

Module 6 : Reaction Kinetics and Dynamics

Lecture 28 : Elementary Reactions and Reaction Mechanisms

Objectives

In this Lecture you will learn to do the following

- Define what is an elementary reaction.
- Sketch the time evolution of concentration in a consecutive reaction.
- Illustrate the use of the steady state approximation and preequilibrium.
- Construct reaction mechanisms using elementary reactions for a few example of rate processes.
- Use the concept of preequilibrium in describing enzyme kinetics.
- Outline a mechanism for unimolecular reactions.
- Outline the principle of relaxation methods.

28.1 Introduction

We have seen in the lecture on the integrated rate laws (lecture 26) that the order of a reaction has to be obtained experimentally and it can not be inferred from the stoichiometric coefficients of the chemical reaction. This can be understood as follows.

If the reaction is of the type $2A + 3B \rightarrow \text{products}$ it is highly unlikely that 2 molecules of A and three molecules of B simultaneously collide to give the products. Even if the reaction is of the type $A \rightarrow \text{products}$, this does not imply that it is first order with respect to A. It is possible that A has to be energized to an activated molecule A^* either by collision with other molecules or by the absorption of light. For reactions in solution media, the participation of the solvent molecules in the reaction needs to be considered. These considerations have lead to the identification of elementary reactions in which the order of the reaction is the same as molecularity which is expressed in the stoichiometric equation for the chemical reaction. The overall mechanism(sequence of steps or elementary reactions involved in the reaction of the reaction is then built up in terms of elementary reactions. Unravelling the reaction mechanism is almost like detective work. Many times a prevailing mechanism of a well known reaction may be replaced by a more accurate mechanism when additional intermediates or pathways are detected and illustrated experimentally.

28.2 Elementary Reactions

Elementary reactions are those where in the molecularity of the reaction is the same as the order of the reaction. Note that the converse is not true! We will now give a few examples of elementary reactions.





In all these reactions, no further steps or intermediates are involved in going from left to right.

In 28.1(a) a single molecule of NO "collides" with an oxygen atom to give NO₂. The reaction is bimolecular and of second order.

In 28.1(c) an oxygen molecule breaks up into two oxygen atoms when excited photochemically (by the absorption of light). The rate of decomposition of O₂, d[O₂]/dt is proportional to the concentration of oxygen molecules [O₂].

If more O₂ molecules are present, more of them are likely to absorb light and form the products. The fact that a reaction is elementary has also to be established by experiment alone. It can not be decided by the simplicity of the appearance of the equation.

The mechanism of a chemical reactions consist of the complete set of elementary reactions that contribute to the over all reaction process. Ideally, we need to know the rate constant for all these elementary reactions(both forward and reverse rate constant), but chemists are usually quite happy if they can unambiguously identify all the elementary reactions and the associated transitions state structures and geometries. the transition state or activated complex is a state intermediate between reactions and products and with the current advances in spectroscopy it is possible to identify these transition states. In the present section, we will describe the mechanisms of a few reactions.

In understanding these mechanisms and using the rate constants of the elementary reactions in the over all rate constants certain approximations (or assumptions) help greatly in simplifying the rate equations. We will first elaborate these.

a) The steady state approximation.

In this approximation, it is assumed that the concentrations of the reactive intermediates remain constant and small during the major part of the reaction process. We will illustrate this approximation for the following consecutive reaction scheme.



An example for such a reaction is



Since each step here is an elementary reaction, rate laws can be written as follows,

$$d[A] / dt = - k_a [A] \quad (28.4)$$

We assume that the rate of formation of A from B is too small to be of any significance. For the rate of change B we have,

$$d[B] / dt = k_a [A] - k_b [B] \quad (28.5)$$

This accounts for the formation of B as well as the consumption of B in formation C. Finally,

$$d[C] / dt = k_b [B] \quad (28.6)$$

Let us assume that at the start of the reaction, only A is present with the concentration given $[A]_0$. Then the concentration of A at any later time is given by the integrated expression

$$[A]_t = [A]_0 e^{-k_a t} \quad (28.7)$$

Substituting this in the equation for the rate of change of B and solving for $[B]_t$ we get

$$[B]_t = k_a [A]_0 (e^{-k_a t} - e^{-k_b t}) / (k_b - k_a) \quad (28.8)$$

And since at all times, $[A] + [B] + [C] = [A]_0$,

we have,

$$[C]_t = [A]_0 \left\{ 1 + \left(1 + \frac{k_a e^{-k_a t} - k_b e^{-k_b t}}{k_b - k_a} \right) \right\} \quad (28.9)$$

For more complicated reactions, such explicit expressions for $[A]_t$, $[B]_t$ and $[C]_t$ are hardly available. Therefore, the steady state approximation (SSA) as described below is invoked.

Figure 28.1 The concentrations of $[A]$, $[B]$ and $[C]$ as a function of time t (all relative to $[A]_0$) for a consecutive reaction $A \rightarrow B \rightarrow C$. The time over which the steady state approximation is valid is shown between dashed vertical lines.

After the first few moments, the concentration of [B] reaches a nearly steady value, at which $d[B]/dt = 0$. Substituting this in (28.5), we get for the steady state concentration of

$$B, d[B]/dt = 0 \quad (28.10a)$$

$$[B] = (k_a / k_b) [A] \quad (28.10b)$$

and now (28.6) can be very easily integrated to get

$$\begin{aligned} [C]_t &= k_a [A]_0 \int_0^t e^{-k_a t} dt \\ &= [A]_0 (1 - e^{-k_a t}) \end{aligned} \quad (28.11)$$

this is a much simpler equation than eq (28.9) and far easier to obtain than (28.9) and is valid for a major part (except the very initial part and the tail end of time) of the reaction time. Indeed, (28.11) is a special case of (28.9) when $k_a \gg k_b$. Equations (28.8) and (28.9) could be easily derived because of simplicity of $A \rightarrow B \rightarrow C$. In complex reactions, it is not possible to get integrated concentrations of reactive intermediates and approximations regarding the concentrations of intermediates (such as eq 28.10b) are extremely useful in obtaining final approximate rate expressions.

b) Preequilibria.

Consider the following sequence of reactions



Here, the intermediate (AB) reaches an equilibrium with the reactants as in

$$K_{eq} = \{ [AB] / [A][B] \}_{eq} = k_f / k_r \quad (28.13)$$

Eq (28.13) would be exactly true if AB does not react further to give products C. But if k_p is small, eq (28.13) is valid quite well for a considerable length of time and this is known as preequilibrium. The formation of the product C is now described by

$$d[C]/dt = k_p [AB] = k_p K [A][B] = k [A][B] \quad (28.14)$$

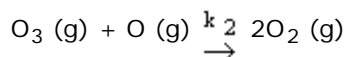
with the final rate constant $k = k_p k_f / k_r$ and the reaction is second order overall.

We can now incorporate these approximations in getting suitable expressions for integrated rate laws in complex reaction schemes.

28.3 Examples of reaction Mechanisms



This reaction is known to occur by the following mechanism



Here M is molecule that collides with O_3 molecules and decomposes the latter through a collision. The intermediate in this reaction is O which we treat using the steady state approximation.

$$\text{The rate equation for [O] is } d[O]/dt = k_1 [O_3][M] - k_{-1} [O_2][O][M] - k_2 [O_3][O] \quad (28.17)$$

Setting $d[O]/dt = 0$, we get the concentration of [O] as

$$[O] = k_1 [O_3][M] / k_{-1} [O_2][M] + k_2 [O_3] \quad (28.18)$$

The rate of change of O_3 is given by

$$d [O_3] / dt = - k_1 [O_3] [M] + k_{-1} [O_2] [O] [M] - k_2 [O] [O_3] \quad (28.19)$$

Using the SSA for $[O]$ we have,

$$d [O_3] / dt = 2 k_1 k_2 [O_3]^2 [M] / k_{-1} [O_2] [M] + k_2 [O_3] \quad (28.20)$$

Needless to say, the result is quite involved. The rate law depends on the value of $[M]$, the concentration of colliding molecules. For small $[M]$ or small pressure or concentrations of M , the rate is nearly first order if k_{-1} is small. For large $[M]$ and small values of k_2 , the rate law is of second order.

b) Oxidation of Nitric oxide

This example is given to illustrate the point that a reaction need not have a unique mechanism. Several paths could lead to the same products and rate laws. The reaction is



Experiments reveal that the rate law is of the form

$$(1/2) d [NO_2] / dt = k_{\text{expt}} [NO]^2 [O_2] \quad (28.22)$$

This may imply that the reaction is elementary. Experiments however indicate that the reaction is not elementary. Two mechanisms have been proposed for the reaction (28.21), one involving a preequilibrium (involving NO_3) and another involving a steady state approximation of an intermediate N_2O_2 .

Mechanism 1



In the first step, a rapid equilibrium is established between the reactants and the NO_3 radical

$$K_{\text{eq}} = k_1 / k_{-1} = [NO_3] / [NO] [O_2] \quad (28.25)$$

For the second step of the mechanism, the rate law is

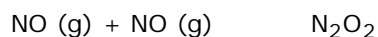
$$(1/2) d [NO_2] / dt = k_2 [NO] [NO_3] \quad (28.26)$$

The second step is the rate determining step, since the preequilibrium eq (28.23) is established rapidly. Substituting eq (28.25) in eq (28.26) we have,

$$(1/2) d [NO_2] / dt = k_2 K_{\text{eq}} [NO]^2 [O_2] \quad (28.27)$$

This is the same as eq (28.22) if k_{expt} is replaced by $k_2 K_{\text{eq}}$. The experimental rate constant is now a product of k_2 and K_{eq} and not the rate constant for an elementary reaction.

Mechanism 2





In this mechanism a rapid equilibrium is not established in eq (28.28) but a steady state approximation can be used for the concentration of N_2O_2 .

$$d [\text{N}_2\text{O}_2] / dt = k_1 [\text{NO}]^2 - k_{-1} [\text{N}_2\text{O}_2] - k_2 [\text{N}_2\text{O}_2] [\text{O}_2] \quad (28.30)$$

Setting this equal to zero we get, for the concentration of $[\text{N}_2\text{O}_2]$,

$$[\text{N}_2\text{O}_2] = k_1 [\text{NO}]^2 / (k_{-1} + k_2 [\text{O}_2]) \quad (28.31)$$

This equation for the constant (steady) value of $[\text{N}_2\text{O}_2]$ is satisfied if k_{-1} is greater than k_2 and k_1 . Only in such a situation is a small value of $[\text{N}_2\text{O}_2]$ is present, satisfying the SSA. In such a situation, $[\text{N}_2\text{O}_2] = (k_1 / k_{-1}) [\text{NO}]^2$ and the rate law for eq (28.29) becomes

$$(1/2) d [\text{NO}_2] / dt = k_2 [\text{N}_2\text{O}_2] [\text{O}_2] = (k_2 k_1 / k_{-1}) [\text{NO}]^2 [\text{O}_2] \quad (28.32)$$

Notice that both mechanisms give the same rate law! The only way to distinguish between the mechanisms is by detecting NO_3 and / or N_2O_2 . At present the second mechanism is favoured.

28.4 Mechanism of unimolecular reactions.

Even for reactions that appear very simple such as $\text{A} \rightarrow [\text{P}]$ where P refers to products, the mechanism can be fairly involved. This is because for reactions to occur, molecules need to be activated or initiated through collisions (unlike radioactivity which is spontaneous!). Collisions could be with other molecules M that are present in the reaction mixture, which are usually in large amounts. The reaction sequence is



If the second step ($\text{A}^* \rightarrow \text{P}$) is slow, this will determine the overall conversion giving first order kinetics. Let us see how this comes about using the steady state approximation for A^*

$$d [\text{A}^*] / dt = k_f [\text{A}] [\text{M}] - k_r [\text{A}^*] [\text{M}] - k_2 [\text{A}^*] \quad (28.34)$$

$$[\text{A}^*] = k_f [\text{A}] [\text{M}] / (k_2 + k_r [\text{M}]) \quad (28.35)$$

substituting in $d [\text{P}] / dt$

$$d [\text{P}] / dt = k_2 [\text{A}^*] = k_2 k_f [\text{A}] [\text{M}] / (k_2 + k_r [\text{M}]) \quad (28.36)$$

This is a general rate expression for the Lindemann - Hinshelwood mechanism outlined above. For low pressures, when $[\text{M}]$ is small, $k_2 \gg k_r [\text{M}]$ and the rate law is of second order

$$d [\text{P}] / dt = (k_2 k_f / k_2) [\text{A}] [\text{M}] = k_f [\text{A}] [\text{M}] \quad (28.37)$$

For high pressures when $k_r [M] \gg k_2$, the rate law becomes

$$d[P] / dt = k_2 k_f / k_r [A], \quad (28.38)$$

which is first order in $[A]$. For many unimolecular reactions such as isomerization of trans CHD = CHD, cis-butadiene, decomposition of N_2O_5 , and so on, the transition from second order at low pressures to first order at high pressures is observed. This also brings out the point that mechanisms for reactions are not ubiquitous but are dependent on reaction conditions and are by no means unique.

28.5 Enzymes Kinetics:

Enzymes are biological catalysts which help in converting substrates (S) into products (P). We will now describe the Michaelis - Menten mechanism for enzyme action. Initially, the enzyme (E) and the substrate form a complex ES^* which later decays into the products regenerating the enzyme. The reaction scheme is written as



The rate of formation of the product is

$$d[P] / dt = k_2 [ES^*] \quad (28.40)$$

Using the steady state approximation for $[ES^*]$, we have

$$d[ES^*] / dt = k_f [E][S] - k_r [ES^*] - k_2 [ES^*] = 0 \quad (28.41)$$

The first term gives the rate of formation of ES^* and the other two terms give the rate of decay of ES^*

$$[ES^*] = k_f [E][S] / (k_r + k_2) \quad (28.42)$$

If $[E]_0$ is the initial (total) concentration of the enzyme and $[E]$ is the concentration of the enzyme which is free to react, then $[E]_0 = [E] + [ES^*]$ which equals the free plus the bound enzyme which has to be equal to $[E]_0$ usually $[E]_0$ is much less than $[S]$, and so $[S]_0 = [S]$ total. Substituting in we get

$$[ES^*] = k_f / (k_r + k_2) [S] \{ [E]_0 - [ES^*] \} \quad (28.43)$$

$$\text{Rearranging, } [ES^*] = k_f [E]_0 [S] / (k_2 + k_r + k_f [S]) \quad (28.44)$$

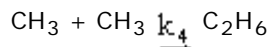
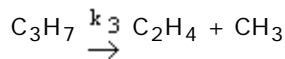
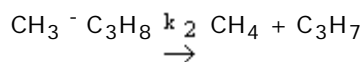
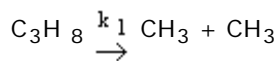
$$\text{and } d[P] / dt = k_2 k_f [E]_0 [S] / (k_2 + k_r + k_f [S]) = k_2 [E]_0 [S] / (k_M + [S]) \quad (28.45)$$

Where $k_M = (k_2 + k_r) / k_f$ is the Michaelis constant. We see that the rate of enzymolysis depends linearly on $[E]_0$ but in a more involved way on $[S]$. When $[S]$ is much larger than k_M , we have $d[P] / dt = k_2 [E]_0$, independent of the substrate and is thus a zero order reaction (in S). This is because too much of S is present to be affected by its depletion into products!

28.6 Problems

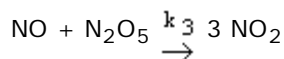
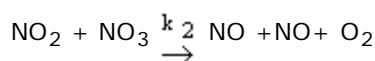
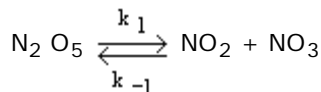
28.1) The Michaelis constant k_M for an enzyme reaction is 0.04M. When the initial substrate concentration is 0.2 M, the reaction rate is $1.2 \times 10^{-3} \text{ Ms}^{-1}$ ($M = \text{mol} / \text{lit}$). How can you maximize the rate of enzymolysis? Under what conditions is the rate of the reaction half its value?

28.2) A mechanism for the decomposition of propane is



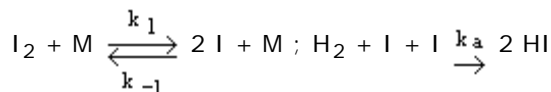
Using the steady state approximation find the expression for the formation of CH_4

28.3) The decomposition of $\text{N}_2\text{O}_5 (\text{g}) \rightarrow 2 \text{NO}_2 (\text{g}) + \text{O}_2 (\text{g})$ is accounted by the mechanism given below



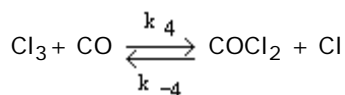
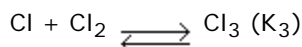
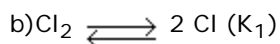
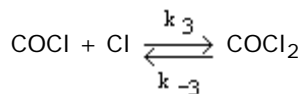
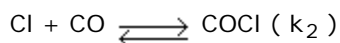
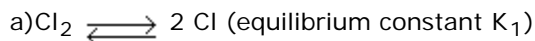
Find an expression for the rate of production of O_2

28.4) There are two mechanisms for the reaction between H_2 and I_2 . In the molecular mechanism, the reaction is of second order, i.e., $d[\text{HI}] / dt = k_m [\text{H}_2] [\text{I}_2]$. In the atomic mechanism, $\text{I} \cdot$ participates, i.e.,



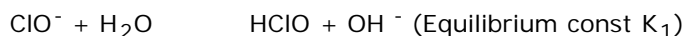
Using the steady state approximation for I obtain the total rate of production of HI .

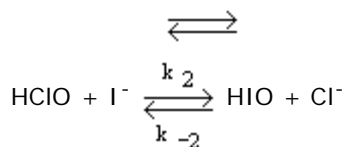
28.5) The formation of phosgene $[\text{COCl}_2 (\text{g})]$ from $\text{CO}(\text{g})$ and $\text{Cl}_2(\text{g})$ can occur by two mechanisms as shown below



For each mechanism, derive the expression for $d[\text{COCl}_2] / dt$. How will you distinguish between the two mechanisms?

28.6) The reaction between I^- and ClO^- is found to have the following mechanism

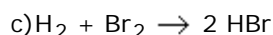
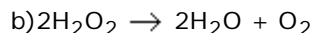
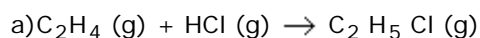




Show that

$$d[\text{Cl}^-] / dt = \{ K_2 K_1 [\text{ClO}^-] [\text{I}^-] - k_{-2} K^{-1}_3 [\text{O}^-] [\text{Cl}^-] \} / [\text{OH}^-]$$

28.7) Propose mechanisms for the following reactions



Recap

In this Lecture you have learnt the following

Summary

The mechanisms of chemical reactions have always kept chemists busy as these studies have led to the discovery of a wide variety of elementary reactions (i.e., reactions in which molecularity is the same as the order with no further possibility of a break up into additional constituent reactions) and the detection of several short lived intermediates. The mechanism of a reaction need not be unique as there could be several pathways leading to the products. In addition, the mechanisms often change when temperature and pressure conditions are changed and when catalysts are added to enhance the reaction rates. Once the steps or the elementary reactions constituting the reaction mechanism are identified we need an equation for the rate law. Convenient approximations (which are valid over significant periods during the reactions) such as the steady state approximation (wherein the small concentration of an intermediate remains constant) and preequilibrium (wherein the reactants quickly come to a near equilibrium with an intermediate) are useful in simplifying the rate equations. Using these, it is possible to identify suitable rate coefficients for reaction process.

Examples of reaction mechanisms of decomposition of ozone, oxidation of nitric oxide, unimolecular reactions and enzymes kinetics have been given in this lecture. With the knowledge gained in this lecture, you will be able to derive the rate law if the reaction mechanism is given to you. Similarly, given the stoichiometry and the order of a reaction you may also be able to propose a mechanism for a given reaction. There is a good chance that your mechanism may be correct!