

KINETICS OF REACTIONS IN SOLUTION

Structure

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9.1 INTRODUCTION

In the previous two units you have learnt about the characteristics and theories of bimolecular and unimolecular gaseous reactions. Having learnt about these elementary reactions in the gas phase, in the present unit we shift our focus to reactions in solution. Fundamentally, the reactions in solution are similar to the ones in the gas phase, as both involve a series of changes in the configuration i.e., the spatial arrangement of the atoms in the species, involved in the reaction step. However, in case of reactions in solution, these configurations may be influenced by the presence of the solvent which becomes an integral part of the reaction. Therefore, we need to take reactant-solvent and solvent-solvent interactions also into account.

We will start the unit by taking up the general aspects of reactions in solution wherein we will broadly outline the differences in gas phase and solution phase reactions. Thereafter, we will discuss the role of solvent in the reactions in the solution phase. This will be followed by a discussion on the theories of reactions in solution. Herein you will learn how the theories of gas phase reactions get modified for reactions in the solution phase. Since in solution phase reactions, specially the ionic reactions, the nature and concentration of the salt plays an important role so we would take up this issue and discuss about the salt effects.

In the next unit we would take up the kinetics of fast reactions.

Expected Learning Outcomes

After studying this unit, you should be able to:

- ❖ outline the general aspects of the kinetics of reactions in solution;
- ❖ discuss the role of solvent in the reactions in solution phase;
- ❖ list the properties of solvent that affect the kinetics of reactions in solution;
- ❖ describe the process of reaction in solution in terms of the encounter pair description;
- ❖ derive the expression for the rate of a reaction in solution in terms of encounter pair description;
- ❖ differentiate between diffusion controlled and activation controlled reactions in solution;
- ❖ explain the absolute reaction rate theory for reactions in solution;
- ❖ define and differentiate between the primary and secondary salt effects;
- ❖ define and calculate the ionic strength of a given solution; and
- ❖ discuss the effect of ionic strength on the rate of a reaction in solution.

9.2 REACTIONS IN SOLUTION: GENERAL ASPECTS

In this course we have so far discussed the reactions in gaseous phase which have been understood to a reasonable extent. The theories of bimolecular and unimolecular reactions discussed in the previous units provide a fairly good agreement with the experimental results. This has been made possible due to the kinetic theory of gases underlying these theories. You would recall that the kinetic theory of gases assumes that the interactions between individual molecules are relatively unimportant and the molecules move around in a random manner. It implies that until the reacting molecules actually collide or interact in the course of the reaction, they can be treated as 'ideal' gas.

However, now we are getting into the domain of reactions in solutions and realise that the behaviour of liquids (solutions) is not as well understood as that of the gases or for that matter of the solids. We know that liquids neither have a completely random structure like gases nor a completely regular structure like solids. As a consequence, their theoretical treatment is highly complicated and does not allow us to proceed in a fundamental manner as we could in case of gases. We need to take up the reactions in solution in a somewhat empirical fashion.

Different reactions in solution behave quite differently. For some reactions, like the thermal decomposition of nitrogen pentoxide, Eq. (9.1), the rates of the reactions are comparable in the gas phase and in solution phase with different types of solvents, Table 9.1.



Here, the solvent appears to play a relatively insignificant role and has only a minor influence on the rate of the reaction.

Table 9.1: The rate constant for the thermal decomposition of N₂O₅ in gas phase and in solutions in different solvents at 298 K

Medium	$k/10^{-5} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$
Gas phase	3.3
Chloroform	3.3
Carbon tetrachloride	4.1
Pentachloroethane	4.3
Nitromethane	3.1

On the other hand, there are solution phase reactions like the formation of the quaternary ammonium salt from ethyl iodide and triethylamine, Eq. (9.2), that do not occur at all in the gas phase.



In such cases, the presence of a solvent is necessary. It probably helps in stabilising the activated complex; and an ionising solvent is found to favour the reaction. The rate increases by about 10^5 times when the solvent is changed from nonpolar hexane to polar DMSO. In gas phase reactions the activated complex predominantly have molecular-type structures whereas for reactions in solution these have charged or charge-separated structures. The increase in the rate can be attributed to the stabilisation of the charges, created during the reaction, by the presence polar solvent. Therefore, the effect of the solvent on the activated complex is crucial.

Further, for the reactions in which the solvent is important its role is determined by the nature of the reactant molecules. The reactions between non polar molecules behave differently than those between the polar molecules which in turn are different from the reactions between ions. Certain reactions involving nonpolar molecules occur in the gas phase as well as in solution, and also have similar rates, entropies and energies of activation in both the cases. For example, the decomposition of nitrogen pentoxide as stated above. In such reactions, the solvent plays a kind of secondary role and the interactions between reactant molecules and solvent molecules are not significant. Similar rates suggest that the number of effective collisions in the two cases are also similar. In such cases we may say that in solution phase the solvent molecules just fill up the space between the reactant molecules.

In a reaction in solution, the concentration of solvent is much larger than that of the solute and it does not change significantly with the progress of the reaction. Therefore, it generally does not appear the rate expression. However, in some cases the solvent does participate in the reaction, and appears in the rate expression. Further, as discussed in Unit 6, in the gas phase reactions the intermediates often acquire steady state concentrations. In contrast, in solution phase reactions, many of the intermediates are at equilibrium concentrations. Since it is easy to determine equilibrium concentrations in the solution phase, the kinetic analysis for reactions in solution is much easier than for the gas phase reactions. On the other hand, in

case of polar molecules or reactions between the ions, the electrostatic forces between solute and solvent molecules exert a significant effect on their kinetic behaviour and hence the rate of the reaction.

One of the important considerations that differentiates the gaseous reactions and the reactions in solutions is the much higher density of the liquid phase. At ambient pressures, in a typical gaseous system the molecules occupy only a tiny volume of the order of about 0.2 percent. Whereas, in a liquid it is more than 50 percent and would depend on the concentration. In a typical liquid solution, due to their massive numbers, the solvent molecules surround the solute molecules. This becomes all the more significant if the solvent can undergo hydrogen bonding e.g., in aqueous solutions.

In such a scenario, we need to visualise the collisions between the reactant molecules in solution differently. Contrary to the truly random motion of gaseous molecules, in solutions the reactant molecules have to find their way through the solvent. Therefore, the frequency of their collision is much less than that in case of the gas. The solvent molecules form a kind of cage around the reactant molecules. The solute molecules keep hopping randomly between these solvent cages. Occasionally, the reactant molecules occupy a common solvent cage where they collide with the solvent molecules that are in excess. In a chance event they may come into contact with each other. Such a meeting of the reactant molecules is termed as an **encounter** and their contact leads to the formation of an **encounter pair**. Now, since the migration of reactant molecules away from a location is also slow, they stay near each other for much longer time than in a gas.

In the solvent cage, the reactant molecules are effectively in a constant state of collision, either amongst themselves or with the solvent molecules. This then may lead to the formation of the product molecules which diffuse out of the cage. Since the reactant molecules are confined in the cage, they may undergo many collisions and if the reaction does not happen in the first such collision it may happen in a subsequent collision. Therefore, once the encounter pair is formed, the reactant molecules get a number of chances to acquire sufficient energy to cross over the critical energy barrier. That is, the probability of the reaction increases. The cage effect, discussed above, is known as the **Franck-Rabinovitch effect**. It is important to note that the activation energy of a reaction in solution is a much more complicated quantity than in a gaseous reaction. It is so because the reactants in the encounter pair are surrounded by solvent, and we need to consider combined energy of the reactant and solvent molecules.

In light of the above discussion, the reactions in solution can be considered to take place in three steps, viz.,

- I. diffusion of reactant molecules through the solvent towards each other
- II. encounters between the reactant molecules with the formation of activated complex (encounter pair) followed by formation of the product
- III. diffusion of products out of the cage

It may appear that one of the two diffusion steps (step I and III) is the rate determining step in this sequence. However, vast majority of the reactions are associated with an activation energy of 40-80 kJ mol⁻¹, whereas the diffusion processes, have an activation energy of about 20 kJ mol⁻¹ and would depend on the temperature and the viscosity of the solution. Therefore, generally the second step is the rate determining step. This conclusion may change in case of reactions having low activation energies like the ones involving ions as these occur very fast and have very small activation energies. Let us understand the process of reaction in solution with the help of an example. Let us take the following general reaction in solution phase



As per the encounter pair description of the reaction in solution, the reaction process can be represented as:



In the first step, the reactants diffuse into the solvent cage; the rate constant for this step is k_D . The reactants form the encounter pair XY which can either dissociate with a rate k_d or form the product with rate constant k_r .

The reaction rate consistent with this scheme can be written as

$$\text{Rate} = k_r [XY] \quad \dots(9.7)$$

Since XY is an intermediate species, we can apply the steady-state approximation to it. For this, we can represent the rate of change of concentration of the encounter pair as

$$\frac{d[XY]}{dt} = k_D [X][Y] - k_d [XY] - k_r [XY] \quad \dots(9.8)$$

Applying steady state condition to [XY], i.e., $\frac{d[XY]}{dt} = 0$, we get

$$[XY] = \frac{k_D [X][Y]}{k_d + k_r} \quad \dots(9.9)$$

Substituting in Eq. (9.7), we get the rate of the reaction as

$$\text{Rate} = \frac{k_r k_D}{k_d + k_r} [X][Y] \quad \dots(9.10)$$

There are two limiting conditions here. The first being that the rate constant for product formation is much greater than that for the dissociation of the encounter pair to re-form the reactants i.e., $k_r \gg k_d$. Under these conditions the rate expression becomes

$$\text{Rate} = k_D [X][Y] \quad \dots(9.11)$$

That is, the rate of reaction is controlled by the rate of diffusion of the reactants, k_D . It is called diffusional control limit and the reaction is said to be a

diffusion-controlled reaction. Since the rate of diffusion depends on the viscosity of the solvent, the rate of such reactions depends on the viscosity. The other possibility is that the rate constant for product formation is much smaller than the rate of dissociation of encounter pair i.e., $k_d \gg k_r$. Under these conditions the rate expression becomes

$$\text{Rate} = \frac{k_r k_D}{k_d} [X][Y] \quad \dots(9.12)$$

That is, the rate of the reaction depends on the energetics of the reaction i.e., the rate is controlled by the activation step. It is called activation control limit and the reaction is said to be a **activation-controlled reaction**.

Having learnt the general aspects of reactions in solution and in what way the solution phase reactions are different from the gas phase reactions, let us now learn about the role of solvents in the kinetics of reactions in solution.

However, before that answer the following simple questions to assess your understanding.

SAQ 1

In what way are the gas phase collisions different from encounters in the solution phase reactions?

SAQ 2

In what way is the activation energy for a solution phase reaction different from that of a gas phase reaction?

9.3 ROLE OF SOLVENT IN REACTIONS IN SOLUTION

We have learnt above that in many reactions the kinetics is influenced by the presence and the nature of the solvent. Let us learn, how does the solvent influence the kinetics of the reaction? In this context we need to consider three properties of the solvent. These are:

- i. the permittivity of the solvent,
- ii. the viscosity of the solvent and
- iii. the polarizability of the solvent molecules.

You know that in solution the solvent acts as a dielectric that modifies the electrostatic interactions between charged species. It reduces their field strength, the forces acting on them and the potential energy of interaction between them. The extent of such a reduction is measured in terms of the quantity called relative permittivity. The permittivity of the solvent may affect the reaction by changing the structure and the charge distribution in the activated complex (encounter pair). A higher value of relative permittivity means lesser interaction between the charged species. This aspect is significant in reactions involving polar molecules or ions.

Further, the movement of molecules through a solvent is expected to depend on its viscosity as the solvent molecules restrict such movement. A solvent with higher viscosity is expected to slow down the movement to a greater extent. Further, as you know that the polarisability of a molecule is a measure of the extent to which the electronic distribution over it can be distorted by the electric field of charged particles, or dipolar molecules. Therefore, the polarisability of solvent may have a role in the stabilisation of the activated complex.

Thus, we can say that these properties of the solvent may affect the reaction in terms of changing its mechanism or the magnitude of the rate constant. These may also act by altering ion pairing, complexation, hydrogen bonding or any other phenomena involved in the reaction.

In addition to the properties of the solvent and their role discussed above, there is another important consideration in the effect of solvent on the kinetics of reactions in solution. It is the **solvation** of the reactants and/or the activated complex by the solvent. Let us consider different possibilities for a reaction. In the first, we assume that neither the reactants nor the activated complex is solvated, the potential energy profile for such a case is given as in curve (I) in Fig. 9.1.

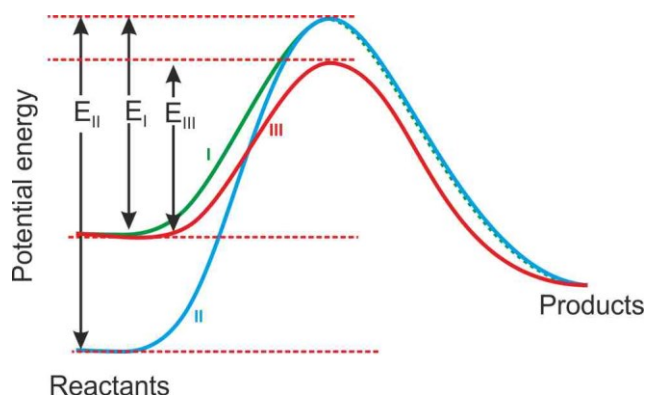


Fig. 9.1: The potential energy curves for (I) reaction with no solvation of the reactants or the activated complex, (II) reaction with solvation of the reactants but not of the activated complex (III) reaction with solvation of the activated complex but not of the reactants.

Here, we find that the activation energy of the reaction has a certain value and correspondingly, the reaction has a certain rate. Now we take a situation in which the reactants are solvated, but the activated complex is not. In such a case, the energy of the reactants decreases whereas that of the activated complex remains unaffected (curve (II)). The activation energy of the reaction increases and causes the rate of the reaction to decrease. In the third case we take up a situation in which the activated complex is solvated, but the reactants are not. In such a case the energy of the activated complex decreases whereas that of the reactants remains unaffected (curve (III)). Here, the activation energy decreases and the rate increases. What would you expect in a case where the solvent solvates the reactants as well as the activated complex? Write your answer in the space provided below.

Yes, you are right. In case where the solvent solvates the reactants as well as the activated complex there may be a small change in the activation energy depending on the difference in the solvation of reactants and the activated complex and rate of the reaction may change accordingly.

Having learnt about the general aspects of reactions in solution and the role of solvent in the kinetics of reactions in solution, let us now take up the theory of rates of reactions in solution. However, before that answer the following.

SAQ 3

The solvation of products has no effect on the rate of reaction. Justify.

9.4 THEORY OF ABSOLUTE REACTION RATES

You have learnt in Unit 6 that according to the transition state theory, the rate constant for the reactions between gaseous molecules, can be determined in terms of partition functions of reactants and the transition state. For activation-controlled reactions in solution we may be tempted to use the transition state theory because of similar mechanistic considerations. However, such an approach cannot be applied because due to the involvement of the solvent, the evaluation of partition functions in such cases is very difficult. As a way out, we extend the transition state theory as applicable to gas phase reactions to the reactions in solution by incorporating activity coefficients. You would recall from your understanding of the concept of activity that

$$\text{Activity} = \text{Concentration} \times \text{Activity coefficient}$$

You also know that in the limits of highly dilute solutions the activity coefficient tends to 1 and the activity becomes equal to the concentration. You would learn in detail about activity and activity coefficients in Unit 13 of this course.

Let us once again consider the reaction



The reaction scheme according to transition state theory is represented as



As discussed in Unit 6, the rate of reaction is directly proportional to the concentration of the activated complex, Eq. (6.50). For infinitely dilute solution, i.e. in the ideal state, rate for solution phase reaction will be given by

$$(\text{Rate}_s)_0 = \frac{k_B T}{h} [XY^\ddagger] \quad \dots(9.14)$$

Here, the subscript s indicates solution phase and 0 represents the standard state and $[XY^\ddagger]$ is the concentration of the activated complex. The concentration of activated complex can be obtained by applying the equilibrium conditions. The equilibrium constant, K^\ddagger for the formation of activated complex under ideal conditions is given as

$$(K_s^\ddagger)_0 = \frac{[XY^\ddagger]}{[X][Y]} \quad \dots(9.15)$$

Rearranging, we get

$$[XY^\ddagger] = (K_s^\ddagger)_0 [X][Y] \quad \dots(9.16)$$

Substituting in Eq. (9.14), we get the expression for the rate of reaction in an ideal solution.

$$(\text{Rate}_s)_0 = \frac{k_B T}{h} (K_s^\ddagger)_0 [X][Y] \quad \dots(9.17)$$

For the rate of elementary reaction in Eq. (9.3) under ideal conditions we can write

$$(\text{Rate})_0 = k_0 [X][Y] \quad \dots(9.18)$$

Comparing, Eq. (9.17) and Eq. (9.18), we can write the rate constant for the reaction in ideal solution as

$$k_0 = \frac{k_B T}{h} (K_s^\ddagger)_0 \quad \dots(9.19)$$

Now, for a non-ideal solution, the rate of reaction will be given by

$$(\text{Rate}_s) = \frac{k_B T}{h} [XY^\ddagger] \quad \dots(9.20)$$

As stated above, for non-ideal solutions we need to invoke activity coefficients.

The equilibrium constant, K_s^\ddagger for a non ideal solution will be given as

$$K_s^\ddagger = \frac{\gamma_\ddagger [XY^\ddagger]}{\gamma_X [X] \gamma_Y [Y]} \quad \dots(9.21)$$

Where, γ_X and γ_Y are the activity coefficients for the reactants respectively, and γ_\ddagger is the activity coefficient for the activated complex. Rearranging, we get the expression for $[XY^\ddagger]$ as

$$[XY^\ddagger] = K_s^\ddagger \frac{\gamma_X \gamma_Y}{\gamma_\ddagger} [X][Y] \quad \dots(9.22)$$

Substituting in Eq. (9.20) we get the expression for the rate of reaction under nonideal conditions as

$$\text{Rate}_s = \frac{k_B T}{h} K_s^\ddagger \frac{\gamma_X \gamma_Y}{\gamma_\ddagger} [X][Y] \quad \dots(9.23)$$

For the rate of elementary reaction in Eq. (9.3) under non-ideal conditions we can write

$$\text{Rate}_s = k_s [X][Y] \quad \dots(9.24)$$

You will learn about the concept of activity and activity coefficients in Unit 12. For now, it is sufficient to know that the activity refers to effective concentration of the species and the activity coefficient is the fraction that determines the effective concentration.

Comparing, Eq. (9.23) and Eq. (9.24), we can write the rate constant under non ideal conditions as

$$k_s = \frac{k_B T}{h} K_s^\ddagger \frac{\gamma_X \gamma_Y}{\gamma_\ddagger} \quad \dots(9.25)$$

If the reaction given in Eq. (9.3) were to occur in gaseous phase, and the reactants are in their standard states, the rate constant for this gas phase reaction can be written as

$$(k_g)_0 = \frac{k_B T}{h} K_g^\ddagger \quad \dots(9.26)$$

Here, the subscript g indicates gas phase and 0 represents the standard state and K_g^\ddagger is equilibrium constant for the activation step.

For reactions in solution, we consider the reference standard state to be the gaseous state. Now, since the activity of very dilute solution and the fugacity of ideal gas, both are equal to 1, we can write

$$K_s^\ddagger = K_g^\ddagger \quad \dots(9.27)$$

Substituting in Eq. (9.25), we get

$$k_s = \frac{k_B T}{h} K_g^\ddagger \frac{\gamma_X \gamma_Y}{\gamma_\ddagger} \quad \dots(9.28)$$

Using Eq. (9.26) we get

$$k_s = k_g \frac{\gamma_X \gamma_Y}{\gamma_\ddagger} \quad \dots(9.29)$$

The Eq. (9.29) can be used for relating the rate constant in solution with that in the gas phase.

In case of unimolecular reactions like the decomposition of N_2O_5 , the rate constants in the gas phase and in solution are equal. This is so because the structures of the activated complexes in the two systems are similar. On the other hand, in case of a closely related reaction viz., the decomposition of nitric acid, the reaction rate is observed to be significantly lower in solution than in the gas phase. This probably is as a result of complexation between the reactant and solvent. Having learnt about the absolute reaction rate theory of reactions in solution, let us take up the effect of salt (electrolyte) concentration on the rate of reactions in solution. However, before that answer the following simple question to assess your understanding.

SAQ 4

Under what conditions does the equilibrium constant for the formation of activated complex equal for the reaction in gas phase and in the solution phase?

You may note that the expression for the rate and rate constant contain the term related to the activity coefficient of the transition state. This is so because the concentration of activated complex is expressed in terms of the equilibrium constant for the activation step (Eq. 9.18).

9.5 SALT EFFECTS

It has been observed that the rate of reaction in solution is altered by the presence of inert ionic species in the solution. The effect is observed for most of the reactions. However, it is more significant for reactions between ions. In such cases, the rate of reaction may alter even at low concentration of the salt. Such an effect of ionic species on the rate of reaction is called as **salt effect**. These salt effects are manifested in two different ways and are classified as primary and the secondary salt effects. The primary salt effect is related to the influence of the added electrolyte concentration on the activity coefficient of the reactants and hence on the rate of reaction. On the other hand, the secondary salt effect refers to the change in the concentration of the reacting ions due to the addition of the electrolytes. Let us discuss these effects.

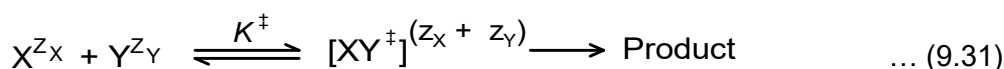
9.5.1 Primary Salt Effect

In case of reactions in solution involving ions, the magnitude of the electrostatic forces between the ions affects the kinetics of the reactions. These forces in turn are affected by the presence of electrolytes whether they are as reactants, products, or an added inert salt. You may note here that an inert salt is the one whose ions do not react either with the reactant (s) or product (s). This effect of inert salts in the reaction rate is called **primary salt effect**. The effect of added inert electrolyte concentration on the rate constants of reactions involving ions in aqueous solutions can be explained in terms of transition state theory, discussed above, and the Debye-Hückel theory which you will learn in Units 13 and 14.

Let us consider the following reaction between a cation, X having a charge Z_X and an anion, Y having a charge, Z_Y



As above, the reaction scheme can be represented as



For such a reaction the activated complex, $[XY^\ddagger]^{(Z_X + Z_Y)}$ will have a charge equal to $(Z_X + Z_Y)$. For sake of simplicity the charges on the species are not shown from now on. As explained above, the equilibrium constant for the formation of the transition state can be written in terms of the activities of the species as

$$K_s^\ddagger = \frac{\gamma_\ddagger [XY^\ddagger]}{\gamma_X [X] \gamma_Y [Y]} \quad \dots (9.21)$$

The rate constant can be expressed as per Eq. (9.25) viz.,

$$k_s = \frac{k_B T}{h} K_s^\ddagger \frac{\gamma_X \gamma_Y}{\gamma_\ddagger} \quad \dots (9.25)$$

Taking logarithm of Eq. (9.25) and expanding the terms we get,

$$\log k_s = \log \frac{k_B T}{h} K_s^\ddagger + \log \gamma_X + \log \gamma_Y - \log \gamma_\ddagger \quad \dots (9.32)$$

The activity coefficients vary with the concentration especially in the presence of added electrolyte. To understand this, Lewis and Randall introduced the quantity called **ionic strength**. It is a unitless quantity that accounts for the charge and concentration of all ions in a solution and is a measure of the intensity of the electric field due to the ions in a solution.

Mathematically, it is given as

$$I = \frac{1}{2} \sum m_i Z_i^2 \quad \text{or} \quad \frac{1}{2} \sum C_i Z_i^2 \quad \dots(9.33)$$

Where, where m_i or C_i is the molar concentration of each individual ion, and Z_i is the charge of each ion. In other words, it is the sum of the terms obtained by multiplying the molarity (concentration) of each ion present in solution by the square of charge on it. Let us take an example to understand the calculation of ionic strength.

Example1: Determine the ionic strength of a 0.10 M solution of MgCl_2 at a pH of 7.0.

Solution: The concentration of all the ions present in the solution will be as follows:

$$[\text{Mg}^{2+}] = 0.10 \text{ M} \quad [\text{Cl}^-] = 0.20 \text{ M} \quad [\text{H}^+] = 1.0 \times 10^{-7} \text{ M} \quad [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

Since the concentrations of hydrogen and hydroxide ions are negligible as compared to the other ions, we use the concentrations and charges for Mg^{2+} and Cl^- for calculating the ionic strength as

$$I = \frac{1}{2} [(0.1)(+2)^2 + (0.2)(-1)^2] = 0.3$$

If the solution is sufficiently dilute, the dependence of activity coefficient on ionic strength is given by Debye-Huckel limiting law about which you will learn in Unit 13. According to the law,

$$\log \gamma_i = -0.509 Z_i^2 I^{1/2} \quad \dots(9.34)$$

where Z_i is the charge on the species, and I is the ionic strength of the solution. Substituting in Eq. (9.33) we get,

$$\log k_s = \log \frac{kT}{h} K_s^\ddagger - 0.509 (Z_X^2 + Z_Y^2 - Z_\ddagger^2) I^{1/2} \quad \dots(9.35)$$

Now, since the charge on the activated complex is $(Z_X + Z_Y)$, we can write

$$Z_\ddagger^2 = (Z_X + Z_Y)^2 = Z_X^2 + Z_Y^2 + 2Z_X Z_Y \quad \dots(9.36)$$

Substituting in Eq. (9.35), and simplifying we get

$$\log k_s = \log \frac{kT}{h} K_s^\ddagger + 1.018 Z_X Z_Y I^{1/2} \quad \dots(9.37)$$

As per Eq. (9.19) the first term in Eq. (9.37) represents $\log k_0$, so we can write

$$\log k_s = \log k_0 + 1.018 Z_X Z_Y I^{1/2} \quad \dots(9.38)$$

In logarithmic form the equation can be written as

$$\log \frac{k_s}{k_o} = 1.018 Z_X Z_Y I^{1/2} \quad \dots(9.39)$$

The Eq. (9. 38) and Eq. (9.39) are known as the Brønsted-Bjerrum equations and predict that a plot of $\log k$ or $\log \frac{k}{k_o}$ versus the square root of ionic

strength, I should be a straight line. For an aqueous solution, the slope is nearly equal to $Z_X Z_Y$, i.e., the product of the ionic charges and the sign of $Z_X Z_Y$ determines the direction of slope as shown in Fig. 9.2.

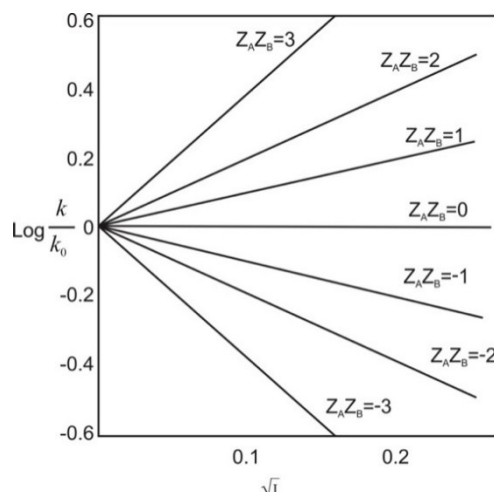


Fig. 9.2: Schematic Brønsted-Bjerrum plot of $\log k$ versus the square root of ionic strength I for different types of ionic reactions in solution.

There are three special cases possible:

- I. If Z_X and Z_Y have the same sign (i.e., both the ions are either positive or negative), then $Z_X Z_Y$ is positive and the rate constant increases with ionic strength. This can be rationalised in terms of the fact that when the ionic strength is high, the solvated ions change the dielectric behaviour of the solution in such a way that the ions of like charge do not repel each other significantly. This allows them to approach more closely, whereby increasing the collision frequency and hence an increased reaction rate.
- II. If Z_X and Z_Y have different signs, $Z_X Z_Y$ is negative and the rate constant decreases with ionic strength. In this case, an increase in the concentration of ions in the solvent causes a decrease in the attraction between the ions thereby decreasing the number of collisions and thence the decrease in the rate of the reaction between them.
- III. If any one of the reactants is uncharged, $Z_X Z_Y$ is zero and the rate constant is independent of the ionic strength.

In order to test these equations we need to make measurements of rate constant of the reaction at different ionic strengths. These are then plotted as a function of square root of the ionic strength. These plots are found to be linear with intercept $\log k_o$. In fact the equation has been verified for a large number of systems and is found to be valid. Some of these reactions are given in Table 9.2.

Now, for reactions involving uncharged reactants, the ionic strength of the solution is expected to have little or no effect on the reaction rate. In cases where the ions are consumed or generated, the overall ionic strength of the medium will change with the progress of the reaction. This may alter the kinetics of the reaction. Therefore, we need to factor in the change in ionic strength with the progress of reaction. In one of the ways to do so is to determine the change in ionic strength during the reaction and adjust results to compensate for the change. Alternatively, the reaction is carried out at a relatively high ionic strength by using a medium containing a large concentration of an inert electrolyte. Minor changes in the concentrations of the ions of reactants and or products do not change the ionic strength of the medium.

Table 9.2: Some of the ionic reactions studied in solution phase

Sunol.	Reaction	S.No.	Reaction
1.	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{Hg}^{2+} \rightarrow 2+$	5.	$\text{CH}_3\text{COOC}_2\text{H}_5 + \text{OH}^- \rightarrow$
2.	$\text{S}_2\text{O}_8^{2-} + \text{I}^- \rightarrow$	6.	$\text{H}^+ + \text{Br}^- + \text{H}_2\text{O}_2 \rightarrow$
3.	$\text{Co}(\text{OC}_2\text{H}_5)_5\text{N}:\text{NO}_2^- + \text{OH}^- \rightarrow$	7.	$\text{Co}(\text{NH}_3)_5\text{Br}^{2+} + \text{OH}^- \rightarrow$
4.	$[\text{Cr}(\text{urea})_6]^{3+} + \text{H}_2\text{O} \rightarrow$	8.	$\text{Fe}^{2+} + \text{Co}(\text{C}_2\text{O}_4)^{3-} \rightarrow$

9.5.2 Secondary Salt Effects

In case of the reactions in which one of the species is neutral ($z=0$), ionic strength should not have any effect as shown above by the Bjerrum equation. However, in practice, for catalytic reactions, especially the ones catalysed by acids or bases there are small effects of changing ionic strength. These effects are not manifested in terms of the change in activity coefficient, instead these are a consequence of the change in the effective concentration of the catalysing species due to the addition of the electrolytes. This phenomenon is independent of primary salt effect and is known as the **secondary salt effect**. In the reactions catalysed by acids or bases, the addition of inert electrolyte affects the concentration of H^+ or OH^- ions. This in turn, alters the rate of the reaction. Let us consider a reaction which is catalysed by H^+ ions produced by a weak acid HA. The ionisation equilibrium of the weak acid is given as



The corresponding thermodynamic ionisation constant is given by the following expression

$$K = \frac{a_{\text{H}^+} \times a_{\text{A}^-}}{a_{\text{HA}}} \quad \dots(9.41)$$

You know that the activity of a species equals the product of activity coefficient and the concentration. Substituting in the above equation we get,

$$K = \frac{\gamma_{H^+} [H^+] \times \gamma_{A^-} [A^-]}{\gamma_{HA} [HA]} \quad \dots(9.42)$$

$$\text{or, } K = \frac{[H^+] \times [A^-]}{[HA]} \frac{\gamma_{H^+} \gamma_{A^-}}{\gamma_{HA}} \quad \dots(9.43)$$

Rearranging, we get

$$[H^+] = K \frac{[HA]}{[A^-]} \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} \quad \dots(9.44)$$

Since, for a given acid salt mixture the ratio $\frac{[HA]}{[A^-]}$ is a constant, we can write

$$[H^+] = K' \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} \quad \dots(9.45)$$

Where K' is a constant. Now since the rate of the reaction depends on the concentration of hydrogen ions besides other species, we can write rate constant expression as

$$k = k_0 \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} \quad \dots(9.46)$$

Where, k_0 is the rate constant in the absence of secondary salt effect. It includes the primary salt effect. Taking logarithms, we get

$$\log k = \log k_0 + \log \frac{\gamma_{HA}}{\gamma_{H^+} \gamma_{A^-}} \quad \dots(9.47)$$

The second term on the right-side equals $1.018\sqrt{I}$, so we get

$$\log k = \log k_0 + 1.018\sqrt{I} \quad \dots(9.48)$$

Thus, an increase in the ionic strength increases the rate constant and hence the rate. The Eq. (9.48) suggests that while studying acid / base catalysed reactions we must keep the ionic strength constant. Else the rate will keep varying.

Let us sum up what have we learnt in this unit. However, before that answer the following simple questions.

SAQ 5

Refer the data given in Table 9.2 and answer the following about the slope of Brønsted-Bjerrum plot:

- Which reaction will have the most negative slope
 - For which reaction(s) the rate constant will be independent of the ionic strength
 - The slope for the reaction at serial number 6 will be positive or negative?
 - Which of the reactions between 2 and 7 will have a positive slope?
-

SAQ 6

What are inert electrolytes?

SAQ 7

Predict the nature (slope) of Brønsted-Bjerrum plot for the following reactions.

1. $\text{CH}_2\text{ClCOO}^- + \text{OH}^- \rightarrow$
 2. $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+} + \text{OH}^- \rightarrow$
 3. $\text{NH}_4^+ + \text{OCN}^- \rightarrow$
 4. $\text{CH}_3\text{I} + \text{H}_2\text{O} \rightarrow$
-

9.6 SUMMARY

In this unit we have taken up different aspects of kinetics of reactions in solution. We started the unit by taking up the general aspects of reactions in solution wherein we broadly outlined the differences in gas phase and solution phase reactions. Then, we described the process of reaction in solution in terms of the encounter pair description and derived the expression for the rate of a reaction in terms of this description. In this context we differentiated between diffusion controlled and activation-controlled reactions in solution. Thereafter, we discussed the role of solvent in the reactions occurring in the solution phase. In this context we pointed out that the solvent manifests its influence in terms of its permittivity, viscosity, and the polarizability. Besides these we also discussed the role of solvation in terms of its effect on the activation energy.

This was followed by a discussion on the theories of reactions in solution. Herein, we discussed how the theories of gas phase reactions get modified for reactions in solution phase. On changing the of medium from gas phase to solutions the theory gets modified, and the influence of the solvent is incorporated in terms of the activity coefficient. In solution phase reactions, especially the ionic reactions, the nature and concentration of the salt plays an important role and the effect of ionic species on the rate of reaction is called salt effect. We discussed the primary and the secondary salt effects. The primary salt effect is related to the influence of the added electrolyte concentration on the activity coefficient and hence on the rate of reaction. Whereas the secondary salt effect refers to the change in the concentration of the reacting ions due to the addition of the electrolytes.

9.7 TERMINAL QUESTIONS

1. List the properties of solvent that affect the kinetics of reaction in solution.
2. Differentiate between diffusion controlled and activation-controlled reactions.

3. Predict the nature (slope) of Brønsted-Bjerrum plot for the following reactions.
- $\text{S}_2\text{O}_3^{2-} + \text{SO}_3^{2-} \rightarrow$
 - $\text{Fe}^{2+} + (\text{Co}(\text{C}_2\text{O}_4)_3)^{2-} \rightarrow$
 - $\text{Co}(\text{NH}_3)_3\text{Br}^{2+} + \text{Hg}^{2+} \rightarrow$
 - $\text{Fe}(\text{CN})_6^{4-} + \text{S}_2\text{O}_8^{2-} \rightarrow$
 - $\text{CH}_3\text{I} + \text{OH}^- \rightarrow$
4. Calculate the ionic strength of a 0.20 M solution of AlCl_3 .
5. Why should the ionic strength be kept constant while studying reactions catalysed by weak acids / bases.

9.8 ANSWERS

Self-Assessment Questions

- In gas phase the molecules move around in a random manner and undergo collisions amongst themselves as well as with the wall of the container. Whereas in case of solutions the reactant molecules have to find their way through the solvent to collide and undergo reaction. The solvent molecules form a kind of cage around the reactant molecules which keep hopping randomly between these solvent cages.

Occasionally the reactant molecules occupy a common solvent cage where they collide with the solvent molecules that are in excess. In a chance event they may come into contact with each other. Such a meeting of the reactant molecules is termed as an encounter and their contact leads to the formation of an encounter pair.
- The activation energy for a solution phase reaction is different from that of a gas phase reaction because the reactants in the encounter pair are surrounded by solvent, and we need to consider combined energy of the reactant and solvent molecules. On the other hand, in case of gas phase reactions we consider the energies of the reactant molecules only.
- Since the solvation of products does not cause any change in the activation energy therefore it has no effect on the rate of reaction.
- The equilibrium constant for the formation of activated complex for gas phase reactions where the reactants behave as ideal gases, and the for solution phase reaction in very dilute solutions is equal. This is so because, the activity of very dilute solution and the fugacity of ideal gas, both are equal to 1.
- i) The slope of Brønsted-Bjerrum plot for the reaction number 8 will have the most negative slope

- ii) For reactions 4 & 5 the rate constant will be independent of the ionic strength
 - iii) The slope for the reaction at serial number 6 will be negative.
 - iv) Between reaction 2 and 7, the reaction at number 2 will have a positive slope.
6. The electrolytes whose ions do not react either with the reactant(s) or the product (s) are called inert electrolytes.
7. The nature (slope) of Brønsted-Bjerrum plot for the given reactions will be
- i. Positive (as the charges on both the reactants is equal to -1 , the value of $Z_X Z_Y$ will be positive and the rate constant will increase with ionic strength).
 - ii. Negative (as the charges on the reactants are $+2$ and -1 , the value of $Z_X Z_Y$ will be negative and the rate constant will decrease with ionic strength).
 - iii. Negative (as the charges on the reactants are $+1$ and -1 , the value of $Z_X Z_Y$ will be negative and the rate constant will decrease with ionic strength).
 - iv. Zero (as the reactants are neutral, the value of $Z_X Z_Y$ will be zero and the rate constant will not change with ionic strength. That is, the rate constant will be independent of the ionic strength).

Terminal Questions

1. The properties of solvent that affect the kinetics of reaction in solution are:
 - i. the permittivity of the solvent,
 - ii. the viscosity of the solvent and
 - iii. the polarizability of the solvent molecules.
2. The reactions in solution can be considered to take place in three steps, viz.,
 - i. diffusion of reactant molecules through the solvent towards each other
 - ii. encounters between the reactant molecules with the formation of activated complex (encounter pair) followed by formation of the product, and
 - iii. diffusion of products away from each other.

If the rate of reaction is limited by the rate of diffusion of the reactants, it is said to be a diffusion-controlled reaction. This happens when the rate of formation of products from the activated complex is far greater than the rate of its dissociation (i.e., $k_r \gg k_d$). On the other hand, when the rate constant for product formation is much smaller than the rate of dissociation of encounter pair (i.e., $k_d \gg k_r$) the rate of the reaction depends on the energetics of the reaction and is said to be an activation-controlled reaction.

3. The nature (slope) of Brønsted-Bjerrum plot for the given reactions will be
- Positive (as the charges on both the reactants is equal to -2 , the value of $Z_x Z_y$ will be positive and the rate constant will increase with ionic strength).
 - Negative (as the charges on the reactants are $+2$ and -3 respectively, the value of $Z_x Z_y$ will be negative and the rate constant will decrease with ionic strength).
 - Positive (as the charges on both the reactants is equal to $+2$, the value of $Z_x Z_y$ will be positive and the rate constant will increase with ionic strength).
 - Positive (as the charges on the reactants are -4 and -2 respectively, the value of $Z_x Z_y$ will be positive and the rate constant will increase with ionic strength).
 - Zero (as the charges on the reactants are zero and -1 respectively, the value of $Z_x Z_y$ will be zero and the rate constant will not change with ionic strength. That is, the rate constant will be independent of the ionic strength).

4. The concentration of all the ions present in the solution will be as follows:

$$[\text{Al}^{3+}] = 0.20 \text{ M} \quad [\text{Cl}^-] = 0.60 \text{ M} \quad [\text{H}^+] = 1.0 \times 10^{-7} \text{ M} \quad [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

Since the concentrations of hydrogen and hydroxide ions are negligible as compared to the other ions, we use the concentrations and charges for Al^{3+} and Cl^- for the calculation of ionic strength.

$$I = \frac{1}{2} [(0.2)(+3)^2 + (0.6)(-1)^2] = 1.2$$

5. The presence of ions influences the ionisation of weak acids or bases thereby changes the concentration of the catalysing species and hence the rate of reaction. Therefore, the ionic strength be kept constant while studying reactions catalysed by weak acid/base.