinite dilution in equation (198) to find out the specific conductivity. First of all, one must determine the equivalent conductivity at concentration 'c', which is possible from the Debye-Huckel-Onsager equation if the values of constants A and B are known. Hence, to proceed further, we must recall the Debye-Huckel-Onsager equation for the non-aqueous solution first, i.e.,

$$\Lambda = \Lambda^0 - (A + B\Lambda^0)\sqrt{c} \tag{199}$$

Where the two constants, A and B, are defined as

$$A = \frac{FZe_0}{3\pi\eta}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} \tag{200}$$

$$B = \frac{e_0^2\omega}{6\varepsilon kT}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} \tag{201}$$

Where F is the Faraday constant and N_A is the Avogadro number. The symbol ε represents the dielectric constant of the medium whereas η is the coefficient of viscosity. Z is charge numbers of the cation and anion. The symbol e_0 simply shows the electronic charge. ω is a parameter defined earlier in this chapter.

Figure 20. The variation of equivalent conductivity vs $c^{1/2}$ in any arbitrary solvent.

It can be clearly seen that both the constants in the slope have the dielectric constant ε in the denominator, and therefore, the equivalent conductivity as well as specific conductivity show decrease with the increasing ε. In other words, we can say that the lower dielectric constant would result in stronger ion-ion interaction and vice-versa. Therefore, in the case of non-aqueous solvents with very low dielectric constants, the relative variation in the magnitude of equivalent conductivity with the square root of the concentration is very large. Consequently, all this result in a very low specific conductivity at any practical electrolytic concentration in non-aqueous solution than in water. Furthermore, in addition to the larger electrolytic resistance, non-aqueous solutions are hard to keep so because they can always absorb some moisture from the atmosphere.

❖ Effect of Ion Association Upon Conductivity (Debye-Huckel-Bjerrum Equation)

According to the Debye-Huckel theory of ion-ion interaction, the ions produced by the dissociation of electrolytes are randomly distributed in the solution with oppositely charged ionic-cloud surrounding them. Nevertheless, the possibility that some negative ions might get very close to the positively charged reference ion was neglected. In such a situation, the translational thermal energy would not be enough to make the ions to move independently, and an ionic-pair may be formed. Being a combined entity of two equal and opposite charges, these ion pairs are completely neutral and distributed randomly in the electrolytic solutions. These neutral ion-pairs are not influenced by the reference ion under consideration. Therefore, the fraction of ions participating in these ion pairs must be obtained for a more accurate picture of the electrochemical properties of the solutions.

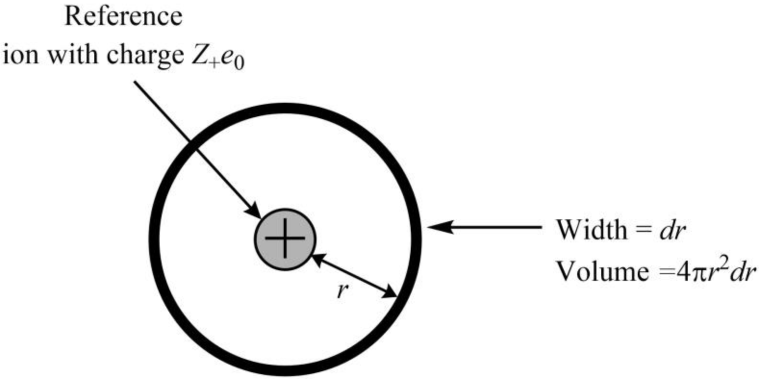


Figure 21. The probability of finding an oppositely charged ion i.e. Z_-e_0 at distance r in dr thickness around the reference ion.

In order to understand the concept, imagine a spherical shell at a distance r from the reference ion with dr thickness. The probability of finding the anion (P_r) in the spherical shell is proportional to three main factors. The first one is the ratio $4\pi r^2$dr volume element to the total volume V, the second one is the total number of anions i.e. N_- and the third is the $e^{-U/kT}$ (U represents the potential energy of anion situated at distance r). Mathematically, we can formulate this as

$$P_r = \left(\frac{4\pi r^2 dr}{V}\right)(N_-)\left(e^{-U/kT}\right) \tag{202}$$

Now because N_-/V represents the anions' concentration n_-^0, the above equation takes the form

$$P_r = 4\pi r^2 dr\, n_-^0 e^{-U/kT} \tag{203}$$

Furthermore, after recalling the value of U, i.e.,

$$U = -\frac{Z_+Z_-e_0^2}{\varepsilon r} \tag{204}$$

Equation (203) becomes

$$P_r = 4\pi r^2\, n_-^0 e^{Z_+Z_-e_0^2/\varepsilon rkT} dr \tag{205}$$

Where *ε* is the dielectric constant of the medium and e_0 is the electronic charge. Now define a new parameter λ as

$$\lambda = \frac{Z_+Z_-e_0^2}{\varepsilon kT} \tag{206}$$

Therefore, we can write

$$P_r = (4\pi\, n_-^0)e^{\lambda/r} r^2 dr \tag{207}$$

Similarly, the probability of finding a positively charged ion at distance *r* in *dr* thickness around a negatively charged reference ion will be

$$P_r = (4\pi\, n_+^0)e^{\lambda/r} r^2 dr \tag{208}$$

Therefore, the probability of finding *i*th type of ion at distance *r* in *dr* thickness around a *k*th type of reference ion can be formulated as

$$P_r = (4\pi\, n_i^0)e^{\lambda/r} r^2 dr \tag{208}$$

where

$$\lambda = \frac{Z_iZ_ke_0^2}{\varepsilon kT} \tag{209}$$

The variation of probability of finding one type ion around other types shows a strange behavior with distance.

Table 1. The total number of oppositely charged ions as a function of distance.

r (pm)	Number of ions in shell × 10^{22}
200	1.77
250	1.37
300	1.22
350	1.17
400	1.21

When r varies from very small to moderate value, the magnitude of P_r decreases because of the factor $e^{\lambda/r}$. However, after a certain value, the probability starts to rise due to the dominance of the directly correlated factor of r^2. Hence, we can say that the probability of finding the oppositely charged ion at distance r from the reference ion first decreases and then increases as we move away from the central ion.

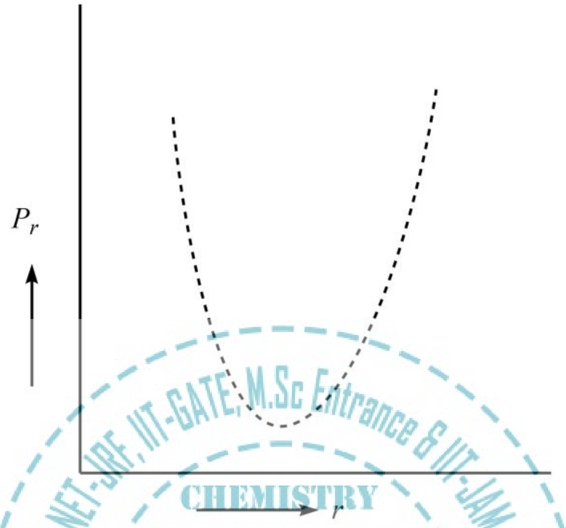


Figure 22. The variation of the overall probability of finding an ion around ion under consideration as a function of distance.

Since the probability of finding a negative ion within a certain distance around a positive ion is obtained by applying the lower and upper bounds, we need to find these limits first. Now, because the ion-pair can be formed only if the participating ions close enough so that the electrostatic attraction can outshine the thermal forces; let this distance be represented by q.

In other words, we can say that the formation of ion-pair takes place only if the separation between the cation and anion is less than q. Since the cation and anion cannot approach each other closer than the ionic-size parameter (a), i.e., (the distance of closest approach), the ion-pair will be formed for an interionic separation of greater than a but less than q. The probability of the ion-pair formation is the number of ith type of ion participating in the ion-association to the total number of the same type of ions. Therefore, the probability of ion-pair formation (θ) can be formulated as

$$\theta = \int_a^q P_r dr = \int_a^q (4\pi\, n_i^0) e^{\lambda/r} r^2 dr \tag{210}$$

Owing to the divergent nature of the integral, the upper limit can be set to the overall probability minima (q) as shown below.

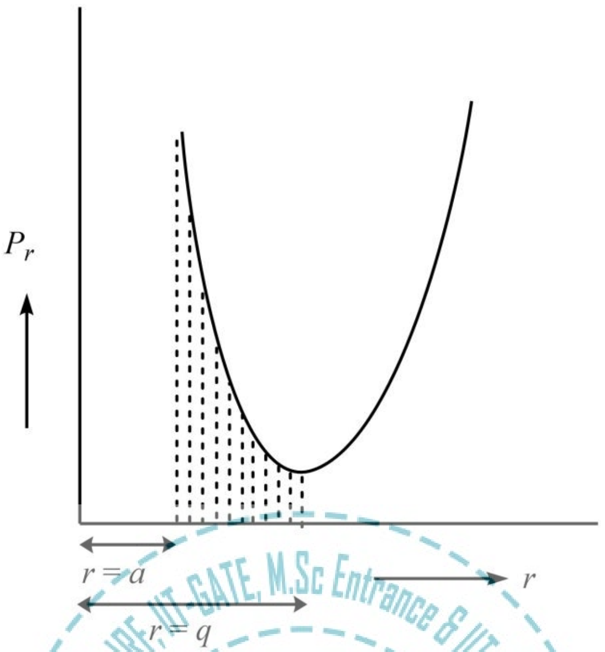


Figure 23. The depiction of the overall probability of finding an oppositely charged ion around reference ion from *a* to *q*.

To find the minima, differentiate equation (208) with respect to *r* and then put equal to zero, i.e.,

$$\frac{dP_r}{dr} = 4\pi\, n_i^0 e^{\frac{\lambda}{r}}\, 2r - 4\pi\, n_i^0\, r^2 e^{\frac{\lambda}{r}} \frac{\lambda}{r^2} \tag{211}$$

or

$$2r_{min} - \lambda = 0 \tag{212}$$

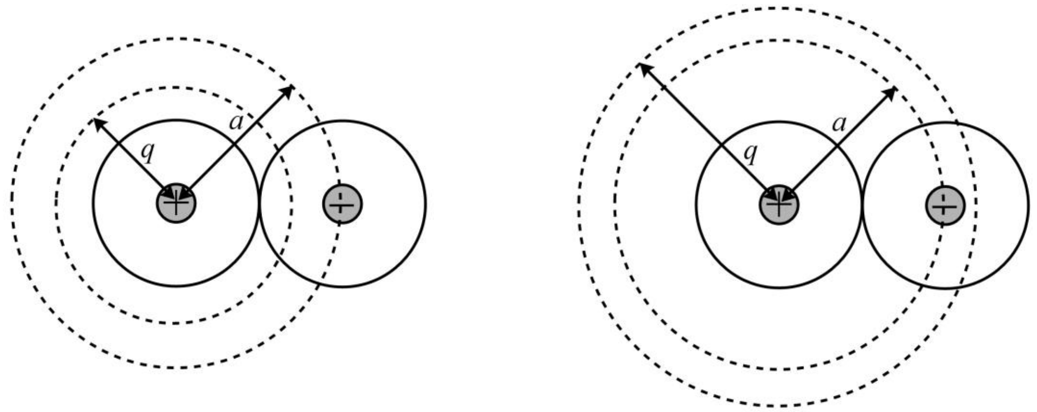
or

$$q = r_{min} = \frac{\lambda}{2} \tag{213}$$

After putting the value of λ from equation (206) into (213), we get

$$q = \frac{Z_+ Z_- e_0^2}{2\varepsilon kT} \tag{214}$$

Bjerrum claimed that only Coulombic interactions (short-range) lead to the formation of ion-pair; and if the separation of cation and anion larger than *q*, they should be treated as free ions. In other words, we can say that the formation of ion-pair is feasible if *a* < *q* and infeasible if *a* > *q*.



$a > q$
Ion-pair formation in not possible

$a < q$
Ion-pair formation in possible

Figure 24. The pictorial representation of ion-pair in the electrolytic solution.

Using the upper limit as $q = \lambda/2$, the probability of ion-pair formation (θ) becomes

$$\theta = 4\pi\, n_i^0 \int_a^{\lambda/2} e^{\lambda/r} r^2\, dr \tag{215}$$

At this stage, after define a new variable for simplicity $y = \lambda/r = 2q/r$ and a new constant $b = \lambda/a$, the above equation takes the form

$$\theta = 4\pi\, n_i^0 \left(\frac{Z_+ Z_- e_0^2}{\varepsilon kT}\right)^3 \int_2^b e^y y^{-4}\, dy \tag{216}$$

Hence, using the above equation we can easily determine the fraction of the ions reserved in pairing and cannot move freely. Nevertheless, it would be more beneficial if we could use some other simple number to quantify the magnitude of ion-pair formation instead of θ.

From the Arrhenius theory of electrolytic dissociation, we know that the A^+B^- type electrolyte would give monovalent cations and anions in water i.e.

$$AB \rightleftharpoons A^+ + B_- \tag{217}$$

Using the law of mass action, the dissociation constant can be given as

$$K = \frac{a_A^+ a_B^-}{a_{AB}} \tag{218}$$

Similarly, if a cation M^+ and anion A^- form an ion-pair i.e.

$$M^{+} + A^{-} \rightleftharpoons IP \tag{219}$$

The law of mass action can also be used to give association constant as

$$K_A = \frac{a_{IP}}{a_M^{+} a_A^{-}} \tag{220}$$

Where a_M^{+}, a_A^{-} and a_{IP} are the activities of the cation, anion and ion-pair, respectively. Moreover, it can also be seen that the association constant is just the reciprocal of dissociation constant. Now, θ is the fraction of ions forming ion-pair, whereas θc and $(1-\theta)c$ are the concentrations of ion-pair and free ions, respectively. Therefore, the association constant in terms of activity coefficients can be written as

$$K_A = \frac{\theta c f_{IP}}{(1-\theta)cf_{+}(1-\theta)cf_{-}} \tag{221}$$

or

$$K_A = \frac{\theta}{(1-\theta)^2}\frac{1}{c}\frac{f_{IP}}{f_{+}f_{-}} \tag{222}$$

Where f_+, f_- and f_{IP} are the activity coefficients for cation, anion and ion-pair, respectively. In terms of mean ionic activity coefficient and analytical concentration c_a, the equation (222) can also be written as

$$K_A = \frac{\theta}{(1-\theta)^2}\frac{1}{c_a}\frac{f_{IP}}{f_{\pm}^2} \tag{223}$$

Now because the ion pairs are neutral species, and therefore, do not participate in ion-ion interactions; the activity coefficients ion-pairs can be taken as unity. Therefore, equation (223) can be written as

$$K_A = \frac{\theta}{(1-\theta)^2}\frac{1}{c_a}\frac{1}{f_{\pm}^2} \tag{224}$$

or

$$\theta = K_A(1-\theta)^2 c_a f_{\pm}^2 \tag{225}$$

At this stage, the only thing that is needed for further treatment is the relation between θ and the conductivity of the electrolyte used. To do so, recall the correlation between the concentration of free ions and specific conductivity (σ) i.e.

$$\sigma = ZF(u_{+} + u_{-})c_{free\ ions} \tag{226}$$

Where F is the Faraday constant.

$$\sigma = ZF(u_{+} + u_{-})\frac{c_{free\ ions}}{c_a}c_a \tag{227}$$

The term $c_{free\ ions}/c_a$ is the fraction of ions that are free (not associated), and therefore

$$\frac{c_{free\ ions}}{c_a} = 1 - \theta \tag{228}$$

Using the result of equation (228) in equation (227), we get

$$\sigma = ZF(u_+ + u_-)(1 - \theta)c_a \tag{229}$$

Furthermore, after converting the specific conductivity to equivalent conductivity ($\Lambda = \sigma/Zc_a$), the equation (229) takes the form

$$\Lambda = F(u_+ + u_-)(1 - \theta) \tag{230}$$

Imagine a situation if no ion-association occurs ($\theta = 0$), then the equation (230) would reduce to

$$\Lambda_{\theta=0} = F(u_+ + u_-) \tag{231}$$

Using equation (231) in equation (230), we get

$$\Lambda = \Lambda_{\theta=0}(1 - \theta) \tag{232}$$

or

$$\frac{\Lambda}{\Lambda_{\theta=0}} = 1 - \theta \tag{233}$$

or

$$\theta = 1 - \frac{\Lambda}{\Lambda_{\theta=0}} \tag{234}$$

Now putting the values of θ and 1−θ from equation (234) and (233) in equation (225), we have

$$1 - \frac{\Lambda}{\Lambda_{\theta=0}} = K_A\left(\frac{\Lambda}{\Lambda_{\theta=0}}\right)^2 c_a f_\pm^2 \tag{235}$$

Rearranging, we get

$$\frac{1}{\Lambda} = \frac{1}{\Lambda_{\theta=0}} + \frac{K_A f_\pm^2}{\Lambda_{\theta=0}^2}\Lambda c_a \tag{236}$$

Rearranging equation (229) for $F(u_+ + u_-)$ and putting in equation (231), we get

$$\Lambda_{\theta=0} = F(u_+ + u_-) = \frac{\sigma}{Z(1 - \theta)c_a} \tag{237}$$

The above equation shows equivalent conductivity at zero ion-association at $(1-\theta)c_a$ concentration. Therefore, we must use Debye-Huckel-Onsager equation to express the more appropriate conductivity at small concentrations i.e.

$$\Lambda_{\theta=0} = \Lambda^0 - (A + B\Lambda^0)\sqrt{1-\theta}\sqrt{c_a} \tag{238}$$

Where the two constants, A and B, are defined as

$$A = \frac{FZe_0}{3\pi\eta}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} \quad and \quad B = \frac{e_0^2\omega}{6\varepsilon kT}\left(\frac{8\pi Z^2 e_0^2 N_A}{1000\varepsilon kT}\right)^{\frac{1}{2}} \tag{239}$$

Where F is the Faraday constant and N_A is the Avogadro number. The symbol ε represents the dielectric constant of the medium whereas η is the coefficient of viscosity. Z is charge numbers of the cation and anion. The symbol e_0 simply shows the electronic charge. ω is a parameter defined earlier in this chapter. The equation (238) can be simplified as

$$\Lambda_{\theta=0} = \Lambda^0 W \tag{240}$$

Where W represents a continued fraction i.e.

$$W = 1 - w\left\{1 - w\left[1 - w(\dots)^{-1/2}\right]^{-1/2}\right\}^{-1/2} \tag{241}$$

Provided that

$$w = \frac{(A + B\Lambda^0)\sqrt{c_a}\sqrt{\Lambda}}{(\Lambda^0)^{3/2}} \tag{242}$$

Using the result of equation (240) into (236), we get

$$\frac{1}{\Lambda} = \frac{1}{\Lambda^0 W} + \frac{K_A f_\pm^2}{(\Lambda^0 W)^2}\Lambda c_a \tag{243}$$

or

$$\frac{W}{\Lambda} = \frac{W}{\Lambda^0} + \frac{K_A}{(\Lambda^0)^2}\frac{f_\pm^2 \Lambda c_a}{W} \tag{244}$$

After looking at the above equation, it is obvious that the formation of ion-pairs has changed the variation of equivalent conductivity with concentration drastically. When the formation of ion-pairs was ignored, the variation of equivalent conductivity with concentration was empirically explained by the Kohlrausch's law.

Nevertheless, in the case of non-aqueous solvents with low dielectric constant, a significant amount of ion-pair formation occurs, and therefore, W/Λ is plotted vs $f_\pm^2\Lambda c_a/W$ with W/Λ^0 as intercept and $K_A/(\Lambda^0)^2$ as slope.

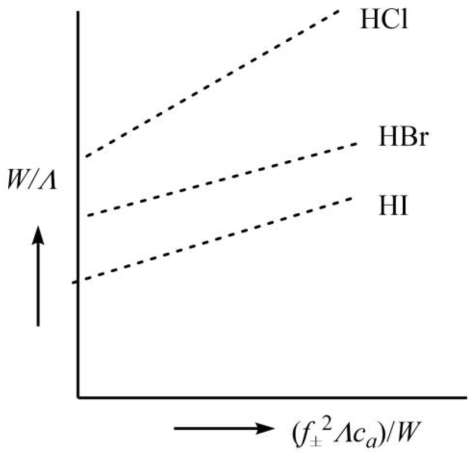


Figure 25. The variation of W/Λ is plotted vs $f_{\pm}^{2}\Lambda c_a/W$ for some typical electrolytic solutions.

❖ Problems

Q 1. Discuss the Debye-Huckel theory of ion-ion interaction in detail.

Q 2. What is excess charge density? How does it vary with the distance from the central ion?

Q 3. Define Debye-Huckel reciprocal length.

Q 4. Derive the expression for the contribution of the ionic cloud to the total potential at a particular distance from the reference ion in strong electrolytes.

Q 5. State and explain the Debye-Huckel limiting law of activity coefficient. Also, discuss its limitations.

Q 6. What is the ion-size parameter? How does it affect total potential around the central ion?

Q 7. Discuss the asymmetry effect in the conductance of strong electrolytes?

Q 8. Derive and discuss the Debye-Huckel-Onsager equation for aqueous solutions.

Q 9. Discuss the effect of the nature of the solvent on the ionic mobility at infinite dilution.

Q 10. How does the equivalent conductivity vary with the square root of the concentration if the dielectric constant of the solvent is very low?

Q 11. Define ion-association in strong electrolytic solutions. How does this affect overall conductivity?

❖ Bibliography

[1] J. Bockris, A. Reddy, *Modern Electrochemistry – Volume 1: Ionics*, Kluwer Academic Publishers, New York, USA 2002.

[2] B. R. Puri, L. R. Sharma, M. S. Pathania, *Principles of Physical Chemistry*, Vishal Publications, Jalandhar, India, 2008.

[3] P. Atkins, J. Paula, *Physical Chemistry*, Oxford University Press, Oxford, UK, 2010.

[4] E. Steiner, *The Chemistry Maths Book*, Oxford University Press, Oxford, UK, 2008.

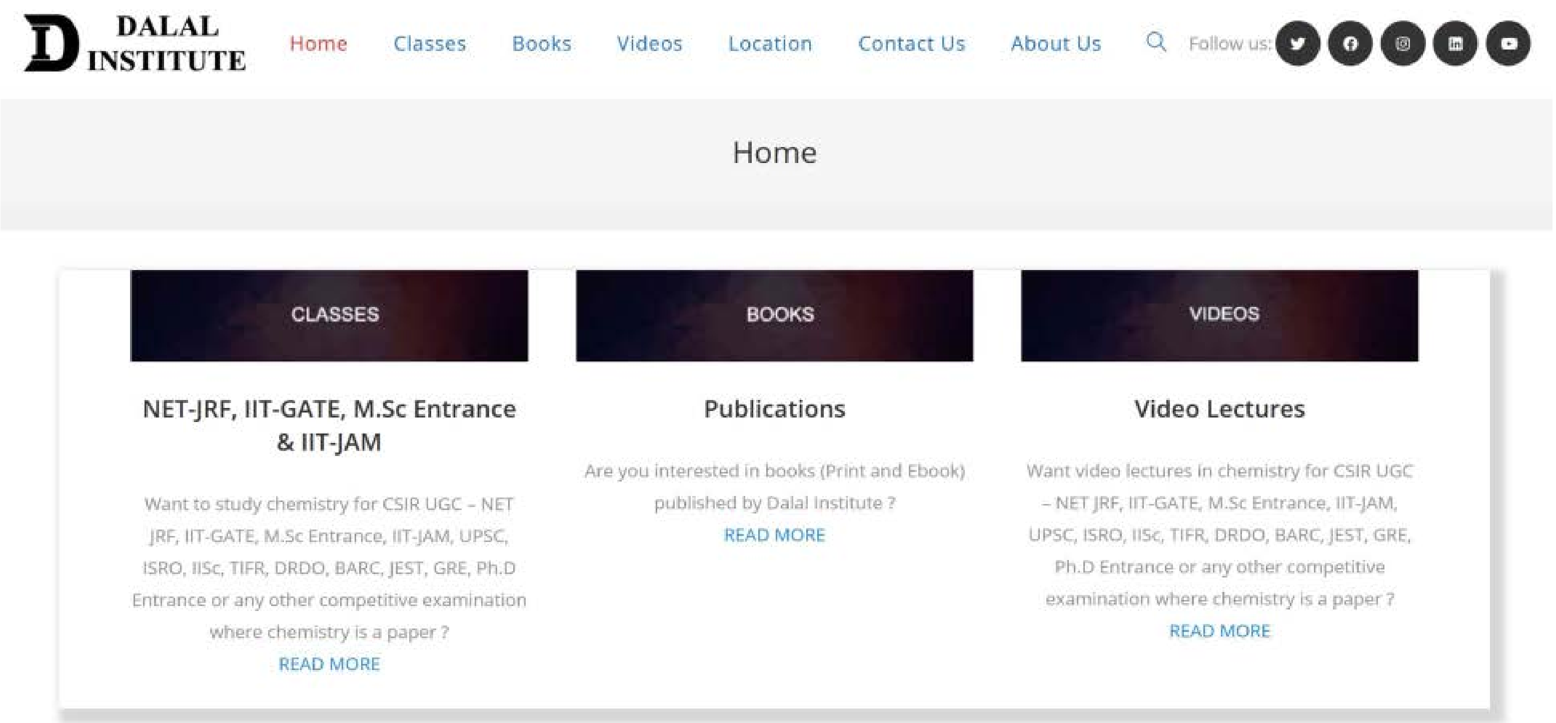
[5] M. R. Wright, *An Introduction to Aqueous Electrolyte Solutions*, John Wiley & Sons Ltd, Sussex, UK, 2007.

[6] P. Debye, E. Hückel, *The Theory of Electrolytes. I. Lowering of Freezing Point and Related Phenomena*, Physikalische Zeitschrift., 24 (1923) 185-206.

[7] V. S. Bagotsky, *Fundamentals of Electrochemistry*, John Wiley & Sons, New Jersey, USA, 2006.

[8] R.R. Netz, H. Orland, *Beyond Poisson-Boltzmann: Fluctuation effects and correlation functions*, The European Physical Journal E, 1 (2000) 203-214.

LEGAL NOTICE



NET-JRF, IIT-GATE, M.Sc Entrance & IIT-JAM

Want to study chemistry for CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

Publications

Are you interested in books (Print and Ebook) published by Dalal Institute ?

Video Lectures

Want video lectures in chemistry for CSIR UGC – NET JRF, IIT-GATE, M.Sc Entrance, IIT-JAM, UPSC, ISRO, IISc, TIFR, DRDO, BARC, JEST, GRE, Ph.D Entrance or any other competitive examination where chemistry is a paper ?

Home: https://www.dalalinstitute.com/
Classes: https://www.dalalinstitute.com/classes/
Books: https://www.dalalinstitute.com/books/
Videos: https://www.dalalinstitute.com/videos/
Location: https://www.dalalinstitute.com/location/
Contact Us: https://www.dalalinstitute.com/contact-us/
About Us: https://www.dalalinstitute.com/about-us/

Postgraduate Level Classes
(NET-JRF & IIT-GATE)
Admission
Regular Program Distance Learning
Test Series Result

Undergraduate Level Classes
(M.Sc Entrance & IIT-JAM)
Admission
Regular Program Distance Learning
Test Series Result

A Textbook of Physical Chemistry – Volume 1

"A Textbook of Physical Chemistry – Volume 1 by Mandeep Dalal" is now available globally; including India, America and most of the European continent. Please ask at your local bookshop or get it online here.
READ MORE

Join the revolution by becoming a part of our community and get all of the member benefits like downloading any PDF document for your personal preview.

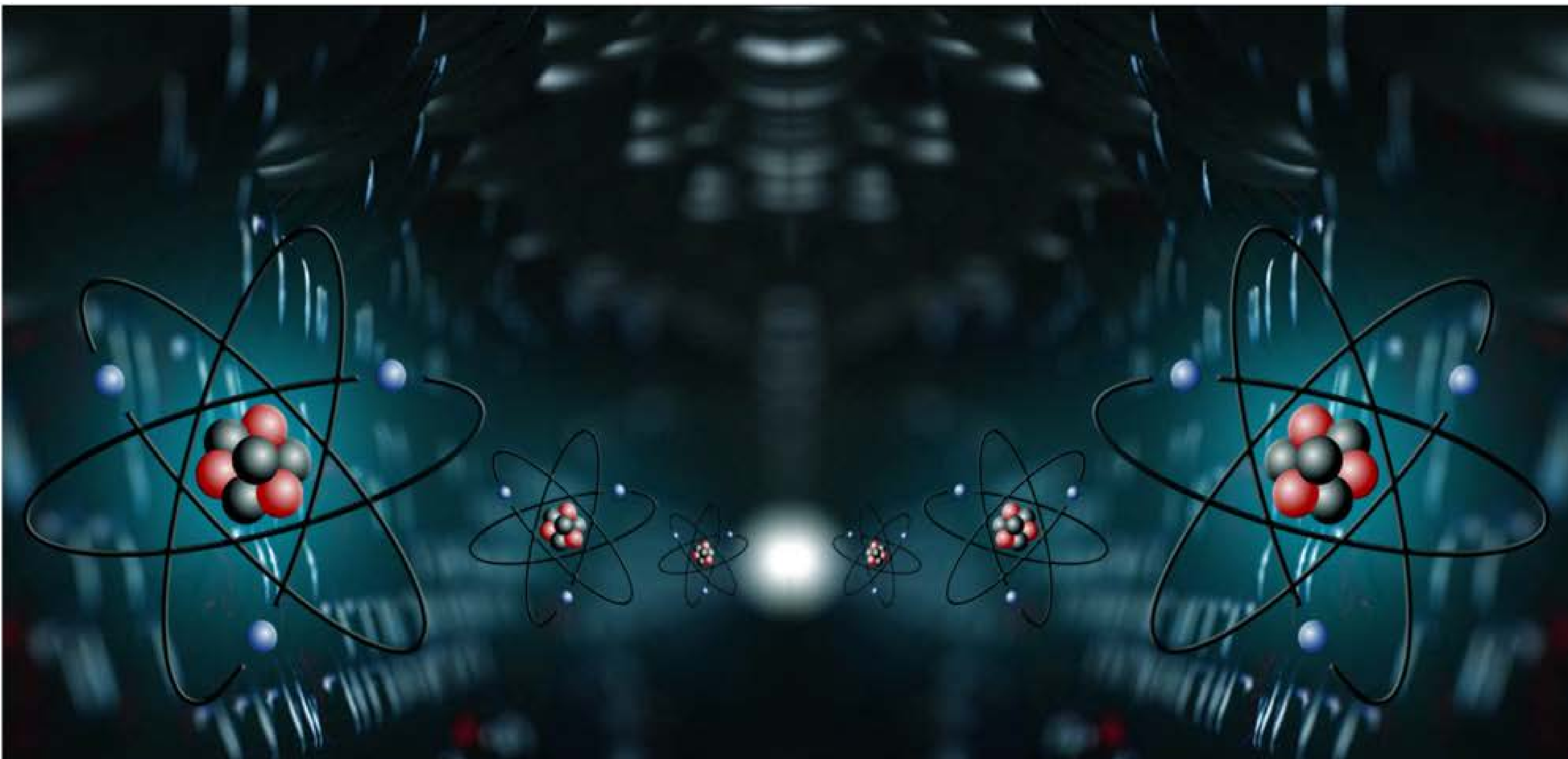
Sign Up

International
Edition

A TEXTBOOK OF PHYSICAL CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

DALAL INSTITUTE

Table of Contents

Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

Mandeep Dalal is an Indian research scholar who is primarily working in the field of Science and Philosophy. He received his Ph.D in Chemistry from Maharshi Dayanand University, Rohtak, in 2018. He is also the Founder and Director of "Dalal Institute", an India-based educational organization which is trying to revolutionize the mode of higher education in Chemistry across the globe. He has published more than 40 research papers in various international scientific journals, including mostly from Elsevier (USA), IOP (UK) and Springer (Netherlands) .

Other Books by the Author

A TEXTBOOK OF INORGANIC CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF PHYSICAL CHEMISTRY - VOLUME I, II, III, IV

A TEXTBOOK OF ORGANIC CHEMISTRY - VOLUME I, II, III, IV

ISBN: 978-81-938720-1-7
9 788193 872017 >
MRP: Rs 800.00

DALAL INSTITUTE
Main Market, Sector-14, Rohtak, Haryana-124001
(+91-9802825820, info@dalalinstitute.com)
www.dalalinstitute.com