

CHAPTER 3

Chemical Dynamics – I

❖ Effect of Temperature on Reaction Rates

The temperature of the system shows a very marked effect on the overall rate of the reaction. In fact, it has been observed that the rate of a chemical reaction typically gets doubled with every 10°C rise in the temperature. However, this ratio may differ considerably and may reach up to 3 for different reactions. Besides, this ratio also varies as the temperature of the reaction increases gradually. The ratio of rate constant at two different temperatures is called as “temperature coefficient” of the reaction. Although we can determine the temperature coefficient between any two temperatures for any chemical reaction, generally it is calculated for 10°C difference.

$$\text{Temperature Coefficient} = \frac{k_{T+10}}{k_T} = 2 - 3 \quad (1)$$

Where k_T and k_{T+10} are rate constants at temperature T and $T+10$, respectively. Now, if once the temperature coefficient is known, you can determine the relative increase or decrease in the overall reaction-rate by using the following relation.

$$\frac{R_2}{R_1} = \frac{k_2}{k_1} = (\text{Temperature Coefficient})^{\frac{T_2-T_1}{\Delta T_{tc}}} \quad (2)$$

Where R_2 and R_1 are the reaction-rates at temperatures T_2 and T_1 , respectively. The ΔT_{tc} is the temperature range for the temperature coefficient.

In order to illustrate the dominance of the effect of temperature change on the reaction rate, consider a reaction in which the temperature of the system is raised from 310°C to 400°C. Now, if the temperature coefficient for 10°C temperature-rise is 2, the relative increase in the rate constant or rate will be

$$\frac{R_2}{R_1} = \frac{k_2}{k_1} = (2)^{\frac{400-310}{10}} \quad (3)$$

$$\frac{R_2}{R_1} = \frac{k_2}{k_1} = (2)^9 = 512 \quad (4)$$

$$\frac{R_2}{R_1} = 512 \quad (5)$$

Hence, a 90°C rise in temperature increases the rate of reaction 512 times, which is definitely huge. Now the question arises, why is it so? What did the temperature do that made this happen? In this section, we will answer these questions.

➤ **Fundamentals of Temperature-Rate Correlation**

Before we discuss the effect of temperature on the reaction rate, we must understand the cause of a reaction itself first. The primary requirement for a reaction to occur is the collision between the reacting molecules. In other words, the reactant molecules must collide with each other to form the product. Therefore, if we assume that every collision results in the formation of the product, the rate of reaction should simply be equal to the collision frequency of the reacting system.

For a reaction between A and B , the collision frequency (Z) is the number of collisions between A and B occurring in the container per unit volume per unit time.

$$Z = n_A n_B \theta_{AB} \sqrt{\frac{8k_B T}{\pi \mu_{AB}}} \quad (6)$$

Where n_A and n_B are the number densities (in the units of m^{-3}) of particles A and B , respectively. The term θ_{AB} is the reaction cross-section (in m^2) when particle A with radius r_A and B with radius r_B collide with each other i.e. $\theta_{AB} = \pi (\sigma_{AB})^2 = \pi (r_A + r_B)^2 = \pi (\sigma_A/2 + \sigma_B/2)^2$. k_B is the Boltzmann's constant ($m^2 kg s^{-2} K^{-1}$). T represents the temperature of the system. The term μ_{AB} represents the reduced mass of the reactants A and B i.e. $\mu_{AB} = m_A m_B / m_A + m_B$. From equation (6), it follows that when we heat the substance, the particles collide more frequently and hence increase the collision frequency. Now one may think that this collision frequency would result in a larger rate of reaction, and therefore, the mystery is solved. However, this isn't sufficient to rationalize the experimental observations. For instance, if we increase the temperature from 300 K to 310 K, the relative increase in the collision frequency (n_Z), and hence in reaction rate, from equation (6) can be determined as given below.

$$n_Z = \sqrt{\frac{310}{300}} = 1.0165 \quad (7)$$

This is only 1.65% increase for a 10° rise in temperature. This is pretty far from the reality i.e. reaction-rate almost gets double (100% increase). So, the actual mechanism is still behind the scene and must be understood.

At this point we must introduce the concept of activation energy, otherwise, the concept cannot be discussed further. The collision of reacting molecules would result in the chemical reaction only if they possess a certain amount of minimum energy i.e. threshold energy. Since every molecule does have some energy, the energy it needs to reach the threshold is less than the actual threshold energy. The energy required by reactant molecules to cross the barrier is called the activation energy or the enthalpy of activation for the reaction. A simple equation can be used to deduce their relationships as given below.

$$\text{Activation energy} = \text{Threshold energy} - \text{Energy actually possessed by the molecules}$$

The rate of a chemical reaction is inversely proportional to the magnitude of the activation energy i.e. larger the activation energy, slower will be the reaction and vice-versa.

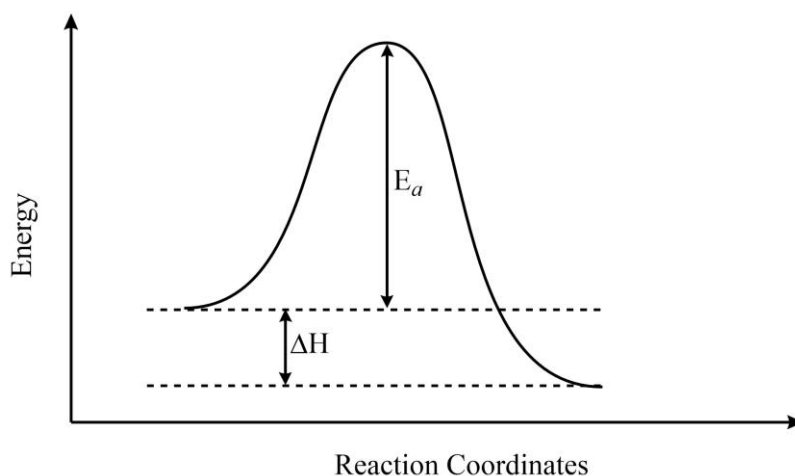


Figure 1. The reaction coordinate diagram for a typical chemical reaction.

Hence, we can say that only effective collisions would result in the chemical reactions, but how can we find the number of molecules having energy high enough to react with each other. For this, we need to go into the basics of energy distribution among a large number of particles i.e. Maxwell's distribution of energies.

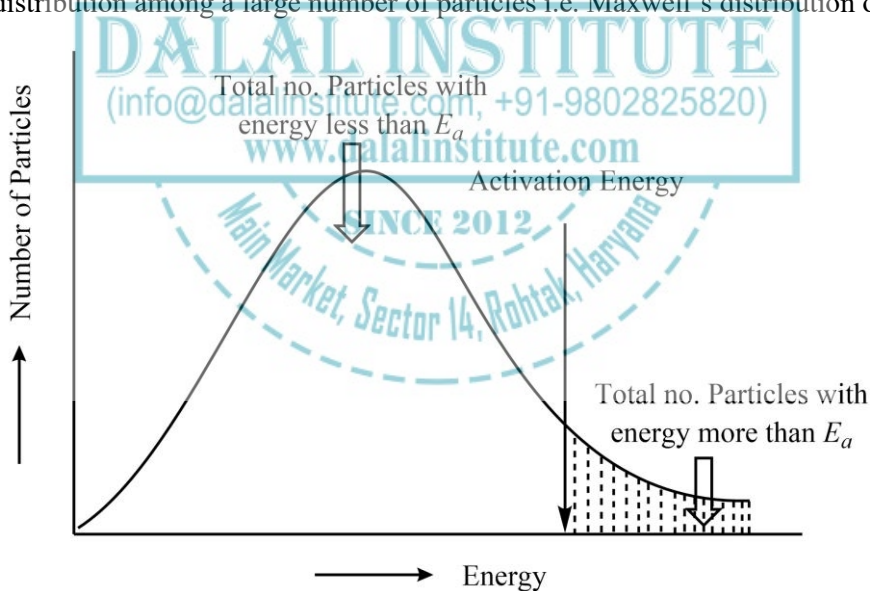


Figure 2. The Maxwell-Boltzmann distribution of energies at temperature T.

After marking the activation energy on the Maxwell-Boltzmann distribution curve, the particle with sufficient energy to react can easily be found from the area under the corresponding curve i.e. dashed area. The undashed area at a particular temperature is quite large, and therefore, represents the number particle whose collision would not result in any reaction chemical change. It can be clearly seen that most of the particles don't have

enough energy, and hence, are unable to yield the product. The reaction-rate will be very small if there are very few particles with enough energy at any time.

However, if the temperature is raised, the maxima of the Maxwell-Boltzmann distribution curve shifts towards higher energy. This makes the number of “efficient particles” to increase and thereby increases the number of effective collisions too. Consider the Maxwell-Boltzmann energy distributions at temperature T and $T+10$.

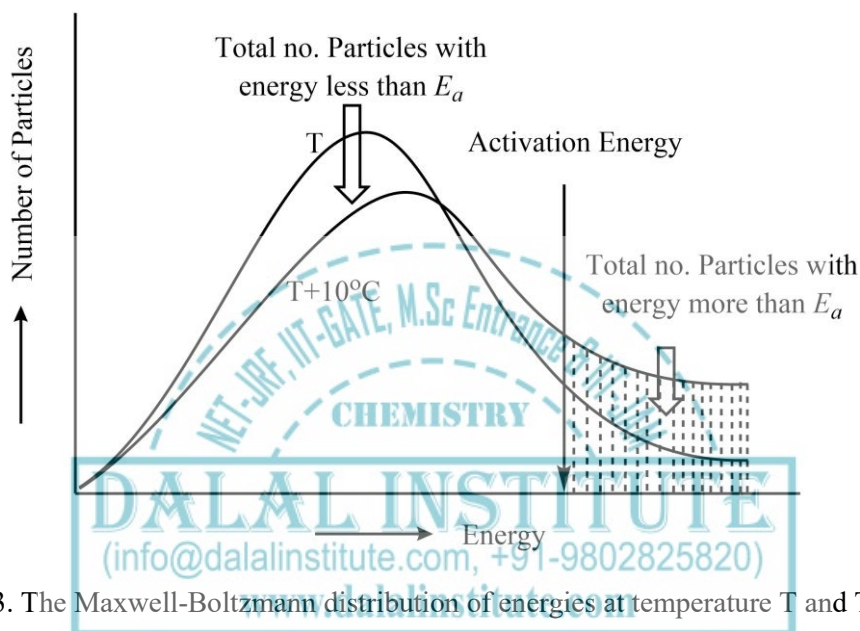


Figure 3. The Maxwell-Boltzmann distribution of energies at temperature T and $T+10^\circ\text{C}$.

Now although the area under the whole curve remains the same, the dashed area is doubled. Thus, the primary reason for almost 100% rise in the overall rate of reaction for every 10°C is the 100% increase in the number of effective collisions.

➤ The Arrhenius Equation

In 1884, the famous Dutch chemist Jacobus Henricus Van't Hoff realized that his equation (Van't Hoff equation) could also be used to suggest a formula for the rates of both forward and backward reactions. In 1889, Svante Arrhenius immediately noticed the importance of this invention and proposed an empirical equation based on Van't Hoff's work. This equation is extremely useful in the modeling of the temperature variation of many chemical reactions. The equation proposed by Arrhenius is

$$k = A e^{-E_a/RT} \quad (8)$$

Where the symbol k , R and T represent rate constant, gas constant and temperature, respectively. A is popularly known as the pre-exponential factor or Arrhenius constant with the units identical to those of the rate constant used, and therefore, will vary depending on the order of the reaction. The term E_a represents the activation energy measured in joule mole^{-1} .

Another popular form of the Arrhenius equation is

$$k = A e^{-E_a/k_B T} \quad (9)$$

The only difference in the equation (8) and equation (9) is the energy units of E_a ; the former one uses energy per mole, which is more common in chemistry, while the latter form uses energy per molecule directly, which is common in physics. The different units are accounted for in using either the gas constant, R , or the Boltzmann constant, k_B , as the multiplier of temperature T . If the reaction is first order, A will have the units of s^{-1} and can be called as collision frequency or frequency factor.

The physical significance of k is that it represents the number of collisions that result in a reaction per second; A is the number of collisions (leading to a reaction or not) per second occurring with the proper orientation to react. The exponential factor is the probability that any given collision will result in a reaction. It can also be seen that either increasing the temperature or decreasing the activation energy (for example through the use of catalysts) will result in an increase in the rate of reaction. Taking the natural logarithm of both side of equation (8), we get

$$\ln k = \ln A + \ln e^{-E_a/RT} \quad (10)$$

$$\ln k = \ln A - \frac{E_a}{RT} \quad (11)$$

Rearrange the above equation, we get

$$\ln k = -\frac{E_a}{RT} + \ln A \quad (12)$$

The equation (12) has the same form as the equation of straight line i.e. $y = mx + c$; which means that if we plot " $\ln k$ " vs $1/T$, the slope and intercept will yield " $-E_a/R$ " and " $\ln A$ ", respectively.

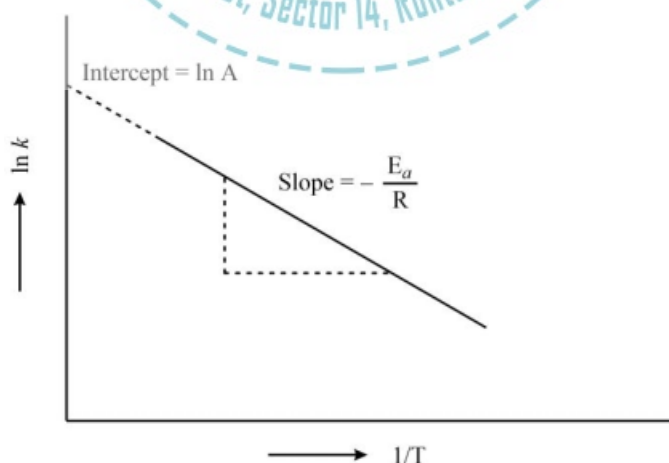


Figure 4. The Arrhenius plot of $\ln k$ vs $1/T$.

In addition to the equation (12), one of the more popular forms of the Arrhenius equation can be derived by converting it to the common logarithm as given below.

$$2.303 \log k = -\frac{E_a}{RT} + 2.303 \log A \quad (13)$$

or

$$\log k = -\frac{E_a}{2.303 RT} + \log A \quad (14)$$

The equation (14) also has the same form as the equation of straight line i.e. $y = mx + c$; which means that if we plot “ $\log k$ ” vs $1/T$, the slope and intercept will yield “ $-E_a/2.303R$ ” and “ $\log A$ ”, respectively.



Figure 5. The Arrhenius plot of $\log k$ vs $1/T$.

To obtain the integrated form of the Arrhenius equation, differentiate the equation (12) as given below.

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \quad (15)$$

Now integrating the above equation between temperature T_1 and T_2 , we get

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \text{or} \quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (16)$$

The above equation can be used to find the activation energy if rate constants are known at two different temperatures.

❖ Rate Law for Opposing Reactions of 1st Order and 2nd Order

A reaction will be called as the opposing or reversible reaction if the reactants react together to form a product and the products also react to yield the reactants simultaneously under the same conditions.

In a simple context, we can say these reactions proceed not only in the forward direction but also in the backward direction. These reactions can be classified into the following categories based upon the kinetic order of the reactions involved.

➤ First Order Opposed by First Order

In order to understand the kinetic profile of first-order reactions opposed by the first order, consider a general reaction in which the reactant A forms product B i.e.



Now, if $k_f \gg k_b$, k_b can be neglected. However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. To do so, suppose that a is the initial concentration of the reactant A and x is the decrease in the concentration of A after ' t ' time. The concentration of the product after the same time would also be equal to x . Hence, the rates of forward reaction (R_f) and backward reaction (R_b) can be given as:

$$R_f = k_f[A] = k_f(a - x) \quad (17)$$

$$R_b = k_b[B] = k_b x \quad (18)$$

The net reaction rate i.e. rate of formation of the product can be given as

$$\frac{dx}{dt} = k_f(a - x) - k_b x \quad (19)$$

However, when the equilibrium is attained, the rate of forward reaction will be equal to the rate of backward reaction i.e. $R_f = R_b$. Therefore, the will take the form

$$k_f(a - x_{eq}) = k_b x_{eq} \quad (20)$$

Where x_{eq} is the concentration of product B or the decrease in the concentration of reactant A at equilibrium. Now putting the value of k_b from equation (20) into equation (19), we get

$$\frac{dx}{dt} = k_f(a - x) - \frac{k_f(a - x_{eq})}{x_{eq}} x \quad (21)$$

$$\frac{dx}{dt} = k_f \left[(a - x) - \frac{(a - x_{eq})}{x_{eq}} x \right] \quad (22)$$

or

$$\frac{dx}{dt} = k_f \left[\frac{(a-x)x_{eq} - (a-x_{eq})x}{x_{eq}} \right] \quad (23)$$

$$\frac{dx}{dt} = k_f \frac{ax_{eq} - ax}{x_{eq}} = \frac{k_f a(x_{eq} - x)}{x_{eq}} \quad (24)$$

or

$$\frac{x_{eq}}{(x_{eq} - x)} dx = k_f a dt \quad (25)$$

Integrating equation (25), we get

$$-x_{eq} \ln(x_{eq} - x) = k_f a t + C \quad (26)$$

Where C is the constant of integration. When $t = 0$, $x = 0$; putting these values in equation (26), we get

$$-x_{eq} \ln x_{eq} = C \quad (27)$$

Using the value of C from equation (27) in (26)

$$-x_{eq} \ln(x_{eq} - x) = k_f a t - x_{eq} \ln x_{eq} \quad (28)$$

or

$$x_{eq} \ln x_{eq} - x_{eq} \ln(x_{eq} - x) = k_f a t \quad (29)$$

$$k_f = \frac{x_{eq}}{at} \ln \frac{x_{eq}}{x_{eq} - x} \quad (30)$$

Using equation (30), the rate constant for the forward reaction can easily be determined by measuring simple quantities like a , t , x_{eq} and x . Now rearranging equation (29) for k_b

$$k_b = \frac{k_f(a - x_{eq})}{x_{eq}} \quad (31)$$

$$k_b = \frac{k_f(a - x_{eq})}{x_{eq}} = k_f \left(\frac{a}{x_{eq}} - \frac{x_{eq}}{x_{eq}} \right) = k_f \left(\frac{a}{x_{eq}} - 1 \right) \quad (32)$$

Now putting the value k_f from equation (30) in equation (32), we get

$$k_b = \left(\frac{1}{t} \ln \frac{x_{eq}}{x_{eq} - x} \right) - \frac{x_{eq}}{at} \ln \frac{x_{eq}}{x_{eq} - x} \quad (33)$$

Hence, the value of the rate constant for backward reaction can also be obtained just by measuring t , x_{eq} and x ; or in other words, the k_f eventually yields the k_b also.

Alternatively, the values of k_f and k_b can also be obtained a slightly different route. Rearranging equation (30), we get

$$\frac{a k_f}{x_{eq}} = \frac{1}{t} \ln \frac{x_{eq}}{x_{eq} - x} \quad (34)$$

Also rearranging equation (20), we have

$$\frac{k_f a}{x_{eq}} = k_b + k_f \quad (35)$$

Equating the right-hand sides of equation (34) and (35), we get

$$\frac{1}{t} \ln \frac{x_{eq}}{x_{eq} - x} = k_b + k_f \quad (36)$$

$$\ln \frac{x_{eq}}{x_{eq} - x} = (k_b + k_f)t \quad (37)$$

or

$$\log \frac{x_{eq}}{x_{eq} - x} = \frac{(k_b + k_f)}{2.303} t \quad (38)$$

Equation (37) and (38) are the equations of straight line ($y = mx + c$) with zero intercept.

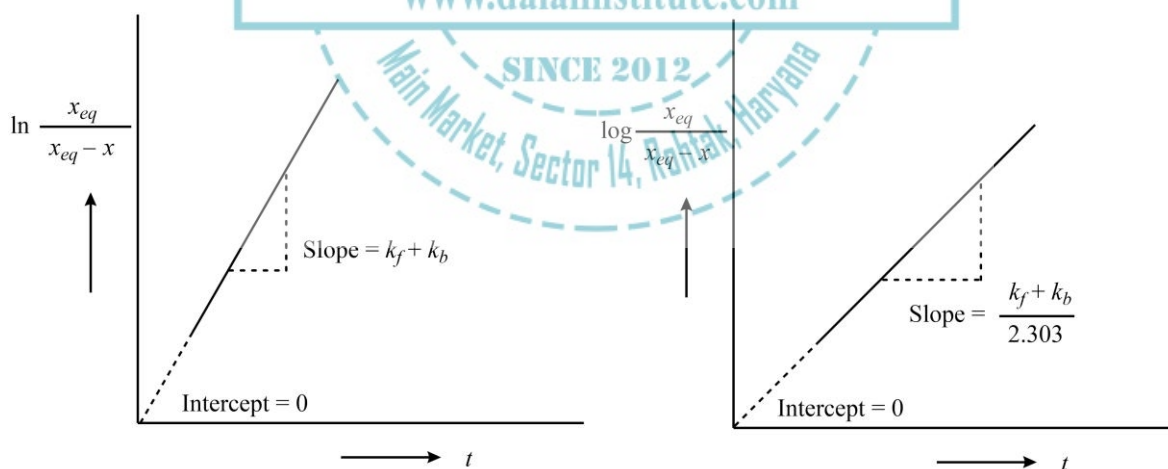


Figure 6. The plot of $\ln \frac{x_{eq}}{x_{eq} - x}$ and $\log \frac{x_{eq}}{x_{eq} - x}$ vs time for first order opposed by the first order.

Now, finding $k_f + k_b$ from slope and k_f/k_b from equilibrium constant, k_f and k_b can easily be obtained from the elimination method. It should also be noted that if plot $\ln \frac{x_{eq} - x}{x_{eq}}$ and $\log \frac{x_{eq} - x}{x_{eq}}$, the slopes will become negative.

➤ **First Order Opposed by Second Order**

In order to understand the kinetic profile of first-order reactions opposed by second-order, consider a general reaction in which the reactant A forms product B and C i.e.



Now, if $k_f \gg k_b$, k_b can be neglected. However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. To do so, suppose that a is the initial concentration of the reactant A and x is the decrease in the concentration of A after 't' time. The concentration of both the products after same time would also be equal to x . Hence, the rates of forward reaction (R_f) and backward reaction (R_b) can be given as:

$$R_f = k_f[A] = k_f(a - x) \quad (40)$$

$$R_b = k_b[B][C] = k_b x^2 \quad (41)$$

The net reaction rate i.e. rate of formation of the product can be given as

$$\frac{dx}{dt} = k_f(a - x) - k_b x^2 \quad (42)$$

However, when the equilibrium is attained, the rate of forward reaction will be equal to the rate of backward reaction i.e. $R_f = R_b$. Therefore, the equation (42) will take the form

$$k_f(a - x_{eq}) = k_b x_{eq}^2 \quad (43)$$

Where x_{eq} is the concentration of product B and C or the decrease in the concentration of reactant A at equilibrium. Now putting the value of k_b from equation (43) into equation (42), we get

$$\frac{dx}{dt} = k_f(a - x) - \frac{k_f(a - x_{eq})}{x_{eq}^2} x^2 \quad (44)$$

$$\frac{dx}{dt} = k_f \left[(a - x) - \frac{(a - x_{eq})}{x_{eq}^2} x^2 \right] \quad (45)$$

or

$$\frac{dx}{dt} = k_f \left[\frac{(a - x)x_{eq}^2 - (a - x_{eq})x^2}{x_{eq}^2} \right] \quad (46)$$

$$\frac{dx}{dt} = k_f \left[\frac{ax_{eq}^2 - xx_{eq}^2 - ax^2 + x_{eq}x^2}{x_{eq}^2} \right] \quad (47)$$

or

$$\frac{x_{eq}^2}{(ax_{eq}^2 - xx_{eq}^2 - ax^2 + x_{eq}x^2)} dx = k_f dt \quad (48)$$

Integrating equation (48), and then rearranging

$$k_f = \frac{x_{eq}}{t(2a - x_{eq})} \ln \frac{ax_{eq} + x_{eq}(a - x_{eq})}{a(x_{eq} - x)} \quad (49)$$

Using equation (49), the rate constant for the forward reaction can easily be determined by measuring simple quantities like a , t , x_{eq} and x . Now, we know that the equilibrium constant for the first order opposed by second-order will be

$$K = \frac{[B][C]}{[A]} \quad (50)$$

also

$$K = \frac{k_f}{k_b} \quad (51)$$

Now putting the value of k_f from equation (49) in equation (51) and the rearranging for k_b , we get

$$k_b = \frac{x_{eq}}{t(2a - x_{eq})K} \ln \frac{ax_{eq} + x_{eq}(a - x_{eq})}{a(x_{eq} - x)} \quad (52)$$

Hence, the value of the rate constant for backward reaction can also be obtained just by measuring t , x_{eq} and x and the equilibrium constant from equation (50).

➤ Second Order Opposed by First Order

In order to understand the kinetic profile of second-order reactions opposed by first order, consider a general reaction in which two reactants A and B form product C i.e.



Now, if $k_f \gg k_b$, k_b can be neglected. However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. To do so, suppose that a is the initial concentration of both the reactant A and B ; while x is the decrease in the concentrations of both reactants after ' t ' time. The concentration of the product after the same time would also be equal to x . Hence, the rates of forward reaction (R_f) and backward reaction (R_b) can be given as:

$$R_f = k_f[A][B] = k_f(a - x)^2 \quad (54)$$

$$R_b = k_b[C] = k_b x \quad (55)$$

The net reaction rate i.e. rate of formation of the product can be given as

$$\frac{dx}{dt} = k_f(a-x)^2 - k_b x \quad (56)$$

However, when the equilibrium is attained, the rate of forward reaction will be equal to the rate of backward reaction i.e. $R_f = R_b$. Therefore, the equation (56) will take the form

$$k_f(a-x_{eq})^2 = k_b x_{eq} \quad (57)$$

Where x_{eq} is the concentration of the product C or the decrease in the concentration of reactant A or B at equilibrium. Now putting the value of k_b from equation (57) into equation (56), we get

$$\frac{dx}{dt} = k_f(a-x)^2 - \frac{k_f(a-x_{eq})^2}{x_{eq}} x \quad (58)$$

$$\frac{dx}{dt} = k_f \left[(a-x)^2 - \frac{(a-x_{eq})^2}{x_{eq}} x \right] \quad (59)$$

or

$$\frac{dx}{dt} = k_f \left[\frac{(a-x)^2 x_{eq} - (a-x_{eq})^2 x}{x_{eq}} \right] \quad (60)$$

$$\frac{dx}{dt} = k_f \left[\frac{(a^2 + x^2 - 2ax)x_{eq} - (a^2 + x_{eq}^2 - 2ax_{eq})x}{x_{eq}} \right] \quad (61)$$

$$\frac{dx}{dt} = k_f \left[\frac{a^2 x_{eq} + x^2 x_{eq} - 2ax x_{eq} - a^2 x - x_{eq}^2 x + 2ax_{eq} x}{x_{eq}} \right] \quad (62)$$

$$\frac{dx}{dt} = k_f \left[\frac{a^2 x_{eq} + x^2 x_{eq} - a^2 x - x_{eq}^2 x}{x_{eq}} \right] \quad (63)$$

or

$$\frac{x_{eq}}{(a^2 x_{eq} + x^2 x_{eq} - a^2 x - x_{eq}^2 x)} dx = k_f dt \quad (64)$$

Integrating equation (64), and then rearranging

$$k_f = \frac{x_{eq}}{t(a^2 - x_{eq}^2)} \ln \frac{x_{eq}(a^2 - x_{eq}x)}{a^2(x_{eq} - x)} \quad (65)$$

Using equation (66), the rate constant for the forward reaction can easily be determined by measuring simple quantities like a , t , x_{eq} and x . Now, we know that the equilibrium constant for a second-order reaction opposed by first order will be

$$K = \frac{[C]}{[A][B]} \quad (66)$$

$$K = \frac{k_f}{k_b} \quad (67)$$

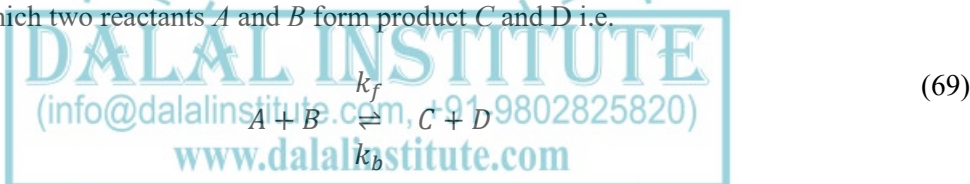
Now putting the value of k_f from equation (65) in equation (67) and the rearranging for k_b , we get

$$k_b = \frac{x_{eq}}{t(a^2 - x_{eq}^2)K} \ln \frac{x_{eq}(a^2 - x_{eq}x)}{a^2(x_{eq} - x)} \quad (68)$$

Hence, the value of the rate constant for backward reaction can also be obtained just by measuring t , x_{eq} and x and the equilibrium constant from equation (66).

➤ **Second Order Opposed by Second Order**

In order to understand the kinetic profile of second-order reactions opposed by second-order, consider a general reaction in which two reactants A and B form product C and D i.e.



Now, if $k_f \gg k_b$, k_b can be neglected. However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. To do so, suppose that a is the initial concentration of both the reactant A and B ; while x is the decrease in the concentrations of both reactants after 't' time. The concentration of the products after the same time would also be equal to x . Hence, the rates of forward reaction (R_f) and backward reaction (R_b) can be given as:

$$R_f = k_f[A][B] = k_f(a - x)^2 \quad (70)$$

$$R_b = k_b[C][D] = k_b x^2 \quad (71)$$

The net reaction rate i.e. rate of formation of the product can be given as

$$\frac{dx}{dt} = k_f(a - x)^2 - k_b x^2 \quad (72)$$

However, when the equilibrium is attained, the rate of forward reaction will be equal to the rate of backward reaction i.e. $R_f = R_b$. Therefore, the equation (72) will take the form

$$k_f(a - x_{eq})^2 = k_b x_{eq}^2 \quad (73)$$

Where x_{eq} is the concentration of the product C and D or the decrease in the concentration of reactant A or B at equilibrium. Now putting the value of k_b from equation (73) into equation (72), we get

$$\frac{dx}{dt} = k_f(a-x)^2 - \frac{k_f(a-x_{eq})^2}{x_{eq}^2}x^2 \quad (74)$$

$$\frac{dx}{dt} = k_f \left[(a-x)^2 - \frac{(a-x_{eq})^2}{x_{eq}^2}x^2 \right] \quad (75)$$

or

$$\frac{dx}{dt} = k_f \left[\frac{(a-x)^2x_{eq}^2 - (a-x_{eq})^2x^2}{x_{eq}^2} \right] \quad (76)$$

$$\frac{dx}{dt} = k_f \left[\frac{a^2x_{eq}^2 + x^2x_{eq}^2 - 2axx_{eq}^2 - a^2x^2 - x_{eq}^2x^2 + 2ax_{eq}x^2}{x_{eq}^2} \right] \quad (78)$$

or

$$\frac{x_{eq}^2}{(a^2x_{eq}^2 - 2axx_{eq}^2 - a^2x^2 + 2ax_{eq}x^2)} dx = k_f dt \quad (80)$$

Integrating equation (80), and then rearranging

$$k_f = \frac{x_{eq}}{2at(a-x_{eq})} \ln \frac{x(a-2x_{eq}) + ax_{eq}}{a(x_{eq}-x)} \quad (81)$$

Using equation (81), the rate constant for the forward reaction can easily be determined by measuring simple quantities like a , t , x_{eq} and x . Now, we know that the equilibrium constant for a second-order reaction opposed by second-order will be

$$K = \frac{[C][D]}{[A][B]} \quad (82)$$

$$K = \frac{k_f}{k_b} \quad (83)$$

Now putting the value of k_f from equation (81) in equation (83) and the rearranging for k_b , we get

$$k_b = \frac{x_{eq}}{2at(a-x_{eq})K} \ln \frac{x(a-2x_{eq}) + ax_{eq}}{a(x_{eq}-x)} \quad (84)$$

Hence, the value of the rate constant for backward reaction can also be obtained just by measuring t , x_{eq} and x and the equilibrium constant from equation (84).

❖ Rate Law for Consecutive & Parallel Reactions of Ist Order Reactions

In addition to the opposing or reversible reactions, two other types of simultaneous reactions are consecutive and parallel reactions. In this section, we will discuss the kinetic profiles of these two types of reactions up to the first order only.

➤ Consecutive Reactions

In many complex reactions, the order of the reaction has not been found equal to the molecularity noted from the stoichiometry. So, these reactions must take place in multiple steps rather than a single step. These multiple steps are individually labeled as consecutive reactions.

The consecutive reactions may be defined as the single-step reactions which can be written to represent an overall reaction.

In order to understand the kinetic profile of consecutive reactions, consider two first-order reactions in which reactant A converts to B which in turn converts to product C .



Where k_1 and k_2 are the rate constants for the first and second steps, respectively. In other words, A is the reactant, B is simply the intermediate and C is the final product.

However, k_f and k_b have comparable values, a rate law depending upon both the constants can be written. Now suppose that the initial concentrations of reactant A is C_0 ; while the concentrations of A , B and C after time t are C_A , C_B and C_C , respectively. So, we can say that

$$C_0 = C_A + C_B + C_C \quad (86)$$

Now, the rate can be deduced in terms of C_A , C_B and C_C as given below.

1. Rate law in terms of C_A : The rate of disappearance reactant of A in the given reaction can be given by the following relation.

$$-\frac{d[C_A]}{dt} = k_1 C_A \quad (87)$$

or

$$-\frac{d[C_A]}{C_A} = k_1 dt \quad (88)$$

Integrating both sides, we get

$$-\ln C_A = k_1 t + I \quad (89)$$

Where I is the constant of integration. However, when $t = 0$, $C_A = C_0$, the equation (89) takes the form

$$-\ln C_0 = I \quad (90)$$

Using the value of integration constant from equation (90) in equation (89), we get

$$-\ln C_A = k_1 t - \ln C_0 \quad (91)$$

or

$$\ln C_0 - \ln C_A = k_1 t \quad (92)$$

or

$$-\ln \frac{C_A}{C_0} = k_1 t \quad (93)$$

or

$$\ln \frac{C_A}{C_0} = -k_1 t \quad (94)$$

or

$$\frac{C_A}{C_0} = e^{-k_1 t} \quad (95)$$

or

$$C_A = C_0 e^{-k_1 t} \quad (96)$$

2. Rate law in terms of C_B : The rate of formation of intermediate B can be given by the following relation.

$$\frac{d[C_B]}{dt} = k_2 C_B + k_1 C_A \quad (97)$$

or

$$\frac{d[C_B]}{dt} = k_1 C_A - k_2 C_B \quad (98)$$

After putting the value of C_A from equation (96) in equation (98), we get a linear differential equation of first order i.e.

$$\frac{d[C_B]}{dt} = k_1 C_0 e^{-k_1 t} - k_2 C_B \quad (99)$$

Integrating and then rearranging equation (99), both side, we get

$$[C_B] = C_0 \left(\frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \quad (100)$$

3. Rate law in terms of C_C : The overall rate of formation of the product C in the given reaction can be given by the following relation.

$$\frac{d[C_C]}{dt} = k_2 C_B \quad (101)$$

After putting the value of C_A and C_B from equation (96) and equation (100) into equation (86), we get the following result.

$$C_C = C_0 - C_0 e^{-k_1 t} - C_0 \left(\frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \quad (102)$$

or

$$= C_0 \left[1 - e^{-k_1 t} - \left(\frac{k_1}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \right] \quad (103)$$

or

$$= C_0 \left[1 - e^{-k_1 t} - \frac{k_1 e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right] \quad (104)$$

or

$$= C_0 \left[1 - \left(e^{-k_1 t} + \frac{k_1 e^{-k_1 t}}{k_2 - k_1} - \frac{k_1 e^{-k_2 t}}{k_2 - k_1} \right) \right] \quad (105)$$

or

$$= C_0 \left[1 - \left(\frac{(k_2 - k_1) e^{-k_1 t} + k_1 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right) \right] \quad (106)$$

$$= C_0 \left[1 - \left(\frac{k_2 e^{-k_1 t} - k_1 e^{-k_1 t} + k_1 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right) \right] \quad (107)$$

$$= C_0 \left[1 - \left(\frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right) \right] \quad (108)$$

or

$$C_C = C_0 \left[1 - \frac{1}{(k_2 - k_1)} (k_2 e^{-k_1 t} - k_1 e^{-k_2 t}) \right] \quad (109)$$

The equation (96), (100) and (109) can be used to plot the time-dependent variation of C_A , C_B and C_C , respectively.

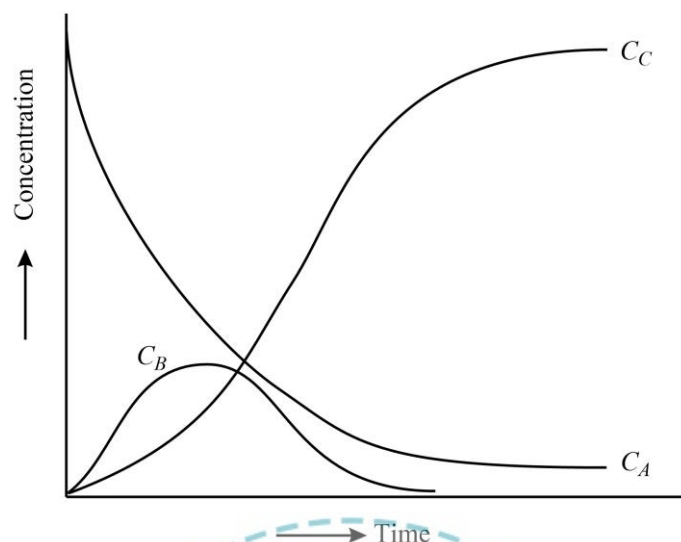


Figure 7. The plot C_A , C_B and C_C as a function of time in a typical consecutive reaction.

It can be clearly seen that the concentration of A decreases exponentially, while the concentration of B increases first and then declines. The concentration of C increases continuously and finally becomes equal to the concentration of A .

Maxima in the concentration of B : In addition to the time-dependent concentration variation of different species, one more important parameter to measure is the maximum B concentration. Since, for this the value of $[dC_B]/dt = 0$, the differentiation of equation (100) and then putting equal to zero gives

$$\frac{d[C_B]}{dt} = C_0 \left(\frac{k_1}{k_2 - k_1} \right) (-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}) = 0 \quad (110)$$

$$-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} = 0 \quad (111)$$

or

$$k_1 e^{-k_1 t} = k_2 e^{-k_2 t} \quad (112)$$

or

$$\frac{k_1}{k_2} = \frac{e^{-k_2 t}}{e^{-k_1 t}} \quad (113)$$

$$\frac{k_1}{k_2} = e^{(k_1 - k_2)t} \quad (114)$$

Taking logarithm both side, we get

$$\ln \frac{k_1}{k_2} = \ln e^{(k_1 - k_2)t} \quad (115)$$

$$\ln \frac{k_1}{k_2} = (k_1 - k_2)t \quad (116)$$

$$t_{max} = \frac{1}{(k_1 - k_2)} \ln \frac{k_1}{k_2} \quad (117)$$

Now putting the value of t from equation (117) in equation (100), we get

$$[C_B] = C_0 \left(\frac{k_1}{k_2 - k_1} \right) \left[\exp \left\{ \frac{-k_1 \ln(k_1/k_2)}{k_1 - k_2} \right\} - \exp \left\{ \frac{-k_2 \ln(k_1/k_2)}{k_1 - k_2} \right\} \right] \quad (118)$$

Simplifying and then rearranging the above equation, we get

$$[C_B]_{max} = C_0 \left(\frac{k_2}{k_1} \right) e^{k_2/(k_1 - k_2)} \quad (119)$$

Rate law in special cases: In addition to the typical consecutive reaction i.e. $k_1 = k_2$, two special cases also arise from the nature of the step reactions discussed below.

i) When $k_2 \gg k_1$: In these types of reactions, the value of k_1 can be neglected. Therefore, the equation (109) takes the form

$$C_A = C_0(1 - e^{-k_1 t}) \quad (120)$$

Graphically,

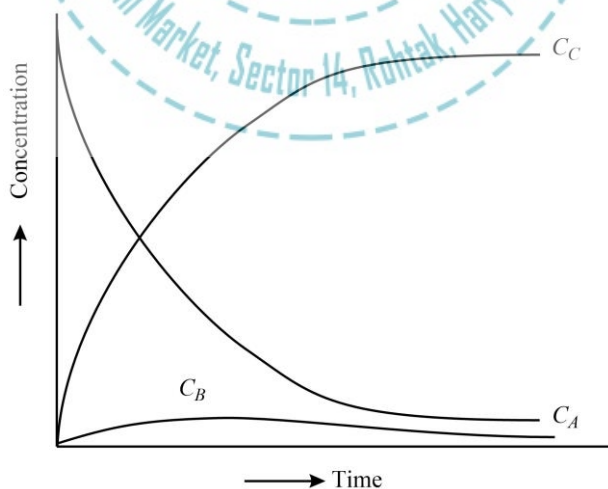


Figure 8. The plot C_A , C_B and C_C vs time in a typical consecutive reaction when $k_2 \gg k_1$.

It can be clearly seen that the concentration of the intermediate practically remains constant, and therefore, the steady-state approximation can be applied in this case.

ii) When $k_1 \gg k_2$: In these types of reactions, the value of k_2 can be neglected. Therefore, the equation (109) takes the form

$$C_C = C_0(1 - e^{-k_2 t}) \quad (121)$$

Graphically,

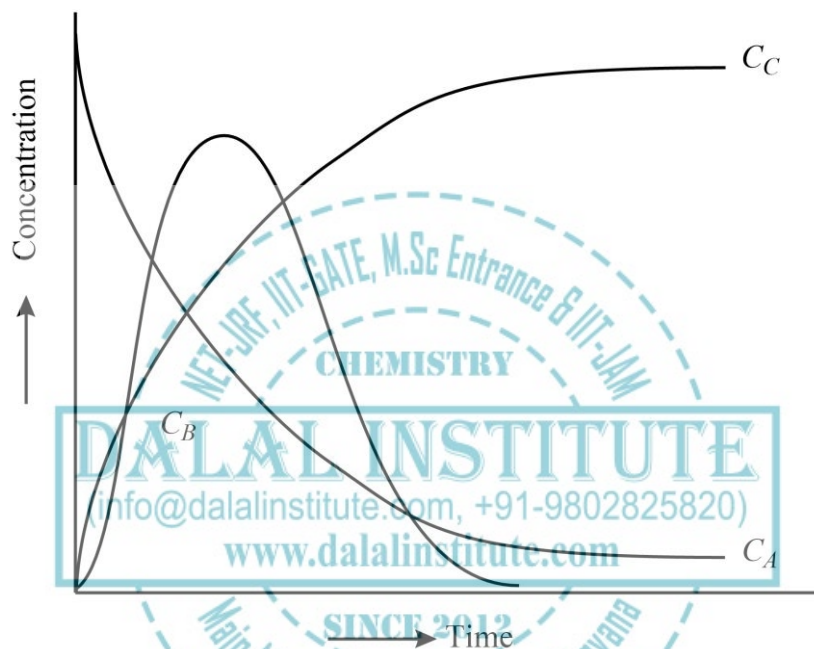


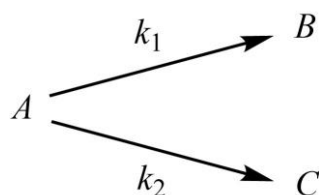
Figure 9. The plot C_A , C_B and C_C vs time in a typical consecutive reaction when $k_1 \gg k_2$.

➤ Parallel Reactions

In many reactions, the reactant reacts to form more than one product simultaneously. If the amount of one the reaction product is very large in comparison to the others, then we can simply neglect these other reactions. However, if the amount of the product formed by other reactions are significant, we must refine the overall rate equation to represent this.

The parallel or side reactions may simply be defined as the reactions in which initial species react to give multiple products simultaneously.

In order to understand the kinetics of parallel reactions of the first order, suppose that a reactant A reacts to form product B and C simultaneously. A typical depiction of the parallel or side reaction with two pathways is given below.



Where k_1 and k_2 are the rate constants. Now suppose that a is the initial concentration of the reactant A , while x is the decrease in the concentrations of the reactant after ‘ t ’ time. Hence, the rates of first (R_1) and second reaction (R_2) can be given as:

$$R_1 = \frac{d[B]}{dt} = k_1[A] = k_1(a - x) \quad (122)$$

or

$$R_2 = \frac{d[C]}{dt} = k_2[A] = k_2(a - x) \quad (123)$$

The overall reaction rate can be obtained by adding equation (122) and equation (123) as

$$\frac{dx}{dt} = \frac{d[B]}{dt} + \frac{d[C]}{dt} = k_1(a - x) + k_2(a - x) \quad (124)$$

or

$$\frac{dx}{dt} = (k_1 + k_2)(a - x) \quad (125)$$

or

$$\frac{dx}{(a - x)} = (k_1 + k_2)dt \quad (126)$$

Integrating the equation (126) and then rearranging, we get

$$k_1 + k_2 = \frac{1}{t} \ln \frac{a}{(a - x)} \quad (127)$$

Also, dividing equation (122) by (123), we get

$$\frac{R_1}{R_2} = \frac{k_1(a - x)}{k_2(a - x)} \quad (128)$$

Which implies that

$$\frac{R_1}{R_2} = \frac{k_1}{k_2} \quad (129)$$

Hence, the value of rate constants involved, i.e., k_1 and k_2 can easily be obtained from the use of equation (127) and equation (129).

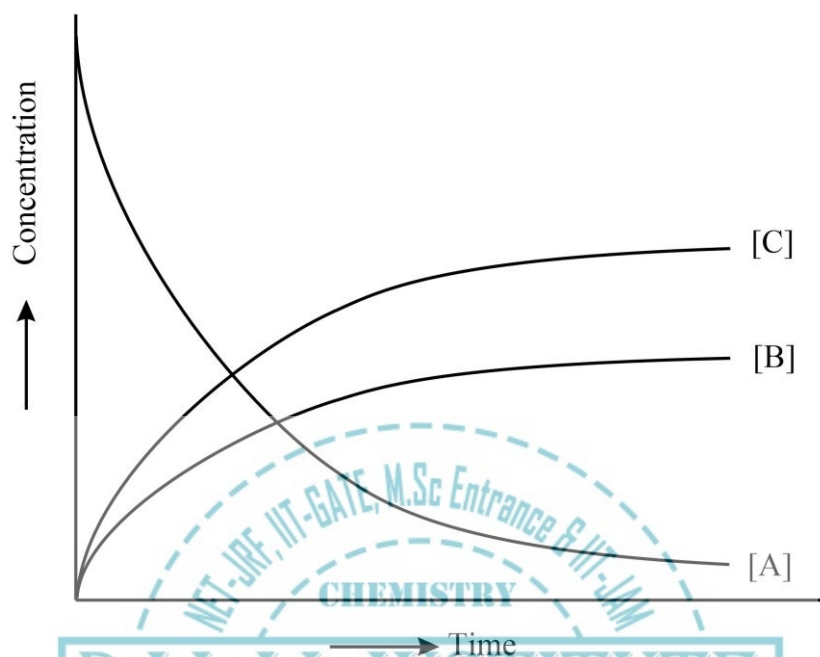


Figure 10. The variation of the concentrations of reactants and products as a function of time in a typical parallel reaction.

It should also be noted from the equation (129) that the ratio of the concentration of products remains the same with time. Furthermore, the percentage of both products can also be obtained from the knowledge of rate constants using the relations given below.

$$\text{Fractional Quantum Yield of A} = \frac{k_1}{k_1 + k_2} \quad (130)$$

also

$$\text{Fractional Quantum Yield of B} = \frac{k_2}{k_1 + k_2} \quad (131)$$

The percentage is obtained by multiplying corresponding fractional quantum yields by 100. Similarly, parts per thousand (ppt) and parts per million (ppm) can be obtained by multiplying equations (130) and (131) by 10^3 and 10^6 , respectively.

❖ Collision Theory of Reaction Rates and Its Limitations

In 1916, a German chemist Max Trautz proposed a theory based on the collisions of reacting molecules to explain reaction kinetics. Two years later, a British chemist William Lewis published similar results, however, he was completely unaware of Trautz's work. The remarkable work of these two gentlemen was extremely beneficial in explaining the rate of many chemical reactions.

The collision theory states that when the right reactant particles strike each other, only a definite fraction of the collisions induce any significant or noticeable chemical change; these successful changes are called successful collisions and are possible only if reacting molecules have sufficient energy at the moment of impact to break the pre-existing bonds and form all new bonds.

The minimum energy required to make a collision successful is called as the activation energy, and these types of collisions result in the products of the reaction. The rise in reactant concentration or increasing the temperature, both result in more collisions and hence more successful collisions, and therefore, increase the reaction rate. Sometimes, a catalyst is involved in the collision between the reactant molecules that decreases the energy required for the chemical change to take place, and so more collisions would have sufficient energy for the reaction to happen. In this section, we will discuss the collision theory of bimolecular and unimolecular reactions in the gaseous phase.

➤ Collision Theory for Bimolecular Reactions

In order to understand the collision theory for bimolecular reactions, we must understand the cause of a reaction itself first. The primary requirement for a reaction to occur is the collision between the reacting molecules. Therefore, if we assume that every collision results in the formation of the product, the rate of reaction should simply be equal to collision frequency (Z) of the reacting system i.e. the number of collisions occurring in the container per unit volume per unit time. Mathematically, we can say that

$$\text{Rate} = Z \quad (132)$$

However, the actual rate would be much less than what is predicted by the equation (132); which is obviously due to the fact that all the collisions are not effective. Therefore, equation (132) must be modified to represent this factor. If f is the fraction of the molecules which are activated, the rate expression can be written as given below.

$$\text{Rate} = Z \times f \quad (133)$$

Now, according to the Maxwell-Boltzmann distribution of energies, the fraction of the molecules having energy greater than a particular energy E is

$$f = \frac{\Delta N}{N} = e^{-E/RT} \quad (134)$$

Where N is the total number of molecules while ΔN represents the number of molecules having energy greater than E . However, if $E = E_a$, the fraction of activated molecules can be written as

$$f = \frac{\Delta N}{N} = e^{-E_a/RT} \quad (135)$$

Where R is the gas constant and T is the reaction temperature. After putting the value of f from equation (135) into equation (133), we get

$$\text{Rate} = Z e^{-E_a/RT} \quad (136)$$

At this point, two possibilities arise; one, when the colliding molecules are similar and other, is when the colliding molecules are dissimilar. We will discuss these cases one by one.

1. Rate of reaction when the colliding molecules are dissimilar: Consider a bimolecular reaction between different molecules A and B yielding product P as



The number of collisions between A and B occurring in the container per unit volume per unit time can be given by the following relation.

$$Z = n_A n_B \sigma_{AB}^2 \sqrt{\frac{8\pi k_B T}{\mu_{AB}}} \quad (138)$$

Where n_A and n_B are the number densities (in the units of m^{-3}) of particles A and B , respectively. The term σ_{AB} is simply the average collision diameter i.e. $\sigma_{AB} = (\sigma_A + \sigma_B)/2$. k_B is the Boltzmann's constant ($m^2 kg s^{-2} K^{-1}$). T represents the temperature of the system. The term μ_{AB} represents the reduced mass of the reactants A and B i.e. $\mu_{AB} = m_A m_B / (m_A + m_B)$.

The equation (138) can also be expressed in terms of molar masses by putting $m_A = M_A/N$, $m_B = M_B/N$ and $k = R/N$; where M_A and M_B are molar masses of the reactants, R is the gas constant and N represents to Avogadro number. Therefore, equation (138) takes the form

$$Z = \sigma_{AB}^2 \sqrt{\frac{8\pi \left(\frac{R}{N}\right) T \left(\frac{M_A}{N} + \frac{M_B}{N}\right)}{\frac{M_A}{N} \times \frac{M_B}{N}}} n_A n_B \quad (139)$$

or

$$Z = \sigma_{AB}^2 \sqrt{\frac{8\pi R T (M_A + M_B)}{M_A M_B}} n_A n_B \quad (140)$$

Also, as we know that the reaction rate can be written in terms of molecules of reactants reacting per cm^3 per second as

$$\text{Rate} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = Ze^{-E_a/RT} \quad (141)$$

or

$$\text{Rate} = -\frac{dn_A}{dt} = -\frac{dn_B}{dt} = \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} \times n_A n_B \times e^{-E_a/RT} \quad (142)$$

Now, in order to express the rate in terms of molar concentrations, we need to recall some typical relations like

$$n_A = \frac{N[A]}{10^3} \quad \text{and} \quad n_B = \frac{N[B]}{10^3} \quad (143)$$

also

$$dn_A = \frac{N}{10^3} d[A] \quad \text{and} \quad dn_B = \frac{N}{10^3} d[B] \quad (144)$$

Using the results of equation (143) and (144) in equation (142), we get

$$\text{Rate} = -\frac{N}{10^3} \frac{d[A]}{dt} = -\frac{N}{10^3} \frac{d[B]}{dt} = \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} \frac{N[A]}{10^3} \frac{N[B]}{10^3} e^{-E_a/RT} \quad (145)$$

or

$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} [A][B] e^{-E_a/RT} \quad (146)$$

Comparing equation (146) with general rate law expressed in molar concentrations i.e. $\text{Rate} = k[A][B]$, we get

$$k = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} e^{-E_a/RT} \quad (147)$$

Comparing equation (147) with Arrhenius rate constant i.e. $k = Ae^{-E_a/RT}$, we get

$$A = \frac{N}{10^3} \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} \quad (148)$$

2. Rate of reaction when the colliding molecules are similar: Consider a bimolecular reaction between similar molecules A and A yielding product P as



The number of collisions between A and A occurring in the container per unit volume per unit time can be given by the following relation.

$$Z = n_A^2 \sigma^2 \sqrt{\frac{4\pi k_B T}{m_A}} \quad (150)$$

Where n_A is the number density (in the units of m^{-3}) of particle A . The term σ is simply the average collision diameter. k_B is the Boltzmann's constant ($m^2 kg s^{-2} K^{-1}$). T represents the temperature of the system. The term m_A represents the mass of the reactants A .

The equation (150) can also be expressed in terms of molar masses by putting $m_A = M_A/N$ and $k = R/N$; where M_A is the molar mass of the reactant, R is the gas constant and N represents to Avogadro number. Therefore, equation (150) takes the form

$$Z = \sigma^2 \sqrt{\frac{4\pi \left(\frac{R}{N}\right) T}{\frac{M_A}{N}}} n_A^2 \quad (151)$$

or

$$Z = \sigma^2 \sqrt{\frac{4\pi RT}{M_A}} n_A^2 \quad (152)$$

Also, as we know that the reaction rate can be written in terms of molecules of reactants reacting per cm^3 per second as

$$\frac{1}{2} \frac{dn_A}{dt} = Z e^{-E_a/RT} \quad (153)$$

or

$$\text{Rate} = -\frac{dn_A}{dt} = 2 \left(\sigma^2 \sqrt{\frac{4\pi RT}{M_A}} \times n_A^2 \times e^{-E_a/RT} \right) \quad (154)$$

Now, in order to express the rate in terms of molar concentrations, we need to recall some typical relations like

$$n_A = \frac{N[A]}{10^3} \quad (155)$$

also

$$dn_A = \frac{N}{10^3} d[A] \quad (156)$$

Using the results of equation (155) and (156) in equation (154), we get

$$\text{Rate} = -\frac{N}{10^3} \frac{d[A]}{dt} = 2 \left(\sigma^2 \sqrt{\frac{4\pi RT}{M_A}} \times \frac{N^2 [A]^2}{10^6} \times e^{-E_a/RT} \right) \quad (157)$$

or

$$\text{Rate} = -\frac{d[A]}{dt} = \frac{4N}{10^3} \sigma^2 \sqrt{\frac{\pi RT}{M_A}} \times [A]^2 \times e^{-E_a/RT} \quad (158)$$

Comparing equation (158) with general rate law expressed in molar concentrations i.e. $\text{Rate} = k[A]^2$, we get

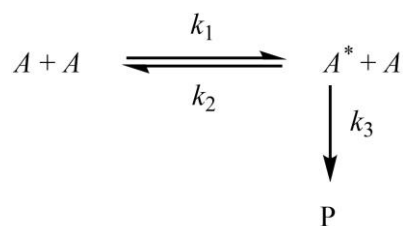
$$k = \frac{4N}{10^3} \sigma^2 \sqrt{\frac{\pi RT}{M_A}} e^{-E_a/RT} \quad (159)$$

Comparing equation (159) with Arrhenius rate constant i.e. $k = Ae^{-E_a/RT}$, we get

$$A = \frac{4N}{10^3} \sigma^2 \sqrt{\frac{\pi RT}{M_A}} \quad (160)$$

➤ Collision Theory for Unimolecular Reactions

In order to understand the collision theory for unimolecular reactions, we must understand the root cause of these reactions. In a typical unimolecular reaction, a single molecule converts into the product by simply rearranging itself. However, the question that arises here is how these molecules get activated. The mystery was solved by a British physicist, Frederick Alexander Lindemann, who proposed a time-lag between activation and actual reaction. In other words, when ordinary molecules collide with each other, some of them get activated, and the rate depends only upon these molecules but not the ordinary ones i.e.



Where k_1 , k_2 and k_3 are the rate constants for the different processes; while A and A^* are the ordinary and activated molecule. The overall rate of formation of the product can be given as

$$\frac{d[P]}{dt} = k_3[A^*] \quad (161)$$

Now, since the molar concentration of $[A^*]$ is unknown we must apply the steady-state approximation on $[A^*]$.

At steady state

Rate of formation of $[A^*]$ = Rate of disappearance of $[A^*]$

$$k_1[A]^2 = k_2[A^*][A] + k_3[A^*] \quad (162)$$

or

$$k_1[A]^2 = (k_2[A] + k_3)[A^*] \quad (163)$$

$$[A^*] = \frac{k_1[A]^2}{k_2[A] + k_3} \quad (164)$$

Using the value of $[A^*]$ from equation (164) in equation (161), we get

$$\text{Rate} = \frac{d[P]}{dt} = \frac{k_3 k_1 [A]^2}{k_2 [A] + k_3} \quad (165)$$

Equation (165) gives rise to two possibilities discussed below.

1. If the concentration of reactant A is very high: In this situation, $k_2[A] \gg k_3$, and k_3 can be neglected, therefore, the equation (165) takes the form

$$\text{Rate} = \frac{d[P]}{dt} = \frac{k_3 k_1 [A]^2}{k_2 [A]} \quad (166)$$

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or

$$\frac{d[P]}{dt} = \frac{k_3 k_1}{k_2} [A] \quad (167)$$

$$\frac{d[P]}{dt} = k_o [A] \quad (168)$$

Where k_o is the overall rate constant. It is clear from the above result that the unimolecular reactions follow first-order kinetics in such cases.

2. If the concentration of reactant A is very low: In this situation, $k_3 \gg k_2[A]$ and $k_2[A]$ can be neglected, therefore, the equation (165) takes the form

$$\text{Rate} = \frac{d[P]}{dt} = \frac{k_3 k_1 [A]^2}{k_3} \quad (169)$$

$$\frac{d[P]}{dt} = k_1 [A]^2 \quad (170)$$

Where k_1 is the overall rate constant. It is clear from the above result that the unimolecular reactions follow second-order kinetics in such cases.

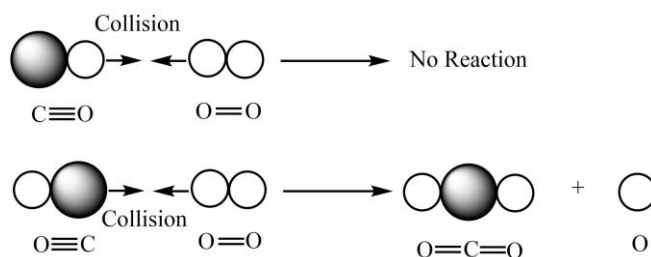
➤ Limitations of Collision Theory

The collision theory of reaction rate is extremely successful in rationalizing the kinetics of many reactions, however, it does suffer from some serious limitations discussed below.

1. This theory finds application only to reactions occurring in the gas phase and solution having simple reactant molecules.
2. The rate constants obtained by employing collision theory are found to be comparable to what has been obtained from the Arrhenius equation only for the simple reactions but not for complex reactions.
3. This theory tells nothing about the exact mechanism behind the chemical reaction i.e. making and breaking of chemical bonds.
4. The collision theory considers only the kinetic energy of reacting molecules and just ignored rotational and vibrational energy which also plays an important role in reaction rate.
5. This theory did not consider the steric factor at all i.e. the proper orientation of the colliding molecules needed to result in the chemical change.

❖ Steric Factor

One of the most glaring limitations of the collision is that the predicted values of rate constants for many reactions were found to be considerably different from the values obtained experimentally. Moreover, it was also noticed that more the complexity, the higher was the deviation. This happened because the collision theory supposed that the particles participating in the chemical reaction are completely spherical, and thus, are able to react in every direction. However, this is far from the truth since the orientation of the collisions is not always appropriate to result in the chemical change. For instance, in the hydrogenation of ethylene, the dihydrogen molecule must approach the bonding zone between the atoms, and not all the possible collisions would be able to satisfy this requirement. For more clear view, consider the formation of CO_2 as shown below.



To solve this problem, the concept of steric factor (ρ) was introduced, which is simply the ratio of experimental value to the predicted value of the rate constant. In other words, the steric factor may be defined as the ratio between the frequency factor and the collision frequency i.e.

$$\rho = \frac{A_{\text{observed}}}{Z_{\text{calculated}}} \quad (171)$$

It is worthy to note that the value of the steric factor most of the cases is less than unity. Typically, it has been seen that more the complex the reactant molecules are, the lower is the steric factor. However, some reactions do have steric factors higher than unity; for instance, the harpoon reactions in which atoms involved exchange electrons generating ions. The deviation from unity may arise due to different reasons such as non-spherical shape of reacting molecules, or the partial delivery of kinetic energy, the presence of a solvent when applied to solutions.

In order to derive the expression for modified collision theory that does consider the reactants steric, recall the rate constant calculated from simple collision theory first i.e.

$$\text{Rate} = Z e^{-E_a/RT} \quad (172)$$

For experimental rate, multiply the equation (172) by the probability or steric factor i.e.

$$\text{Rate} = \rho Z e^{-E_a/RT} \quad (173)$$

Now considering both the possibilities i.e. whether the reacting species are the same or different, we can simplify the above equation in two ways:

i) For dissimilar molecules:

If the colliding molecules are not the same, the exponential part in equation (173) takes the form

$$A = \rho \frac{N}{10^3} \sigma_{AB}^2 \sqrt{\frac{8\pi RT(M_A + M_B)}{M_A M_B}} \quad (174)$$

Substituting the values of different constants, we get

$$A = 2.753 \times 10^{29} \times \rho \times \sigma_{AB}^2 \sqrt{\frac{T(M_A + M_B)}{M_A M_B}} \quad (175)$$

ii) For similar molecules:

If the colliding molecules are the same, the exponential part in equation (173) takes the form

$$A = \rho \frac{N}{10^3} 4\sigma^2 \sqrt{\frac{\pi RT}{M_A}} \quad (176)$$

$$A = 3.893 \times 10^{29} \times \rho \times \sigma^2 \sqrt{\frac{T}{M_A}} \quad (177)$$

This modified collision theory can account for probability factors up to 10^{-4} but not less than that. This limitation can be overcome by “transition state theory” discussed in the next section.

❖ Activated Complex Theory

In 1935, an American chemist Henry Eyring; alongside two British chemists, Meredith Gwynne Evans and Michael Polanyi; proposed a new theory to rationalize the rate of different chemical reactions which was based upon the formation of an activated intermediate complex. This theory is also known as the "transition state theory", "theory of absolute reaction rates", and "absolute-rate theory".

The activated complex theory states that the rates of various elementary chemical reactions can be explained by assuming a special type of chemical equilibria (quasi-equilibrium) between reactants and activated complexes.

Before the development of activated complex theory, the Arrhenius rate law was popularly used to determine energies for the potential barrier. However, the Arrhenius equation was based on empirical observations rather than mechanistic investigations as if one or more intermediates are involved in the conversion or not. For that reason, more development was essential to know the two factors present in the Arrhenius equation, the activation energy (E_a) and the pre-exponential factor (A). The Eyring equation from transition state theory successfully addresses these two issues and therefore contributed significantly to the conceptual understanding of reaction kinetics.

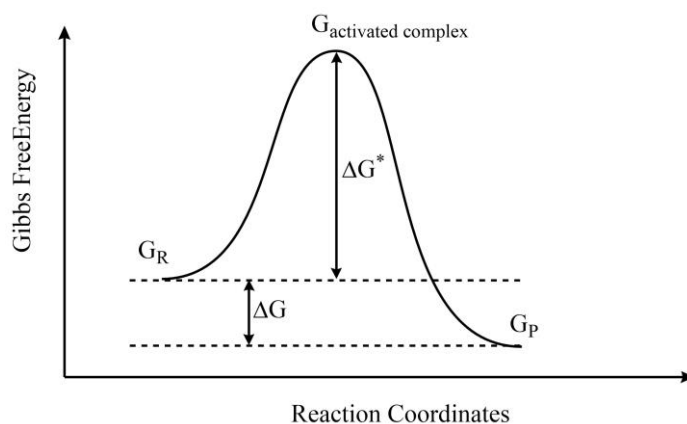


Figure 11. The variation of free energy as the reaction proceeds.

To explore the concept mathematically, consider a reaction between reactant A and B forming a product P via the activated complex X^* as:



The equilibrium constant for reactants to activated complex conversion is

$$K^* = \frac{[X^*]}{[A][B]} \quad (179)$$

Henry Eyring showed that the rate constant for a chemical reaction with any order or molecularity can be given by the following relation.

$$k = \frac{RT}{Nh} K^* \quad (180)$$

Where K^* is the equilibrium constant for reactants to activated complex conversion at temperature T. Whereas, R , N and h represent the gas constant, Avogadro number and Planck's constant, respectively. Now, as we know from thermodynamics

$$\Delta G^* = -RT \ln K^* \quad (181)$$

$$-\frac{\Delta G^*}{RT} = \ln K^* \quad (182)$$

$$K^* = e^{-\frac{\Delta G^*}{RT}} \quad (183)$$

Where ΔG^* is the free energy of activation for reactants to activated complex conversion step. Using the value of K^* from equation (183) into equation (180), we get

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G^*}{RT}} \quad (184)$$

If we put the thermodynamic value of free energy i.e. $\Delta G^* = \Delta H^* - T\Delta S^*$ in equation (184), we get

$$k = \frac{RT}{Nh} e^{-\frac{(\Delta H^* - T\Delta S^*)}{RT}} \quad (185)$$

or

$$k = \frac{RT}{Nh} \times e^{\frac{\Delta S^*}{R}} \times e^{-\frac{\Delta H^*}{RT}} \quad (186)$$

Where ΔH^* and ΔS^* are enthalpy change and the entropy change of the activation step. Equation (186) is popularly known as the Eyring equation. Now, since the equation (186) contains very fundamental factors of the reacting species, that is why this theory got its name of "theory of absolute reaction rates".

➤ Significance of Entropy of Activation and Enthalpy of Activation

As far as the equation (184) is concerned, it can easily be seen that as the free energy change of the activation step increases, the rate constant would decrease. However, if we look at the simplified form i.e. equation (186), we find three factors; one is RT/Nh which is constant if the temperature is kept constant. The second factor involves ΔS^* , and therefore, we can conclude that the reaction rate would show exponential increase if the entropy of activation increases. The third factor includes ΔH^* , and therefore, we can conclude that the reaction rate would show exponential decrease if the enthalpy of activation increases. It is also worthy to note that the first two terms collectively make the frequency factor.

➤ **Comparison with Arrhenius Rate Constant**

Like the collision theory, the validity of the “activated complex theory” must also be checked against the results of the Arrhenius rate equation. In order to do so, recall the Arrhenius equation i.e.

$$k = A e^{-\frac{E_a}{RT}} \quad (187)$$

By looking at the analogy with equation (187), we get

$$A = \frac{RT}{Nh} \times e^{\frac{\Delta S^*}{R}} \quad (188)$$

and

$$e^{-\frac{E_a}{RT}} = e^{-\frac{\Delta H^*}{RT}} \quad (189)$$

Now we can use equation (188) and (189) to determine the value of entropy of activation and enthalpy of activation.

1. Calculation of entropy of activation: In order to determine the entropy change of the activation step, take the natural logarithm of the equation (188) i.e.

$$\ln A = \ln \frac{RT}{Nh} + \ln e^{\frac{\Delta S^*}{R}} \quad (190)$$

$$\ln A = \ln \frac{RT}{Nh} + \frac{\Delta S^*}{R} \quad (191)$$

or

$$\frac{\Delta S^*}{R} = \ln A - \ln \frac{RT}{Nh} \quad (192)$$

$$\Delta S^* = R \ln A - R \ln \frac{RT}{Nh} \quad (193)$$

Thus, higher is the value of the frequency factor, larger will be the entropy of activation.

2. Calculation of enthalpy of activation: In order to determine the enthalpy change of the activation step, we must look at the equation (189) which suggests that the enthalpy change of the activation step as exactly equal to the activation energy of the reaction dictating the rate considerably i.e. $\Delta H^* = E_a$. However, it has been observed that the exact value of activation energy is slightly different than the enthalpy of activation. In order to prove the aforementioned statement, rewrite the equation (186) as:

$$k = \frac{R}{Nh} e^{\frac{\Delta S^*}{R}} \times T \times e^{-\frac{\Delta H^*}{RT}} \quad (194)$$

or

$$k = C \times T \times e^{-\frac{\Delta H^*}{RT}} \quad (195)$$

Where C is another constant. Now taking natural logarithm both side, equation (195) takes the form

$$\ln k = \ln C + \ln T + \ln e^{-\frac{\Delta H^*}{RT}} \quad (196)$$

or

$$\ln k = \ln C + \ln T - \frac{\Delta H^*}{RT} \quad (197)$$

Now, differentiating both side w.r.t temperature, we get

$$\frac{d \ln k}{dt} = \frac{1}{T} + \frac{\Delta H^*}{RT^2} \quad (198)$$

We also know from the Arrhenius equation that

$$k = A e^{-\frac{E_a}{RT}} \quad (199)$$

Now taking natural logarithm both side, equation (199) takes the form

$$\ln k = \ln A + \ln e^{-\frac{E_a}{RT}} \quad (200)$$

or

$$\ln k = \ln A - \frac{E_a}{RT} \quad (201)$$

Now, differentiating both side w.r.t temperature, we get

$$\frac{d \ln k}{dt} = \frac{E_a}{RT^2} \quad (202)$$

Comparing (198) and (202), we get

$$\frac{1}{T} + \frac{\Delta H^*}{RT^2} = \frac{E_a}{RT^2} \quad (203)$$

$$\frac{RT + \Delta H^*}{RT^2} = \frac{E_a}{RT^2} \quad (204)$$

$$\Delta H^* = E_a - RT \quad (205)$$

If n is the change in the number of moles of gas in going from reactant to activated complex, the result of equation (205) takes the form $\Delta H^* = E_a - \Delta n_g RT$.

❖ 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.

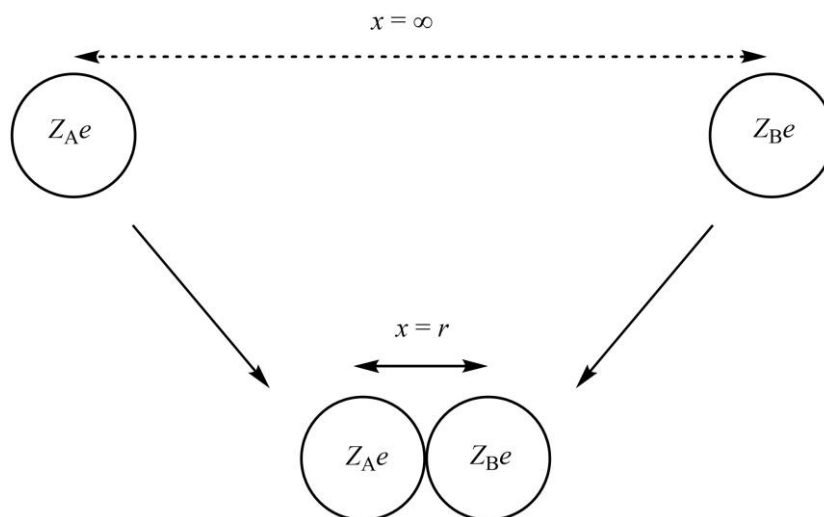


Figure 12. The pictorial depiction of the double-sphere model of ionic reactions.

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:

$$F_{AB} = \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon x^2} \quad (206)$$

Where ϵ_0 and ϵ are permittivities of the vacuum ($8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) and the dielectric constant of the solvent used, respectively. The symbol e represents the elementary charge and has a value equal to $1.6 \times 10^{-19} \text{ C}$. 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

$$\text{work} = \text{force} \times \text{displacement} \quad (207)$$

$$dw = F_{AB} \times dx \quad (208)$$

$$dw = -\frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon x^2} dx \quad (209)$$

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 $x = \infty$ to $x = r$ will be

$$w = -\int_{\infty}^r \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon x^2} dx \quad (210)$$

$$w = -\frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon r} \quad (211)$$

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.

$$\Delta G_{EI}^* = \frac{N Z_A Z_B e^2}{4\pi\epsilon_0\epsilon r} \quad (212)$$

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.

$$\Delta G^* = \Delta G_{NEI}^* + \Delta G_{EI}^* = \Delta G_{NEI}^* + \frac{N Z_A Z_B e^2}{4\pi\epsilon_0\epsilon r} \quad (213)$$

Also, from the activated complex theory, we know that

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

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

$$k = \frac{RT}{Nh} e^{-\left(\frac{\Delta G_{NEI}^*}{RT} + \frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r}\right)} \quad (215)$$

$$k = \frac{RT}{Nh} e^{-\frac{\Delta G_{NEI}^*}{RT}} \cdot e^{-\frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r}} \quad (216)$$

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

$$\ln k = \ln \frac{RT}{Nh} + \ln e^{-\frac{\Delta G_{NEI}^*}{RT}} + \ln e^{-\frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r}} \quad (217)$$

or

$$\ln k = \ln \frac{RT}{Nh} - \frac{\Delta G_{NEI}^*}{RT} - \frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r} \quad (218)$$

Which can also be expressed as

$$\ln k = \ln k_0 - \frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r} \quad (219)$$

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.

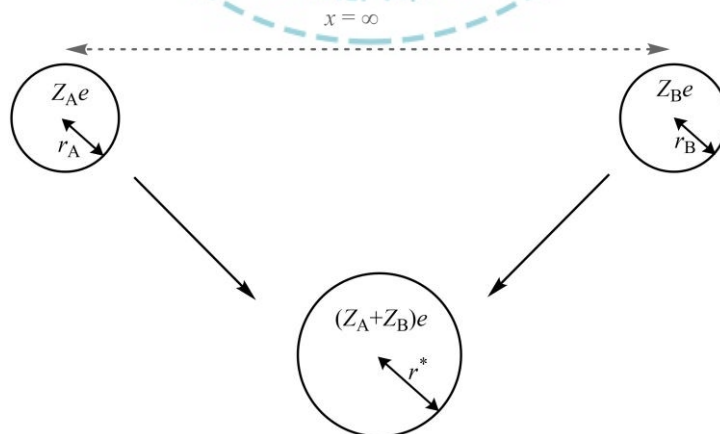


Figure 12. The pictorial depiction of the single-sphere model of ionic reactions.

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:

$$dF = \frac{\lambda e^2 d\lambda}{4\pi\epsilon_0\epsilon x^2} \quad (220)$$

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

$$dw = dF \times dx \quad (221)$$

$$dw = \frac{\lambda e^2 d\lambda}{4\pi\epsilon_0\epsilon x^2} dx \quad (222)$$

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.

$$w = \frac{e^2}{4\pi\epsilon_0\epsilon} \int_0^Z \int_{\infty}^r \frac{\lambda}{x^2} d\lambda dx \quad (223)$$

$$w = \frac{Z^2 e^2}{8\pi\epsilon_0\epsilon r} \quad (224)$$

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

$$G_{EI} = \frac{Z^2 e^2}{8\pi\epsilon_0\epsilon r} \quad (225)$$

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

$$G_{EI}(A) = \frac{Z_A^2 e^2}{8\pi\epsilon_0\epsilon r_A} \quad (225)$$

$$G_{EI}(B) = \frac{Z_B^2 e^2}{8\pi\epsilon_0\epsilon r_B} \quad (226)$$

$$G_{EI}^* = \frac{(Z_B + Z_A)^2 e^2}{8\pi\epsilon_0\epsilon r^*} \quad (227)$$

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

$$\Delta G_{EI}^* = \frac{(Z_B + Z_A)^2 e^2}{8\pi\epsilon_0\epsilon r^*} - \frac{Z_A^2 e^2}{8\pi\epsilon_0\epsilon r_A} - \frac{Z_B^2 e^2}{8\pi\epsilon_0\epsilon r_B} \quad (228)$$

or

$$\Delta G_{EI}^* = \frac{e^2}{8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (229)$$

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.

$$\Delta G^* = \Delta G_{NEI}^* + \Delta G_{EI}^* = \Delta G_{NEI}^* + \frac{Ne^2}{8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (230)$$

Also, from the activated complex theory, we know that

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

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

$$k = \frac{RT}{Nh} e^{-\left(\frac{\Delta G_{NEI}^*}{RT} + \frac{Ne^2}{RT8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \right)} \quad (232)$$

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

$$\ln k = \ln \frac{RT}{Nh} - \frac{\Delta G_{NEI}^*}{RT} - \frac{Ne^2}{RT8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (233)$$

Which can also be expressed as

$$\ln k = \ln k_0 - \frac{Ne^2}{RT8\pi\epsilon_0\epsilon} \left[\frac{(Z_B + Z_A)^2}{r^*} - \frac{Z_A^2}{r_A} - \frac{Z_B^2}{r_B} \right] \quad (234)$$

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.

❖ 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.

$$\ln k = \ln k_0 - \frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0\epsilon r} \quad (235)$$

Where ϵ_0 and ϵ are permittivities of the vacuum ($8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$) and the dielectric constant of the solvent used, respectively. The symbol e represents the elementary charge and has a value equal to $1.6 \times 10^{-19} \text{ C}$. 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

$$\ln k = -\frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0 r \epsilon} + \ln k_0 \quad (236)$$

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.

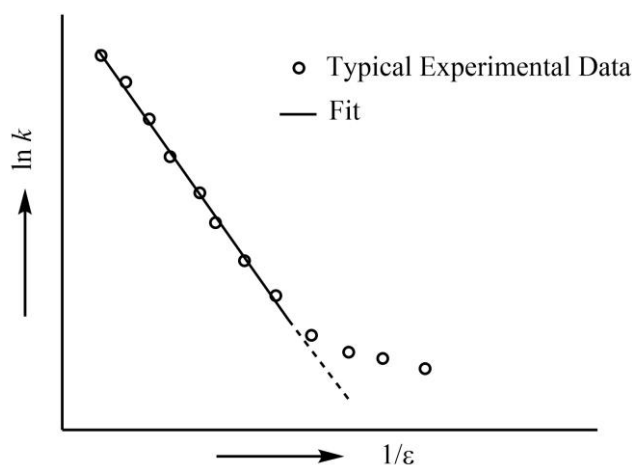


Figure 13. The plot of $\ln k$ vs $1/\epsilon$ for a typical ionic reaction.

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

$$m = -\frac{NZ_A Z_B e^2}{RT4\pi\epsilon_0 r} \quad (237)$$

Every term in the above equation is known apart from r , suggesting its straight forward determination from the slope of $\ln k$ vs $1/\epsilon$. 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

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

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

$$\Delta G_{EI}^* = \frac{NZ_A Z_B e^2}{4\pi\epsilon_0 \epsilon r} \quad (239)$$

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

$$\Delta S_{EI}^* = -\left(\frac{\partial(\Delta G_{EI}^*)}{\partial T}\right)_P = -\frac{NZ_A Z_B e^2}{4\pi\epsilon_0 r} \left(\frac{\partial(1/\epsilon)}{\partial T}\right)_P \quad (240)$$

or

$$\Delta S_{EI}^* = \frac{NZ_A Z_B e^2}{4\pi\epsilon_0 \epsilon^2 r} \left(\frac{\partial\epsilon}{\partial T}\right)_P \quad (241)$$

or

$$\Delta S_{EI}^* = \frac{NZ_A Z_B e^2}{4\pi\epsilon_0 \epsilon r} \left(\frac{\partial \ln \epsilon}{\partial T}\right)_P \quad (242)$$

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 $Z_A Z_B$.

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.

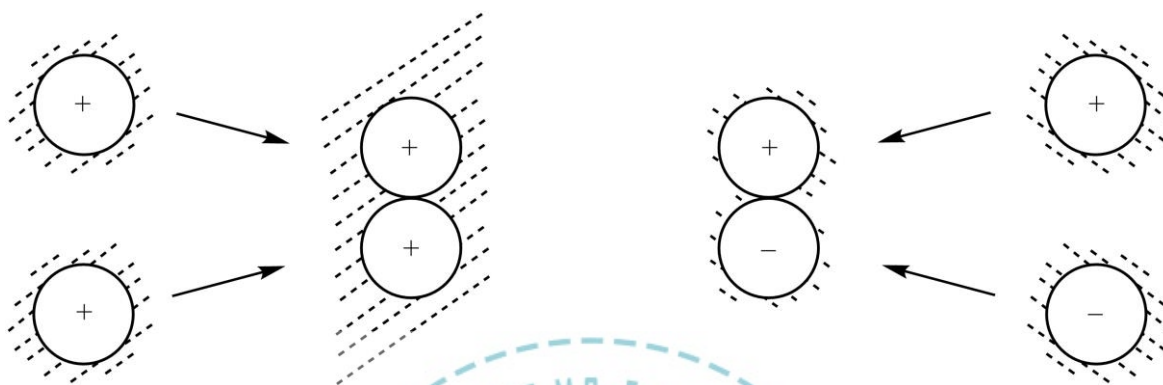


Figure 14. The dependence of entropy of activation on the solvent electrostriction in case of (left) same charges and (right) opposite charges.

➤ 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.

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

Where m_i and z_i are the molarity and charge number of i th 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 Danish physical chemist, J. N. Brønsted, proposed the rate equation relating reaction-rate (R) and activity coefficient as

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

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 $y_A y_B / y_X$ as the “kinetic activity factor”, and it was found to be quite accurate with experimental data. Now, rearranging equation (245), we get

$$\frac{R}{[A][B]} = k_0 \frac{y_A y_B}{y_X} \quad (246)$$

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

$$k = k_0 \frac{y_A y_B}{y_X} \quad (247)$$

Taking logarithm both side, we get

$$\log k = \log k_0 + \log \frac{y_A y_B}{y_X} \quad (248)$$

or

$$\log k = \log k_0 + \log y_A + \log y_B - \log y_X \quad (249)$$

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

$$\log \gamma_i = -B z_i^2 \sqrt{I} \quad (250)$$

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

$$\log k = \log k_0 - B z_A^2 \sqrt{I} - B z_B^2 \sqrt{I} + B z_X^2 \sqrt{I} \quad (251)$$

or

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

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

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

or simply

$$\log k = \log k_0 + 2B z_A z_B \sqrt{I} \quad (255)$$

Rearranging the above equation, we get

$$\log k = 2B z_A z_B \sqrt{I} + \log k_0 \quad (256)$$

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

$$\log k - \log k_0 = 1.02 z_A z_B \sqrt{I} \quad (257)$$

or

$$\log \frac{k}{k_0} = 1.02 z_A z_B \sqrt{I} \quad (258)$$

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.

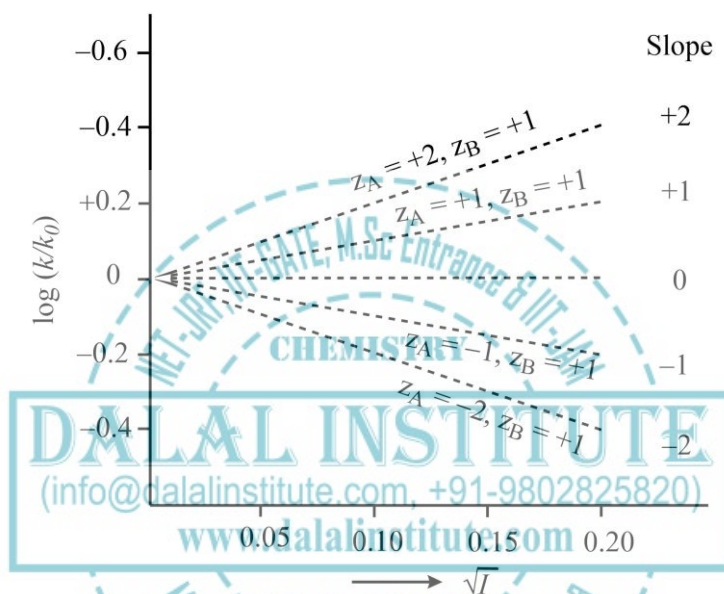
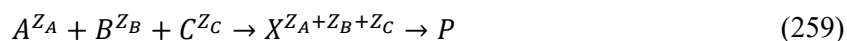


Figure 15. The plot of $\log (k/k_0)$ vs $(I)^{1/2}$ for different ionic reactions in aqueous solution at 25°C.

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



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

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

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

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 $(z_A z_B + z_B z_C + z_C z_A)$.

❖ The Comparison of Collision and Activated Complex Theory

After studying the collision as well as the transition state theories in detail, it is time to highlight the key points of similarities and differences between the two. A comparative analysis of both theories is quite beneficial as far as the practicality is concerned.

Table 1. The side-by-side comparison between the collision theory and transition state theory.

Collision Theory	Activated Complex Theory
1. According to the collision theory, the chemical reactions occur when the reactant molecules collide with a sufficient amount of kinetic energy.	1. According to the transition state theory, the primary cause of the reaction is actually the formation of an activated complex or the transition state, which in turn, converts to the final product.
2. It is based upon the kinetic theory of gases.	2. It is derived from the fundamentals of thermodynamics.
3. This theory considers the activation energy as the minimum energy required to make the collision effective.	3. This theory assumes the activation energy as the difference between the energy of the reacting molecules and the energy of the activated complex.
4. This theory tells nothing about the entropy of activation.	4. The transition state theory enables us to measure the entropy of activation.
5. Collision theory is applicable to simple chemical reactions and large deviations with experimental results are observed as the complexity increases.	5. This theory provided reasonable predictions even for the complex reactions.
6. The incorporation of the correction factor in modified collision theory was arbitrary.	6. The incorporation of correction factor was justified in terms of entropy of activation i.e. ΔS^\ddagger .
7. This theory tells nothing about the mechanism involved.	7. The formation of the activated complex is very much correlated with the actual mechanism going on.

❖ Problems

- Q 1. Discuss the fundamental concept of the effect of temperature on the reaction-rate with special reference to Maxwell-Boltzmann distribution of energies.
- Q 2. Derive Arrhenius equation for the rate of reactions. How it can be used to determine the activation energy?
- Q 3. Deduce the rate expression for the first order opposed by first-order reactions. How it can be used to yield the value of backward reaction too?
- Q 4. Derive and discuss the rate law for second-order opposed by second order.
- Q 5. What are the consecutive reactions? Discuss the condition required to apply the steady-state approximation to a typical consecutive reaction.
- Q 6. Define concurrent or parallel reactions. Derive the rate law for the first-order case.
- Q 7. Discuss the collision of the theory bimolecular reaction when the colliding particles are dissimilar.
- Q 8. What are unimolecular reactions? How they are treated in the collision framework?
- Q 9. Discuss the limitations of collision theory and the incorporation of the steric factor?
- Q 10. Derive the rate law in the activated complex framework. How it can be used to determine the entropy of activation?
- Q 11. What is the single-sphere model of ionic reactions? How is it different from the double sphere model?
- Q 12. Discuss the influence of ionic strength on the rate of ionic reactions of the third order.
- Q 13. Give five points of difference between the collision and activated complex theory.

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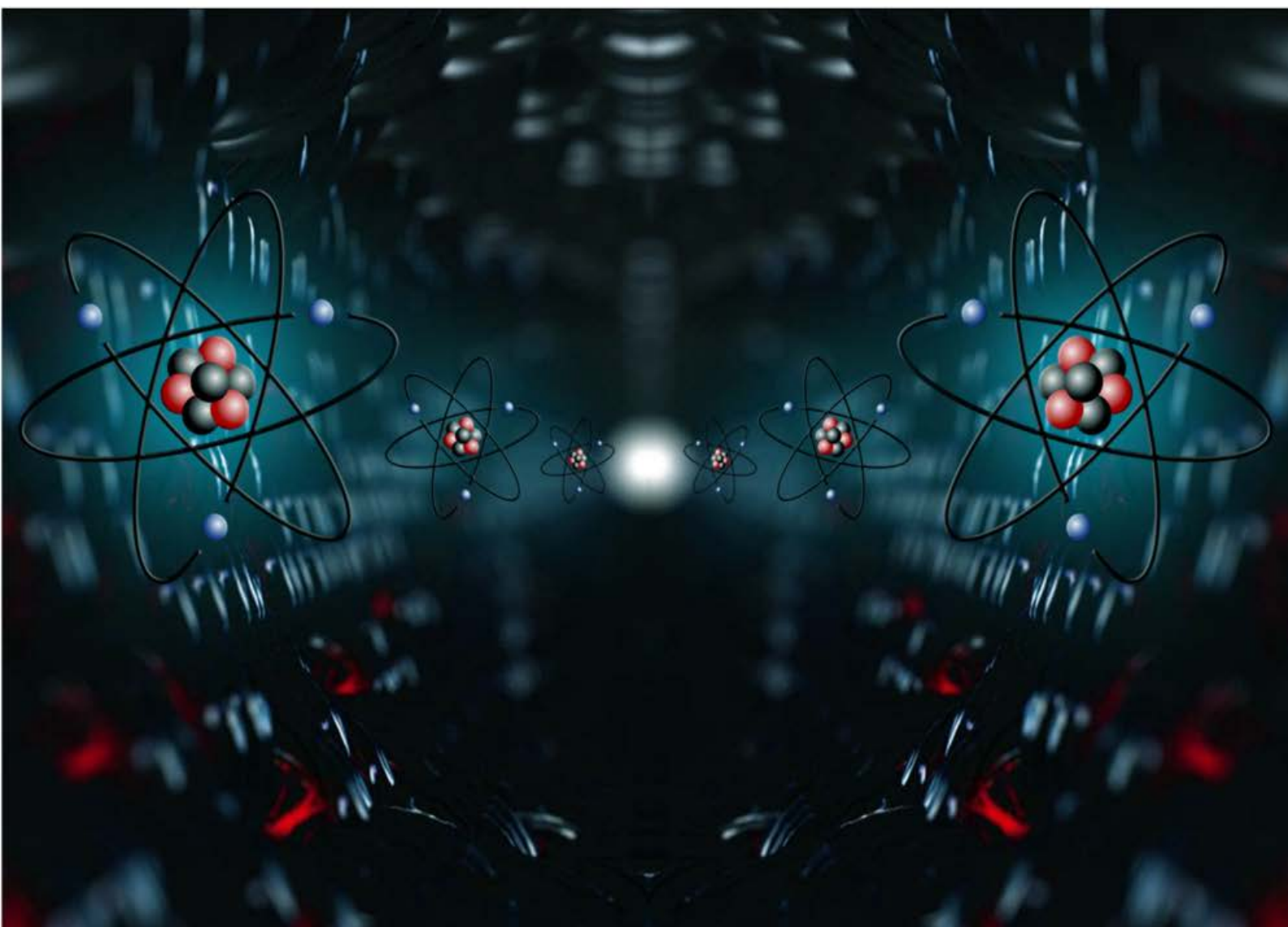
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