❖ Ionic Reactions: Single and Double Sphere Models

It is a quite well-known fact that the rate of ionic reactions is generally small, which is obviously due to the larger magnitude of activation energies arising from the very strong nature of electrostatic interactions. The magnitude of the frequency factor in ionic reactions is a function of ionic charges. The frequency factors have larger values if the charges on the participating ions are opposite, while smaller values are obtained in the case of like-charged ions. This behavior can be explained in terms of the kinetic theory of gases; which suggests that oppositely charged ions are more prone to collision due to attraction than the ions colliding with same charges (repulsive forces). Besides the collision theory, the activated complex theory also provides an alternate explanation for the ionic reactions. In this section, we will discuss the rationalization of ionic reactions on the basis of the single-sphere model and the double-sphere model in detail.

➢ *Double Sphere Model*

Before we discuss the double sphere model of the ionic reactions, a simplified surrounding must be assumed. Although it would be an oversimplification of the actual situation, it is highly beneficial as far as conceptual and quantitative understanding is concerned. To do so, the solvent is considered as continuous surrounding with a ε as the dielectric constant.

According to this model, two ions, which can same or opposite charges, combine together to form an activated complex. In the initial state, the ions are considered as discrete; while in the final state, they assumed to form a dumbbell like coordination with '*r*' as the distance of separation between their centers.

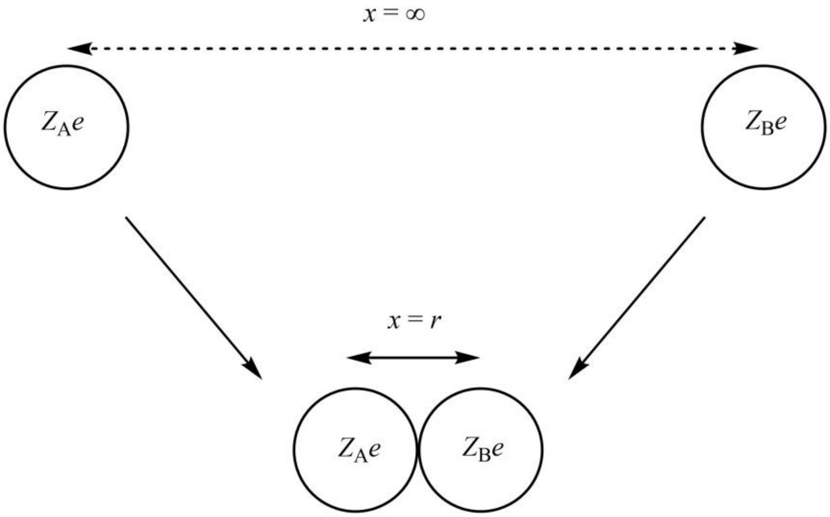


Figure 12. The pictorial depiction of the double-sphere model of ionic reactions.

Now, if Z_A and Z_B are the charge numbers of the participating ions and x as the distance of separation, the force of electrostatic interaction (F_{AB}) between them can be given from the Coulomb's law as:

$$F_{AB} = \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 \varepsilon x^2} \tag{206}$$

Where ε₀ and ε are permittivities of the vacuum (8.854×10^{-12} C^2 N^{-1} m^{-2}) and the dielectric constant of the solvent used, respectively. The symbol *e* represents the elementary charge and has a value equal to 1.6×10^{-19} *C*. The value of parameter varies from ∞ to *r* with the mutual approach of two ions. The amount of work done in moving the two ions closer by an extant *dx* will be

$$work = force \times displacement \tag{207}$$

$$dw = F_{AB} \times dx \tag{208}$$

$$dw = -\frac{Z_A Z_B e^2}{4\pi\varepsilon_0 \varepsilon x^2} dx \tag{209}$$

The negative sign is an indicator of decreasing separation i.e. distance is reduced by *dx*. The total amount of work done in moving the two ions from *x* = ∞ to *x* = *r* will be

$$w = -\int_{\infty}^{r} \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 \varepsilon x^2} dx \tag{210}$$

$$w = \frac{Z_A Z_B e^2}{4\pi\varepsilon_0 \varepsilon\, r} \tag{211}$$

The work given the above equation is actually the potential energy of the system which would have a negative sign for oppositely charged ions and positive sign if the ions have same charges. Furthermore, we can also say that this work is the free energy change due to electrostatic interactions, therefore, multiplying it by Avogadro number (*N*) would give the value of the corresponding molar free energy change (ΔG^*_{EI}) i.e.

$$\Delta G^*_{EI} = \frac{N Z_A Z_B e^2}{4\pi\varepsilon_0 \varepsilon\, r} \tag{212}$$

Correcting the above equation for non-electrostatic contribution ΔG^*_{NEI}, the total molar free energy change for the whole process can be given by the following relation.

$$\Delta G^* = \Delta G^*_{NEI} + \Delta G^*_{EI} = \Delta G^*_{NEI} + \frac{N Z_A Z_B e^2}{4\pi\varepsilon_0 \varepsilon\, r} \tag{213}$$

Also, from the activated complex theory, we know that

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^*}{RT}} \tag{214}$$

After putting the value of ΔG^* from equation (213) into equation (214), we get

$$k = \frac{RT}{Nh} e^{-\left(\frac{\Delta G^{*}_{NEI}}{RT} + \frac{N Z_A Z_B e^2}{RT 4\pi\varepsilon_0 \varepsilon\, r}\right)} \tag{215}$$

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^{*}_{NEI}}{RT}} . e^{-\frac{N Z_A Z_B e^2}{RT 4\pi\varepsilon_0 \varepsilon\, r}} \tag{216}$$

Taking natural logarithm both side of equation (216), we get

$$\ln k = \ln \frac{RT}{Nh} + \ln e^{-\frac{\Delta G^{*}_{NEI}}{RT}} + \ln e^{-\frac{N Z_A Z_B e^2}{RT 4\pi\varepsilon_0 \varepsilon\, r}} \tag{217}$$

or

$$\ln k = \ln \frac{RT}{Nh} - \frac{\Delta G^{*}_{NEI}}{RT} - \frac{N Z_A Z_B e^2}{RT 4\pi\varepsilon_0 \varepsilon\, r} \tag{218}$$

Which can also be expressed as

$$\ln k = \ln k_0 - \frac{N Z_A Z_B e^2}{RT 4\pi\varepsilon_0 \varepsilon\, r} \tag{219}$$

Where k_0 represents the magnitude of the rate constant for the ionic reaction carried out in a solvent of infinite dielectric constant so that the electrostatic interactions become zero.

- ***Single Sphere Model***

Besides the double-sphere model, another theoretical model that is quite rationalizing is a single-sphere model. Just like the double-sphere model, the solvent is also considered as a continuum with a ε as the dielectric constant. However, the primary differentiating aspect of this model is that it considers the two ions, which can same or opposite charges, to form a single-sphere activated complex.

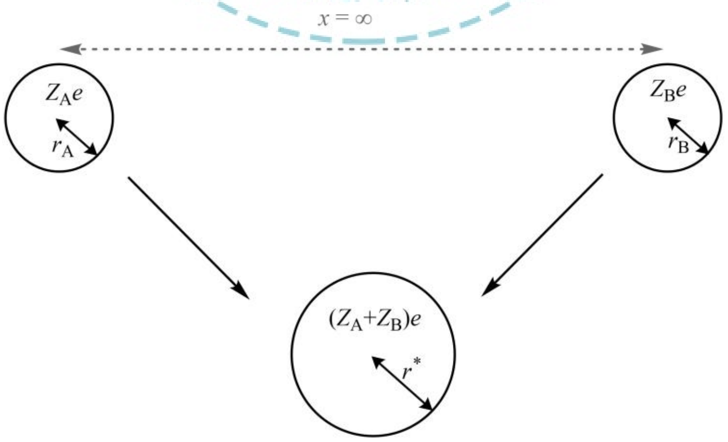


Figure 12. The pictorial depiction of the single-sphere model of ionic reactions.

In the initial state, the ions are considered as discrete; while in the final state, they assumed to form a single-sphere activated complex with 'r^*' as the overall radius. The rate law for this case was derived by Born by considering the energy required to charge an ion in solution. Now suppose that we need to charge a conducting sphere of radius r from an initial value of zero to the final value Ze. This can be visualized as a process in which a very small charge is $e.d\lambda$ ($\lambda = 0 - Z$) is carried from infinite to this sphere.

Now, if Z_A and Z_B are the charge numbers of the participating ions and x as the distance of separation between the sphere and the "increment" at any time, the force of electrostatic interaction (dF) between them can be given from the Coulomb's law as:

$$dF = \frac{\lambda e^2 d\lambda}{4\pi\varepsilon_0\varepsilon x^2} \tag{220}$$

Where ε_0 and ε are permittivities of the vacuum ($8.854 \times 10^{-12}\ C^2\ \mathrm{N}^{-1}\ \mathrm{m}^{-2}$) and the dielectric constant of the solvent used, respectively. The symbol e represents the elementary charge and has a value equal to 1.6×10^{-19} C. The amount of work done in moving the "increment" closer by an extant dx will be

$$dw = dF \times dx \tag{221}$$

$$dw = \frac{\lambda e^2 d\lambda}{4\pi\varepsilon_0\varepsilon x^2} dx \tag{222}$$

The total amount of work done can be obtained by carrying out the double integration with respect to $x = \infty - r$ and $\lambda = 0 - Z$ i.e.

$$w = \frac{e^2}{4\pi\varepsilon_0\varepsilon} \int_0^Z \int_\infty^r \frac{\lambda}{x^2} d\lambda\, dx \tag{223}$$

$$w = \frac{Z^2 e^2}{8\pi\varepsilon_0\varepsilon\, r} \tag{224}$$

The work given the above equation is actually the contribution of the electrostatic interactions to the Gibbs energy of the ion i.e.

$$G_{EI} = \frac{Z^2 e^2}{8\pi\varepsilon_0\varepsilon\, r} \tag{225}$$

In the light of the above correlation, the electrostatic contribution to the Gibbs free energy of discrete ions and activated complex can be written as

$$G_{EI}(A) = \frac{Z_A^2 e^2}{8\pi\varepsilon_0\varepsilon\, r_A} \tag{225}$$

$$G_{EI}(B) = \frac{Z_B^2 e^2}{8\pi\varepsilon_0 \varepsilon\, r_B} \tag{226}$$

$$G_{EI}^* = \frac{(Z_B + Z_B)^2 e^2}{8\pi\varepsilon_0 \varepsilon\, r^*} \tag{227}$$

Hence, the change in electrostatic contribution can be obtained simply by subtracting the sum of individual contributions from the overall contribution i.e.

$$\Delta G_{EI}^* = \frac{(Z_B + Z_B)^2 e^2}{8\pi\varepsilon_0 \varepsilon\, r^*} - \frac{Z_A^2 e^2}{8\pi\varepsilon_0 \varepsilon\, r_A} - \frac{Z_B^2 e^2}{8\pi\varepsilon_0 \varepsilon\, r_B} \tag{228}$$

or

$$\Delta G_{EI}^* = \frac{e^2}{8\pi\varepsilon_0 \varepsilon}\left[\frac{(Z_B + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B}\right] \tag{229}$$

Correcting the above equation for non-electrostatic contribution ΔG_{NEI}^*, the total molar free energy change for the whole process can be given by the following relation.

$$\Delta G^* = \Delta G_{NEI}^* + \Delta G_{EI}^* = \Delta G_{NEI}^* + \frac{Ne^2}{8\pi\varepsilon_0 \varepsilon}\left[\frac{(Z_B + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B}\right] \tag{230}$$

Also, from the activated complex theory, we know that

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^*}{RT}} \tag{231}$$

After putting the value of ΔG^* from equation (230) into equation (231), we get

$$k = \frac{RT}{Nh} e^{-\left(\frac{\Delta G_{NEI}^*}{RT} + \frac{Ne^2}{RT8\pi\varepsilon_0 \varepsilon}\left[\frac{(Z_B + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B}\right]\right)} \tag{232}$$

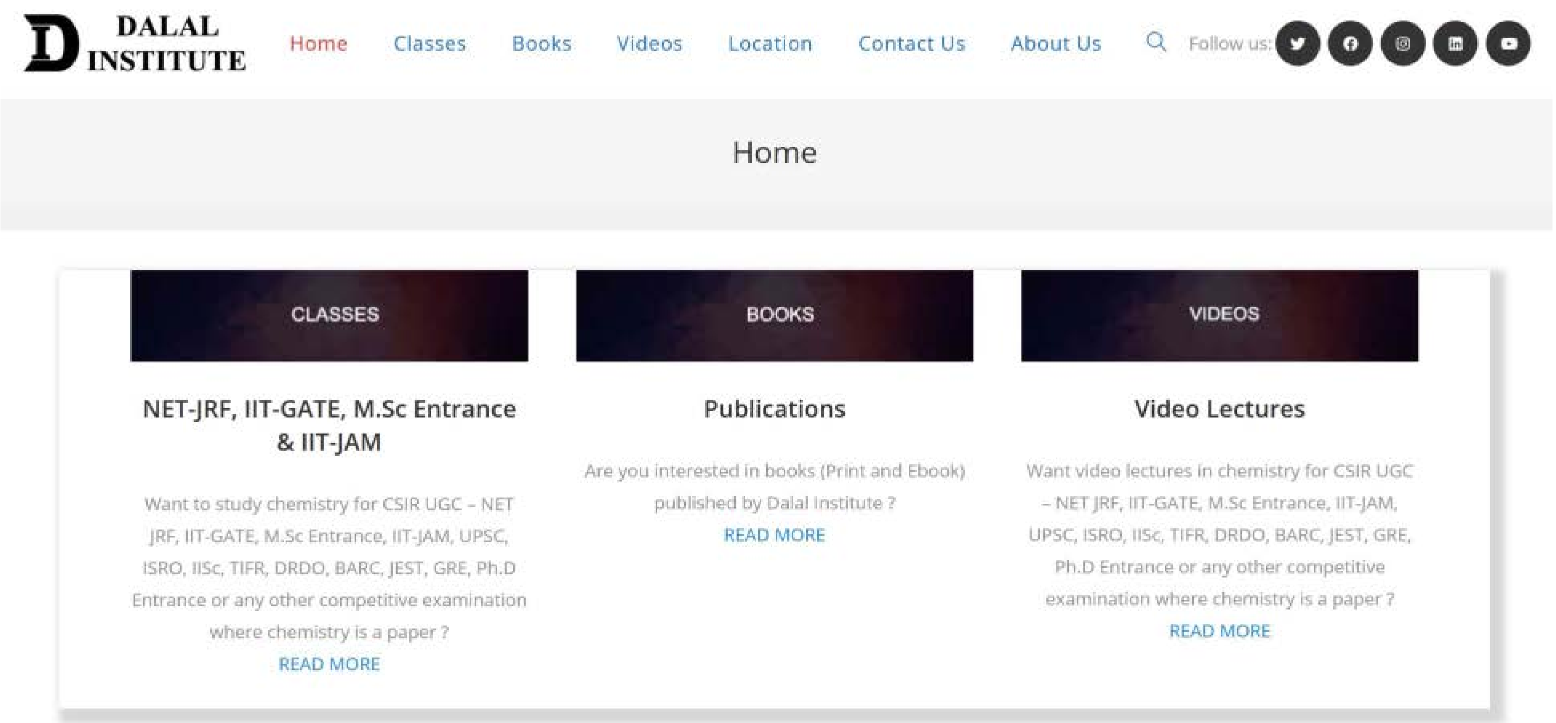
Taking natural logarithm both side of equation (232) and rearranging, we get

$$\ln k = \ln \frac{RT}{Nh} - \frac{\Delta G_{NEI}^*}{RT} - \frac{Ne^2}{RT8\pi\varepsilon_0 \varepsilon}\left[\frac{(Z_B + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B}\right] \tag{233}$$

Which can also be expressed as

$$\ln k = \ln k_0 - \frac{Ne^2}{RT8\pi\varepsilon_0 \varepsilon}\left[\frac{(Z_B + Z_B)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B}\right] \tag{234}$$

Where k_0 represents the magnitude of the rate constant for the ionic reaction carried out in a solvent of infinite dielectric constant so that the electrostatic interactions become zero.



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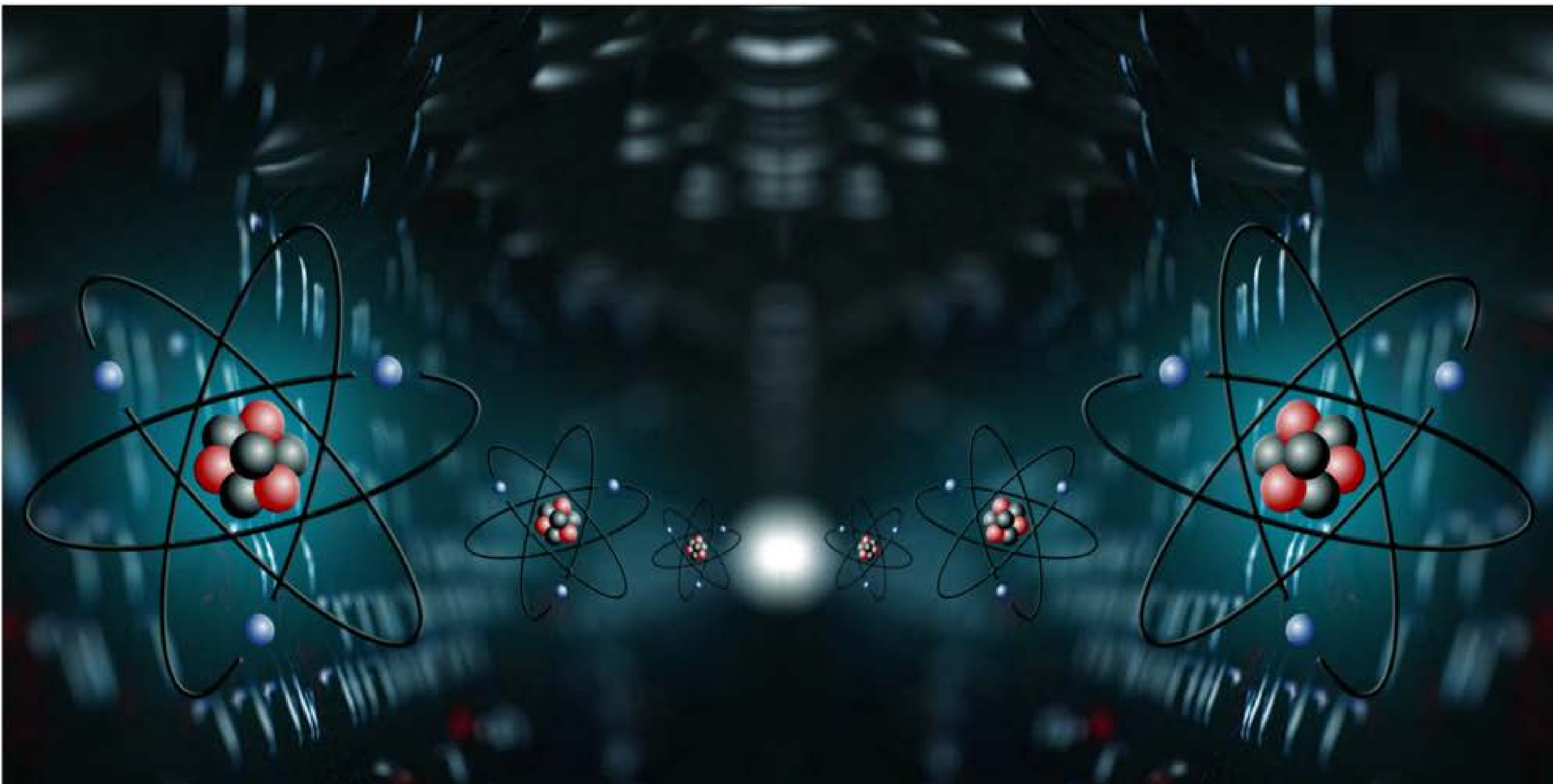

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Mandeep Dalal
(M.Sc, Ph.D, CSIR UGC - NET JRF, IIT - GATE)
Founder & Director, Dalal Institute
Contact No: +91-9802825820
Homepage: www.mandeepdalal.com
E-Mail: dr.mandeep.dalal@gmail.com

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) .

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

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