NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM 407

COURSE TITLE: REACTION KINETICS

COURSE GUIDE

CHM 407
REACTION KINETICS

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INTRODUCTION

CHM 407: Reaction Kinetics concerns with the speed or rates of chemical reactions. The study of reaction rates allows for the prediction of how fast it will take a reaction mixture to reach equilibrium. It also account for how the reaction rate would be optimised by controlling certain factors such as temperature, pressure and the presence of a catalyst. The study of rate often reveals the sequence of elementary steps that lead to the product formation from the reactants, which is referred to as the reaction mechanism.

Many reactions of technologies and biological importance involve complex sequence of steps, or proceed at a useful rate only in the presence of catalysts. Many gas reactions of industrial importance also occur only on the surface of solids which act as catalysts. The mode of action of such surface reactions are discussed in this course. Light is a form of energy and light energy can be used to initiate or sustain chemical reaction. This will also be discussed in this course.

WHAT YOU WILL LEARN IN THIS COURSE

The course consists of main course and the course guide. The course guide tells you briefly what the course is all about, what course materials you will be using and how you can work with these materials. In addition, it advocates some general guidelines for the amount of time you are likely to spend on each unit of the course in order to complete it successfully.

It gives you guidance in respect of your Tutor-Marked Assignment which will be made available in the assignment file. There will be regular tutorial classes that are related to the course. It is advisable for you to attend these tutorial sessions

COURSE AIMS

The course aims to introduce you to the fundamental concepts in the study of rate and mechanism in order to explain the natural phenomena of technological and biological importance.

COURSE OBJECTIVES

To achieve the aims set out, the course has a set of objectives. Each unit also has specific objectives which are included at the beginning of the unit. You should read these objectives before you study the unit. You may wish to refer to them during your study to check on your progress.

Below are the comprehensive objectives of the course as a whole. By meeting these objectives, you should have achieved the aims of the course as a whole. In addition to the aims above, this course sets to achieve some objectives. Thus, after going through the course, you should be able to:

- define rate law, rate constant and order of reaction
- differential between order of reaction and stoichiometry
- state the experimental methods for studying the reaction rate
- derive integrated rate laws for first order, second order and zeroth order reactions and use them for calculating rate constants
- state the methods for determining the order of reaction
- define elementary reaction and molecularity
- explain the modes of action of heterogeneous and homogeneous catalysts
- account for acid-base catalysis using the Bronsted theory
- explain the significance of the Michael's county in enzyme catalysis.
- explain the terms, concurrent, reversible and consecutive reactions
- analysis experimental results for complex reactions i.e. how product concentration or reactant concentration varies with time of reaction
- define and use the Langumair absorption isotherm
- explain order for a surface reaction
- state Beer-Lamberts law
- calculate quantum yield
- list some examples of photochemical reactions
- derive rate expressions for some photochemical reactions
- list some applications of photochemical studies.

WORKING THROUGH THIS COURSE

This course involves that you would be required to spend a lot of time to read. The content of this material is very dense and require you spending great time in studying it. This accounts for the great effort put into its development in the attempt to make it more comprehensive. Nevertheless, the effort required of you is still tremendous. You are advised to avail yourself the opportunity of attending the tutorial sessions where you would have the opportunity of comparing knowledge with your peers.

COURSE MATERIALS

You will be provided with the following material:

1. Course Guide
2. Study Units

In addition, there are lists of recommended textbooks in this course which are not compulsory for you to acquire or indeed read, but necessary as supplements to the course material.

STUDY UNITS

Module 1 Chemical Kinetics

Unit 1 Some Fundamental Concepts of Rate Laws
Unit 2 First and Second Order Reactions
Unit 3 Higher Order of Reaction

Module 2 Some Reaction Mechanisms

Unit 1 Mechanism of Simple Reactions
Unit 2 Theory of Unimolecular Reactions
Unit 3 Complex Reaction

Module 3 Heterogeneous Reactions and Catalysis

Unit 1 Surface Tension of Solutions
Unit 2 Catalysis

Module 4 Photochemistry

Unit 1 Laws of Photochemistry
Unit 2 Photochemical Dissociation

In Module 1, the different types of complex reactions namely; concurrent, reversible and consecutive (chain) reactions will be discussed. The analyses of experimental results for such reaction are also explained in the unit. Zeroth, third and fast reaction and determination of reaction order were also discussed

In Module 2, the mechanism of uni and bimolecular reactions and chain reactions are discussed. Theories to harmonise observed rates and mechanism are equally discussed.

In Module 3, we introduce surface chemistry and catalysis. Physorption and chemisorption processes are discussed and the different types of reaction isotherms are explained. The mode of action of the heterogeneous catalyst is further explained and examples and applications of heterogeneous catalysts discussed.

In Module 4, we discuss light induced reactions (photochemistry). In photochemistry, we study the absorption and emission of light by matter and in photochemical reactions; reactions acquire the necessary activation energy through light absorption.

PRESENTATION SCHEDULE

The course materials have important dates for the timely completion and submission of your TMAs and tutorial lessons. You are vividly reminded of the need to promptly submit answers to tutorials and assignments as and when due.

ASSESSMENT

The course assessment consists of three aspects namely the self-assessment exercise, the tutor-marked assignment and the written examination/end of course examination.

It is essential that you attempt all exercises and assignments and submit appropriately to the course facilitator for grading. Let your answers be concise and as accurate as possible. You are expected to consult other material course in addition to your course materials in order to be able to present accurate answers to the questions. Kindly note that the tutor marked assignment covers only 30% of the total marked for the course.

TUTOR-MARKED ASSIGNMENT

The TMA is a continuous assessment component of this course. It accounts for 30% of the total score. You will be given a number of TMAs to answer. Nearly all of them must be answered before you are allowed to sit for the end of the course examination. The TMAs will be given to you by your facilitator and returned after you have done the assignment. Note that these assignments are already contained in the assignment file to be given to you. You may do yourself good by reading and researching well before you attempt to answer the questions.

You are advised to submit these assignments to the facilitator at the stipulated time as could be seen in the assignment file. However, if for any reason you are unable to meet the deadline, you are advised to intimate the facilitator of your problem before the due date and seek for an extension which may be granted or not.

FINAL EXAMINATION AND GRADING

The end of the course examination for this course will be for about 3 hours with a score value of 70% of the total course work. The examination will be made up of questions which normally reflect on what you have learnt in the course materials/further reading. In addition, they may be prototype of the self-assessment exercises and the TMAs. The end of the course examination is intended to cover information from all parts of the course.

Avail yourself the opportunity of the time-lag between the completion of the course content and the beginning of the examination to revise as much as possible the whole course materials, the exercise and assignments.

COURSE MARKING SCHEME

Assignment	**Marks**
Assignments	The best three marks of the submitted assignments count at 10% each i.e. 30% of the course marks
End of Course Examination	70% of overall course marks
Total	100% of the course materials

FACILITATION/TUTORS AND TUTORIALS

There are few hours of tutorials provided in support of this course. You will be informed appropriately of the name, telephone number and e-mail address of your facilitator. In addition, the time, dates and location of the tutorial lessons will be communicated beforehand. You are required to mail or submit your Tutor Marked Assignment to your facilitator, at least two working days, before the schedule date. Note that all the submitted assignments will be duly marked by the facilitator with further comments that can improve on your performances. The facilitator will from time to time takes track record of your comprehension, progress and difficulty in the course.

Be kind enough to attend tutorial lessons at the fixed appointment. It is probably the only avenue to meet face to face and discuss with you facilitator. There, you will be able to ask question or seek clarification on seemingly grey area in the course material. You may as well have prepared questions and comments for your facilitator before the due date. An active participation during the tutorial lessons will be an added advantage to boost confidence level.

In case any of the situations listed below arises, do not hesitate to intimate your facilitator using his or her telephone number or via e-mail address:

- **y**ou do not understand any part of the study or the assigned readings
- **y**ou are not skill enough to attempt the self assessment exercise
- **y**ou The questions in the TMAs are not clearly understood.

Accept our best wishes in this course and we do hope that you will benefit considerably from its application.

MAIN COURSE

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MODULE 1 CHEMICAL KINETICS

UNIT 1 SOME FUNDAMENTAL CONCEPTS OF RATE LAW

CONTENTS

1.0 INTRODUCTION

Chemical kinetics is the study of rates and mechanisms of chemical reactions. The rate of a reaction depends on many factors such as the concentration of the reactants, temperature, catalyst etc.

We shall start this unit by explaining the dependence of rate of reaction on the concentrations of the reactants. In this process, we shall be defining the terms such as rate equation, rate law and order of reaction. We shall then derive the first and second orders of reaction.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define rate law, rate constant and order of reaction
- differentiate between order of reaction and stoichiometry
- state the experimental methods for studying the reaction rates.

3.0 MAIN CONTENT

3.1 Some Fundamental Concepts

In this course, the following shall apply:

- the phrase 'rate of reaction' means instantaneous reaction rate
- the symbol ' � ' is to be read as delta. It denotes change in a property.

Convention for Expressing Reaction Rates

In order to obtain a single value for the reaction rate, it is necessary to divide the rate of consumption of a reactant or the rate of formation of a product by the stoichiometric coefficient of the respective species. To illustrate this, let us consider the reaction:

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D}$$

In this reaction, A and B are reactants while C and D are products; *a, b, c* and *d* are the stoichiometric coefficients. The reaction rate is related to the rates of consumption of the reactants and the rates of formation of the products as follows:

Reaction rate

$$= \frac{1}{a}\left(\frac{-d\,[A]}{dt}\right) = \frac{1}{b}\left(\frac{-d\,[B]}{dt}\right)$$

$$= \frac{1}{c}\,\frac{-d\,[C]}{dt} = \frac{1}{d}\left(\frac{-d\,[D]}{dt}\right) \qquad \ldots (1.1)$$

Using this general equation, you examine E.q 1.1

- The number preceding the formula of a substance in the balanced equation is its stoichiometric coefficient

3.1.1 Rate of Reaction

The rate of reaction or the velocity of reaction at a specified time is defined as the decrease in the concentration of a reactant or the increase in the concentration of a product per unit time. The rate of reaction at a specified time is also known as instantaneous rate of reaction; it can be generally defined as the rate of change of concentration of a specified species at a particular instant. While specifying the reaction rate, it is appropriate to mention the component with respect to which it is stated. Let us consider a simple reaction:

$A \rightarrow B$

With respect to the reaction stoichiometry, one molecule of B is formed for every molecule of A consumed. The reaction rate can be specified in the following ways:

- we can measure the concentration of the reactant A at various time intervals. From these values, we can specify the decrease in concentration of A with respect to time at any particular instant. The reaction rate thus obtained is the rate of consumption of A.

Rate of consumption of A = $\frac{\text{Decrease in the concentration of A}}{\text{Change in time}}$

$$= \frac{-\Delta[A]}{\Delta t}$$

- Δ [A] means change in the concentration of A and - Δ [A] means the decrease in the concentration of A. While writing a rate expression with respect to a reactant, there is a preceding negative sign (since it is customary to express the rate of a reaction as a positive quantity).
- we can measure the concentration of the product B at various time intervals. From these values, we can arrive at the rate of formation of B at any particular instant.

Rate of formation of B = $\frac{\text{Increase in the concentration of B}}{\text{Change in time}}$

$$= \frac{-\Delta[B]}{\Delta t}$$

The rates of consumption of reactants and the rates of formation of products are related through their stoichiometric coefficients.

For example, consider the decomposition of NO_2.

$$2NO_2(g) \rightarrow 2NO(g) + O_2(g)$$

We can write the relationship between the rates of consumption of NO_2 and the rates of formation of NO and O_2 as follows:

½(Rate of consumption of NO_2) = ½ (Rate of formation of NO) … (1.1)

= Rate of formation of O_2

Using the convention as expressed by Eq. 1.2, we can write as shown below;

$$\text{Reaction rate} = \frac{1}{2} \times \frac{-d\,[NO_2]}{dt} = \frac{1}{2} \times \frac{d\,[NO]}{dt} = \frac{d\,[O_2]}{dt} \quad ....(1.2)$$

You will deduct from the above relationship that for every two molecules of NO_2 consumed, two molecules of NO and one molecule of O_2 are formed. In other words, the reaction rate is equal to:

- half the rate of consumption of NO_2
- half the rate of formation of NO, and
- the rate of formation of O_2

3.2 Calculation of Reaction Rate

You may be curious to know how the reaction rates are calculated. Take for instance the following reaction:

$2NO_2\,(g) \rightarrow 2NO(g) + O_2(g)$

In Figure 1.1, you can see the graph of concentration (c) against time (*t*) plots for NO_2, NO and O_2 from the values given in Table 18.1. In these figures, the graphical method of calculating the reaction rates for the consumption of NO_2 and for the formation of NO and NO_2 are illustrated. The reaction rate at any particular instant is obtained by calculating the slope of a line tangent to the curve at that point.

Table 1.1: Concentration of NO_2, NO and O_2 at Different Time Interval at 673 K

Time(s)	$[NO_2]$(M)	[NO](M)	$[O_2]$(M)
0	0.00100	0	0
50	0.0079	0.0021	0.0011
100	0.0065	0.0035	0.0018
150	0.0055	0.0045	0.0023
200	0.0048	0.0052	0.0026
250	0.0043	0.0057	0.0029
300	0.0038	0.0062	0.0031
350	0.0034	0.0066	0.0033

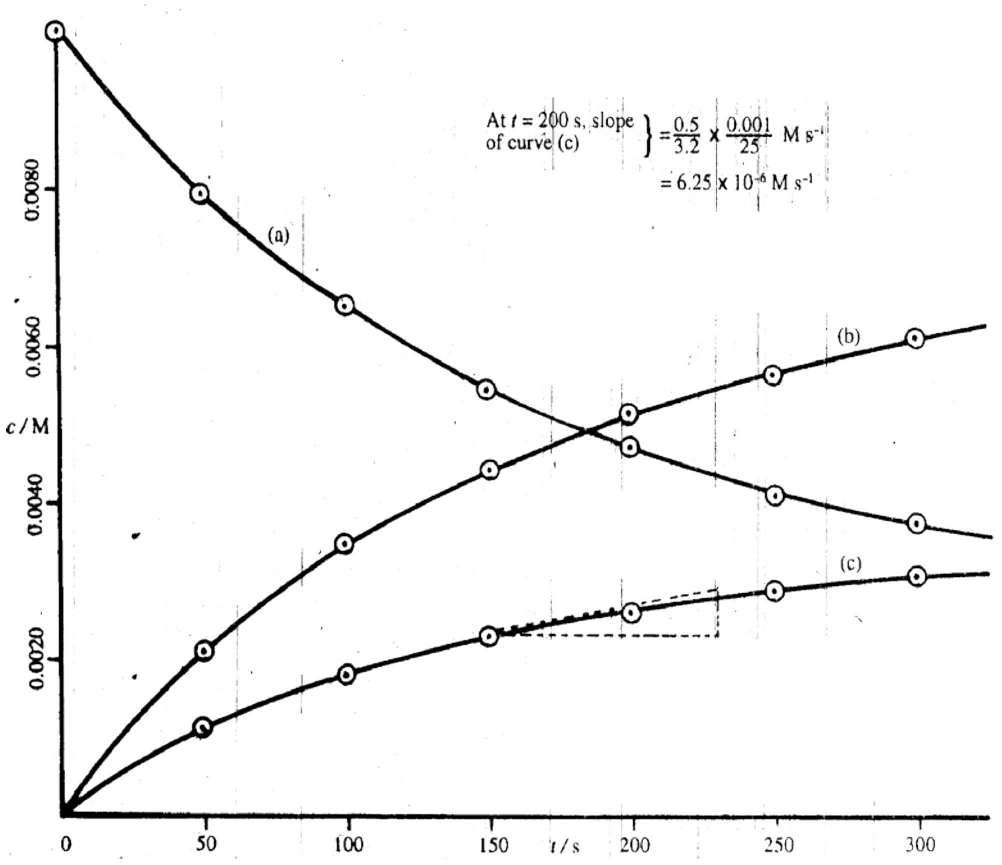

Fig. 1.1: a) Concentration against Time Plot for NO_2, NO and O_2 Note the falling nature of the curve which is characteristic of concentration against time plot for a reactant.

Note:

a = Concentration against time plot for NO_2
b = Concentration against time plot for NO
c = Concentration against time plot for O_2

From the slope of the tangent time drawn (corresponding to a particular time) to the concentration (c) against time (t) curve for a component, we can obtain the rate of the reaction.

Rate of reaction

$$= -\frac{\text{(Slope of tangent to the c against } t \text{ curve for the reactant)}}{\text{Stoichiometric coefficient of the reactant}}$$

$$= \frac{\text{(Slope of tangent to the c against } t \text{ curve for the product)}}{\text{Stoichiometric coefficient of the product}}$$

The concentration of components are given in molarity (M) unit where 1M = 1 mol/dm^3

Rate of consumption of NO_2; = - Slope of the tangent line at *t* = 200 *s*
at *t* = 200 *s*

$= -(-1.31\times10^{-5})\ Ms^{-1}$
$= 1.31\times10^{-5}\ Ms^{-1}$

Reaction rate $= \frac{1}{2}$(Rate of consumption of NO_2) = $\frac{1}{2} \times 1.31\times10^{-5}\ Ms^{-1}$

$= 6.55 \times 10^{-6}\ Ms^{-1}$

b) Concentration against time plot for NO; note the rising nature of the curve which is characteristic of concentration against time plot for a product.

Rate of formation of NO = Slope of the tangent line at *t* = 200 *s*
at t = 200 *s*
$- 1.30 \times 10^{-5}\ Ms^{-1}$

Reaction rate $= \frac{1}{2}$(Rate of formation of NO)

$= 1/2 \times 1.30 \times 10^{-5}\ Ms^{-1}$
$= 6.50 \times 10^{-6}\ Ms^{-1}$

c) Concentration against time plot for O_2; note again the rising curve. Compared to the curve for NO, the curve for O_2 rises slowly.

Rate of formation of O_2 = Slope of the tangent line at *t* = 200 *s*
at *t* =200 *s*
$- 6.25 \times 10^{-4}\ Ms^{-1}$
Reaction rate = Rate of formation of O_2
$= 6.25 \times 10^{-6}\ Ms^{-1}$

Also note that for the curves (a) and (b), the tangents are not indicated.

From the slope values at *t* = 200 *s*, you can see that the following relationship is nearly correct.

Reaction rate = $\frac{1}{2}$(Rate of consumption NO_2= $\frac{1}{2}$(Rate of formation of NO)

= Rate of formation of O_2

In our discussion, we are mainly interested in the concentration against time plots for the reactants. In other words, we are studying the reactions under conditions where the rate of the forward reaction is significant but the reverse reaction rate is low. This is made possible, if we study the reaction upto a point where the product amounts are not high. For example, in the decomposition of NO_2, there could be a decrease in the concentration of NO_2 upto a particular time. Afterwards, enough nitric oxide and oxygen are formed and the reverse reaction also could take place leading to the formation of NO_2. In order to simplify the situation, it is better to study the reaction rates before significant amounts of products are formed. In general, the rates of reactions are complex functions of the concentrations of the reactants and the products at a given the temperature. However, there are some reactions in which the rates are proportional to the simple powers of the concentrations of the reactants. We shall be mostly concerned with this class of reactions.

Example 2: Decomposition of N_2O_5

The decomposition of N_2O_5 in the gas phase was studied at 323 K

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The instantaneous rates of this reaction calculated from $[N_2O_5]$ against time plot (similar to Fig. 1.1) are given in Table 1.2

Table 1.2: Rates for the Decomposition of N_2O_5 at 323 K

$[N_2O_5]$/M	Rate/Ms^{-1}	Rate s $\overline{[N_2O_5]}$
(i)	(ii)	(iii)
0.300	2.73×10^{-4}	9.1×10^{-4}
0.150	$1.37 \times l0^{-4}$	9.1×10^{-4}
0.100	$9.10 \times l0^{-3}$	9.1×10^{-4}

From columns (i) and (ii), you can see that the rate for the decomposition of N_2O_5 decreases with the decrease in the concentration of N_2O_5. Further, column (iii) gives the ratio of the rate to the concentration of N_2O_5. In all the three cases, it is a constant. This shows that the rate is directly proportional to the concentration of N_2O_5.

$$\frac{\text{Rate}}{[N_2O_5]} = k \qquad \ldots (1.3)$$

Hence, rate = $k\,[N_2O_5]$ … (1.4)

Where k is the proportionality constant.

Example 3: Decomposition of Hydrogen Iodide

The decomposition of hydrogen iodide was followed at a constant temperature

$$2HI(g) \rightarrow H_2(g) + I_2(g)$$

The instantaneous rates of this reaction were calculated using the [HI] against time plot like that of Fig. 1.1. These values are given in Table 1.3

Table 1.3: Rates for the Decomposition of HI

[HI]/M (i)	Rate/Ms^{-1} (ii)	Rate [HI] (iii)	Rate Ms^{-1} [HI]^2 (iv)
3.00×10^{-2}	3.60×10^{-5}	1.2×10^{-3}	4.00×10^{-2}
2.00×10^{-2}	1.60×10^{-3}	8.0×10^{-4}	4.00×10^{-2}
1.50×10^{-2}	9.01×10^{-6}	6.0×10^{-4}	4.00×10^{-2}

From Table 1.3, you can see that the rate of decomposition of HI decreases with decrease in the concentration of HI, as in the case of the decomposition of N_2O_5. Further, it is evident from column (iii) that rate/[HI] is not a constant. But for column (iv), rate/[HI]^2 is a constant.

From the table given above, it is evident that
Rate / [HI]^2 = k …(1.5)
Hence, rate = k [HI]^2 … (1.6)

Where k is the proportionality constant

For many chemical reactions, the relationship between the reaction rate and the concentration can be expressed in a simple way as in Eq. 1.4 or 1.6. We shall first consider these simple cases and later discuss those reactions, for which the rate concentration relationship is more complex.

3.3 The Rate Law and the Rate Constant

The relationship expressed as in Eq. 1.4 or Eq. 1.6 is called the **rate law**. A rate law is an equation expressing the relationship between the instantaneous reaction rate and the concentrations of the reactants in given a reaction.

The rate law for a simple reaction with one reactant is given below:

Reaction rate $= k\,[\text{Reactant}]^n$ …(1.7)

Where k *is* called the rate constant or rate coefficient or the specific rate or the reaction.

Thus by definition, the rate constant is independent of concentration, but it may depend on other factors. In this equation, *n* refers to the order of the reaction. The order with respect to a component is the power to which the concentration of that component is raised in the rate law. Comparing Eq. 1.7 with Eqs. 1.4 and 1.6 we can conclude that:

i) $n = 1$ in Eq. 1.4; i.e.; decomposition of N_2O_5 is a **first order** reaction. The significance of this statement is that the reaction rate is proportional to the first power of concentration of N_2O_5.

i.e., Rate $= k\,[N_2O_5]^1$ … (1.8)

Where k is the **first order rate constant**

From Eq. 1.7, it can be seen that if [reactant] = l then k = rate. For this reason, k is called the specific rate.

ii) $n = 2$ for the decomposition of HI; i.e. the decomposition of HI is a **second order reaction**. Again, this implies that the decomposition rate of HI is proportional to the second power or square of the concentration of HI.

i.e., Rate $= k\,[HI]^2$ …(1.9)

Where k is the **second order rate constant**.

3.4 Order of Reaction and Stoichiometry

The rate laws as well as the order of the reaction are normally determined experimentally; these cannot be predicted from the stoichiometry of the reaction. The stoichiometry of reaction gives the relationship between the amounts of the reactants and the amount of the product. The stoichiometry of a reaction must be differentiated from the order of a reaction. Let us consider the following examples:

Example 1

The gas-phase decomposition of N_2O_5 yields NO_2 and O_2 at a particular temperature.

$2N_2O_5\,(g) \longrightarrow 4\,NO_2\,(g) + O_2\,(g)$

The experimentally observes rate law for the reaction rate = $k\,[N_2O_5]$
Can you comment on the order and the stoichiometry of the reaction?

Solution

It can be seen that the stoichiometric coefficient of N_2O_5 is 2 whereas the order of reaction is 1.

Example 2

The balanced equation for the decomposition of nitrous oxide is given below:

$2N_2O_5\,(g)\quad 2NO_2\,(g) + O_2\,(g)$

The rate law is,

Rate = $k\,[\,N_2O_5\,]$

Comment on the order of the reaction and the stoichiometry.

Solution

Again the stoichiometric coefficient of N_2O_5 is 2 whereas the order of reaction is 1.

In the above two examples, the order of reaction and the stoichiometry are not identical, but there are cases where the order and stoichiometric coefficient are identical. One of those cases can be seen in the following reaction:

$2HI(g) \rightarrow H_2\,(g) + I_2(g)$

Rate = $k\,[HI]^2$

In the decomposition of HI, the order of reaction is two. The stoichiometric coefficient of HI is also 2.

From the above examples, it can be deduced that the stoichiometric coefficient and the order of the reaction need not be the same always. You must bear in mind the following points while arriving at a rate law.

i) In the case of simple reactions, the concentrations of the reactants appear in rate law; but the concentrations of the products do not appear in the rate law because the rate measurements are done under the conditions where the reverse reaction rate is negligibly low.

ii) The order of the reaction must be determined experimentally; the experimental methods will be discussed in the next section.

iii) The order of reaction need not be identical with the stoichiometric coefficient of the reactant.

So far we have considered the reactions involving only one reactant. In case of reactions involving many reactants, the rate of reaction may depend on the concentrations of more than one reactant. In such cases, we can calculate the order of the reaction with respect to the individual reactant as well as the *overall order*. The overall order is the sum of the powers to which the individual concentrations are raised in the rate law.

Generally, for a given reaction;

$A + B + C \rightarrow$ products … (1.10)

If the rate law is experimentally found to be,

Rate = $k\,[\,A\,]^m\,[\,B\,]^n\,[\,C]^p$

Then, the overall order of the reaction = $m + n + p$.

For example in the following reaction,

BrO_3 (aq) + 5 Br^- (aq) + $6H^+$ (aq) $\rightarrow$ 3 Br_2 (aq) + 3 H2O (l) … (1.11)

Rate = $k\,[BrO_3]\,[Br^-]\,[H^+]^2$

The overall rate of the reaction is four, being first order in BrO^-_3, first order in Br^- second order in H^+

The rate laws discussed so far are called *differential rate laws*. Such rate laws describe the dependence of reaction rate on concentration. From these differential rate laws, we can obtain the *integrated rate laws* through integration. These integrated rate laws help us in relating the concentration of a substance to time. In order words, using the integrated rate laws, we can calculate the concentration of a substance at any specific time. We shall discuss the derivation of the integrated forms of rate laws later in this course. In the next section, we shall discuss some experimental methods of studying the reaction rates.

For the BrO_3^- – Br^- – H^+ reaction let us compare the order of reaction and the stoichiometric coefficient for each reactant.

	BrO_3^-	Br^-	H^+
Order	1	1	1
Stoichiometric Coefficient	1	5	6

It may be deduced that the stoichiometric coefficients and the respective orders of reaction are not identical throughout.

3.5 Experimental Methods of Rate Studies

Many physical and chemical methods are available for studying the reaction rates. Some of them are listed below:

i) Volume or Pressure Measurement

When one or more of the components are gases, the reaction rate can be followed by measuring the volume or pressure change. The partial pressures of the species are to be calculated using the reaction stoichiometry.

Spectrophotometers have arrangements for generation of nearly monochromatic radiation in visible and ultraviolet regions and also for the measurement of radiation transmitted by the absorbing substance.

Nowadays, many sophisticated instrument such as nuclear magnetic resonance spectrometer, mass spectrometer etc, are used in reaction kinetics. We shall not discuss these aspects.

ii) Titrimetry

Using acid-base or oxidation-reduction titrations, the reaction course can be followed if at least one of the components in the reaction is an acid, a base, an oxidising agent or a reducing agent.

iii) Conductometry or Potentiometry

If one or more of the ions are present or produced in the reaction, suitable methods can be designed based on conductivity or potentiometric measurements.

iv) Spectrophotometry

When a component of the reaction has a strong absorption band at a particular wavelength region, spectrophotometers could be used for measuring the reaction rate. Photoelectric colorimeters are cheaper instruments and are mainly useful for reaction rate studies in visible region.

v) **Polarimetry**

When at least one of the components of a reaction is optically active, the reaction rate can be studied from the measurements of optical rotation.

Depending of the reaction under study, the concentration of a reactant or a product is followed at various time intervals using any of the methods explained above. These values are then used for calculating the rate constant. Examples are worked out later in this unit to illustrate how to calculate the rate constant. Before studying these examples, we shall discuss the method of arriving at the integrated forms of rate laws.

4.0 CONCLUSION

Reaction rates are determined by measuring the change in the concentration of a reactant or product over a period of time.

5.0 SUMMARY

In this unit, we have discussed the fundamentals concepts of rate law and the experimental methods of rate studies. These experimental methods of rate studies include; volume or pressure measurement, titrimetry, conductometry or potentiometry, spectrophotometry and polarimetry.

6.0 TUTOR-MARKED ASSIGNMENT

i. (a) At 323K, the rate of reaction for the decomposition of N_2O_5 at a particular instant is 2.74×10^{-4} Ms^{-1}. Calculate the rate of formation of O_2.

The reaction is represented below:

$2N_2O_5(g) \rightarrow 4NO_2\ (g) + O_2\ (g)$

(b) In the decomposition of hydrogen iodide, what is the relationship between the rate of decomposition of HI and the rate of formation of H_2?

ii. State the name of a suitable experimental method that can be followed to monitor the reaction rate in each of the following cases.

i) $H_2\,(g) + Br_2\,(g) \rightarrow 2HBr\,(g)$

Hint: Bromine absorbs strongly in the visible region, while hydrogen and hydrogen bromide are not.

iii. $CH_3COOC_2H_5\,(aq) + OH^-\,(aq) \rightarrow CH_3COO^-\,(aq) + C_2H_5OH\,(aq)$

iv. $CH_3CHO^-\,(g) \rightarrow CH_4\,(g) + CO\,(g)$ (at constant volume conditions)

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UNIT 2 FIRST AND SECOND ORDER REACTIONS

CONTENTS

1.0 INTRODUCTION

In the last unit, we examined the fundamental concept of rate law. We equally discussed the experimental methods of rate studies. In this section, we shall derive integrated rate laws for first and second order reactions and apply these laws in calculating the rate constants.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- derive integrated rate laws for first order reaction
- derive integrated rate laws for second order reaction
- use the integrated laws derived above for calculating rate constants.

3.0 MAIN CONTENT

3.1 Integrated Rate Law for First Order Reactions

Let us consider the following reaction, which is experimentally found to be first order

$$A \rightarrow \text{Product} \qquad \ldots\ldots\ldots (1.12)$$

Applying Eq. 1.7 we can write

$$\text{Rate} = \frac{-d[A]}{dt} = k\,[A]^1 \qquad \ldots (1.13)$$

Where k is the first order rate constant and $n = 1$. This means that the rate of consumption of A at any given time is directly proportional to the first power of the concentration of A at that time.

In order to obtain the integrated rate for first order reaction, concentrations of A at the beginning of the reaction and at a time t as mentioned below:

At time = 0 (i.e., at the start), the concentration of A = $[A]^o$

At time = A the concentration of A - $[A]_t$

Using these limits of concentration and time, we can integrate Eq. 1.13 after rearranging it as follows:

$$\int_{[A]_0}^{[A]_t} - \frac{d\ [A]}{[A]} = \int_0^t k\, dt \qquad \text{… (1.14)}$$

$$- \qquad = \qquad k\, dt$$

$$\text{i.e., } - \{\ln [A]\} = k[t] \int_0^t {}_{[A]_0}^{[A]_t} \qquad \text{… (1.15)}$$

$$- \{\ln [A]_t - \ln [A]\ 0\} = k\ (t - 0) \qquad \text{…. (1.16)}$$

$$\ln [A]_0 - \ln [A]_t = kt \qquad \text{…(1.17)}$$

Hence,

$$\ln \frac{[A]_0}{[A]_t} = kt \qquad \text{…. (1.18)}$$

Eq. 1.18 can be written in the exponential form as follows:

$$[A]_t = [A]_0\, e^{-kt} \qquad \text{…(1.19)}$$

Note: In order to understand the transformation of Eq. into Eq 1.16.

The transformation of Eq. l.18 into Eq. 1.19 could be explained as follows

$$\ln\frac{[A]_o}{[A]_t} = kt$$

$$-\ln \frac{[A]_t}{[A]_0} = kt$$

Taking antilogarithms

$$\frac{[A]_t}{[A]_o} = e^{-kt}$$

$$[A]t = [A]_0 \, e^{-kt} \qquad 1.19$$

Corresponding to Eq. 1.19, we can draw the concentration vs time plot for a first order reaction. This curve is of the type shown in Fig. 1.2. Such a curve is called an exponential decay curve. In an exponential decay curve, there is an initial steep decrease in concentration; this is followed by a slow decrease in concentration. Note that the decay curve goes parallel to *x*-axis after longer time intervals indicate that the reaction will take infinite time for completion.

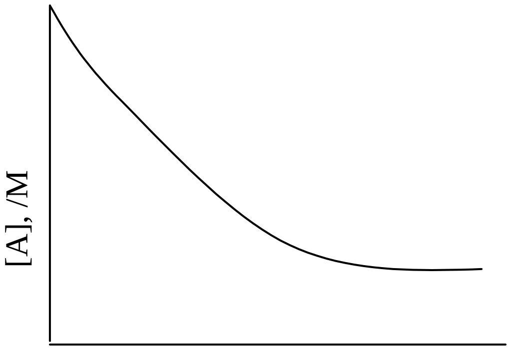

Fig 1.2: Exponential Decay of A

Radioactive decay is a good example of first order/reaction.

From Eq. 1.18, it is convenient to work with logarithms to the base 10 (known as common logarithms). Hence, we can rewrite Eq. 1.18 as follows:

Also note that: ln *x* = 2.303 log *x*

$$2.303 \log\frac{[A]_0}{[A\,]_t} = kt$$

$$\ldots (1.20)$$

$$k = \frac{2.303}{t} \log\frac{[A]_0}{[A]_t}$$

Eq. 1.20 is useful in calculating the concentration of the reactant at a time *t* (i.e., $[A]_t$) provided, its initial concentration (i.e., $[A]_0$), *k* and *t* are known. Also, k can be calculated if $[A]_0$, $[A]_t$ and *t* are known. Using the graphical method, we can test whether a reactant follows first order or not.

3.2 Graphical Method of Calculating First Order Rate Constant

In order to facilitate graphical representation, Eq. 1.20 is modified as follows:

$$\log \frac{[A]_o}{[A]t} = \frac{kt}{2.303} \qquad \ldots (1.21)$$

Hence, $$\log[A]_0 - \log [A]_t = \frac{k\,t}{2.303} \qquad \ldots. (1.22)$$

i.e., $$-\log [A]_t = \frac{k\,t}{2.303} - \log [A]_0 \qquad \ldots. (1.23)$$

$$\log [A]_t = \frac{-k}{2.303}\, t + \log [A]_0 \qquad \ldots (1.24)$$

From Eq 1.21, we can derive Eq. 1.22 by substituting the concentrations of A at the intervals t_1, and t_2 as follow:

At time = $t_1,$ the concentration of A = $[A]_1$

At lime = t_2, the concentration of A = $[A]_2$

$$\log \frac{[A]_0}{[A]_1} = \frac{k\,t_1}{2.303}$$

$$\log \frac{[A]_0}{[A]_2} = \frac{k\,t_2}{2.303}$$

Hence:

$$\log \frac{[A]_0}{[A]_2} - \log \frac{[A]_0}{[A]_1}$$

$$= \frac{k}{2.303}(t_2 - t1) \qquad \ldots(1.25)$$

$$\text{i.e } \log \frac{[A]_1}{[A]_2} = \frac{k}{2.303}(t_2 - t_1) \qquad \ldots(1.26)$$

By comparing Eq. 1.24 with the equation for a straight line,

$y = \mathrm{mx} + c,$

We can infer that by plotting log; [A] against time t, a straight line must be obtained for a first order reaction. Such plots are shown in Figures

1.3 and 1.5. The rate constant can be calculated from the slope as follows:

k = -2.303 × slope … (1.27)

Knowing the concentration of a reactant undergoing first order reaction at a particular time, it is possible to calculate its concentration at another time interval using Eq. 1.28

$$\log \frac{[A]_1}{[A]_2} = kt \, \frac{(t_2 - t_1)}{2.303} \qquad \ldots (1.28)$$

The following hints may be useful while calculating the rate constant using the integrated rate law.

i) If the concentrations of the reactant are given at various time intervals, the concentration at $t = 0$ is equal to] $[\ A\ ]_0$ and the concentration at any given time is $[A]_t$ *;* log $[A]_t$ against t plot is made as described earlier. This principle is followed in Example 3.

ii) Instead of giving the concentrations of a reactant at various time intervals, parameters such as partial pressures, absorbances, volumes, titre values etc. which are proportional to the concentration of the reactant may be given. In these cases, the measurements made at zero time and at any given time t may be used instead of [A]d and $[\ A\ ]_{t.}$. For example, we can substitute the partial pressure of the reactant instead of its concentration in Eq. 1.2l and obtain Eq. 1.28.

$$\log \frac{(PA)_0}{(PA)_t} = \frac{kt}{2.303}$$

Where $(PA)_0$ and $(PA)_t$ are the partial pressures of the reactant at the start and after a time, t. In Example 4, we Use this method.

iii) Sometimes, the rates of measurement are made in terms of the concentrations of the product formed. If the stoichiometry of the reaction is such that one molecule of the product is formed when one molecule of the reactant is consumed then the concentration of the product at $t = \infty$ must be equal to initial concentration of the reactant. Let us assume that the concentration of the product at any given time is x. Then x also represents the decrease in the concentration of the reactant after a time, t. Thus $[A]_0$ = concentration of the product at $t = \infty$ and $[\ A\ ]_t = [\ A\ ]_0 - x$.

Using these (relationships, Eq. 1.2l could be written as,

$$\log \frac{[A]_0}{[A]_{0-x}} = \frac{k\,t}{2.303}$$

Calculation of this type is illustrated in Example 5.

Let us work out some examples to illustrate the calculation of *k* by graphical method.

Example 3

On heating cyclopropane to 770K, it was converted into propene. In one experiment, the following data were obtained:

t/s.	0	300	600	900
$\frac{[\text{Cyclopropane}]}{\text{M}}$	1.50×10^{-3}	1.24×10^{-3}	1.00×10^{-3}	8.3×10^{-4}

Using graphical method, test whether the above data satisfy first order rate equation. Calculate the rate constant.

Solution

Using the data, log [cyclopropane]/M values are calculated and tabulated along with *t* values.

log [cycIppropane]/M	–2.82	–2.91	–3.00	–3.08
t/s	0	300	400	900

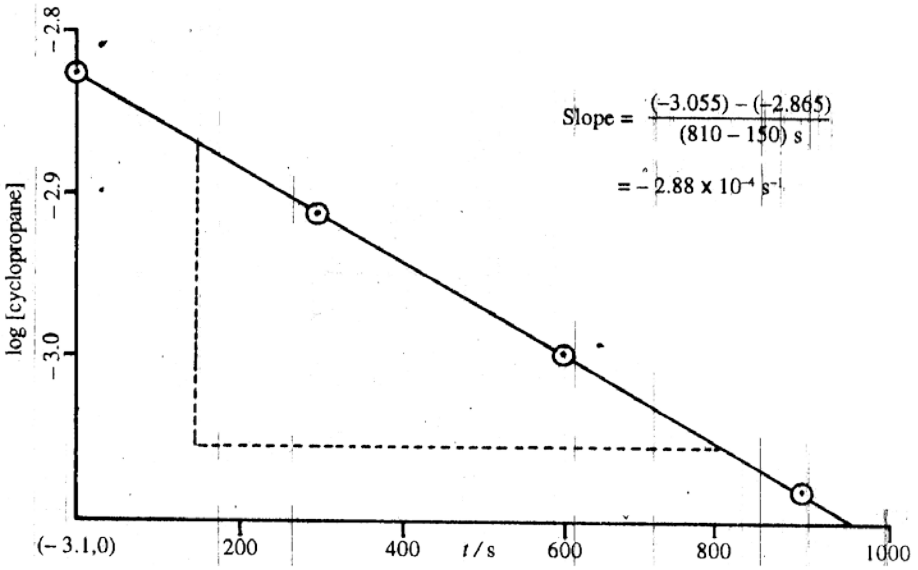

Fig. 1.3: log [cyclopropane] against *t* Plot

Figure 1.3 shows the log [cyclopropane] vs. *t* plot. The graph is a straight line, confirming that the reaction is first order.

$$k = -2.303 \times \text{slope} = -2.303 \times (-2.88 \times 10^{-4})\ \text{s}^{-1}$$
$$= -6.63 \times 10^{-4}\ \text{s}^{-1}$$

Example 4

Azomethane ($CH_3 - N = N - CH_3$) decomposes at 600 k as pr the equation:

$$CH_3 - N = N - CH_3(g) \longrightarrow C_2H_6\,(g) + N_2\,(g)$$

The reaction rate was followed by measuring the partial pressure of azomethane (PA) at different time intervals and the data are given below:

PA/pa	10.9	7.6	5.3	*3.7*	2.6
t/s	0	1000	2000	3000	4000

Using the data, test whether the reaction follows first order kinetics and calculate the rate constant.

Solution

The concentration of azomethane (CA) can be related **to its partial pressure** (*PA.*) as follows:

PA = *C*ART or *PA* α *CA*

So, we can use partial pressure of azomethane in Eq. 1.21 instead of concentration as shown in Eq. 1.28.

Where (PA) o and *(PA.)$_t$* are the partial pressures of azomethane at the start and after a time, *t.* We tabulate the data accordingly:

log(PA)t/Pa	1.04	0.88	0.72	0.57	0.41
t/s	0	1000	2000	3000	4000

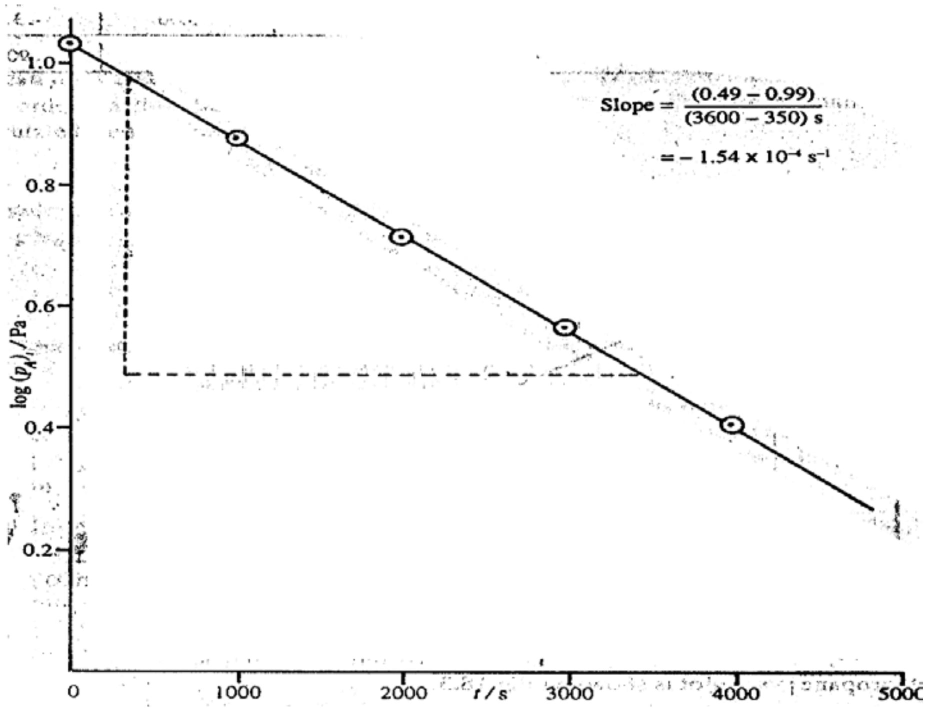

Fig. 1.4: log (Pa)t against t Plot for the Decomposition of Azomethane

log (*PA*)$_t$, is plotted against *t* as shown in Fig.l.4

From Figure l.4, we could see that the graph is a straight line. Hence, the decomposition of azomethane is a first order reaction.

Slope = l.54 $\times 10^{-4} s^{-1}$

k = - 2.303 × slope, = -2.303 × (-1.54×10^{-4} s^{-1})

$= 3.55 \times 10^{-4}$ s^{-1}

Example 5

The hydrolysis rate of benzene diazonium chloride ($C_6H_5N = NCI$) in its aqueous solution was followed by measuring the volume of nitrogen evolved at different time intervals. The reaction was found to be first order. Using the data given below, calculate the first order rate constant.

Time /s	0	1500	3000	4500	∞
Volume of N_2 / Cm^3	0	6.4	12.1	17.6	81

Solution

In this example, the rate measurement is done in terms of the product. The volume (V_t) of nitrogen produced at any given time, *t*, is proportional to the concentration of benzene diazonium chloride reacted (*x*). The volume at *t* ∞ (i.e., V_∞) indicates the volume of nitrogen produced by the complete hydrolysis of benzene diazonium chloride and, it is proportional to the initial concentration of benzene diazonium chloride.

So, $[A]_0 \infty V_\infty$

$x \,\alpha\, V_t$

And $[A]_0 - x \;\alpha\; V_\infty - V_t$

Hence $$\frac{[A]_0}{[A]_0 - x} = \frac{V_\infty}{V_\infty - V_t}$$

Using this relationship in Eq.1.29,

$$\log \frac{V_\infty}{V_\infty - V_t} = \frac{kt}{2.303}$$

I.e., $$\log (V_\infty - V_t) = \log V_\infty - \frac{kt}{2.303}$$

Using the data given above, ($V_\infty - V_t$) and log ($V_\infty - V_t$) values are tabulated for different *t* values.

Time/s	0	1500	3000	4500
$(V_\infty - V_t)/cm^3$	81	74.6	68.9	63.4
$\log (V_\infty - V_t)/cm^3$	1.908	1.873	1.838	1.802

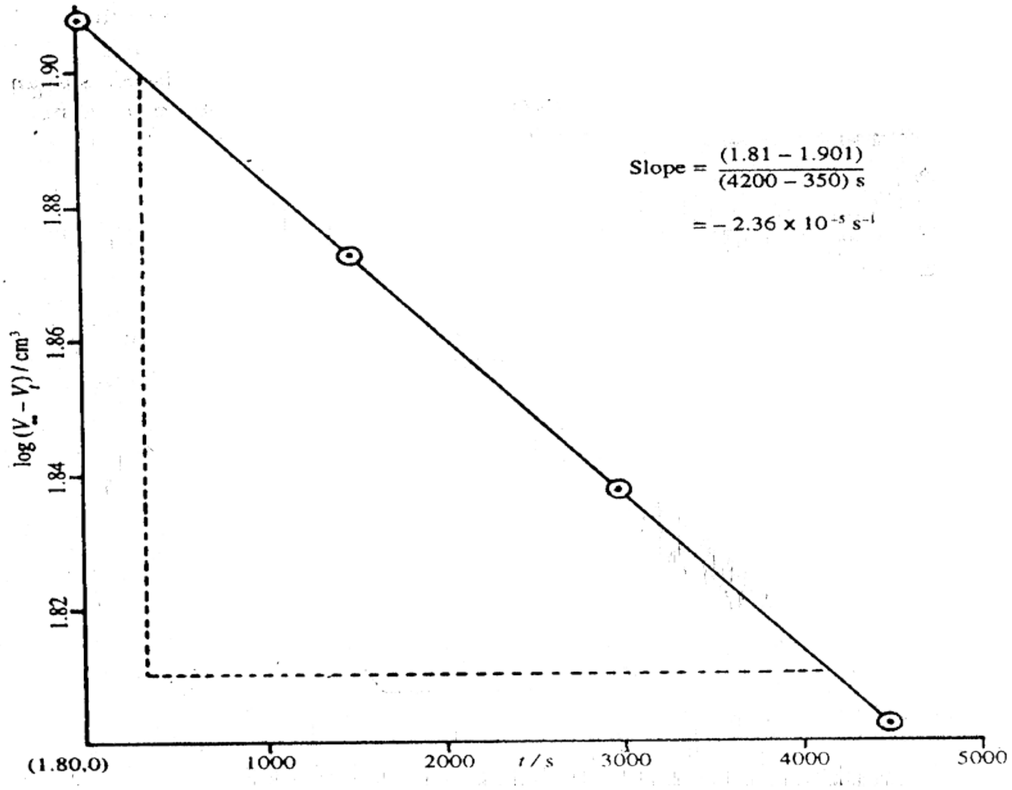

Fig. 1.5: log (v_∞ – v_t) against t Plot for the Hydrolysis of Benzene Diazonium Chloride

In a first order reaction, the amount of the reactant remaining after *n* half-life periods is given by the formula:

log ($V_\infty – V_t$) as plotted against *t* (Fig. l.5)

From figure l.5

$$\text{Slope} = –2.36 \times 10^{-5}\ s^{-1}$$
$$k = – 2.303 \times \text{slope}$$
$$= 2.303 \text{ x } (–2.36 \times l0^{-5}\ s^{-1})$$
$$= 5.44 \times l0^{-5}\ s^{-1}$$

In a first order reaction, the amount of the reactant remaining after n half-life periods is given by the formula:

Concentration of the reactant remaining after = *n* half-lives Initial concentration of the reactant

3.3 Half-Life of First Order Reactions

The time taken for the concentration of a reactant to fall to half its initial value is called the *half-life of a reaction.* It is denoted by the symbol, *t.* We can derive an expression useful in calculating the half-life of a substance undergoing first order reaction using Eq. 1.21.

$$\log \frac{[A]_0}{[A]_t} = \frac{kt}{2.303} \qquad \ldots(1.29)$$

We must bear in mind that when:

$$t = t^1/_{2,}\, [A]t = \frac{[A]_0}{2}$$

Using these relationships in Eq. 1.29, will give:

$$\log \frac{[A]_0}{[A]_0/2} = \frac{kt_{½}}{2.303} \qquad \ldots(1.30)$$

I.e. $$\log 2 = \frac{kt_{½}}{2.303}$$

or $$t_{½} = \frac{2.303 \log 2}{k} = \frac{0.693}{k} \qquad \ldots(1.31)$$

From Eq. 1.31; we understand that t½ does not depend on initial concentration of the substance in the case of a first order reaction. This means that for a given first order reaction, half-life period is the same, whatever be the initial concentration; this leads to an interesting result that the time taken for the changes in the concentrations of the reactant such as,

$$[A]_0 \rightarrow \frac{[A]_0}{2}$$

or $[A]_0/2 \rightarrow [A]_0/4$

or $[A]_0/4 \rightarrow [A]_0/8$

is the same. The half-life periods required to bring about decrease in concentration of a reactant up to 12.5% of its initial concentration can be represented as in Figure 1.6.

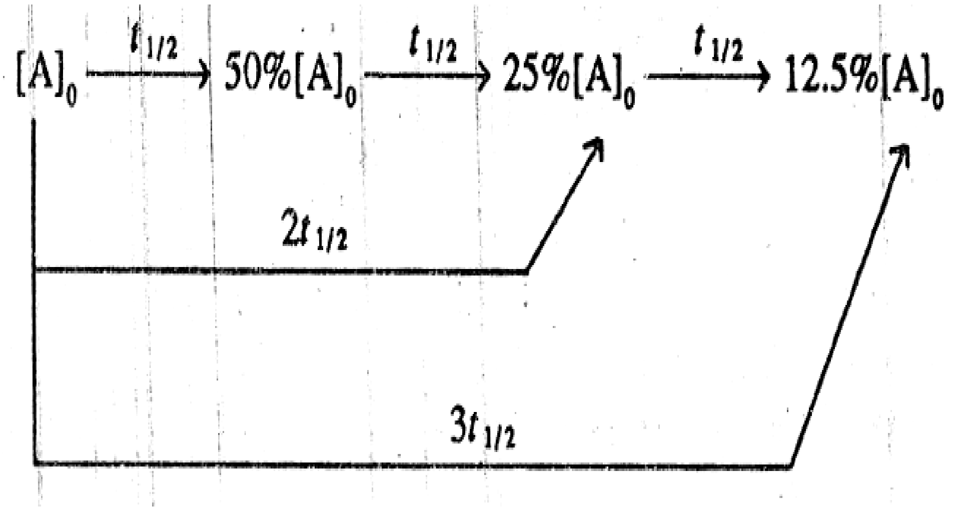

Fig. 1.6: Change in % [A]o over the first three half-life periods of a first order reaction) *t ½ is* the half-life period for the conversion, [A]o →50% [A]o.

Example 6

The first-order rate constant for the decomposition of N_2O_5 at 340K is $5.20 \times 10^{-3}\ s^{-1}$. Calculate the time required for the concentration of N_2O_5 to fall to (a) one-half and (b) one-fourth of its initial value.

Solution

a) Using Eq. 1.30, $t_{½} = \frac{0.693}{k}$

$$= \frac{0.693}{5.20 \times 10^{-3}\ s^{-1}}$$

$= 133s$

Hence, time taken for the concentration of N_20_5 to decrease by 50% is 133 s.

b) The time required for the decrease in the concentration of N_2O_5 to 25% of its initial value is twice the half-life period, i.e., 266 s.

Having studied the equations useful in calculating the first order rate constant half-life period of the reactant, let us derive similar equations for second order reactions.

3.4 Integrated Rate Laws for Second Order Reactions

There are two types of second order reactions:

i) A single reactant could give rise to products through a second order reaction.

$$A \rightarrow \text{Products} \qquad \ldots(1.32)$$

The rate equation is

$$\text{rate} = \frac{-d[A]}{dt} = k[A]^2 \qquad \ldots(1.33)$$

Where *k* is the second order rate constant.

Two examples of this type are given below:

$2NO_2\,(g) \rightarrow 2NO\,(g) + O_2\,(g)$
$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$

ii) Two different reactant molecules could react to give products through a second order reaction.

$$A + B \rightarrow \text{Products} \qquad \ldots(1.34)$$

The rate equation is given as:

$$\text{Reaction rate} = k[A][B] \qquad \ldots(1.35)$$

Examples of this type are given below. Note that the stoichiometric ratio to the reactant is 1:1.

$H_2(g) + I_2(g) \rightarrow 2\,HI(g)$

$CH_3Br\,(aq) + OH^-\,(aq) \rightarrow CH_3OH\,(aq) + Br^-\,(aq)$

$CH_3COOC_2H_5\,(aq) + OH^-\,(aq) \rightarrow CH_3COO^-\,(aq) + C_2H_5OH\,(aq)$

Again the study of these reactions could be simplified if the initial concentrations of both the reactants ($[A]_0$ and $[B]_0$) are the same, i.e..,

i.e. $[A]_0 - [B]_0$ and so $[A] = [B]$
Where $[A]$ and $-[B]$ are concentrations of the reactants at any given time, *t*
Then, Eq. 1.35 takes the same form as Eq.1.33

$$\text{Rate} = \frac{-d[A]}{dt} = k[A][B] = k[A][A] \qquad \ldots(1.36)$$

$$= k\,[A]^2$$

Thus, we could see that the rate equation takes the same form for a second order reaction, if the reaction is:

i) second order in a single reactant or
ii) first order in each of the two reactants such that the concentrations of the two are same throughout the reaction.

We use Eq.1.33 as the rate law for both these two types. We derive the integrated rate law for these two under case (i).

Case (i): Integrated rate law for a reaction that follows differential rate law with respect to Eq. 1.33.

We start with the differential rate law

$$-\frac{d[A]}{dt} = k\,[A]^2$$

The integrated form of this equation can be obtained using the following limiting conditions:

At time t = 0 (i.e., at the start), the concentration of A = [A]o. At time = t, the concentration of A = [A]t.

Applying these limits on the rearranged form of Eq. 1.33, we get:

$$-\int_{[A]_0}^{[A]_t} - \frac{d\,[A]}{[A]^2} = \int_0^t k\,dt \quad \ldots(1.37)$$

i.e.,

$$-\left(-\frac{1}{[A]}\right)_{[A]_0}^{[A]_t} = k(t-0) \quad \ldots(1.38)$$

$$-\left(\frac{1}{[A]_t} + \frac{1}{[A]_0}\right) = kt \quad \ldots(1.39)$$

$$\frac{1}{[A]_t} + \frac{1}{[A]_0} = kt \quad \ldots(1.40)$$

or

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt \quad \ldots(1.41)$$

The second order rate constant can be calculated by plotting $l/[A]_t$ against t. A straight line curve must be obtained, if the reaction is second order in the reactant. The slope of the straight line gives the second order rate constant.

k = Slope ...(1.42)

Note: Each successive half-life is double the preceding half-life in a second order reaction. In a first order reaction, all successive half-life periods are same.

3.5 Half-Life of a Second Order Reaction

For reactions following second order rate with respect to Eq. 1.33, an equation could be derived which is useful in calculating the half-life period.

At the half-life period ($t = t_{½}$), $[\ A\ ]_t\ -\ [\ A_0\ ]/2$. Using this in Eq.1.41 gives:

$$\frac{1}{[A]_0/2} = \frac{1}{[A]_0} + kt_{/2}$$

i.e., $$\frac{2}{[A]_0} = \frac{1}{[A]_0} = kt½$$

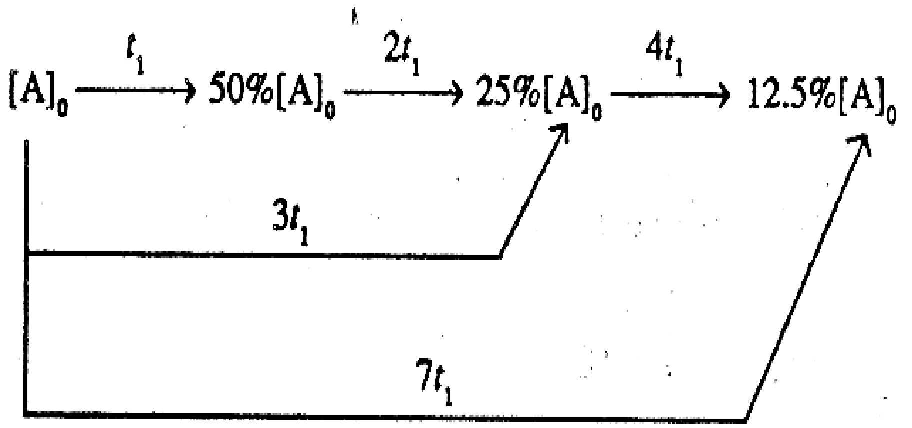

Fig. 1.7: Change in % [A]0 over three successive half-lives in a second order reaction t1 refers to half-life for the change in concentration from [A]0 to 50% [A]0 …(1.43)

$$t_{½} = \frac{1}{k\,[A]_0}$$

From Eq.1.43, we understand that $t_{½}$ is inversely proportional to initial concentration for a second order reaction. As initial concentration of the reactant decreases, $t_{½}$ increases. If for the decrease in concentration of A to 50% of its initial value, time required is 100 s, then for the change from 50% A to 25% A, it will require 200s.

Three successive half-lives for a second order reaction can be represented by Fig.1.7

Example 7

At 700K, the second order rate constant for the reaction,

$$2HI\ (g) \rightarrow H_2(g) + I_2(g)$$

is $1.83 \times 10^{-3}\ M^{-1}\ s^{-1}$. Calculate the time taken for 1.00×10^{-2} M HI to fall to

(a) one-half and (b) one-eighth of its initial concentration.

Solution

a) Using Eq. 1.42, $t_{½} = \dfrac{1}{k\,[A]_0} = \dfrac{1}{1.83 \times 10^{-3} \times 1.00 \times 10^{-2}}$

$= 5.46 \times 10^4$ s.

Time needed for the decrease in concentration of HI to one-eighth of its initial value is seven times the value calculated above as shown in Fig. 1.7; i.e. time needed is 3.82×10^5 s.

Now we derive the integrated rate law for a reaction that is second order overall and is first order in each of the two reactants having different initial concentrations.

Case (ii): Integrated rate law for a reaction that follows rate law with respect to Eq. 1.35.

Let us start the reaction between A and B with different initial concentrations,

$[A]_0$ and $[B]_0$. Let these two react to give products with respect to the rate law given in Eq.l.35
A + B → Products
Reaction rate = k[A] [B]

For simplicity, we have taken the reaction in which the stoichiometric coefficients of the reactants are same. But similar methods can be followed for reactions with different stoichiometric coefficients.

As per the reaction stoichiometry, A and B react in the ratio 1:1. After t seconds, let the concentrations of A and B be $[A]_0 - x$ and $[B]_0 - x$.

Hence, the reaction rate = $\frac{-d\,[A]}{dt} = \frac{-d\,[B]}{dt} = k\,[A][B]$

i.e. $= \frac{-d\,\{[A]o - x\}}{dt} = k\,\{[A]o - x\}\,\{[B]o - x\}$

i.e. $= \frac{-d\,\{[A]o}{dt} + \frac{dx}{dt} = k\,\{[A]o - x\}\,\{[B]o - x\}$

Therefore $\frac{dx}{dx} = k\,\{[A]_0 - x\}\{[B]o - x\}$ … (1.44)

$\frac{d\,[A]_0}{dt} = 0$ since [A] o is a constant.

In order to get the integrated form, we have to transform Eq. 1.44 as shown below:

$$\frac{dx}{\{[A]0 - x\}\{[B]0 - x\}} = k\,dt \qquad \text{…. (1.45)}$$

Let us write the expression, $\frac{1}{\{[A]0 - x\}\{[B]0 - x\}}$ as follows:

$$\frac{1}{\{[A]0 - x\}\{[B]0 - x\}} = \frac{p}{\{[A]0 - x\}} + \frac{q}{\{[B]0 - x\}} \qquad \text{….(1.46)}$$

i.e., $\frac{1}{\{[A]0 - x\}\{[B]0 - x\}} = \frac{p\,\{[B]0 - x\} + q\,\{[A]0 - x\}}{\{[A]0 - x\}\{[B]0 - x\}}$

In other words, $p\,\{[B]0 - x\} + q\,\{[A]0 - x\} = 1$ …(1.47)

Put x = [A]0, then $p\,\{[B]0 - [A]0 = 1$

or $p = \frac{1}{[B]0 - [A]0}$ … (1.48)

Hence, $p = -\frac{1}{[A]0 - [B]_0}$ … (1.49)

Put $x = [B]0$ in Eq. 1.46

Hence $q\{[A]0 - [B]0\} = 1$

or $$q = \frac{1}{[A]0 - [B]_0} \quad \ldots(1.50)$$

From Eqs. 1.46, 1.49 and 1.50

$$\frac{1}{\{[A]0 - x\}\{[B]0 - x\}} = -\frac{1}{\{[A]0 - [B]0\}\{[A]0 - x\}} + \frac{1}{\{[A]0 - [B]0\}\{[B]0 - x\}} \quad \ldots.\ (1.51)$$

We have adopted the **partial fraction procedure** in the above steps.

Using Eq. 1.51 in Eq. 1.45

$$-\frac{dx}{\{[A]0 - [B]0\}\{[A]0 - x\}} + \frac{dx}{\{[A]0 - [B]0\}\{[B]0 - x\}} = k\,dt \quad \ldots\ (1.52)$$

You can see that the two terms in the L.H.S. of Eq 1.51 contain either {[A]0 – x} or {[B0] – x} in the denominator. The splitting of the expression in L.H.S of Eq. 1.45 through partial fraction method facilitates usage of Formula.

At time = 0, $x = 0$ ("x" denotes the change in concentration of A or B due to reaction)

At time = t, $x = t$

$$\int_0^{x_t} \frac{dx}{\{[A]0 - [B]0\}\{[B]0 - x\}} \int_0^{x_t} \frac{dx}{\{[A]0 - [B]0\}\{[A]0 - x\}} = k\int_0^t dt \quad \ldots(1.53)$$

$$\frac{1}{[A]0 - [B]0}\Big(-\ln([B]\,0 - x)\Big)_0^{x_t} - \frac{1}{[A]0 - [B]0}\Big(-\ln([A]\,0 - x)\Big)_0^{x_t} = kt$$

$$\frac{-1}{[A]_0 - [B]_0}\{\ln([B]_0 - xt) - \ln[B]_0\} + \frac{1}{[A]_0 - [B]_0}\{\ln([A]_0 - xt) - \ln[A]_0\} = kt$$

$$\frac{1}{[A]_0 - [B]_0} \ln \frac{([A]_0 - xt)\,[B]_0}{([B]_0 - xt)\,[A]_0} = kt \quad \ldots(1.54)$$

$$\log \frac{([A]_0 - xt)\ [B]_0}{([B]_0 - xt)\ [A]_0} = \frac{k\{[A]_0 - [B]_0\}\,t}{2.303} \quad \ldots(1.55)$$

$$\log \frac{[A]_0 - xt}{[B]_0 - xt} = \log \frac{[A]_0}{[B]_0} + \frac{k\ ([A]_0 - [B]_0)\,t}{2.303} \quad \ldots(1.56)$$

By plotting log $\underline{[A]_0 - xt}$ against t, a straight line graph is obtained.

$[B]_0 - xt$

The slope of the straight line is equal to $k\frac{([A]_0 - [B]_0)}{2.303}$

$$k = \frac{2.303 \times \text{slope}}{([A]_0 - [B]_0)} \quad \ldots (1.57)$$

The name saponification is derived from the fact that soaps are produced by the hydrolysis of esters of long-chain fatty acids using alkalis.

Let us discuss the saponification of ester as an example for the calculation of second order rate constant. The hydrolysis of ester by an alkali is called saponification. For example, the saponification of methyl acetate can be represented by the following equation:

$CH_3COOCH_3 + OH^- \rightarrow CH_3COO^- + CH_3OH$

The saponification rate is studied as follows:

A reaction mixture is prepared with known concentrations of alkali and ester. At regular intervals, certain volume of the solution is withdrawn and titrated against standard HCl. From the titre values, the concentrations of the unreacted alkali and the unreacted ester could be determined at various time intervals.

The rate constant can be determined using,

i) Eq. 1.40 and 1.41. if the initial concentrations of ester and alkali are same;
ii) Eqs. 1.56 and 1.57, if their initial concentrations are different

Now, let us study the following example:

Example 8

The saponification of methyl acetate using sodium hydroxide was studied at 298 K. The initial concentrations of the alkali and ester in the reaction mixture were both 1.00×10^{-2} M. The reaction rate was followed by titration of a definite volume of the reaction mixture with standard HC1. The concentrations of unreacted alkali, $[A]_t$, at various time intervals are given below:

Time / s	240	550	720 '	1000 ;	1550
$10^3[A]_t$/M	6.85	4.81	4.17	3.38	2.49

Calculate the second order rate constant.

Solution

Since the initial concentrations of the alkali and the ester are same, we can use

Eqs. 1.40 and 1.41 for solving this problem. We tabulate the t values Against $[A]_t$ at various time intervals as follows:

$\frac{1}{[A]_t}$ M	146	208	240	296	402
t/s	240	550	720	1000	1550

As suggested by Eq. 1.40, 1/[A]t against t plot is a straight line (Fig. 1.8) showing that the application of methyl acetic follows second order kinetics.

Using Eq. 1.41, k = Slope

$= 0.194\ M^{-1}\ s^{-1}$

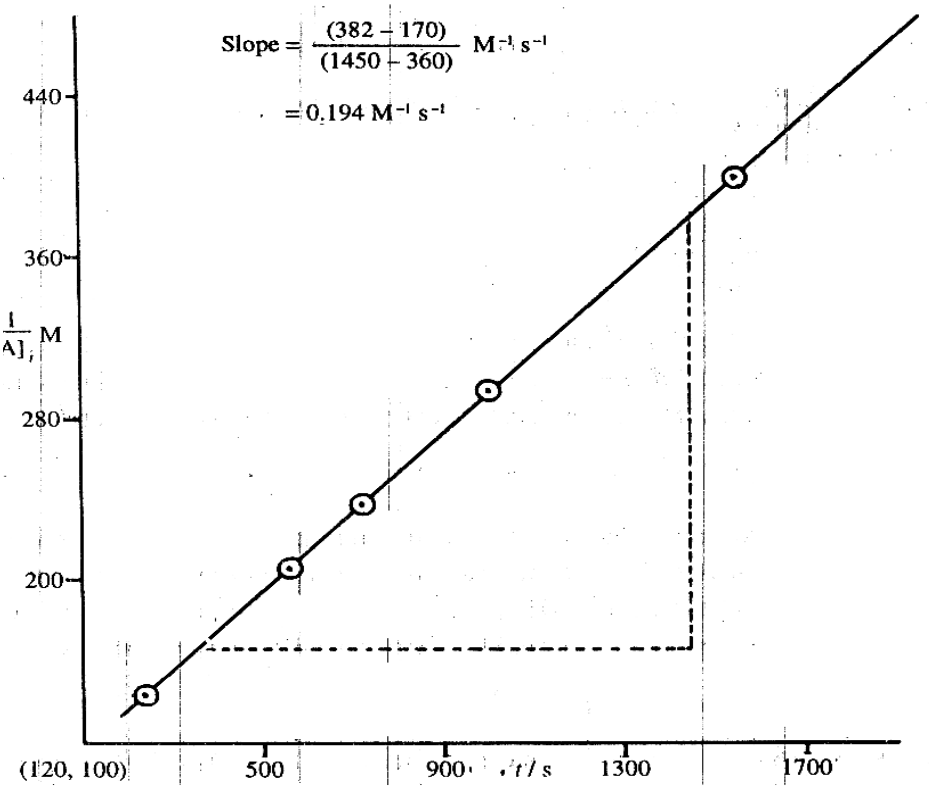

Fig. 1.8: **$1/[A]_t$ against *t* Plot for the Saponification of Methyl acetate**

Since we have some experiences of the differential and the integrated forms of rate laws for first order and second order reactions, we shall discuss zeroth order reactions in the next section. Also, we shall give some examples of third order reactions.

4.0 CONCLUSION

The curve for a first-order reaction is always a curve of a special type. It is an exponential. The equation for the line is always of the form:
$[A]t = [A]_0 e^{-kt}$

Where $[A]t$ is the concentration at a time t and $[A]_{0,}$ the starting concentration.
The graphs of concentration against time for a second order reaction are also curves. However, they are not exponentials, and do not have a constant half-life.

5.0 SUMMARY

In this unit, we have examined the integrated rate law for first order reactions; the graphical method of calculating first order rate constant; the half-life of first order reactions and the integrated rate laws for second order reactions.

6.0 TUTOR-MARKED ASSIGNMENT

i. a. State the units of the rate constants for zeroth order, first order and second order reactions. The rate of reaction is measured in $M\ s^{-1}$
   b. The decomposition of HI is a second order reaction. At 700 K the rate constant for the reaction is $1.83 \times 10^{-3}\ M^{-1}\ s^{-1}$. If the initial concentration of HI is 1.00 × 10-2 M, calculate its concentration after $1.68\ ^{x}\ 105$ s.

7.0 REFERENCES/FURTHER READING

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UNIT 3 HIGHER ORDER OF REACTION

CONTENTS

1.0 INTRODUCTION

In this unit, we shall study the zeroth and third order reactions. These equations will be used in calculating the rate constants for the reactions. We shall then explain the methods of determining the order of reaction. Finally, the methods of studying fast reactions will be dealt with.

2.0 OBJECTIVES

At the end of this unit, you should be able to**:**

- derive integrated rate laws for zeroth, pseudo-first and third order reactions
- apply the integrated rate laws above for calculating rate constants
- state the methods for determining the order of reaction
- predict the nature of fast reaction.

3.0 MAIN CONTENT

3.1 Zeroth Order Reaction

It is easy to spot a zeroth order reaction because the rate stays constant even though the reactant is being used up. The rate law for a zeroth order reaction is of the following form:

$$-\frac{d[A]}{dt} = k[A]^0 = k \qquad \ldots (1.58)$$

Since $[A]^0 = 1$

Note that zeroth order reaction is generally a heterogeneous reaction.

In a zeroth reaction, the reaction rate is independent of the concentrations of the reactant.

Some examples of zeroth order reactions are given below:

i. Decomposition of ammonia on a hot platinum surface

$$2NH_3 (g) \xrightarrow{Pt} 2N_2 (g) + 3H_2 (g)$$

ii. Decomposition of nitrous oxide on a hot platinum surface

$$2N_2O (g) \xrightarrow{Pt} 2N_2 (g) + O_2 (g)$$

iii. Decomposition of hydrogen iodide on finely divided gold at 320 K

$$2HI (g) \xrightarrow{Au} H_2 (g) + I_2 (g)$$

Let us derive the integrated rate law for a zeroth order reaction.

3.1.1 Integrated Rate Law for Zeroth Order Reaction

Let us consider the zeroth order reaction:

$$A \rightarrow \text{Products}$$

Let the concentration of A at the beginning be [A]o and its concentration at the time t be $[A]_t$.

The integrated form of Eq.l.58 can be derived as follows:

$$\int_{[A]_0}^{[A]_t} -d[A] = \int_0^t k\,dt \qquad \ldots (1.59)$$

$$-\Big\{ [A] \Big\}_{[A]_0}^{[A]_t} = k(t-0)$$

$- [A]_t + [A]0 = kt$

i.e $[A]0 – [A]_t = kt$

or $[A]_t = [A]_0 – kt$ … (1.60)

On plotting $[A]_t$, against t, a straight line is obtained for a zeroth order rejection. The slope s equal to – k

K = Slope … (1.61)

Example 1

The decomposition of hydrogen iodide on gold at 323K is zeroth order reaction and the rate constant is $1.20 \times l0^{-4}$ Ms^{-1}

a) If the initial concentration of hydrogen iodide is 0.500M, calculate its concentration after 3.00×10^3s.

b) How long will it take for all of the hydrogen iodide to decompose?

Solution

(a) Using Eq. 1.60, $[A]_t = [A]_0 - kt$

$= (0.500 - (1.20 \times 10^{-4} \times 3.00 \times 10^3))$ M

$= 0.140$M

(b) If hydrogen iodide completely decomposes, then $[A\ ]_t, = 0$

or $t = \frac{[A]_0}{k} = \frac{0.500\ M}{120 \times 10^{-4}\ M\ s^{-1}}$

$= 4.17 \times 10^3$ s

Hence, the reaction will be complete after 4.17×10^3s.

3.1.2 Half-Life of a Zeroth Order Reaction

As discussed for the first and second order reactions,

$[A]_t = [A\ ]o/2$ when $t = t½$,

Hence, Eq. 1.60 becomes,

$[A]o/|2 - [A]o — kt½$

or $kt½ = [A]o/2$

$$t_{1/2} = \frac{[A]_0}{2k} \quad \ldots. (1.62)$$

This implies that the half-life of a zeroth order reaction is directly proportional to the initial concentration of the reactant.

Example 2

Calculate the half-life for the decomposition of hydrogen iodide on gold at 323K. Use the data from Example 9.

Solution

Using the data from Example 9 in Eq.1.62,

$$t_{1/2} = \frac{[A]0}{2k} = \frac{0.500\ \mathrm{M}}{2 \times 1.20 \times 10^{-4}\ \mathrm{M}^{\mathrm{s}-}1} = 2.08 \times 103$$

From Examples 1 and 2, you can understand that the zeroth order reaction is complete in two half-lives as shown in Fig. 1.9

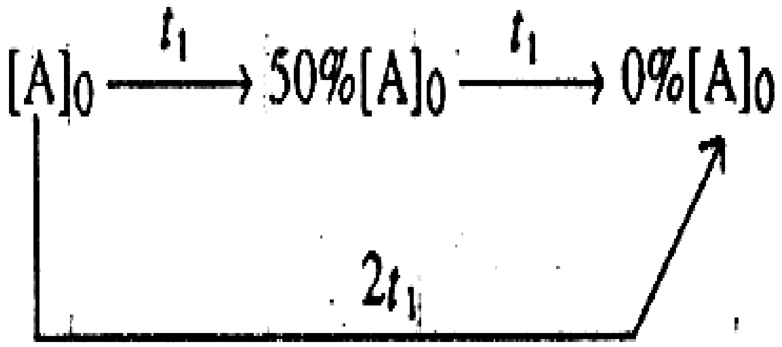

Fig. 1.9: Completion of a Zeroth Order Reaction; t1 is the time taken for both the conversions, $[A]_0$ → 50% [A]0 → 0% $[A]_0$

3.2 Third Order Reactions

There are few third order reactions; two examples are given below:

$$2NO\ (g) + O_2\ (g) \rightarrow 2NO_2\ (g)$$
$$2NO\ (g) + Br_2\ (g) \rightarrow 2NOBr\ (g)$$

The methods of arriving at differential and integrated rate laws for third order reactions are similar to those of first and second order reactions. We are not going to discuss the same.

SELF-ASSESSMENT EXERCISE

Using the data in Example 1, calculate the time required for the decomposition of HI at 323 K to proceed to 75%.

3.3 Pseudo-Flrst Order Reactions

One of the ways of simplifying the study of reactions involving more than one reactants is to study the pseudo-first order conditions. For example, considered the reaction:

$CH_3Br\ (aq) + OH^{-}\ (aq) \rightarrow CH_3OH\ (aq) + Br\ (aq)$ ….63)

Reactions rate = $k\ [CH_3Br]\ [OH^{-}]$ …. (1.64)

If the concentrations of CH_3Br and OH^{-} are comparable, then the reaction is second order overall as indicated by Eq. 1.46. Suppose that the concentration of HO^{-} is much larger (say, 10 times or more) than the concentration of CH_3Br. In such cases, the concentration of OH^{-} will not change much during the reaction and can be considered constant. Hence, the reaction rate depends on the concentration of CH_3Br only.

Reaction rate = $k'\ [CH_3Br]$

Where $k' = k[HO^{-}]$; k' is the pseudo-first order rate constant. The reaction can be treated as first order for calculation purposes. Hence, the integrated rate law is similar to Eq. 1.21

$$\log \frac{[CH3Br]0}{[CH3Br]_t} = \frac{k'\,t}{2.303}$$

In general, the reactions like the above that are effectively first order due to large excess of one of the reactions are called pseudo-first order reactions.

Let us discuss the following two reactions which are studied under pseudo-first order condition.

i) Acid Hydrolysis of Ester

The hydrolysis of ethyl acetate in presence of a mineral acid (say, HCl) can be represented by the following equation:
$CH_3COOC_2H_5 + H_2O + H_3O^{+} \rightarrow CH_3COOH + C_2H_5OH + H_3O^{+}$

The reaction rate depends on [ester], [water] and $[H_3O^{+}]$. Here H_3O^{+} ion is a catalyst. Since the concentration of the catalyst does not change during the reaction, and water is present in large amount, the reaction becomes pseudo first order in ester.

Rate = *k'* [ester]

Where *k'* includes concentration and H_3O^+. If the reaction is carried out on a solvent other than water, the first order dependence on [water] also could be seen.

The pseudo-first order rate constant is determined by titrating a definite volume of the reaction mixture containing ester to HCl with standard alkali. Let $V_{0,}$ V_t and $V\infty$ be the volumes of standard alkali at the start, after a time t and after the completion of the reaction.

Note that infinite reading ($V\infty$) is usually taken after heating the reaction mixture for a few minutes or after keeping the reaction mixture at the experimental temperature for a long time.

$V\infty$ = Volume of alkali equivalent to:

(i) Acetic acid librated after the completion of the reaction and
(ii) HCl present.

V_t = Volume of alkali equivalent to:

(i) Acetic acid and produced at the time t and
(ii) HCl present.

V_0 = Volume of alkali equivalent to volume HCl only.

Since the concentration of HCl is constant throughout the experiments,

$[A]_0$ (i.e. Initial concentration of ester)

α ($V\infty$ - V_0) and $[A]_t$ (i.e. concentration of ester remaining unreached at *t*) α ($V\infty$ - V_0)

We can calculate pseudo-first order rate constant for the acid hydrolysis of ethyl acetate by using the following modified form of Eq. 1.21.

$$\frac{k' t}{2.303} = \log \frac{[A]0}{[A]_t} = \log \frac{V\infty - V0}{V\infty - V0} \qquad \ldots (1.65)$$

Where k' is the pseudo first order rate constant.

ii) Inversion of Sucrose

The hydrolysis of sucrose to form glucose and fructose in the presence of mineral acid is similar to the acid hydrolysis of ester as far as the reaction kinetics is concerned.

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O + H_3O^+ \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6} + H_3O^+$$

Sucrose turns the plane-polarised light to the right, (i.e., it is dextro-rotatory). Glucose also turns the plane-polarised light to the light, while fructose turns it to the left (i.e., it is laevo-rotatory). On completion of the reaction, the reaction mixture is laevo-rotatory, since the angle of rotation is more for fructose than for glucose. To start with, the reaction mixture is dextrorotatory due to sucrose. Thus, the completion of reaction (infinite reading) is marked by the change in the sign of rotation. Due to this reason, the reaction is called inversion of sucrose.

If r_0, r_t, and r_∞ are, the angles of rotation at the beginning, after time *t;* and after completion of the reaction, then the pseudo first order rate constant (*k'*) for the inversion of sucrose is given by:

$$k' = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty} \qquad (1.66)$$

Eq. 18.66 is a modified form of Eq. 18.21, where [A]o is proportional to $(r_0 - r_\infty)$ and $[A]_t$ and is proportional to $(r_0 - r_\infty)$.

3.4 Determining the Order of Reaction

In order to write the rate law, we must know the order of reaction with respect to each reactant. In this section, we shall discuss some methods for determining the order of reaction.

1) Method of Initial Rates

The instantaneous rate of reaction extrapolated to the instant when the reagents were just mixed is called the initial rate of the reaction. Let us consider the reaction

$$A + B \rightarrow \text{Products}$$

Let the rate of reaction be represented as:

$$v = k\,[A]^m\,[B]^n$$

Where the reaction is m^{th} order in A and n^{th} order in B. The rate constant for the reaction is *k*. We have to obtain the initial rates from at least two experiments in which the initial concentrations of A (a_1 and a_2) are different while the initial concentration of B (b_1,) is constant

Rate in Experiment I $= k a_1^m b_1^n$

Rate in Experiment II $v_2 = k a_2^m b_1^n$

From the ratio $v_1 \div v_2$, we can calculate m, since a_1 and a_2 are known.

$$\frac{\text{Rate in Experiment I}}{\text{Rate in Experiment II}} = \frac{v_1}{v_2} = \frac{k a_1^m b_1^n}{k a_2^m b_1^n} = \left(\frac{a_1}{a_2}\right)^m \quad \text{... (1.67)}$$

Taking logarithms we can write,

$$\log \frac{v_1}{v_2} = m \log \frac{a_1}{a_2} \quad \text{...(1.68)}$$

Extrapolation is the process of extending a curve up to a desired *x* or *y* coordinate to obtain the corresponding y or *x* value.

Initial reaction rate could be graphically arrived at by plotting the concentration of a reactant against time. The tangent to the concentration curve is drawn at the very start of the reaction and its slope is calculated. The negative of the slope value is the initial rate.

Similarly, the rate is measured for one more experiment in which the initial concentration of A is a_2 and the initial concentration of B is b_2.

So rate in experiment III $v3 = k\, a_2^m b_2^n$

$$\frac{\text{Rate in experiment I}}{\text{Rate in experiment II}} = \frac{v_2}{v_2} = \frac{k a_2^m b_1^n}{k a_2^m b_2^n} = \left(\frac{b_1}{b_2}\right)^n \quad \text{...(1.69)}$$

$$\log \frac{v_2}{v_3} = m \log \frac{b_1}{b_2}$$

Since v_2, v_3 b_1 and b_2 are known, *n* can be calculated. The overall reaction order = *m* + *n*. You can understand this method from the following example.

Example 3

For the reaction $Cl_2\,(g) + 2NO\,(g) \longrightarrow 2NOCl\,(g)$

The initial concentration $[Cl_2]_0$ and $[NO]_0$ are given along with initial rates.

$$\text{Rate} = \frac{-d[Cl_2]}{dt}$$

$[Cl_2]_0$/M	$[NO]_0$/M	Initial rate/Ms^{-1}
0.10	0.10	3.0×10^{-3}
0.20	0.10	6.0×10^{-3}
0.20	0.20	2.4×10^{-2}

Calculate (i) order of the reaction with respect to each of the reactants and the overall order: (ii) what is the rate law? (iii) calculate the rate constant.

Solution

i) We can write the rate law as, $k\,[Cl_2]^m\,[NO]^{n.}$

Similar to Eq. 1.68 and 1.70, we can write the logarithm ratios and, calculate *m* and *n* as follows:

$$v_1 = k\,(0.10)^m\,(0.10)^n = 3.0 \times 10^{-3}\ \text{M s}^{-1}$$

$$v_2 = k\,(0.20)^m\,(0.10)^n = 6.0 \times 10^{-3}\ \text{M s}^{-1}$$

$$v_3 = k\,(0.20)^m\,(0.20)^n = 2.4 \times 10^{-2}\ \text{M s}^{-1}$$

Using Eq. 1.68,
$$m = \frac{\log \dfrac{3.0 \times 10^{-3}}{6.0 \times 10^{-3}}}{\log \dfrac{0.10}{0.20}} = \frac{\log \dfrac{6.0}{3.0}}{\log \dfrac{0.20}{0.10}} = 1$$

Using Eq. 1.70,
$$n = \frac{\log \dfrac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}}}{\log \dfrac{0.10}{0.20}} = \frac{\log \dfrac{2.4}{6.0}}{\log \dfrac{0.20}{0.10}} = 1$$

Hence, the reaction is second order in NO and first order in Cl_2. The overall order is
2 + 1 = 3.

ii) The rate law is given below:

$$\text{Rate} = k\,[Cl_2]\,[NO]^2$$

$[A]_0/10^{-2}$ M	5.00	4.00
t ½ /s	240	300

Calculate the order of reaction.

3.5 Fast Reactions

Many reactions are of fast that ordinary experimental methods mentioned in section 1.3 are inadequate to make measurement of reaction rates or the rate constants. Such reactions are called fast reactions and the half-life periods of fast reactions are less than 10^{-2}s. Some of the special techniques used for measuring the constants of fast reactions are:

- flash photolysis
- flow methods, and
- relaxation methods.

Of the above three, we will discuss the first method in CHE 411. Now we consider the principles of the other two methods.

3.5.1 Flow Methods

Two techniques are available under flow method. In continuous flow method (Fig. 1.10 the reacting solutions or gases are taken in separate containers (A and B) and are allowed to flow through the mixing chamber (C) into an observation tube (D). At various points along the observation tube, the composition of the mixture is determined by some physical methods.

iii) The rate constant can be calculated using any one of the three rates given above.

$$v_1 = 3\,.0 \times 10^{-3}\ \text{M s}^{-1} = k\,(0.10\text{M})\,(0.10\ \text{M})^2$$

$$k = \frac{3.0 \times 1^{-3}}{(0.10)^3}\ \text{M}^{-2}\ \text{s}^{-1} = 3.0\ \text{M}^{-2}\ \text{s}^{-1}$$

Care must be taken in applying the method of initial rates. For complex reactions like the formation of HBr (discussed in the next section), the product also affects the rate. The method of initial rates is applicable to simple reactions only.

1. Clock Reactions

In the ease of some reactions, the time taken for the colour change of the reaction mixture can be used for measuring the initial rate. Such self-indicating reactions are known as clock reactions. For example, the kinetics of the following reaction can be monitored as a clock reaction. A reaction mixture is prepared using potassium perdisulphate and potassium iodide in a higher concentration and sodium thiosulphate in much lower concentration. A qroup of (starch is also present in the reaction mixture. The reaction mixture colourless in the beginning and it turns blue after some time.

$$2KI + K_2S_2O_8 \rightarrow 2K_2SO_4 + I_2$$

Potassium
perdisulphate

The time, Δ_t, between the mixing of me reactants and the appearance of blue colour noted. The blue colour develops due to the liberation of free iodine, after sodium thiosulphate (present in less concentration) is consumed completely as per the reaction:

$$2\ Na_2S_2O_0 + I_2 \rightarrow 2NaI + Na_2S_4O_6$$

Sodium
tetrathionate

The order of the reaction with respect to KI (m) and the order of the reaction with respect to $K_2S_2O_8$ (n) can be calculated by using the following formula:

$$\log (1/\Delta t) = m \log [KI] + n \log [K_2S_2O_8] + \text{constant}$$

A plot of log $(1/\Delta t)$ against log [KI] is made using Δt values obtained by varying [KI] and keeping $[K_2S_2O_8]$ constant. The slope of the straight line gives m. Similarly n is obtained from the slope of the straight line got by plotting log $(1/\Delta t)$ against $[K_2S_2O_8]$. For the second plot, Δt is obtained by varying $[K_2S_2O_8]$ and keeping [KI] constant.

Experimentally it has been found that m = 1 and n = 1

$$\text{Hence, } -d[K_2S_2O_8] = k\ [KI]\ [K_2S_2O_8]$$

For clock reactions, two more examples are given below:

1) Acid catalysed iodination of acetone
2) Saponification of ester (using phenolphthalein indicator).

Some methods of studying fast reactions will be discussed in Sec. 1.72.

2) Trial and Error Method

We can determine the order of reaction:

i) By substituting the experimental data into Eqs. 1.21, 1.40 and 1.60
ii) By graphical method using plots such as log [A] against *t*, 1/[A] against *t* and [A] against *t*. The order of the reaction is one, two or zero depending on
i) Which of the equations gives rise to a constant value for *k* or

ii) Which of the plots gives a straight line.

3) Half-Life Method

The half-lives are determined using different initial concentrations of; the reactant. If the half-life is independent of initial concentration, the reaction is first order. If the half-life is inversely proportional to the power of initial concentration, the reaction is second order. If the half-life is directly proportional to the first power of initial concentration, the reaction is zeroth order.

In general, half-life period (t) is proportional to $[A]_0^{1-n}$ where $[A]_0$ is the initial concentration of the reactant and n is the order of the reaction.

If the half-life periods ate t_1 and t_2 corresponding to the initial concentrations

$[A]_1$ and $[A]_2$ of a reactant, then

$$\frac{t_2}{t_1} = \left(\frac{[A]_2}{[A]_1}\right)^{1-n} = \left(\frac{[A]_1}{[A]_2}\right)^{n-1}$$

$$n - 1 = \frac{\log t_2/t_1}{\log [A]_1/[A]_2}$$

$$n = 1 + \frac{\log t_2/t_1}{\log [A]_1/[A]_2} \quad \ldots(1.71)$$

Example 4

For the decomposition of acetaldehyde in gas-phase at 791 K, the half-life periods are 328 s and 572 s corresponding to the initial concentration 9.72×10^{-3} M and 4.56×10^{-3} M.

Solution

Using Eq. 1.71

$$n = 1 + \frac{\log 572/328}{\log 9.72 \times 10^{-3}/4.56 \times 10^{-3}} = 1 + \frac{0.2415}{0.3287} = 1.735$$

The order of the reaction is 1.735. Note that the order of the reaction is fractional.

4. Isolation Method

In the case of reaction having more than one reactant, the rate law can be simplified if the concentrations of all reactants except one are taken in excess. The reaction rate then depends on the reactant present in lesser quantity. The order of the reaction is determined by one of the methods given above. It is equal to the order in the reactant present in lesser quantity. This procedure is repeated in turn with each of the reactants being in lesser amount while others are in excess. The procedure is called *Vant Hoff's isolation method*.

For example, consider the reaction,

$$A + B \rightarrow \text{Products}$$

For which the rate law is,

$$\text{Rate} = k\,[A]^m\,[B]^n \qquad \ldots (1.72)$$

In the first set of experiments B is in excess as compared to A, such that the rate depends on A only.

Hence, the rate – $k_1[A]^m$ … (1.73)

Where $k_1 = k$ (Initial concentration of B)^n … (1.74)

Since B is in excess as compared to A, the concentration of B almost remains a constant throughout the experiment. From the rate the measurements, *m* can be found out using graphical method.

In the second set of experiments, [A] is much large as compared to [B]. The rate measurements are made and using the rate law stated below, *n* is calculated.

$$\text{Rate} = k_2[B]^n \quad . . .(1.75)$$

where $k_2 = k$ (Initial concentration of A]^m . . . (176)

The overall order of the reaction is $m + n$.

SELF-ASSESSMENT EXERCISE

For the alkaline hydrolysis of ethyl nitrobenzoate, the half-life periods and the initial concentrations are given below:

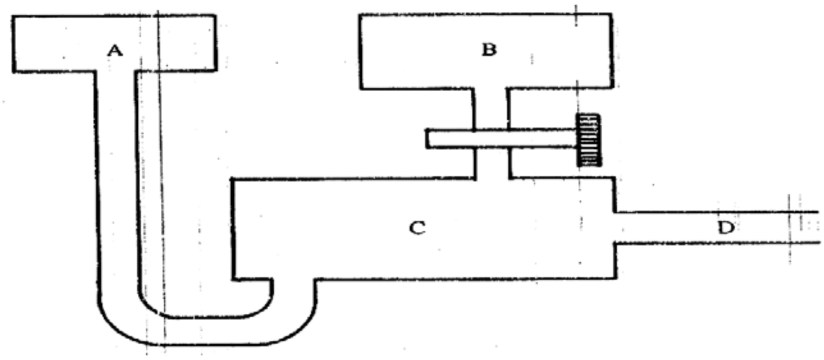

Fig. 1.10: Apparatus for Continuous Flow Method

Using this method, reactions which get completed within 10^{-3} s can be studied. But this method requires a large volume of the reactants. In order to study the reaction rates using small volumes of samples, a refined method is used which is known as stopped flow method. The reacting solutions are forced through jets into a mixing chamber where mixing occurs very rapidly (within 10^{-3} s.) The solution passes at once into the reaction vessel from the mixing chamber. The flow is then stopped and measurements are made using suitable physical methods. This method is widely used for the study of enzymes kinetics.

3.5.2 Relaxation Method

For studying reactions, which are complete within 10^{-5} s or even less, one of the problems encountered is that the time of mixing the reactants should be much smaller than the time taken for the completion of the reaction. To avoid this problem, relaxation methods have been developed. In a relaxation method, we disturb a reaction at equilibrium using an external influence such as sudden variation of pressure or, temperature (known as pressure jump or temperature jump). The system is said to be perturbed from its equilibrium position.

The perturbed system then returns to a new equilibrium position. Relaxation refers to the passage of a perturbed system to the new equilibrium. The concentration of the perturbed system is recorded at various time intervals, using suitable physical methods. From these measurements, it is possible to measure the rate constants.

4.0 CONCLUSION

Zeroth order reaction is a heterogeneous reaction and the reaction rate is independent of the concentrations of the reactant. The integrated rate law for zeroth order reaction is given as $[A]_t = [A]_0 - kt$. There are few third order reactions and the methods of arriving at differential and integrated rate laws for third order reactions are similar to those of first and second order reactions.

5.0 SUMMARY

We derived the integrated forms of rate expressions for third order and zeroth order reactions. We defined and illustrated the pseudo first order reactions. We explained the methods of determination of order of reaction.

Finally, we gave an outline of the methods of studying fast reactions.

6.0 TUTOR-MARKED ASSIGNMENT

Give the details of the graphical method of obtaining the pseudo-first order rate constant for

i. acid hydrolysis bf ethyl acetate
ii. inversion of sucrose.

7.0 REFERENCES/FURTHER READING

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APPENDIX I

Use of Eq. 2.66 in Calculating Total Collision Frequency

To understand the derivation of Eq. 2.79 for the total collision frequency among the molecules of two gases, X and Y, it is better to recapitulate the derivation of Eq, 2.52 given in Sec. 2.11 of Unit 2. Using a different procedure, Eq. 2.52 was derived for calculating the total collision frequency among the molecules of a Single gas.

Eq. 2.66 can be used for deriving the total collision frequency among the molecules of a single or two different gases. Now, let us see how Eq. 2.66 could be used to derive the total collision frequency among the molecules of a single gas.

Collision diameter of a single gas = σ

$$\left\{\begin{array}{l}\text{The reduced mass of a system}\\\text{of two molecules of the same}\\\text{gas which undergo collision}\end{array}\right\} = \mu = \frac{m^2}{2m} = \frac{m}{2}$$

Mass of each molecule (m) *is* same and $m_x = m_Y, = m$ in Eq. 2.70

Mass of one molecule of a gas (m)

$$= \frac{\text{Molar mass } (M_m)}{\text{Avogadro constant } (N_A)}$$

And $k_b N_A = R$

Note that while dealing with relative motion of molecules, we must use reduced mass of a system of two molecules put not the mass of a molecule. Using the μ value given above in Eq. 2.68

average relative speed of two molecules of a gas

$$= \left(\frac{8k_b T}{\pi m/2}\right)^{1/2} = 2^{1/2}\left(\frac{8k_b T}{\pi m}\right)^{1/2} = 2^{1/2}\left(\frac{8k_bTN_A}{\pi m N_A}\right)^{1/2} = 2^{1/2}\left(\frac{8RT}{\pi M_m}\right)^{1/2}$$

i.e., Average relative speed of two molecules of gas

$$\left(\frac{8RT}{\pi M_m}\right)^{1/2}$$

$$= 2½\, u$$

Mass of one molecule of a gas (m)
$\dfrac{\text{Molar mass (Mm)}}{\text{Avogadro constant } (N_A)}$
and $k_b\, N_A = R$

Number density of the gas = n_o

Now, let us come to the correction factor required while calculating the total collision frequency among the molecules of a single gas. Suppose there are *N* molecules in a gas with labels, 1, 2, 3, 4 ... *N*. To Calculate the total number of collisions, we use the following method:

First, imaging that molecule 1 is colliding with each of the molecules 2; 3, 4....... *N* and count the number of collisions

Then, assume that molecule 2 is colliding with each of the molecules, l, 3, 4 ... N and count the number of collisions

Continue the above procedure till the Nth molecule colliding with each of the molecules, 1, 2, 3 ... (N - l) and count the number of collisions in each case.

Add the number of collisions obtained in each case. In this procedure, each collision would have been counted twice. For example the collision between molecules 1 and 2 is counted twice as if, molecule 1 is colliding with molecule 2 and, molecule 2 is colliding with molecule 1. Hence the correction factor, 1*/2,* must be included in Eq. 2.68 while calculating the total collision frequency among the molecules of a gas, so that each collision is counted only once;

i.e., correction factor = 1/2

Substituting the various factors in Eq. 2.66

$$\left\{\begin{matrix}\text{Total collision frequency}\\ \text{among the molecules of a gas}\\ \text{(denoted as } Z_{11} \text{ in Sec. 2.11)}\end{matrix}\right\} = \pi\sigma^2 \,.\, 2½\,^{-}.\, u \,.\, n_0 \,.\, n_0 \,.\, ½$$

$$= \frac{1}{\sqrt{2}}\ \pi\, \sigma 2\, \overset{2}{u}\, n_0$$

While calculating the total collision frequency among the molecules of two different gases such as X and Y discussed in this section, there is no necessity for the corrector factor. We add up the number of collisions that each molecule of X will make with each molecules of Y as follows: Let the molecules of gas X have labels,

X_1, X_2 X_3 ….. X_N

Let the molecules of gas Y have labels,

Y_1, Y_2 Y_3 …..Y_N

Count the number *of* collisions as indicated below:

Let the molecule X_1 collide with each of the molecules, Y_1, Y_2 Y_3 …..Y_N and count the number of collisions.

Repeat the process and count the number of collisions that X_2 makes with Y_1, Y_2 Y_3 …..Y_N. Continue the process and calculate the number of collisions up to the molecule XN colliding with each of the molecules, Y_1, Y_2 Y_3 …..Y_N

Add the number of collision us in each case.

In this process, each collision between a molecule of X and a molecule of Y is counted once only. Hence there is no necessity for correction factor while calculating the total collision frequency among the molecules of different gases. In this case we have not **counted**

i) the collision **among** the molecules of X only or
ii) the collisions **among** the molecules of Y only.

MODULE 2 SOME REACTIONS MECHANISMS

UNIT 1 MECHANISM OF SIMPLE REACTIONS

CONTENTS

1.0 INTRODUCTION

Chemical kinetics is the study of rates and mechanisms of chemical reactions. The rate of a reaction depends on many factors such as the concentration of the reactants, temperature, catalysts, etc. We shall discuss the mechanism of simple reactions and also illustrate the significance of rate determining step in explaining the rate law. We shall study the effect of temperature on reaction rates and state the theories of reaction rates.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define elementary reaction and molecularity
- propose mechanisms for simple reactions using the experimental rate law.

3.0 MAIN CONTENT

3.1 Some Reaction Mechanisms

Many chemical reactions take place through a series of steps. Each step is known as an **elementary reaction.** A **reaction mechanism** is a series of elementary reactions proposed for explaining the rate law for the overall reaction. The elementary reactions are written as chemical equations. Such chemical equations give a possible explanation for the reaction path.

For an elementary reaction, the molecularity is the same as the order of reaction.

The rate law for each elementary reaction can be written using **molecularity**. The molecularity is the number of reactant molecules or atoms in an elementary reaction. If there is only one reactant molecule (or atom) in an elementary reaction, the reaction is said to be unimolecular. An elementary reaction in which two molecules (or atoms) react together is bimolecular reaction. Most reaction mechanisms consider mainly unimolecular and bimolecular reactions. The chance of termolecular reactions (where three species are to combine) occurring is much less, because the probability of three species colliding simultaneously is quite low. An example each for unimolecuar and bimolecular reactions is given below.

Unimolecular Reaction

$$O_3(g) \rightarrow O_2(g) + O(g) \qquad \ldots (2.1)$$

A unimolecular reaction has a first order rate law; hence the rate of decomposition of O_3 could be represented as follows;

$$\text{Rate} = k\,[\,O_3\,] \qquad \ldots(2.2)$$

Bimolecular Reaction

$$2O_3\,(g) \rightarrow O_2\,(g) + 2O_2\,(g) \qquad \ldots(2.3)$$

A bimolecular reaction has an overall second order rate law, being first order in each reactant. Hence, for the elementary reaction given in Eq. 1.79, rate can be expressed as follows:

$$\text{Rate} = k\,[\,O\,]\,[\,O_3\,] \qquad \ldots(2.4)$$

Some of the guidelines followed in suggesting reaction mechanisms are given below:

1) The elementary reactions when added must be equal to the coverall balanced chemical equation for the reaction.

For example, the overall reaction in the decomposition of O_3 in the upper atmosphere is,

$$2O_3\,(g) \rightarrow 3O_2(g) \quad \ldots(2.5)$$

This reaction could be taken as the result of the following two elementary reactions:

Step (i): $O_3(g) \rightarrow O_2\,(g) + O\,(g)$ …(2.1)

Step (ii): $O_3\,(g) + O\,(g) \rightarrow 2O_2.\,(g)$ …(2.3)

Overall reaction: $2O_3\,(g) \rightarrow 3O_2\,(g)$ (Same as in Eq 2.5)

2) While writing such a mechanism, one possible support is proving the presence of *intermediates***.** For example, in the mechanism suggested above, atomic oxygen is an intermediate. Such intermediates can be detected by physical or chemical methods. They are generally reactive species. Further an intermediate is produced and ultimately used up.

3) The mechanism must agree with the overall rate law determined experimentally. In other words, the rate laws for the elementary reactions must be combined in such a way that the overall rate law is explained. In order to accomplish this, we must be able to decide the *rate determining step*. Out of the elementary reactions suggested, the slowest one is called the rate determining step. The overall reaction rate cannot be faster than the slowest step in a mechanism. The rate determining step decides the rate of the overall reaction.

For example, in the mechanism suggested for the decomposition of ozone,

Step ii (i.e. Eq 2.3) is possibly the rate determining step. We shall explain this shortly.

4) The possibilities of both forward and reverse reactions occurring fast must also be considered! That is, the possibility of a dynamic equilibrium must also be examined. This is one of the ways to

- find a suitable relationship for expressing the concentration of an intermediate and
- eliminate the term denoting the concentration of the intermediate from the rate expression for the overall reaction.

5) Kinetic information can only support a proposed mechanism; it should not be taken as a proof since a mechanism cannot be proved absolutely.

Only a few guidelines are given here for proposing a reaction mechanism. However, these are sufficient for studying the reaction mechanisms of simple reactions.

Studies on organic and inorganic reaction mechanisms have led to the growth of separate branches of chemistry. You are advised to take up the course on Organic Reaction Mechanisms, if you desire to study theories of organic reactions.

Now, we shall discuss the reaction mechanism involving:

- a fast equilibrium followed by a slow step
- a slow step followed by a fast step, and
- a chain reaction.

We shall also state the following types with an example in each case without discussing the reaction mechanisms.

- Consecutive reasons
- Opposing reactions
- Parallel reactions

Example 1

For the decomposition Of $O_{3,}$

$$2O_3(g) \rightarrow 3O_2\,(g) \quad \ldots..(2.5)$$

The overall rate law is given below:

$$\text{Overall rate} = k\,\frac{[O_3]^2}{[O_2]} \quad \ldots\,(2.6)$$

Suggest a possible mechanism to explain the observed rate law.

Solution

You can see that the overall rate contains the term for the concentration of oxygen which is a product. This indicates that the mechanism consists of more than one step. A possible mechanism is suggested through eqs. 2.7 and 2.3

$$\text{Step i):} \quad O_3\,(g) \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2\,(g) + O\,(g)\ (\text{fast}) \qquad \ldots (2.7)$$

$$\text{Step ii):} \quad O_3\,(g) + O\,(g) \xrightarrow{k_2} 2O_2\,(g)\ \ (\text{slow}) \qquad \ldots(2.3)$$

Note that the addition of Eq 2.3 and the forward reaction of eq. 2.7 give the overall balanced equation as per eq. 1.8l. In the mechanism suggested above, k_1 and k_{-1} are the rate constants for the forward and the reverse reactions as per Eq.1.83; k_2 is the rate constant for the reaction with respect to eq. 2.3

With respect to the mechanism suggested above,

$$\text{Overall rate} = k_2\ [O_3]\,[O] \quad \ldots(2.4)$$

Now we shall eliminate [O] in eq. 1.80. For this purpose, we shall assume the following:

Rate of formation of O = Rate of Consumption of O . . .(2.8)

i.e., $k_1\,[O_3] = k_{-1}[O_2][O] + k_2[O_3][O]$ . . .(2.9)

This assumption is valid because [O] is extremely small at any given time. Its variation with time (d[O]/dt is still small and it may be taken to be zero. This type of assumption is called steady state approximation and we shall discuss it in Section 2.3.

The above equation is written in the basis of the proposed mechanism which implies that oxygen atom is formed in the forward reaction of step (i) and is consumed in the reverse reaction of step (i) and, in step (ii). The forward and reverse reactions are as given in step (i) are much fast than the reaction as given in step (ii). In other words, $k_2\,[O_3]\,[O]$ is negligibly smaller than $k_{-1}[O]\,[O]$.

Hence Eq. 2.9 becomes,

$$k_1 [O_3] = k_{-1}[O_2] [O] \qquad \ldots(2.10)$$

or $$[O] = \frac{k_1 [O_3]}{k_{-1} [O_2]} \qquad \ldots(2.11)$$

Using Eq. 2.11 in Eq 2.4

Overall rate $= k_2[O_3][O]$

$$= \frac{k_1 k_2}{k_{-1}} \frac{[O_3][O_3]}{[O_2]} \qquad \ldots(2.12)$$

i.e., Overall rate $= k \frac{[O_3]^2}{[O_2]} \qquad \ldots(2.13)$

Where k is the composite rate constant since it combines the rate constants, k_1, k_2 and k_{-1} for the equation,

$$k = \frac{k_1 k_2}{k_{-1}} \qquad \ldots(2.14)$$

You can see that Eq. 2.13 is the same as Eq 2.6

Example 2

The rate expression for the reaction, below is given as: Overall rate = $k [NO_2]^2$

$$NO_2 (g) + CO (g) \rightarrow NO (g) + CO_2 (g)$$

Spectroscopically, NO_3 radical has been detected. Suggest a mechanism in keeping with these facts.

Solution

While suggesting the mechanism, the following facts must be borne in mind:

i) The stoichiometry for the overall reaction must be as given in Eq 2.18

ii) With respect to Eq. 2.19, the rate does not depend on [CO] but depends on $[NO_2]^2$. This implies that the reaction consists of more than one step and CO does not take part in the rate determining step.

iii) NO_3 is a probable intermediate in the reaction. Keeping in view the above features, the following mechanism is proposed:

Step i): $NO_2\,(g) + NO_2\,(g) \rightarrow NO_3\,(g) + NO\,(g)$ (slow) … (2.20)

Step ii) $NO_3\,(g) + CO\,(g) \rightarrow NO_2\,(g) + CO_2\,(g)$ (fast) … (2.21)

Overall reaction: $NO_2\,(g) + CO\,(g) \rightarrow NO\,(g) + CO_2\,(g)$

The stoichiometry is as given in Eq. 2.18. Since [CO] does not appear in the rate expression step, step (i) is assumed to be slower than step (ii). It is almost assumed that the intermediate, NO_3, is consumed at a faster rate than it is formed.

i.e., overall rate = rate of formation of NO_3

But rate of formation of NO_3 (as given in Eq. 2.20) $= k\,[NO2]^2$

Note that this is the same as Eq. 2.19

Example 3

The rate for the reaction between hydrogen and bromine is quite complex as given by Eq. 2.23

$H_2\,(g) + Br_2\,(g) \rightarrow 2HBr\,(g)$ …(2.22)

$$\frac{d\,[HBr]}{dt} = \frac{k\,[H_2]\,[Br_2]^{1/2}}{1 + \frac{k'\,[HBr]}{[Br_2]}} \qquad \text{…(2.23)}$$

Suggest a mechanism which could explain in the above rate law.

Solution

To explain the rate law, a reaction sequence is proposed as follows:

$Br_2 \xrightarrow{k_1} 2Br$ Chain initiation … (2.24)

$Br + H_2 \xrightarrow{k_2} HBr + H$ …(2.25)

$H + Br_2 \xrightarrow{k_3} HBr + Br$ Chain termination …(2.26)

$$H + HBr \xrightarrow{k_4} H_2 + Br \qquad \ldots (2.27)$$

$$2Br \xrightarrow{k_5} Br_2 \quad \text{Chain termination} \qquad \ldots (2.28)$$

The rate of reaction can be represented by Eq. 2.27 noting that HBr is formed as given in Eqs. 2.25 and 2.26 and consumed as it is in Eq. 2.27.

$$\frac{d[HBr]}{dt} = k_2 [Br][H_2] + k_3 [H] [Br_2] - k_4 [H] [HBr] \quad \ldots(2.29)$$

The negative sign preceding k_4 [H] [HBr] in Eq. 2.29 is due to the consumption of HBr is given in Eq. 2.27. The reaction sequence given above is an example of a chain reaction. In a chain reaction, an intermediate reacts to produce another intermediate. For example, Br, a radical intermediate produced as given in Eq. 2.24 reacts with H_2 to produce another radical intermediate, H. Again H reacts with Br_2 as it is in Eq. 2.26 to give Br and so on. Reaction represented by Eq. 2.24 is the *chain initiation* reaction, since it is the start of the chain reaction.

Reactions such as Eqs 2.25 - 2. 27 are known as *chain propagation* reactions. Although Eq. 2.27 represents a propagation reaction producing Br, it also results in the consumption of HBr. For the latter reason, Eq. 2.27 represents an *inhibiting reaction***.** Eq. 2.28 is a *chain terminating reaction* since the intermediates combine to give a molecule.

Note that: Often an intermediate in a chain reaction is a free radical. A free radical is an atom or a fragment of a molecule and has an unpaired electron.

TO simplify Eq. 2.29, we must express [H] and [Br] in terms of [Br2], [H2] and

[HBr]. Such a step is required since the concentrations of the intermediates are not easy to measure whereas the concentrations of the reactants and products could be measured. Such a simplification is possible assuming that the net rates of formations of intermediates are equal to zero.

i.e., $$\frac{d[Br]}{dt} = 0 \qquad \ldots (2.30)$$

and $$\frac{d[H]}{dt} = 0 \qquad \ldots(2.31)$$

With respect to the elementary reactions given above, Br is formed as given in Eqs. 2.24, 2.26 and 2.27; Br is consumed as shown in Eqs. 2.25 and 2.28. Also, two bromine atoms are consumed in Eq. 2.24 for every bromine molecule dissociated and two bromine atoms are consumed in Eq. 2.28 for every bromine molecule formed. Using these ideas and Eq. 2.26, we can write,

$$\frac{d[Br]}{dt} = 0 = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 \qquad \ldots(2.32)$$

Similarly, H is formed in Eq. 1.98 and consumed in Eqs 2.26 and 2.27. Using these ideas and Eq.2.31 we can write,

$$\frac{d[H]}{dt} = 0 = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] \qquad \ldots(2.33)$$

By adding Eq. 2.32 and 2.33, we get,

$$2k_1[Br_2] = 2k_5[Br]^2$$

$$\text{or} \qquad [Br] = \left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2} \qquad \ldots(2.34)$$

From Eq. 2.33 we can write,

$$[H] = \frac{k_2[H_2][Br]}{k_3[Br_2] + k_4[HBr]} \qquad \ldots(2.35)$$

Using Eqs. 2.34 and 2.35, we get

$$[H] = \frac{k_2\left(\frac{k_1}{k_5}\right)^{1/2}[H_2][Br_2]^{1/2}}{k_3[Br_2] + k_4[HBr]} \qquad \ldots(2.36)$$

Rearranging Eq. 2.29, gives

$$\frac{d[HBr]}{dt} = k_2[H_2][Br] + [H](k_3[Br_2] - k_4[HBr] \qquad \ldots(2.37)$$

Using Eqs. 2.34, 2.36 and 2.37, we get

$$\frac{d[HBr]}{dt} = k_2\left(\frac{k_1}{k_5}\right)^{1/2}[Br_2]^{1/2}[H_2] + \frac{(k_3[Br_2] - k_4[HBr])(k_2(k_1/k_5)^{1/2}[H_2]}{k_3[Br_2] + k_4[HBr]}$$

$$= \underline{2k_2k_3(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]} \qquad \ldots(2.38)$$

$$k_3\,[Br_2] + k_4\,[HBr]$$

Dividing the numerator and denominator of R.H.S by k_3 $[Br_2]$,

$$\frac{d\,[HBr]}{dt} = \frac{2k_2\,(k_1/k_5)^{1/2}\;[H_2]\,[Br_2]^{1/2}}{1 + \dfrac{k_4\,[HBr]}{k_3\,[Br_2]}} \qquad \ldots (2.39)$$

By comparism, you can see that Eqs. 2.23 and 2.39 are the same, where

$$k = 2k_2\left(\frac{k_1}{k_5}\right)^{1/2} \text{ and } k' = \frac{k_4}{k_3}$$

The presence of the term $[HBr]/[Br_2]$ in the denominator of Eq. 2.23 or Eq 2.39, has the following significance.

- HBr formed inhibits the rate of the reaction
- At high $[Br_2]$, the inhibition is less

Both these predictions have been verified experimentally.

In the H_2-Br_2 reaction, inhibition takes place due to the product formed. Sometimes, impurities are deliberately added to some materials to inhibit undesirable reactions. For example, food products generally get spoiled due to chain reactions involving oxidation. To preserve the food products, it is customary to use the preservatives which inhibit oxidation by removing chain-propagating radicals. Such "antioxidants" are also added to plastics and rubber to prevent their degradation.

3.2 Free-Radical Reactions

In H_2 - Br_2 reaction, H and Br atoms have unpaired elections and these are free-radicals. In 1929, Paneth and Hofeditz reported the formation of polyatomic free radicals (CH_3 radicals) by the thermal decomposition of lead tetramethyl. It was found that lead was deposited as a mirror, in the hot portion of a tube through which hydrogen gas carrying lead tetramethyl vapour was passed.

$$C_2H_6 \xrightarrow{k_1} 2CH_3$$

$$CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$$

$$C_2H_5 \xrightarrow{k_3} C_2H_4 + H$$

$$H + C_2H_6 \xrightarrow{k_4} H_2 + C_2H_5$$

$$H + C_2H_5 \xrightarrow{k_5} C_2H_6$$

The free-radicals such as CH_3 and C_2H_5 are detected by direct experimental methods or from the products they give. Experimentally obtained rate law is given by the equation.

$$\text{Rate} = k\,[C_2H_6] \qquad \dots (2.41)$$

Where k is the overall rate constant: k is the complex combination of the rate constants of the individual elementary reactions.

3.3 Consecutive Reactions

We have postulated the existence of intermediates. In many cases, the intermediate in one step is the reactant in the next. Such reactions are called consecutive reactions. The rates of consecutive reactions could be stated in terms of the concentrations of the reactants taken initially and the products formed in each stage. Example is the acid hydrolysis of diethyl adipate.

The radical intermediates can be removed by using substances like NO. Since NO molecule has an unpaired electron, it combines with a radical intermediate which also has an unpaired electron. This could result in chain termination. Here, NO molecule is called the radical scavenger and it is said to quench the chain reaction. To prove the chain mechanism, such radical scavengers are used.

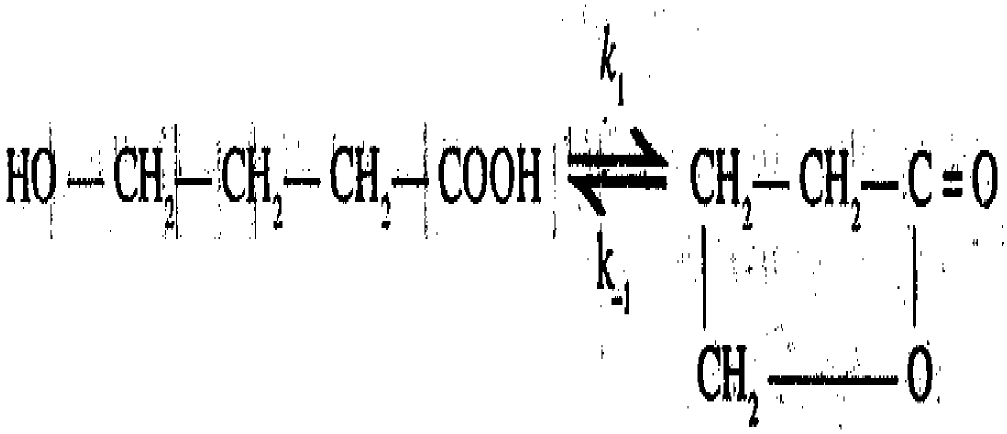
Just as we can terminate a chain reaction using radical scavengers, we can start a chain reaction using free radical sensitisers such as Pb (CH_3). or $Hg(CH_3)_2$. To increase the decomposition rate of an organic compound, $Pb(CH_3)$ or $Hg(CH_3)_2$ is added. These substances decompose, and introduce CH_3, radicals into the system. This starts the decomposition of the organic compounds through a chain reaction. $Pb(CH_3)_4$ and $Hg(CH_3)_2$ are said to sensitise the decomposition of organic compounds.

3.4 Opposing Reactions

In opposing reactions, rates of forward and reverse reactions are both appreciable. While in proposing a mechanism, both the reaction rates must be considered.

Example

Formation of butyrolactone from γ-hydroxybutyric acid goes through the process below:

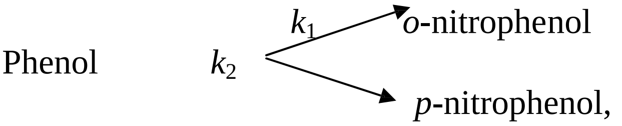


3.5 Parallel Reactions

If a reactant can undergo more than one reaction, the resulting reactions are called parallel reactions. The rates of a set of parallel reactions can be measured as the concentrations of the products formed in each case.

Example

Nitration of phenol yielding *o*-nitrophenol and *p*-nitrophenol,



In the next section, we shall explain the theory of unimolecular reaction rates.

4.0 CONCLUSION

In this unit, you have learnt about the mechanisms of simple reactions. We explained that chemical reactions take place through a series of elementary reaction. We also discussed that a reaction mechanism is a series of elementary reactions proposed for explaining the rate law for the overall reaction. The following were equally discussed in this unit:

- Free-radical reactions
- Consecutive reactions
- Opposing reaction
- Parallel reactions.

5.0 SUMMARY

The mechanism of a reaction is the explanation of how the reaction takes place. The slowest step in a reaction governs the rate of the reaction. Before changing into products, reactants form a transition state. The molecularity of a reaction is the numbers of species form the transition state.

6.0 TUTOR-MARKED ASSIGNMENT

i. A). For the following elementary reactions, write the rate laws:

  - $O_3\,(g) + NO\,(g) \rightarrow O_2\,(g) + NO_2\,(g)$
  - $CH_3NC\,(g) \rightarrow CH_3CN\,(g)$
  - $CI_2\,(g) \rightarrow 2Cl\,(g)$

B. For the reaction,
$2NO\,(g) + O_2\,(g) \rightarrow 2HO_2\,(g)$

the rate law is given below:

Rate = $k[NO]^2\,[O_2]$

Is the following mechanism consistent with the rate law?

Step i) $NO + O_2 \underset{k_2}{\overset{k_1}{\leftrightarrows}} NO_3$ both rates are fast and equal

Step ii) $NO_3 + NO \xrightarrow{k_3} 2NO_2$ Slow

Hint: Consider NO_3 as an intermediate.

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UNIT 2 THEORY OF UNIMOLECULAR REACTIONS

CONTENTS

1.0 INTRODUCTION

An elementary reaction in which only one molecule or a radical reacts is known as the unimolecular reaction. In this unit, we shall study the theory of unimolecular reactions and the general theories of reaction rates; the collision and the Arrhenius theories. Also, we shall examine the activated complex theory.

2.0 OBJECTIVES

At the end of the unit, you should be able to:

- discuss the theory of unimolecular reactions
- explain Arrhenius equation, collision theory and activated complex theory
- describe the methods of studying fast reactions.

3.0 MAIN CONTENT

3.1 Theory of Unimolecular Reactions

A unimolecular reaction is an elementary reaction in which only one molecule or a radical reacts. The unimolecular reactions follow first order kinetics. A number of gas phase reactions follow first order kinetics. These reactions are assumed to proceed through unimolecular rate-determining step. But how does the reactant molecule attain the activation energy? The activation energy is the minimum energy needed for the reactant molecules to react and yield products. If the molecules obtain their activation energy through collisions, it is difficult to explain first order kinetics. A collision process needs at least two molecules and hence, second order kinetics could be expected but not first order kinetics. In 1992, Lindemann and Hinshelwood proposed a mechanism which could explain the unimolecular reactions in which molecules attain their activation energy through collision.

Let two molecules of the reactant gas (*X*) collide yielding an activate molecule

(X^*) and a normal molecule (*X*). Such a collision is called an activating collision.

$$X + X \xrightarrow{k_a} X^* + X \qquad \ldots(2.42)$$

Rate of activation of $X = k_a [X] [X]$ …..(2.45)

The activated molecule, X^*, can undergo either of the following reactions:

i) X^* can undergo collision with another molecule *X* and lose its excess energy. Such a collision is called a deactivating collision

$$X^* + X \xrightarrow{k'_a} X + X$$

Rate of decay of X* =’k_a [X*] [X]

ii) Alternatively, of X^* can decay to yield the product, Y.

$$X^* \xrightarrow{k_b} Y \qquad \ldots(2.46)$$

Rate of decay of X^* = Rate of product formation = $\frac{d[Y]}{dt} = k_b [X^*]$(2.47)

Note that decay of X^* is a unimolecular reaction.

If the decay of X^* yielding products is the rate-determining step, then the overall rate of the reaction is given by the following expression.

$$\text{Rate} = k_b [X^*] \qquad \ldots(2.48)$$

In order to express the concentration of X^*, an active species, in terms of concentrations of reactants (or products) in the ground state, *steady-state approximation* is used. According to this procedure, it is assumed that a steady-state is reached after a reaction starts such that the concentration of the activated species is more or less a constant and does not change with time.

i.e. $$\frac{d[X^*]}{dt} = 0 \qquad \ldots(2.49)$$

According to steady-state approximation, the concentrations of all reactive intermediates are constant and small during the major part of the reaction.

This means that the activated species, X^*, is consumed as soon as it is formed. Since X^* is formed and consumed (Eqs. 2.44 and 2.46),

$$\frac{d[X^*]}{dt} = 0 = k_a[X]^2 - k_4[X][X^*] - k_b[X^*] \qquad \ldots(2.50)$$

i.e., $$[X^*](k'_a[X] + k_b) = k_a[X]^2$$

or $$[X^*] = \frac{k_a[X]^2}{(k'_a[X] + k_b)} \qquad \ldots(2.51)$$

Using Eqs. 2.48 and 2.51

$$\text{Rate} = \frac{k_a k_b [X]^2}{(k'_a[X] + k_b)} \qquad \ldots(2.52)$$

From p = cRT *or* p α c. Hence, when the pressure of a gas is high, its concentration is high and consequently, there will be large number of collisions.

A. At High Pressures

At high pressures, the number of collisions is large and the probability of deactivating collisions occurring is high that is' the rate of deactivation is larger than the rate of product formation (through decay); the unimolecular decay of X^* is the rate-determining step at high pressures; i.e.

Eq. Such as 2.54 or 2.37 are instances of limiting conditions. Using such approximation procedure, it is possible to simplify a complicated equation as Eq. 2.52.

$k'_a [X^*] [X] >> k_b [X^*]$

or $k'_a [X] >> k_b$ …(2.53)

In other words, $k'_a [X] + k_b \simeq k'_a [X]$ …(2.54)

Using this in Eq. 2.52, we get

$$\text{Rate} = \frac{k_a k_b [X]^2}{k'_a [X]} = \frac{k_a k_b}{'k_a} [X] \qquad \ldots(2.55)$$

This implies that the rate is first order at high pressures.

B. At Low Pressures

At low pressures, the number of collisions decreases. This means that the activated molecule yields the product as soon it is formed and there is not much time left for deactivating collision to occur. In other words, the bimolecular formation of X^* is the rate-determining step. Furthermore, the rate of deactivating collisions is much small as compared to the rate of product formation.

$k_b [X^*] >> k'_a [X^*] [X]$

or $k_b >> k'_a [X]$ …(2.56)

or $k'_a [X] + k_b \simeq k_b$ …(2.57)

Using this in Eqs.2.55,

$$\text{Rate} = \frac{k_a k_b [X]^2}{k_b} = k_a [X]^2 \qquad \ldots(2.58)$$

Hence the reaction follows second order kinetics at low pressures.

Using this Lindemann -Hinshelwood theory, we could explain the unimolecular decomposition of N_2O_5 at high pressures.

3.2 Theories of Reaction Rates

The rates of many reactions increase with the rise in temperature. Arrhenius proposed the following empirical relationship between the rate constant, *k*, and temperature, *T*.

$\ln k = \ln A - E_a/RT$ …(2.59)

or $\log k = \log A - E_a/2.303RT$ …(2.60)

Where A is called the Arrhenius factor or frequency factor or pre-exponential factor and E_a is the activation energy. *Activation energy is the threshold energy that the reactant molecules must have in order to react.* If log k is plotted against 1, a straight line (Fig. 2.1) is obtained for many reactions. In such cases, the *T* slope of the line is – Ea/2.303R and the intercept as 1 = 0 gives log A.

T

Eqs. 2.59 is also written in the exponential form as follows:

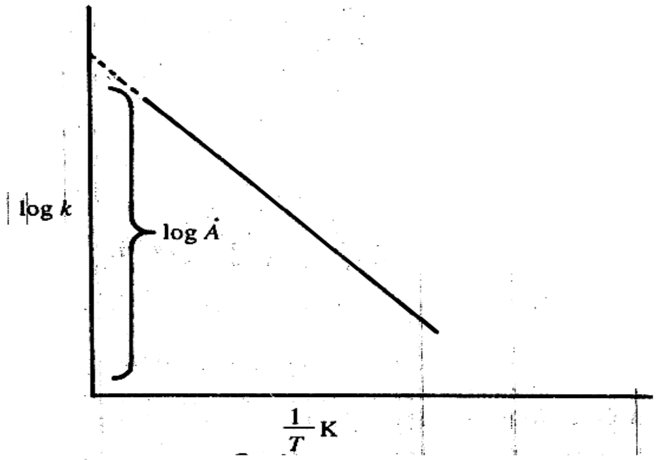

Fig. 2.1: Plot of log k against $\frac{1}{T}$

$$\mathbf{k = A\,e^{-Ea/RT}} \quad ...(2.61)$$

A possible reason for the deviation from Arrhenius equation in some reactions is that *A* and E_a may vary with temperature. The temperature dependence of Arrhenius factor will be discussed in collision theory. In the present discussion, we consider that A and E_a are constant for a reaction. If the activation energy is high for a reaction, it means that the temperature dependence of the reaction rate is also high. In such cases, even a small change of temperature results in a large change in the rate constant.

Although activation energy of a reaction can be calculated Wm log *k* vs l/*T* plot, another way of obtaining it is to calculate rate constants (k_1 and k_2) at two temperatures (T_1 and T_2). Assuming E_a *and A* to be constant and using Eq. 2.60, we get.

$$\log k_1 = \log A - E_a/2.303RT_1 \quad ...(2.62)$$

and $$\log k_2 = \log A - E_a/2.303\,RT_2 \quad ...(2.63)$$

Subtracting the terms in Eq. 2.63 from those in Eq. 2.62,

$$\log \frac{k_2}{k_1} = \frac{-E_a}{2.303R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$= \frac{-E_a}{2.303R}\,\frac{(T_2 - T_2)}{T_1\,T_2}$$

$$\text{i.e.,}\quad \log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\,\frac{(T_2 - T_1)}{T_1\,T_2} \qquad \ldots(2.64)$$

Note that the unit of *A* depends on the unit of *k*. For first order reactions, *A* has s^{-1} unit which is the same as the unit for frequency. This could be a reason for its name, frequency factor. *A* is also called the pre-exponential factor since it precedes the exponential term in Eq. 2.61

Let us work out an example.

Example 4

The rate constants for the decomposition of SO_2C1_2 are $1.01 \times 10^{-6}\ s^{-1}$ at 552 K and $3.85 \times 10^{-5}\ s^{-1}$ at 600K. Calculate the activation energy and the frequency factor; assuming them to be independent of temperature.

Solution

From Eq. 2.64,

$$E_a = 2.303\ \frac{RT_1T_2}{(T_2 - T_1)} \log \frac{k_2}{k_1}$$

$$E_a = \left(\frac{2.303 \times 8.314 \times 552 \times 600}{48} \log \frac{3.85 \times 10^{-5}}{1.01 \times 10^{-6}}\right) \text{J mol}^{-1}$$

Substituting for *T* = 600 K, E_a - 2.09 ×I0^5 J mol^{-1} and $k = 3.85 \times 10^{-5}\ s^{-1}$ in
Eq. 2.60 gives, $\log A = \log k + Ea/2.303RT$

$$= -4.4145 + \frac{2.09 \times 10^5}{2.303 \times 8.314 \times 600}$$

$$\log A = -4.4145 + 18.1924 = 13.7779$$

A = Antilog of 13.7779

$A = 6.00 \times 10^{13}\ s^{-1}$

We can understand the significance of the terms, E_a, *A* and $e^{-Ea/RT}$ during the discussion on collision theory of reaction rates.

3.3 Collision Theory

Collision theory is applicable to bimolecular reactions in gas phase. With some modifications, this can be applied to unimolecular (see Sec. 18.9) and termolecular reactions also. We explain collision theory using a gas-phase bimolecular elementary reaction of the following.

$$X + Y \rightarrow \text{Product} \quad \ldots(2.65)$$

With respect to collision theory, the rate of a bimolecular reaction depends on:

- The total collision frequency and
- Boltzmann factor.

Although the stearic factor is also to be considered while calculating the reaction rate, it will be treated under the refinement of collision theory.

To understand the significance of Eq. 2.26, see Appendix I.

Average speed of a gas molecule (u) $= \left\{\frac{8RT}{\pi m}\right\}^{1/2}$

Hence average relative speed of the molecules of X and Y $= \left\{\frac{8k_bT}{\pi m}\right\}^{1/2}$

Since R = N_Ak_b, Mm = $N_A\, m$

Where M_m is the molar mass and m is the mass of one molecule of gas and N_A is Avogadro constant.

While calculating the relative motion of particles, it is customary to use reduced mass in the place of mass of one molecule of the gas.

Hence, average relative speed of a molecule(u) $\left\{\frac{8k_bT}{\pi m}\right\}^{1/2}$

Which is same as Eq. . . . 2.68

$$\mu = \frac{M_x M_Y}{M_x + M_Y} \frac{1}{N_A} \quad \ldots 2.72$$

Where M_X , M_Y and N_A are the molar mass of X molar mass of Y and Avogadro constant

Eq. 2.72 comes from Eq. 2.70 since,

Mass of one molecule of a substance

$$= \frac{\text{Molar mass}}{\text{Avogadro constant}}$$

3.3.1 Total Collision Frequency

Total collision frequency (ZXY) is the number of collision between the molecules of X and the molecule of Y in unit time in unit volume. Only X-Y collision are counted but not X-X or Y –Y collisions, since only X-Y collisions are possible for the reaction indicated in Eq. 2.65

The total collision frequency (Z) in general can be derived using the following relationship:

$$Z = \begin{cases} \pi \times (\text{collision diameter})^2 \\ \times (\text{average relative speed of gas molecules}) \\ \times (\text{number density}) \\ \times (\text{number density}) \\ \times (\text{correction factor}) \end{cases} \quad \ldots(2.66)$$

For calculating the total collision frequency (ZXY) among the molecules of X and Y, in respect to Eq. 2.66, we use the following relationship:

i) Collision diameter = $\sigma_{XY} = \frac{1}{2}(\sigma_X + \sigma_Y)$ ….(2.67)

Where σ_X and σ_Y are the diameters of the molecules, X and Y respectively. The collision diameter σ_{XY} is the distance of closest approach between a molecule of X and a molecule of Y.

ii) Average relative speed of X and Y molecules

$$= \left(\frac{8\, k_b T}{\pi\mu}\right)^{1/2} \quad \ldots \quad (2.68)$$

Where k_b is the Boltzmann constant (subscript b is added to k to differentiate it from the rate constant), T is temperature and μ is reduced mass.

Note that $\frac{1}{\mu} = \frac{1}{m_X} + \frac{1}{m_Y}$ … (2.69)

or $\mu = \frac{m_X m_Y}{m_X + m_Y}$ . . .(2.70)

Where m_X and m_Y are the masses of one molecule of X and Y, representatively.

iii) Let us now calculate the factor, (number density) x (number density). Since we have two types of molecules, X and Y, we have to consider number densities of both X and Y. Using Eq. 2.75

That is: (number density of X) × (number density of Y)

In the case of collision between the molecules of X and Y (i.e., between molecules of different gases), there is no necessity for the correction factor. It is because we calculate the collisions between; each molecule of X and each molecule of Y. Each collision is counted only once. So omitting the correction factor and using Eqs. 2.66, 2.68 and 2.79, we get,

$$Z_{XY} = \pi\sigma_{XY}^2 \left(\frac{8k_bT}{\pi\mu}\right)^{1/2} N_A^2 [X][Y] \ldots. \quad \textbf{\textit{(2.79)}}$$

Thus we have obtained a relationship useful in calculating the total collision frequency for the collision between each molecule of X and ea0h molecule of Y. Next we study the significance of Boltzmann factor.

3.3.2 Boltzmann Factor

You must realise that not all collisions between the molecules of X and Y would result in the product formation. Only those collisions, in which, the energy of the colliding molecules equals or exceeds some critical value Ea (known as activation energy as per Arrhenius equation), are effective in bringing about the reaction between X and Y. If Ea >>RT, then the Boltzmann factor, e –Ea/RT gives the fraction pf the collisions in which the colliding molecules possess energy equal to or greater than the activation energy.

Boltzmann factor = e –Ea/RT **…*(2.80)***

3.3.4 Calculation of Reaction Rate

The product of the total collision frequency and the Boltzmann factor gives the *number of molecules of X or Y in unit volume reacting per unit time.* This follows from the definitions of the terms, total collision frequency and the Boltzmann factor. In order to obtain the reaction rate in terms of concentrations of X or Y (or the *number of moles of X or Y*) consumed per unit time, we have to divide the product, Z_{XY} e-$^{Ea/RT}$ by Avogadro constant;

$$\text{Reaction rate} = \frac{-d[X]}{dt} = \frac{-d[Y]}{dt}$$

$$= \frac{Z_{XY}\, e^{-E_a/RT}}{N_A} \qquad \ldots(2.81)$$

Using Eqs. 2.79 and 2.81,

$$\text{Reaction rate} = \pi\, cr_{XY}^{2} \left(\frac{8k_bT}{\pi\,\mu}\right)^{\frac{1}{2}} N_A^{2}\, [X]\, [Y] e^{-E_a/RT}\ \frac{1}{N_A} \qquad \ldots..(2.82)$$

$$= \pi\, cr_{XY}^{2} \left(\frac{8k_bT}{\pi\,\mu}\right)^{\frac{1}{2}} N_A\, [X]\, [Y] e^{-E_a/RT}$$

By definition, the reaction rate for a bimolecular elementary reaction with respect to Eq.2.65 is as follows;

$$\text{Reaction rate} = k\, [X]\, [Y] \qquad \ldots\ (2.83)$$

Comparing Eqs. 2.82 and 2.83

$$k = \pi\, \sigma_{XY}^{2} \left(\frac{8k_bT}{\pi\,\mu}\right)^{\frac{1}{2}} N_A\ [X][Y]\ N_A\, e^{-E_a/RT} \ldots\ldots..(2.84)$$

Eq. 2.84 gives the theoretical value of the rate constant for a bimolecular reaction as per collision theory; $\pi\, \sigma_{XY}$ is called the mean collision cross-section.

3.4 Collision Theory and Arrhenius Theory – A Comparison

You compare Arrhenius Equation (Eq. 2.61) with Eq. 2.84. You can see that the frequency factor A is given by:

$$A = \pi\sigma_{XY}^{2} \left(\frac{8k_bT}{\pi\,\mu}\right)^{\frac{1}{2}} N_A \qquad \ldots\ (2.85)$$

From Eq. 2.85, you can see that *A* is not independent of temperature as predicted by Arrhenius equation. However, over a short range of temperature, the variation in *A* is not significant. Arrhenius factor can be written as a product of *A'* and $T^{\frac{1}{2}}$ where *A'* is a temperature-independent constant and *T* is temperature.

$$A = A'\, T^{\frac{1}{2}}$$

Where $A' = \pi\sigma_{XY\frac{1}{2}}^{2} \left(\frac{8k_bT}{\pi\,\mu}\right)^{\frac{1}{2}} N_A$

The factor $T^{½}$ indicated the temperature dependence of A as given in Eq. 2.85

Hence $\log A = \log A' T^{½} = \log A' + 1/2 \log T$

Using this in Eq. 2.60

$$\log k = \log A' + 1/2 \log T - \frac{E_a}{2.303\,RT}$$

or $\log k - 1/2 \log \mathrm{T} = \log A' - E_a/2.303\,RT$

A better method of arriving at the experimental values of Ea and A is to plot $\log k - 1/2 \log T$ against $1/T$.

The slope of the plot gives E_a value since

$$\text{Slope} = -E_a/2.303\,R$$

The intercept gives $\log A'$ value from A' values, A at any temperature can be found out since:

$$A = A' T^{½}$$

The value of A so obtained is the experimental value.

It was found that in the case of reaction between simple molecules, the agreement between the experimental value of A and the value obtained from collision theory (Eq. 2.85) is fairly good. In the case of reactions involving complex molecules, there is a discrepancy between the two values of A. To explain this discrepancy, a refinement was suggested for Eqs. 2.84 and 2.85 in terms of steric factor.

Steric Factor

Although the molecular collision may have requisite energy, the reaction would take place only if the molecules have proper orientation. In other words, the reacting species must have proper spatial orientation for the reaction to occur. In the case of complex molecules, the probability of attaining proper orientation for the reaction is much less as compared to simple molecules. To stress the need for the poor spatial requirement, **steric factor or probability factor** (P) was also added to the right hand side of Eq. 2.84

Hence $$k = \mathrm{P}\ \pi\sigma_{XY}^{2} \left(\frac{8k_bT}{\pi\mu}\right)^{½} N_A\ N_A e^{-E_a/RT} \qquad \ldots (2.86)$$

$$A = P\,\pi\sigma_{XY}^{2}\left(\frac{8k_bT}{\pi\mu}\right)^{½} N_A \qquad \ldots (2.87)$$

Also, $$P = \frac{A_{\text{Experimental}}}{A_{\text{Theoretical}}} \qquad \ldots (2.88)$$

The steric factor is smaller for reaction between complex molecules. We expect the steric factor to be less than unity. But many fast reactions are known for which the steric factor is much greater than unity in collision theory. Collision theory cannot explain such cases. Let us now discuss the *Activated Complex Theory* which gives a better method for calculating reaction rates.

3.5 Activated Complex Theory

The activated complex theory or the absolute theory of reaction rates depicts the formation of activated complex ($A^{\ddagger}$) from the reactants (X and Y) as a preceding step for the formation of the product, P.

$$X + Y \rightarrow A^{\ddagger}$$

$$A^{\ddagger} \rightarrow P$$

The main features of the activated complex theory are given here:

The reactant molecules come into contact with each other. In this process, a few bonds get distorted; some bonds start forming with the exchange or release of atom or groups. The composite molecule so formed from the reactants prior to the formation of the product is called the activated complex. The activated complex then decomposes to give the product. The reaction sequence could be represented as given in Figure 2.2.

Activated complex is the configuration of the atoms which the reactant molecules have near the top of the energy barrier that separates the reactants from the products. Transition state is the highest point in the potential energy curve.

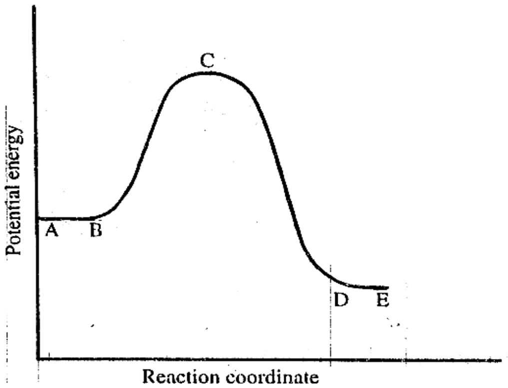

Fig. 2.2: Graphical Representation of the Change in Potential Energy as a Function of Reaction Coordinates

The total potential energy of the system is depended in the y-axis and the **reaction coordinate** in the *x*-axis. Reaction coordinate is the sequence of simultaneous changes in bond distances and bond angles. Such changes result during the formation of the products from the reactants.

Consider the reaction between a molecule of H_2 and a molecule of I_2. To start with, let us imagine that the two molecules are far apart and the total potential energy of the system is the sum of the potential energies of H_2 and I_2. This part of the reaction course is represented by the horizontal portion AB of the curve in Figure. 2.2. As the two molecules approach each other to such an extent that the orbital begin to overlap (appoint B in the curve), H–H and I–I bonds begin to stretch and H–I bond begins to form. The total potential energy starts increasing and this is represented by raising portion of the curve BC. As the extention of H–H and I–I bond breakage and H–I bond formation increase, a point is reached when the potential energy is maximum (point C). The activated complex, represented below as a composite molecule, has the maximum potential energy.

Activated complex is the configuration of the atoms which the reactant molecules have near the top of the energy barrier that separates the reactants from the products. Transition state is the highest point in the potential energy curve.

The bond-breaking is an energy demanding process and the bond-making is an energy releasing process. The net energy requirement for the formation of the activated complex and its decomposition to products must be available through the translational or the vibrational energy of the reactants.

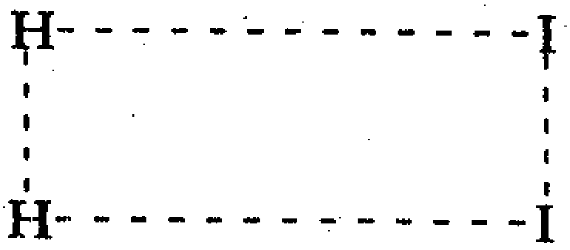

Fig. 2.3: Activated Complex

The maxima point in the potential energy curve is called the transition state. Even a slight distortion of the bonds in the form of compression of H – I bond and stretching of H – H and I – I bonds enables the activated complex pass through the transition state. The path along CD in Figure 2.2 represents the course of the events which result in the complete breakage of H – H and I – I bonds along with the formation of H – I bond. The horizontal portion DE represents the total potential energy of two H – I molecules. Although a fraction of the activated complex molecules could form the reactants (along the path CB) the formation of the products is almost a certainty, once the activated complex is at the transition state. The fraction of the activated complex converted into products is called the transmission coefficient and in majority of cases, it is unity.

3.5.1 Energy Requirement for the Reaction

Now let us consider the energy criteria for the reaction. The energy requirement for the reactants to cross the energy barrier is to be met from translational or the vibrational energy of the molecules. At the transition state, the activated complex has some complicated vibration like motion of all atoms. The activated complex has one particular mode of vibration along which it is unstable. If the activated complex vibrates with the frequency corresponding to this vibrational mode, the activated complex decomposes into products.

3.5.2 Rate Constant Calculation using Activated Complex Theory

Based on statistical thermodynamics, Eyring developed the activated complex theory. The basic postulate of the theory is that there exists equilibrium between the activated complex and the reactants. Let us consider the *bimolecular gas phase reaction*

$$X + Y \rightarrow A^{\ddagger} \qquad \ldots (2.89)$$

where X and Y are the reactants and $A^{\ddagger}$ is the activated complex: The activated complex then decomposes to give the product, P

$$A^{\ddagger} \rightarrow P \qquad \ldots (2.90)$$

The rate of formation of the product depends on:

i) the concentration of the activated complex and

ii) the frequency which is being converted into the product. This is the frequency of one of the vibrational nodes with respect to which the activated complex is unstable. Using detailed calculations, it is possible to derive an expression useful in calculating the rate constant (*k*) the elementary reaction,

$$X + Y \rightarrow P$$

(for which the steps are given in Eqs. 2.89 and 2.90). We shall only state the final expression without going through the derivation in full.

$$k = \frac{RT}{P^0} \cdot \frac{k_b T}{h} k_p = \frac{R k_b T^2}{p^0 h} k_p \qquad \ldots (2.91)$$

where K_p = The equilibrium constant for the formation of the activated complex after adjusting for its vibration with respect to which it is unstable.

T = Temperature

k_b = Boltzmann constant

RT / p^0 is the correction term where p^0 is the standard pressure (1bar)

h = Planck constant

R = Gas constant

Using van’t Hoff isotherm … (2.92)

$$\Delta G^{\ddagger} = - RT \ln K_p$$

where $\Delta G^{\ddagger}$ is molar Gibbs energy of activation. … (2.93)

Hence, $K_p = e^{-\Delta G^{\ddagger}/RT}$

Using Eq. 2.93 in Eq. 2.91

$$k = \frac{R k_b T^2}{hp^0} e^{-\Delta G^{\ddagger}/RT} \qquad \ldots (2.94)$$

Using

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger} \qquad \ldots (2.95)$$

where $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the molar enthalpy of activation and entropy of activation respectively.

Using Eq. 2.95 and 2.94

$$k = \frac{R k_b T^2}{hp^0} e^{-(\Delta H^{\ddagger} - T\Delta S^{\ddagger})/RT}$$

$$k = \frac{Rk_bT^2}{hp^0} \; e^{-(\Delta H^\ddagger - /RT} \; e^{\Delta S^\ddagger/R} \qquad \ldots (2.96)$$

Applying the differential form of Eq. 2.59, it is possible to find the following relationship for a bimolecular gas phase reaction:

$$\Delta H^\ddagger = E_a - 2RT \qquad \ldots(2.97)$$

Using Eq.s 2.96 and 2.97

$$k = \frac{Rk_bT^2}{hp^0} \; e^{-(E_a - 2RT)\,/RT} \; e^{\Delta S^\ddagger/R}$$

$$k = \frac{Rk_bT^2}{hp^0} \; e^{-E_a/RT} e^{2} \; e^{\Delta S^\ddagger/R} \qquad \ldots\ (2.98)$$

Comparing Arrhenius equation Eq 2.61 and with Eq. 2.98

$$A = \frac{Rk_bT^2}{hp^0} \; e^2 \; e^{\Delta S^\ddagger/R} \qquad \ldots (2.99)$$

$$\text{Hence} \quad e^{\Delta S^\ddagger/R} = \frac{hp^0}{Rk_bT^2\, e^2} A$$

$$\text{i.e.,} \quad e^{\Delta S^\ddagger/R} = 7.8119 \times 10^{-11} \frac{A}{T^2} \quad \ldots (2.10)$$

Substituting for the constants and taking natural logarithms,

$$\Delta S^\ddagger/R = \text{In } 7.8119 \times 10^{-11} \frac{A}{T^2}$$

$$\Delta S^\ddagger = 2.303R\,(\log 7.8119 \times 10^{-11} + \log A/T^2)$$

$$= (19.15 \log A/T^2 - 193.6)\ \text{J mol}^{-1}\ \text{K}^{-1} \qquad \ldots (2.101)$$

Note that while discussing collision theory or the activated complex theory, we consider only the gas-phase reactions. The study of reaction rates in solutions is complicated due to the role of the solvent. In this course, we shall not discuss the reaction rates in solutions.

Thus $\Delta H^\ddagger$, $\Delta S^\ddagger$ and $\Delta G^\ddagger$ can be calculated at any given temperature. If A and E_a are known from Arrhenius graph (Fig. 2.1).

To account for the discrepancy between the experimentally obtained value of *A* and the value calculated using collision theory, we had to introduce steric factor in Eq. 18.157. The activated complex theory has the factor, e which takes care of the steric factor automatically.

It is observed that $LS^{\ddagger}$ is negative for many reactions. Such a negative value indicates decrease in disorderliness. This is understandable since during collisions, the particles have to approach each other, thereby causing a decrease in randomness. The negative value of $LS^{\ddagger}$ brings down the value of e and hence of *A* as given in Eq. 18.-170. A large negative value for the entropy of activation is generally observed for reactions involving complex molecules, the demand for proper orientation is more in the case of a complex molecule and this causes larger reduction in randomness. Thus, the entropy of activation, and hence the frequency factor could be expected to be much less for reactions involving complex molecules.

4.0 CONCLUSION

A unimolecular reaction is an elementary reaction in which only one molecule or a radical reacts. The unimolecular reactions follow first order kinetics. A number of gas phase reactions follow first order kinetics. These reactions are assumed to proceed through unimolecular rate-determining step. The activated complex theory or the absolute theory of reaction rates depicts the formation of activated complex ($A^{\ddagger}$) from the reactants (X and Y) as a preceding step for the formation of the product, P.

$X + Y \rightarrow A^{\ddagger}$

$A^{\ddagger} \rightarrow P$

5.0 SUMMARY

In this unit, you have learnt about the following:

- theory of unimolecular reactions
- theory of reaction rates
- collision theory
- collision theory and Arrhenius theory – a comparison
- activated complex theory

6.0 TUTOR-MARKED ASSIGNMENT

i. The second order rate constants of a reaction are given below at two temperatures:

T/K	298	308
$10^5 \times k$ / M^{-1} s^{-1}	8.8	28

Calculate the activation energy of the reaction.

ii. For the reaction,

$2NOCl \rightarrow 2NO + Cl_2$

Arrhenius factor at 298 k is 9.4×10^9 M^{-1} s^{-1}, Calculate entropy of activation for this reaction at 298K.

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UNIT 3 COMPLEX REACTIONS

CONTENTS

1.0 INTRODUCTION

In the preceding units, we discussed the rate of chemical reactions and factors influencing it. Emphases were made on the rate laws of first and second order reactions which are the simple reactions. In this unit, we will consider increasingly complex reaction schemes, and see how to construct and solve the corresponding rate laws.

2.0 OBJECTIVES

At the end of the unit, you should be able to:

- discuss the theory of complex reactions
- explain parallel reactions
- describe the nature of reactions in equilibra.

30 MAIN CONTENT

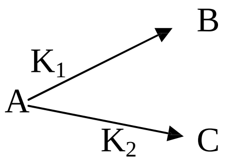
3.1 Complex Reactions

Not all chemical reactions proceed to a stage at which the concentration of the reactions becomes vanishingly small. Such a reaction proceeds via a more complex reaction mechanism. Most industrial chemical reactions, the type likely to be encountered in a chemical laboratory or plant, involve multiple steps between the reaction and products.

Such reactions are called complex reactions.

3.2 Parallel Reaction

It is not uncommon for a reaction to produce more than one product, and the reaction is often kinetic and thermodynamic. The sequence is



$$Rate = \frac{d[A]}{dt} - K_1[A] + K_2[A]$$
$$[A] = ae^{-(K_1+K_2)t}$$

The rate of the formation of the products is given as:

$$\frac{d[B]}{dt} = K_1[A]$$
$$= K_1 ae^{-(K_1+K_2)t}$$

and

$$\frac{d[C]}{dt} = K_2[A]$$
$$= K_2 ae^{-(K_1+K_2)t}$$

Integrating the equation gives:

$$[B] = \frac{K_1 a}{K_1 + K_2}\left(1 - e^{-(K_1+K_2)t}\right)$$

and

$$[C] = \frac{k_2 a}{K_1 + K_2}\left(1 -^{e-(K_1+K_2)t}\right)$$

The rate of the products formed is proportional to their rate constant.

$$\frac{[B]}{[C]} = \frac{K_1}{K_2}$$

3.3 Reactions Approaching Equilibrium

Consider a reaction in which both forward and reverse reaction are first order as given by the scheme below.

$$A \rightleftharpoons B$$

The rate of change of [A] has two contributions. It is depleted by the forward reaction at a rate K [A] but is replenished by the reverse reaction at a rate $K^1[B]$. The net rate of change is therefore

$$\frac{d[A]}{df} = -K[A] + K^1[B]$$

If the critical concentration of A and [B]o is [A]o and there is no B present initially, at all times [A]+[B] = [A]o, and so

$$\frac{d[A]}{dt} = -K[A] + K^1([A]o - [A])$$
$$= -(K + K^1)[A] + K^1[A]o$$

The solution of this first order differential equation, with the critical condition [A] = [A]o is

$$[A]t = [A]o\left(\frac{K^1 + Ke^{-(K+K^1)t}}{K_1 + K^1}\right)$$

When time t approaches infinity the concentrations reach their equilibrium values

$[A]_\alpha = K^1[A]_o/(K_1 + K^1)$ and
$[B]_\alpha = [A]_o - [A] = K[A]_o/(K+K_1)$

The ratio of these equilibrium concentrations, which is the equilibrium constant is

$$K_c = [B]_\alpha/[A]_\alpha = K/K^1$$

3.4 Other Types of Equilibria

In the case of a reaction that is bimolecular and second-order in both directions as shown by the scheme below

$$A + B \rightleftharpoons C + D$$

The rate of change of the concentration of A, as a result of the forward, and reverse reactions are:

$A + B \rightarrow C + D \qquad \upsilon A = -K[A][B]$

and

$C + D \rightarrow A = B \qquad \upsilon A = K^1[C][D]$

At equilibrium, the net rate of change is zero. Hence, at equilibrium:

$$-K[A][B] + K^1[C][D] = 0$$

Also,

$$K_C = \left(\frac{[C][D]}{[A][B]}\right)_{eq} = \frac{K}{K^1}$$

In the case of a reaction which proceeds by a sequence of simple reactions, such as:

$A + B \rightleftharpoons C + D$

$C \rightleftharpoons E + F$

υ_A forward = $-Ka[A][B]$

υ_A reverse = $K^1a[C][D]$

υ_C forward = $-Kb[C]$

υ_C reverse = $Kb^1[E][F]$

At equilibrium, all the reactions are individually at equilibrium, such that:

$$\left(\frac{[C][D]}{[A][B]}\right)_{eq} = \frac{Ka}{K^1_a} \text{ and } \left(\frac{[E][F]}{[C]}\right)_{eq} = \frac{Kb}{K^1b}$$

The overall reaction equilibrium is

$$A + B \rightleftharpoons D + E + F$$

$$K = \left(\frac{[D][E][F]}{[A][B]}\right)_{eq} = \left(\frac{[C][D][E][F]}{[A][B][C]}\right)_{eq}$$

$$= \left(\frac{[C][D]}{[A][B]}\right)_{eq} \left(\frac{[E][F]}{[C]}\right)_{eq} = \frac{Ka\ Kb}{K^1_a K^1_b}$$

When the overall reaction is the sum of a sequence of steps

$$K = \frac{Ka\ Kb}{K^1_a K^1_B}$$

Where K_∂ is the rate constants for the individual steps and K^1 refers to the corresponding reverse reaction steps.

3.5 Consecutive Reactions

Some reactions proceed through the formation of an intermediate as in radioactive decay:

$$2^{39}U \rightarrow {}^{239}Np \rightarrow {}^{239}Pu$$

Consider a first-order consecutive reaction as given below:

$$A \xrightarrow{K_1} B \xrightarrow{K_2} C$$

The rate of disappearance of A is

$$\frac{d[A]}{dt} = -K[A]$$

And rate of formations of B and C are:

$$\frac{d[B]}{dt} = K_1[A] - K_2[B]$$

$$\frac{d[C]}{dt} = K_2[B]$$

At initial time t = 0, concentration of $[A] = [A]_o$ and those of $[B] = 0$ and $[C] = 0$

The first equation is a first order rate law, and so $[A] = [A]_o\text{-}f^{-K1t}$
The rate of second equation is

$$\frac{d[B]}{dt} = K_1[A]_o \mathbf{l} - K_1 t - K_2[B]$$

$$\frac{d[B]}{dt} = K_2[B] = K_1[A]_o \mathbf{l}^{-K1t}$$

By integrating the equation, the solution is:

$$[B] = \frac{K_1}{K_2 - K_1}[A]_o \left(1 + K\left(\frac{e^{-K_1 t} - {}_2\mathbf{l}^{-K_2 t}}{K_2 - K_1}\right)\right)$$

3.6 Pre-Equilibria

In this case, a consecutive reaction in which an intermediate reaches equilibrium with the reactions before forming a product, as given in the scheme below

$$A + B \underset{K^1_2}{\overset{K_1}{\rightleftharpoons}} (AB) \rightarrow C$$

Since we assume that A, B and (AB) are in equilibrium, we can write

$$K = \left(\frac{[(AB)]}{[A][B]}\right)$$

$\square_{eq}$

with $K = \frac{K_1}{K_2}$

By ignoring the fact that [AB] is slowly leaking away as it forms C. The rate of formation of C may now be written as:

$$\frac{d[C]}{dt} = K_2[(AB)]$$
$$= K_2K_1[A]\,[B]$$
$$K\,[A]\,[B]$$

Where $K = \frac{K_1K_2}{K_2}$

3.7 Enzyme Reaction

Another example of a pre-equilibrium reaction is the Michaelis-Menten mechanism of enzyme action. The proposed mechanism is

$$\mathrm{E + S} \rightleftharpoons \mathrm{(ES)} \rightarrow \mathrm{P + E}$$
$$\frac{d(p)}{dt} + K_3\big[(ES)\big]$$

(ES) denotes a bound state of the enzyme E and its substrates S. In order to relate [(es)] to the enzyme concentration we write its rate law and then impose the steady-state approximation

$$\frac{d[(ES)]}{dt} = K_1[E][S] - K_2[(ES)] - K_3[(ES)] = 0$$

This rearranges to

$$[(ES)] = \left(\frac{K_1}{(K_2 + K_3)}\right)[E]\,[S]$$

[E] and [S] are concentration of the enzyme and substrate and $[E]_o$ in total concentration of enzyme

$$[E] + [(ES)] = [E]_o, \text{ a constant}$$

since only few E is added, we can ignore the fact that [S] differs slightly from [S] total.

Therefore

$$[(ES)] = \left(\frac{K_1}{K_2 + K_3}\right)\big\{[E]_o - [(ES)]\big\}[S]$$

which can also rearranges to

$$[ES] = \frac{K_1[E]_o[S]}{K_3 + K_2 + K_1[S]}$$

It follows that the rate of formation of products is

$$\frac{d[P]}{dt} = \frac{K_3K_1[E]_o[S]}{K_3 + K_2 + K_1[S]}$$

$$= \frac{K_3[E]_o[S]}{Km + [S]}$$

where km is the Michael constant is

$$Km = \frac{(K_3 + K_2)}{K_1}$$

3.8 Unimolecular Reaction

A number of gas phase reactions follows first-order kinesis and are believed to proceed through a unimolecular rate – determining stage. These are called unimolecular reactions. In the Lindemann-Heinshelwood mechanism it is supposed that a reactant molecule A collides with another M, a diluents gas molecule, and becomes energetically excited at the expense of M's translational kinetic energy,

$A + M \rightarrow A^* + M$ $d[A^*]/dt = K_1[A][M]$

and the energised molecule might lose its excess energy by colliding with another

$A + M \rightarrow A + M$ $d[A^*]/dt = K_2[A^*][M]$

or the excited molecule might shake itself apart and form product

$A^* \rightarrow P$ $d[b]/dt = K_3 [A^*]$

$$\frac{d[A^*]}{dt} = -K_3[A^*]$$

By applying steady state approximation to the net rate of formation of A^*,

$$\frac{d[A^*]}{dt} = K_1[A][M] - K_2[A^*][M] - K_3[A^*] = 0$$

This solves to

$$[A^*] = \frac{K_1[A][M]}{K_3 + K_2[M]}$$

and so the rate law for the formation of P is

$$\frac{d[P]}{dt} = K_3[A] = \frac{K_1K_3[A][M]}{K_3 + K_2[M]}$$

If the rate of deactivation by A^*, M collisions is much greater than the rate of unimolecular decay, so that

$K_2[A^*]\,[M] >> K_3\,[A^*]$ or $K_2\,[M] >> K_3$

Then we neglect K_3 in the denominator and obtain

$$\frac{d[P]}{dt} = \frac{K_1K_3[A][M]}{K_2[M]} = \left(\frac{K_1K_3}{K_2}\right)[A]$$

a first-order rate law, as we set out to show.

The Lindemann-Hinshelwood Mechanism can be tested because it predicts that as the concentration of M is reduced, the reaction should switch to overall second-order kinetics. This is because when $K_2[M] << K_3$, the rate is approximately

$$\frac{d[P]}{dt} = \frac{K_1K_3[M][A]}{K_3} = K_1[A][M]$$

The physical reason for the change of order is that at low pressure the rate-determining step is the bimolecular formation of $[A^*]$, if we write the full rate law as

$$\frac{d[P]}{dt} = Keff[A]$$

$$Keff = \frac{K_1K_3[M]}{K_3 + K_2[M]}$$

then the expression for the effective rate constant can be rearranged to

$$\frac{1}{Keff} = \frac{1}{Ki[M] + \frac{K_2}{K_1K_3}}$$

4.0 CONCLUSION

Those chemical reactions that proceed to a stage at which the concentration of the reactions becomes vanishingly small are known as complex reactions. Complex reactions proceed via a more complex reaction mechanism. Most industrial chemical reactions, like those encountered in a chemical laboratory or plant, involve multiple steps between the reaction and products. Such reactions are known as complex reactions.

5.0 SUMMARY

In this unit we discussed the steps followed in arriving at the mechanisms of simple reactions. We described the theory of unimolecular reaction rates. Arrhenius equation, collision theory and the activated complex were discussed.

6.0 TUTOR-MARKED ASSIGNMENT

The rate law for the reaction $2A+B \rightarrow X + 3D$ was expressed as rate = K [A][B], what are the units of K? Express the rate law in terms of the rate of change of concentration of (a) A, (b) c.

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MODULE 3 HETEROGENEOUS REACTIONS AND CATALYSIS

Unit 1 Surface Tension of Solutions
Unit 2 Catalysis

UNIT 1 SURFACE TENSION OF SOLUTIONS

CONTENTS

1.0 INTRODUCTION

In this unit, we shall discuss the effect of surface on chemical reactivity.

Surface, in the chemical sense, is a phase boundary. Geometrically a surface has an area but no thickness. Surface is an **interface region** where one phase ends and the other begins. Chemically, it is a region in which the properties vary from one phase to another. The transition occurs over distance of molecular dimensions. Thus for a chemist, surface has a thickness which shrinks to zero in an ideal condition of a geometrical description. In this unit, we shall discuss the properties of an interface which may be liquid/vapour, solid/liquid or solid/gas. We shall discuss adsorption of gases on solid surface. Such a discussion is important since many of the chemical reactions in industry or in the biological systems take place on the interface.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define an interface

- state the relationship between the concentration of a surface active solute and the surface tension of a solution
- discuss different isotherms for adsorption on solid surfaces.

3.0 MAIN CONTENT

3.1 Surface Tension of Solutions

Liquids assume a shape with minimum surface area. The bulk molecules have less energy than the molecules in the surface, since a molecule in the bulk interacts with larger number of molecules as compared to a molecule on the surface. You are aware that every system tries to assume a state in which it has minimum energy. Hence, a liquid strives to take a shape which has the least surface area. The shape assumed is spherical, as a sphere has the smallest surface to volume ratio. The force that opposes the increase in area of a liquid is referred to as surface tension. Surface tension is a force per unit length acting on the surface opposing the expansion of surface area. Alternative definition suggests that surface tension is the surface energy per unit area of the surface. Normally, the surface tension values reported are for the liquid-vapour interface in presence of air.

When we dissolve a solute in a solvent, the surface tension of the solution changes. A relationship could be derived to establish the fact that the concentration of the solute that lowers the surface tension would tend to be more on the surface of a solvent as compared to that in the bulk. This is the basis of *Gibbs adsorption isotherm*, about which this section does not intend to give a detailed discussion. Substances which produce a remarkable lowering of interfacial tension are called ‘surface active agents or surfactants’. We have seen one of the applications of the surfactants which is the cleaning action of soaps and detergents. Another application of surfactants is in the formation of surface films. Some insoluble substances such as long-chain fatty acids and alcohols could spread on water surface to form a thin film. The formation of such surface films using long-chain alcohols has been helpful in retarding the evaporation of water from reservoirs.

3.2 Adsorption on Solids

We noted earlier that the molecules on the surface of a liquid experience an inward pull. The liquid surface is thus in a state of unsaturation. The surface of a solid also behaves in a similar manner. In a solid, the ions or the molecules at the surface of a crystal do not have all their *valencies* satisfied by union with other particles. Such forces also arise due to the fact that when a new solid surface is created by breaking a solid, some inter-atomic bonds are broken and some of the valencies of surface atoms are left unsatisfied. As a result of these residual forces, the surface of the solid has a tendency to attract and retain available molecules and other particles towards itself; such a condition is helpful in decreasing the surface energy of a solid. The molecules so attracted are retained on the surface than in the bulk of the solid. This phenomenon of higher concentration of a substance on the surface of a solid is called *adsorption*. The substance attracted to the surface is called *adsorbate* while the substance to which it is attached is called *adsorbent.* For example, charcoal adsorbs acetic acid when kept in contact with it; here, acetic acid is adsorbate and charcoal is adsorbent.

Adsorption should be clearly distinguished from absorption. In absorption, the substance is not only retained on the surface but passes through the surface and is distributed throughout the bulk of the solid. Thus, anhydrous calcium chloride absorbs water to form a hydrate while acetic acid is adsorbed from its solution by charcoal. Sometimes the word ‘sorption’ is used when there is a doubt whether a process is true adsorption or absorption.

Note: Porous substance is a substance having tiny opening through which fluids or air could pass.

The extent of adsorption by charcoal can be increased by subjecting charcoal to a process of activation. It involves heating of wood charcoal between 625K and 1275K in vacuum, air, steam, chlorine or carbon dioxide. During activation, hydrocarbons and other impurities are removed from charcoal leading thereby to a large surface area for adsorption. The resulting substance is called activated charcoal.

3.3 Adsorption of Gases by Solids

The studies of the adsorption of gases by solids are similar to those of the adsorption of liquids by solids. In this unit, we shall mainly study the adsorption of gases by solids.

Although all solids adsorb gases, the effects are not evident unless the adsorbent is porous and has a very large area for a given mass. That is why silica gel and charcoal, which have porous structure, are very effective as adsorbing agents.

The amount of a gas adsorbed by a solid depends on:

- the nature of the gas and adsorbent,
- the surface area of the adsorbent, and
- the temperature and pressure of the adsorbent-adsorbate system

Table 2.1 gives the volume of various gases adsorbed by 1.00kg of charcoal at 288K. The volumes of gases have all been reduced to 273K and 1.013 x 10^5 Pa pressure. It can be seen from Table 2.1 that gases which can be liquefied easily are more readily absorbed.

Table 2.1: Adsorption of Gases on Charcoal

Gas	Volume adsorbed	Critical temperature
	m^3	k
H_2	4.7 x 10^{-3}	33
N_2	8.0 x 10^{-3}	126
CO	9.3 x 10^{-3}	134
CO_2	4.8 x 10^{-2}	304
HCI	7.2 x 10^{-2}	324
H_2S	9.9 x 10^{-2}	373
NH_3	1.8 x 10^{-1}	406

The total amount of the gas adsorbed increases with the surface area of the adsorbent. During adsorption, equilibrium is established between the gas in contact with the solid and the gas on the surface. An increase in temperature decreases the amount of gas adsorbed.

In the text section, we shall discuss quantitative relationships regarding adsorption.

3.4 Adsorption Isotherms

The amount of a substance adsorbed by an adsorbent temperature depends upon the concentration or pressure of an adsorbate. For the adsorption of a substance (adsorbate) present in a solution by a solid adsorbent, Freundlich gave an empirical equation. This equation gives the relationship between the mass of the adsorbate *(x)* adsorbed by a particular mass *(m)* of the adsorbent and the equilibrium concentration of the adsorbate *(c)* in the solution at a particular temperature as given below:

$$\frac{x}{m} Kc1^{/n} \qquad \text{....3.1}$$

where K and n are constants. Eq. 3.1 is a form of Freundich adsorption isotherm. By plotting log $x/_{m}$ against log c (Fig. 1.1), we can evaluate K and n. the values of K and n depend on

- nature of the adsorbate
- nature and particle size of the adsorbent
- temperature.

It is worth mentioning that as the particles size becomes smaller, the surface area increases enormously. This increases the adsorbing capacity of an adsorbent.

Eq. 3.1 could be slightly modified to express the adsorption of a gas by a solid as given below:

$$\frac{x}{m} = Kp^{1/n} \qquad \cdots\cdots 3.2$$

In this equation, *p* stands for the pressure of the gas adsorbate; other terms have the same significance as given in Eq. 3.1

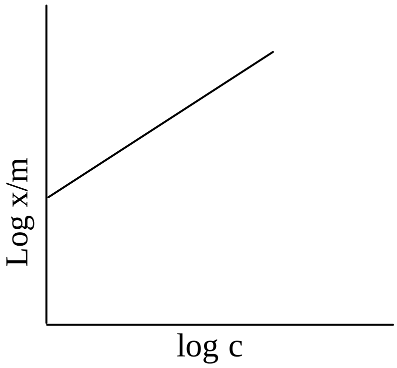

Fig 3.1: Graphical Representation of Freundlich Adsorption Isotherm

Note that Freundlich isotherm (Eq 2.1 or 2.2) is applicable only if the concentration or pressure of the adsorbate is low.

3.5 Langmuir Adsorption Isotherm

Langmuir obtained a relationship for the adsorption of a gas by a solid. Langmuir started with the assumptions stated below:

- the adsorbed gas behaves ideally in the vapour phase; there are no attractive or repulsive forces among the gas molecules
- the surface of a solid is homogeneous and there are a fixed number of adsorption sites. Each site has the same attraction for the gas molecules.
- each adsorption site can adsorb only one molecule. A solid surface cannot form a layer more than a single molecule in depth. In other words, the adsorption of a gas could lead only to the formation of unimolecular layer on the solid
- there is an equilibrium between the condensation of gas molecules on the adsorbent and their desorption from it. The initial rate of condensation of gas molecules on the solid surface is high and it decreases as the surface available for adsorption decreases. The desorption can occur by thermal agitation and the rate of desorption will depend upon the amount of solid surface

covered by gas molecules. It will increase as the surface becomes more and more saturated. At a certain stage, the rates of condensation and desorption become equal and an equilibrium is established.

- using the above assumptions, Langmuir equation for adsorption can be derived as follows:

Note:

Desorption is the process of release of the adsorbed molecules. Desorption may also be called the evaporation of the adsorbed molecules.

Let the fraction of the total surface covered by gas molecules be 0; then the surface available for adsorption is 1 –0. According to kinetic theory of gases, the rate at which the molecules strike the unit area of surface is proportional to the pressure of the gas. If *p* is the equilibrium gas pressure, then, the rate of condensation is given as follows:
Rate of condensation = a (1-0) p

or rate of condensation = k_1 (1-0)p ……3.3
where k_1 is a constant of proportionality.
Rate of evaporation from the surface will be proportional only to the fraction of the surface which has adsorbed gas molecules on it. Thus,

Rate of evaporation = k_2 0 …….3.4
k_2 is also a proportionality constant.
At equilibrium, the rates of condensation and evaporation are equal. Hence,
K_1 (1-0) p = k_2 0 ……3.5
Rearranging Eq. 3.5, we can get,

$$0=\frac{k_1p}{k_2+k_1p}=\frac{(k_1/k_2)p}{1+(k_1/k_2)p}$$ (Dividing the numerator and Denominator by K_2)

$$0=\frac{Kp}{1+Kp}$$ (where k_1/k_2 = K, another constant) ……...3.6

Eq. 3.6 could be modified to find a relationship between the amount of gas adsorbed and the gas pressure. The amount of gas adsorbed (*y*) at a pressure p is proportional to the fraction of the total surface covered (0) by the gas molecules.
i.e., $y \alpha 0$

Hence, $y = y_m0$ or $y/y_m = 0$ ……3.7

Where y_m is the proportionality constant and is equal to the amount of the gas molecules required to form a unimolecular layer; i.e., $y = y_m$ when 0 = 1

Using Eqs. 3.6 and 3.7

$$\frac{y}{y_m} = \frac{kp}{1+kp}$$

$$y = \frac{y_m kp}{1+kp}$$

$$\text{or } \frac{p}{y} = \frac{1+Kp}{y_m K} = \frac{1}{y_m K} = \frac{p}{y_m} \qquad \text{….3.8}$$

Eq. 3.8 is known as Langmuir adsorption isotherm.

When the gas pressure is low, p/y_m is small when compared to $\frac{1}{y_m k}$ hence $\frac{p}{y} = \frac{1}{y_m k}$ or p/y = constant, since y_m and K are constants.

Or $p \alpha y$

This means that at low pressures, the amount of gas adsorbed is proportional to gas pressure.

When the gas pressure is high, $\frac{p}{y_m}$ is much larger than $1/y_m k$. Hence, Eq. 3.8 could be written as:

$$\frac{p}{y} = \frac{p}{y_m}$$

or $y = y_m$ which means that at high pressures, the amount of gas adsorbed is sufficient to form a unimolecular layer. A way to verify Langmuir adsorption isotherm (Eq. 3.8) is to plot p/y against p. A straight line must be obtained. ((Fig. 2.2)

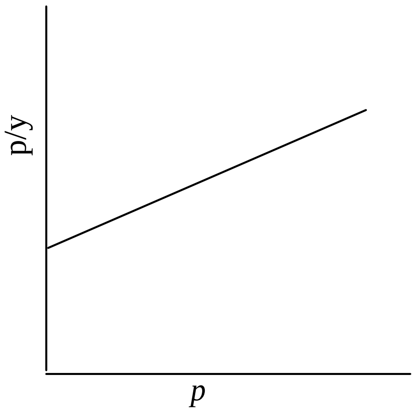

Fig. 3.2: Graphical Representation of Langmuir Adsorption Isotherm

It is observed that straight line plots are obtained when the surfaces are smooth and nonporous, and when the pressures are not too high. Under these conditions, Eq. 3.8 is obeyed. Deviations from Langmuir adsorption isotherm are seen if;

- Surface is porous (i.e. a good adsorbent) and
- Pressure is very high.

Under these conditions, gas molecules give rise to multilayer adsorption on the solid surface which accounts for derivations from Eq. 3.8. For explaining multilayer adsorption, **B**runauer, **E**mmet and **T**eller have proposed a model which is known as **BET** isotherm which we are not going to discuss in detail.

4.0 CONCLUSION

Adsorption means the taking up by the surface of a solid or liquid (adsorbent) of the atoms, ions, or molecules of a gas or other liquid (adsorbate). Porous or finely divided solids can hold more adsorbate because of the relatively large surface area exposed. Similarly, the adsorbent surface of a quantity of liquid is increased if the liquid is divided into fine droplets. In some cases, the atoms of the adsorbate share electrons with atoms of the adsorbent surface forming a thin layer of chemical compound. Adsorption is also an important part of catalysis and other chemical processes. Absorption occurs when the molecules of adsorbate penetrate the bulk of the solid or liquid adsorbent.

5.0 SUMMARY

In this unit, we have discussed surface tension of solutions under the following headings:

- Adsorption on solids

- Adsorption of gases by solids
- The adsorption isotherms
- The Langmuir adsorption isotherm.

6.0 TUTOR-MARKED ASSIGNMENT

i. Starting from Eq. 3.6, derive the following equation:

$$P = \frac{0}{K(1 - 0)}$$

ii. What is the essential characteristic of the surface active agent?

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UNIT 2 CATALYSIS

CONTENTS

1.0 INTRODUCTION

Catalysis can be defined as the alteration of the speed of a chemical reaction, through the presence of an additional substance, known as a catalyst, which remains chemically unchanged by the reaction. Enzymes, which are among the most powerful catalysts, play an essential role in living organisms, where they accelerate reactions that otherwise would require temperatures that would destroy most of the organic matter. In this unit, we shall discuss catalysis in details; physisorption, chemisorptions, the modern methods of surface studies, types of catalyst and the mechanisms of catalytic reactions.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define catalysis
- differentiate between physisorption and chemisorption
- state the role of photoelectron spectroscopy in surface chemical analysis
- describe the functions of different types of catalysts
- explain the inhibition of chemical reactions and poisoning of catalysts.

3.0 MAIN CONTENT

3.1 Catalysis

Catalysis is the alteration of the speed of a chemical reaction, through the presence of an additional substance, known as a catalyst. Catalyst remains chemically unchanged by the reaction. A catalyst in a solution with—or in the same phase as—the reactants is called a homogeneous catalyst. The catalyst combines with one of the reactants to form an intermediate compound that reacts more readily with the other reactant. The catalyst, however, does not influence the equilibrium of the reaction, because the decomposition of the products into the reactants is speeded up to a similar degree. An example of homogeneous catalysis is the formation of sulfur trioxide by the reaction of sulfur dioxide with oxygen, in which nitrogen dioxide serves as a catalyst. Under extreme heat, sulfur dioxide and nitrogen dioxide react to form sulfur trioxide and the intermediate compound nitric oxide, which then reacts with oxygen to re-form nitrogen dioxide. The same amount of nitrogen dioxide exists at both the beginning and end of the reaction.

Depending on the type of interaction, adsorption is of two-type-physisorption (physical adsorption) and chemisorption (chemical adsorption).

Both physisorption and chemisorption are generally exothermic process. This should be noted while discussing about enthalpy decrease while comparing energies of physisorption and chemisorption.

3.1.1 Physisorption

If the adsorbate molecules are weakly bounded to the adsorbent, it is classified as physisorption. It is also known as van der Waals adsorption since the forces involved are of van der Waals type and are of the same magnitude. Example is in the liquefaction of gases. The enthalpy decrease (-DH) associated with physisorption is much low (< 40 kJ mol^{-1}) and is of the same order as the enthalpy of condensation of the adsorbate. Increase of temperature is not favourable to physisorption. Adsorption of gases by charcoal is an example of pysisorption. Physisorption is generally independent of the chemical nature of the adsorbent. All gases exhibit van der Walls adsorption.

Note

The unsatisfied valencies of the surface may cause breakage of the bonds in the chemisorbed molecules. The fragments that results in the process are responsible for the increased chemical activity.

3.1.2 Chemisorption

If the adsorbed molecules react chemically with the surface, we call it chemisorption. The enthalpy decrease associated with chemisorption is much high (between 40KJ mol^{-1} and 400KJ mol^{-1}) and is of the order of bond enthalpies. We shall discuss later how the type of bonding caused by chemisorption between the adsorbent and the adsorbate determines the reactivity pattern. Many chemisorption processes involve activation energy as in a chemical reaction. In such cases, the rates of chemisorption and desorption increase with temperature in contrast with the rate of physisorption.

Note:

High bond enthalpy of nitrogen (945KJ mol^{-1}) is mainly responsible for its low reactivity.

Let us see how the type of adsorption of nitrogen on iron surface varies with temperature. The studies on the adsorption of nitrogen on iron surface indicate that at about 770K (the temperature chosen for Haber process), nitrogen is chemisorbed on the iron surface. Chemisorption results in large release of energy. The optimum temperature chosen for the reaction and the energy released during chemisorption are helpful in overcoming the large bond enthalpy of nitrogen. Hence, when nitrogen is chemisorbed at 770K, it present as nitrogen atoms and not as molecules.

Note:

One of the methods followed in scientific reasoning is to arrive at the same conclusion through more than one method. Take for instance, the manufacture of ammonia. Based on Le Chatelier principle as discussed in CHM 103, high pressure (200-300 atm.) and optimum temperature (670-870K) are needed for a good yield of ammonia. These conclusions could be reached from surface studies also. In this section, we have explained that around 770K, nitrogen is chemisorbed on iron to a large extent and, this facilitates the formation of ammonia.

At temperatures less than 770K, there is no much of chemisorption of nitrogen on iron surface. At room temperature, iron does not adsorb nitrogen at all. But as temperature is lowered and bought near 80K (the boiling point of liquid nitrogen), iron adsorbs nitrogen gas physically as nitrogen molecules! In short, near 770K, nitrogen is chemisorbed by iron as nitrogen atoms and near 80K, it is physisorbed as nitrogen molecules.

The dissociation of nitrogen molecule on iron surface at 770 K could facilitate its further reaction such as the formation of ammonia through Haber process. Although the mechanism of iron catalysis in Haber process is not completely understood, the chemisorption of nitrogen on iron certainly plays a role in it.

3.2 Modern Methods of Surface Studies

The composition of the adsorbent surface, the nature of binding between the adsorbent and the adsorbate and the extent of surface coverage could be studied by using methods such as X-ray or UV photoelectron spectroscopy. Auger spectroscopy and low energy electron diffraction (LEED). Of these methods, we shall explain the principle of X-ray and UV photoelectron spectroscopy only.

Note:

Auger effect is the emission of a second electron after high energy radiation has expelled on electron. Auger effect is the basis of Auger spectroscopy and is much used in microelectronics industry.

Low energy electron diffraction is the diffraction caused by atoms on the surface by using low energy electrons. The LEED pattern depicts the two dimensional structure of a surface. Low energy electrons are used to ensure diffraction by atoms on the surface only, but not by atoms in the bulk.

As you have thought in *Atoms and Molecules,* your hundred level course, we explained the photoelectric effect, according to which photoelectrons could be ejected by irradiating a metal surface with UV rays. The minimum energy that UV rays must possess for photoelectron emission corresponds to the ionisation energy of the valence electrons. If we are interested in the emission of inner electrons, we must use X-ray or UV photoelectron. Since such photoelectron spectroscopy studies are useful in obtaining the fingerprint of the materials present in a surface of a material, these methods are known as *electron spectroscopy for chemical analysis* (ESCA). It is possible to identify the elements present in a given surface using X-ray photoelectron spectroscopy since each element has characteristic inner shell ionisation energies. The surface study using ESCA is made possible by the fact that the ejected electrons cannot escape except from within a few nanometers from the surface. The nature of chemisorption between a catalyst surface and the reactant molecules could be established by ESCA studies.

3.3 Types of Catalysts

We have discussed earlier that the rate of a chemical reaction can be increased by raising the temperature. This increases the fraction of molecules having energies in excess of some threshold energy (nearly equal to activation energy). Another way to increase the rate of chemical reaction is to find an alternate path for a chemical reaction that has lower activation energy. A catalyst produces this alternate path for a chemical reaction. The sole function of the catalyst is to lower the activation energy of a reaction. Thus, a small amount of manganese dioxide increases the rate of decomposition of $KCl0_3$; the decomposition of nitrous oxide is accelerated by iodine; in presence of Ni, unsaturated hydrocarbons can be hydrogenated to saturated hydrocarbons. The amount of a catalyst remains unchanged at the end of a reaction and may be used repeatedly. *A substance which can influence the rate of a chemical reaction but itself remains unchanged chemically is called a catalyst*. A catalyst cannot start a chemical reaction that could not take place in its absence. A catalyst does not alter the position of equilibrium; in other words, it cannot change the relative amounts of the reactants and products at the equilibrium. Consequently, a catalyst must accelerate equally both the forward and the reverse reactions. A catalyst is highly specific in its action, for example, MnO_2 can catalyse the decomposition of $KClO_3$ but not that of KNO_3. In certain reactions, one of the products could catalyse the reaction. For instance, in the oxidation of oxalic acid by acidified $KMnO_4$, Mn^{2+} ions formed during the reaction increase the rate of the reaction. This type of phenomenon is called *auto-catalysis*.

Catalysis may be of homogenous or heterogeneous type. In homogenous catalysis, the catalyst forms a single phase with the reactants and products, whereas in heterogeneous catalysis, it constitutes a separate phase.

There is another type of catalysis known as enzyme catalysis. Enzymes have high relative molecular masses and are protein molecules. The enzymes catalyse a variety of chemical reactions in living organisms. The enzyme reaction medium is colloidal in nature and strictly, enzyme catalysis does not fall under homogenous or heterogeneous catalysis. The enzymes are specific in catalysing only a particular set of reactions. Enzyme activity depends on pH of the medium.

Examples of all the three types of catalysis are provided in Table 2.2

Table 3.2: The Three Types of Catalysis

Types		Illustrative reaction	Catalyst
Homogeneous catalysis	1)	$2SO_2(g) + 0_2(g) \rightarrow 2SO_3(g)$	NO (g)
	2)	$CH_3COOC_2H_5(1) + H_2O(1) \rightarrow CH_3COOH(1) + C_2H_5OH(1)$	$H_3O^+(aq)$
Heterogeneous catalysis	1)	$HCOOH(g) \rightarrow H_2O(g) + CO(g)$	$A1_2O_3(s)$
	2)	$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$	Pt (s)
Enzyme cataysis	1)	$NH_2CONH_2 + H_2O \rightarrow 2NH_3 + CO_2$	Urease
	2)	$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$	Zymase

- Note that in enzyme catalysis, we have not specified the states of the substances.

In the next unit, we shall discuss the theories of catalysis.

3.4 Mechanisms of Catalytic Reactions

In homogenous or enzyme catalysis, a reaction intermediate is formed between the reactant and the catalyst or the enzyme. The intermediate compound then decomposes to give the product. The reaction sequence can be represented as follows:

Step (i) Formation of the intermediate compound S + C!:+SC
Step (ii) Decomposition of the intermediate compound $SC \rightarrow P + C$

Where S and P are the reactant and the product respectively, and C is the catalyst or the enzyme; SC is the intermediate compound. The role of the catalyst or the enzyme is to lower the activation energies of the forward and reverse reactions. In Figure 3.3, E_c is the activation energy for the conversion of a reactant to a product in the presence of a catalyst and E_{uc} is the activation energy for the same reaction in the absence of catalyst. You can see that $E_c < E_{uc}$. The same is true for the reverse reaction.

It is interesting to note that many of the biological reactions are catalysed by enzymes. This is facilitated by the fact that the enzyme catalysed reactions have much lower activation energies than systems containing chemical catalyst. Table 2.3 indicates the activation energies for the decomposition of hydrogen peroxide under different conditions; can you make your own judgment!

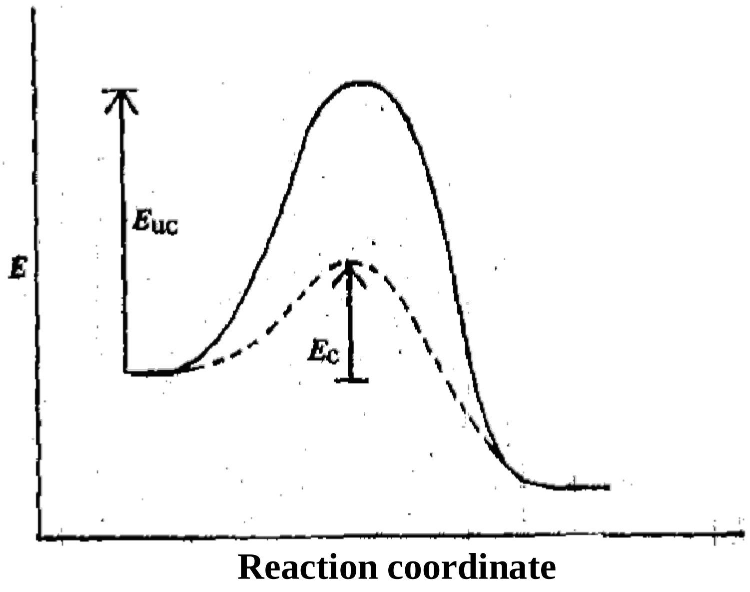

Fig. 3.3: Relative Activation Energies for Catalysed and Uncatalysed Reactions

Table 3.3: Activation Energies for the Decomposition of Hydrogen Peroxide Solution

Catalyst	Activation energy/kJ mol	Relative rate of reacti
None	75.3	1
1$^-$ (*aq*) (homogenous)	56.5	2.0×10^3
Pt (s) (heterogeneous	49.0	4.1×10^4
Catalase (enzyme)	8	6.3×10^{11}

Note

You can have an idea about the importance of enzyme reactions from the fact that ammonia produced from nitrogen by nitrogenase enzyme is ten times more than that produced by Haber process. Furthermore, the enzyme gives good yields of ammonia at room temperature and pressure. Compare this with the experimental conditions needed for Haber process (200-300 atmospheric pressure and 670-870K).

In heterogeneous catalysis, the role of the catalyst surface is to bring down the activation energies of the reactions. This happens due to chemisorption which is similar to intermediate compound formation in homogenous catalysis. The ability of a surface to have chemisorption of the reactant molecules depends on the chemical nature of the surface. ESCA studies (Sec. 2.6) are helpful in deciding the nature of chemisorption between the surface and the reactant molecules. The difference in the nature of chemisorption could lead to different products even from the same reactant.

For example, ethyl alcohol is dehydrogenated on Ni, Pd or Pt catalysts to give acetaldehyde.

$$CH_3CH_2OH \xrightarrow{\text{Ni, Pd or Pt}} \rightarrow CH_3CHO + H_2$$

On the other hand, ethyl alcohol undergoes dehydration reaction on alumina.

$$CH_3CH_2OH \rightarrow \xrightarrow{\text{Alumina}} CH_2 = CH_2 + H_2O$$

On Ni, Pd or Pt surfaces, the linkage of ethyl alcohol is through two hydrogen atoms (Fig. 3.4). The strong affinity between Ni and hydrogen accounts for the removal of two hydrogen atoms from ethyl alcohol.

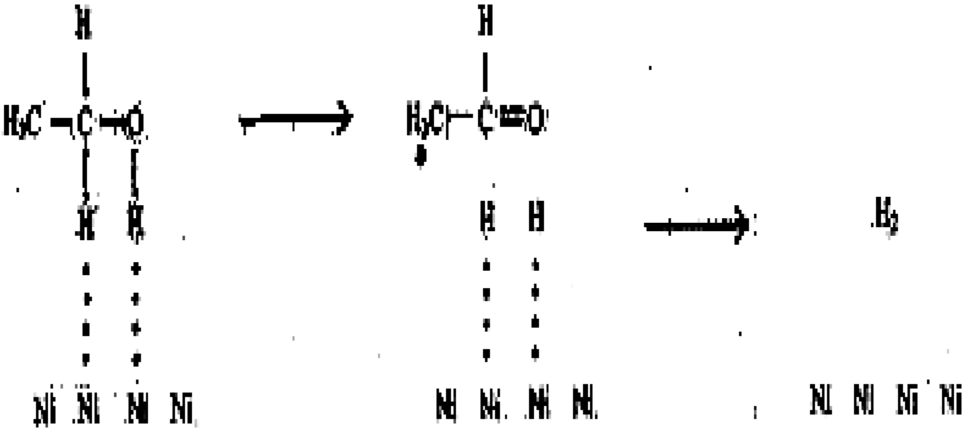

Fig. 3.4: Dehydrogenation Process on Ni

On the other hand, alumina acts differently due to its different structure. Alumina has both oxide groups and hydroxyl groups. The linkage of ethyl alcohol to alumina is through hydrogen and oxygen atoms as shown in figure 3.5. The removal of hydrogen and hydroxyl groups from adjacent carbon atoms leads to the dehydration reaction.

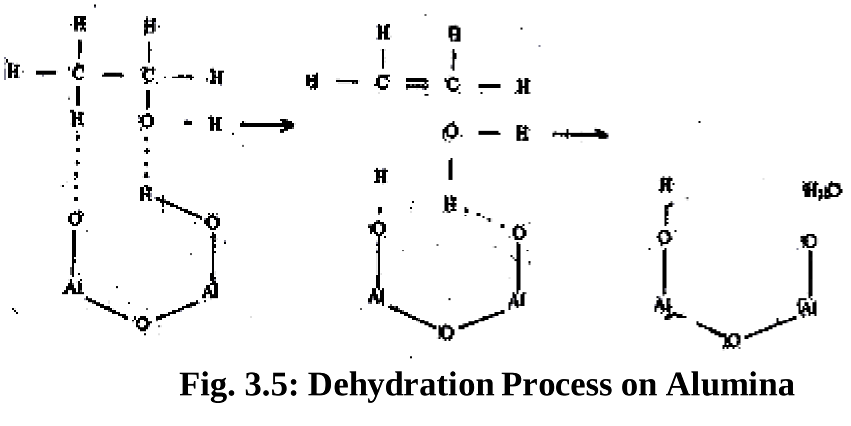

Fig. 3.5: Dehydration Process on Alumina

Certain substances improve the activity of a catalyst. Such substances are called *promoters*. These substances may not themselves be effective catalysts. A promoter may increase the number of active sites on a catalyst surface. In the light of this discussion, let us examine the catalysis in Haber process of manufacturing ammonia. A mixture of iron, potassium and aluminium oxides facilitates this reaction. The hydrogen atmosphere reduces iron oxide into porous iron which has large surface area that acts as the catalyst. The mixture of potassium oxide and aluminium oxide acts as promoters.

Let us now see a few applications of catalysts in chemical industries.

- In the preparation of edible fats from vegetable and animal fats, controlled partial hydrogenation with a catalyst such as nickel helps in removing some of the double bonds. In the absence of hydrogenation, these double bonds could be oxidised by air which impart the oil the rancid odour on storage.
- Careful studies of the catalytic surface have been helpful in preferential formation of a product starting from a reactant. Thus, it is possible to prepare various oxidation products of ethylene such as ethanol, acetaldehyde, vinyl chloride or vinyl acetate by proper choice of catalysts and reaction conditions.
- You may be aware that ‘cracking’ is the process of producing small organic molecules by the breaking of long-chain hydrocarbon molecules. Usually, silica-alumina catalysts are used for this purpose. Cracking is required to produce branched-chain isometric hydrocarbons which have more fuel efficiency in automobile engines.

3.5 Inhibition and Poisoning

You have learnt earlier that the reactants are to be adsorbed on the surface for the chemical reaction to be influenced by the surface. For the enhancement of the reaction rate, the reactants must be adsorbed more or less to same extent. If one of the reactants is more strongly adsorbed than the other or if a product is adsorbed to a greater extent than the reactants, then the active centres on the catalyst surface would not be completely available for the reaction and the reaction rate decreases. Such a condition is called *inhibition* of the catalyst. One of the reactants or the products which gets strongly adsorbed and thereby decreases the reaction rate is called the inhibitor. For example, in the decomposition of ammonia on platinum surface, hydrogen (a product) is strongly adsorbed and inhibits the reaction.

It is possible that the reaction could be inhibited by a foreign molecule that does not take part in a reaction. This type of inhibition is called *catalytic poisoning*. It is observed that even small amount of the catalytic poison could be effective in stopping a reaction. This phenomenon could be explained by the fact that the active centres constitute only a small fraction of the total surface sites on a catalyst and, the meager amount of poison could occupy these positions. This prevents the reactant molecules from occupying such positions. For example, in the contact process of manufacturing sulphuric acid, a small amount of arsenic impurity can even poisons the platinised asbestos catalyst and the reaction almost stops.

SELF-ASSESSMENT EXERCISE

State the conditions under which a catalyst loses its influence over a reaction?

- described the types of catalyst and indicated the mechanisms of their activity
- discussed the inhibition and poisoning of catalyst.

4.0 CONCLUSION

Rates of reaction increase in the presence of catalysts, substances that provide a new, faster reaction mechanism but are themselves regenerated so that they can continue the process. Mixtures of hydrogen and oxygen gases at room temperature do not explode. But the introduction of powdered platinum leads to an explosion as the platinum surface becomes covered with adsorbed oxygen. The platinum atoms stretch the bonds of the O_2 molecules, weakening them and lowering the activation energy. The oxygen atoms then react rapidly with hydrogen molecules, colliding with them, forming water, and regenerating the catalyst. The steps by which a reaction occurs are called the reaction mechanism.

5.0 SUMMARY

In this unit, we have discussed the role of surface in chemical reactions. Hence, we have:

- defined a surface active agent
- discussed the significance of adsorption isotherms
- explained physisorption and chemisorption
- outlined the modern methods of surface studies.

6.0 TUTOR-MARKED ASSIGNMENT

i. Assuming that chemisorption of nitrogen on iron at 770K follows Langmuir isotherm, could you justify the use of high pressure in Haber process for the manufacture of ammonia?

ii. What is the basis principle for ESCA studies of the surface?

iii. a). At 310 K (blood temperature), sucrose could be hydrolysed using an enzyme, saccharase or a mineral acid. The reaction rate for one reaction is 10^{12} times higher than the other. Identify the faster reaction.

b). It has been explained that the rate of a reaction is proportional to $e^{-E/RT}$. The activation energy of the reaction $H_2(g) + 1_2(g)$ (2HI(g) is reduced from 184 kJ mol^{-1} to 59 kJ mol^{-1} in the presence of platinum catalyst. By what factor will the reaction rate be increased by platinum at 600K? Assume that the frequency factor remains unchanged.

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MODULE 4 PHOTOCHEMISTRY

UNIT 1 LAWS OF PHOTOCHEMISTRY

CONTENTS

1.0 INTRODUCTION

You have learnt in your 300 level course that free energy must decrease for a physical or a chemical process to be feasible. This is applicable to thermal reactions (also known as dark reactions). The conversion of carbon dioxide and water into starch is a reaction in which free energy increases. Under laboratory conditions, this reaction is not possible. But plants carry out starch synthesis using sunlight. Ozonisation of oxygen and decomposition of ammonia are also non-spontaneous reactions under laboratory conditions. However, these could take place by using light of proper energy. Such possibilities of new reactions and new synthetic methods encouraged the scientists to probe into light-initiated reactions.

In photochemistry, we shall study the absorption and emission of light by matter. It includes the study of various photophysical processes and photochemical reactions. Two important photophysical processes are fluorescence and phosphorescence. During fluorescence, light emission takes place in the presence of exciting radiation; but the emission stops once the exciting radiation is removed. In contrast to this, during phosphorescence, light emission takes place even after the removal of the exciting radiation.

In photochemical reactions, the substances acquire the necessary activation energy through light absorption. Again, this is in contrast to the thermal reactions in which the reactants acquire their activation energy through collisions between molecules.

In this unit, we shall discuss the laws of photochemistry. We shall then describe some photochemical reactions and photophysical processes. We shall also explain some photosensitised reactions. Finally, we shall discuss the applications of photochemical studies.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain the mathematical form of Beer-Lambert law
- state Grotthuss-Draper law and Stark Einstein law
- calculate the quantum yield of a reaction using the given experimental data
- explain the reason for the higher energy requirement for the photochemical dissociation of a molecule as compared to its thermal dissociation
- derive rate expressions for simple photochemical reactions
- explain some photophysical properties such as fluorescence and phosphorescence
- list some photosensitised reactions
- state the applications of photochemical studies
- define chemiluminescence.

3.0 MAIN CONTENT

3.1 Laws of Photochemistry

Grotthuss-Drapper law and Stark-Einstein law are the two laws concerning the interaction between matter and light. Before discussing these two laws, let us state the mathematical form of Beer-Lambert law which was discussed in Unit 8 of *Atoms and Molecules*; your hundred level course.

Beer-Lambert law is useful in calculating the concentration of a solution on the basis of its light absorption. This law relates the intensity of the transmitted monochromatic light to the concentration of the solution and the thickness of the cell in which the solution is kept.

Mathematical forms of Beer-Lambert law is given below:
Log $l_0/1 = A = ecl$ ……3.1

Where 1_0 = Intensity of the incident radiation

1 = Intensity of the transmitted radiation

A = log $1_0/1$ = Absorbance or optical density of the solution

c = concentration of the solution expressed in mol m^{-3}

1 = thickness of the cell

€ = molar extinction coefficient; expressed in m^2 mol^{-1}

The molar extinction coefficient of a substance can be determined using a colorimeter or a spectrophotometer as follows. The different absorbances of a solution are measured at different known concentrations using a cell of known thickness (1). The plot of A against ç gives a straight line (Fig. 1.1) and its slope is equal to $_E$ 1.

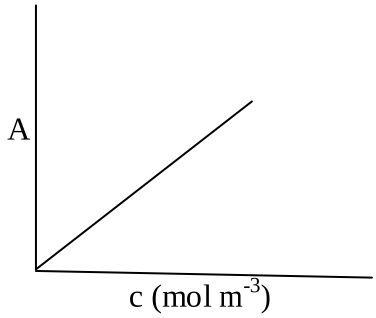


Fig: 4.1: The Graph of A vs C Plot

Hence, $= e\,\frac{\text{slope}}{1}$

Since l is known, e can be calculated. Using this e value, the concentration of a solution can be determined by measuring its absorbance.

Colorimeters and spectrophotometers are commercially available for the measurement of adsorbances. In colorimeters, colour filters are used to get the incident radiation in a particular wavelength range. Spectrophotometers have arrangements for obtaining nearly monochromatic incident radiation. Both colorimeters and spectrophotometers have devices for converting the light transmitted into suitable signal through detector devices (Sec. 3.3). The signal generated from transmitted light is directly read as absorbance values.

Study the following example carefully: the calculation shown below is used in chemical actinometers (example 3 in Section 3.3) for estimating the intensity of the light absorbed during a photochemical reaction. The example illustrates the use of Eq. 1.1 in calculating the concentration of a solution.

Example 1

A solution of the red complex formed by Fe^{2+} ion with 1, 10-phenanthroline is taken in a cell of the thickness 1.00cm. If e for the complex is $1.11 \times 10^3 m^2 mol^{-1}$ and the absorbance of the solution is 0.391, calculate the concentration of the complex in mol^{-3}.

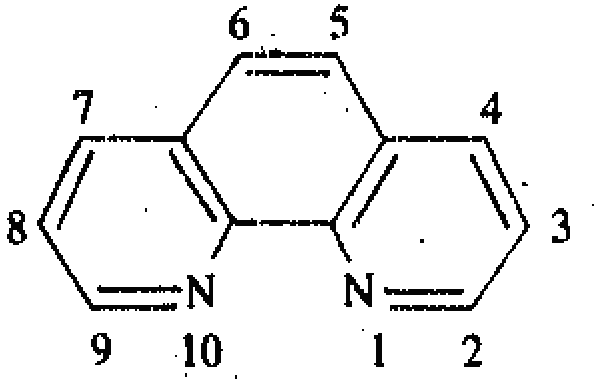
Solution

$$A = 0.391; l = 1.00cm = 1.00 \times 10^{-2} m;$$
$$e = 1.11 \times 10^3 m^2 mol^{-1}$$

Rearranging Eq. 3.1, $c = \frac{A}{e!} = \frac{0.391}{1.11x10^3 x1.00x10^{-2}} mol\ m^{-3}$

$$= 0.0352 mol\ m^{-3}$$

Note



1,10 – Phenanthroline (Phen)

We shall now state the two laws of photochemistry.

3.1.1 Grotthuss-Draper Law

According to this law, only the light that is absorbed by a molecule can produce a photochemical change in it. This means that it is not sufficient to pass through a substance to bring about a chemical reaction; but the light must be absorbed by it. Stark-Einstein law of photochemical equivalence provides a quantum mechanical form to Grotthuss-Draper law.

3.1.2 Stark-Einstein Law of Photochemical Equivalence

Stark-Einstein law of photochemical equivalence can be stated as follows:

Each molecule taking part in a photochemical reaction absorbs one quantum of radiation which causes the reaction.

Note

Stark-Einstein law is applicable only if the intensity of light is not very high.

This law is applicable to the primary act of excitation of a molecule by light adsorption. This law helps in calculating the quantum efficiency (F) which is a measure of the efficiency of the use of light in a photochemical reaction.

The quantum efficiencies for the formation of a product and for the disappearance of the reactant are defined below:

$$\text{The quantum efficiency for the formation of Product (fR)} = \frac{\text{Number of molecules of product formed in 1 second}}{\text{Number of quanta absorbed in 1 second}}$$

$$= \frac{dN_P / dt}{l_a} \qquad ..\ 3.2$$

In this equation, dN_p/dt denotes the rate of formation of the product. The units for $\frac{dN_p}{dt}$ are molecules per second. l_a refers to the number of photons absorbed per second. Similarly, we can define the quantum efficiency for the disappearance of a reactant.

The quantum efficiency for the disappearance of the reactant (fR) $= \dfrac{\text{Number of molecules of reactant consumed in 1 second}}{\text{Number of quanta absorbed in 1 second}}$

$$= \frac{-\ dN_P\ / dt}{1_a} \qquad \text{..... 3.3}$$

Where $-dN_R/dt$ is the rate of consumption of the reactant. The minus sign in $-dN_R/dt$ is due to the decrease in concentration of the reactant with time.

With respect to Stark – Einstein law, each reacting molecule absorbs one quantum of light. Hence,

The energy absorbed by one mole of substance undergoing Photochemical reaction $= N_A h v = \dfrac{N_A hc}{l}$ 3.4

This unit of energy is also called Einstein and, as apparent from Eq. 3.4, the value of Einstein depends on v or l .

Where $N_A = 6.022 \times 10^{23}\ mol^{-1}$

$h = 6.626 \times 10^{-34}$ J s

$c = 3 \times 10^{8}\ m\ s^{-1}$

l = wavelength of the light in m unit

V = frequency in s^{-1} unit.

To calculate the quantum efficiency, use the following steps:

i) Calculation of Energy Absorbed per Quantum

Energy per quantum of radiation absorbed $= hv = \dfrac{hc}{l}$

ii) Calculation of *I*a

Usually intensity of light absorbed is given in Js^{-1} units. From this, I_a could be calculated using the following equation:

Intensity in terms of number of photons absorbed in 1 second (1)

$$= \frac{\text{Intensity in J s}^{-1}\text{ units}}{\text{Energy per quantum}}$$

Note:

Unit for energy per quantum = joule photon $^{-1}$

Unit for l = $\frac{\text{joule second}^{-1}}{\text{joulephoton}^{-1}}$

= photon second^{-1}

iii) Calculation of $\frac{-dN_R}{dt}$ or $\frac{dN_P}{dt}$

First, we have to obtain the number of moles of reactant consumed or of product formed **in 1 second** by dividing the respective amount by the time in second unit.

In order to calculate the rate of formation or rate of disappearance in molecule per second units, we have to use the following equations:

$$\frac{-dN_R}{dt} = \text{Number of moles of reactant Decomposed in 1 second} \times N_A \qquad \ldots 3.5$$

Also, $\frac{dN_P}{dt}$ = Number of moles of product formed in 1 second x N_A ` … 3.6

iv) Calculation of Quantum Efficiency

Using Eq. 3.2 or 3.3, f p or f R can be calculated.

Let us illustrate the calculation of quantum efficiency for a reaction.

Example 2

In photochemical decomposition of acetone using 313 nm light, 7.57 x 10^{-6} mol of carbon monoxide is formed in 20 minutes. If the light absorbed corresponds to 2.41 x 10^{-3} Js^{-1}, calculate the quantum efficiency for the formation of carbon monoxide.

i) energy absorbed per quantum= $\frac{hc}{l} = \frac{6.626x10^{-34}x3x10^{8}}{313x10^{-9}}$ joule photon^{-1}

$$= 6.35 \text{ x } 10^{-19} \text{ joule photon}^{-1}$$

ii) $l_a = \frac{\text{Intensity in joule second}^{-1}}{6.35x10^{-19} \text{ joule photon}^{-1}}$

$$= \frac{2.14x10^{-3} \text{ joule second}^{-1}}{6.35x10^{-19} \text{ joule photon}^{-1}}$$

i.e. $l_a =$ 3.80 x 10^{15} photons second^{-1}

iii) $\frac{\text{Amount of carbon monoxide}}{\text{formed in 1 second}} = \frac{7.57x10^{-6} \text{ mol}}{20x60 \text{ s}}$

$$= 6.31 \text{ x } 10^{-9} \text{ mol s}^{-1}$$

$$\frac{dN_{co}}{dt} = 6.31 \text{ x } 10^{-9} \text{ x } 6.022 \text{ x } 10^{23} \text{ molecule second}^{-1}$$

$$= 3.80 \text{ x } 10^{15} \text{ molecule second}^{-1}$$

iv) Using Eq. 3.2 f_{CO} = $\frac{\text{Quantum efficiency for the}}{\text{formation of carbon monoxide}}$

$$= \frac{\frac{dN_{CO}}{dt}}{l_a} = 1$$

In the next section, we shall discuss the experimental method of determining the quantum efficiency of a reaction.

3.2 Experimental Determination of Quantum Efficiency

For the determination of quantum efficiency of a photochemical reaction, it is important we measure the following:

- the rate of decomposition of the reactants or the rate of formation of the products;
- the number of quanta absorbed in the given time.

In short, we need a method for measuring the amount of light absorbed, if we can devise a method for estimating the intensity of the incident light (l_o) and the intensity of the light transmitted (l) by the reaction mixture, the intensity of the light absorbed (l_a) can be calculated using the relationship;

$$I_a = l_o – l$$

For measuring l_o and l, same cell is used. I_o corresponds to the measurement of intensity with empty cell (known as blank) and l, to the measurement using the cell containing the reaction mixture.

The experimental set-up used for measuring the intensity of light is shown in Figure 4.2

As a source (A) of visible light, a high intensity tungsten lamp or quartz halogen lamp or xenon arc lamp can be used. For obtaining ultraviolet light, hydrogen or deuterium lamps are good sources. The light is first passed through a lens, B (to get a parallel beam of light), and then through a monochromator (C). The monochromator yields a narrow band of light in the desired wavelength. The monochromatic light then passes through the reaction cell (D). The light transmitted by the reaction cell reaches the detector (E).

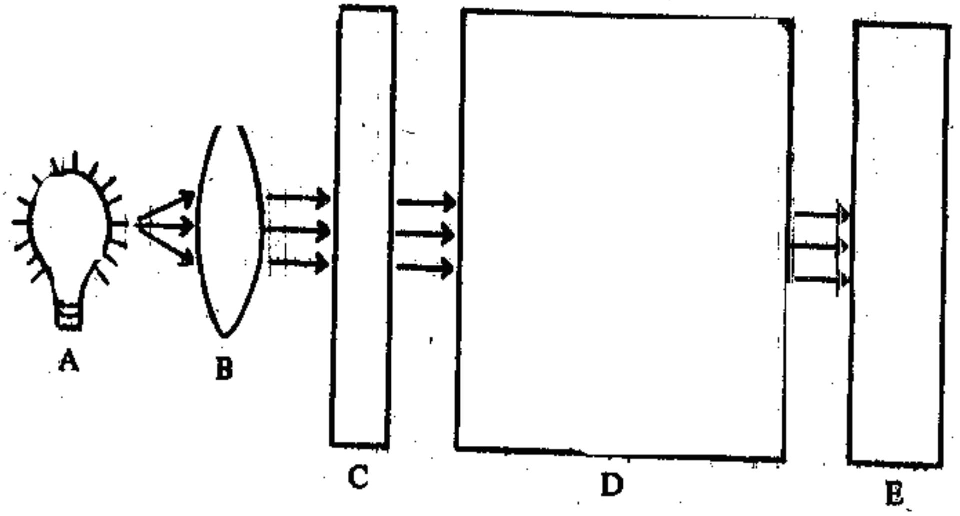


Fig 4.2: Measurement of Intensity of Light during a Photochemical Reaction

Note

- While using ultraviolet light as a source of radiation, quartz cuvettes (cells) and lenses must be used.
- Since pyrex glass absorbs light below 300nm, it can be used for radiation above 300nm only.
- The visible light has the wavelength region, 800-380nm. The ultraviolet light has wavelength below 380nm and above 199nm.

The detector is used for measuring the intensity of light. The quantitative measurement of light intensity based on energy conversion or on chemical reaction is called **actinometry**. Detectors such as thermopiles and the photoelectric cells function on energy conversion principle. We discuss each of them in brief below:

3.2.1 Thermopile

Thermopile (Fig. 4.3) is a device useful for converting light into heat, and then, heat into electricity. It has a set of junctions of different metals having a blackened surface. This black coating is to ensure absorption of all radiation falling on it. The energy so absorbed increases the temperature of the metals. Thermopile converts this temperature increase into a potential difference. Light intensity is related to electricity generated by it. The detector device must be calibrated against a standard light source. Thermopile could be used as a detector for light of any wavelength.

Note:
Thermopile consists of thermocouples connected in series and it generates electricity on heating

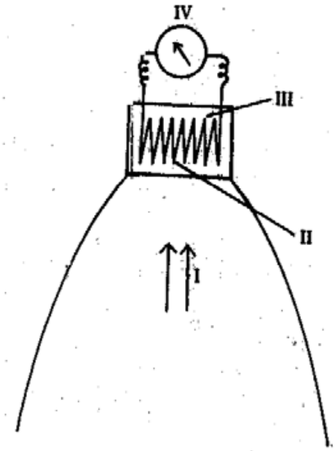


Fig. 4.3: Thermopile: I. Light radiation, II. Blackened surface exposed to radiation III. Unexposed surface at the back; IV. Galvanometer

3.2.2 Photoelectric Cells

Photoelectric cell converts light directly into electricity. The current generated is directly proportional to light intensity. Photoelectric cell is an evacuated bulb with a photosensitive cathode. Light radiation results in the emission of electrons from the cathode and then collected at the anode. Thus, the flow of current is caused. The photoelectric cell is sensitive to the wavelength of the light used and must be calibrated using a thermopile.

3.2.3 Chemical Actinometers

Light intensity could be estimated by a quantitative estimation of a substance formed or decomposed by light. The photochemical decomposition of $K_3Fe\ (C_2O_4)_3$ is a widely used chemical method for estimating intensity of light between the wavelength range 250nm and 577nm. Light within this wavelength range causes $K_3Fe(C_2O_4)_3$ dissolved in sulphuric acid to react as follows:

$2\ Fe^{3+} + 2e^- \longrightarrow 2\ Fe^{2+}$
$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-$

The concentration of Fe^{2+} is estimated calorimetrically through complex formation with 1,10-phenanthroline (see example 1). This complex has a deep red colour. The concentration of the complex is equal to the concentration of Fe^{2+} present before complexation occurs. The following example is worked out to illustrate this method.

Example 3

In a potassium ferrioxalate actinometer, the quantum efficiency for Fe^{2+} production (f FS) at 480 nm wavelength is 0.95. After irradiating the potassium ferrioxalate solution for 20 minutes, it is completely transferred to a $200cm^3$ volumetric flask, mixed with required quantity of 1,10-phenanthroline for complex formation and made up to mark with a buffer solution. For colorimetric estimation, a sample of this complex is taken in a cell of 1.00cm thickness. The complex has an absorbance value of 0.391 and its e is $1.11 \times 10^3 m^2\ mol^{-1}$.

Calculate:

i) the concentration of complex
ii) the number of Fe^{2+} ions formed in the actinometer due to irradiation
iii) the rate of formation of Fe^{2+} ions (dN_{FS}/dt)
iv) l_a (number of photons absorbed per second)

Assume that one Fe^{2+} ion forms one complex molecule with 1,10-phenanthroline.

Solution

i) Note that the concentration of the complex is same as that calculated in Example using Eq. 1.1; c = concentration of complex = 0.0352 mol m^{-3}

Also, concentration of Fe^{2+} ion = concentration of the complex

= 0.0352 mol m^{-3}

ii) Number of moles of Fe^{2+} Present in 200Cm^3 of the solution =

Concentration x Volume of the of Fe^{2+} solution in m^3 unit

= 0.0352 x 200 x 10^{-6} mol

= 7.04 x 10^{-6} mol

Because 200cm^3 = 200 x 10^{-6} m^3

Hence the number of moles of Fe^{2+} formed in the actinometer

= 7.04 x 10^{-6}mol

The number of Fe^{2+} ions formed in the actinometer

= 7.04 x 10^{-6} x 6.022 x 10^{23} ions

= 4.24 x 10^{18} ions

iii) $$\frac{dN_{FS}}{dt} = \frac{\text{Number of Fe}^{2+}\text{ ions formed}}{\text{Time in sec onds}} = \frac{4.24x10^{18}}{1200}\text{ ions second}^{-1}$$

= 3.53 x 10^{15} ions second^{-1}

(iv) Using Eq. 4.2 = $\frac{dN_{FS}/dt}{l_a}$

Given that f_{FS} = 0.95

Hence l_a = $-\frac{dN_{FS}}{x\ dt}\ \frac{1}{0.95}$

$$= \frac{3.53x10^{15}}{0.95}\text{ photons second}^{-1}$$

= 3.72 x 10^{15} photons second^{-1}

3.3 The Quantum Efficiencies of Some Reactions

If a photochemical reaction follows Stark-Einstein law, then f must be unity. Studies on a large number of photochemical reactions indicate that while some of them follow Stark-Einstein law, many others do not. The quantum efficiencies of some photochemical reactions along with their effective wavelengths are given in Table 4.1

Table 4.1: Quantum Efficiencies and Effective Wavelengths of Some Photochemical Reactions

Reaction	Effective wavelength/nm	f
$2NH_3 \rightarrow N_2 + 3H_2$	Đ210	0.2
$2NO_2 \rightarrow 2NO + 0_2$	Đ366	0.7
$H_2 + Br_2 \rightarrow 2HBr$	Đ511	0.01
$H_2S \rightarrow H_2 + S$	Đ208	1.0
$2HI \rightarrow H_2 + 1_2$	Đ327	2.0
$30_2 \rightarrow 20_3$	Đ175	3.0
$H_2 + Cl_2 \rightarrow 2HCl$	Đ478	10^6

The photochemical reactions for which quantum efficiency is a small integer are said to follow Stark-Einstein law. Examples are the dissociation of H_2S or ozonisation of oxygen etc. Reactions like the formation of hydrogen chloride or hydrogen bromide do not follow Stark-Einstein law. The quantum efficiency for the former reaction ($H_2 + Cl_2 \longrightarrow 2HCl$) is very high while it is much low for the latter ($H_2 + Br_2 \longrightarrow 2HB_r$). In order to explain these discrepancies, Bodenstein pointed out that photochemical reaction involved two distinct processes: the primary and the secondary processes.

i) In the primary process, absorption of one quantum of light results in the excitation of one molecule or an atom (A) to form the excited species, A^{D}

$$\underset{\text{Atom or molecule}}{A + hv} \longrightarrow \underset{\text{Excited species}}{A}$$

ii) In the secondary process, the excited species undergoes a chemical change

$$A \longrightarrow \text{Products}$$

According to Bodenstein, the deviations from Stark-Einstein law are due to the secondary processes.

In the case of reactions having low quantum yields, the number of molecules decomposed by the absorption of one quantum of radiation is less than one. The probable reasons for the low quantum yields are given below:

- The excited species formed at the first step may be deactivated by collisions before the product could be formed. This process is called *quenching*. Sometimes, the presence of paramagnetic substances like oxygen or nitric oxide could result in quenching leading to low quantum yield for a chemical reaction.
- One or more of the reactions in the secondary/primary processes may be endothermic. High energy requirement could decrease the reaction rate. The quantum yield for the formation of hydrogen bromide is low due to the endothermic nature of the reaction between Br and H_2 (see Example 5 in Sec. 3.5).
- The excited species may recombine to give the reactant molecule. In the hydrogen bromide formation, another reason for the low quantum yield is the recombination of bromine atoms which are formed in the primary step.

In the case of reactions with high quantum yields, the excited species formed in the first step could initiate a series of chain reactions. This causes a large number of molecules to react by absorption of one quantum of light, as in the case of hydrogen chloride formation (see Sec. 3.5).

4.0 CONCLUSION

Photochemistry is the study of chemical changes that are initiated by light. The first law of photochemistry, known as the Grotthuss-Draper law, states that light must be absorbed by a chemical substance in order for a photochemical reaction to take place. In other words, molecules that do not absorb light of a particular frequency will not undergo a photochemical reaction when irradiated at that frequency. The second law of photochemistry, the Stark-Einstein law, states that for each photon of light absorbed by a chemical system, only one molecule is activated for photochemical reaction. This latter law is also known as the photoequivalence law and was derived by Albert Einstein

5.0 SUMMARY

Photoreactions take place easily (provided absorption of light can occur) because the absorption of light promotes the molecule to an excited state that contains more energy than the stable ground state. Because the excited molecule contains more energy, it is more reactive. The advantage of photochemistry, where it works, is that it provides a short, direct route for chemical reaction.

6.0 TUTOR-MARKED ASSIGNMENT

i. A radiation of 250nm incident in H1 results in the decomposition 1.85×10^{-2} mol within a particular time interval. Light energy absorbed during this time interval is 4.18 k J.
Calculate the quantum efficiency for the decomposition of H1.

ii. The quantum yield for the photochemical formation of hydrogen chloride is high in the absence of oxygen but low when oxygen is present. Explain.

7.0 REFERENCES/FURTHER READING

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UNIT 2 PHOTOCHEMICAL DISSOCIATION

CONTENTS

1.0 INTRODUCTION

Photochemical dissociation involves the dissociation of chemicals by light. In this unit, some photochemical reactions and some photophysical processes will be discussed. Also, we shall examine the application of photochemistry.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- explain the reason for the higher energy requirement for the photochemical dissociation of a molecule as compared to its thermal dissociation
- derive rate expressions for simple photochemical reactions
- explain some photophysical properties such as fluorescence and phosphorescence
- list some photosensitised reactions
- state the applications of photochemical studies
- define chemiluminescence.

3.0 MAIN CONTENT

3.1 Photochemical Dissociation

It has been stated that the bond enthalpy gives an estimate of the average energy required to break a particular bond. These bond enthalpies are derived from thermochemical calculations. It is generally seen that the energy required for the dissociation of a particular bond by light absorption is much greater than its bond enthalpy value. In Table 4.2, we illustrate this for some diatomic molecules.

Table 4.2: Comparison of Photochemical Dissociation Energies and Bond Enthalpies

Dissociating molecules	l /nm	(Photochemical dissociation' energy) kJmol^{-1}	Bond enthalpy' kJ mol^{-1}
H_2	84.5	1420	436
$C1_2$	478	250	242
Br_2	511	235	193
HI	327	367	299
O_2	176	682	497

Note

Bond enthalpy of a diatomic molecule indicates the energy requirement for its thermal dissociation.

- value corresponds to maximum wavelength of light required for decompositions by direct irradiation.
- Photochemical dissociation energy for one mole is calculated by substituting for l in Eq. 3.4

The reasons for the higher photochemical dissociation energies as compared to bond enthalpies are given below:

- For dissociating a molecule through light absorption, there must be an upper electronic state with appropriate energy levels. There is no such restriction for thermal decomposition.
- During photochemical dissociation, the product species could be an excited state and/or in ground state. For example, decomposition of bromine by absorption of light of wavelength 511 nm can be shown as below:

$$Br_2 + h\,v \longrightarrow Br^{D} + Br \qquad l = 511 \text{ nm}$$

The atom with asterisk sign indicates excited state. Thus, photochemical decomposition of bromine needs 235kJmol^{-1}. But thermal decomposition of bromine needs 193kJ mol^{-1} only, since both the bromine atoms are formed in ground state.

The photochemical dissociation of molecules is also known as *photolysis*. The photolysis can be understood using potential energy diagrams.

In Figure 4.4, the ground state and the excited state are represented using potential energy diagrams I and II, respectively. The quantized vibrational sublevels in each state are shown by horizontal lines such as AB, EF etc.

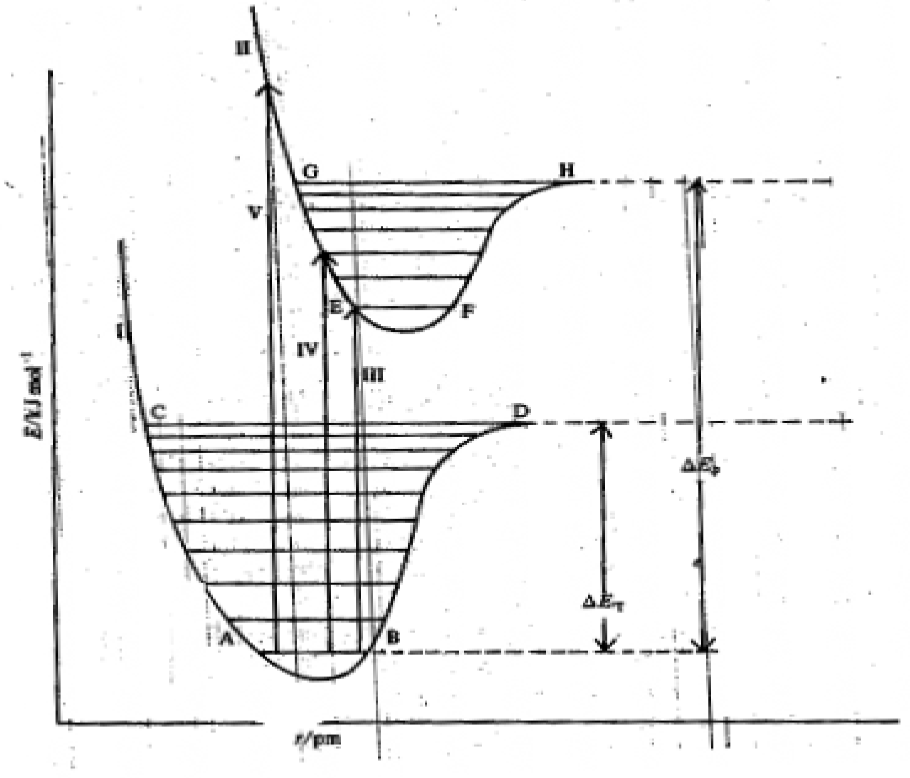


Fig. 4.4: Electronic Excitation; *E* (potential energy) vs *r* (internuclear distance)

When a molecule is excited from zero vibrational level AB of ground electronic state of any of the vibrational levels *below GH* in the upper electronic state, the resultant electronic spectrum shows an absorption band with vibration – rotation fine structure. The fine structure is due to numerous transitions (such as III, IV etc.) possible from the zero vibrational level (AB) in the lower electronic state to any of the quantised vibrational levels in the upper electronic state. This can further be understood from the fact that each vibrational level has its own rotational sublevels.

When a molecule absorbs sufficient energy such that it is transferred from the ground state to or above GH in the upper electronic state, then the molecule undergoes photochemical dissociation. The spectrum shows a continuum (lack for discrete lines), once the molecule dissociates. The difference in energy between the levels AB and GH (Ep) is the *photochemical dissociation energy*. *The thermal dissociation energy* (Et) is equal to the bond enthalpy in the case of diatomic molecules and it is the energy difference between the lowest and uppermost vibrational levels (AB and CD) in the ground state. Note that $E_p > E_T$.

We have disused photolysis in detail so far because it is initial reaction in many photochemical reactions. The excited atom or radical formed due to photolysis of a molecule often starts a chain reaction. We shall use this principle in the next section in the study of some photochemical reactions.

3.2 Some Photochemical Reactions

In this section, we shall discuss the mechanism of some photochemical reactions and explain flash photolysis. For the first two reactions given below, we derive rate equations also. You should go through these derivations carefully. These two examples could give you an idea as on how the photochemical rate expressions are written.

The first step in the both examples is photolysis. The rate of the photolysis step is expressed as I_a which is the rate of absorption of light (number of quanta absorbed per second). The initial photolysis is followed by thermal (or dark) reactions for which kinetic expressions are as similar to those discussed earlier in this course.

3.3 Photochemical Decomposition of Hydrogen Iodide

Let us derive expressions useful in calculating the rate of decomposition of HI and the quantum efficiency for this reaction. HI undergoes photochemical decomposition below 327 um. The mechanism is given below:

$$HI + h\nu \rightarrow H + I \qquad \frac{\text{Rate of}}{\text{photolysis}} = I_a \qquad \ldots 3.7$$

$H + HI \xrightarrow{K} H_2 + I$ …3.8

$I + I \xrightarrow{k} I_2$ …3.9

Such steps are written based on energy considerations.

Note

While deriving rate expressions, we try to eliminate terms contain active species using steady state principle.

HI is consumed in two ways as given in Eqs. 3.7 and 3.8. The rate of disappearance of HI can be written as follows:

$$\frac{-\,d[HI]}{dt} = I_a + k_2\,[H]\,[HI] \qquad \ldots 3.10$$

With respect to the steady state approximation, the concentration of the active species H is constants. In other words, its concentration does not vary with time.

i.e., $$\frac{d[H]}{dt} = 0 = I_a - k_2\,[H]\,[HI] \qquad \ldots.3.11$$

Note that H is formed as given in Eq. 3.7 and is used as highlighted in Eq. 3.8

Or $k_2\,[H]\,[HI] = I_a$ …3.12

Using Eqs. 3.10 and 3.12, we get,

$$\frac{-\,d[HI]}{dt} = 2\,I_a \qquad \ldots.3.13$$

Experimentally it has been observed that the quantum efficiency for HI decomposition is 2. It is worth nothing that the rate of decomposition of HI depends on the intensity of the absorbed light as given in Eq. 3.13.

Example

Photochemical Reaction between H_2 and Br_2

Hydrogen and bromine combine at wavelengths below 511 nm to give HBr as shown in the mechanism below. Let us calculate the rate of formation of HBr and also the quantum efficiency for this reaction.

$Br_2 + h\nu \rightarrow Br + Br$ $\text{Rate of photolysis} = I_a$ …..3.14

$Br + H_2 \leftrightarrow HBr + Br$ ….3.15

$H + Br_2 \leftrightarrow HBr + Br$ ….3.16

$H + HBr \xrightarrow{k_4} H_2 + Br$ ….3.17

$Br + Br \xrightarrow{k_5} Br_2$ …3.18

The rate of formation of HBr can be written as:

$$\frac{d[HBr]}{dt} = k_2 [Br] [H_2] + k_3 [H] [Br_2] - k_2 [H] [HBr] \quad ….3.19$$

Note that Br and H are active species and we can apply steady state approximation for these two.

$$\frac{d[H]}{dt} = 0 = 2I_a - k_2 [Br] [H_2] + k_3 [H] [Br_2] - k_4 [H] [HBr] -2k_5[Br] \quad .....3.20$$

The coefficient 2 in $2I_a$ and $2k_5 [Br]^2$ are due to the formation or disappearance of two bromine atoms in the respective steps.

$$\frac{d[H]}{dt} = 0 = k_2 [Br] [H_2] - k_3 [H] [Br_2] - k_4 [H] [HBr] \quad ….3.21$$

Adding Eq. 3.20 and using Eq 3.21 and rearranging we get,

$$2 k_5 [Br]^2 = 2I_a \quad ....3.22$$

Or

$$[Br] = (I_a / k_5)^{½} \quad …3.23$$

Rearranging Eq. 3.21 and using Eq. 3.23 we get,

$$[H] = \frac{k_2 [Br] [H_2]}{k_4 [HBr] + k_3 [Br_2]} = \frac{k_2 [H_2] (I_a/k_5)^{1/2}}{k_4 [HBr] + k_3 [Br_2]} \quad ….3.24$$

Using Eqs. 3.19, 3.23 and 3.24

$$\frac{d[HBr]}{dt} = k2\ (I_a/k_5)^{1/2}\ [H_2] + (k_3[Br_2] – k_4 [HBr])$$

$$\frac{k_2 [H_2] (I_a/k_5)^{1/2}}{k_4 [HBr] + k_3 [Br_2]} = \frac{2k_2k_3 (I_a/k_5)^{1/2} [H_2] [Br_2]}{k_4 [HBr] + k_3 [Br_2]}$$

Dividing the numerator and the denominator of R.H.S by $k_3 [Br_2]$

$$\frac{d[HBr]}{dt} = \frac{2k_2k_5^{-½} I_a [H_2]}{1 + k_4 [HBr] / k_3 [Br_2]} \quad …..3.25$$

i.e., $\frac{d[HBr]}{dt}$ a I_a½ ….3.26

This shows that the rate of hydrogen bromide formation is proportional to the square root of the absorbed intensity. This has been proved experimentally.

In the above two cases, we derived rate expressions. Next, we shall study the reaction between H_2 and $C1_2$ in a qualitative way, and then, study the principles of flash photolysis.

Hydrogen-Chloride Reaction

The quantum efficiency for the photochemical combination of hydrogen and chlorine is very high. When exposed to light of wavelength 478nm, the primary process in the photochemical reactions is the decomposition of chlorine.

$$C1_2 + hv \rightarrow 2\ C1 \quad ….3.27$$

This is followed by the following secondary processes:

$$C1 + H_2 \rightarrow HC1 + H \quad ….3.28$$
$$H + C1_2 \rightarrow HC1 + C1 \quad ….3.29$$

The reaction between C1 and H_2 (Eq. 3.28) is exothermic and much faster. This results in the propagation of chain reaction with high quantum efficiency. The chain-terminating step is the recombination of chloride atoms on the walls of the vessel to form chloride molecule.

$$C1 + C1 \rightarrow C1_2 \qquad \text{.....3.30}$$

Let us explain briefly the main features of flash photolysis. Flash photolysis is useful in detecting the short-lived intermediates in a reaction sequence. The reaction mechanisms are proposed based on flash photolysis results.

3.4 Flash Photolysis

Flash photolysis was developed by Norrish and Porter in 1949. In ordinary photolysis, the steady state concentrations of the intermediates are so small that these cannot be detected by absorption spectrophotometers. In flash photolysis, a high-intensity flash of microsecond duration is used for the photolysis substance and the products are identified using absorption spectrophotometers. The flash duration must match the decay rate of the intermediates. Flash lamps work for a time of around 15 µ s. This restricts their use to the study of intermediate of life time around 100 µs. In recent years, laser flash sources have been developed. The flash duration is around 10^{-9} s.

As far as this section is concerned, make sure that you understand the derivations for calculating the rate of decomposition of hydrogen iodide and the rate of formation of hydrogen bromide. This could help you in arriving at the rate expressions for simple photochemical reactions for which reaction sequence (like Eq. 3.14 to Eq.3.18) is known. You can build up confidence by answering the SAE given below. The aim of this SAE is to make you derive expression for the rate of formation of carbon monoxide in the photolysis of acetaldehyde. You are guided through a series of steps with helpful hints. This guidance has added to the length of the problem.

SELF-ASSESSMENT EXERCISE

Given the reaction sequence for the photolysis of acetaldehyde:

$$CH_3CHO + h\nu \rightarrow CH_3 + CHO \quad \begin{array}{c}\text{Rate of}\\ \text{photolysis}\end{array} - I_a \qquad \text{...(1)}$$

$$CH_3 + CH_3CHO \leftrightarrow CH_4 + CH_3CO \qquad \text{...(2)}$$

$$CH_3CO \leftrightarrow CH_3 + CO \qquad \text{...(3)}$$

$$CH_3 + CH_3 \leftrightarrow C_2H_6 \qquad \text{....(4)}$$

I_a is the absorbed light intensity and it represents the rate of photochemical excitation (as per Eq.(1).

Using the above mechanism, derive expressions for the following:

i) $\frac{d[CH_3CO]}{dt}$ ii) $\frac{d[CH_3]}{dt}$

Hints: CH_3CO and CH_3 are active species. CH_3CO is formed as given in Eq. (2) and consumed as per Eq. (3). CH_3 is formed (Eqs. (1) and (3)). CH_3CO is used up as given in Eqs. (2) and (4). The answers for (i) and (ii) are to be arrived at using Eqs. 3.21and 3.22 as models. Note that with respect to Eq. (4), two CH_3 radicals are consumed for every molecule of ethane formed).

iii) Derive the combined expression for $\frac{d[CH_3CO]}{dt} + \frac{d[CH_3]}{dt}$

Hints: Add up the expressions you have got as answers for (i) and (ii)

Note:

For a 2-election system, the first three singlet states are represented below:

iv) Find the relationship between $[CH_3]$and I_a

Hint: Rearrange the answer for (iii)

v) State the relationship between $\frac{d[CO]}{dt}$ and $[CH_3CO]$

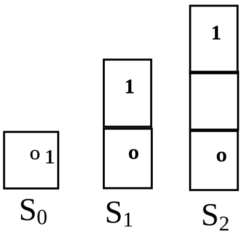
(**Hint**: Use Eq. (3).

vi) Find the relationship between the rate of formation of CO and the absorbed light intensity.

(**Hint**: First combine answers for (v) and (i). Then use the answer for (iv)

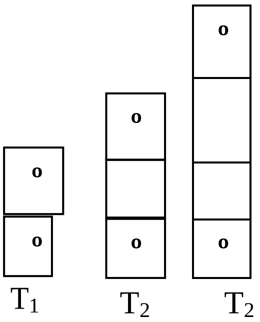
Note

For a 2-electron system, the first three singlet states are represented below:



Note that $E_{s2} > E_{s1}$ where E stands for the energy of a particular level.

Similarly, the first three triple states are represented below for a 2-electron system:



$E_{T3}>E_{T2}>E_{T1}$

3.5 Photophysical Processes

The light absorbed by a molecule is not always used up in producing a chemical reaction. The absorbed energy can be lost through various physical processes. In this section, we shall examine such physical processes.

The adsorption of ultraviolet or visible light results in the increase of electronic energy from the ground to the excited states. Usually, electronic excitation is also accompanied by an increase in the rotational and vibrational energy levels. In our discussion, for convenience, we shall depict only transitions between electronic energy levels. In order to understand the nature of electronic transitions, it is essential to know the concept of spin multiplicity. A molecule with electrons pairs and with anti-parallel spins is said to be in single ground state (S_o). An excited molecule with *two of its electrons unpaired and, with anti-parallel spins* is said to be in the excited singlet state such as S_1, S_2, S_3,…etc. An excited molecule with *two of its electrons unpaired, but with parallel spins* is said to be in the excited triple state such as T_1, T_2, T_3…etc.

Note

Normally excitation of a ground state molecule leads only to one of the excited singlet states. But in some specified cases, direct excitation from S_0 to a triplet level is possible. We restrict our discussion to S_0S_1 ,S_0 S_2 etc, transitions only.

Multiplicity of state is given by the expression 2*S* + 1, where *S* (note the italicised type) is the sum of spin values of electrons. This symbol *S* should not be confused with S (Roman type) for singlet state.

Imagine a molecule in the singlet state, that has two electrons with anti-parallel spins (such as ^{o1}). Then, sum of the electron spins

$= S = +\frac{1}{2} - \frac{1}{2} = 0$

Hence multiplicity
$= 2S + 1 = (2x0) + 1 = 1$

Normally, a molecule in the S_0 state on absorbing a quantum of light gets two of its paired electron unpaired and gets transferred to S_1 or S_2 or S_3…etc., levels, but not to T_1 or T_2 or T_3…etc. levels. This implies that due to excitation, spin multiplicity is not generally altered. This condition is called the *selection rule for electronic transition*. In other words, absorption of energy by the molecule in the ground state leads to allowed transition such as $S_0 \longrightarrow S_1$, $S_0 \longrightarrow S_2$, $S_0 \longrightarrow S_3$ and so on. Such excitations and the subsequent energy loss while reaching the ground state are shown by Jablonski diagram (Fig. 4.5). The solid arrows pointing upwards refer to absorption of energy. The solid arrows pointing downwards refer to energy emission as light, known as *radiative transition*. The wavy horizontal arrows stand for transition between excited singlet and triplet state without energy loss, while wavy vertical arrows stand for transition between singlet-singlet or triplet-triplet levels with energy loss as heat (the latter is not shown in Fig. 4.5). These wavy arrows stand for *non-radiative transition* (transitions without light emission).

Note

Thus, the singlet state has two electrons with anti-parallel spins and its (2*S* + 1) value is equal to 1. In the presence of a magnetic field, a molecule in the singlet state does not split further.

A molecule in the triplet state has two electrons with parallel spins (such as **ºº**). The sum of electron spins.

$= S = \frac{1}{2} + \frac{1}{2} = 1$

Hence the multiplicity = (2*S* + 1) = 3

So, a molecule in the triplet state has two electrons with parallel spins and its (2*S* + 1) value is equal to 3. In the presence of a magnetic field, a triplet state splits into three energy levels.

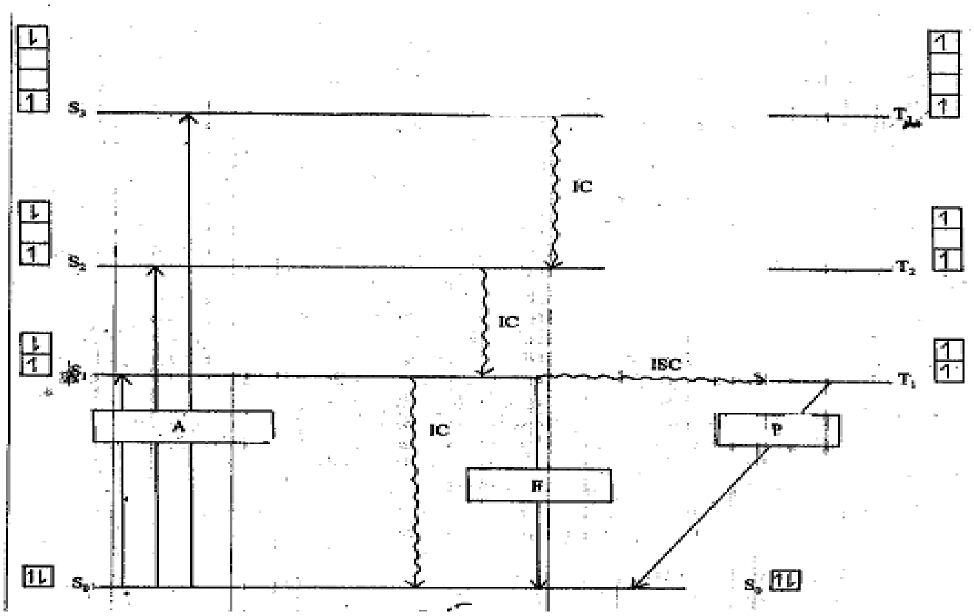


Fig. 4.5: Jablonski Diagram

In Fig. 4.5, the excitation from the singlet ground state to the excited singlet levels; S_1, S_2 and S_3 are shown by vertical arrows marked A. The excited species at S_2 and S_3 have very short life span and these species, quickly lose their energy as heat to the medium in about 10^{-11} second and reach S_1 level. Such a singlet-singlet transition is called an **internal conversion** (IC). The molecule at S_1 state has a life time 10^{-8}-10^{-10} second. The system at S_1 may undergo any of the following transitions.

A = Absorption of quanta leading to excitation to S_1, S_2 and S_3 levels.
Note the anti-parallel spins at various S levels
IC = Internal conversion from S_3 to S_2, from S_2 to S_1 and from S_1 to S_0
F = Fluorescence; a transition from $S_1 \longrightarrow S_0$ with light emission
ISC = Intersystem crossing; $S_1 \longrightarrow T_1$ transition. Note the parallel spins at various T levels
P = Phosphorescence; a transition from $T_1 \longrightarrow S_0$ with light emission

For clarity, transition to and from T_2 and T_3 are not shown.

Note

The name "fluorescence" is derived from the name of the mineral, "fluorite", which emits visible light on exposing to ultraviolet radiation.

i) Fluorescence

The excited molecule could undergo the transition, $S_1 \longrightarrow S_0$, with emission of light. This phenomenon is called fluorescence (F). Since S_1 S_0 transition is allowed by selection rule, it is very fast. In other words, substances fluoresce in the presence of the exciting radiation. Once the exciting radiation is stopped, the fluorescence stops.

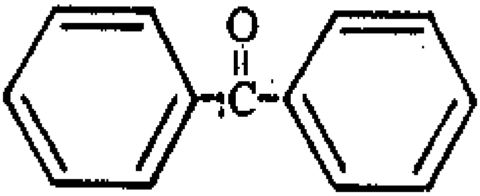
ii) Internal Conversion

The excess energy may be lost as heat while $S_1 \longrightarrow S_0$ transition takes place which is again a case of internal conversion and a radiationless transition.

iii) Intersystem Crossing

The excited molecule could cross over to the first triplet state through S_1 T_1 transition. Such a transition involves spin inversion. For such intersystem crossing (ISC) to be efficient, the energy gap between S_1 and T_1 levels must be low.

Ketones have very low energy gap between S_1 and T_1 levels and have high efficiency for intersystem crossing. Thus benzophenone has 100% efficiency for intersystem crossing. Compared to ketones, aromatic hydrocarbons are less efficient in intersystem crossing and olefins are still less efficient. Let us now study two of the processes by which the molecule in the triplet state could reach the ground state.



Benzophenone

1) Phosphorescence

An interesting physical process by which an excited species at T_1 level may undergo transition to S_0 level is by emitting light; $T_1 \longrightarrow S_0$ transition with emission of light is called *phosphorescence (P)*. This is a process with a spin change and is a forbidden transition. Hence, in contrast to fluorescence, light emission during phosphorescence is slow and it lasts even after the removal of exciting radiation.

2) Energy Transfer

Another process by which a molecule in the triplet state (called a donor molecule) may lose its excess energy is by energy transfer to an acceptor molecule. This is an instance of *sensitisation* which we shall discuss later in this unit.

Let us now see some of the applications of the study of the physical processes. Study of fluorescent behaviours of substances has led to the development of fluorescence spectroscopy. Using spectrofluorometers, it is possible to identify several fluorescing substances present in the same solution; provided they have sufficiently different fluorescent such as 10^{-9}g/cm^{3} could be detected. For example, this method is quite useful in the analysis of drugs, pesticides and atmospheric pollutants which are present in trace amounts. Studies based on fluorescence and phosphorescence provides important data on the properties excited states such as lifetime, energy and electronic configuration.

On the commercial side, fluorescent lamp is one of the applications of the phenomenon of florescence. A florescent lamp consists of a glass tube with

- a small amount of mercury
- two electrodes
- a coating of phosphor.

A phosphor is a solid substance which emits fluorescent light when excited with an ultraviolet radiation. The electrodes initiate an electric arc which helps in vaporising and exciting mercury atoms. The excited mercury atoms emit ultraviolet radiation. The phosphor, being excited by ultraviolet radiation, emits fluorescence.

Some other commercial applications of fluorescence are given below:

- Optical brighteners are added to detergents to give extra-brightness to the clothes. Optical brighteners fluoresce in sunlight.
- Fluorescent paints are manufactured using suitable additives.
- TV screens of different colours are produced using phosphors.

Although molecules in the excited singlet and triple states could show interesting chemical behaviour, their studies are included in Organic Reaction Mechanism, your second semester course. In the next section, we shall discuss photosensitisation; this discussion could make you understand how a substance gains photochemical activity in the presence of another photochemically excited substance. Based on the materials of this section, answer the following SAQ.

SELF-ASSESSMENT EXERCISE

State two differences between fluorescence and phosphorescence.

3.6 Photosensitisation

Photosensitisation is the process of exciting a molecule by energy transfer from an excited molecule. In this process, a donor molecule (D) absorbs a quantum light and forms an excited molecule ($D^{\cdot}$). The excited donor molecule then transfers its excitation energy to an acceptor molecule (A) in the ground state in order to excite it. This can be explained using the following reaction sequence:

- Light absorption : $D + hv \rightarrow D^{\cdot}$
- Sensitisation : $D^{\cdot} + A \rightarrow A^{\cdot} + D$

The donor molecule is called sensitiser. We have earlier mentioned about such energy transfer by the excited molecule. The excited acceptor molecule A could take part either in chemical reactions or in physical processes which we shall discuss now.

3.7 Photosensitised Chemical Reactions

If the excited molecule A has obtained sufficient energy, it will get dissociated and start a chemical reaction. The advantage in photosensitised dissociation of a molecule is that it is enough to transfer energy equivalent to its bond enthalpy to dissociate it. This is so since the photosensitised molecule gets dissociated in the ground state. This is in contrast to direct photochemical decomposition for which much higher energy is required due to the necessity of exciting a molecule to upper electronic state. Thus, the energy required for photosensitised dissociation of a molecule is less than that of photochemical dissociation.

Let us consider an example. When irradiated with 253.7 nm light, hydrogen and oxygen react in presence of mercury vapour but not in its absence. Mercury vapour acts as a sensitiser. The reaction sequence is given below:

$$Hg + hv \rightarrow Hg^{D}$$
$$Hg^{D} + H_2 \rightarrow H + H + Hg$$
$$H + O_2 \rightarrow OH + O$$

The chain reaction continues further. The energy transferred to hydrogen molecule by excited mercury atom is equal to 472 kJ mol^{-1} (as given in Eq. 3:4 where l = 253.7nm). This energy is sufficient for thermal dissociation of hydrogen since its bond enthalpy is 436 kJ mol^{-1}. Note that excited mercury atom cannot directly dissociate oxygen molecule since its bond enthalpy is higher (497 kJ mol^{-1}). Further in the absence of mercury vapour, light of 253.7 nm (or 472 kJ mol^{-1} energy) cannot photolyse hydrogen or oxygen directly, since the energies needed for their photochemical dissociation are much higher (1420 kJ mol^{-1} and 682 kJ mol^{-1} respectively). Hence mercury vapour is essential as a sensitiser for H_2-0_2 photochemical reaction as l = 253.7 nm.

A well-known photosensitised reaction is photosynthesis. Chlorophyl ("chl") and other plant pigments act as photosensitiser in the synthesis of starch from carbon dioxide and water. A simplified reaction sequence is as follows:

$$\text{chl} + h\nu \rightarrow \text{chl}^{\cdot} \quad \text{Starch}$$

$$\text{chl}^{\cdot} \quad CO_2 + H_2O \rightarrow \frac{1}{n}\left(CH_2O\right)_n + 0_2 + \text{chl}$$

Note:

Chlorophyll is the name given for a group of compounds with minor variation in structure. Chlorophyll absorbs effectively in the red region of sunlight; the red light is in abundance in sunlight.

The reaction mechanism is very complex. Energy calculations show that apart from chlorophyll, there must be other coloured light-absorbing materials (pigments) which also provide energy required for the synthesis of starch.

Photosensitisation is frequently used by chemists for preparing compounds which cannot be formed by thermal or direct irradiation methods.

3.8 Sensitised Fluorescence

Let us at this juncture, discuss a physical process which proceeds through sensations. Thallium vapour does not give rise to fluorescence when directly irradiated with light of wavelength 253.7nm. But if mercury vapour is also included in the reaction vessel, thallium exhibits fluorescence. Mercury atoms get excited first and transfer energy to thallium atoms to excite them. The excited thallium atoms emit fluorescent as they go down to the ground level.

Using the ideas learnt in this section, answer the following SAE.

3.9 Applications of Photochemistry

We have earlier indicated the applications of the study of fluorescence, phosphorescence, flash photolysis and photosensitisation. Apart from the above, a few are worth mentioning.

Synthetic organic chemists have increasingly started using photochemical methods for synthesis due to greater efficiency and selectively as compared to dark reaction. Photochemistry offers a method of conducting reactions which are not possible thermodynamically.

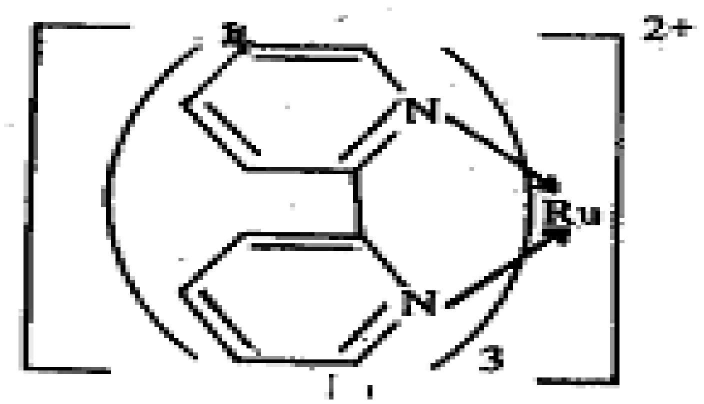
In the analysis of pollutants, photochemistry plays an important role. For example, photochemical studies have indicated how ozone layer is affected by chlorofluorocarbons (Freon) used as refrigerants, solvents and spray-propellants. The simplest Freon is CF_2CI_2. Freon is chemically inert and remains as such for years. But when it stratosphere (10 to 50km above the earth’s surface), Freon decomposes and gives out free chlorine atoms. These chlorine atoms can react with ozone decomposing it. This can cause depletion on ozone layer. It is a matter of serious concern since ozone layers protects our planet from low wavelength portion of sun’s rays (290nm-320nm wavelength). Irradiation with such high energy radiation could product skin cancer. As a result of photochemical studies, alternatives are tried for Freon.

The present energy crisis has compelled the scientists to look for alternatives. Solar energy, if properly utilised through suitable photochemical reactions, could offer a solution for this energy problem. In this connection, we shall now discuss the functioning of a photogalvanic cell which is help for solar energy conversion through chemical reactions.

Notes:

Three common types of cells used for converting light into electricity are given below:

i) Photoelectric cells or photo cells convert light into electricity using photosensitive cathode.
ii) Photovoltaic cells have two dissimilar silicon (or germanium) crystals in close contact. Irradiation of light causes flow of electrons from one crystal to other. Solar cells used in calculators are photovoltaic cells.
iii) Photogalvanic cells convert light into electricity through chemical reactions.



Tris – (2,2’ – bipyridine)
Ruthenium (II) ion

3.9.1 Photogalvanic Cell

A reversible cell which converts light into electricity through an intermediate chemical reaction is called photogalvanic cell. It undergoes cyclic charging and recharging process as explained below:

3.9.2 Charging in Presence of Light

Two substances undergo oxidation – reduction in presence of light

$$OA_1 + RA_2 \rightarrow OA_2 + RA_1$$

In this OA_1 and RA_1 refer to oxidised and reduced from of substance 1, while OA_2 and $RA_2$to those of substance 2. In this process, light is used in conducting a chemical reaction. This photochemical reaction is thermodynamically non-spontaneous ($\Delta G>0$). By the above photochemical process, the cell is charged.

3.9.3 Discharging in the Absence of Light

In the absence of light, the reaction reverses spontaneously. $\Delta G>0$).

$$OA_2 + RA_1 \longrightarrow OA_1 + RA_2$$

The chemical energy gained during charging is converted into electrical energy and the cell is discharged.

An example of such systems is given below:

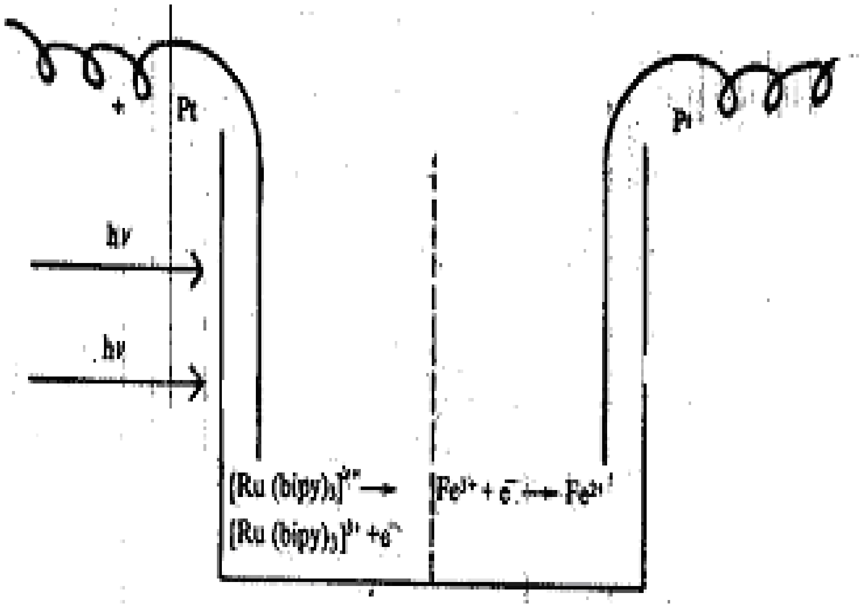


Fig. 4.6: Photogalvanic Cell

Fe^{3+} + Ru $(bipy)_3$ → Ru (bipy) $_3$ + fe^{2+}

In this system, tris- (2,2'-bipyridine) ruthenium (II) – tris- (2,2'-bipyridine) ruthenium (III) and iron (II) – irons (III) are the two redox pairs. The platinum electrodes serve as electrical contacts (Fig. 3.6).

In the next section, we shall discuss chemiluminescence, which in a way, is the reverse of photochemical reaction.

Note:

Photocheomism is the light induced reversible colour change. The colour change is brought about by reversible reactions. Photochromic sunglasses darken in sunlight and protect the eyes from the excess light. The sunglasses contain Ag' and react reversibly as follows:

In presence of sunlight:

Ag^{+} (s) + $Cu^{+\ (s)}$→ Ag (s) + Cu^{2+} (s)

Silver formed is responsible for the darkening of the glasses.

In the absence of sunlight:

Ag (s) + Cu^{2+} (s) →Ag^{+} (s) + Cu^{+} (s)

3.9.4 Chemiluminescence

Chemiluminescence is the emission of light as a result of chemical reaction at room temperature. It must be clearly understood that chemiluminescence is not due to any photophysical process like fluorescence or phosphorescence. Some examples of chemiluminescence are given below:

- Glow of phosphorus is due to slow oxidation; it is not due to phosphorescence as name suggests.
- Oxidation of Grignard compounds by air or oxygen results in greenish-blue luminescence
- *Will-o-the-wisp* (mistaken as light produced by evil spirits) is the glow caused by the oxidation of decaying wood in marshy places.
- Emission of light by firefly is due to oxidation of some proteins in its body (this is also called bioluminescence).

4.0 CONCLUSION

In this unit, we have dealt with some of the important physical processes of photochemistry as well as some of the applications of the study of the physical processes.

5.0 SUMMARY

In this unit, we have discussed the physical and chemical processes accompanying light absorption. The photophysical processes have been explained. The applications of fluorescence and phosphorescence have equally been stated while photosensitisation and chemiluminescence have been explained with examples.

6.0 TUTOR-MARKED ASSIGNMENT

i. In the photochemical dissociation of HI, the first step is given below:

$HI + h\nu \rightarrow H + I$

Note

The excess energy ($\Delta E_p. - \Delta E_T$) that a photochemical decomposition demands as compared to thermal decomposition is given to one of the atoms formed. This atom is said to be in the excited state.

Assume that H atom formed is in excited state while I atom is in ground state. Calculate the excess energy that the excited hydrogen atom carries as (use Table 19.2) compared to a ground state hydrogen atom.

ii. Oxalic acid is not decomposed directly by light of wavelength, 335 nm. Irradiation in presence of uranyl $\left(\mathrm{UO}_2^+\right)$ ion results in the decomposition of oxalic acid to carbon monoxide and carbon dioxide.
   a. How do you explain this reaction?
   b. Suggest a reaction sequence.

(**Note**: the above procedure was used in the earlier chemical actinometrical method of determining the light intensity. Oxalic acid solution of known concentration was irradiated in presence of uranyl ion and the reacted oxalic acid was estimated using potassium permanganate solution. From the amount of oxalic acid reacted, the intensity of light was calculated using f for a particular wavelength.)

iii. Suggest a basic difference between galvanic cells (discussed in CHM 112 and photogalvanic cells

7.0 REFERENCES/FURTHER READING

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APPPENDIX II

Derivation of Eq. 2.97: $\Delta H^{\ddagger} = \boldsymbol{E_a} - \mathbf{2RT}$

According to Eq. 2.59, ln k = in A – E_a/RT. Differentiating with respect to temperature and assuming A and E_a to be independent of temperature,

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

or $$Ea = RT^2 \frac{d \ln k}{dT}$$

This equation can be represented in the following form under constant volume conditions:

The change in concentration of a species is related to

- the change in the amount
- the change in the volume of the system.

If volume of the system is kept constant, the change in concentration of the species could be directly related to the change in the amount of species.

Keeping this in view, many reaction rates are measured under constant volume conditions. Reactions taking place in closed vessels are examples of this type.

$$E_a = RT^2 \left(\frac{\partial \ln k}{\partial T}\right)_v \quad \text{…(A.1)}$$

$$E_a = RT^2 \left(\frac{\partial k/k}{\partial T}\right)_v = \frac{RT^2}{k}\left(\frac{\partial k}{\partial T}\right)_v \quad \text{…(A.2)}$$

Rewriting Eq. 2.91

$$K = \frac{RT}{p^0}\frac{k_bT}{h} K_p$$

$$K = V^0 \frac{k_bT}{h} K_p \text{………(A.3)}$$

RT

P^0

where —— $= V^0$ = standard volume

$$\left(\frac{\partial k}{\partial T}\right)_v = \frac{V^0 k_b}{h}\frac{\partial (TK_p)}{\partial T}_v$$

$$\left(\frac{\partial k}{\partial T}\right)_v = \frac{V^0 k_b}{h}\left[K_p + T\left(\frac{\partial K_p}{\partial T}\right)\right]_v \quad \ldots(A.4)$$

Using Eqs. A.3 and A.4

$$\frac{1}{k}\left(\frac{\partial k}{\partial T}\right)_v = \frac{h}{V k_b TKp}\,\frac{V^0 k_b}{h}\left[K_p + T\left(\frac{\partial K_p}{\partial T}\right)_v\right]$$

$$= \frac{1}{TK_p}\left[K_p + T\left(\frac{\partial k_p}{\partial T}\right)\right]_v \quad \ldots\ldots\ldots (A.5)$$

$$\frac{RT^2}{k}\left(\frac{\partial k}{\partial T}\right)_v = \frac{RT^2}{TK_p}\left[K_p + T\left(\frac{\partial k_p}{\partial T}\right)\right]_v$$

$$= \frac{RT}{K_P}\left[K_P + T\left(\frac{\partial K_p}{\partial T}\right)\right]_v$$

$$= RT\left[1 + T\,.\,\frac{1}{K_p}\left(\frac{\partial K_p}{\partial T}\right)_v\right]$$

$$\frac{RT^2}{k}\left(\frac{\partial k}{\partial T}\right)_v = RT + RT^2\left(\frac{\partial \ln k_p}{\partial T}\right)_v \quad \ldots(A.6)$$

Using (A.2) and (A.6)

$$E_a = RT + RT^2\left(\frac{\partial \text{ in } k_p}{\partial T}\right)_v \quad \ldots (A.7)$$

$$- d \ln k_p = \frac{11H^o}{RT^2} \quad \ldots\ldots\ldots\ldots (2.102)$$

Under constant volume conditions, takes the form.

$$RT^{2}\left(\frac{\partial \ln k_{p}}{\text{v}}\right)_{\partial T} = \Delta U^{\ddagger} \qquad \ldots \text{(A.8)}$$

where $\Delta U^{\ddagger}$ is the molar activation internal energy.

From Eqs. A.7 and A.8,

$$E_{a} = RT + \Delta U^{\ddagger} \qquad \ldots \text{(A.9)}$$

Applying Eq. 4.15 pf CHE 112 for the formation of the activated complex,

$$\Delta H^{\ddagger} = \Delta U^{\ddagger} + \Delta n_{g}RT$$

Δn_{g} = Difference in the number of moles between the gaseous reactants and the gaseous products.

= -1 (for the formation of the activated complex as per Eq. 2.89) …(A.10)

Hence $\Delta H^{\ddagger =} \Delta U^{\ddagger} - RT$

Using Eqs. A.9 and A.10,

$$E_{a} = \Delta H^{\ddagger} = \Delta U^{\ddagger} + 2RT$$

or $\Delta H^{\ddagger} = E_{a} - 2RT$

The last one is Eq. 2.97

Eq. A.160 written below specifying the physical state $X(g) + Y \rightarrow A^{\ddagger}(g)$