❖ 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.

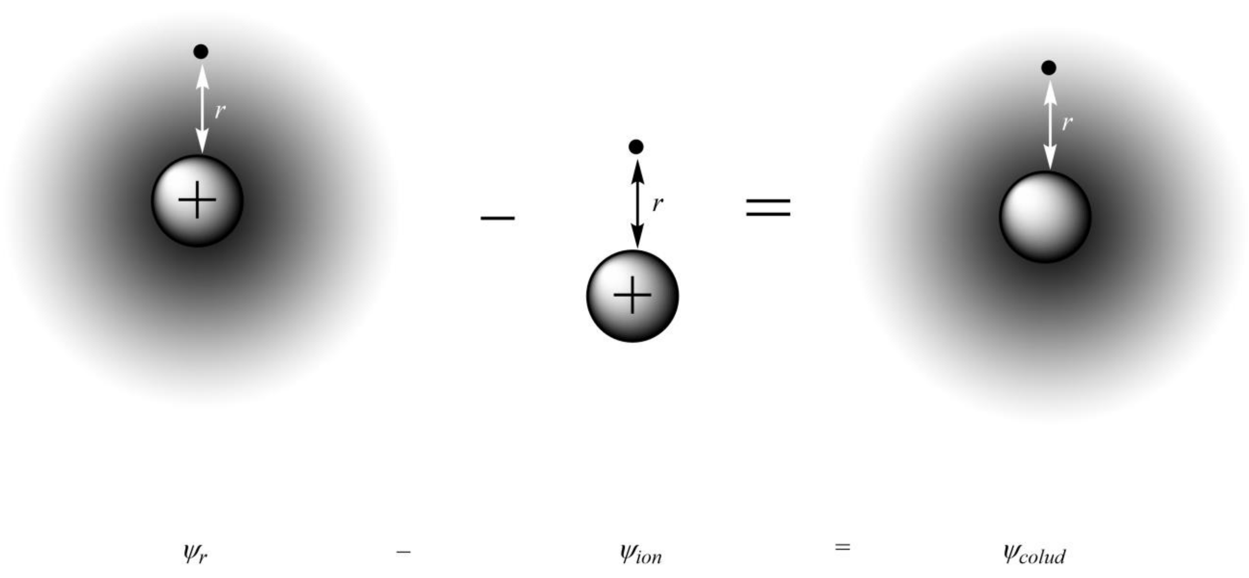

Figure 11. The pictorial representation of the superposition of the potentials at distance r from the reference ion due to the ionic cloud ion and the potential due to the central ion itself.

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.

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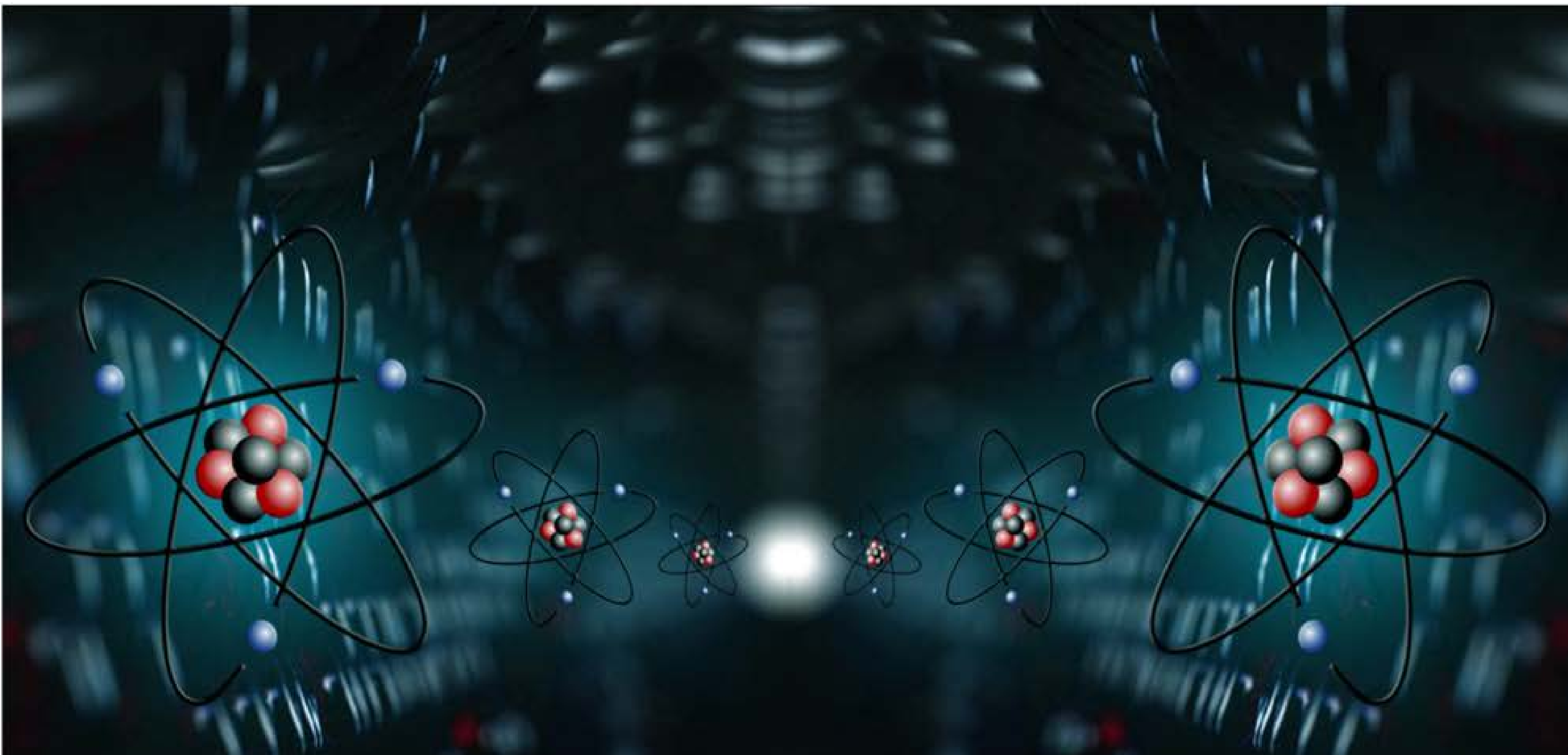

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