❖ 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.

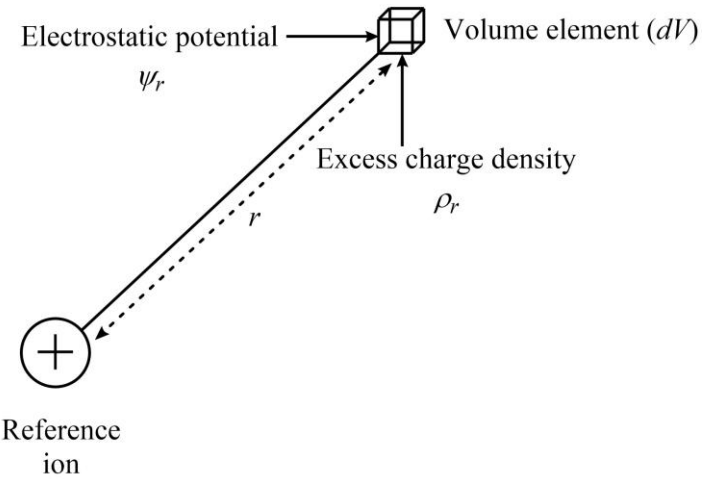


Figure 6. The depiction of electrostatic potential and excess charge density in *dV* volume element at distance *r* from the reference ion.

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.

$$\rho_r = n_1 Z_1 e_0 + n_2 Z_2 e_0 + n_3 Z_3 e_0 \ldots\ldots n_i Z_i e_0 \tag{34}$$

or

$$\rho_r = \sum n_i Z_i e_0 \tag{35}$$

Where n_1 is the number of first kind ions with $Z_1 e_0$ charge, n_2 is the number of second kind ions with $Z_2 e_0$ 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 *i*th 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.

$$\psi_r = \frac{Z_i e_0}{\varepsilon r} \tag{59}$$

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.

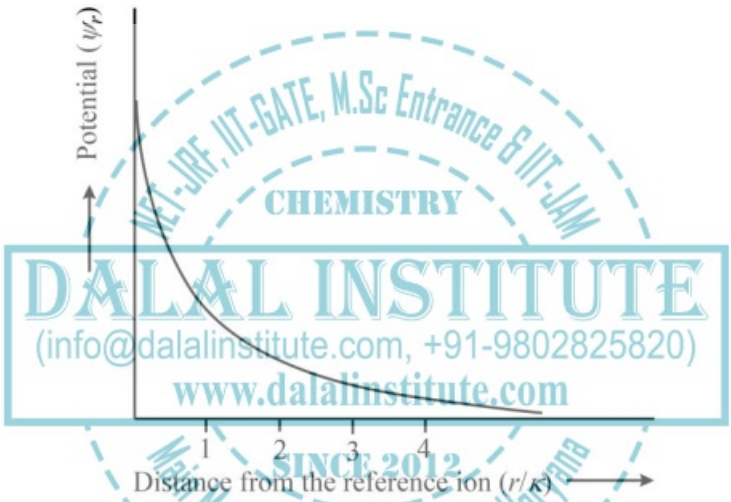


Figure 7. The variation of electrostatic potential as a function of the distance r from the reference ion.

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.

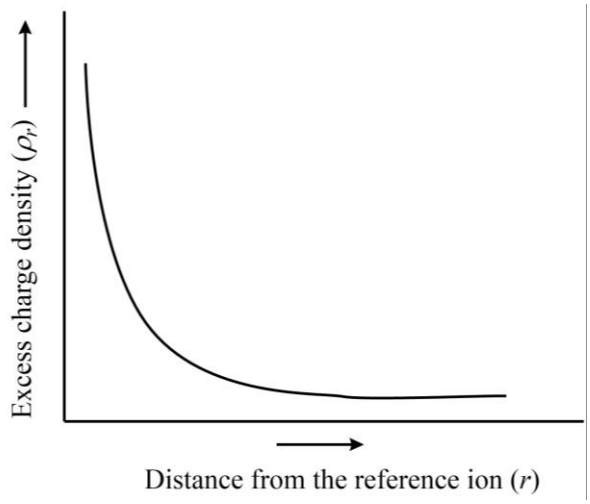
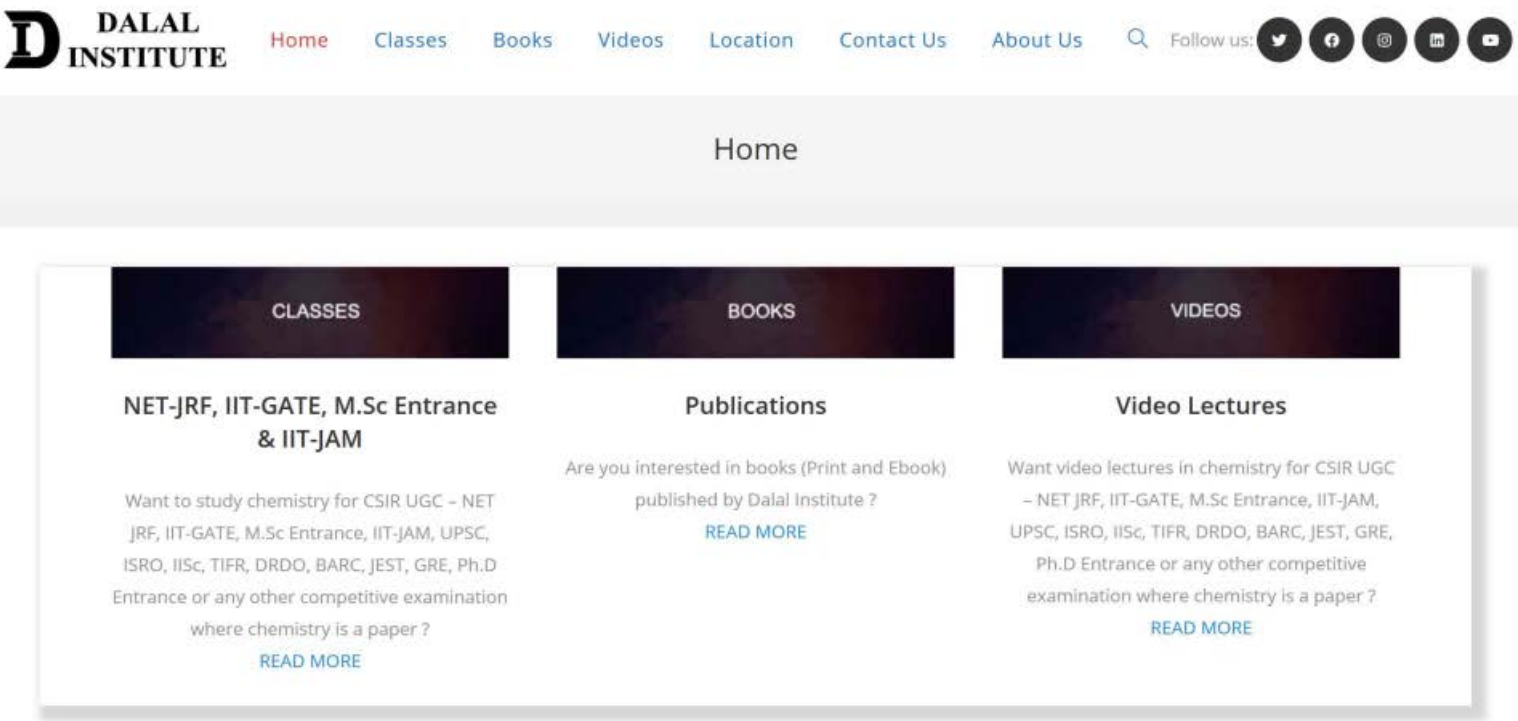


Figure 8. The variation of excess charge density as a function of the distance r from the reference ion.

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.



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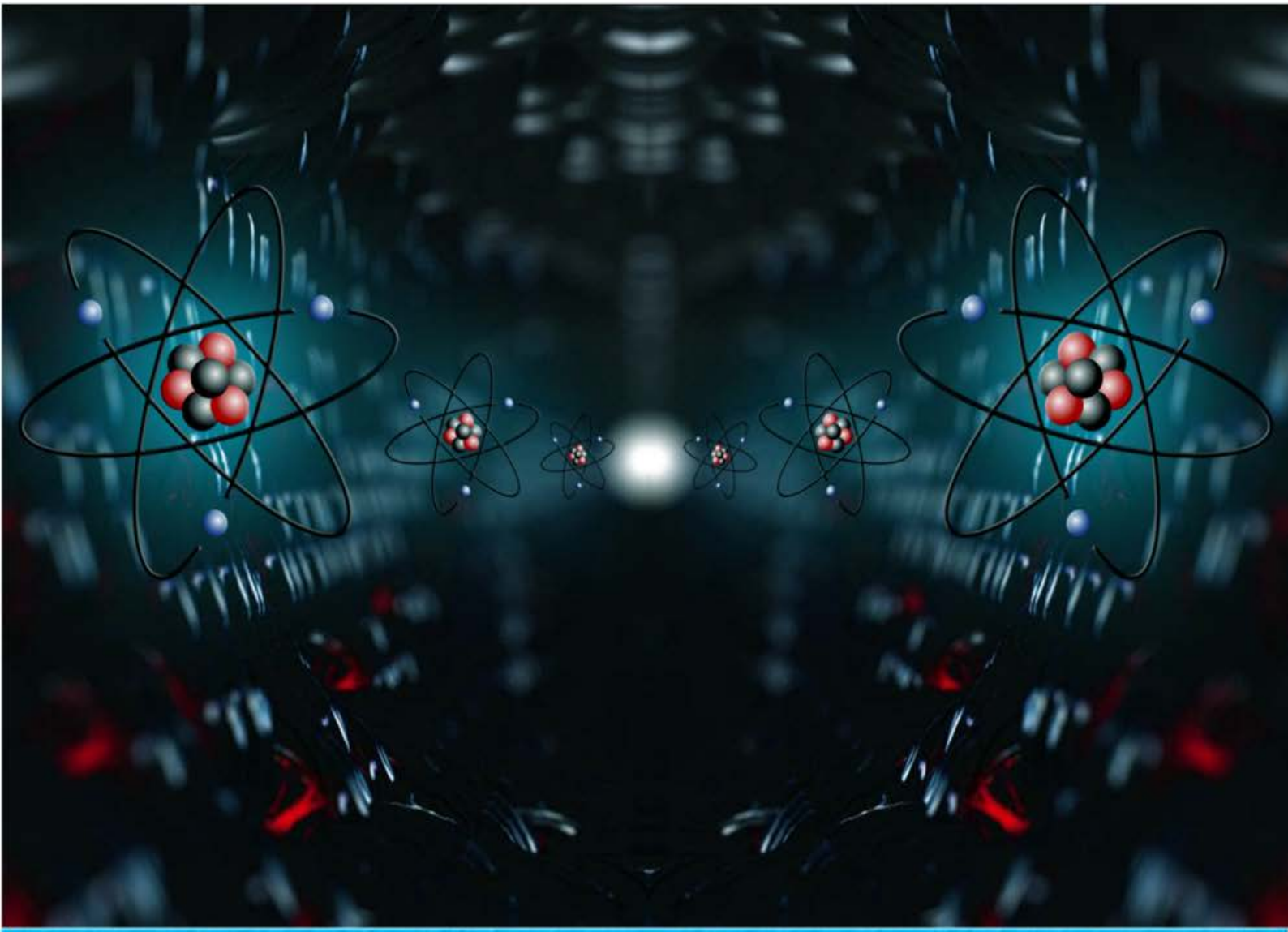

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ISBN: 978-81-938720-1-7

MRP: Rs 800.00

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