❖ Influence of Solvent and Ionic Strength

The rate of reaction in the case of ionic reactions is strongly dependent upon the nature of the solvent used and the ionic strength. The single and double-sphere treatment of these reactions enables us to study their effect in detail. In this section, we discuss the application and validity of solvent influence and ionic strength on the reaction rate.

➢ *Influence of the Solvent*

In order to study the influence of solvent on the rate of ionic reactions, recall the rate equation derived using the double sphere model i.e.

$$\ln k = \ln k_0 - \frac{NZ_AZ_Be^2}{RT4\pi\varepsilon_0\varepsilon\, r} \tag{235}$$

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. 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. Z_A and Z_B are the charge numbers of the participating ions. The symbol N and R represents the Avogadro number and gas constant, respectively. Rearranging equation (235), we get

$$\ln k = -\frac{NZ_AZ_Be^2}{RT4\pi\varepsilon_0\, r}\frac{1}{\varepsilon} + \ln k_0 \tag{236}$$

Which is clearly the equation of the straight line ($y = mx + c$) with a negative slope and positive intercept. Therefore, it is obvious that the logarithm of the rate constant shows a linear variation with the reciprocal of dielectric constant.

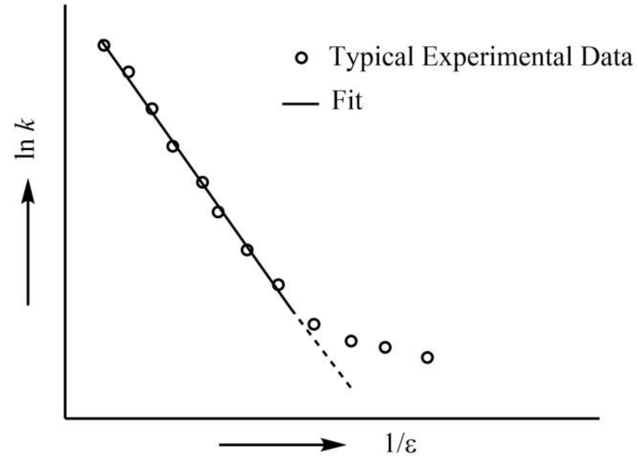


Figure 13. The plot of ln k vs 1/ε for a typical ionic reaction.

It is quite obvious from the plot that equation (236) holds very good over a wide range of dielectric contents; however, as the large deviations are observed at lower values of ε. Moreover, if '*m*' is the experimental slope then from equation (236), we have

$$m = -\frac{NZ_AZ_Be^2}{RT4\pi\varepsilon_0\, r} \tag{237}$$

Every term in the above equation is known apart from *r*, suggesting its straight forward determination from the slope of ln *k* vs 1/ε. The values of *r* obtained from equation (237) are found to be quite comparable to other methods, which in turn suggests its practical application.

Besides the calculation of *r*, the influence of dielectric constant of solvent can also be used to explain the entropy of activation. In order to do so, recall from the principles of thermodynamics

$$\left(\frac{\partial G}{\partial T}\right)_P = -S \tag{238}$$

Also, the electrostatic contribution to the Gibbs free energy using the double sphere model is

$$\Delta G_{EI}^* = \frac{NZ_AZ_Be^2}{4\pi\varepsilon_0\varepsilon\, r} \tag{239}$$

However, the only quantity which is temperature-dependent in the above equation is ε. Therefore, differentiating equation (239) with respect to temperature at constant pressure gives

$$\Delta S_{EI}^* = -\left(\frac{\partial(\Delta G_{EI}^*)}{\partial T}\right)_P = -\frac{NZ_AZ_Be^2}{4\pi\varepsilon_0\, r}\left(\frac{\partial(1/\varepsilon)}{\partial T}\right)_P \tag{240}$$

or

$$\Delta S_{EI}^* = \frac{NZ_AZ_Be^2}{4\pi\varepsilon_0\varepsilon^2\, r}\left(\frac{\partial\varepsilon}{\partial T}\right)_P \tag{241}$$

or

$$\Delta S_{EI}^* = \frac{NZ_AZ_Be^2}{4\pi\varepsilon_0\varepsilon\, r}\left(\frac{\partial \ln\varepsilon}{\partial T}\right)_P \tag{242}$$

Therefore, knowing the dielectric constant of the solvent and *r*, the entropy of activation can be obtained. Moreover, it is also worthy to note that the entropy of activation is negative and decreases with an increase in Z_AZ_B.

One more factor that affects the entropy of activation is the phenomena of "electrostriction" or the solvent binding. This can be explained by considering the combination of two ions as of same and opposite charges. If the ions forming activated complex are having one-unit positive charge each, the double-sphere will have a total of two-unit positive charge. This would result in a very strong interaction between the activated complex and the surrounding solvent molecules. This would eventually result in a restriction of free movement and hence decreased entropy. On the other hand, If the ions forming activated complex possess opposite charges, the double-sphere would have less charge resulting in decreased electrostriction, and therefore, increased entropy.

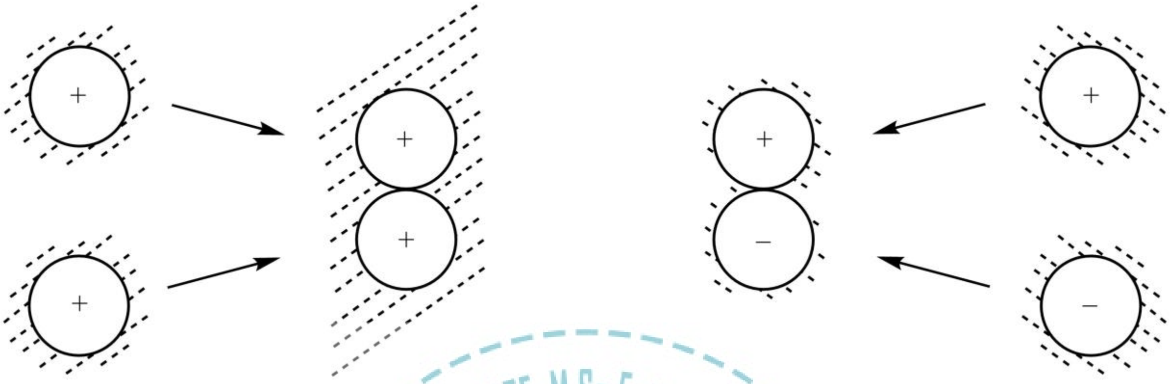


Figure 14. The dependence of entropy of activation on the solvent electrostriction in case of (left) same charges and (right) opposite charges.

- ***Influence of Ionic Strength***

In order to study the influence of ionic strength (I) on the rate of ionic reactions, we need to recall the quantity itself first i.e.

$$I = \frac{1}{2}\sum_{i=1}^{i=n} m_i z_i^2 \tag{243}$$

Where m_i and z_i are the molarity and charge number of ith species, respectively. For instance, the value of z for Ca^{2+} and Cl^- in $CaCl_2$ are +2 and −1, respectively. It has been found that an increase the ionic strength increases the rate of reaction if charges on the reacting species are of the same sign. On the other hand, the reaction rate has been found to follow a declining trend with increasing ionic strength if reaction ions are of opposite sign. The mathematical treatment of the abovementioned statement is discussed below.

To rationalize the effect of ionic strength of the solution on the rate of reaction in case of ionic reactions, consider a typical case i.e.

$$A^{Z_A} + B^{Z_B} \rightarrow X^{Z_A+Z_B} \rightarrow P \tag{244}$$

A Danish physical chemist, J. N. Brønsted, proposed the rate equation relating reaction-rate (R) and activity coefficient as

$$R = k_0[A][B]\frac{y_A y_B}{y_X} \tag{245}$$

Where y_A, y_B and y_X are the activity coefficients for the reactant A, B and the activated complex X, respectively. Brønsted collectively labeled the term y_Ay_B/y_X as the “kinetic activity factor”, and it was found be quite accurate with experimental data. Now, rearranging equation (245), we get

$$\frac{R}{[A][B]} = k_0\frac{y_Ay_B}{y_X} \tag{246}$$

Since the left-hand side simply equals to a second-order rate constant, the above equation takes the form

$$k = k_0\frac{y_Ay_B}{y_X} \tag{247}$$

Taking logarithm both side, we get

$$\log k = \log k_0 + \log\frac{y_Ay_B}{y_X} \tag{248}$$

or

$$\log k = \log k_0 + \log y_A + \log y_B - \log y_X \tag{249}$$

Now the correlation of mean ionic activity coefficient with the ionic strength is given by famous Debye-Huckel theory i.e.

$$\log y_i = -Bz_i^2\sqrt{I} \tag{250}$$

Where B is the Debye-Huckel constant. Using the concept of equation (250) in equation (249), we get

$$\log k = \log k_0 - Bz_A^2\sqrt{I} - Bz_B^2\sqrt{I} + Bz_X^2\sqrt{I} \tag{251}$$

or

$$\log k = \log k_0 - Bz_A^2\sqrt{I} - Bz_B^2\sqrt{I} + B(z_A + z_B)^2\sqrt{I} \tag{252}$$

$$\log k = \log k_0 + B[(z_A + z_B)^2 - z_A^2 - z_B^2]\sqrt{I} \tag{253}$$

$$\log k = \log k_0 + B[z_A^2 + z_B^2 + 2z_Az_B - z_A^2 - z_B^2]\sqrt{I} \tag{254}$$

or simply

$$\log k = \log k_0 + 2Bz_Az_B\sqrt{I} \tag{255}$$

Rearranging the above equation, we get

$$\log k = 2Bz_Az_B\sqrt{I} + \log k_0 \tag{256}$$

Which is clearly the equation of straight line ($y = mx + c$) with a positive slope ($2Bz_Az_B$) and positive intercept ($\log k_0$). For aqueous solutions at 25°C, $2B$ = 1.02, equation (256) takes the form

$$\log k - \log k_0 = 1.02\, z_A z_B \sqrt{I} \tag{257}$$

or

$$\log \frac{k}{k_0} = 1.02\, z_A z_B \sqrt{I} \tag{258}$$

Where k_0 is the rate constant at zero ionic strength and can be obtained by the extrapolation of log k_0 vs square root of the ionic strength.

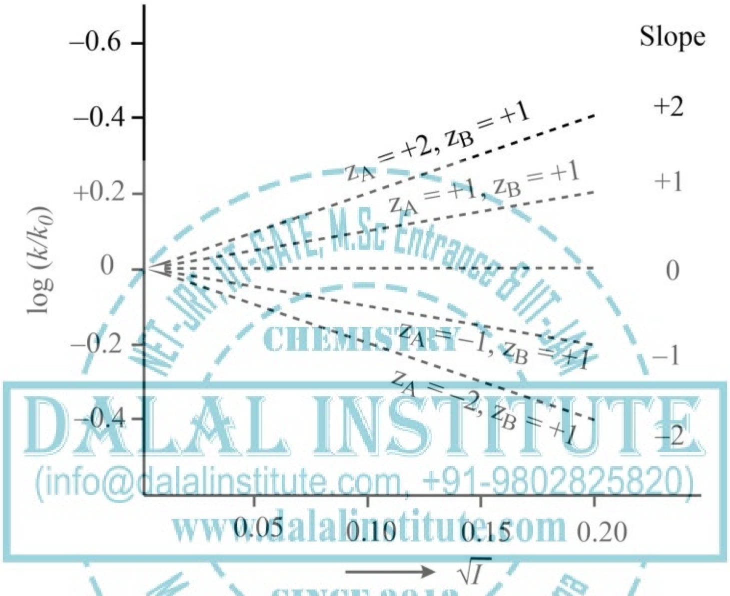


Figure 15. The plot of log (k/k_0) vs $(I)^{1/2}$ for different ionic reactions in aqueous solution at 25°C.

The above equation can also be extended to explain the dependence of reaction-rate on ionic strength for third-order reactions. To do so, consider

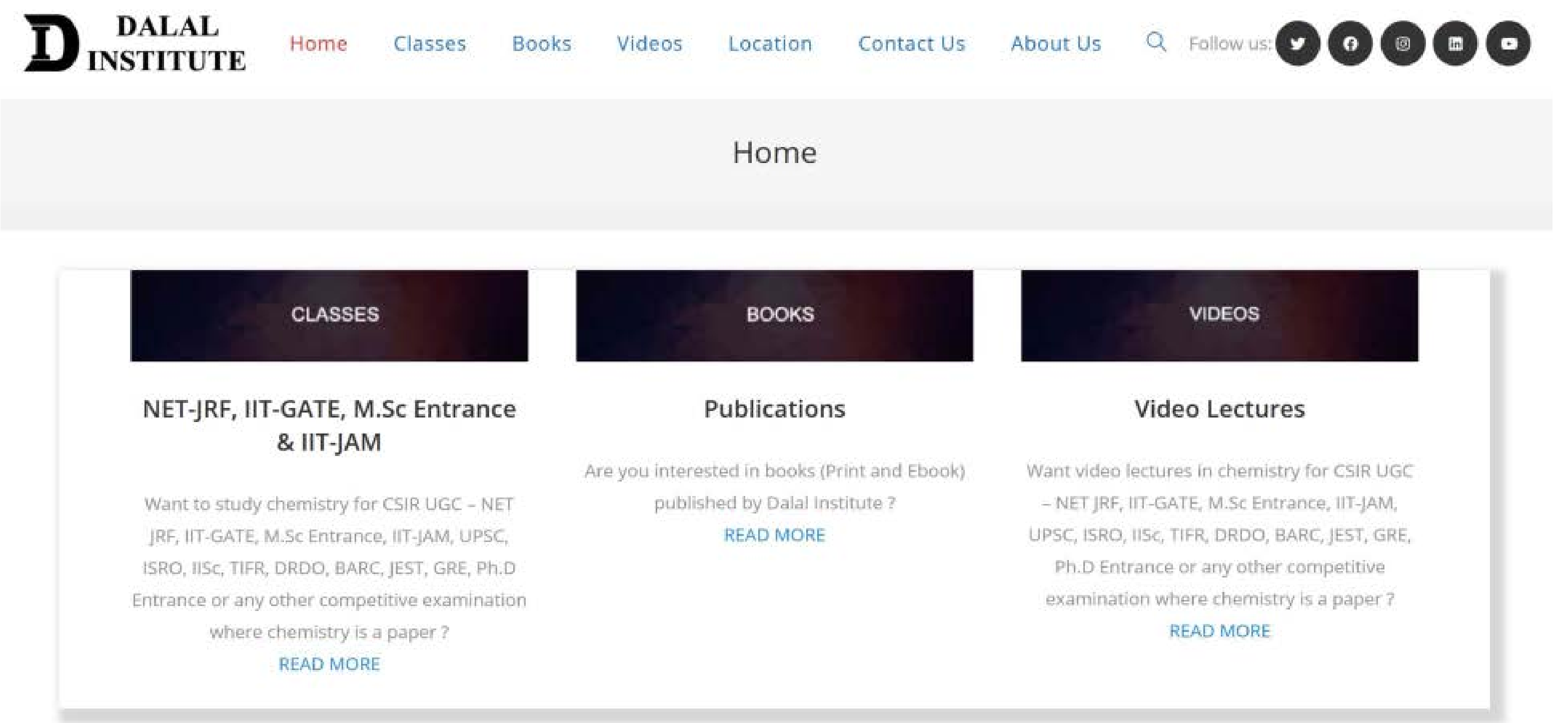
$$A^{Z_A} + B^{Z_B} + C^{Z_C} \rightarrow X^{Z_A+Z_B+Z_C} \rightarrow P \tag{259}$$

Following the same route as in second-order reactions, we will get

$$\log k = \log k_0 + B[(z_A + z_B + z_C)^2 - z_A^2 - z_B^2 - z_C^2]\sqrt{I} \tag{260}$$

$$\log k = \log k_0 + 2B(z_A z_B + z_B z_C + z_C z_A)\sqrt{I} \tag{261}$$

Therefore, a negative slope will be observed if $(z_A z_B + z_B z_C + z_C z_A)$ is negative while a positive slope is expected for a positive value of $(z_A z_B + z_B z_C + z_C z_A)$.



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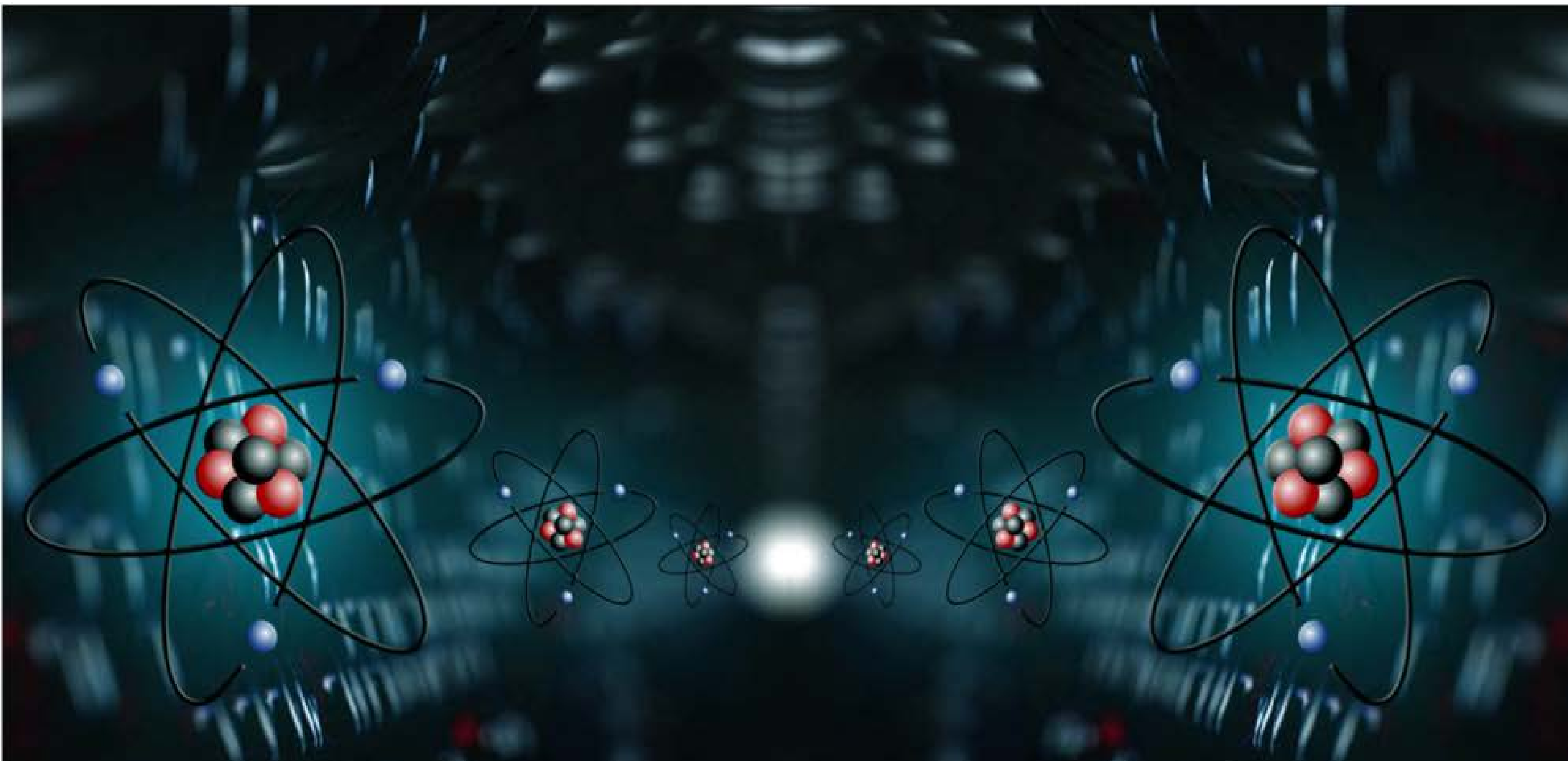

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