

Module 7 : Theories of Reaction Rates

Lecture 32 : Theories Of Reaction Rates - I : Collision Theory

Objectives

After studying this lecture you will be able to do the following.

- Calculate collision frequency using kinetic theory.
- Distinguish between collision cross section and reaction cross section.
- Compare collision theory with Arrhenius theory and experiments.
- Define the steric factor.
- Rationalize the departure of collision theory from experiments for ionic reactions using the harpoon mechanism.

32.1 Introduction

In the earlier lectures on chemical kinetics, we have studied the empirical aspects in detail. We now begin the theoretical explanations of chemical rate processes. This is one of the most challenging areas in chemistry. Molecular structure is fairly well understood through the advances in spectroscopy and quantum chemistry. With the knowledge of the same molecular structures and intermolecular forces, chemical equilibrium (thermodynamics) can be predicted quite accurately. An understanding the rates of processes microscopically requires answers to several interesting questions. Some of the main questions are as follows. How close should the molecules approach one another for the reaction to occur? Does the reaction "occur" only after reaching this separation or does it start well before the distance of closest separation is reached? Do all the reactants react identically or is there a distribution over several possibilities? Do all "encounters" between the reactants produce the products? How closely can we monitor the progress of the reaction theoretically (as well as experimentally)? Over the last four decades, the time resolution of this monitoring has improved dramatically from microseconds to femtoseconds.

While most of the above questions relate to gas phase processes, solution reactions have the additional contributions from the participation of the solvent. We shall take up these issues one by one in modest details. We first begin with the gas phase collision theory. This is followed by the transition state theory (lecture 33). Potential energy surfaces are introduced in lecture 34 and the trajectories over potential energy surfaces will be considered in lecture 35.

32.2 Bimolecular gas phase collision theory

Consider the following gas phase reaction



The rate of the reaction, $r = dP/dt$, depends on the following factors: a) The concentrations or the number densities of molecules A and B, i.e., N_A and N_B (N_A = numbers of molecules in unit volume of the container, similarly N_B), b) number of collisions between of A and B in unit time. This is the collision rate. Larger the relative velocity between A and B, larger the collision rate. The relative speed between A and B is obtained from $\frac{1}{2} \mu \bar{v}^2 = \frac{1}{2} k_B T$ or \bar{v} , the relative velocity $= (k_B T / \mu)^{1/2}$ is determined by the temperature T at equilibrium; and thirdly, c) the collision cross section, σ . The collision cross section is the area within which the center of A should be around the target B so that a collision can be said to have occurred. Let us first calculate the collision frequency between A and B.

Figure 32.1 Collision cross section and the collision cylinder.

All the molecules that come inside the range of the collision cylinder will collide with the central molecule on the extreme left. All those outside this cylinder do not collide with molecule A.

To calculate the collision frequency, consider the motion of the molecule labeled A. In time Δt , the molecule moves a distance $\bar{c} \Delta t$ where \bar{c} is the average speed of the molecule. Any other molecule which is within the volume of the cylinder $\pi \bar{c} \Delta t d^2$ spanned by molecule A, will collide with molecule A. Here πd^2 is the area of the cylinder spanned by A. This collision cylinder is shown in Fig 32.1. All the molecules that collide with A can be easily identified in the figure. During collisions, the directions of molecules change and the cylinder is not a rigid space but the effectively available space for the molecules. Since all molecules are moving, we need to use the relative speeds between molecules. From kinetic theory of gases, the average relative speed between molecules A and B is

$$\bar{c}_{\text{rel}} = (8 k_B T / \pi \mu)^{1/2}, \mu^{-1} = m_A^{-1} + m_B^{-1} \quad (32.2)$$

Where μ is the reduced mass between A and B. For identical molecules, $\bar{c}_{\text{rel}} = \sqrt{2} \bar{c}$, where the latter is calculated with m in the denominator of Eq. (32.2) in place of the reduced mass. The factor $2^{1/2}$ is because $\mu = m / 2$. The area of the cylinder is called the collision cross section. Molecules outside this area do not collide with A. If N_A is the number of molecules of A in volume V , the collision frequency is given by

$$z = \sqrt{2} \sigma \bar{c} N_A / V \quad (32.3)$$

This z is the number of collisions encounter by a single molecule. Since there are N_A molecules in volume V , the number of collisions between molecules of A in unit time and unit volume, Z_{AA}

$$Z_{AA} = (1/2) z N_A / V \quad (32.4)$$

Substituting the values of all the factors, we have

$$Z_{AA} = \sigma (4 k_B T / \pi m)^{1/2} (N_A / V)^2$$

If n_A is the number of moles of A in volume V , then, $[A] = \text{molar concentration of A} = n_A / V$. Since $N_A = n_A L$ where $L = \text{Avogadro number}$, we have for Z_{AA}

$$Z_{AA} = \sigma (4 k_B T / \pi m)^{1/2} L^2 [A]^2 \quad (32.5)$$

If the collision is between molecules of type A with molecules of type B, the factor of 1/2 in eq. (32.4) drops out. If two molecules of A collide it is counted as one collision. When molecules of A collide with

molecules of B, there are distinct AB collisions, AA and BB collisions. The total number of collisions between A and B molecules in unit time and unit volume is given by

$$Z_{AB} = \sigma (8 k_B T / \pi \mu)^{1/2} L^2 [A] [B] \quad (32.6)$$

Substitution of the values of all the factors in eq (32.5) and (32.6) gives values of Z_{AA} or Z_{AB} in the range of 10^{34} collisions in a volume of 1 m^3 in a second.

If we assume that each collision leads to the formation of the products then the rate of the reaction $r = -d[A] / dt$ will equal Z_{AB} / L . The division by L is to get the correct molar unit of (moles / volume) / s. Since all collisions are not effective but only those collisions with energy greater than some E'_a are effective, the rate may be expressed as

$$r = -d[A] / dt = -(Z_{AB} / L) e^{-E'_a / RT} \quad (32.7)$$

E'_a is slightly different from the activation energy E_a (see below)

Expanding eq. (32.7) we get,

$$-d[A] / dt = -\sigma (8 k_B T / \pi \mu)^{1/2} L [A] [B] e^{-E'_a / RT} \quad (32.8)$$

$= -k_c [A] [B]$ where

$$k_c = \sigma (8 k_B T / \pi \mu)^{1/2} L e^{-E'_a / RT} \quad (32.9)$$

Where k_c is the rate constant in the collision theory. Notice that unlike the Arrhenius theory, the prefactor depends on \sqrt{T} . If we insist on rewriting $d[A] / dt = -k [A] [B]$ where $k = A e^{-E_a / RT}$ with A independent of T , then the activation energy E_a of the Arrhenius equation is given by $E_a = RT^2 d \ln k / dT$. Applying this formula to eq. (32.9) we get

$$E_a = RT^2 d \ln k_c / dT = E'_a + 1/2 RT \quad (32.10)$$

It is for this reason that E'_a in (32.8) was distinguished from E_a of (32.10). Since $(1/2) RT$ is much smaller than E'_a , the difference between E_a and E'_a is generally not of great significance.

Let us compare some experimental results with the results of collision theory. These are shown in Table 32.1

Reactions	Arrhenius Parameters from experiments		Collision theory $A / (\text{M}^{-1} \text{s}^{-1})$	$A_{\text{Arrhenius}} / A_{\text{Collision Theory}}$
	$A / (\text{M}^{-1} \text{s}^{-1})$	$E_a / (\text{kJ} / \text{mol})$		
$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}$	9.4×10^9	102.0	5.9×10^{10}	0.16
$2\text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	6.3×10^7	0.0	2.5×10^{10}	2.5×10^{-3}
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	1.24×10^6	180.0	7.3×10^{11}	1.7×10^{-6}
$\text{K}_2 + \text{Br}_2 \rightarrow 2\text{KBr}$	1.0×10^{12}	0	2.1×10^{11}	4.8

Table 32.1 Arrhenius parameters (from Eq. 32.10) and collision theory results for a few gas phase reactions.

The comparisons are not encouraging. The above collision theory can not predict E_a . In the first three reactions, the experimental collision frequency is much lower than the collision theory results while in the last reaction, it is higher. Rather than discarding the theory, we seek to improve it and learn a lot in the process (in a manner similar to getting improved equations of state, starting with the ideal gas equation of state). An explanation of the above difference in the values of A is that the actual "reactive" cross section σ^* is different from the collision cross section σ . Consider the collisions between H_2 and C_2H_4 shown in

Figure 32.2 Various collisions of H₂ with C₂ H₄

Most collisions are in random directions and only a small fraction of collisions with the correct relative alignments lead to the products. This requirement of "proper relative" alignment between molecules is called the steric effect and we can define the steric factor P as

$$\sigma^* = \sigma P \quad (32.11)$$

For the four reactions in Table 32., the values of P are 0.16, 2.5×10^{-3} , 1.7×10^{-6} and 4.8 respectively. Before we consider σ^* being larger than σ , we will consider the dependence of σ^* on energy or velocity of molecules. When the steric factor is small, very few collisions occur with suitable relative orientations of reactants.

The above discussion brings out the central role of reaction cross sections (σ^*) in chemical dynamics. In addition to the dependence of the reaction cross section on the relative orientations of reactants, σ^* depends on the relative velocity (or relative kinetic energy) as well. For smaller relative velocities, the reactants often have more time to feel the presence of one another.

Figure 32.3 Dependence of σ^* (reaction cross section) on relative velocity (v_{rel}).

To calculate the collision frequency, consider the motion of the molecule labeled A. In time Δt , the molecule moves a distance $\bar{c} \Delta t$ where \bar{c} is the average speed of the molecule. Any other molecule which is within the volume of the cylinder $\pi \bar{c} \Delta t d^2$ spanned by molecule A, will collide with molecule A. Here

πd^2 is the area of the cylinder spanned by A. This collision cylinder is shown in Fig 32.1. All the molecules that collide with A can be easily identified in the figure. During collisions, the directions of molecules change and the cylinder is not a rigid space but the effectively available space for the molecules. Since all molecules are moving, we need to use the relative speeds between molecules. From kinetic theory of gases, the average relative speed between molecules A and B is

$$\bar{c}_{rel} = (8 k_B T / \pi \mu)^{1/2}, \mu^{-1} = m_A^{-1} + m_B^{-1} \quad (32.2)$$

Where μ is the reduced mass between A and B. For identical molecules, $\bar{c}_{rel} = \sqrt{2} \bar{c}$, where the latter

is calculated with m in the denominator of Eq. (32.2) in place of the reduced mass. The factor $2^{1/2}$ is because $\mu = m / 2$. The area of the cylinder is called the collision cross section. Molecules outside this area do not collide with A. If N_A is the number of molecules of A in volume V , the collision frequency is given by

$$Z = \sqrt{2} \sigma \bar{c} N_A / V \quad (32.3)$$

This z is the number of collisions encounter by a single molecule. Since there are N_A molecules in volume V , the number of collisions between molecules of A in unit time and unit volume, Z_{AA}

$$Z_{AA} = (1/2) z N_A / V \quad (32.4)$$

Substituting the values of all the factors, we have

$$Z_{AA} = \sigma (4 k_B T / \pi m)^{1/2} (N_A / V)^2$$

If n_A is the number of moles of A in volume V , then, $[A] = \text{molar concentration of A} = n_A / V$. Since $N_A = n_A L$ where $L = \text{Avogadro number}$, we have for Z_{AA}

$$Z_{AA} = \sigma (4 k_B T / \pi m)^{1/2} L^2 [A]^2 \quad (32.5)$$

Since the cross section depends on relative energy, we need to integrate over the distribution function of energy to get the rate constant, i.e.,

$$d[A] / dt = - \sigma(\epsilon) v_{rel} L [A] [B] \text{ becomes} \quad (32.12)$$

$$d[A] / dt = - \left\{ \int_0^{\infty} \sigma(\epsilon) v_{rel} f(\epsilon) d\epsilon \right\} L [A] [B] \quad (32.13)$$

$$\text{and with } v_{rel} = (2\epsilon / \mu)^{1/2} \text{ from } \epsilon = 1/2 \mu v_{rel}^2 \quad (32.14)$$

Substituting velocities by energies by using the above substitutions, we have

$$k_c = L \int_0^{\infty} \sigma(\epsilon) (2\epsilon / \mu)^{1/2} f(\epsilon) d\epsilon \quad (32.15)$$

The primary reason for converting from v_{rel} to relative kinetic energy ϵ is that experimentally cross sections are often tabulated as functions of energy. Let us first convert the Maxwell Boltzmann velocity distribution into an energy distribution.

$$f(v) dv = 4\pi (m / 2\pi k_B T)^{3/2} v^2 \exp(-m v^2 / k_B T) dv \quad (32.16)$$

$$= 4 \pi (m / 2 \pi k_B T)^{3/2} (2 \varepsilon / m) e^{-\varepsilon_a / k_B T} d\varepsilon / (2m\varepsilon)^{1/2} \quad (32.17)$$

Where we have used that $d\psi = d\varepsilon / (2m\varepsilon)^{1/2}$ from $\varepsilon = m\psi^2/2$

$$= 2 \pi (m / \pi k_B T)^{3/2} \varepsilon^{1/2} e^{-\varepsilon_a / k_B T} d\varepsilon = f(\varepsilon) d\varepsilon \quad (32.18)$$

Substituting this in (32.15) we get

$$k_C = (8 / \pi k_B T)^{1/2} (1 / k_B T) \int_0^{\infty} \varepsilon \sigma(\varepsilon) e^{-\varepsilon_a / k_B T} d\varepsilon \quad (32.19)$$

An experimental cross section data is shown in Fig 32.4.

Figure 32.4 Experimental $\sigma(\varepsilon)$ for the reaction $H + D_2 \rightarrow HD + D$

To integrate eq (32.19) we need a functional form of $\sigma(\varepsilon)$. Using an approximate form for $\sigma(\varepsilon)$ vs ε for the above figure as follows,

$\sigma(\varepsilon) = 0$ if $\varepsilon < \varepsilon_a$

$$\sigma(\varepsilon) = (1 - \varepsilon_a / \varepsilon) \sigma \text{ for } \varepsilon > \varepsilon_a \quad (32.20)$$

The integral of eq (32.19) becomes

$$\int_0^{\infty} \varepsilon \sigma(\varepsilon) e^{-\varepsilon_a / k_B T} d\varepsilon = \int_0^{\infty} \varepsilon (1 - \varepsilon_a / \varepsilon) \sigma e^{-\varepsilon_a / k_B T} d\varepsilon \quad (32.21)$$

$$= \sigma (\pi k_B T / \mu)^{1/2} e^{-\varepsilon_a / k_B T} \quad (32.22)$$

We see that, while the exponent has the Arrhenius form, the preexponential is not a constant (as in the Arrhenius case) but a temperature dependent function. The additional temperature dependence of this factor is determined by the distribution function as well as the detailed form of the cross sections.

In Table 32.1, for the reaction in the last row, the reaction cross section was larger than the collision cross section. This can be understood through the harpoon mechanism as described below.

32.3 The Harpoon Mechanism.

For reaction involving strongly electropositive and electronegative elements we find that σ^* can be greater than σ . This is due to the harpoon mechanism in which the electrostatic attraction enhances the reaction cross section. When the reactants K and Br₂ approach each other in the reaction,



at a certain close distance, an electron of K (the harpoon) is captured by Br₂ to give Br₂⁻. Once the ionic intermediates K⁺ and Br₂⁻ are formed, they are strongly attracted towards each other and move towards one another with greater velocity (enhanced reactivity) leading to a larger value of σ^* .

Let us understand the above description quantitatively by studying the potential energy diagram of K + Br₂ and K⁺ + Br₂⁻ as a function of the separation between K and Br₂. The diagram is shown in Fig 32.5.

Figure 32 . 5 The harpoon mechanism for the K + Br₂ reaction.

At large distances, neutral K and Br₂ have lower energy than ionic K⁺ and Br₂⁻ because more energy is needed to separate the ionic species. For all r greater than r*, the potential energy curve for the neutral reactants lies lower than the potential energy for the ionic reactants. At r = r*, the two potential energies are equal and for r values less than r*, the ionic potential energy curve is lower than the neutral reactants curve, because of the strong electrostatic attraction between K⁺ and Br₂⁻. The difference in the energy (ΔE) between the charged pair (K⁺ and Br₂⁻) and the neutral pair is

$$\Delta E = (I - E_a - e^2 / r) - E_{\text{neutral pair}} \quad (32.24)$$

Where I is the ionization energy of K, E_a, the electron affinity of Br₂ and - e²/r, the electrostatic attraction. For r < r*, ΔE is negative (more attractive) and therefore the distance at which the electron jumps from K to Br is when r = r*, where the term in brackets goes to zero, i.e.,

$$e^2 / r^* = I - E_a \text{ or } r^* = e^2 / (I - E_a) \quad (32.25)$$

Since the electron or the harpoon shoots across from K to Br₂ when $r = r^*$, $\pi (r^*)^2$ may be identified as the reaction cross section. It is after this transfer that the reactants are further accelerated towards each other and finally depart as products KBr and Br. This reaction cross section may be compared with the collision cross section πd^2 where d is the contact distance between K and Br₂. This ratio is the steric factor P discussed earlier.

$$P = \sigma^* / \sigma = (r^* / d)^2 = \{ e^2 / d (I - E_a) \}^2 \quad (32.26)$$

For K, $I = 420 \text{ kJ/mol}$, E_a of Br₂ is 250 kJ/mol and $d = \text{contact distance} = [d(K) + d(\text{Br}_2)] / 2 = 400 \text{ pm}$. $d(K)$ is the diameter of K and $d(\text{Br}_2)$ is the average diameter of Br₂. We note that this calculated value of $P \approx 5$ which matches with the experimental value of P .

To find the reaction cross section of reactions, one needs to know the potential energy curves (surfaces when more than one independent variable like r above are involved) and other details such as probabilities of passage from reactants to products. These involve detailed microscopic calculations. Experiments involve crossed molecular beams which will be outlined in a later lecture.

32.4 Problems

- 32.1) If z is the collision frequency, $1/z$ may be thought of as the mean time before successive collisions. If we multiply the mean time with the mean speed, we get a length, which is now the mean or average distance a particle travels before undergoing a collision. This is called the mean free path. Show that the mean free path for A - A collisions, $\lambda = \bar{c} / z = (k_B T / p) / (2^{1/2} \sigma)$
- 32.2) Calculate the volume of the collision cylinder for sodium atoms at 300 K. Calculate the average velocity from $\bar{c} = (8 kT / \pi \mu)^{1/2}$, where $\mu = m / 2$ and m is the mass of a sodium atom. Use $\Delta t = 100 \text{ ps}$ (pico seconds)
- 32.3) The value of P for the reaction between NO and Cl₂ giving NOCl and Cl is 0.018 at 298 K. If the experimental value of A is $4.0 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$, estimate the collision diameter for the reaction. If the collision cross section of NO is 0.42 nm^2 , what is the collision cross section of Cl₂?
- 32.4) The P factor for the harpoon mechanism between Na and Cl₂ is 2.3. If the value of d for the reactants is 3.5 \AA , what is the value of $I - E_a$ for the reaction? Compute the value of I if E_a is 225 kJ/mol .
- 32.5) Calculate the collision frequencies and collision densities at 298 K and 1 bar pressure for: a) pure N₂, b) pure O₂ c) equimolar mixture of N₂ and O₂. The collision diameters for N₂ and O₂ are 280 pm and 300 pm respectively. $1 \text{ pm} = 10^{-12} \text{ m} = 100 \text{ \AA}$
- 32.6) At 300 K, if the activation energy of the reaction is 15 kJ/mol , what fraction of collisions occur with the required kinetic energy? How does this fraction change at 1000K and 2000K?
- 32.7) Even though C₂H₄ and C₆H₆ are not spherical, collision diameters are used in calculations involving these molecules. How can this be justified?
- 32.8) The collision cross sections in nm² for atoms/ molecules are given in parenthesis below against the atoms / molecules He (0.21), Ar (0.36), O₂ (0.4), Cl₂ (0.93), CO₂ (0.52), CH₄ (0.46), C₂H₆ (0.64), C₆H₆ (0.88). For some of these, try to estimate these values from the information on molecular / atomic sizes and bond lengths.

- 32.9) How can you calculate the mean free path (the average distance a molecule traverses before a collision) from mean velocity and the collision frequency?
- 32.10) Calculate the collision theory rate constant at 500K for the bimolecular reaction $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g})$. The activation energy is 170 kJ / mol. Use the reduced mass in your calculation.
- 32.11) In the present lecture, we have verified the value of P for the $\text{H}_2 + \text{C}_2\text{H}_4$ reaction. Verify the values of P for the reactions in the Table 32.1 involving reactions of NOCl and ClO

Recap

In this Lecture you have learnt the following

Summary

In the present lecture, we have been introduced to the collision theory of reaction rates. Collision frequency between reactants is calculated using the results of kinetic theory of gases. In a preliminary definition of a collision, two molecules are said to collide if the second molecule approaches the first molecule within an area called the collision cross section which equals πd^2 where d is the average diameter of the two molecules. The rate constant is expressed as a product of the cross section, relative velocity and a Boltzmann factor accounting for the fraction of activated molecules.

This simple collision theory departs significantly from experimental results. This is rationalized by noting that the reaction cross sections are different from collision cross sections. Most collisions (as exemplified using the collision between C_2H_4 and H_2) do not occur with the correct orientations of the reactants. The effect of these orientations can be incorporated using a steric factor. The reaction cross section depends on relative velocities as well. This can be taken into account by including the experimental energy (or speed) dependent cross sections along with the Maxwell Boltzmann velocity distribution. In reactions where ionic interactions can contribute, the reaction cross section can be larger than the collision cross section. This was explained using the harpoon mechanism in the $\text{K} + \text{Br}_2$ reaction. The experimental determination of reactive cross sections and their theoretical estimation is yet a challenge in chemical kinetics, but very significant progress has been made in the case of several elementary reactions.