COURSE GUIDE

CHM 407
CHEMICAL KINETICS

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Reviewed 2020

Printed 2021

ISBN: 978-978-058-096-4

COURSE GUIDE

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INTRODUCTION

The origin of chemical kinetics has been traced to several scientist. For example, in 1864, Peter Waage and Caton Guldberg pioneered the development of chemical kinetics by proposing the law of mass action, which now form the basis of elementary reaction. Vant Hoff studied and discovered chemical dynamics and osmotic pressure in 1884 and was awarded the first Noble Prize in Chemistry in 1901. After van’t Hoff, chemical kinetics was expanded to contain experimental determination of reaction rates from which rate law and rate constants were discovered. In recent times, chemical kinetics has been fully developed to address numerous industrial, environmental, health, agriculture, astronomy and other life processes.

Chemical kinetics is a branch of chemistry that study the rate of chemical reaction and how the rate can be controlled for optimum productivity in the affected areas. Concepts common in chemical kinetics are rate of reaction, which describes how much reactant is consumed with time or how much product is formed with time), order of reaction, molecularity of a reaction (which describes the number of molecule associated with the rate determining step), rate law (experimental rate equation), etc. In order to unfold its beauty, chemical kinetics employs several mathematical tools such as integration, differentiation, inequality, etc. In analysing the kinetic of any chemical processes, chemical kinetics must necessarily employ mathematical and chemical tools to derive equation that can stand as a model for the various stages that gives the product.

The study of chemical kinetics has widely captured various life and industrial processes. For example, kinetics of photochemistry captures photosynthesis and photography while kinetic of catalysis captures industrial production, environmental safety, etc.

COURSE COMPETENCIES

Electrochemistry (CHM 409) is a course which addresses first, second and third order rate equations. Rate constants, and equilibrium constant collision theory, transition state theory, reaction coordinates. Unimolecular reaction theory, Bimolecular reaction mechanism: Chain reaction mechanisms; catalysis and heterogeneous reactions. Photochemical reactions mechanism.

This course is aimed to bring the student to the knowledge of fundamental aspect, theory and laws in chemical kinetics, catalysis and photochemistry. Derivation of rate equations and other equation is give strong emphasis in this course. Worked examples are provided in each unit

COURSE OBJECTIVES

- To introduce the students to chemical kinetics concepts
- To introduce the student to order of reaction and derivation of rate law for first, second and third order
- To introduce the student to the concept of elementary reactions and model unimolecular, bimolecular and termolecular elementary reactions
- To introduce the concept of theories of chemical reactions and explain qualitative and quantitative significant of Arrhenius, collision and Transition state theories
- To explain catalysis in details and use qualitative and quantitative models to simplify the concept
- To review in details, the concept of photochemistry, classification, application and associated kinetic equation

WORKING THROUGH THIS COURSE

The course is structured into sic study sections. It is necessary that for the student to study and understand the content of all the units in the respective modules.

STUDY UNITS

You will be provided with the following materials:

1. Course Guide

2. Modules: There are three modules in this course. Each module consists of two study units.

Module 1

Study Unit 1 introduces chemical kinetics, how to calculate rate of equation, expressions for theoretical rate equation and rate law. It also explains order of reaction (zero, first, second and third order) and finally explain pseudo order reactions. Derivation of integrated rate equations have been done for each of the kinetic order.

Study Unit 2 explain theories of chemical reaction including Arrhenius, collision and Transition state theories.

Module 2

Study Unit 1 explain the concept of elementary reactions and give explanations for unimolecular, bimolecular and termolecular reaction. Molecularity of a reaction has been deeply explained. Theories on rate of reaction including Lindeman theory have been explained and associated integrated rate laws have been derived. The session ends by explanation of the concept of steady state approximation.

In Study Unit 2 explanations are given to various concepts of complex reaction. Integrated rate laws are derived for opposing reaction, consecutive reaction, competitive reaction and for chain reaction. Chain reaction is singled out for elaborate detail discussion because of its significant.

Module 3

Study Unit 1 explains catalysis in details (what they are, what they do and where they are needed). Classification of catalyst base on various approaches have been explained. Industrial application of catalyst and their characteristics have been discussed in details. Integrated rate equations have been derived for autocatalysis, acid catalysis and enzyme catalysis.

Study Unit 2 discusses photochemistry in details. Laws of photochemistry, differentiation between photophysical and photochemical processes, mechanism of photochemical processes, experimental monitoring of photochemical reactions and photochemistry of vision were discussed in details.

REFERENCES AND FURTHER READINGS

Textbooks referred to in the development of each units are presented at the end of the units. However, list of some General references is presented below:

Albini, A., Fasani, E. And Prott, S. (2018). *Photochemistry*. Vol 45. Royal Society of Chemistry, UK.

Ameta, R. And Amet, S. C. (2017). *Photocatalysis: Principles and Application*. CRC press, UK.

Atkins, P. and de Paula, J. (2018). *Atkins'Physical chemistry*. 11th Edition. Oxford University Press. UK.

Engel T. and Reid, P. (2005). *Physical chemistry*. Pearson Cummings. San Francisco. New York.

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Evans, R. C., Douglas, P., Burrow, H. D. (Eds.) (2015). *Applied photochemistry*. Springer International Pub. UK.

Hammerich, O. and Speiser, B. (2015) *Organic electrochemistry* 5th edition, revised and expanded. Taylor & Francis Publication, UK. ISBN: 978-1-4200-8401-6 (hardback), 978-1-4200-8402-3

Jack, R. and Scholz, F. (2017). *Wilhelm Ostwald. The Autobiography*. Springer, Germany, ISBN: 978-319-46955-3, and 978-3-319-46953 (print)

Kulikovsky, A. (2018). *Analytical models for PEM fuel cell impedance*. Andrei Kulikovsky, USA. 2018, ISBN: 9781521470749

Levine, N. I. (2018). *Physical chemistry*.5th Edition. Higher Education. Boston.

Molina, A. and Gonzalez, J. (2016). *Pulse voltammetry in physical electrochemistry and electroanalysis. Theory and applications*. Springer, UK, ISBN: 978-3-319-21250-0

Monk, P. (2004). *Physical chemistry: Understanding the Chemical World*. John Wiley and Sons Ltd. England.

Perico, M. And Granuci, G. (2018). *Photochemistry: A modern theoretical perspective*. Springer International Pub. UK.

Politano, F. And Mansilla, G. O. (2018). Light on the horizon: current research and future perspective in flow photochemistry. *Organic Process Research and Development* 22: 1045-1062.

PRESENTATION SCHEDULE

This course is presented in three different modules. Each module consists of two study units. Each module begins with introduction, study outcomes and main content. Within the main content, fundamental facts are presented along with inline worked examples and answers. Each unit ends with summary, conclusion, bibliography, self assessment questions/answers and activity for student to test their comprehension.

ASSESSMENT

There are two aspects of assessment for this course: the tutor-marked assignment (TMA) and end of course examination. The TMAs shall constitute the continuous assessment component of the course. They will be marked by the tutor and equally account for 30 % of the total course score. Each learner shall be examined in four TMAs before the end of course examination. The end of course examination shall constitute 70% of the total course score.

HOW TO GET THE MOST FROM THE COURSE

Student are expected to comprehends best information out of this course through careful study of each units. It is recommended that student should test their ability to answer questions that follow each unit as well as questions in reference materials related to this course

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MODULE 1

STUDY UNIT 1: INTEGRATED RATE LAWS

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1.0 Introduction

Chemical kinetics is the study of the rate of chemical reactions or processes. This include the study of the effects of various variables, re-arrangement or orientation of molecules on the rate of chemical reaction. The rate of a chemical process can be approached in terms of the amount of product formed per unit time or the amount of reactant consumed per unit time. However, in some chemical processes, not all reactants are converted to product, some reactions may be characterised by side reactions or progress through the formation of an intermediate, in other cases, the orientation of the reactant molecules may affect the formation of product and hence the rate of chemical reaction. Chemical kinetics can be viewed in terms of macroscopic and microscopic components. In the macroscopic level, the amount of reactant that has reacted or the amount of product formed as well as the rate of their formation/consumption are considered. However, at the microscopic level, orientation of the molecules before collision, collision of the molecule and the availability of enough energy, needed to activate the reaction are the essential factors.

The rate of a chemical reaction can be defined as the rate of change of concentration of the reactant or the product. Before a chemical reaction starts, the concentration of the reactant will be zero at the initial time (i.e. t = 0). However, when the reaction starts, the concentration of the reactant will decrease with time while that of the product will increase with time. Therefore, for a hypothetical reaction such as the one expressed in equation 1, the theoretical rate of the reaction can be expressed according to equation 2,

$$aA + bB \rightarrow cC + dD \qquad 1.1$$

$$R_{Theor} = -\frac{1}{a}.\frac{d[A]}{dt} = -\frac{1}{b}.\frac{d[B]}{dt} = \frac{1}{c}.\frac{d[C]}{dt} = \frac{1}{d}.\frac{d[D]}{dt} \qquad 1.2$$

where a, b, c and d are the number of moles of A, B, C and D respectively. t is the time. If the concentration has a unit of moles and the time second, then the rate of reaction will have a unit of mole/second. Other units are g/s, lb/s, kg/day etc. Equation 1.2 reveals that the rate of a chemical reaction can be expressed in terms of decrease in concentration of the reactant (justifying the use of negative sign) or in terms of increase in concentration of the product (justifying the use of positive sign) with time. Let us consider the reaction between hydrogen and iodine, which leads to the formation of hydrogen iodide according to the following equation,

$$H_{2_{(g)}} + I_{2_{(g)}} = 2HI_{(g)} \qquad 1.3$$

Before the reaction begins, the concentrations of hydrogen and iodine are maximum while that of hydrogen iodide is zero but when the reaction proceeds, concentrations of hydrogen and iodine begins to decrease while that of hydrogen iodide will begin to increase. According to the law of conservation of matter, matter cannot be destroyed or created but change from one form to another. Therefore, for every loss of x mole of reactant, x mole of product is formed. Therefore, the variation of concentration of reactants and product with time can be represented graphically as shown in Fig. 4.1

Frome equation two and Fig.4. 1, it is evidence that the rate of formation of HI is twice the rate of disappearance of H_2 and I_2. Applying equation 1.2, we can write the rate equation for this reaction as follows (equation 4),

$$\frac{1}{2}\frac{d[HI]}{dt} = -\frac{d[H_2]}{dt} = -\frac{d[I_2]}{dt} \qquad 1.4$$

Equation 14 also implies that the slope of either plots should give the value of the rate of reaction. Hence rate of reaction is the change in concentration of the reactant or product with time.

The major short coming arising from the use of equations 1.2 in estimating the rate of a chemical reaction is that it is based on the expressed chemical equation and its stoichiometry. However, it has been found that the theoretical expressed rate equation may not always agree with the experimentally derived equation. An experimentally derived rate equation is called rate law. The essential features of a rate law for a given reaction can be written as,

$$Rate = k_n[A]^x.[B]^y \qquad 1.5$$

where, k_n is the rate constant with respect to the overall order of reaction, x is the order of reaction with respect to the reactant, A while y is the order of reaction with respect to the concentration, B. The overall order of the reaction is the sum of the individual order (i.e. $x + y = n$). An experimental derived equation such as the one expressed inequation 5 shows that the rate of reaction is proportional to the concentrations of reactant raised to certain power. If the order of reaction is 1,2, 3....n, the reaction is said to be first order, second order, third order, n order. It is possible to have zero and even fractional order of reaction.

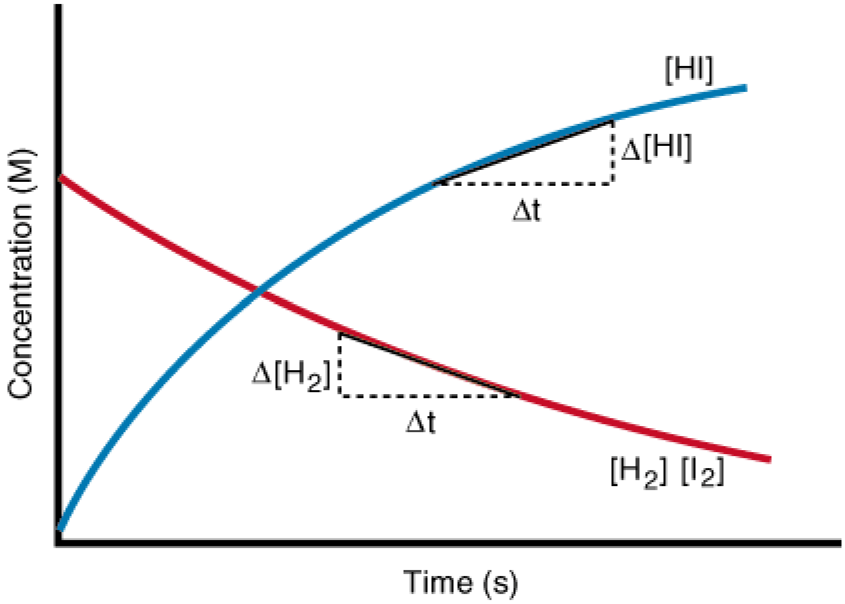


Fig. 1.1: Variation of concentrations of reactant and product with time

2.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

(i) understand what is chemical kinetics

(ii) understand and differentiate between rate law and theoretical rate equation

(iii) understand what is order of reaction

(iv) derive integrated rate equation for zero order, first order, second order and third order kinetics

(v) know how to identify the order of a reaction given some data

(vi) derive kinetic equation for a pseudo order kinetics

(vii) solve mathematical problems associated with order of reaction

3.0 Main Content

3.1 Integrated Rate law

3.1.1 Derivation of integrated rate equation

The rate equation is often represented as a differential equation, which indicates that it can be most useful if integrated. In this section, integrated rate equations are derived for some reactions orders.

3.1.2 Zero order reaction

A zero-order reaction is characterised by a non dependency of the rate of the reaction on concentration. Example of a zero-order reaction is the decomposition or cracking of ammonia using tungsten as a catalyst. The reaction proceeds independent of the concentration of ammonia. Generally, a first order reaction can be represented according to equation 1.6, which re-arranges to .equation 1.7,

$$Rate = -\frac{d[A]}{dt} = k_0[A]^0 \qquad 1.6$$

$$-\frac{d[A]}{d[A]^0} = k_0 dt \qquad 1.7$$

Integration of equation 7, within the concentration's limits, 'a_0' and 'a_t' (corresponding to time, t = 0 and t respectively) yields equations1.8 and 1.9,

$$-\int_{a_0}^{a_t} d[A\} = \int_0^t k_0 dt \qquad 1.8$$

$$-(a_t - a_0) = k_0(t - 0) \qquad 1.9$$

$$a_0 - a_t = k_0 t \qquad 1.10$$

Equation 1.10 is the integrated rate law for a zero-order reaction. In order to test whether a given reaction is a zero order, equation 1.10 is suitable. If equation 1.10 is linearized, it becomes, $a_t = k_0 t - a_0$, which is in the form, y = mx + C, indicating that a plot of values of 'a' versus values of t should yields a straight line with slope and intercept equal to k_0 and a_0 (see Fig.1. 2).

The half-life of a chemical reaction is the time taken for the concentration of the reactant to be reduced by half its initial value. This implies that if the initial concentration of the reactant is ‘a_t’. Then at half-life, the concentration will become, $a_0/2$. Using this concept, the half-life for a zero-order reaction can be derived as follows,

$$\frac{a_0}{1} - \frac{a_0}{2} = k_0 t_{\frac{1}{2}} \qquad 1.11$$

$$t_{\frac{1}{2}} = \frac{a_0}{2k_0} \qquad 1.12$$

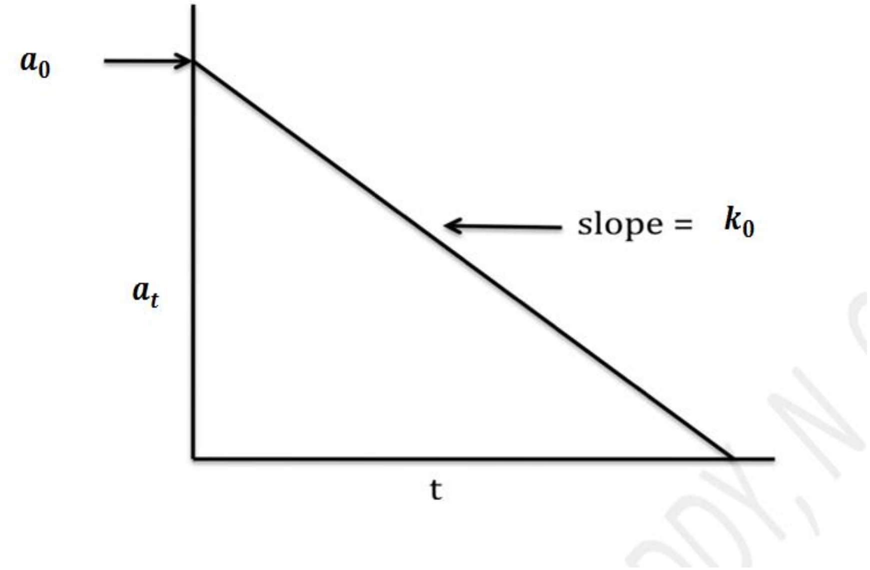


Fig. 1.2: Variation of concentration with time for a zero order reaction

Worked example 1

(a) Given that for a zero-order reaction, a reactant A decomposes to give a product, P. Derive an integrated rate law for the reaction

(b) How can you test and confirm that a given reaction is zero order?

(c) Derive an expression for the half-life of a zero order reaction hence, calculate the half-life of the reaction If the concentration of A changes from 0.1 M to 0.25 M after 30 minutes,

(d) Radioactivity of a sample (z = 22) decreases 90 % after 20 years. What will be the half-life of the sample?

Solution

(a) The rate law for the reaction can be written as

$$Rate = -\frac{d[A]}{dt} = k_0[A]^0 \qquad 1$$

$$-\frac{d[A]}{d[A]^0} = k_0 dt \qquad 2$$

Integration of equation 2, within the concentration's limits, 'a$_0$' and 'a_t' (corresponding to time, t = 0 and t respectively) yields equations 3 and 4, which simplifies to 5

$$\int_{a_0}^{a_t} d[A\} = \int_0^t k_0 dt \qquad 3$$

$$-(a_t - a_0) = k_0(t - 0) \qquad 4$$

$$a_0 - a_t = k_0 t \qquad 5$$

Equation 10 is the integrated rate law for a zero-order reaction.

(b) In order to test whether a given reaction is a zero order, equation 5 is suitable. If equation 5 is linearized, it becomes $a_t = k_0 t - a_0$, which is in the form, y = mx + C, indicating that a plot of values of 'a' versus values of t should yields a straight line with slope and intercept equal to k_0 and a_0.

(c) The half-life of a chemical reaction is the time taken for the concentration of the reactant to be reduced by half its initial value. This implies that if the initial concentration of the reactant was 'a_t', at half life, the concentration will become, $a_0/2$. Using this concept, the half-life for a zero-order reaction can be derived from equation 5 as follow,

$$\frac{a_0}{1} - \frac{a_0}{2} = k_0 t_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{a_0}{2k_0}$$

In order to calculate the half-life, we need to know the values of a_0 (a_0 = 0.1 M, the initial concentration) and k_0, the rate constant. Since a_0 , a_t and t are given, we can use equation 5 to calculate k_0, that is

$$a_0 - a_t = k_0 t$$

$$[0.1\,M] - [0.025\,M] = k_0(30\ x\ 60)$$

$$k_0 = \frac{0.076\,M}{1800s} = 4.22 \times 10^{-5}\,M/s$$

$$t_{\frac{1}{2}} = \frac{[0.1M]}{2(4.22 \times 10^{-5}\,M/s)} = 1.18 \times 10^3\,s$$

(d) A radioactive decay is a first order reaction. Therefore, the half-life is given as $t_{\frac{1}{2}} = \frac{0.693}{k_1}$. Hence, we need to know the rate constant, which can be gotten from the equation, $ln\left(\frac{a_t}{a_0}\right) = -k_1 t$,

Let the initial concentration of the reactant be x M. That means the concentration after twenty years will be 90 % less, i.e. x – 90x/100 = (100x – 90x)/100 = 10x/100 . Hence a_0 = x, a_t = (100x – 90)/100 and t = 20 years. Therefore

$$ln\left(\frac{10\text{x}/100}{x}\right) = -k_1(20\,years)$$

$$ln(0.1) = -k_1(20\,years)$$

$$-2.30259 = -k_1(20\,years)$$

$$k_1 = \frac{2.30259}{20\,years} = 1.15 \times 10^{-1}/\text{years}$$

Therefore, the half-life is $t_{\frac{1}{2}} = \frac{0.693}{k_1} = \frac{0.693}{1.15 \times 10^{-1}/\text{year}} = 6.03\,years$

3.1.3 First order reaction

A first order reaction is a one in which the rate of reaction is proportional to the concentration of the reactant raised to the power of unity. Therefore, the rate law for a first order reaction, given as A = product, 1.can be written as,

$$Rate = -\frac{d[A]}{dt} = k_1[A] \qquad 1.13$$

$$-\frac{d[A]}{[A]} = k_1 dt \qquad 1.14$$

where k_1 is the first order rate constant, [A] is the concentration of the reactant and t is the time. If at time, t = 0 and at some other time, t, the concentrations of the reactant are 'a_0' and 'a_t' respectively, then equation 1.14 can be integrated within these limits to obtain equations 1.15 to 1.18 as follows,

$$\int_{a_0}^{a_t} -\frac{d[A]}{[A]} = \int_0^t k_1 dt \qquad 1.15$$

$$[-\ln[A]]_{a_0}^{a_t} = k_1[t]_0^t \qquad 1.16$$

$$-(lna_t - lna_0) = k_1\,(t-0) \qquad 1.17$$

$$lna_t - lna_0 = -k_1 t \qquad 1.18$$

Equation 1.18 is the integrated rate equation for a first order reaction. However, the equation can be simplified to the forms expressed in equations 1.19 and 1.20,

$$ln\left(\frac{a_t}{a_0}\right) = -k_1t \qquad 1.19$$

$$a_t = a_0e^{-k_1t} \qquad 1.20$$

Equations 1.19 and 1.20 are the various forms of integrated rate equations for the first order equation. From equation 1.19, a reaction can be confirmed to be a first order reaction if a plot of $ln\left(\frac{a_t}{a_0}\right)$ versus t gives a straight line. This approach follows the linearised model of the equation, thus, $ln\left(\frac{a_t}{a_0}\right) = -k_1t + 0$, which compares with the general linear model, y = mx + C. Such plots will give a negative slope equal to k_1 (as shown in Fig.1.3)

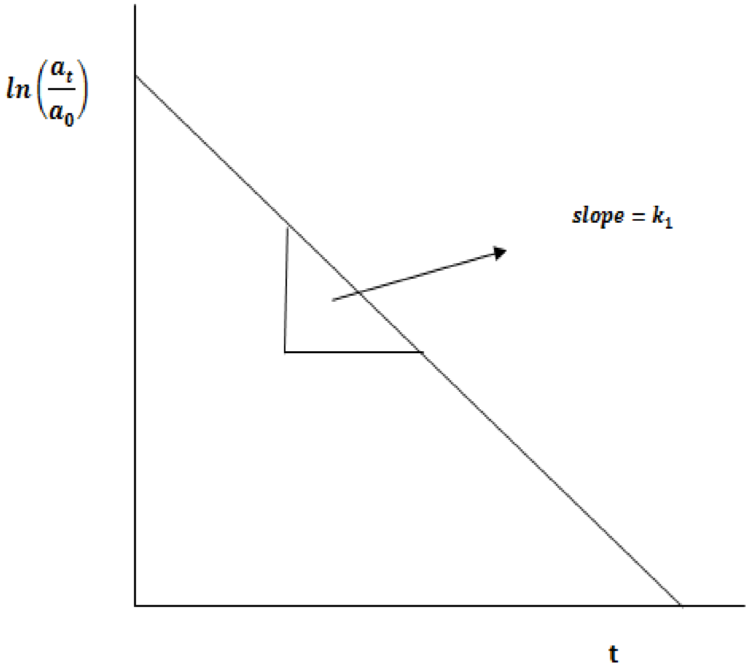


Fig. 1.3: Variation of $ln\left(\frac{a_t}{a_0}\right)$ with t for a first order reaction

The half-life of a first order reaction can be derived using equation 19. As stated before, at half life, $a_t = a_0/2$, hence,

$$ln\left(\frac{\frac{a_0}{2}}{a_0}\right) = -k_1t_{\frac{1}{2}} \qquad 1.21$$

$$t_{\frac{1}{2}} = -\ln\frac{\left(\frac{1}{2}\right)}{k_1} \qquad 1.22$$

$$t_{\frac{1}{2}} = \frac{ln2}{k_1} = \frac{0.683}{k_1} \qquad 1.23$$

Equation 1.23 reveals that the half-life of a first order reaction is independent of the concentration of the reactant but is a function of the rate constant.

There are other ways of analysing a first order reaction. For example, consider a reactant, A reacting to give a product, P. If the number of moles of A reacting is a_0 at time, t=0 and the number of moles of product formed after some time, t, is x moles. Then at time t, the concentration of a must have decrease to (a_0 – x) while that of P is x. This indicates that an expression for a first order reaction can be written in the forms expressed by equations 1.24 and 1.25,

$$-\frac{d(a_0-x)}{dt} = k_1(a_0-x) \qquad 1.24$$

$$\frac{dx}{dt} = k_1(a_0-x) \qquad 1.25$$

Rearrangement, integration and simplification of equation 1.25 yields equations1.26 to 1.3030

$$\int_0^x \frac{dx}{(a_0-x)} = k_1 dt \qquad 1.26$$

$$[-ln(a_0-x)]_0^x = k_1[t]_0^t \qquad 1.27$$

$$-ln(a_0-x)-(-lna_0) = k_1 t \qquad 1.28$$

$$lna_0 - ln(a_0-x) = k_1 t \qquad 1.29$$

$$ln\left(\frac{a_0}{a_0-x}\right) = k_1 t \qquad 1.30$$

The significant of equation 30 is that a plot of $ln\left(\frac{a_0}{a_0-x}\right)$ versus t should be linear with slope equal to k_1. This derivation also reveals that the integrated equation for a first order reaction can also be presented in terms of the concentration of product (that is x). The expression for the half-life of the reaction is the same as the one earlier derived (equation 1.29). This can be proved by inserting x = a_0/2 into equation 30. This gives $ln\left(\frac{a_0}{a_0-a_0/2}\right) = ln\left(\frac{a_0}{a_0/2}\right) = k_1 t_{\frac{1}{2}}$ hence $t_{\frac{1}{2}} = \frac{ln2}{k_1} = \frac{0.639}{k_1}$ as before.

Worked example 2

Given that for a first order reaction, the concentration of the reactant changes from 0.1 M to 0.025 M in 60 minutes. Calculate

1. the rate of reaction, when the concentration of A is 0.05 M
2. The half-life of the reaction

Solution

i. A first order rate equation can be expressed as $a_t = a_0 e^{-k_1 t}$, which translate to $ln\left(\frac{a_t}{a_0}\right) = -k_1 t$. From the question

$a_0 = [0.1]$ (i.e initial concentration)

$a_t = [0.025]$, that is the concentration after time, t

$$t = 60\ minutes = 60\ x\ 60s = 3600s$$

If these values are substituted into the rate equation, the rat constant becomes,

$$k_1 = \frac{-ln\left(\frac{a_t}{a_0}\right)}{t} = \frac{-ln\left(\frac{0.025M}{0.1M}\right)}{3600s} = \frac{1.3863}{3600} = 3.85\ \times 10^{-4} s^{=1}$$

When the concentration of A = 0.05 M. It implies that a_t = [0.05M] and since the reaction proceeds with the same rate constant and is a first order reaction, the rate can be expressed as

$$Rate = k_1[A] = 3.85\ \times 10^{-4} s^{=1}[0.05\text{ M}] = \mathbf{19.2\ \times 10^{-6}\ Ms^{-1}}$$

ii. The half-life of a first order reaction is given as, $t_{\frac{1}{2}} = \frac{0.693}{k_1} = \frac{0.693}{3.85} \times 10^4\ s = \mathbf{1.80\ \ 10^3\ s}$

Worked example 3

(a) A reactant A undergoes first order kinetics. Show that the time variation of the reactant concentration a_t at any time t is given by $a_t = a_0 e^{-k_1 t}$where a_0 is the initial concentration of the reactant and k_1 is the first order rate constant. How can you prove that a given equation is first order? Hence derive an expression for the half life of the reaction.

(b) For a particular first order reaction at 300 K, the concentration of reactant is reduced to one half of its initial value after 5000 s. At 310 K, the concentration is halved after 1000 s. Calculate:
(i) the rate constant for the reaction at 300 and 310 K
(ii) the time required for the concentration to be reduced to one quarter of its initial value at 300 K
(iii) the activation energy of the reaction.

Solution

(a) A first order reaction is a one in which the rate of reaction is proportional to the concentration of the reactant raised to the power of unity. Therefore, the rate law for a first order reaction, given as A = product, can be written as,

$$Rate = -\frac{d[A]}{dt} = k_1[A] \qquad (1)$$

$$-\frac{d[A]}{d[A]} = k_1 dt \qquad (2)$$

where k_1 is the first order rate constant, [A] is the concentration of the reactant and t is the time. If at time, t = 0 and at some other time, t, the concentrations of the reactant are 'a_0' and 'a_t'

respectively, then equation 2 can be integrated within these limits to yields equations 3 to 6 as the solutions,

$$\int_{a_0}^{a_t} -\frac{d[A]}{d[A]} = \int_0^t k_1 dt \qquad (3)$$

$$[-\ln[A]]_{a_0}^{a_t} = k_1[t]_0^t \qquad (4)$$

$$-(lna_t - (-lna_0) = k_1\ (t-0) \qquad (5)$$

$$lna_t - lna_0 = -k_1 t \qquad (6)$$

Equation 6 is the integrated rate equation for a first order reaction. However, the equation can be simplified and re-presented in the following forms,

$$ln\left(\frac{a_t}{a_0}\right) = -k_1 t \qquad (7)$$

$$a_t = a_0 e^{-k_1 t} \qquad (8)$$

Equation 8 is the required equation. A first order reaction can be tested and confirmed if a plot of $ln\left(\frac{a_t}{a_0}\right)$ versus t gives a straight line. This approach follows the linearised model of the equation, thus, $ln\left(\frac{a_t}{a_0}\right) = -k_1 t + 0$, which compares with the general linear model, y = mx + C. Such plots will give a negative slope equal to k_1

The half-life of a first order reaction can be derived using equation 7 since at half-life, $a_t = a_0/2$, the equation becomes

$$ln\left(\frac{\frac{a_0}{2}}{a_0}\right) = -k_1 t_{\frac{1}{2}} \qquad (9)$$

$$t_{\frac{1}{2}} = -\ln\frac{\left(\frac{1}{2}\right)}{k_1} \qquad (10)$$

$$t_{\frac{1}{2}} = \frac{ln2}{k_1} = \frac{0.693}{k_1}$$ (1))1

(b)

(i) The rate constant can be calculated from the half-life, thus, $k_1 = \frac{0.693}{t_{\frac{1}{2}}}$.

At 300 K, $t_{\frac{1}{2}}$ = 5000, therefore, $k_1 = \frac{0.693}{5000} = 1.39 \times 10^{=4} s^{-1}$

At 310 K, $t_{\frac{1}{2}}$ = 1000, therefore, $k_1 = \frac{0.693}{1000} = 6.93 \times 10^{=4} s^{-1}$

(ii) The time required can be calculated from the integrated rate law, i.e., $ln\left(\frac{a_t}{a_0}\right) = -k_1 t$. From the question, $a_t = \frac{a_0}{4}$. At 300 K, $k_1 = 1.39 \times 10^{=4} s^{-1}$, Therefore,

$$ln\left(\frac{\frac{a_0}{4}}{a_0}\right) = -1.39 \times 10^{=4}s^{-1}t$$

$$ln(0.25) = -1.39 \times 10^{=4}s^{-1}t$$

$$t = -\frac{ln(0.25)}{1.39} \times 10^4\ s = 9.9733 \times 10^3\ s$$

(iii) The activation energy can be calculated using the following equation, $ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$, where k$_2$ and k$_1$ are the rate constants at 310 and 300 K. Substituting the values into the equation, we have,

$$ln\left(\frac{0.000693}{0.000139}\right) = \frac{E_a}{8.314}\left(\frac{1}{300} - \frac{1}{310}\right)$$

$$ln(4.9856) = \frac{E_a}{8.314}(0.000108)$$

$$1.6066 = \frac{E_a}{8.314}(0.000108)$$

$$E_a = \frac{1.6066 \times 8.314}{0.000108} = 123\ 678.45\ Jmol^{-1} = 123.68\ kJmol^{-1}$$

3.1.4 Second order reaction

A second order reaction can arise in two different ways. These are,

(i) A single reactant, giving a product, P. That is A = Product. The rate law in this case is $-\frac{d[A]}{dt} = k_2[A]^2$

(ii) Two reactants reacting to give a single product, P such as A + B = P. In this case, the rate law can be written as $-\frac{d[A]}{dt} = k_2[A][B]\ or -\frac{d[B]}{dt} = k_2[A][B]$

Considering the first case, we have equation 1.31, which is integrated to give equation 1.32.

$$-\frac{d[A]}{[A]^2} = k_2dt \qquad 1.31$$

$$-\int_{a_0}^{a_t}\frac{d[A]}{[A]^2} = k_2\int_0^t dt \qquad 1.32$$

Simplification of equation 1.32 gives equation 1.33 and 1.34

$$\left[\frac{1}{A}\right]_{a_0}^{a_t} = k_2[t]_0^t \qquad 1.33$$

$$\frac{1}{a_t} - \frac{1}{a_0} = k_2t \qquad 1.34$$

Equation 1.34 is the integrated rate equation for a second order reaction, involving one reactant. The unique future of this equation is that it is a function of concentrations. From equation 1.34, a given reaction can be proven to be a second order if a plot of $\frac{1}{a_t}$ versus t gives a straight line. In such case, the slope and intercept of the plot will be t and $\frac{1}{a_0}$ respectively (the linear form of equation 34 is $\frac{1}{a_t} = k_2 t + \frac{1}{a_0}$). Also, the half life of a second order reaction can be derived by substituting for t and a_t. i. E, a_t = a_0/t and t = $t_{\frac{1}{2}}$. Hence,

$$\frac{1}{\frac{a_0}{2}} - \frac{1}{a_0} = k_2 t_{\frac{1}{2}} \qquad 1.35$$

$$\frac{2}{a_0} - \frac{1}{a_0} = k_2 t_{\frac{1}{2}} \qquad 1.36$$

$$\frac{1}{a_0} = k_2 t_{\frac{1}{2}} \; or \; t_{\frac{1}{2}} = \frac{1}{k_2 a_0} \qquad 1.37$$

Therefore, the half-life of a second order reaction depends on the initial concentration of the reactant and on the rate constant.

On the t hand, the second case 2 of a second order rate equation rearranges to

$$-\frac{d[A]}{[A][B]} = k_2 dt \qquad 1.38$$

Let the initial concentrations of A and B be a_0 and b_0. If x mole of the product is formed after time, t, concentrations of A and B will reduce to (a_0 –x) and (b_0 – x) respectively. Consequently, substituting [A] and [B] into equation 1.38 yields,

$$-\frac{d(a_0-x)}{(a_0-x)(b_0-x)} = k_2 dt \qquad 1.39$$

$$\frac{dx}{(a_0-x)(b_0-x)} = k_2 dt \qquad 1.40$$

Equation 1.40 can best be solved by treating it as a partial fraction. This enables the equation to be divided into parts that can easily be integrated,

$$\frac{dx}{(a_0-x)(b_0-x)} \equiv dx\left[\frac{C}{(a_0-x)} + \frac{D}{(b_0-x)}\right] \qquad 1.41a$$

In the first approach, the equation is simplified thus,

$$\frac{1}{(a_0-x)(b_0-x)} \equiv \frac{C}{(a_0-x)} + \frac{D}{(b_0-x)} \qquad 1.41b$$

The LCM of the denominators of equation 1.41b is $(a_0 - x)(b_0 - x)$. Upon simplification, equation 42 becomes,

$$1 \equiv C(b_0 - x) + D(a_0 - x) \qquad 1.42$$

The first approach can be applied as follow. Putting x = a0 into equation 42, we have,

$$1 = C(b_0 - a_0) + D(a_0 - a_0),$$

$$C(b_0 - a_0) = 1 \text{ and } C = \frac{1}{(b_0 - a_0)}.$$

Again, putting x = b0, into equation 42, we have,

$$1 = C(b_0 - b_0) + D(a_0 - b_0).$$

$$1 = D(a_0 - b_0) \text{ and } D = \frac{1}{(a_0 - b_0)}$$

Second approach

In the second approach, the equation is expanded and the constant terms and terms associated with the coefficient of x are used to approximate the constants, C and D. Therefore, expansion of equation gives, $1 \equiv Cb_0 - Cx + Da_0 - Dx$, which rearranges to

$$1 \equiv (Cb_0 + Da_0) - (C + D)x \qquad 1.43$$

Comparing the coefficients of x in the right and left hand side of equation 43, we have, C + D = 0 or C = - D. Similarly, comparing the coefficient of the constant, we have, $Cb_0 + Da_0 = 1$. Since C = -D, we have,

$$-Db_0 + Da_0 = 1 \; or D(a_0 - b_0) = 1,$$

$$D = \frac{1}{(a_0 - b_0)}.$$

Similarly, C = -D also implies that D = -C hence,

$$Cb_0 + Da_0 = 1,$$

$$-Cb_0 - Ca_0 = 1$$

$$\text{or } C(b_0 - a_0) = 1 \text{ and } C = \frac{1}{(b_0 - a_0)} \text{ as before.}$$

Generally, the two methods give the same solution. Substituting for C and D into equation 1.41 and resetting the original equation, we have,

$$\frac{dx}{(a_0 - x)(b_0 - x)} \equiv \left[\frac{1}{(b_0 - a_0)(a_0 - x)} + \frac{1}{(a_0 - b_0)(b_0 - x)}\right] dx = k_2 dt \qquad 1.44$$

Equation 44 can easily be integrated by part, i.e. splitting the equation,

$$\int_{\mathbf{0}}^{\boldsymbol{x}} \frac{dx}{(b_0 - a_0)(a_0 - x)} + \int_{\mathbf{0}}^{\boldsymbol{x}} \frac{dx}{(a_0 - b_0)(b_0 - x)} = \int_{\mathbf{0}}^{\boldsymbol{t}} k_2 dt \qquad \mathbf{1.}45$$

The solution to equation 44 is gotten through the steps expressed below

$$\frac{1}{(b_0 - a_0)} \int_0^x \frac{dx}{(a_0 - x)} + \frac{1}{(a_0 - b_0)} \int_0^x \frac{dx}{(b_0 - x)} = \int_0^t k_2 dt \qquad 1.46$$

$$\frac{1}{(b_0 - a_0)} [-ln(a_0 - x)]_0^x + \frac{1}{(a_0 - b_0)} [-ln(b_0 - x)]_0^x = [t]_0^t \qquad 1.47$$

$$\frac{1}{(b_0-a_0)}(-ln(a_0-x)-(-ln(a_0-0)+\frac{1}{(a_0-b_0)}(-ln(b_0-x)-(-ln(b_0-0) = k_2t \qquad 1.48$$

$$\frac{1}{(b_0-a_0)}[lna_0-ln(a_0-x)]+\frac{1}{(a_0-b_0)}[lnb_0-ln(b_0-x)\,] = k_2t \qquad 1.49$$

$$\frac{1}{(b_0-a_0)}ln\left(\frac{a_0}{a_0-x}\right)+\frac{1}{(a_0-b_0)}ln\left(\frac{b_0}{b_0-x}\right) = k_2t \qquad 1.50$$

$$\frac{1}{(a_0-b_0)}ln\left(\frac{b_0}{b_0-x}\right)-\frac{1}{(a_0-b_0)}ln\left(\frac{a_0-x}{a_0}\right) = k_2t \qquad 1.51$$

$$\frac{1}{(a_0-b_0)}ln\left(\frac{b_0}{b_0-x}\,.\frac{a_0-x}{a_0}\right) = -k_2t \qquad 1.52$$

$$\frac{1}{(a_0-b_0)}ln\left\{\frac{b_0}{a_0}\left(\frac{a_0-x}{b_0-x}\right)\right\} = -k_2t \qquad 1.55$$

$$\frac{1}{(a_0-b_0)}log\left\{\frac{b_0}{a_0}\left(\frac{a_0-x}{b_0-x}\right)\right\} = -\frac{k_2}{2.303}\,\mathrm{t} \qquad 1.56$$

Equations 1.55 and 1.56 gives the integrated rate law for the second order reaction arising from two reactants combining to give a product.

Worked example 4

Consider the following reaction, 2Mg + O_2 = 2MgO. If the rate equation can be written as,

$$Rate \;=\; k_n[Mg]^x[O_2]^y$$

The results of some three trial experiments generated the data given in the Table below

Experiment No	**Initial [Mg] mol/L**	**Initial [[O_2] mol/L**	**Measured rate (mol/Ls)**
1	0.10	0.10	0.002
2	0.20	0.10	0.004
3	0.10	0.20	0.008

Answer the following questions

i. What is the rate law for the reaction?

ii. What is the overall order of the reaction?

iii. Calculate the value of the rate constant, k_n

Solution

(i) The expected rate law should take the form, $Rate \;=\; k_n[Mg]^x[O_2]^y$.

(ii) From the data provided, when the concentration of O_2 is held constant at 0.10 mol, then we can obtain the order for Mg (using experiments 1 and 2) as follows,

$$\frac{[0.2]}{[0.1]} = \frac{[0.04]}{[0.02]}$$

This gives 2 = 2^1 which means that the order of the reaction with respect to Mg is 1. Similarly, when the concentration of Mg is held constant in experiments 1 and 3, we have,

$$\frac{[0.2]}{[0.1]} = \frac{[0.08]}{[0.02]}$$

which gives, 2 = 2^2 hence the order of the reaction with respect to oxygen is 2 and the overall order is 3rd order, i.e. termolecular reaction.

iii. Using data obtained from experiment 1, we can obtain the value of the rate constant.

Thus,

$0.002 = k_n(0.01)^1(0.01)^2$, which gives $k_n = 2.0 \times 10^4$. This means that the rate equation can be re-written as $Rate \ = \ 20000[Mg][O_2]^2$

Worked example 5

During the kinetic study of the reaction, 2A + B → C + D, following results were obtained:

Run	**[A]/mol L^{-1}**	**[B]/mol L^{-1}**	**Initial rate of formation of D/mol L^{-1} min^{-1}**
I	0.1	0.1	6.0×10^{-3}
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88×10^{-1}
IV	0.4	0.1	2.40×10^{-2}

(i) Determine the order of the reaction

(ii) Calculate the value of the rate constant

(iii) Write the rate law for the reaction

Solution

(i) In runs I and IV, the concentrations of B are held constant at 0.01 mol. Therefore,

$$\frac{[0.4]}{[0.1]} = \frac{[0.024]}{[0.006]}$$

Which gives, $4^1 = 4^1$ hence the order with respect to A is 1. Similarly, in runs II and III, concentrations of A are held constant, hence,

$$\frac{[0.4]}{[0.2]} = \frac{[0.28]}{[0.072]}$$

Which gives $2^1 = 2^2$, hence the order of the reaction with respect to B is 2

The rate law for the reaction can be written as, $Rate\ =\ k_n[A]^1[B]^2$, which gives overall order of 3. That is termolecular reaction.

(ii)`The rate constant can be obtained by substituting for the variables indicated in the rate law. If we choose run IV, we have

$$0.024\ =\ k_n[0.4]^1[0.1]^2$$

This gives $k_n = 6$

(ii) The rate law can be written as $Rate\ =\ 6[A]^1[B]^2$

Worked example 6

Thermal decomposition of NO_2 at 330 ° C occurs according to the following equation

$$2NO_{2(g)} \overset{\Delta}{\rightarrow} 2NO_{(g)}\ +\ \ O_{2(g)}$$

The data obtained from the experiment are presented in the Table below,

Time (s)	**$[NO_2]$(M)**
0	1.00×10^{-2}
60	6.83×10^{-3}
120	5.18×10^{-3}
180	4.18×10^{-3}
240	3.00×10^{-3}
300	3.01×10^{-3}
360	2.64×10^{-3}

Use the above information to answer the following questions

(i) Show that the mechanism of the reaction is consistent with a second order

(ii) Calculate the rate constant of the reaction

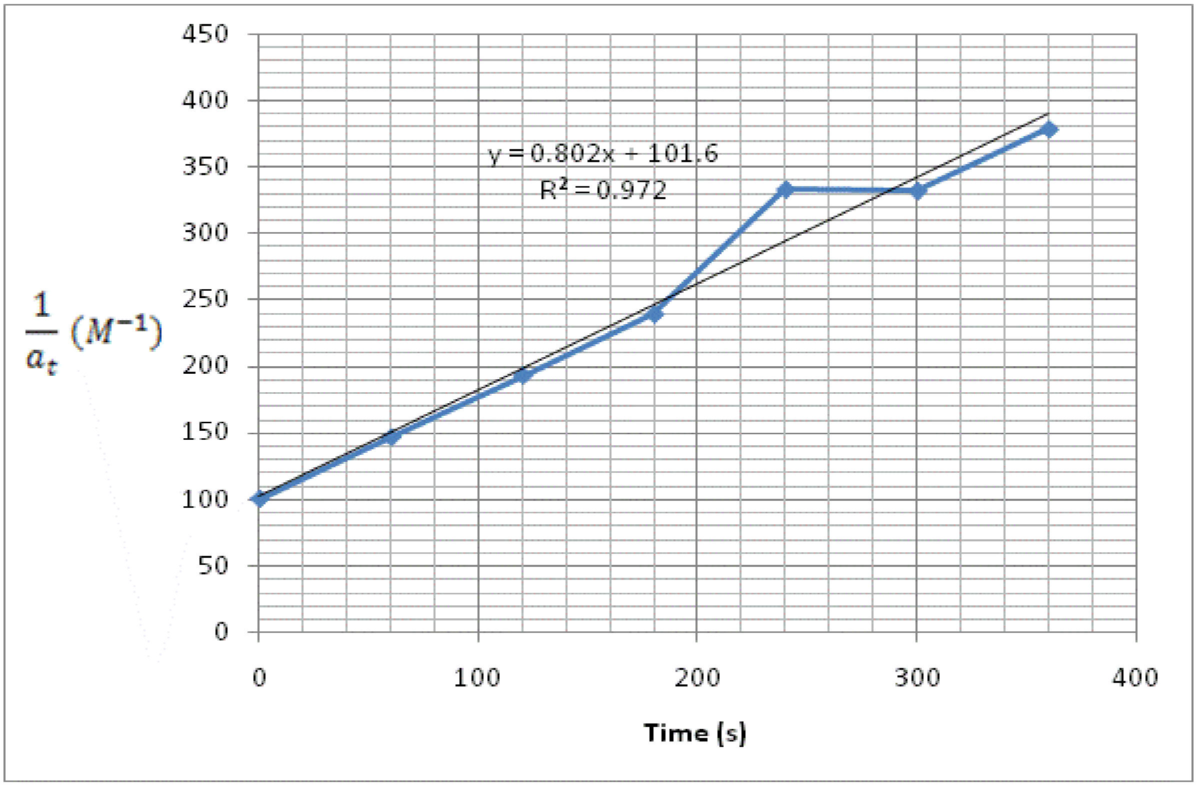
(iii) Write the rate law for the reaction

(iv) Derive an expression for the half-life of the reaction, hence calculate the half life

Solution

For a second order reaction, the integrated rate law is $\frac{1}{a_t} - \frac{1}{a_0} = k_2 t$. Therefore, a plot of $\frac{1}{a_t}$ versus t should be linear. The Table of content and the plot are shown below

Time (s)	$\boldsymbol{\frac{1}{a_t}}$ $(\boldsymbol{M^{-1}})$
0	100
60	146.4129
120	193.0502
180	239.2344
240	333.3333
300	332.2259
360	3787.879



(i) A close examination of the above plots indicates that the data fitted a second order reaction model.

(ii) Since the reaction is a second order, it obeys the equation, $\frac{1}{a_t} - \frac{1}{a_0} = k_2 t$. Hence the rate constant is the slope of the plot, $k_2 = 0.802\ M^{-1}s^{-1}$

(iii) The rate law for the reaction is $Rate = 0.802[NO_2]^2$

(iv) From the integrated law, the half-life can be derived. At half-life, $t = t_{1/2}$, $a_t = a_0/2$. Therefore,

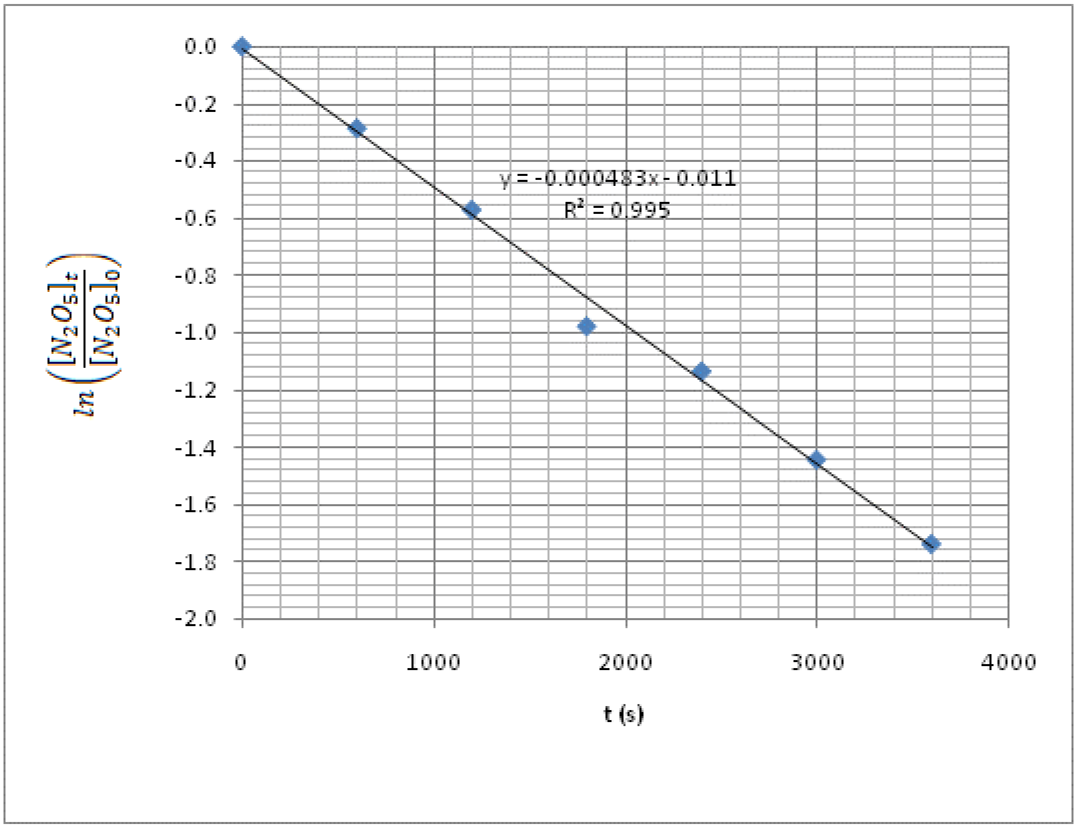
$$\frac{1}{\frac{a_0}{2}} - \frac{1}{a_0} = k_2 t_{\frac{1}{2}}$$

$$\frac{2}{a_0} - \frac{1}{a_0} = k_2 t_{\frac{1}{2}}$$

$$\frac{1}{a_0} = k_2 t_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{1}{a_0 k_2} = \frac{1}{0.802\ M^{-1}s^{-1}(0.01\ \mathrm{M})} = 124.69\ s$$

Worked example 7



3.1.5 Third order reaction

A third order reaction may be regarded as a termolecular reaction in which the rate of reaction depends on three concentration variables. Generally, a termolecular reaction can be represented as a reaction in which three reactants combine to give a product as shown in equation 1.57,

$$A + B + C \quad \rightarrow Product \qquad 1.57$$

The rate law for the above reaction can be written as,

$$-\frac{d[A]}{dt} = -\frac{d[B\}}{dt} = -\frac{d[C]}{dt} = k_3[A][B][C] \qquad 1.58$$

If A = B = C, equation 1.59 replaces equation 1.58 and upon rearrangement, equation 1.60 is obtained

$$-\frac{d[A]}{dt} = k_3[A]^3 \qquad 1.59$$

$$-\frac{d[A]}{[A]^3} = k_3 dt \qquad 1.60$$

Integrating equation 1.60 within the limits, a_0 and a_t (which correspond to time t = 0 and t respectively), leads to equations 1.61,

$$\int_{a_0}^{a_t} -\frac{d[A]}{[A]^3} = k_3 \int_0^t dt \qquad 1.61$$

$$\left[\frac{1}{2A^2}\right]_{a_0}^{a_t} = k_3[t]_0^t \qquad 1.62$$

$$\frac{1}{2a_t^2} - \frac{1}{2a_0^2} = k_3 t \qquad 1.63$$

An expression for the half-life of a third order reaction (of the form, expressed by equation 1.62) can be derived as follows,

$$\frac{1}{2(\frac{a_0^2}{4})} - \frac{1}{2a_0^2} = k_3 t_{\frac{1}{2}} \qquad 1.64$$

$$\frac{4}{2a_0^2} - \frac{1}{2a_0^2} = k_3 t_{\frac{1}{2}} \qquad 1.65$$

$$\frac{3}{2a_0^2} = k_3 t_{\frac{1}{2}} \qquad 1.66$$

$$t_{\frac{1}{2}} = \frac{3}{2k_3 a_0^2} \qquad 1.67$$

From the above, it seen that the half-life of a third order reaction depends on the rate constant and on the square of the initial concentration of the reactant.

Another approach to the derivation of an integrated rate law for a third order reaction is to consider the initial concentrations of A, B and C to be a_0, b_0 and c_0 at time, t = 0. If the number of moles of the product formed at time, t is x mole, then the concentrations of A, B and C will be (a_0 –x), (b_0 –x) and (c_0 – x) respectively. Again, if A = B = C, then the rate equation can be represented as,

$$\frac{dx}{dt} = k_3[a_0 - x]^3 \qquad 1.68$$

$$\frac{dx}{[a_0 - x]^3} = k_3 dt \qquad 1.68$$

Integration of equation 1.68 and the solution to the integration are presented below,

$$\int_0^x \frac{dx}{[(a_0 - x)]^3} = k_3 \int_0^t dt \qquad 1.69$$

$$\left[\frac{1}{2(a_0 - x)^2}\right]_0^x = k_3[t]_0^t \qquad 1.70$$

$$\frac{1}{2(a_0 - x)^2} - \frac{1}{2a_0^2} = k_3 t \qquad 1.71$$

$$\frac{1}{(a_0 - x)^2} - \frac{1}{a_0^2} = 2k_3 t \qquad 1.72$$

It is significant to note that the half-life based, on equation 1.67 is virtually the same as the one derived from equation 61. In order to achieved these results, we note that at $t_{\frac{1}{2}}$, x = a_0/2. Substituting for x n equation 66 yields,

$$\frac{1}{2(a_0 - \frac{a_0}{2})^2} - \frac{1}{2a_0^2} = k_3 t_{\frac{1}{2}} \qquad 1.73$$

$$\frac{1}{2(-\frac{a_0}{2})^2} - \frac{1}{2a_0^2} = k_3 t_{\frac{1}{2}} \qquad 1.74$$

$$\frac{4}{2a_0^2} - \frac{1}{2a_0^2} = k_3 t_{\frac{1}{2}} \qquad 1.75$$

$$\frac{3}{2a_0^2} = k_3 t_{\frac{1}{2}} \qquad 1.76$$

$$t_{\frac{1}{2}} = \frac{3}{2k_3 a_0^2} \qquad 1.77$$

Worked example 8

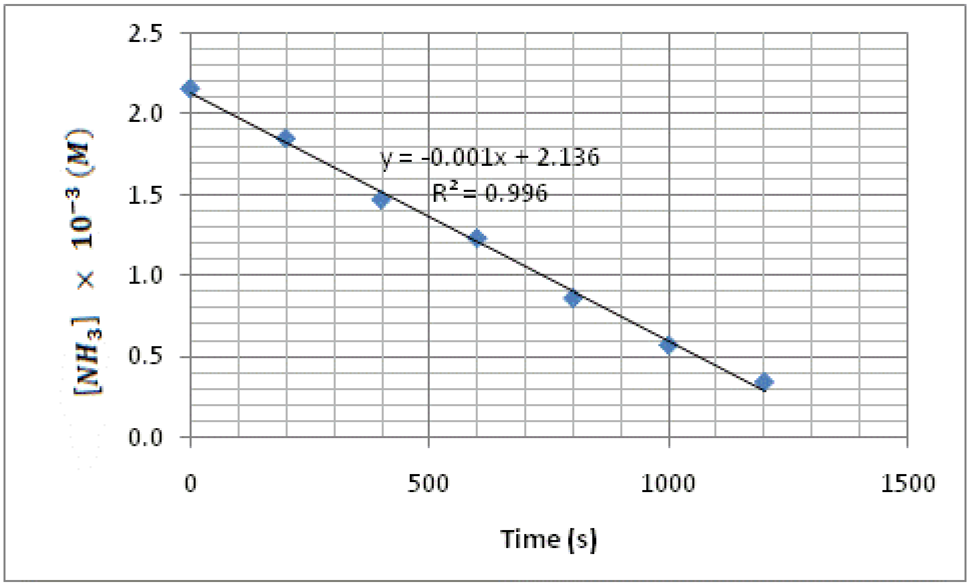
The decomposition of ammonia on a platinum surface at 1129 K occurs according to the following reaction: 2 $NH_{3(g)} \rightarrow N2_{(g)} + 3H_{2(g)}$. It occurs via zero order kinetics. Use the following kinetic data which report the variation of ammonia concentration in the gas phase with time t to evaluate the rate constant for the reaction at 1129 K.

t(s)	$[NH_3] \times 10^{-3}\ (M)$

0	2.16
200	1.85
400	1.47
600	1.23
800	0.86
1000	0.57
1200	0.34

Solution

For a zero-order reaction, the integrated rate equation is $a_0 - a_t = k_0 t$, which rearranges to $a_t = -k_0 t + a_0$. Therefore, the rate constant can be estimate as the slope of the plot of concentration of ammonia against time (t). The graph is shown below,



From the graph, the slope is equal to -0.001, therefore, the rate constant, $k_0 = 0.001$ Ms^{-1}.

Worked example 9.

Given that the rate of the reaction, A + B = C vary with concentration according to the data presented in the Table below, determine the order of the reaction and calculate the rate constant for the reaction.

[A] x 10^{-2} M	**Rate x 10^{-5} M/min**
0.50	0.30

1.78	3.80
7.22	62.20
19.90	47.50

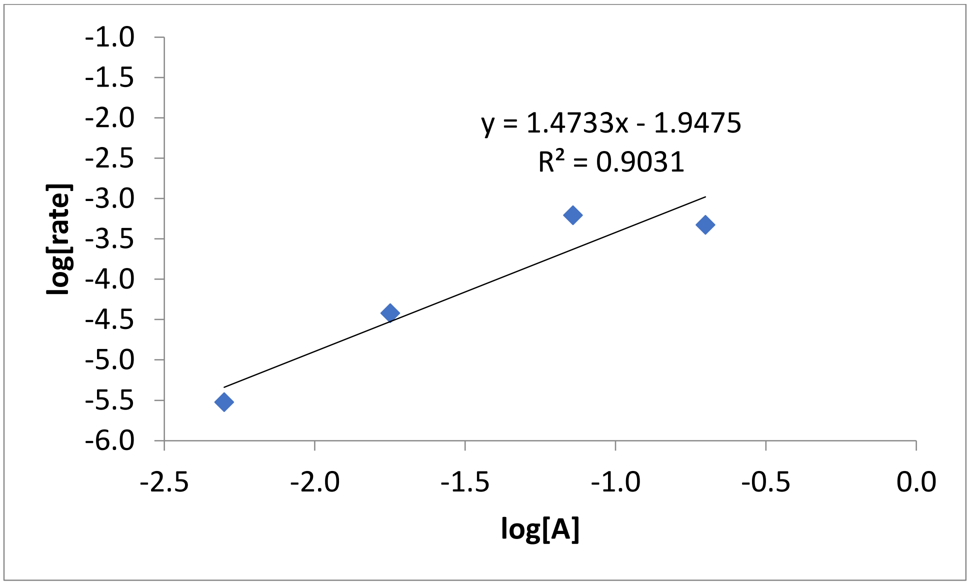
(b) The rate law of the reaction can be proposed to take the form,

$$Rate = k_n[A]^n$$

Taking logarithm of both sides of the equation gives, the following expression is obtained.

$$\log(Rate) = logk_n + nlog[A]$$

Therefore, a plot of log(rate) versus log(A) should be linear with slope equal to n and intercept equal to k_n. From the graph shown below, the slope is equal to 1.473 which approximate to 1. Hence the kinetic of the reaction is first order. Also, the intercept on the plot is 1.947 which indicate that log(k) = 1.947, hence the rate constant, k = $\log^{-1}$(k) = 0.01129 = 1.129 x 10^{-4} s^{-1}



3.2 Pseudo order reaction

A pseudo order reaction occurs when the concentration of one of the reactants remains constant during the reaction because it is present as a catalyst or because it is presence in a very large concentration. For example, a pseudo first order reaction is a second order reaction that is made to behave like a first order reaction.

The integrated rate law for a second order reaction involving two reactant was derived as $\frac{1}{(a_0-b_0)} ln\left\{\frac{b_0}{a_0}\left(\frac{a_0-x}{b_0-x}\right)\right\} = k_2$t, Which can also be written as

$$\frac{1}{([A]_0-[B]_0)} ln\left\{\frac{[B]_0}{[A]_0}\left(\frac{[A\}}{[B\}}\right)\right\} = k_2 t$$

The equation is applicable when $[A]_0 > [B]_0$. However, when $[A]_0 \gg [B]_0$ then $[A]_0$ tend to [A] and the equation becomes,

$$\frac{1}{[A]_0} ln\left\{\frac{[B]_0}{[A]}\left(\frac{[A]}{[B\}}\right)\right\} = kt$$

$$\frac{1}{[A]_0} ln\left\{\frac{[B]_0}{[B]}\right\} = kt$$

$$ln\left\{\frac{[B]_0}{[B]}\right\} = [A]_0 kt$$

$$\frac{[B]}{[B]_0} = e^{-[A]_0 kt}$$

$$[B] = [B]_0 e^{-[A]_0 kt}$$

The above equation is a functional form of a first order reaction and the system is said to operate under a pseudo first order reaction. Thus, a second order reaction is made to behave like a first order reaction because one of the reactants is presence in excessively large concentration (such that the concentration will remain constant because the change in concentration will be very negligible) while the other is present in low concentration.

The half-life of a pseudo first order reaction can also be derived as follows,

$$ln\left\{\frac{[B]_0}{0.5[B]_0}\right\} = [A]_0 kt_{\frac{1}{2}}$$

$$ln\left\{\frac{1}{0.5}\right\} = [A]_0 kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{-\ln(0.5)}{[A]_0 k} = \frac{0.6931}{[A]_0 k}$$

4.0 (i) Self Assessment Questions and Answers

1. Using the following data, which is the correct rate law of the sample reaction?

A + 5B + 6C → 3D + 3E

Experiment	[A] (M)	[B] (M)	[C] (M)	Initial Rate (M/s)
1	0.35	0.35	0.35	8.0×10^{-4}
2	0.70	0.35	0.35	3.2×10^{-3}
3	0.70	0.70	0.35	6.4×10^{-3}
4	0.70	0.35	0.70	3.2×10^{-3}

(a) Calculate the order of the reaction with respect to the reactant, A

(b) Calculate the order of reaction with respect to the reactant, B

(c) Calculate the order of the reaction with respect to the reactant, C

(d) Calculate the overall order of reaction

(e) Write the rate law for the reaction and calculate the rate constant for the reaction

2. The initial rate for the underlisted equation is given in the Table

$$2NO_{2(g)} + 2H_{2(g)} \rightarrow N_{2(g)} + 2H_2O_{(l)} \ at \ 1280\ °C$$

Experiment	[NO] (M)	[H_2] (M)	Initial rate (M/s)
1	0.0050	0.0020	1.25×10^{-5}
2	0.0100	0.0020	5.00×10^{-5}
3	0.0100	0.0040	1.00×10^{-4}

(a) Calculate the order of the reaction with respect to NO and H_2
(b) Write the rate law and hence, calculate the rate constant

3. What is the major condition required for a zero-order reaction to occur?

4. State (with example), if a fractional order reaction is possible for a normal reaction or otherwise.

5.(a) What is a pseudo order reaction?

(b) If the integrated rate law for a second order reaction is written as,

$$\frac{1}{([A]_0 - [B]_0)} ln\left\{\frac{[B]_0}{[A]_0}\left(\frac{[A\}}{[B\}}\right)\right\} = k_2t$$

Derive equation for the functional form of the system if it operates under a pseudo first order kinetics.

(c) Derive equation for the half-life of the pseudo first order reaction.

1.6.1 Answers to Self Assessment Questions

1. (a) In experiment 1 and experiment 2, concentrations of **B** and **C** are constant (i.e., 0.35 M) and the rate law changes from $3.2 \times 10^{-3}\ M/s$ to $8.0 \times 10^{-4}\ M/S$, therefore,

$$\frac{0.70}{0.35} = \frac{3.2 \times 10^{-3}\ M/s}{8.0 \times 10^{-4}\ M/S}$$

which gives, $2^1 = 2^2$

Hence the order of the reaction with respect to A is 2

(b) In experiments 2 and 3, **A** and **C** have a constant concentration of 0.7 M and 0.35 M respectively, while the concentration of B changes from 0.35 M to 0.70 M. The rate constant changes from $6.4 \times 10^{-3}\ M/s$ to $3.2 \times 10^{-3}\ M/s$, hence

$$\frac{0.70}{0.35} = \frac{6.4 \times 10^{-3}\ M/s}{3.2 \times 10^{-3}\ M/s}$$

$$2^1 = 2^1$$

Therefore, the reaction is first order with respect to B and the order is 1

(c) In experiments 2 and 4, the concentrations of **A** and **B** are constant at 0.70 M and 0.35 M respectively while that of C changes from 0.35 to 0.70 M. The rate constant remains unchanged, at $3.2 \times 10^{-3}\ M/s$

$$\frac{0.70}{0.35} = \frac{3.2 \times 10^{-3}\ M/s}{3.2 \times 10^{-3}\ M/s}$$

$$2^1 = 2^0$$

This means that the reaction is zero order with respect to C

(c) The overall order is obtained by adding all the exponents for the reactants, = 2+1+0 = 3, which represent third order

(d) The rate law can be written as,

$$Rate = k_3[A]^2[B]^1[C]^0 = k_3[A]^2[B]^1$$

The rate constant can be calculated by substituting values of the reactants into the equation. For example, if we chose experiment 2, Rate = $3.2 \times 10^{-3}\ M/s$ and [B] = 0.35 M, [A] = 0.70 M, hence,

$$k_3 = \frac{Rate}{[A]^2[B]^1} = \frac{3.2 \times 10^{-3}\ M/s}{[0.70\ M]^2[0.35\ M]^1} = 1.866 \times 10^{-2}\ M^{-2}s^{-1}$$

(a) In experiments 1 and 2, concentration of H_2 is constant at 0.0020 M while that of NO changes from 0.0050 to 0.0100 M, The rate constant changes from 5.00 x 10^5 to 1.25 x 10^{-4} M/s, therefore,

$$\frac{0.0100}{0.0050} = \frac{5.00 \times 10^{-5} M/s}{1.25 \times 10^{-5}\ M/s}$$

$$2^1 = 2^2$$

This mean the reaction is second order with respect to NO

Similarly, in experiments 2 and 3, concentration of NO is constant at 0.0100 M while that of H_2 changes from 0.0020 to 0.0040 M. The rate constant changes from 5.00 x 10^{-5} M/s to 1.00 x 10^{-4-} M/s, therefore,

$$\frac{0.0040}{0.0020} = \frac{1.00 \times 10^{-4} M/s}{5..00 \times 10^{-5}\ M/s}$$

$$2^1 = 2^1$$

Hence, the reaction is first order with respect to H_2 and the order of the reaction is 2+1 = 3rd order.

(b) The rate law can be written as,

$$Rate = k_3[NO]^2[H_2]^1$$

$$k_3 = \frac{Rate}{[NO]^2[H_2]^1} = \frac{5..00 \times 10^{-5} M/s}{[0.0100]^2[0.0020]^1} = 2.5 \times 1\,0^{-4} M^{-2}s^{-1}$$

3. Zero-order reactions are typically found when a material that is required for the reaction to proceed, such as a surface or a catalyst, is saturated by the reactants. A reaction is zero-order if concentration data is plotted versus time and the result is a straight line.

4. Fractional order reactions, the order is a non-integer, which often indicates a chemical chain reaction or other complex reaction mechanism. For example, the pyrolysis of acetaldehyde (CH_3CHO) into methane and carbon monoxide proceeds with an order of 1.5.

5.(a) A pseudo order reaction occurs when the concentration of one of the reactants remains constant during the reaction because it is present as a catalyst or because it is presence in a very large concentration. For example, a pseudo first order reaction is a second order reaction that is made to behave like a first order reaction.

(b) Given that for a second order reaction, the integrated rate law is

$$\frac{1}{([A]_0 - [B]_0)} ln\left\{\frac{[B]_0}{[A]_0}\left(\frac{[A\}}{[B\}}\right)\right\} = k_2 t$$

The equation is applicable when $[A]_0 > [B]_0$. However, when $[A]_0 \gg [B]_0$ then $[A]_0$ tend to [A] and the equation becomes,

$$\frac{1}{[A]_0} ln\left\{\frac{[B]_0}{[A]}\left(\frac{[A]}{[B\}}\right)\right\} = kt$$

$$\frac{1}{[A]_0} ln\left\{\frac{[B]_0}{[B]}\right\} = kt$$

$$ln\left\{\frac{[B]_0}{[B]}\right\} = [A]_0 kt$$

$$\frac{[B]}{[B]_0} = e^{-[A]_0 kt}$$

$$[B] = [B]_0 e^{-[A]_0 kt}$$

The above equation is a functional form of a first order reaction and the system is said to operate under a pseudo first order reaction.

(c) The half-life of a pseudo first order reaction can also be derived as follows,

$$ln\left\{\frac{[B]_0}{0.5[B]_0}\right\} = [A]_0 kt_{\frac{1}{2}}$$

$$ln\left\{\frac{1}{0.5}\right\} = [A]_0 kt_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{-\ln(0.5)}{[A]_0 k} = \frac{0.6931}{[A]_0 k}$$

(ii) Class Activity

1. Consider some common reactions such as (i) Decomposition of hydrogen peroxide (ii)Adsorption of nickel catalyst (iii) Radioactive reaction of Uranium. Provide the order for each of the listed reaction (6 minutes)

2. Under what relation can a first order reaction obeys an exponential reaction (5 minutes)

3. Is fractional order reaction common?. Give example is yes (3 minutes)

4. Derive an integrated rate equation for a zero order reaction and for its half life (10 miniutes)

5. 0 Conclusion

Chemical reactions can be monitored through the knowledge of the reaction order they obeys. Basically, reactions can be zero, first second, third or fractional order. However, complex reactions shows different kinetic behaviour and their order is built up from the various steps that characterised such a reaction. Knowledge of reaction order also provide information on the half life of the reaction, which is a significant factor in analysing some useful reaction functions such as decay rate, etc.

6.0 Summary

Chemical kinetics studies the rate of chemical reactions and creates a mathematical link between concentrations and time. The commonest order of reactions is zero order, first order, second order and third order. A pseudo order reaction set in when the concentration of one of the reactants is in excess. Rate law for the various orders differs greatly but interesting factor in the derived rate law is the possibility of calculating half-life which is a parameter that can link with several properties. The rate law of zero, first, second and third law as well as their half-lives depends on time and differ from each other. Dependent of rate law on concentration is not applicable to applicable to a zero-order reaction. However, rate laws of first, second and third order reactions are concentration and time dependent. Rate law provides a theoretical modelling step for envisaging time dependent progress of a given reaction.

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MODULE 1

STUDY UNIT 2: KINETICS MODELS

1.0 Introduction

Temperature affects reaction rate in several ways but generally, reaction rates are known to increase with increase in temperature. However, this concept does not operate in all cases because they are some reaction rate that decreases with increase in temperature. In order to understand the disparity in reaction rate temperature relationship, it is necessary to consider internal processes that occurs inside the molecules including collision and other molecular motions. Some theories of reaction have been proposed to explain how the internal molecular properties can affect the rate of chemical reaction. Most accepted theories are Arrhenius theory, collision theory and transition state theory. These theories are considered in this section.

2.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

(i) understand the relationship between temperature and rate of reaction
(ii) understand how Arrhenius theory explains the progress of chemical reaction
(iii) understand the role of collision theory in predicting the rate of chemical reaction

(iv) understand the transition state model and its explanation for the rate of chemical reactions.

(v) derive equations for the various models that relates rate constant with thermodynamic parameters or molecular properties

(vi) solve mathematical problems related to Arrhenius and reaction theories

3.0 Main Content

3.1 Effect of temperature on the rate of reaction

It has long been established that temperature affects the rate of a chemical reaction. As a rule, reaction rate doubles for every 10 ° C rise in temperature. Increase in the rate of a chemical reaction will be accompanied by increase in the rate constant. Several reactions show various respond to the variation of the rate of reaction with temperature. Fig. 2.1 shows different types of plots for the variation of rate of reaction with temperature. Figs. 2.1a and 2.1b clearly show that the rate of reaction increases with temperature while Fig. 2.1c and 2.1d show that the rate of reaction decreases with increase in temperature. Fig. 2.1a is a typical Arrhenius plot while others are anti-Arrhenius plots. The first empirical equation relating the rate constant of a chemical reaction with temperature was given by Hood who stated that the logarithm of the rate constant is proportional to the inverse of temperature as shown in equation 2.1,

$$logk = A - \frac{B}{T} \qquad 2.1$$

As at then Hood's equation revealed that a plot of logk versus 1/T gives a straight line with slope and intercept equal to B and A. However, Hood was unable to give the physical significant of the constants, A and B. On the progressive path, Van;t Hoff found that there exists a relationship between equilibrium constant and temperature while Arrhenius gave an equation for the variation of reaction rate constant with temperature (equation 2.2 which is rearranged to 2.3),

$$\frac{dlnk}{dT} = \frac{E_a}{RT^2} \qquad 2.2$$

$$dlnk = \frac{E_a}{R} . \frac{dT}{T^2} \qquad 2.3$$

Where k is the rate constant, T is the temperature, R is the Universal gas constant and E_a is the activation energy, defined as the minimum energy required for a reaction to proceeds. Integration of equation 2.3 yields the following results,

$$\int dlnk = \frac{E_a}{R} \int \frac{dT}{T^2} \qquad 2.4$$

$$lnk = -\frac{E_a}{RT} + Constant \qquad 2.5$$

The constant included in equation 2.5 was found to be lnA, where A is the Arrhenius or pre-exponential factor. Therefore, equation 2.5 becomes,

$$lnk = lnA - \frac{E_a}{RT} \qquad 2.6$$

The exponential form of the Arrhenius equation can be written as, $k = Ae^{-\frac{E_a}{RT}}$. Generally, from the Arrhenius equation, a plot of rate constant against the reciprocal of temperature is linear and is characterised by slope and intercept equal to $\frac{E_a}{R}$ and lnA respectively (see Fig.2.1). The Arrhenius equation can also be applied if the rate constants (k_1 and k_2) at two different temperatures (T_1 and T_2) are known. Inserting the corresponding rate constant and temperatures successively, into equation 73, gives the following expressions (2.7 and 2.8):

$$lnk_{\mathbf{1}} = lnA - \frac{E_a}{RT_1} \qquad 2.7$$

$$lnk_{\mathbf{2}} = lnA - \frac{E_a}{RT_2} \qquad 2.8$$

Subtracting equation 2.7 from 2.8, gives equation 2.9 and equation 2.10 upon simplification

$$lnk_{\mathbf{2}} - lnk_{\mathbf{1}} = (lnA - lnA) - \left(\frac{E_a}{RT_2} - \frac{E_a}{RT_1}\right) \qquad 2.9$$

$$ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad 2.10$$

From equation 2.10, it is evident that Arrhenius equation can be used to estimate the value of the activation energy is the values of the rate constant at two different temperatures are known.

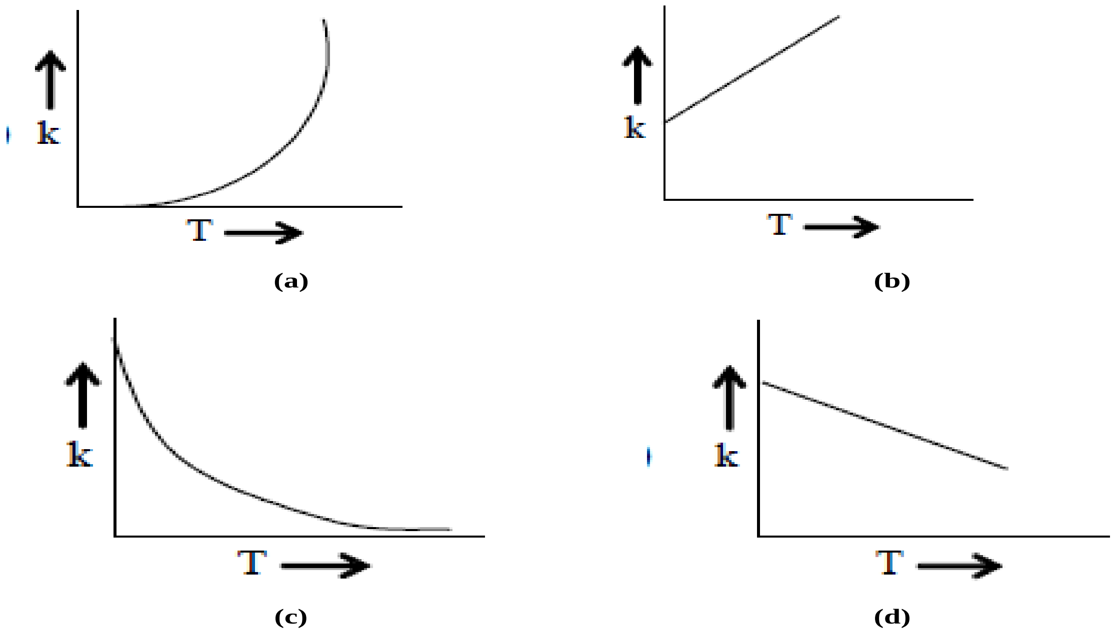


Fig. 2.1: Various types of variation of rate constant with temperature

Worked example 1

(a) Write down the Arrhenius equation relating the rate constant k and the activation energy Ea. Explain each term used in the equation.

(b) Describe how the activation energy could be measured experimentally and indicate how the data could be manipulated graphically to obtain a numerical estimate of Ea.

(c) A rate constant of a chemical reaction is $1.78 \times 10^{-4} Lmol^{-1}s^{-1}$ at 40 °C and $1.38 \times 10^{-3} Lmol^{-1}s^{-1}$ at 80 °C. Evaluate the activation energy for the reaction.

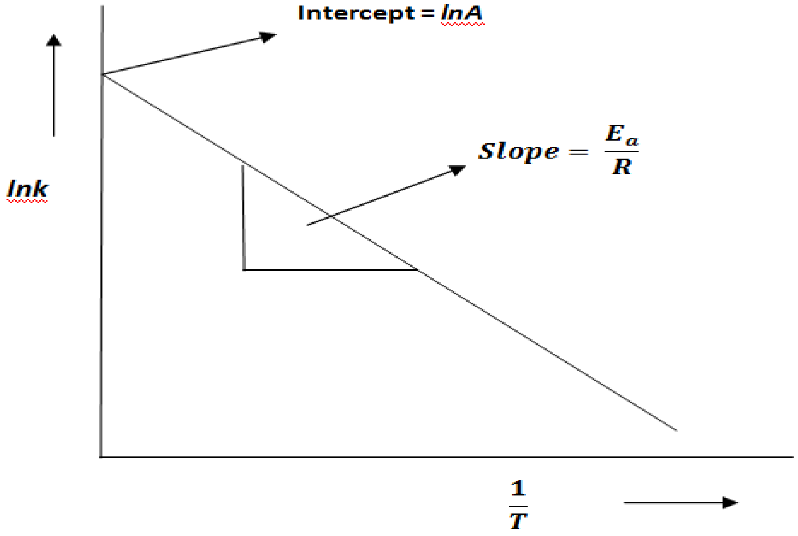
Solution

(a) The Arrhenius equation can be written as, $k = Aexp\left(\frac{-E_a}{RT}\right)$, where k is the rate constant, E_a is the activation energy (i.e., the minimum energy needed before a reaction can proceeds), R is the gas constant and T is the temperature.

(b) The activation energy can be measured experimentally by measuring values of the rate constant at different temperatures. The rate constant itself can be calculated from known rate of reaction (whose order is known). From the Arrhenius equation, $k = Aexp\left(\frac{-E_a}{RT}\right)$, the logarithm of both sides yields,

$$lnk = lnA - \frac{E_a}{RT}$$

This implies that a plot of lnk versus 1/T will give a straight line with slope equal to –E_a/R (-E_a/8.314 J/mol/K) and intercept equal to lnA. This enable the activation energy to be easily calculated. The Figure shown below is the nature of plot expected.



(c) Given,

$k_1 = 1.78 \times 10^{-4}$ $Lmol^{-1}s^{-1}$, T_1 =40°C = 273 + 40 = 313 K

$k_2 = 1.38 \times 10^{-3}$ $Lmol^{-1}s^{-1}$, T_2 = 80°C = 273 + 80 = 353 K

The activation energy can be calculated from the equation, $ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Therefore,

$$ln\left(\frac{0.00138 \text{ Lmol} - 1\text{s} - 1}{0.000178 \text{ Lmol} - 1\text{s} - 1}\right) = \frac{E_a}{8.314\,Jmol^{-1}K^{-1}}\left(\frac{1}{313\,K} - \frac{1}{353\,K}\right)$$

$$ln\left(\frac{0.00138}{0.000178}\right) = \frac{E_a}{8.314\,Jmol^{-1}}\left(\frac{1}{313} - \frac{1}{353}\right)$$

$$ln(7.7528) = \frac{E_a}{8.314\,Jmol^{-1}}(0.003194 - 0.002833)$$

$$ln(7.7528) = \frac{E_a}{8.314\,Jmol^{-1}}(0.000361)$$

$$E_a = \frac{2.04805 \times 8.314\,Jmol^{-1}}{0.000361} = 47167.65\,Jmol^{-1} = 47.17\,Jmol^{-1}$$

Worked example 2

(a) Values of the rate constant for the bromination of propanone as a function of temperature are presented in the following table. Show that the data obey the Arrhenius equation and evaluate the activation energy of the reaction and the pre-exponential factor A.

T (° C)	**K x $10^{-8}s^{-1}$**
90	4.53
110	59.30
120	197.21
130	613.02

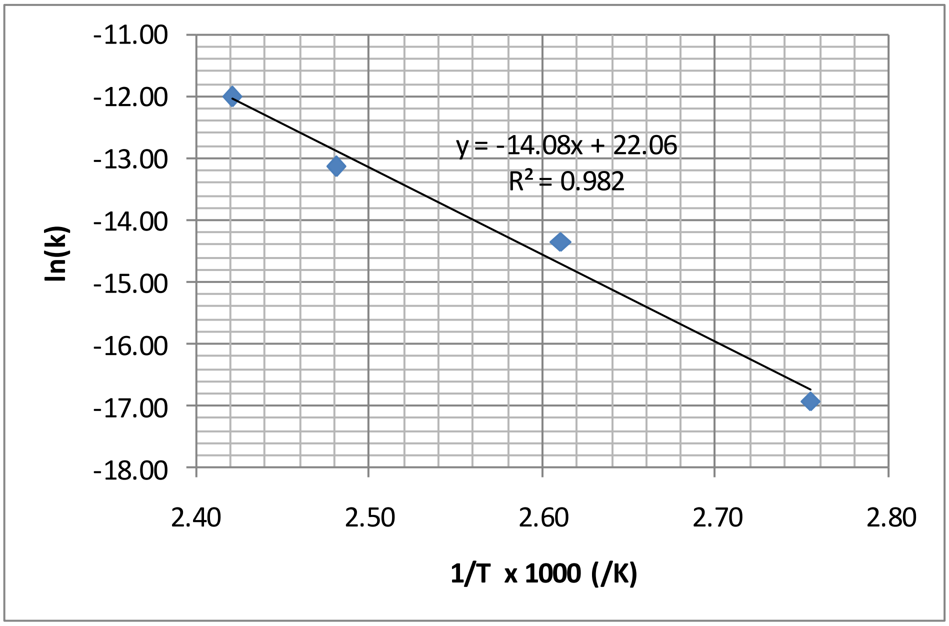
(b) The major mechanism for removing methane from the atmosphere is the reaction with hydroxyl radicals $CH_4 + OH^* \rightarrow CH_3^* + H_2O$. The activation energy for the reaction is approximately 20 kJ mol^{-1}. Calculate the ratio of the rate constants for the reaction at the earth's surface (T= 295 K) and at the top of the troposphere (where T = 220 K).

Solution

In order to determine the activation energy, the Arrhenius equation is used. The equation can be written as $lnk = lnA - \frac{E_a}{RT}$. This implies that a graph of lnk versus 1/T will should give a straight line if the equation is obeyed. The data needed for the plotting and the produced graph are presented below. The slope of the graph is -14.08, which indicate that $-\frac{E_a}{R}$ = -14.08. Therefore, E_a = 8.314 x 14.08 = 117.06 J/mol.

T (K)	**K x 10^{-8} s^{-1}**	**1/T x 1000 (/K)**	**lnk**
363	4.53	2.75	-16.9100

383	59.30	2.61	-14.3381
403	197.21	2.48	-13.1364
413	613.02	2.42	-12.0023



(b) The problem can be solved using the Arrhenius equation. i.e. $ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$.

Given,

E_a = 20.00 kJ/mol = 20000.00 J/mol

T_1 = 220 K

T_2 = 295 K

R = 8.314 J/mol/K

Therefore,

$$ln\left(\frac{k_2}{k_1}\right) = \frac{20000\, J/mol}{8.314\, J/mol}\left(\frac{1}{220\ K} - \frac{1}{295\ K}\right)$$

$$ln\left(\frac{k_2}{k_1}\right) = 2405.58(0.001156) = 2.7800$$

$$\frac{k_2}{k_1} = 16.12$$

Therefore, the ratio of the rate constants for the reaction at the earth's surface (T= 295 K) and at the top of the troposphere (where T = 220 K) is 16.12.

Worked example 3

In the homogeneous decomposition of nitrous oxide N_2O to form nitrogen and oxygen, it is found that at constant temperature the time needed for half the reaction to be completed is inversely proportional to the initial pressure (P_0) of N_2O. On varying the temperature, the following
results were obtained

T (K)	P_0 (Torr)	$t_{1/2}$
962	294	1520
1030	360	212
1085	345	53

You should note that 1 atm = 760 Torr = 101.325 kPa, and you may assume that N_2O behaves as an ideal gas. Use the above information to answer the following questions

(i) Determine the order of the reaction

(ii) Calculate the rate constant for the reaction at the various temperatures

(iii) The activation energy of the reaction and the pre-exponential factor.

Solution

(i) Since the time needed for half the reaction to be completed is inversely proportional to the initial pressure (P_0) of N_2O and the pressure of the gas is directly proportional to the concentration, it means that the order of the reaction is second order and not zero or first order. The following analysis suffice,

For a zero-order reaction, the half-life is directly proportional to the concentration, i.e. $t_{\frac{1}{2}} = \frac{a_0}{2k_0}$

For a first order, the half-life is independent of the concentration i.e. $t_{\frac{1}{2}} = \frac{0.693}{k_1}$

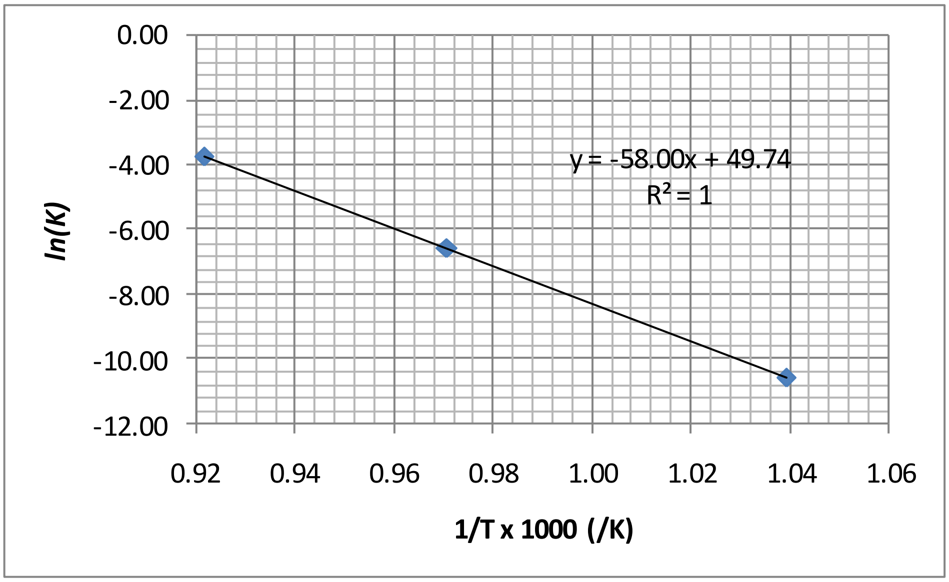
For a second order reaction, the half-life is inversely proportional to the concentration. i.e. $t_{\frac{1}{2}} = \frac{1}{a_0k_2}$. Therefore, the reaction is second order.

(ii) The data must be subjected to further conversion before it can be useful for the calculations. The pressure must be converted to S.I unit (N/m^2). 1atm = 760 mm/g (Torr) = 101325 Nm^2Since the gas is an ideal gas, then it obey the equation, $PV = nRT$ where P is the pressure, V is the volume, n is the number of mole, R is the gas constant and T is the temperature. From the equation, $P = \left(\frac{n}{V}\right) RT = CRT$, where C is the concentration (note n/V = concentration in mol/dm^3). Therefore, $C = \frac{P}{RT}$. This unit enable us to convert the pressure to concentration. These data are shown in the Table below,

T (K)	**P_0 (Torr)**	**P (Nm^2)**	**$t_{1/2}$**	**C (mol/dm^3)**	**k (moldm^{3}s^{-1})**
962	294	202650	1520	25.33737	2.60 x 10^{-5}
1030	360	28264.34	212	3.30059	1.43 x 10^{-3}
1085	345	7066.086	53	0.78332	2.41 x 10^{-2}

For a second order reaction, the rate constant can be derived from the equation for half-life. That is $t_{\frac{1}{2}} = \frac{1}{a_0 k_2}$ indicating that $k_2 = \frac{1}{a_0 t_{\frac{1}{2}}}$. Calculated values of k_2 are presented in the above table.

(iii) In order to determine the activation energy, the Arrhenius equation is used. The equation can be written as $lnk = lnA - \frac{E_a}{RT}$. This implies that a graph of lnk versus 1/T will should give a straight line with slope and intercept equal to $-\frac{E_a}{R}$ and ln A respectively. The Arrhenius plot for the data is presented below.



From the graph, the slope is -58.00 while the intercept is 49.74. These imply that

$$-\frac{E_a}{R} = -58.00\, and\ E_a = -58.00\, x\, \frac{8.314}{-1} = 482.21\, J/mol$$

$$\text{Also, } lnA = 49.74, therefore, A = 4.00 \times 10^{21}$$

3.2 Theories of chemical reaction

Theories of chemical reaction explains the various steps connected with the effect of variables such as energy and temperature on chemical reaction. Theories of chemical reactions use established models to explain how the rate constant is related to thermodynamic variables, thus creating a link between chemical kinetics and thermodynamics. There are three major theories of chemical reactions. These are,

(i) The Arrhenius theory
(ii) The Collision theory
(iii) The Transition state theory.

Each of these theories, its applications and limitations are examined in this section.

3.2.1 The Arrhenius theory

Arrhenius suggested that reaction occurs when molecules collide and that not all collision leads to chemical reaction. The collision that leads to chemical reaction are called effective collision. According to the Arrhenius concept, collision must produce energy equal to or higher than the minimum energy (activation energy) before it can be effective. This implies that there is an energy barrier that must be overcome (i.e. the activation energy). In order to overcome this barrier, the energy produce by collision must be equal to or higher than the activation energy. According to Boltzmann equation, the fraction of molecules having energy, equal to or greater than the activation energy (i.e. the fraction of molecules that have energy enough to be converted to the product) can be expressed as

$$\frac{n_{Ea}}{n_T} = e^{\frac{-E\,a}{kT}} \qquad 2.11$$

where n_{E_a} is the number of molecules having energy equal to E_a and n_T is the total number of molecules. From equation 2.11, it is evident that the rate of reaction will be proportional to the rate molecules are converted to products, which in turn is proportional to n_{E_a}. Hence it can be stated that the rate of the chemical reaction is proportional to $n_T e^{\frac{-E\,a}{kT}}$ as shown in equation 2.12,

$$Rate \propto n_T e^{\frac{-E_a}{kT}} \qquad 2.12$$

It is known that the concentration of the reactant can significantly affect the rate of chemical reaction. Therefore,

$$Rate \propto [concentration\ of\ reactant]\ n_T e^{\frac{-E_a}{kT}} \qquad 2.13$$

$$Rate = Ae^{\frac{-E_a}{kT}}[concentration\ of\ reactant] \qquad 2.14$$

where A is the Arrhenius or pre-exponential factor. Since the rate of a chemical reaction can also be expressed as rate = k[concentration of the reactant], it implies that the rate constant, k = rate/[concentration of reactant], hence $\frac{An_T e^{\frac{-E_a}{RT}}[concentration\ of\ reactant]}{[Concentration\ of\ reactant]} = Rate.$ Therefore, equation 2.14 becomes,

$$k = Ae^{\frac{-E_a}{RT}} \qquad 2.15$$

Equation 2.15 is the Arrhenius equation, in which the Boltzmann constant, k is replaced with the gas constant, R. It can be seen from the above derivation that the probability of a molecule to go into a reaction is the function of its collision frequency.

The Arrhenius equation is widely applied in solving problems related to chemical system (by plotting lnk versus 1/T as shown in Fig. 2.2). However, it has some shortcomings. For example,

i. the equation is most applicable to gaseous systems,
ii. it doesn’t explain how molecules becomes activated
iii. It is unable to explain the physical meaning of the frequency factor, A

In view of these and other problems, the collision theory was introduced.

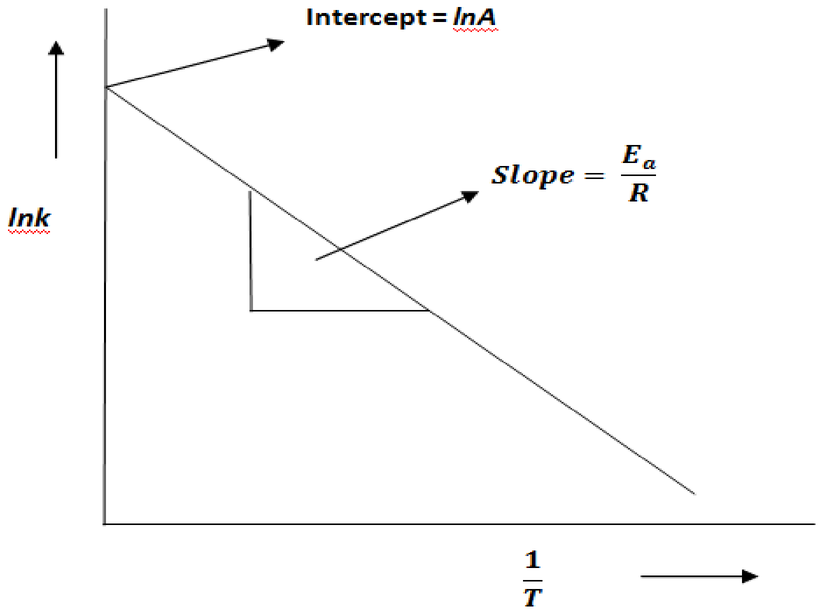
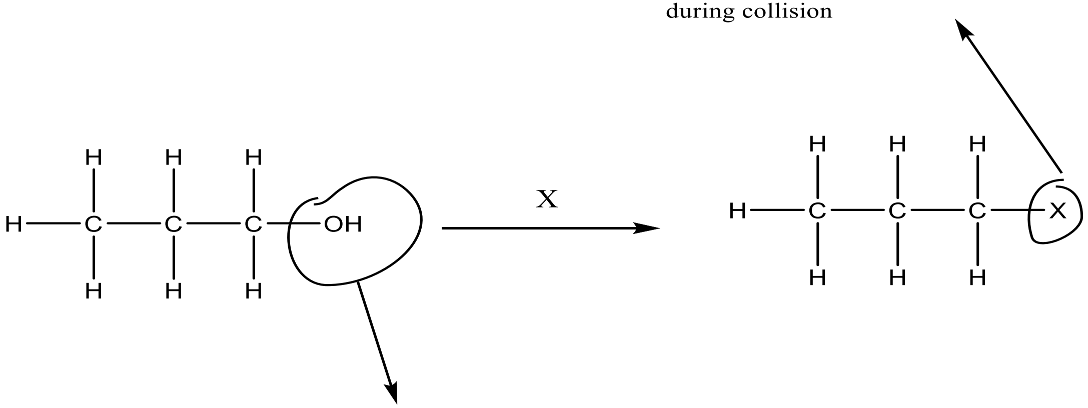


Fig. 2.2: Typical pattern of Arrhenius plot

3.2.2 The Collision theory

The collision theory applies the assumptions of the Arrhenius equation but in addition, it has an additional assumption which requires that the molecule must be properly oriented at the point of collision. This implies that even if there could be several bonds in a molecule, the collision must take place at the appropriate bond. For example, in the molecule shown below, the collision that will be effective in overcoming the energy barrier will be the one that takes place at the OH group. Therefore, even if the molecule has activation energy, it will not collide to produce product until it is properly oriented.

Effective collision leads to the formation of product, through the bond that was broken during collision



Acording to the collision theory, colision that must lead to the formation of product must takes place at this bond

Introducing collision factor into the Arrhenius equation, the rate of reaction can be expressed according to equations 2.16 and 2.17

$$Rate\ =\ Z_{AB}e^{\frac{-E_a}{RT}}[concentration\ of\ reactant] \tag{2.16}$$

$$Rate\ =\ Z_{AB}e^{\frac{-E_a}{RT}}[A][B] \tag{2.17}$$

where [A][B] is the concentration of the reactants and is related to the rate constant, k and to the rate of reaction. Generally, Rate of reaction = k[A][B]. Therefore, rate/[A][B] = k. This enables equation 83 to be written in the form shown in equation 2.18

$$k\ =\ Z_{AB}e^{\frac{-E_a}{RT}} \tag{2.18}$$

The Arrhenius equation state that $k\ =\ Ae^{\frac{-E_a}{RT}}$, which compares with the equation given by the collision theory to explain the physical meaning of ‘A’. i.e $A =\ Z_{AB}$, indicating that it represents effective collision in the system. However, it has been found that the theoretical value of k obtained through Z_{AB} is often found to be higher than the experimental value. This difference is compensated by introducing a steric factor, which explains the probability that the molecule is properly oriented at the point of reaction. The collision number, which is the number of collisions per unit volume per unit time, is related to the average velocity of the molecule (v), the collision diameter (d_{AB}) and to the number of molecules. Therefore,

$$Z_{AB}\ =\ n_A n_B d_{AB}^2 v\pi \tag{2.19}$$

The velocity of the molecule is given as, $v = \sqrt{\frac{8\pi RT}{\mu}}$, where μ is the reduced mass of the molecule. For two molecules consisting of A and B atoms with molecular mass given as M_A and M_B, the reduced mass is given as, $M_AM_B/(M_A + M_B)$. Inserting $v =\ \sqrt{\frac{8\pi RT}{\mu}}$ into equation 85, we have,

$$Z_{AB}\ =\ n_A n_B d_{AB}^2 \pi\sqrt{\frac{8\pi RT}{\mu}} \tag{2.20}$$

From the Arrhenius equation, which states that $=\ Z_{AB}e^{\frac{-E_a}{RT}}$, we can substitute for Z_{AB} and the results is given in equation 87,

$$k\ =\ n_A n_B d_{AB}^2 \pi\sqrt{\frac{8\pi RT}{\mu}}.\,e^{\frac{-E_a}{RT}} \tag{2.21}$$

From the above, it can be seen that the collision theory explains the Arrhenius factor but still suffer some setbacks because it is most applicable to gaseous reactions and does not provide a way to calculate the probability factor, P.

3.2.3 The Transition state theory

The transition state theory was developed in the 20h century by Eyring, an Irish Chemist. According to the transition state theory, a reaction forming a product, first form an intermediate which is in thermodynamic equilibrium with the molecules of the reactant. The only unique property of the intermediate is that it has an energy that is higher than the energy of either the reactant or the molecule and that it has a short life span. The intermediate is easily converted to the product. This implies that the rate of the reaction depends on two major factors, which are,

(i) The concentration of the activation complex
(ii) The rate of dissociation of the activation complex into the product.

For a simple bimolecular reaction involving molecules A and B, then the reaction can be represented as follows, *

$$A + B \rightleftharpoons [AB]^{++} \xrightarrow{k} \text{Product} \qquad 2.22$$

The rate of reaction can be expressed as the product of the concentration of the intermediate and the frequency of decomposition of the activated complex (equation 2.23),

$$Rate = [AB]^{++}.frequency\ of\ decomposition\ of\ the\ activation\ complex \qquad 2.23$$

From equation 2.23, $[AB]^{++} = k^{++}[A][B]\ or\ k^{++} = \frac{[AB]^{++}}{[A][B]}$. According to Eyring, the specific rate (k) of any reaction is proportional to k^{++} according to equation 2.24,

$$k = \frac{RT}{Nh}k^{++} \qquad 2.24$$

where R is the universal gas constant, T is the temperature, N is the Avogadro's number while h is the Planck constant. The constant, k^{++} can be related to some changes in thermodynamic variables such as ΔG^{++}, ΔS^{++} and ΔH^{++}. Generally, the equilibrium constant, k^{++} is related to ΔG^{++} and can be written as, $\Delta G^{++} = -RTlnk^{++}$ indicating that

$$lnk^{++} = -\frac{\Delta G^{++}}{RT} = -\frac{\Delta H^{++} - T\Delta S^{++}}{RT} \qquad 2.25$$

$$k^{++} = e^{\frac{T\Delta S^{++}}{RT}} e^{-\frac{\Delta H^{++}}{RT}} \qquad 2.26$$

Substituting equation 2.26 into equation 2.27, gives equation 93, which simplifies to equation 2.28

$$k = \frac{RT}{Nh}\left(e^{\frac{T\Delta S^{++}}{RT}}e^{-\frac{\Delta H^{++}}{RT}}\right) \qquad 2.27$$

$$ln\left(\frac{k}{T}\right) = ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^{++}}{R}\right) - \left(\frac{\Delta H^{++}}{RT}\right) \qquad 2.28$$

Equation 2.28 is an expression for Eyring transition state equation. The Transition state equation has some similarities with the Arrhenius equation and can be used to explain Arrhenius parameters. Recall the Arrhenius equation (equation 81), $lnk = lnA - \frac{E_a}{RT}$ while the transition state equation can be expressed as $lnk = ln\left(\frac{RT}{Nh}\right) + \left(\frac{\Delta S^{++}}{R}\right) - \left(\frac{\Delta H^{++}}{RT}\right)$. Then it is obvious that if we equate the two equation, some terms can be compared. i.e.,

$$lnk = lnA - \frac{E_a}{RT} = \left\{ln\left(\frac{RT}{Nh}\right) + \left(\frac{\Delta S^{++}}{R}\right)\right\} - \left(\frac{\Delta H^{++}}{RT}\right)$$

It is evident from the above that A in the Arrhenius equation is related to entropy change while E_a is related to enthalpy change. That is $A = \left(\frac{RT}{Nh}\right).e^{\left(\frac{\Delta S^{++}}{R}\right)} and E_a = \Delta H^{++}$. Therefore, the Arrhenius factor can be estimated in terms of ΔS^{++} and the activation energy can be estimated in terms of E_a.Generally, when volume and pressure are taken into consideration, then$E_a = \Delta H^{++} + \Delta(PV)$. For solids, change in volume is negligible, therefore, $\Delta(PV) \approx 0$ and $E_a \approx \Delta H^{++}$. However, for gases, PV = nRT, therefore $\Delta(PV) = \Delta n^{++}RT$ and $E_a = \Delta H^{++} + \Delta n^{++}RT$

Worked example 4

Given that the rate constants for a first order reaction at 25 and 60 ° C are 2 x 10^{-3} and 8 x 10^{-3} s/mol. Calculate the activation energy for the reaction.

Solution

The logarithm form of the Arrhenius equation can be used for the calculation. The equation is $\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$. Substituting the given values to the equation, we have,

$$ln\left(\frac{0.008}{0.002}\right) = \frac{E_a}{8.314}\left(\frac{1}{298} - \frac{1}{333}\right)$$

$$ln(4) = \frac{E_a}{8.314}(0.000356)$$

$$1.3863 = 4.2819\ x\ 10^{-5}E_a$$

$$E_a = \frac{1.3863}{4.2819} x\ 10^{-5} = 32325.41 \frac{J}{mol} = 32.33\ kJ/mol$$

Worked example 14

Given the reaction, $ClO_3^- + H_2O \rightarrow ClO_4^- + H_2$. If the values of rate constant and temperature are as presented in the Table below,

K(/s)	T (°C)
2 x 10^{-3}	25
4 x 10^{-3}	35
6 x 10^{-3}	45
8 x 10^{-3}	55
1.0 x 10^{-2}	65

Calculate the following,

i. The activation energy for the reaction
ii. The value of the Arrhenius constant for the reaction
iii. Calculate the change in enthalpy and entropy of activation of the reaction
iv. What is the relationship between the Arrhenius parameters and Transition state Parameters?

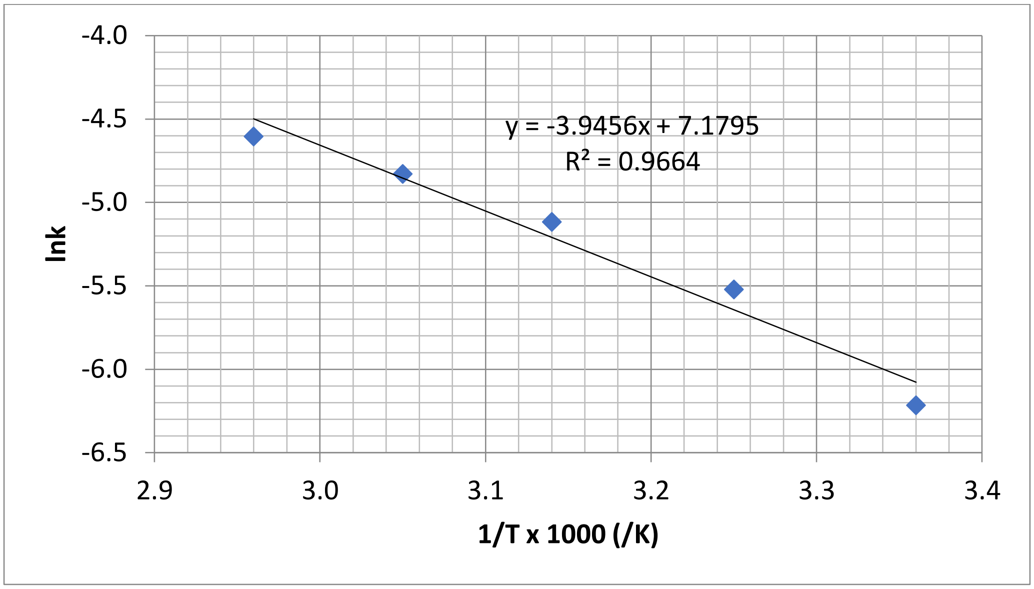
Solution

i. The Arrhenius equation relates the rate constant to the activation energy according to the equation, $k = Ae^{\frac{-E\ a}{kT}}$. The logarithm of the equation gives, $lnk = lnA - \frac{E_a}{RT}$. , which implies that a plot of lnk versus 1/T should be linear with slope and intercept equal to $-\frac{E_a}{R}$ and lnA respectively. The Table of content for the required data is presented below,

k(/s)	T (°C)	1/T x 1000 (K)	lnk
2 x 10^{-3}	298	3.36	-6.2146
4 x 10^{-3}	308	3.25	-5.5215
6 x 10^{-3}	318	3.14	-5.1160
8 x 10^{-3}	328	3.05	-4.8283

1.0 x 10^{-2}	338	2.96	-4.6052

The required graph is presented below,



From the graph, the slope is equal to -3.912, therefore, - 3.945 = -E_a/R (where R is the gas constant. R = 8.314 J/mol/K). Therefore, E_a = 3.912 x 8.314 = 32.80 J/mol

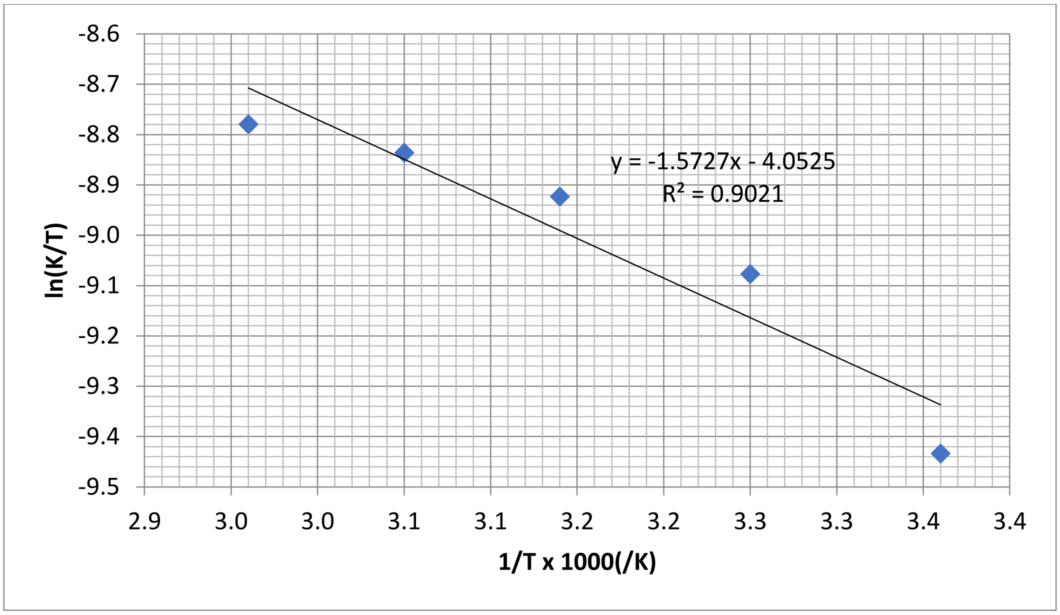
i. The intercept from the graph is 7.179. This indicate that lnA = 6.870 indicating that the Arrhenius constant, A = Exp(7.179) = 1311.59.

ii. The change in entropy and enthalpy of activation of the reaction can be calculated using the Transition state equation, which can be written as, $ln\left(\frac{k}{T}\right) = ln\left(\frac{R}{Nh}\right) + ln\left(\frac{\Delta S^{++}}{R}\right) - \left(\frac{\Delta H^{++}}{RT}\right)$. This indicate that a plot of , $ln\left(\frac{k}{T}\right)$ versus 1/T should be linear with slope and intercept equal to -$\frac{\Delta H^{++}}{R}$ and [$ln\left(\frac{R}{Nh}\right) + ln\left(\frac{\Delta S^{++}}{R}\right)$] . The required Table of value is presented below

k(/s)	**T (°C)**	**1/T x 0.001 (K)**	$ln\left(\frac{k}{T}\right)$
2 x 10^{-3}	298	3.36	-9.4335
4 x 10^{-3}	308	3.25	-9.0768
6 x 10^{-3}	318	3.14	-8.9227

8×10^{-3}	328	3.05	-8.8357
1.0×10^{-2}	338	2.96	-8.7796

The Transition state plots for the given reaction is presented below,



From the plots, the slope is -3.599 indicating that $-\frac{\Delta H^{++}}{R} = --1.572$, hence $\Delta H^{++} = 13.07\, J/mol$. On the other hand, the intercept is -0.133 indicating that $ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S^{++}}{R}\right) = -4.052$. where N is the Avogadro' s number and h is the Planck constant. $ln\left(\frac{R}{Nh}\right) = ln\left(\frac{8.314}{(6.022 \times 10^{23})(6.6226 \times 10^{-34})}\right) = 23.76$. Therefore, 23.76 + $\frac{\Delta S^{++}}{8.314}$ = -4.052, or $\frac{\Delta S^{++}}{8.314} = -27.812$, which gives,

$$\Delta S^{++} = 8.314\, x\, (-27.812) = 231.23\, J/mol$$

iii. The Transition state equation has some similarities with the Arrhenius equation and can be used to explain Arrhenius parameters. Recall the Arrhenius equation (equation 81), $lnk = lnA - \frac{E_a}{RT}$ while the transition state equation can be expressed as $lnk = ln\left(\frac{RT}{Nh}\right) + \left(\frac{\Delta S^{++}}{R}\right) - \left(\frac{\Delta H^{++}}{RT}\right)$. Then it is obvious that if we equate the two equation, some terms can be compared. i.e.,

$$lnk = lnA - \frac{E_a}{RT} = \left\{ln\left(\frac{RT}{Nh}\right) + \left(\frac{\Delta S^{++}}{R}\right)\right\} - \left(\frac{\Delta H^{++}}{RT}\right)$$

It is evident from the above that A in the Arrhenius equation is related to entropy change while E_a is related to enthalpy change. That is $A = \left(\frac{RT}{Nh}\right).e^{\left(\frac{\Delta S^{++}}{R}\right)} and E_a = \Delta H^{++}$. Therefore, the Arrhenius factor can be estimated in terms of ΔS^{++} and the activation energy can be estimated in terms of E_a.Generally, when volume and pressure are taken into consideration, then $E_a = \Delta H^{++} + \Delta(PV)$. For solids, change in volume is negligible, therefore, $\Delta(PV) \approx 0$ and $E_a \approx \Delta H^{++}$. However, for gases, PV = nRT, therefore $\Delta(PV) = \Delta n^{++}RT$ and $E_a = \Delta H^{++} + \Delta n^{++}RT$

4.0 Conclusion

The behaviour of molecular species from the onset of the reaction, through the intermediate level to the product formation states are explained by various theories, each of them which has their scope and limitation. However, comprehensive kinetic behaviour is achieved by considering all the theories and consequent application to real experimental situations. Within the scope of each of these theories, good correlations with experimental data have been recorded to some extent.

5.0 Summary

They are three theories of chemical reaction including the Arrhenius theory, the collision theory and the Transition state theory. Arrhenius theory considers that the rate of chemical reaction is proportional to the frequency of effective collision. The shortcoming of Arrhenius theory lied on the ability to compute the frequency of effective collision. Consequently, the collision theory explains the Arrhenius factor but still suffer some setbacks because it is most applicable to gaseous reactions and does not provide a way to calculate the probability factor, P. The transition state theory relates rate constant to thermodynamics parameters.

The rate of reaction has strong link with frequency of effective collision, Arrhenius factor, the rate of decomposition of the transition state and thermodynamic parameters. However, among all the factors that link rate constant with these parameters, thermodynamic parameters are more feasible and applicable because they can easily be verify by experiments.

6.0 (i) Self Assessment Exercises and Answers

1.(a) Write an equation for the exponential form of the Arrhenius equation and define all the terms in the equation. Which of the terms defines the average kinetic energy of the system?

(b) Comment on the expected magnitude of the rate constant and reaction rate as the temperature increases or decreases

(c) How does the equation compare with exponential decay law

2. (a) The data below is kinetic data obtained for isomerization of cyclopropane to propene. Use the data to calculate the activation energy and pre-exponential factor for the reaction

T	k
477	0.00018
523	0.0027
577	0.03
623	0.26

(b) Why is the calculated value of the activation energy too high?

3. It is generally believed that for most reaction, the rate of reaction doubles for every ten degree rise in temperature (although this thumb rule is not generally obeyed). Calculate the expected activation energy for reactions that obeys this thumb rule

Answer to Self Assessment Exercise

1.(a)

$$k = Aexp\left(\frac{-E_a}{RT}\right)$$

where k is the rate constant, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant and T is the temperature. The average kinetic energy is given as RT.

(b) The exponent of the Arrhenius equation is the ration of the activation energy divided by the average kinetic energy (RT). The larger the ratio, the lower is the rate of rate constant and the faster is the reaction. This means high temperature and low E_a will lead to low values of rate constant and hence a faster reaction.

(c) The decay is not the concentration of a reactant as a function of time, but the magnitude of the rate constant as a function of the exponent $-E_a/RT$

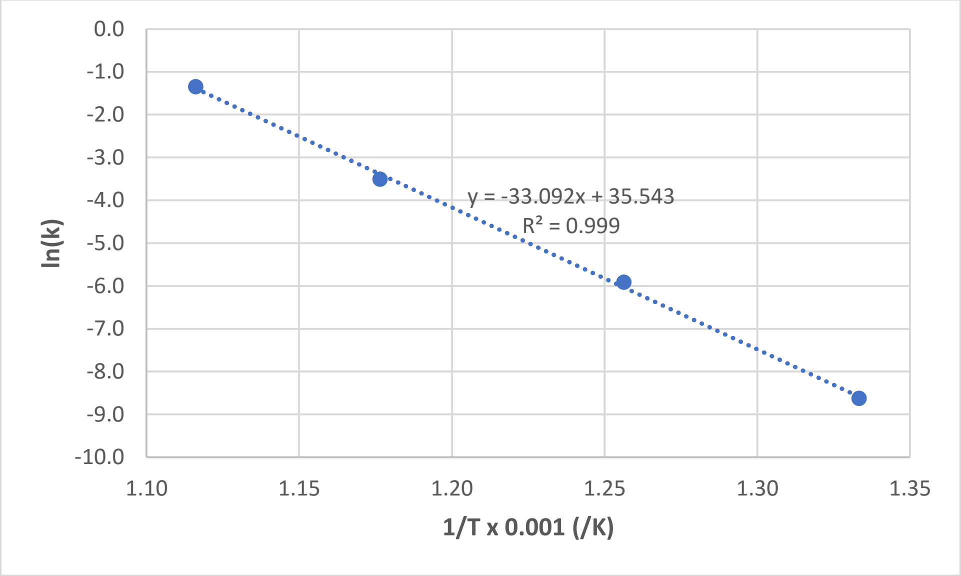
2. The Arrhenius equation can be transformed as follows,

$$k = Aexp\left(\frac{-E_a}{RT}\right)$$

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

The above equation indicates that a plot of ln(k) versus 1/T should be linear with slope equal to E_a/R and intercept equal to ln(A). The Table of values and the Arrhenius plot are presented below,

T (°C)	K (/s)	T (K)	1/T (/K)	lnK
477	0.00018	750	0.001333	-8.62255
523	0.0027	796	0.001256	-5.9145
577	0.03	850	0.001176	-3.50656
623	0.26	896	0.001116	-1.34707



From the plot, the slope = -33.092 indicating that the activation energy is

-33.092 x 1000) (8.314) kJ/mol = 275126.89 J/mol = 275. 13 kJ/mol

The exponential factor can be obtained from the intercept, hence

log(A) = 35.543

A = $\log^{-1}$(35.543) = 3.543 x 10^{35}

(b) This activation energy is high, which is not surprising because a carbon-carbon bond must be broken in order to open the cyclopropane ring. (C–C bond energies are typically around 350 kJ/mol.) This is why the reaction must be carried out at high temperature.

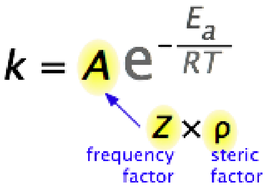
3. The Arrhenius equation can be used if the rate constants for two different temperatures are known. Let k_1 be equal to 1 and $k_2 = 2$, Also $T_1 = 295$ K, then $T_2 = T_1 + 10$ K $= 305$ K

The equation modified equation is,

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

$$E_a = \frac{Rln\left(\frac{k_1}{k_2}\right)}{\left(\frac{1}{T_1} - \frac{1}{T_2}\right)} = \frac{(8.314\, J/K)ln\left(\frac{2}{1}\right)}{\left(\frac{1}{295\, K} - \frac{1}{T305\, K_2}\right)} = 52.4\, kJ/mol$$

4. The most obvious factor that will limit reaction rate is the rate at which reactant molecules come into contact. This can be calculated from kinetic molecular theory and is known as the frequency or collision factor. This can be compared to the Arrhenius equation as follows,



In some reactions, the relative orientation of the molecules at the point of collision is important, so a geometrical or *steric factor* (commonly denoted by ρ can be defined. In general, liken the product, $\rho Z = A$

(ii) Study Activity

(a) Obtain a mild steel sheet. From the sheet, obtained five different coupons (each of dimension, 5 x 4). (ii) Record the weight of each coupon (iii) Prepared solution of 5 M H_2SO_4 and filled it to five different beakers. (iv) To each of the beaker, add one mild steel coupon (v) After 10, 15, 20, 25 and 30 minutes withdraw each coupon, wash each of them with distilled water to remove the corrosion product. And re-weigh them separately. Record the new weight and obtain the difference in weight (i.e original weight -weight after immersion). The corrosion rate can be obtained by dividing weight loss by time (i.e period of immersion). (2 hours)

(b) Plot a graph of corrosion rate against time and obtained the value for the rate of corrosion

(c) Plot a graph of -log(weight loss) against time. From your plot, can it be concluded that the corrosion of mild steel is first order? (30 minutes)

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MODULE 2

STUDY UNIT 1: ELEMENTARY REACTIONS

1.0 Introduction

Different elementary steps combine to give a complex reaction. An elementary step has one transition step, no intermediate and cannot be broken down into simpler reactions (Fig. 3.1)

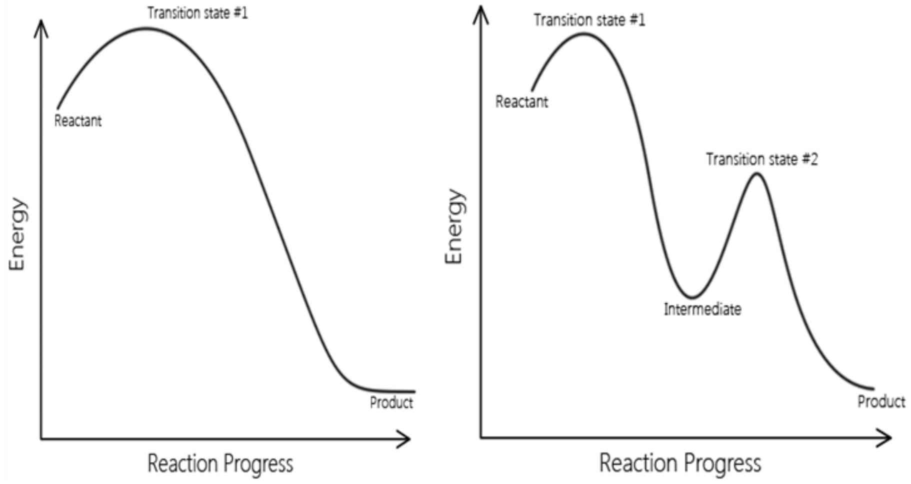
Non-elementary reactions can be described by multiple elementary reaction steps. A set of elementary reactions comprises of a reaction mechanism, which predicts the elementary steps involved in a complex reaction. Fig. 3.1b shows a reaction coordinate of a complex reaction, which involves an intermediate and multiple transition A complex reaction can be explained in terms of elementary reactions.

2.0 IntendedLearning Outcomes

When you have studied this session, you should be able to:

(i) know what is elementary and non elementary reactions
(ii) understand the concept of molecularity of a reaction
(iii) know the mechanism of unimolecular reaction
(iv) know the mechanism of bimolecular reaction
(v) know mechanism of termolecular reaction

(vi) solve problems associated with unimolecular, bimolecular and termolecular reactions.



(a) (b)

Fig. 3.1: Reaction profile diagram for (a) elementary step (b) non elementary step reactions

3.0 Main Content

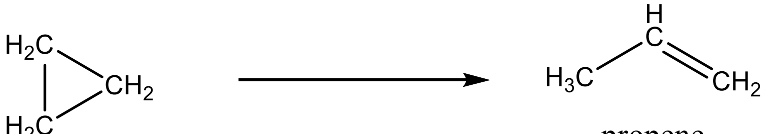
3.1 Molecularity of a reaction

Molecularity of a reaction is the number of molecules that react in an elementary reaction and is numerically equal to the sum of the stoichiometric coefficients of reactants in the elementary reaction. For reaction that proceeds via different steps, some of the steps may be fast and some may be slow. The slowest step is the rate determining or rate limiting step and the number of molecules associated with the slowest step is the molecularity of the reaction.

A reaction is said to be unimolecular, bimolecular or termolecular when one, two or three molecules comes together to form products respectively

3.1.1 Unimolecular reaction

A unimolecular reaction occurs when a single molecule rearranges its atoms to produce one or more products. Example of a unimolecular reaction is the isomerization of cyclopropane to propene as shown below



propene

Some common reactions in chemistry occur via unimolecular process. These include, radioactive decay, cis-trans isomerization, thermal decomposition, ring opening and racemization.

The basic theory in explaining the mechanism of a unimolecular reaction was proposed by Frederick Alexander Linderman (in 1922), who stated that a unimolecular reaction occurs via bimolecular activation step, followed by a rate determining unimolecular step. According to Linderman, a molecule, 'A' reacting to give product will first undergo bimolecular activation to form an intermediate (step1) and the intermediate will decompose to give the product (step 2)

$$\text{A} + \text{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{A} + \text{A}^* \text{ (step 1)}$$

$$\text{A*} \xrightarrow{k_2} \text{Product} \qquad \text{(step 2)}$$

The law of mass action states that the velocity of a chemical reaction is proportional to the concentration of the reactants (the proportionality constant in this case is the rate constant). Therefore, applying the law of mass action to the above reactions, we have,

$$\frac{d[A^*]}{dt} = k_1[A][A] - k_{-1}[A][A^*] - k_2[A^*] \qquad 3.1$$

According to the steady state approximation, the rate of change of the concentration of the intermediate will approximately be zero. That is $\frac{d[A^*]}{dt} = 0$ which implies that the right hand side of the equation can be written as,

$$k_1[A][A] - k_{-1}[A][A^*] - k_2[A^*] = 0 \qquad 3.2$$

$$k_1[A]^2 = k_{-1}[A][A^*] + k_2[A^*] \qquad 3.3$$

$$k_1[A]^2 = [A^*](k_{-1}[A] + k_2) \qquad 3.4$$

$$[A^*] = \frac{k_1[A]^2}{(k_{-1}[A] + k_2)} \qquad 3.5$$

However, the rate of the reaction is given as

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2 k_1[A]^2}{(k_{-1}[A] + k_2)} \qquad 3.6$$

If $k_{-1}[A] \gg k_2$, then k_2 can becomes negligible and the rate becomes

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2 k_1[A]^2}{k_{-1}[A]} = \frac{k_2 k_1[A]}{k_{-1}} = k_{eff}[A] \qquad 3.7$$

where k_{eff} is an effective first order rate constant. $k_{eff} = \frac{k_2 k_1}{k_{-1}}$is a function of pressure and equation 3.7 is prevalent at high pressure, in which collisional deactivation of A* is the rate determining step, resulting in a first order reaction. However, if $k_2 \gg k_{-1}[A]$, equation 3.6 becomes,

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2 k_1 [A]^2}{k_2} = k_1[A]^2 \qquad 3.8$$

which suggest that bimolecular excitation is the rate determining step and is second order with respect to A. This option is prevalent at high pressure.

There are two major shortcomings. The first is that Linderman did not take into account, the dependence of biomolecular activation on energy. The theory also neglects the internal degree of freedom of the molecule and undermine the rate of molecular activation. Secondly, the particular motion required for the unimolecular deactivation was not taken into consideration. These shortcomings, initiated the modification of Linderman mechanism by Hinshelwood. Hinshelwood accounted for internal degrees of freedom during the activation process and modelled the internal modes of A by a hypothetical molecule having ‘s’ equivalent classical harmonic oscillators, and by considering thermal equilibrium and the strong collision assumption (i.e., the probability of deactivation is equal to the collision frequency and that each collision is efficient to deactivate). Without proof, Hinshelwood equation is written according to equation 3.9,

$$k_1 = \frac{Z}{(s-1)!} . \left\{\frac{E_a}{k_B T}\right\}^{s-1} exp\left\{\frac{E_a}{k_B T}\right\} \qquad 3.9$$

Hinshelwood equation has been found to bridge much gap that was created by the Linderman theory.

3.1.2 Bimolecular collision

A bimolecular reaction is characterised by two molecules colliding with one another, leading to the exchange of energy, atom or group of atoms. For example, if molecule A react with molecule B through a bimolecular collision, the equation (equation 3.10) and the rate (equation 3.11) can be written ^{as} follows,

$$A + B \rightarrow Product \qquad 3.10$$

$$-\frac{d[A]}{dt} = k_2[A][B] \qquad 3.11$$

Therefore, the rate of the reaction is proportional to the rate at which the reactants come together. The collision and transition state theories so far discussed covers bimolecular reaction.

3.1.3 Termolecular collision

The probability of three molecules colliding together is very rare, indicating that termolecular reaction is not common. In 1916 Trauts found that values of rate constant calculated through the collision theory for triple collisions are extraordinary higher than the corresponding experimental values. From these findings, he drew conclusion that termolecular reactions takes place in two stages. This may involve the initial bimolecular collision of the two molecules to formed energetically excited intermediate. This intermediate will collide with the third molecule in a second bimolecular reaction, transferring the excess energy to it. For example, the reaction between nitrogen (II) oxide and halide can be represented as follow,

$$2NO + X_2 \quad \rightarrow \quad 2NOX \qquad 3.12$$

The above reaction often takes place through two steps, which can be represented as,

$$\mathrm{NO} \;+\; \mathrm{X_2} \underset{k}{\rightleftharpoons} \mathrm{NOX_2} \quad \text{(step 1)}$$

$$\mathrm{NOX_2} \;+\; \mathrm{NO} \xrightarrow{k_2} \mathrm{2NOX} \quad \text{(step 2)}$$

The equilibrium constant for the first step can be written as,

$$K_{eq} = \frac{[NOX_2]}{[NO][X_2]} \text{ or } [NOX_2] = K_{eq}[NO][X_2] \qquad 3.13$$

The second step is the rate determining step and the rate of the reaction can be written as

$$\frac{d[NOX]}{dt} = k_2[NOX_2][NO] \; = \; k_2K_{eq}[NO]^2[X_2] \qquad 3.14$$

Equation 3.14 reference a third order reaction. The rate of most termolecular reaction tends to decrease with increase in temperature.

3.2 Steady state approximation

Some reactions proceed through the formation of reaction intermediate such as the one shown in the equation below,

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k'_1} \mathrm{C}$$

As the concentration of A decreases, the concentration. ratio of B increases and that of C increases as it is formed. At a certain time, the concentration of B increases from zero to maximum and then drop back to zero as A is consumed even as C dominates (see Fig.3.2, which show how the concentration of the intermediate first increases and becomes constant at the steady state zone before deceasing to zero).

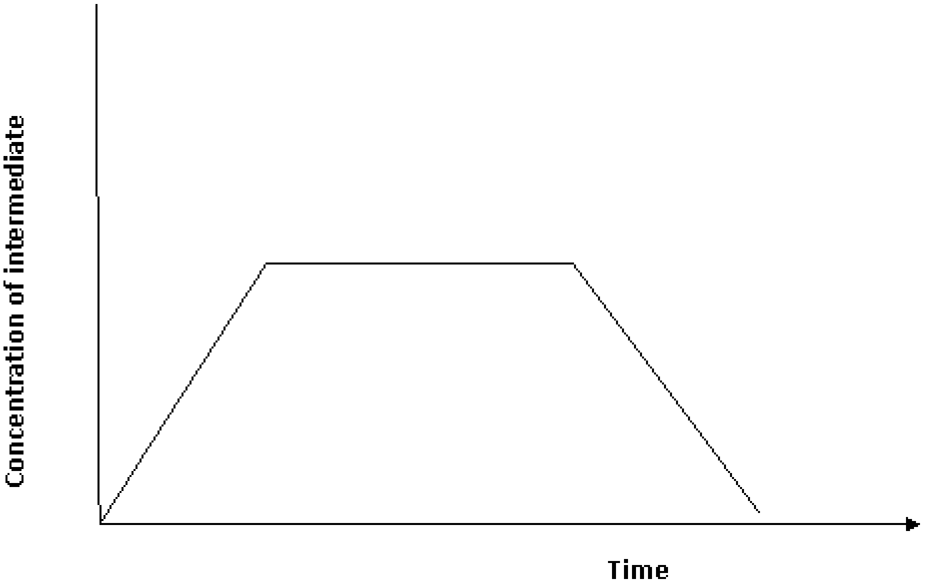


Fig. 3.2: Graph showing the attainment of steady state

Kinetic approach requires development of rate equation. If the rate constant, $k_1^{'} \gg k_1$, then the intermediate will be very reactive and will be consumed once it is formed. Similarly, if A reacts slowly, the concentration of the intermediate will remain at the same minimal value. The assumption that the concentration of the intermediate remains constant for a reasonable period of the reaction is called steady state assumption (SSA).

Worked example 1

(a) Given that a reaction occurs as occurs as shown in the equations below,

$$\text{A} + \text{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{A} + \text{A}^* \text{ (step 1)}$$

$$\text{A}^* \xrightarrow{k_2} \text{Product} \qquad \text{(step 2)}$$

Derive the Linderman mechanism and the law of mass action to derive expression for the integrated rate law

(b) If $k_{-1}[A] \gg k_2$ and if $k_2 \gg k_{-1}[A]$

Solution

(a) The law of mass action states that the velocity of a chemical reaction is proportional to the concentration of the reactants (the proportionality constant in this case is the rate constant). Therefore, applying the law of mass action to the above reactions, we have,

$$\frac{d[A^*]}{dt} = k_1[A][A] - k_{-1}[A][A^*] - k_2[A^*] \qquad (1)$$

According to the steady state approximation, the rate of change of the concentration of the intermediate will approximately be zero. That is $\frac{d[A^*]}{dt} = 0$ which implies that the right hand side of the equation can be written as,

$$k_1[A][A] - k_{-1}[A][A^*] - k_2[A^*] = 0 \qquad (2)$$

$$k_1[A]^2 = k_{-1}[A][A^*] + k_2[A^*] \qquad (3)$$

$$k_1[A]^2 = [A^*](k_{-1}[A] + k_2) \qquad (4)$$

$$[A^*] = \frac{k_1[A]^2}{(k_{-1}[A] + k_2)} \qquad (5)$$

However, the rate of the reaction is given as

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2k_1[A]^2}{(k_{-1}[A] + k_2)} \qquad (6)$$

(b)

If $k_{-1}[A] \gg k_2$, then k_2 can becomes negligible and the rate becomes

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2k_1[A]^2}{k_{-1}[A]} = \frac{k_2k_1[A]}{k_{-1}} = k_{eff}[A] \qquad (7)$$

where k_{eff} is an effective first order rate constant, $k_{eff} = \frac{k_2k_1}{k_{-1}}$is a function of pressure and equation 99 is prevalent at high pressure, in which collisional deactivation of A* is the rate determining step, resulting in a first order reaction.

However, if $k_2 \gg k_{-1}[A]$, equation 6 becomes,

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2k_1[A]^2}{k_2} = k_1[A]^2 \qquad (8)$$

4.0 (i) Self Assessment Exercises and Answers

1.(a) Differentiate between elementary and complicated reactions

(b) Write short note on molecularity of a reaction. Hence what is the molecularity of a reaction that occurs in the following sequences,

Overall Reaction	H_2O_2 = H_2O + 1/2O	
Step 1	H_2O_2 = H_2O + [O]	slow
Step 2	[O] + [O] =)$_2$	Fast

(c) Is there any restriction to values that molecularity of a reaction can assume? Give reason for your answer.

2. (a) According to Linderman mechanism, if A' react to give product and first undergo bimolecular activation to form an intermediate (step1) and the intermediate decomposes to give the product (step 2)

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A + A^* \text{ (step 1)}$$

$$A^* \xrightarrow{k_2} \text{Product} \quad \text{(step 2)}$$

(a) Derive an expression for the rate of decomposition of the intermediate (i.e. $\frac{d[A^*]}{dt}$) using the law of mass action

(b) Use the steady state approximation to show that $\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2 k_1 [A]^2}{(k_{-1}[A] + k_2)}$. Where [P] is the concentration of the product.

(c) What would the reaction rate be if (i) If $k_{-1}[A] \gg k_2$ (ii) If $k_2 \gg k_{-1}[A]$

3a. (a) State Linderman theory of reaction

(b) What are the shortcomings of Linderman theory of reaction mechanism

(c) How did Hinshelwood. Hinshelwood modified the Linderman equation, hence write the modified equation.

4. (a) Show that the reaction $2NO + X_2 = 2NOX$ occurs through termolecular collision if the mechanism of the reaction is

$$NO + X_2 \underset{k}{\rightleftharpoons} NOX_2 \text{ (step 1)}$$

$$NOX_2 + NO \xrightarrow{k_2} 2NOX \text{ (step 2)}$$

(b) Write short note on bimolecular collision and derive a rate equation for a simple bimolecular collision

Answers to Self Assessment questions

1.(a) Elementary reactions are those reactions that take place through only one step while complicated reactions are those that involves sequence of steps. Sequence of step through which complicated reactions takes place is called mechanism.

(b) The molecularity of an elementary reaction is defined as the minimum number of molecules, atoms or ions of the reactants(s) required for the reaction to occur and is equal to the sum of the stoichiometric coefficients of the reactants in the chemical equation of the reaction. It can also be defined as the total number of molecules of reactant in the elementary step

Step 1 is the rate determining step because it is the slowest step, hence the molecularity is two (2) because the number of reactant molecules is two (2)

(c) Molecularity cannot be negative, fractional zero and cannot be more than three because more than three molecules cannot mutually collide with each other.

2. (a) The law of mass action states that the velocity of a chemical reaction is proportional to the concentration of the reactants (the proportionality constant in this case is the rate constant). Therefore, applying the law of mass action to the above reactions, we have,

$$\frac{d[A^*]}{dt} = k_1[A][A] - k_{-1}[A][A^*] - k_2[A^*] \qquad (1)$$

(b) According to the steady state approximation, the rate of change of the concentration of the intermediate will approximately be zero. That is $\frac{d[A^*]}{dt} = 0$ which implies that the right hand side of the equation can be written as,

$$k_1[A][A] - k_{-1}[A][A^*] - k_2[A^*] = 0 \qquad (2)$$

$$k_1[A]^2 = k_{-1}[A][A^*] + k_2[A^*] \qquad (3)$$

$$k_1[A]^2 = [A^*](k_{-1}[A] + k_2) \qquad (4)$$

$$[A^*] = \frac{k_1[A]^2}{(k_{-1}[A] + k_2)} \qquad (5)$$

However, the rate of the reaction is given as

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2k_1[A]^2}{(k_{-1}[A] + k_2)} \qquad (6)$$

(c) If $k_{-1}[A] \gg k_2$, then k_2 can becomes negligible and the rate becomes

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2k_1[A]^2}{k_{-1}[A]} = \frac{k_2k_1[A]}{k_{-1}} = k_{eff}[A] \qquad (7)$$

where k_{eff} is an effective first order rate constant. $k_{eff} = \frac{k_2k_1}{k_{-1}}$is a function of pressure and equation (7) is prevalent at high pressure, in which collisional deactivation of A* is the rate determining step, resulting in a first order reaction. However, if $k_2 \gg k_{-1}[A]$, equation 3.6 becomes,

$$\frac{d[P]}{dt} = k_2[A^*] = \frac{k_2k_1[A]^2}{k_2} = k_1[A]^2 \qquad (8)$$

which suggest that bimolecular excitation is the rate determining step and is second order with respect to A. This option is prevalent at high pressure.

(3) (a) The basic theory in explaining the mechanism of a unimolecular reaction was proposed by Frederick Alexander Linderman (in 1922), who stated that a unimolecular reaction occurs via bimolecular activation step, followed by a rate determining unimolecular step.

(b) There are two major shortcomings. The first is that Linderman did not take into account, the dependence of biomolecular activation on energy. The theory also neglects the internal degree of freedom of the molecule and undermine the rate of molecular activation. Secondly, the particular motion required for the unimolecular deactivation was not taken into consideration

(c) These shortcomings, initiated the modification of Linderman mechanism by Hinshelwood. Hinshelwood accounted for internal degrees of freedom during the activation process and modelled the internal modes of A by a hypothetical molecule having ‘s’ equivalent classical harmonic oscillators. The modified equation is

$$k_1 = \frac{Z}{(s-1)!}.\left\{\frac{E_a}{k_BT}\right\}^{s-1} exp\left\{\frac{E_a}{k_BT}\right\} \qquad (1)$$

Hinshelwood equation has been found to bridge much gap that was created by the Linderman theory.

4. (a) $N2O + X_2 \quad \rightarrow \quad 2NOX$ (1)

The above reaction often takes place through two steps, which can be represented as,

$$NO + X_2 \underset{k}{\rightleftharpoons} NOX_2 \quad \text{(step 1)}$$

$$NOX_2 + NO \xrightarrow{k_2} 2NOX \quad \text{(step 2)}$$

The equilibrium constant for the first step can be written as,

$$K_{eq} = \frac{[NOX_2]}{[NO][X_2]} \text{ or } [NOX_2] = K_{eq}[NO][X_2] \qquad (2)$$

The second step is the rate determining step and the rate of the reaction can be written as

$$\frac{d[NOX]}{dt} = k_2[NOX_2][NO] = k_2K_{eq}[NO]^2[X_2] \qquad (3)$$

Equation 3 reference a third order reaction. The rate of most termolecular reaction tends to decrease with increase in temperature.

(b) A bimolecular reaction is characterised by two molecules colliding with one another, leading to the exchange of energy, atom or group of atoms. For example, if molecule A react with molecule B through a bimolecular collision, the equation (equation 1) and the rate (equation 2) can be written ^{as} follows,

$$A + B \rightarrow Product \qquad (1)$$

$$-\frac{d[A]}{dt} = k_2[A][B] \qquad (2)$$

Therefore, the rate of the reaction is proportional to the rate at which the reactants come together. The collision and transition state theories so far discussed covers bimolecular reaction.

(ii) Class Activity

Identify five chemical reactions that involves (i) Unimolecular (ii) Bimolecular (iii) termolecular reactions path. (20 minutes)

5.0 Conclusion

A chemical reaction can be classified as unimolecular, bimolecular and termolecular based on the molecularity of the reaction and the nature of collision. This classification supports the collision theory.

6.0 Summary

A chemical reaction in which one or more chemical species react directly to form products in a single reaction step and with a single transition state is called an elementary reaction. Though the formation of intermediate is not expected in an elementary reaction, several elementary reactions are known to proceed through step wise reactions characterised by reaction intermediates.

A unimolecular elementary reaction occurs when a molecule dissociates or isomerizes to form a product. At constant temperature, the rate of a unimolecular elementary reaction is proportional to the concentration of the reactant (i.e. A):

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

In a bimolecular elementary reaction, two atoms, or ions or molecules or radical reacts to form a product. At constant temperature, the rate of bimolecular elementary reaction is proportional to the concentrations of the reactants (i.e. A and B):

$$\frac{d[A]}{dt} = -k[A][\mathrm{B}]$$

The mechanism of an elementary reaction may not be straight but could be complicated considering the number of molecules involves. The works of Lindeman and others have offered explanations for the mechanism of elementary reactions

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MODULE 2

STUDY UNIT 2: COMPLEX REACTIONS

1.0 Introduction

There are several gas phase reactions that are complex because they do not follow the derived mechanism strictly but consist of various reaction steps. That is, they involved two or more side reactions. A simple reaction is characterised by one rate constant because the reactant is directly converted to product. But there are some reactions of bimolecular or termolecular nature that has different steps and each step has its own rate constant. Examples of complex reactions are

(i) Reversible or opposing reaction
(ii) Consecutive reaction
(iii) Parallel reaction
(iv) Chain reaction
(v) Polymerization reaction

2.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

(i) To know what is complex reactions and different types of complex reaction
(ii) To understand opposing reaction and derive integrated rate law for opposing reaction
(iii) To understand consecutive reaction and derive integrated rate law for consecutive reaction

(iv) To understand parallel reaction and derive integrated rate law for parallel reaction’

(v) To understand chain reaction and derive integrated rate law for chain reaction

(vi) To know how to characteristics of chain reaction

(vii) To solve problems associated with complex reactions.

3.0 Main Content

3.1 Reversible or opposing reactions

Most chemical reactions are reversible to some extent. This means there as the reactants combine to form the product, the product also become re-converted to reactants. When such systems are close to equilibrium, the rate of forward and backward reactions will be comparable. Based on the order of the forward or backward reactions, three cases can be identified. These are

(i) Those in which forward and backward reactions are first order

(ii) Those in which the forward reaction is second order and the backward reaction is first order

(iii) Those in which both forward and backward reaction are second orders.

3.1.1 Case 1: Forward and backward reaction are first order

If A reacts to give B in the forward reaction and B reacts to A in the reverse reaction such that the rate of forward reaction is represented as K_f while that of the reverse reaction is represented as k_r, then the reaction can be represented as,

$$\mathrm{A} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{B}$$

The rate equation for the above reaction can be written in terms of the decrease in concentration of A with time,

$$-\frac{d[A]}{dt} = k_f[A] - k_r[B] \qquad 4.1$$

Assuming that at time, $t = 0$, $[A] = a_0$ and $[B] = 0$, then at any other time, t, $[A] = a_0 - x$ and $[B] = x$, then equation 106 translates to equations 4.2 and 4.3,

$$-\frac{d(a_0 - x)}{dt} = k_f(a_0 - x) - k_r x \qquad 4.2$$

$$\frac{dx}{dt} = k_f(a_0 - x) - k_r x \qquad 4.3$$

At equilibrium, the rate of forward reaction is equal to the rate of backward reaction indicating that $\frac{dx}{dt} = 0$ and $k_f(a_0 - x) - k_r x = 0$. Therefore, $k_f(a_0 - x) = k_r x$ and $k_r = \frac{k_f(a_0 - x_e)}{x_e}$. X_e is the equilibrium concentration of x. Substituting for k_r in equation 4.3, yields equation 4.4,

$$\frac{dx}{dt} = \frac{k_f(a_0 - x)}{1} - \frac{k_f(a_0 - x_e)x}{x_e} \qquad 4.4$$

The right hand side of the equation can be simplified by taking the LCM of the denominator (LCM of 1 and $x_e = x_e$) and the results of lead to equation 4.5,

$$\frac{dx}{dt} = \frac{k_f(a_0 - x)}{1} - \frac{k_f(a_0 - x_e)x}{x_e} = \frac{x_e k_f(a_0 - x) - k_f(a_0 - x_e)x}{x_e}$$

$$\frac{dx}{dt} = \frac{k_f a_0 x_e - k_f x_e x - k_f a_0 x + k_f x_e x}{x_e} = \frac{k_f a_0(x_e - x)}{x_e}$$

Therefore, $\frac{dx}{dt} = \frac{k_f a_0(x_e - x)}{x_e}$, which rearranges to $\frac{dx}{(x_e - x)} = \frac{k_f a_0}{x_e} dt$ and can be integrated, within the limit of concentration (i.e 0 to x) and time (0 to t) as follows,

$$\int_0^x \frac{dx}{(x_e - x)} = \frac{k_f a_0}{x_e} \int_0^t dt \qquad 4.5$$

$$[-ln(x_e - x)]_0^x = \frac{k_f a_0}{x_e} [t]_0^t \qquad 4.6$$

$$-ln(x_e - x) - \{-ln(x_e - 0)\} = \frac{k_f a_0 t}{x_e} \qquad 4.7$$

$$ln x_e - ln(x_e - x) = \frac{k_f a_0 t}{x_e} \qquad 4.8$$

$$\frac{x_e}{a_0} ln\left(\frac{x_e}{x_e - x}\right) = k_f t \qquad 4.9$$

Equation 4.9 is the integrated rate law for a reversible reaction in which the forward and backward reactions are first order.

Alternative approach to the derivation of an integrated rate law for a reversible reaction that is first order in both directions, is presented as follow,

$$-\frac{d[A]}{dt} = k_f[A] - k_r[B]$$

If the initial concentration of the reactant is [A$_0$] (i.e. at time, t = 0), then the concentrations of A and B at some other time, t are [A] and [A$_0$] – [A] respectively. Therefore, the rate equation becomes,

$$-\frac{d[A]}{dt} = k_f[A] - k_r([A_0] - [A]) \tag{4.10}$$

$$-\frac{d[A]}{dt} = k_f[A] - k_r[A_0] + k_r[A] \tag{4.11}$$

$$-\frac{d[A]}{dt} = (k_f + k_r)[A] - k_r[A_0] \tag{4.12}$$

$$-\frac{d[A]}{dt} = (k_f + k_r)\left\{[A] - \frac{k_r[A_0]}{k_f+k_r}\right\} \tag{4.13}$$

At equilibrium, $\frac{k_f}{k_r} = \frac{[B_{eq}]}{[A_{eq}]} = \frac{[A_0]-[[A_{eq}]]}{[A_{eq}]}$. Therefore, $k_f[A_{eq}] = k_r([A_0] - [A_{eq}])$, which rearranges to give, $(k_f + k_r)[A_{eq}] = k_r[A_0]$ or $[A_{eq}] = \frac{k_r[A_0]}{k_f+k_r}$. Substituting for $\frac{k_r[A_0]}{k_f+k_r}$ in equation 4.13, gives equation 4.14, which rearranges to equation 4.15,

$$-\frac{d[A]}{dt} = (k_f + k_r)\{[A] - [A_{eq}]\} \tag{4.14}$$

$$-\frac{d[A]}{[A]-[A_{eq}]} = (k_f + k_r)dt \tag{4.15}$$

The solution to equation 4.15 can only be gotten through integration within the concentration and time limits as shown below,

$$-\int_{[A_0]}^{[A]} \frac{d[A]}{[A]-[A_{eq}]} = (k_f + k_r)\int_0^t dt \tag{4.16}$$

$$\left[-ln([A] - [A_{eq}])\right]_{[A_0]}^{[A]} = (k_f + k_r)[t]_0^t \tag{4.17}$$

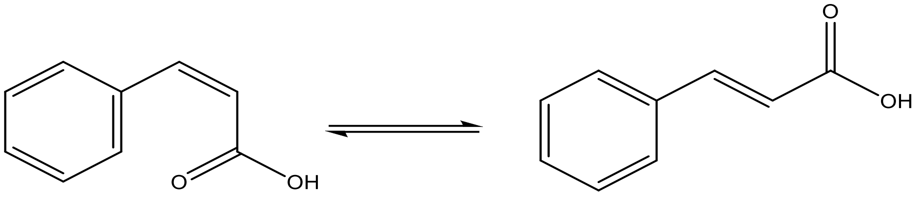
$$-ln([A] - [A_{eq}]) - \{-ln([A_0] - [A_{eq}])\} = (k_f + k_r)t \tag{4.18}$$

$$ln\left(\frac{[A_0]-[A_{eq}]}{[A]-[A_{eq}]}\right) = (k_f + k_r)t \tag{4.19}$$

From equation 4.19, a plot of $ln\left(\frac{[A_0]-[A_{eq}]}{[A]-[A_{eq}]}\right)$ versus t should be linear with slope equal to $k_f + k_r$.The reciprocal of this rate constant is called relaxation time, i.e $\tau = 1/(k_f + k_r)$ and it applies when the system relaxes towards its equilibrium.

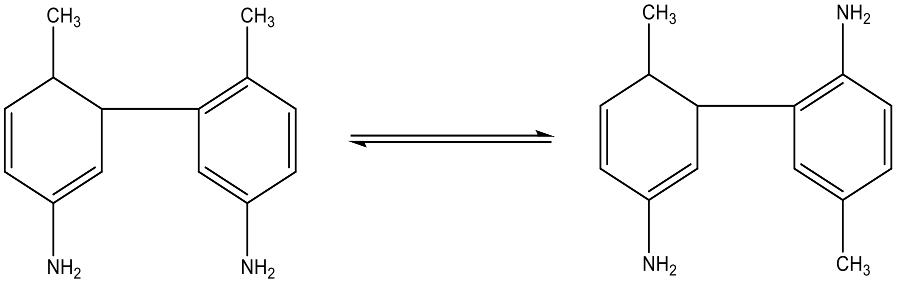
Examples of reversible reactions that are first order in both forward and backward reactions are,

i. Cis-trans isomerisation of cinnamic acid

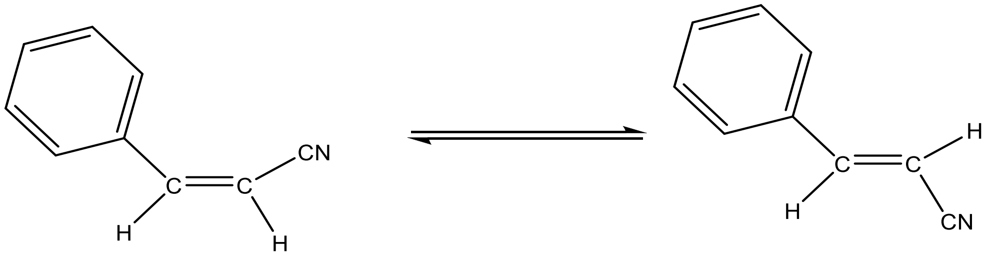


cis-cinnamic acid trans-cinnamic acid

ii. Cis trans racemisation of 3-(3-amino-6-methylcyclohexa-2,4-dienyl)-4-methylaniline



iii. Cis-trans isomerisation of styryl cyanide



3.1.2 Case 2: Forward reaction is second order and backward reaction is first order

This type of reversible reaction may involve two reactants, A and B and one product in the forward reaction. Therefore, the equation for the reaction can be written as,

$$A + B \underset{k_1}{\overset{k_2}{\rightleftharpoons}} C$$

The rate law for the above reaction can be written as,

$$-\frac{d[A]}{dt} = k_2[A][B] - k_1[C] \tag{4.20}$$

(N/B. Further derivation is beyond the scope of this course)

3.1.4 Case 3: Forward and backward reactions are second order

Reversible reactions in which forward and backward reactions are second order may be associated with bimolecular collision in both directions. The general equation for such reactions can be written as,

$$\mathrm{A} + \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C} + \mathrm{D}$$

At time, t = 0, [A] = a_0, [B] =b_0 but at time, t, [C] = x, [D] = x, [A] = a_0-x and [B] = b_0 – x. The rate equation for the above reaction will be

$$-\frac{d(a_0 - x)}{dt} = \frac{dx}{dt} = k_2(a_0 - x)(b_0 - x) - k_{-2}x^2 \tag{4.21}$$

(N/B. Further derivation is beyond the scope of this course)

4.2 Consecutive or Series Reactions

Consecutive reactions are those reactions that proceed through sequence of step called mechanism. Most reactions that are encountered in chemical sciences are consecutive reaction. For example, A may react via unimolecular to give B, which in turn reacts unimolecularly to give C, the final product. These steps can be represented by the equation below,

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{C}$$

A comm. on example of consecutive reaction is the radioactive decay. Since both reactions is first order, the rate equations can be written as follow,

$$-\frac{d[A]}{dt} = k_1[A] \tag{4.22}$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \tag{4.23}$$

$$\frac{d[C]}{dt} = k_2[B] \tag{4.24}$$

At time, t = 0, [A] = a_0, [B] = 0 and [C]=0. From equation 200, we have,

$$-\int_{a_0}^{a_t} \frac{d[A]}{[A]} = \int_0^t k_1 dt \tag{4.25}$$

$$[\ln A]_{a_0}^{a_t} = -k_1 t \tag{4.26}$$

$$a_t = a_0 e^{-k_1 t} \tag{4.27}$$

5unstituting equation 4.27 into equation 4.23, equation 4.28 is obtained

$$\frac{db}{dt} = k_1 a_0 e^{-k_1 t} - k_2 b \qquad 4.28$$

Explanation of the derivation

Equation 4.28 can be solved using integration formula. For a given differential of y with respect to x(P and Q are functions of x), we have,

$$\frac{dy}{dx} + P(x)y = Q(x)$$

The integration factor is given as:

$$R(x) = e^{\int P(x)dx}$$

The final integration can be gotten from the formula,

$$yR(x) = \int Q(x)R(x)dx$$

Applying the above to equation 206, let $P(t) = k_2$ and $Q(t) = k_1 a_0 e^{-k_1 t}$

$$R(t) = e^{\int k_2 dt} = e^{k_2 t}$$

$$yR(x) = bR(t) = be^{k_2 t} = k_1 a_0 \int e^{-k_1 t} . e^{k_2 t} = \frac{k_1 a_0}{k_2 - k_1} e^{(k_2 - k_1)t} + C$$

$$b = \frac{k_1 a_0}{k_2 - k_1} . \frac{e^{(k_2 - k_1)t}}{e^{k_2 t}} + \frac{C}{e^{k_2 t}} \qquad 4.29$$

$$b = \frac{k_1 a_0}{k_2 - k_1} e^{-k_1 t} + Ce^{-k_2 t} \qquad 4.20$$

The value of the constant can be gotten by setting t = 0, when b = 0, this gives, $0 = \frac{k_1 a_0}{k_2 - k_1} + C$.

Therefore, $C = -\frac{k_1 a_0}{k_2 - k_1}$ and equation 4.30 translates to equation 44.31,

$$b = \frac{k_1 a_0}{k_2 - k_1} e^{-k_1 t} - \frac{k_1 a_0}{k_2 - k_1} e^{-k_2 t} \qquad 4.31$$

$$b = \frac{k_1 a_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \qquad 4.32$$

The concentration of C can be evaluated by using the concept of conservation of the number of moles. That is $[A]_0 = [A] + [B] + [C]$ or $a_0 = a_t + b + c$, therefore, $c = a_0 – a_t – b$. Substituting for the listed values gives,

$$[C] = a_0 - a_0 e^{-k_1 t} - \frac{k_1 a_0}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \qquad 4.33$$

$$[C] = a_0 - a_0 e^{-k_1 t} - \frac{k_1 a_0}{k_2 - k_1} e^{-k_1 t} + \frac{k_1 a_0}{k_2 - k_1} e^{-k_2 t} \qquad 4.34$$

Equation 4.34 reveals that the rate depends on two major possibilities. These are $k_2 \gg k_1$ and $k_1 \gg k_2$. When $k_1 \gg k_2$, the nature of variation of concentration with the progress of the reaction is as shown in Fig. 4.1. The Figure indicates that [B] increases from zero to a maximum concentration as [A] decreases from maximum to zero. Finally, [C] increases as A and B become depleted.

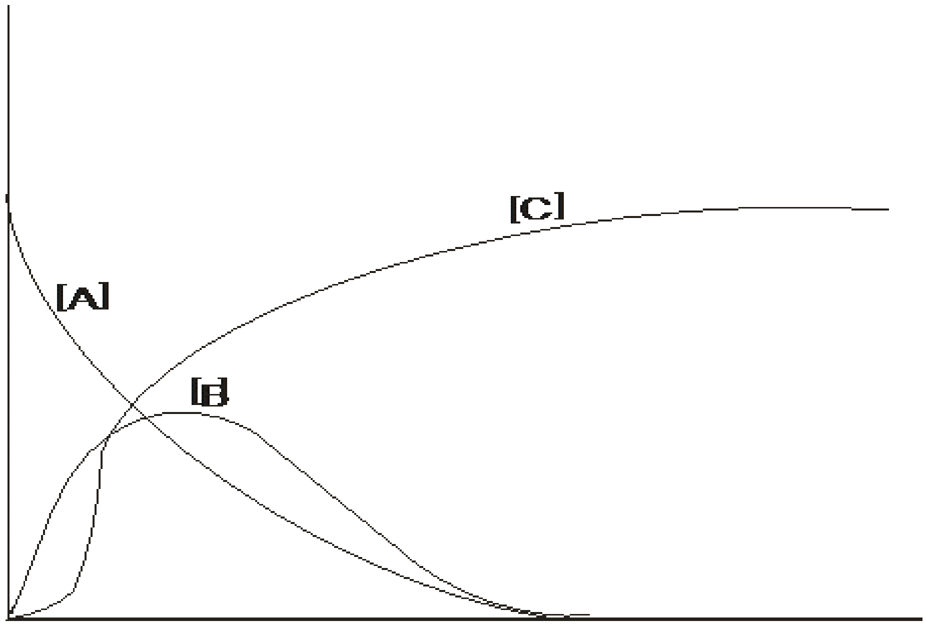


Fig. 4.1: Progress of consecutive reaction when $k_1 \gg k_2$

However, when $k_2 \gg k_1$, the expected plot is shown in Fig 4.2. In this case, the rate of decrease of A correspond to the rate of formation of C. The concentration of B seems to remain fairly constant after reaching its maximum. This is consistent with the steady state approximation. The graph also reveals that the concentration of B remains relatively small indicating that is it been destroyed faster than it is formed. This is most related to the situation where the two rate constants are relatively comparable.

Examples of consecutive reactions are,

i. Pyrolysis of acetone, which occurs through the following steps

$$CH_3COCH_3 \rightarrow CH_2 = CO + CH_4$$

$$CH_2 = CO \rightarrow \frac{1}{2}C_2H_4 + CO$$

ii. The decomposition of dimethyl ether, which follows two steps

$$CH_3OCH_3 \rightarrow CH_4^+ + HCHO$$

$CH_4^+ + HCHO \rightarrow CO + H_2 + CH_4$

iii. Decomposition of sodium hypochlorite in alkaline solution

$2NaClO \rightarrow NaCl + NaClO_2$

$NaClO_2 + NaClO \rightarrow NaCl + NaClO_3$

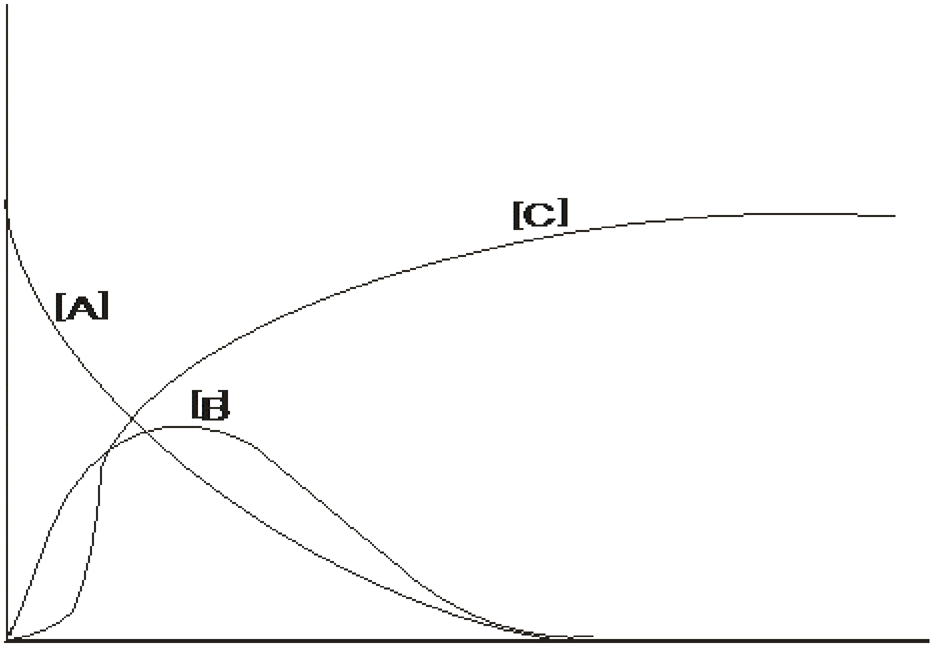
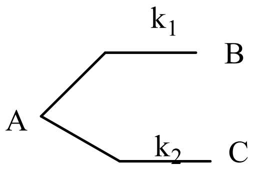


Fig. 4.2: Progress of consecutive reaction when $k_2 \gg k_1$

3.3 Competitive Reactions

Competitive reactions (parallel, simultaneous reactions) are those reactions in which the reactants give more than one product, in more than one way and at the same time. When side reactions take place, the reaction that gives maximum yield of product is called main reaction while the other ones are called side reactions. The kinetics of parallel reaction can be studied but derivation of a general or integrated rule may not be possible because its kinetics depends on the type of reaction. For example, if a reactant, A gives two different products as shown below, then kinetic equation can be derived if the rate at which each step occurs is known



The rate of the above reaction is,

$$Rate = k_1[A] + k_2[A] = [A](k_1 + k_2) \qquad 4.35$$

$$-\frac{d[A]}{dt} = [A](k_1 + k_2) \qquad 4.36$$

$$-\frac{d[A]}{[A]} = (k_1 + k_2)dt \qquad 4.37$$

Integrating the above equation between the, a_0 and a_t at time, t = 0 and at time, t, we have,

$$\int_{a_0}^{a_t} -\frac{d[A]}{[A]} = (k_1 + k_2)\int_0^t dt \qquad 4.38$$

$$ln\left(\frac{a_t}{a_0}\right) = -(k_1 + k_2)t \qquad 4.39$$

$$a_t = a_0 e^{-(k_1 + k_2)t} \qquad 4.40$$

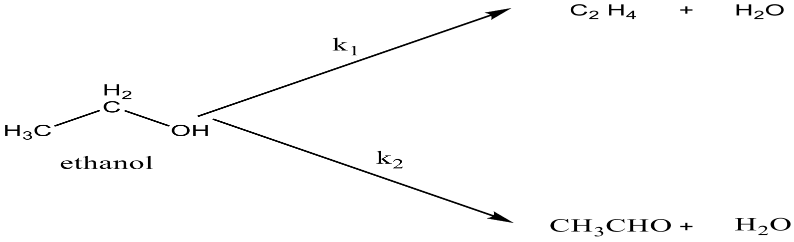
From equation 4.39, the half-life for this reaction can be estimated thus,

$$ln\left(\frac{\frac{a_0}{2}}{a_0}\right) = -(k_1 + k_2)t_{\frac{1}{2}}$$

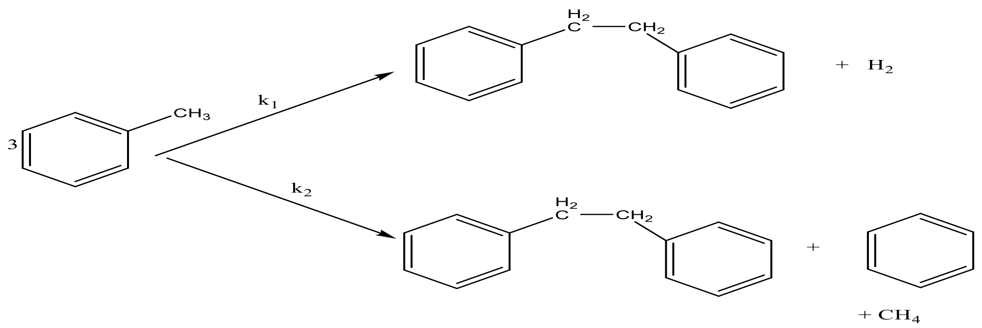
$$t_{\frac{1}{2}} = \frac{ln2}{(k_1 + k_2)} = \frac{0.6931}{(k_1 + k_2)}$$

Example of parallel reactions are,

i. Dehydration of alcohol to olefin and dehydrogenated to aldehyde



ii. Pyrolysis of toluene



4.4 Chain Reaction

There are numerous gas phase reactions that proceeds through the generation, consumption and termination of free radicals and are called chain reactions. The generated free radical, which is a molecular fragment can attack reactant molecule, leading to the formation of product or more free radicals. The sequences of reactions where radicals are generated, or where radical attack product molecules or leads to the formation of required product form the fundamental of chain reaction or free radical reaction.

The major steps in free radical reactions are initiation, propagation, inhibition and termination. The characteristics of each of these steps are highlighted below,

i. **Initiation step**: This is the step involving the formation of free radical from the reactant molecule. For example, $2Br_2 \rightarrow 2Br^*$ or $2Cl_2 \rightarrow 2Cl^*$

Initiation of free radical reaction can be induced by absorption of photon or by molecular collision.

ii. **Propagation step**: This involves the production of more free radicals and it occurs when the primary free radical attack other molecules to produce more free radicals, that will be needed to propagate the reaction. For example, the free radical produced from bromine gas can attack hydrogen gas in its environment and produce hydrogen free radical through the following steps.

$2Br_2 \rightarrow 2Br^*$ (step 1: Initiation step)

$Br^* + H_{2_{(g)}} \rightarrow HBr + Br^*$ (step 2: propagation step)

In a normal chain reaction, one mole of a free radical produce one mole of another free radical but in a branched chain reaction one mole of a free radical produce more than one mole of other free radicals. The example shown above is a normal chain reaction.

iii. **Inhibition**: Inhibition occurs when a free radical attack the product molecule. For example, in the production of HBr, the free radicals involve in the reaction are H* and Br*. These radicals can attack the already produce HBr as shown below,

$2Br_2 \rightarrow 2Br^*$ (step 1: Initiation step)

$Br^* + H_{2_{(g)}} \rightarrow HBr + Br^*$ (step 2: propagation step)

$Br^* + HBr \rightarrow Br_2 + H^*$ (step 3: Inhibition)

$H^* + HBr \rightarrow H_2 + Br^*$ (step 3: Inhibition)

iv. **Termination step**: All free radical reactions end in the termination step. Chain reaction terminates when the reaction ceases and the free radicals are removed. There are several ways or processes that can lead to chain termination but there are two types of chain termination, namely,

(a) linear termination, in which the chain centre is removed at the wall of the reaction vessel.

(b) Quadratic termination, which involves re-combination or disproportionation

Specific ways of chain termination are

(a) Dimerization or recombination. For example, two ethyl free radicals can combine to give butane according to the equation, $CH_3CH_2^* + CH_3CH_2^* \rightarrow CH_3CH_2CH_2CH_3$. This is an example of dimerization because it involves two similar radicals.

(b) Reaction with the wall of the containing vessels.

(c) There are some molecules called inhibitors because they have the tendency to terminate a chain reaction. When such molecules are introduced, they will terminate the chain reaction

(d) Chain termination can be achieved by quenching the reaction. This could be achieved through the control of physical parameters such as pressure or temperature.

3.4.1 Branched chain reaction and explosion

Branched chain reaction occurs when one radical produce at least two other radicals. Branched chain reaction can lead to explosion especially when the reaction is propagated by free radicals. For example, the reaction between the mixture of hydrogen and oxygen gases is very slow at 550 °C and a pressure below 760 mm/Hg. However, increase in pressure will increase the reaction rate slowly and above 760 mm/Hg there will be a sudden explosion.

Generally, at relative low pressure, the rate of reaction is slow. However, kinetic details on explosion can be complicated. It is evident that at 550 °C, the reaction between H_2 and O_2 at 200 and 100 atmospheric pressure respectively is slow and even become slower as the pressure is reduced. However, at a pressure of 98 atmosphere, an explosion will be noticed. Further increase in pressure above the explosion zone, increases the reaction rate until explosion is said to occur.

The effect of pressure on chain reaction is significant. Increase in pressure often has the effect of increasing the rate of formation of free radicals (which will rapidly lead to increase in the rate of reaction and subsequent explosion) against the rate of termination. However, when the rate of formation of free radical is less than the rate of termination, explosion will cease.

Thermal explosion is also possible because at high pressure, the temperature may be very high such that it results in cracking, hence further formation of free radical and subsequent explosion. Under thermal explosion, the reaction rate depends exponentially on the temperature. This implies that if it is not possible for the energy generated during exothermic reaction to escape, the temperature of the system will rise and there will be a rise in the reaction rate, more heat will be produced and since it cannot escape, the reaction will become catastrophically faster. The various step involves in the chain reaction explained above (that is mixture of H_2 and O_2) are indicated below,

$H_2 + O_2 \rightarrow HO_2^* + H^*$ Step 1

$H_2 + HO_2 \rightarrow HO^* + H_2O$ Step 2

$H_2 + HO^* \rightarrow H^* + H_2O$ Step 3

$H^* + O_2 \rightarrow HO^* + O^*$ Step 4

$O^* + H_2 \rightarrow HO^* + O^*$ Step 5

Step 1 is initiation, steps 2 and 3 are propagation while steps 4 and 5 are branching. Alternative mechanism for the explosion reaction between oxygen and hydrogen is also given below,

$H_2 + O_2 \rightarrow 2OH^*$ Step 1
$H_2 \rightarrow 2H^*$ Step 2
$H_2 + OH^* \rightarrow H^* + H_2O$ Step 3
$H^* + O_2 \rightarrow O^* + OH^*$ Step 4
$O^* + H_2 \rightarrow H^* + OH^*$ Step 5

Steps 1 and 2 are initiation, step 3 is propagation, steps 4 and 5 are branching steps.

Another common example of chain reaction is the reaction between H_2 and Br_2 which gives HBr as the product. The equation for this reaction is given as,

$$H_2 + Br_2 \rightarrow 2HBr$$

Therefore, the rate of the reaction is expected to be of the form, $\frac{d[HBr]}{dt} = k[H_2]^x[Br_2]^y$ where x and y are the orders of the reaction with respect to H_2 and Br_2 respectively. x + y is the overall order of the reaction. However, in 1906, Bodenstein and Lind found that the mechanism of the above reaction is complex and were able to show that the rate of the reaction is consistent with the following,

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{\frac{1}{2}}}{1 + k'\frac{[HBr]}{[Br_2]}}$$

3.4.2 Characterization of chain reaction

Chain reactions can be characterised in several ways which include but not limited to the following,

i. Addition of small amount of an inhibitor to a chain reaction will cause the reaction to stop. When a reaction proceeds via a radical intermediate, the simplest techniques to ascertain the reaction involves the introduction of small amount of an inhibitor. Examples of inhibitors are hydroquinone, nitrogen (II) oxide, olefins, phenols, aromatic amines and some nitro compounds.

ii. Some spectroscopic techniques are useful in characterizing free radical reaction. Electron spin resonance spectroscopy (ESR) and mass spectroscopy (MS) are unique techniques that can be used to detect the presence of free radical. Also, some radicals are coloured (even when the compounds from which they are derived from are not coloured). Therefore, colourimetry method may be used to detect the radical. If the radical is not coloured, the rate at which they discharge the colour that is developed through addition of coloured compound can provide an avenue for studying the reaction. Magnetic field paramagnetism, which is associated with presence of unpaired electron forms the principle of using electron spin resonance spectroscopy to study free radical reactions.

iii. Chemical techniques such as the ability of free radicals to initiate the polymerization of a compound such as alkene, can be used to characterise a free radical reaction.

iv. Trapping techniques, involving the addition of a compound that readily reacts with the free radical and trapped the reaction can also be used to characterise a chain reaction.

v. Induction method is based on observing a time lag before a reaction proceeds. Basically, one of the characteristics of chain reaction is that there exists a time lag between the coming together of the reactants and the actual reaction. This is because chain reactions are relatively slow.

vi. The use of metallic mirror technique, designed by Paneth is one of the methods that are often used to characterised free radical reactions. When a free radical strike the inside of the mirror, the mirror will disappear.

Worked example 1

The mechanism for the decomposition of N_2O_5 is given below,

$$N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3$$

$$NO_2 + NO_3 \xrightarrow{k_3} NO + O_2 + NO_2$$

$$NO + NO_3 \xrightarrow{k_4} 2NO_2$$

Use the steady state approximation to obtained the overall rate of decomposition of the compound and show that the kinetic of the decomposition can be first order.

Solution

The rate of decomposition of N_2O_5 is given as,

$$\frac{d[N_2O_5]}{dt} = -k_1[N_2O_5] - k_2[NO_2][NO_3] \qquad (1)$$

However,

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_2[NO_2][NO_3] - k_3[NO_2][NO_3] - k_4[NO][NO_3] \qquad (2)$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - (k_2 + k_3)[NO_2][NO_3] - k_4[NO][NO_3] \qquad (3)$$

Also,

$$\frac{d[NO]}{dt} = k_3[NO_2][NO_3] - k_4[NO][NO_3] \qquad (4)$$

Introducing steady state approximation, equations 3 and 4 translate to equations 5 and 6 respectively,

$$k_1[N_2O_5] - (k_2 + k_3)[NO_2][NO_3] - k_4[NO][NO_3] = 0 \qquad (5)$$

$$k_3[NO_2][NO_3] - k_4[NO][NO_3] = 0 \qquad (6)$$

Subtracting equation 6 from 5 leads to equation 7

$$k_1[N_2O_5] - (k_2 + 2k_3)\,[NO_2][NO_3] = 0 \qquad (7)$$

Therefore, $k_1[N_2O_5] = (k_2 + 2k_3)\,[NO_2][NO_3]$ or $[NO_2][NO_3] = \frac{k_1[N_2O_5]}{(k_2+2k_3)}$. Therefore,

$$[NO_3] = \frac{k_1[N_2O_5]}{(k_2+2k_3)[NO_2]} \qquad (8)$$

Also, since, $k_3[NO_2][NO_3] - k_4[NO][NO_3] = 0$ (equation 6), then,

$$[NO] = \frac{k_3[NO_2][NO_3]}{k_4[NO_3]} = \frac{k_3[NO_2]}{k_4} \qquad (9)$$

Since the rate of decomposition is given as, $-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_2[NO_2][NO_3]$, then equation 10 is obtained after substituting for NO$_3$ and NO (from equations 8 and 9 respectively);

$$\frac{d[N_2O_5]}{dt} = k_2[NO_2]\frac{k_1[N_2O_5]}{(k_2 + 2k_3)[NO_2]} - k_1[N_2O_5]$$

$$= \frac{k_2k_1[N_2O_5]}{(k_2 + 2k_3)} - k_1[N_2O_5]$$

Using the LCM of the above expression, we can simplify it to the form,

$$\frac{d[N_2O_5]}{dt} = \frac{k_2k_1[N_2O_5] - k_1(k_2 + 2k_3)[N_2O_5]}{(k_2 + 2k_3)}$$

$$\frac{d[N_2O_5]}{dt} = \frac{k_2k_1[N_2O_5] - k_1k_2[N_2O_5] - 2k_3k_1[N_2O_5]}{(k_2 + 2k_3)}$$

$$-\frac{d[N_2O_5]}{dt} = \frac{2k_1k_3[N_2O_5]}{(k_2 + 2k_3)}$$

If k$_3$>>k$_2$, the rate of decomposition becomes, $-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$, which effectively is a first order reaction. But is k$_2$>> k$_1$, we have $\frac{d[N_2O_5]}{dt} = \frac{2k_1k_3[N_2O_5]}{k_2} = \frac{2k_1k_3}{k_2}[N_2O_5] = k_{eff}[N_2O_5]$, which is still a first order rate.

Worked example 2

The mechanism of the formation of HBr from H$_2$ and Br$_2$ consist of five steps (given below).

$$Br_2 \xrightarrow{k_1} 2Br^*$$

$$Br^* + H_2 \xrightarrow{k_2} HBr + H^*$$

$$H^* + Br_2 \xrightarrow{k_3} HBr + Br^*$$

$$H^* + HBr \xrightarrow{k_4} H_2 + Br^*$$

$$Br^* + Br^* \xrightarrow{k_5} Br_2$$

Show that the derived rate of the reaction is consistent with the v equation,

$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{\frac{1}{2}}}{1 + k'\frac{[HBr]}{[Br_2]}}$$

Solution

The rate of the reaction is given as,

$$\frac{d[HBr]}{dt} = k_2[Br^*][H_2] + k_3[H^*][Br_2] - k_4[H^*][HBr] \qquad (1)$$

The concentration of the free radicals, H* and Br* cannot be found at ease, therefore, their concentrations must be represented in terms of measurable quantities.

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

$$\frac{d[H^*]}{dt} = k_2[Br^*][H_2] - k_3[H^*][Br_2] - k_4[H^*][HBr] \qquad (3)$$

Invoking the steady state approximation (SSA) to equations 1 to 3, equations 4 to 6 are obtained,

$$k_2[Br^*][H_2] + k_3[H^*][Br_2] - k_4[H^*][HBr] = 0 \qquad (4)$$

$$k_1[Br_2] - k_2[Br^*][H_2] + k_3[H^*][Br_2] + k_4[H^*][HBr] - k_5[Br^*]^2 = 0 \qquad (5)$$

$$k_2[Br^*][H_2] - k_3[H^*][Br_2] - k_4[H^*][HBr] = 0 \qquad (6)$$

From equation 6, $k_2[Br^*][H_2] = (k_4[H^*][HBr] + k_3[H^*][Br_2])$. Therefore, substituting for $k_2[Br^*][H_2]$ in equation 5, we have,

$$k_1[Br_2] - (k_4[H^*][HBr] + k_3[H^*][Br_2]) + k_3[H^*][Br_2] + k_4[H^*][HBr] - k_5[Br^*]^2 = 0$$

$$k_1[Br_2] - k_4[H^*][HBr] - k_3[H^*][Br_2] + k_3[H^*][Br_2] + k_4[H^*][HBr] - k_5[Br^*]^2 = 0$$

$$k_1[Br_2] - k_5[Br^*]^2 = 0 \qquad (7)$$

From equation 7, $k_5[Br^*]^2 = k_1[Br +_2]$, which implies that $[Br^*]^2 = \frac{k_1}{k_5}[Br_2]$ and

$$[Br^*] = \left(\frac{k_1}{k_5}[Br_2]\right)^{\frac{1}{2}} \qquad (8)$$

Rearrangement of equation 6, gives

$$k_2[Br^*][H_2] = k_3[H^*][Br_2] + k_4[H^*][HBr]$$

$$k_2[Br^*][H_2] = [H^*](k_3[Br_2] + k_4[HBr])$$

$$[H^*] = \frac{k_2[Br^*][H_2]}{(k_3[Br_2] + k_4[HBr])}$$

$$[H^*] = \frac{k_2\left(\frac{k_1}{k_5}[Br_2]\right)^{\frac{1}{2}}[H_2]}{(k_3[Br_2]+ k_4[HBr])} \qquad (9)$$

Since the rate is given by $\frac{d[HBr]}{dt} = k_2[Br^*][H_2] + k_3[H^*][Br_2] - k_4[H^*][HBr]$, it follows that, $\frac{d[HBr]}{dt} = k_2\left(\frac{k_1}{k_5}[Br_2]\right)^{\frac{1}{2}}[H_2] + k_3\frac{k_2\left(\frac{k_1}{k_5}[Br_2]\right)^{\frac{1}{2}}[H_2]}{(k_3[Br_2]+ k_4[HBr])}[Br_2] - k_4\frac{k_2\left(\frac{k_1}{k_5}[Br_2]\right)^{\frac{1}{2}}[H_2]}{(k_3[Br_2]+ k_4[HBr])}[HBr]$

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

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

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

The LCM of the denominator of the bracketed term is $(k_3[Br_2] + k_4[HBr])$, which when applied, simplify the above equation to

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

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

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

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

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

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

$$\frac{d[HBr]}{dt} = \left(\frac{k([Br_2])^{\frac{1}{2}}[H_2]}{1+k'\frac{[HBr]}{[Br_2]}}\right)$$

The above equation is the required equation and it shows that rate increase with decrease in the concentration of HBr. where $k = 2k_2\left(\frac{k_1}{k_5}\right)^{\frac{1}{2}}$ and $k' = \left(\frac{k_4}{k_3}\right)$

4.0 Self Assessment Question and Answers

1. The thermal decomposition of acetaldehyde is given by the following equation, $CH_3CHO \rightarrow CH_4 + CO$. Experiment reveals that the reaction is a chain reaction and occurs through the following mechanism,

$$CH_3CHO \xrightarrow{k_1} CH_3^* + CHO$$

$$CH_3CHO + CH_3^* \xrightarrow{k_2} CH_4 + CH_3CO^*$$

$$CH_3CO \xrightarrow{k_3} CH_3^* + CO$$

$$CH_3^* + CH_3^* \xrightarrow{k_4} C_2H_6$$

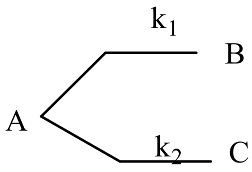
Derive the kinetic equation for the formation of methane, in terms of measurable quantities.

2. If A may react unimolecularly to give B, which in turn reacts unimolecularly to give C, the final product. The step involves is given as,

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Show that $a_t = a_0 e^{-k_1 t}$

3.(a) Given the following parallel reaction,



Show that $a_t = a_0 e^{-(k_1 + k_2)t}$

(b) Derive an expression for the half-life of the parallel reaction.

(c) If the values of the two rate constants are 0.6 and 0.4 /s, calculate the half life

Answers to Self Assessment Questions

1. The rate of formation of methane can be written as, $\frac{d[CH_4]}{dt} = k_2[CH_3CHO][CH_3^*]$. The two radicals in the reactions are CH_3* and CH_3CO*. Application of the steady state approximation to the radicals gives equations 1 and 2.

$$\frac{d[CH_3^*]}{dt} = k_1[CH_3CHO] - k_2[CH_3CHO][CH_3^*] + k_3[CH_3CO^*] - k_4[CH_3^*]^2 = 0 \qquad (1)$$

$$\frac{d[CH_3CO^*]}{dt} = k_2[CH_3CHO][CH_3^*] - k_3[CH_3CO^*] = 0 \qquad (2)$$

From equation, 2, $k_2[CH_3CHO][CH_3^*] = k_3[CH_3CO^*]$, which can be substituted into equation 1 as follows,

$$\frac{d[CH_3^*]}{dt} = k_1[CH_3CHO] - k_3[CH_3CO^*] + k_3[CH_3CO^*] - k_4[CH_3^*]^2$$

$$\frac{d[CH_3^*]}{dt} = k_1[CH_3CHO] - k_4[CH_3^*]^2$$

$$k_1[CH_3CHO] - k_4[CH_3^*]^2$$

$$[CH_3^*] = \left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [CH_3CHO]^{\frac{1}{2}}$$

Therefore, the rate is given as $\frac{d[CH_4]}{dt} = k_2[CH_3CHO][CH_3^*]$, which translate to the following equation,

$$\frac{d[CH_4]}{dt} = k_2[CH_3CHO]\left(\frac{k_1}{k_4}\right)^{\frac{1}{2}} [CH_3CHO]^{\frac{1}{2}}$$

2. From the given equation,

$$-\frac{d[A]}{dt} = k_1[A] \qquad (1)$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B] \qquad (2)$$

$$\frac{d[C]}{dt} = k_2[B] \qquad (3)$$

At time, t = 0, [A] = a_0, [B] = 0 and [C]=0. From equation 200, we have,

$$-\int_{a_0}^{a_t} \frac{d[A]}{[A]} = \int_0^t k_1 dt \qquad (4)$$

$$[\ln A]_{a_0}^{a_t} = -k_1 t \qquad (5)$$

$$a_t = a_0 e^{-k_1 t} \qquad (6)$$

3.(a) The rate of the above reaction is,

$$Rate = k_1[A] + k_2[A] = [A](k_1 + k_2) \qquad (1)$$

$$-\frac{d[A]}{dt} = [A](k_1 + k_2) \qquad (2)$$

$$-\frac{d[A]}{[A]} = (k_1 + k_2)dt \qquad (3)$$

Integrating the above equation between the, a_0 and a_t at time, t = 0 and at time, t, we have,

$$\int_{a_0}^{a_t} -\frac{d[A]}{[A]} = (k_1 + k_2)\int_0^t dt \qquad (4)$$

$$ln\left(\frac{a_t}{a_0}\right) = -(k_1 + k_2)t \qquad (5)$$

$$a_t = a_0 e^{-(k_1 + k_2)t} \qquad (6)$$

(b) From equation 5, the half-life for this reaction can be estimated thus,

$$ln\left(\frac{\frac{a_0}{2}}{a_0}\right) = -(k_1 + k_2)t_{\frac{1}{2}}$$

$$t_{\frac{1}{2}} = \frac{ln2}{(k_1 + k_2)} = \frac{0.6931}{(k_1 + k_2)}$$

(c) If k_1 = 0.6 /s and k_2 = 0.4/s, then the half-life is

$$t_{\frac{1}{2}} = \frac{ln2}{(k_1 + k_2)} = \frac{0.6931}{(0.6/s + 0.4/s)} = 0.6931\,s$$

(ii) Class Activity

(1) Identify five industrial processes whose reaction kinetics follow complex mechanism (30 minutes)

(2) What is the advantage of studying complex reaction mechanism (10 minute)

(3) Outline the mechanism needed for hydrogenation of oil in the presence of a catalyst and state if the process follow a complex mechanism (10 minutes)

7.0 Conclusion

Complex reactions display features that are significantly difference from other reactions indicating that their kinetics are not simple but complicated. Complex reactions are significant because most industrial synthetic routes operate through complex mechanism.

6.0 Summary

Complex reactions are known for complicated mechanism and step wise progress of their action. They constitute kinetics of several industrial processes. Reversible or opposing reactions, consecutive or series reaction, parallel or competitive reaction, chain or free radical reactions and polymerization reactions are basic examples of complex reactions. The mechanism of complex reactions is derived by considering the various reactions that constitute the main reaction. Kinetics of complex reactions is relatively complicated. However, complex reactions also exhibit kinetic equations that reflects concentration time relationship. The study of complex reaction is very relevant in understanding several industrial processes and mechanism of useful reactions.

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MODULE 3

STUDY UNIT 1: CATALYSIS

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1.0 Introduction

A catalyst is any substances that alter the rate of a chemical reaction, when present in minute quantity. The process of using a catalyst to increase or retard the rate of a chemical catalyst is called catalysis. A catalyst that speeds up the rate of a chemical reaction is called positive catalyst while those that slows down the rate of a chemical reaction are called negative catalysts. Generally, a catalyst alters the rate of a chemical reaction by affecting the activation energy. Indeed, a positive catalyst lowers the activation energy and shortens the gap and time between vibrational activation of the reactants and the attainment of the activation complex. On the other hand, a negative catalyst increases the value of the activation energy. The effect of a positive catalyst on the reaction profile is shown in Fig. 5.1 while Fig. 5.2 shows the effect of a negative catalyst on the rate of a chemical reaction

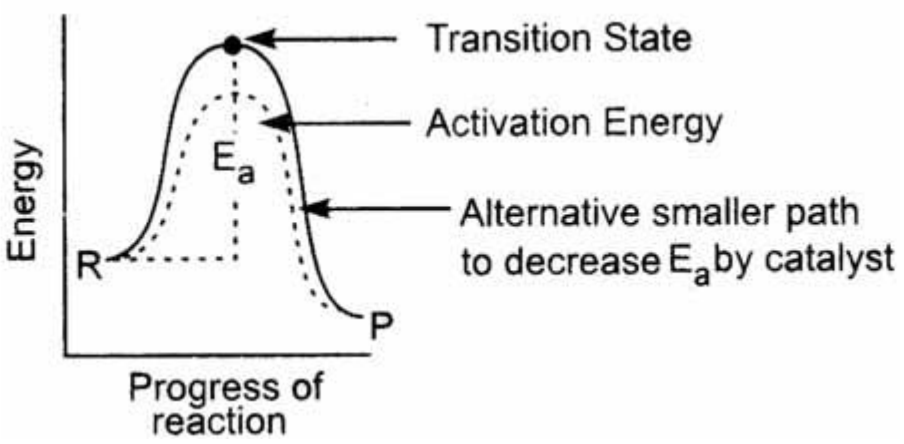
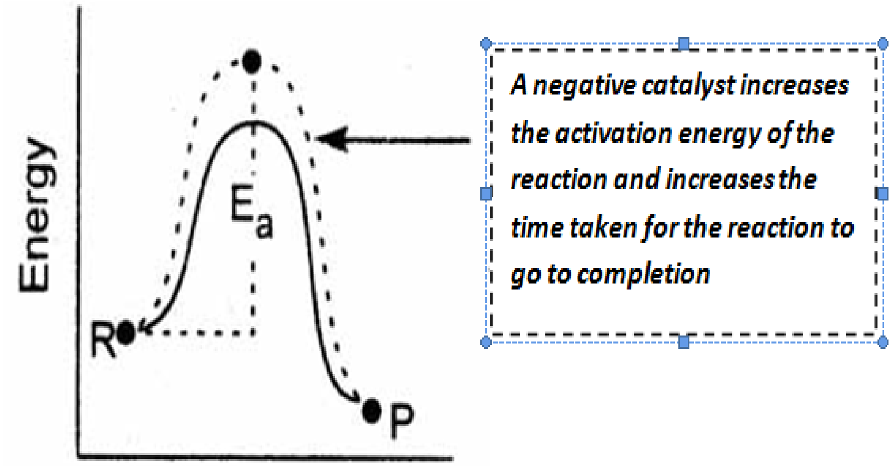


Fig. 5.1: Effect of a positive catalyst on the rate of a chemical reaction



A negative catalyst increases the activation energy of the reaction and increases the time taken for the reaction to go to completion

Fig. 5.2: Effect of a negative catalyst on the rate of a chemical reaction

Examples of reactions catalysed by positive catalysts are

i. $SO_{2(g)} + O_{2(g)} \xrightarrow{Pt(s)} 2SO_{3(g)}$

ii. $N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_{3(g)}$

iii. $CH_2 = CH_{2(g)} + H_{2(g)} \xrightarrow{Ni(s)} CH_3 = CH_{3(g)}$

iv. $2KClO_{3(s)} \xrightarrow{MnO_{2(s)}} 2KCl_{(s)}3O_{2(g)}$

On the other hand, examples of reactions catalysed by negative catalysts are

i. $2H_2O_2 \xrightarrow{H_3PO_{4(s\_}} H_2O_{(g)} + O_{2(g)}$

ii. $2H_2O_2 \xrightarrow{Glycerine} H_2O_{(g)} + O_{2(g)}$

iii. $2H_2O_2 \xrightarrow{Acetamilide} H_2O_{(g)} + O_{2(g)}$

iv. $Na_2SO_{3(s)} \xrightarrow{C_2H_5OH} Na_2SO_{4(s)}$

2.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

- (i) know what is a catalyst, its properties and application
- (ii) understand the effect of a negative and a positive catalyst on the reaction path of exothermic and endothermic reaction
- (iii) understand the what is autocatalysis and to derive the integrated rate law for autocatalysis
- (iv) understand the chemistry of induced catalysis
- (v) understand what are promoters and inhibitors in catalysis
- (vi) understand various forms of acid catalysis and be able to derive integrated law for acid catalysis
- (vii) understand various mechanism of enzyme catalysis and derive integrated rate law for enzyme catalysis
- (viii) solve mathematical problems related to catalysis

3.0 Main Content

3.1 Autocatalysis

Autocatalysis is a catalytic reaction in which one of the products that is formed during the reaction acts as a catalyst. An example of auto catalysis is the hydrolysis of ethyl ethanoate in which one of the products (ethanoic acid) act as an auto catalyst in the reaction,

$$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \rightarrow CH_3COOH_{(l)}(autocatalyst) + C_2H_5OH_{(l)}$$

Other examples are given below,

$$2KMnO_4 + 5H_2C_2O_4 + 3H_2SO_4 \xrightarrow{80\,^{\circ}C} K_2SO_4 + 2MnSO_4(autocatalyst) + 10CO_2 + 8H_2O$$

$$2AsH_3 \rightarrow 2AS\ +\ 3H_2\ (autocatalyst)$$

$$3Cu\ +\ 8HNO_3\ \ \rightarrow\ \ 3Cu(NO_3)_2\ +\ 4H_2O\ +\ 2NO$$

The mechanism of auto catalysis can be derived by assuming that the reaction is catalysed by the product, hence, the under listed equation is applicable,

$$A + P\ \rightarrow 2P$$

The rate law is

$$\frac{dP}{dt} = k[A]\{P]$$

In the course of the reaction, the concentration of A will be decreasing while that P will increase, therefore, we can replace the concentration terms in the above equation by introducing a factor, x. Thus, $[A] =\ [A]_0 -\ x$ and $[P] =\ [P]_0 +\ x$. Consequently, the rate equation becomes,

$$\frac{dP}{dt} = k([A]_0 -\ x)([P]_0 +\ x\ )$$

$$\frac{dP}{([A]_0 -\ x)([P]_0 +\ x)} = kdt$$

The above equation can be solved by integrating using partial fraction method as follows,

$$\frac{1}{([A]_0 -\ x)([P]_0 +\ x)} = \frac{A}{([A]_0 -\ x)} + \frac{B}{([P]_0 +\ x\ )}$$

Taking the LCM of both sides of the equation i.e. LCM = [$([A]_0 -\ x)([P]_0 +\ x)$], we have,

$$1 \equiv \mathrm{B}([A]_0 -\ x) +\ \mathrm{A}([P]_0 +\ x\ )$$

$$1 \equiv \mathrm{B}[A]_0\ +\ A[P]_0 + (A - B)x$$

Comparing coefficient on the left and right sides of the equations, we have,

A- B = 0, which implies that A = B

$\mathrm{B}[A]_0\ +\ A[P]_0 = 1$. This implies that $\mathrm{B}([A]_0\ +\ [P]_0) = 1$ (since A = B) and that $A = B = \frac{1}{([A]_0 + [P]_0)}$. Therefore,

$$\frac{1}{([A]_0 -\ x)([P]_0 +\ x)} = \frac{1}{([A]_0\ +\ [P]_0)}\left\{\frac{1}{([A]_0 -\ x)} + \frac{1}{([P]_0 +\ x\ )}\right\}$$

And the rate equation becomes

$$\frac{dP}{([A]_0 -\ x)([P]_0 +\ x)} = \frac{dP}{([A]_0\ +\ [P]_0)}\left\{\frac{1}{([A]_0 -\ x)} + \frac{1}{([P]_0 +\ x\ )}\right\} = kdt$$

Solving the above equation by integration, we have,

$$\int_0^x \frac{dP}{([A]_0 - x)([P]_0 + x)} = \frac{dP}{([A]_0 + [P]_0)} \int_0^P \frac{dP}{([A]_0 - x)} + \frac{1}{([A]_0 + [P]_0)} \int_0^P \frac{dP}{([P]_0 + x\,)} \quad = = k \int_0^t dt$$

The solution to the above integral is

$$\frac{1}{([A]_0 \, + \, [P]_0)} \, ln\left(\frac{[A]_0([P]_0 + x)}{[P]_0([A]_0 - x)}\right) = kt$$

$$ln\left(\frac{([P]_0 + x)}{([A]_0 - x)}\right) = kt([A]_0 \, + \, [P]_0)\left[\frac{[P]_0}{[A]_0}\right]$$

If $([A]_0 \, + \, [P]_0)k = a \; and \; \frac{[P]_0}{[A]_0} = a$, then the integrated rate equation for auto catalysis can be simplify to,

$$ln\left(\frac{([P]_0 + x)}{([A]_0 - x)}\right) = abt$$

$$\frac{[P]_0 + x)}{[A]_0 - x)} = \; e^{abt}$$

$$[P]_0 + x) = \; [A]_0 - x)e^{abt}$$

3.1.1 Induced catalysis

Induced catalysis involves the use of one reactant to speed up the rate of a reaction, which will not occur ordinary. Such a catalyst is called an induced catalyst. For example, sodium thiosulphite oxidizes readily in air to give sodium thiosulphate but sodium arsenite does not oxidize in air. However, when air is passed through a mixture of sodium thiosulphite and sodium arsenite, the sodium arsenite oxidizes readily. Therefore, sodium thiosulphite is an induced catalyst for the oxidation of sodium arsenite, as the following equations present.

$$Na_2SO_3 \xrightarrow{air} Na_2SO_4$$

$$Na_2AsO_3 \xrightarrow{air} \quad No\ reaction$$

$$Na_2SO_3 \; + \quad Na_2AsO_3 \xrightarrow{air} Na_2SO_4 \;\; + \;\; Na_2AsO_4$$

Another example is the reduction of mercuric chloride ($HgCl_2$) with oxalic acid which is very slow, but potassium permanganate is reduced readily with oxalic acid. If, however, oxalic acid is added to a mixture of potassium permanganate and $HgCl_2$, both are reduced simultaneously. The reduction of potassium permanganate, thus, induces the reduction of mercuric chloride.

3.1.2 Promoters and inhibitors

Substances that increase the efficiency of a catalyst are called promoters while those that decrease the efficiency of a catalyst are called inhibitors. For example, alumina is a promoter to the iron catalyst used in the Haber process for the production of ammonia while arsenic compounds are inhibitors to the platinum catalyst used in the contact process for the conversion of SO_2 to SO_3.

3.2 Some industrial applications of catalysis

Catalysts of various forms and types play significant roles in process optimization, conservation of raw materials, reduction in energy requirement and other factors. Several industrial products will not be economically affordable without a catalyst. On the other hand, negative catalysts may be useful in controlling the rate of some reaction, where speed is not required. Some industrial processes that are feasible through the use of catalyst are listed below,

i. The Haber process: This is the process for the production of ammonia in commercial quantity. The catalyst used in this process is reduced iron.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_{3(g)}$$

ii. The contact process uses vanadium (V) oxide or platinum catalyst for the commercial production of SO_3, which dissolves in water to form H_2SO_4,

$$SO_{2(g)} + O_{2(g)} \xrightarrow{Pt(s)} 2SO_{3(g)}$$

iii. The fermentation process for the conversion of sugar to alcohol uses zymase as a catalyst

$$C_6H_{12}O_{6(aq)} \xrightarrow{zymase} 2C_2H_5OH_{(aq)} + 2CO_2$$

iv. Hydrogenation of oil, which converts unsaturated hydrocarbons to higher degree of saturation, uses nickel catalyst. This form the bases for the production of margarine and similar products

v. Hydrolysis of starch to sugar (an essential product in the food industries) is catalyst by an enzyme called diastase

$$2C_6H_{10}O_{5(aq)} + H_2O_{(l)} \xrightarrow{diastase} C_{12}H_{22}O_{11(aq)}$$

vi. Tetra ethyl lead is an autocatalyst that is often added to petrol in order to decrease the ignition point of petrol.

vii. In the petroleum industries, several processes such as cracking, reforming, refining, hydrotreatment and others, cannot be carried out without a catalyst.

viii. In the petrochemical industries, catalysts are used in the synthesis of intermediate chemicals and polymers

ix. Catalyst are also useful in pollution control, especially in the removal of CO, NO and hydrocarbons from exhaust fumes generated by stationary and mobile engines

3.3 General characteristics of catalysts

Although there are different types of catalyst, all catalysts have the following general properties,

i. A catalyst alters the rate of a chemical reaction by creating new reaction pathway but does not affect the thermodynamic properties of the system

ii. A catalyst will catalyse a chemical reaction, even when present in a minute concentration.

iii. A given catalyst is specific in action in that it may not catalyse other reactions.

iv. A catalyst is sensitive to temperature and pH. This implies that a given catalyst has an optimum pH and temperature ranges in which its functions best. At a temperature and pH, outside its range of sensitivity, a catalyst may be denatured or render inactive.

v. A catalyst remains chemically unchanged at the end of the reaction. However, the physical state of the catalyst may change.

vi. A catalyst has no effect on the position of a chemical equilibrium. However, it may alter the time at which a reaction approaches equilibrium.

3.4 Types of catalysis

Catalysis can generally be classified based on the physical states of the reactants and the catalyst. Therefore, on this basis, there are two types of catalysis, namely: homogenous and heterogeneous catalysis.

3.4.1 Homogeneous catalysis

In homogeneous catalysis, the reactant and the catalysis are in the same phase. There are several examples of homogeneous catalysis including the use of NO in catalysing the reactions between

SO_2 and oxygen, CO_2 and oxygen and the decomposition ofN_2O. These are shown in the chemical equations below,

$$\text{lead chamber process: } 2SO_2 + O_2 \xrightarrow{NO} 2SO_3$$

$$2CO + O_2 \xrightarrow{NO} 2CO_2$$

$$2N_2O \xrightarrow{NO} 2N_2 + O_2$$

The above examples are homogeneous catalysis in gaseous phase. Common examples of homogeneous catalysis in liquid phase are

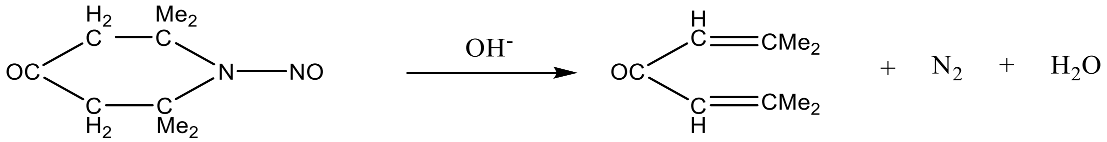
i. Acid hydrolysis of ethyl ethanoate to ethanoic acid and ethanol

$$CH_3COOCH_3 + H_2O \xrightarrow{H^+} CH_3COOH + CH_3OH$$

ii. Inversion of sucrose to glucose and fructose in the presence of acid as a catalyst

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

iii. The decomposition of 2,2,6,6,tetramethyl-1-nitrosopiperidin-4-one, catalysed by OH^-



2,2,6,6-tetramethyl-1-nitrosopiperidin-4-one

2,6-dimethylhepta-2,5-dien-4-one

iv. Conversion of acetone into diacetone

$$CH_3OCH_3 + CH_3OCH_3 \xrightarrow{OH^-} CH_3COCH_2C.(CH_3)_2OH$$

3.4.2 Heterogeneous catalysis

In heterogeneous catalysis, the catalyst and the reactant are in different phases. There are several examples of heterogeneous catalysis including the following,

i. The Haber process: This is the process for the production of ammonia in commercial quantity. The catalyst used in this process is reduced iron.

$$N_{2(g)} + 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_{3(g)}$$

ii. The contact process uses vanadium (V) oxide or platinum catalyst for the commercial production of SO_3, which dissolves in water to form H_2SO_4,

$$SO_{2(g)} + O_{2(g)} \xrightarrow{Pt(s)} 2SO_{3(g)}$$

iii. The fermentation process for the conversion of sugar to alcohol uses zymase as a catalyst

$$C_6H_{12}O_{6(aq)} \xrightarrow{zymase} 2C_2H_5OH_{(aq)} + 2CO_2$$

iv. In the manufacturing of nitric acid by oxidation of ammonia using a mixture of ferric oxide and bismuth oxide

$$4NH_3 + 5O_2 \xrightarrow{Fe_2O_3/Bi_2O_3} 4NO + 6H_2O$$

v. Hydrogenation of unsaturated hydrocarbon using nickel as a catalyst

$$X - CH = CH - Y + H_2 \overset{Ni}{\rightarrow} X - CH_2 - CH_2 - Y$$

vi. Bergius process for synthesis of petrol uses ferric oxide as a catalysis

vii. Bosch process for manufacturing of hydrogen uses mixture of Ferric oxide and chromic oxide as promoter

viii. Deacon’s process for manufacture of chlorine uses cupric chloride as a catalyst

ix. Ostwald’s process for manufacture of nitric acid use platinized asbestos as a catalyst

Differences between homogeneous and heterogeneous catalysis are presented in Table 5.1 below

Table 5.1: Differences between homogeneous and heterogeneous catalysis

Homogeneous catalysis	Heterogeneous catalysis
Homogenous catalyst is found mostly in liquid or gaseous state	Found in liquid, gas and even solid phases
Operative temperature for homogeneous catalysis is generally low except under high pressure	Required significant high operative temperature
Diffusion in homogenous catalysis is usually high because the reactant and the catalyst are in the same phase	Since the catalyst are in different phases, diffusivity and absorbance are usually low
There is usually large heat transfer because the catalyst and the reactant are in the same phase	The heat transfer is relatively low because the reactant molecules and catalysts are in different phase

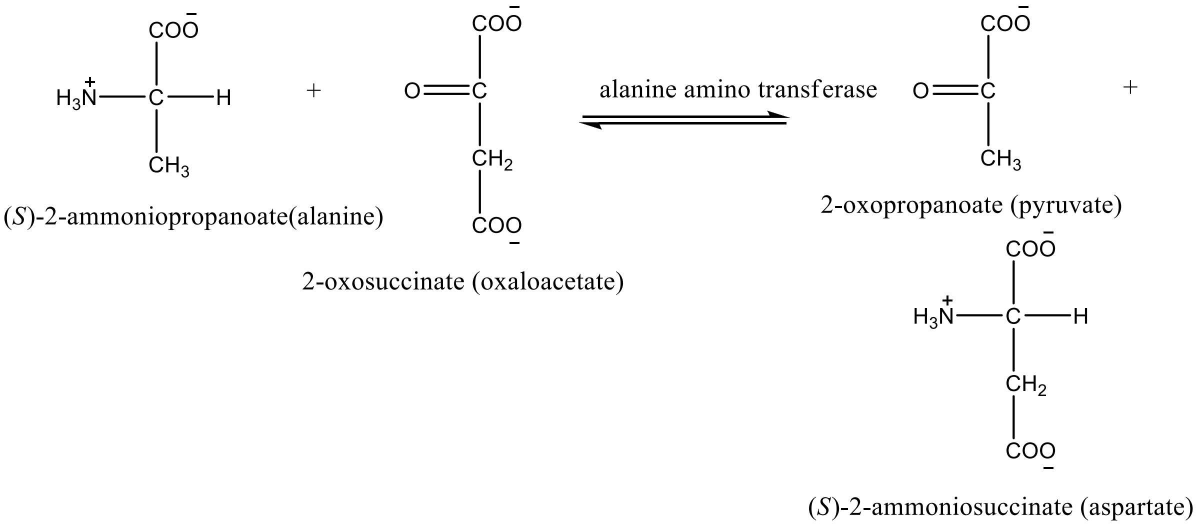
Characterized by well-defined active sites	The active site is not very well defined as different phase sites might have different catalytic properties for the same particle
Recycling methods are not very cost effective	Recycling methods is relatively cost effective
Modification of homogenous catalysts is very easy as it depends upon the tuning of electronic and steric properties on metal	The modification of heterogeneous catalysts is relatively difficult because the controlling methods of particle site as well as the active size at molecular level is difficult

3.5 Enzyme catalysis

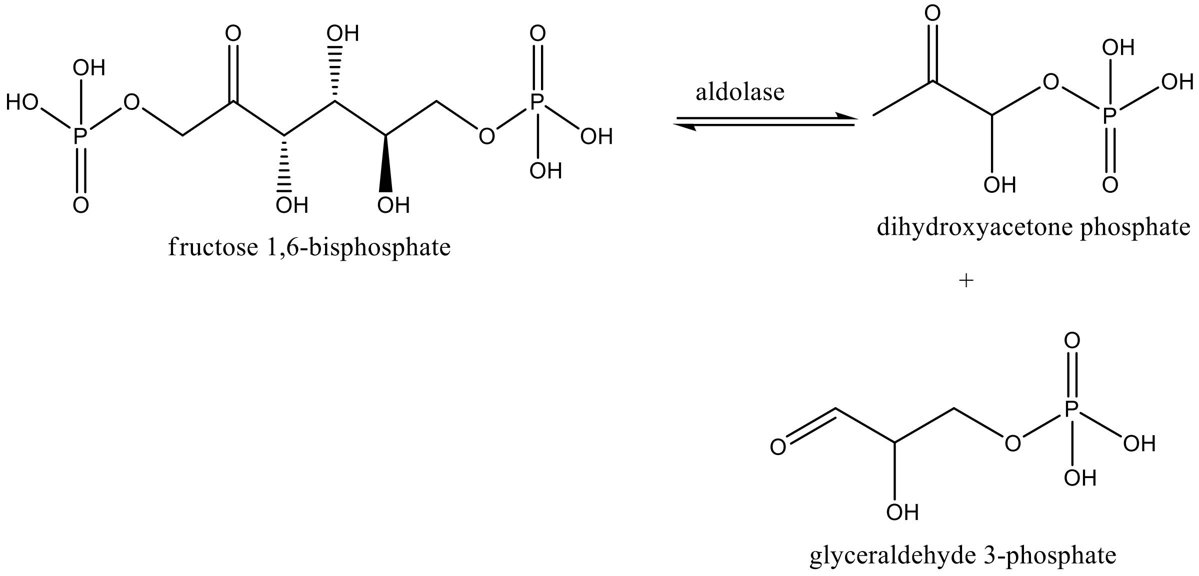
Enzymes are protein and they catalysed various biochemical reactions. Enzymes and enzymes catalysis can generally be classified into six groups. These are,

i. Oxidation reduction (redox) enzymes: These catalyse reactions through the donation and acceptance of electron. Electron is transferred from the reducing agent to the oxidation agent such that the reducing agent is oxidized while the oxidizing agent is reduced. Enzymes in this groups are generally called oxidoreductase.

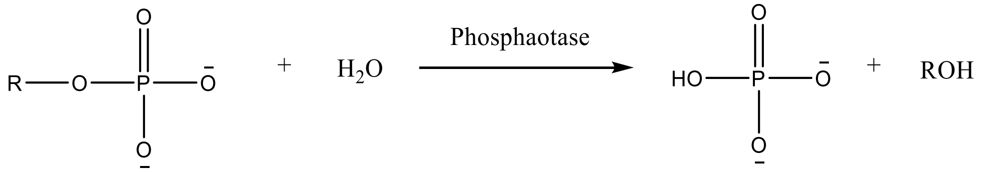
ii. Transferases are enzymes that catalyse group transfer reaction. That is the transfer of functional group from one molecule (called the donor) to another molecule (called the acceptor). Example is the transfer of the alpha amino group between alanine and aspartate by alanine amino transferase



iii. Lyase enzymes are enzymes that breaks chemical bonds and facilitate the formation of double bond or cyclic structure through catalytic path ways. Lyase enzymes cleaves C-C, C-O and C-N bonds through elimination and not oxidation or hydrolysis. For example, the enzyme, aldolase convert fructose 1,6-bisphosphate to dihydroxyacetone phosphate and glyceraldehydes-3-phosphate during glycolysis.

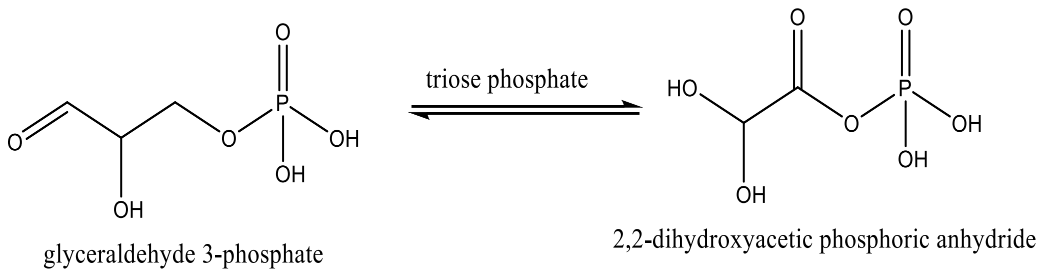


iv. Hydrolytic enzymes (hydrolase) catalyse the hydrolysis of a chemical bond. For example, phosphatise enzyme hydrolysis's phosphate ester by breaking the oxygen-phosphorus bond in phosphate ester as shown below



$$R{-}O{-}\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle \bar{O}}{|}}{P}}}{-}\bar{O} + H_2O \xrightarrow{\text{Phosphaotase}} HO{-}\overset{\displaystyle O}{\overset{\|}{\underset{\underset{\displaystyle \bar{O}}{|}}{P}}}{-}\bar{O} + ROH$$

v. Isomerases are enzymes that convert a molecule to its isomer for example, the enzyme, triose phosphate isomerise can facilitate the conversion of glyceraldehyde 3-phosphate to its isomer, 2,2-dihydroxyacetic phosphoric anhydride as shown below



vi. Ligases # enzymes catalyse the joining two large molecules through hydrolysis, which leads to the formation of chemical bond (mostly covalent bond). When the joining is accomplished by the breaking of pyrophosphate bond in adenine triphosphate (ATP), the enzyme is called synthetases.

Example 1

Write equations to show how catalytic converter in automobile exhaust convert poisonous hydrocarbon (PHC), NO and NO_2 gases to non-poisonous gases.

Solution

$$CO + PHC + O_2 \xrightarrow{Catalytic\ converter} CO_2 + H_2O$$

$$2NO + 2NO_2 \xrightarrow{Catalytic\ converter} 2N_2 + 3O_{2(g)}$$

Example 2

Write equations to show Ostwald process

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt\ catalyst} 4NO_{(g)} + 6H_2O$$

$$2NO + O_{2(g)} \rightarrow 2NO_{2(g)}$$

$$2NO_2 + H_2O \rightarrow HNO_{2(aq)} + HNO_{3(aq)}$$

3.5.1 Mechanism of enzyme catalysis

The basic mechanism for enzyme catalysis is the Michaelis Menton mechanism. An enzyme E, react with the substrate, S to form a complex, ES*. The complex can dissociate in two ways. The first is the backward reaction, which leads to the formation of E and S and the second is the forward reaction, which results in the formation of the product, P and the regeneration of the enzyme.

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES^* \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} E + P$$

However, the second step, i.e., the formation of E and P, usually goes to completion, indicating that the reverse reaction is not significant. Hence, we have,

$$E + S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES^* \xrightarrow{k_2} E + P$$

The rate equation for the above reaction can be written as,

$$\frac{d[ES^*]}{dt} = k_1[E][S] - k_{-1}[ES^*] - k_2[ES^*] \qquad 5.1$$

Application of the steady state approximation to equation 5.1 implies that $\frac{d[ES^*]}{dt} = 0$, hence

$$k_1[E][S] - k_{-1}[ES^*] - k_2[ES^*] = 0 \qquad 5.2$$

$$k_1[E][S] = k_{-1}[ES^*] + k_2[ES^*] \qquad 5.3$$

$$k_1[E][S] = (k_{-1} + k_2)[ES^*] \qquad 5.4$$

$$[ES^*] = \frac{k_1[E][S]}{(k_{-1} + k_2)} \qquad 5.5$$

If the total enzyme concentration before the reaction is [E$_0$], then since enzymes are not destroyed during the reaction, it implies that the total concentration of the enzyme at any given time will be equal to E$_0$. Concentration of the free enzyme is [E] while the concentration of the enzyme that is bound to the substrate, S is [ES]. By conservation, [E$_0$] = [E] + [ES]. Therefore,

$$[E_0] = [E] + \frac{k_1[E][S]}{(k_{-1} + k_2)} \qquad 5.6$$

$$[E_0] = [E]\left\{1 + \frac{k_1[S]}{(k_{-1} + k_2)}\right\} \qquad 5.7$$

$$[E] = \frac{[E_0]}{\left\{1 + \frac{k_1[S]}{(k_{-1} + k_2)}\right\}} \qquad 5.8$$

$$[E] = \frac{[E_0]}{\left\{\frac{k_{-1} + k_2 + k_1[S]}{(k_{-1} + k_2)}\right\}} \qquad 5.9$$

$$[E] = \frac{[E_0](k_{-1} + k_2)}{k_{-1} + k_2 + k_1[S]} \qquad 5.10$$

Since $[ES^*] = \frac{k_1[E][S]}{(k_{-1} + k_2)}$ (i.e equation 5.5), substitution of equation 5.10 into 5.5 gives equation 5.11

$$[ES^*] = \frac{k_1[E_0][S]}{k_{-1} + k_2 + k_1[S]} \qquad 5.11$$

The rate of disappearance of the substrate, S can be written as,

$$\frac{-d[S]}{dt} = k_2[ES^*] = \frac{k_1 k_2[E_0][S]}{k_{-1} + k_2 + k_1[S]} \qquad 5.12$$

Equation 5.12 is called Michaelis Menton equation. The equation reveals that the rate is expressed in terms of measurable quantities. Dividing the numerator and the denominator of equation 5.12 by k_1, we have,

$$\frac{-d[S]}{dt} = \frac{k_2[E_0][S]}{\frac{k_{-1} + k_2}{k_1} + [S]}$$

$$Rate = \frac{k_2[E_0][S]}{k_m + [S]} \qquad 5.13$$

where $k_m = \frac{k_{-1} + k_2}{k_1}$ is called Michaelis Menton constant. Equation 5.13 reveals that the rate depends on the concentration of the enzyme and that of the substrate. Based on the relative values of [S] and k_m, two possibilities can be ascertained. In the first case, [S]>> k_m and the rate equation become, $Rate = k_2[E_0]$. This is a zero-order reaction because [E_0] is constant. On the other hand, if k_m>> [S], then the rate becomes, $Rate = k_{eff}[E_0][S]$. This is a first order reaction.

An interesting method of using the Michaelis Menton equation is the graphical method. The rate equation, $rate = \frac{k_1 k_2[E_0][S]}{k_{-1} + k_2 + k_1[S]}$ (equation 213) can be converted into equation of a straight line by taking the reciprocal of the equation. That is

$$\frac{1}{Rate} = \frac{(k_{-1} + k_2)}{k_1 k_2[E_0][S]} + \frac{1}{k_2[E_0]} \qquad 5.14$$

From equation 215, a plot of reciprocal of the rate against the reciprocal of the substrate concentration is a straight line, with intercept and slope equal to $\frac{1}{k_2[E_0]}$ and $\frac{(k_{-1} + k_2)}{k_1 k_2[E_0]}$ respectively. This type of plot is called Lineweaver Burk plot

Question 3

The kinetic of enzyme reaction can be described in3 terms of Michaelis Menton equation,

$$E \quad + \quad S \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} ES^* \xrightarrow{k_2} E \; + \; P$$

where E is the enzyme, S is the substrate, ES* is the enzyme-substrate complex and P is the product of the catalysed reaction. If the rate of reaction is represented as, Rate = k_2[ES*], show that $Rate\ =\ \frac{k_2[E_0][S]}{k_m\ +\ [S]}$. where k_m= $\frac{k_{-1} + k_2}{k_1}$ is the Michaelis Menton constant

(b) What form does the reaction rate takes when (i) [S] >> [k_m] (ii) [k_m>> [S}

(c) How can you use the Michaelis Menton equation to calculate the values, $\frac{1}{k_2[E_0]}$ and $\frac{(k_{-1} + k_2)}{k_1 k_2[E_0]}$

(d) The variation of rate constant with substrate concentration for an enzyme catalysed reaction is presented in the Table below.

Rate ($ML^{-1}S^{-1}$)	**[S](mmol/L)**
0.0000278	0.00125
0.000052	0.0025
0.0000833	0.005
0.000167	0.020

Develop line-weaver Burk plot to calculate the following parameters,

i. The catalytic rate constant
ii. The Michaelis Menton constant
iii. The catalytic efficiency

The total concentration of the enzyme, [E_0] = 0.0025 moles

Solution

From the given equation, the rate equation for the formation of ES* can be derived and is given as,

$$\frac{d[ES^*]}{dt} = k_1[E][S] - k_{-1}[ES^*] - k_2[ES^*] \qquad (1)$$

Application of the steady state approximation to equation 1 implies that $\frac{d[ES^*]}{dt} = 0$, hence

$$k_1[E][S] - k_{-1}[ES^*] - k_2[ES^*] = 0 \qquad (2)$$

$$k_1[E][S] = k_{-1}[ES^*] + k_2[ES^*] \qquad (3)$$

$$k_1[E][S] = (k_{-1} + k_2)[ES^*] \qquad (4)$$

$$[ES^*] = \frac{k_1[E][S]}{(k_{-1} + k_2)} \qquad (5)$$

If the total enzyme concentration before the reaction is [E$_0$], then since enzymes are not destroyed during the reaction, it implies that the total concentration of the enzyme at any given time will be equal to E$_0$. Concentration of the free enzyme is [E] while the concentration of the enzyme that is bound to the substrate, S is [ES]. By conservation, [E$_0$] = [E] + [ES]. Therefore,

$$[E_0] = [E] + \frac{k_1[E][S]}{(k_{-1} + k_2)} \qquad (6)$$

$$[E_0] = [E]\left\{1 + \frac{k_1[S]}{(k_{-1} + k_2)}\right\} \qquad (7)$$

$$[E] = \frac{[E_0]}{\left\{1 + \frac{k_1[S]}{(k_{-1} + k_2)}\right\}} \qquad (8)$$

$$[E] = \frac{[E_0]}{\left\{\frac{k_{-1} + k_2 + k_1[S]}{(k_{-1} + k_2)}\right\}} \qquad (9)$$

$$[E] = \frac{[E_0](k_{-1} + k_2)}{k_{-1} + k_2 + k_1[S]} \qquad (10)$$

Since $[ES^*] = \frac{k_1[E][S]}{(k_{-1} + k_2)}$ (i.e equation 5), substitution of equation 5 into 10 gives equation 11

$$[ES^*] = \frac{k_1[E_0][S]}{k_{-1} + k_2 + k_1[S]} \qquad (11)$$

The rate of disappearance of the substrate, S can be written as,

$$\frac{-d[S]}{dt} = k_2[ES^*] = \frac{k_1 k_2[E_0][S]}{k_{-1} + k_2 + k_1[S]} \qquad (12)$$

Equation 12 is called Michaelis Menton equation. The equation reveals that the rate can expressed in terms of measurable quantities. Dividing the numerator and the denominator of equation 12 by k_1, we have,

$$\frac{-d[S]}{dt} = \frac{k_2[E_0][S]}{\frac{k_{-1}+k_2}{k_1} + [S]}$$

$$Rate = \frac{k_2[E_0][S]}{k_m + [S]} \qquad (13)$$

where $k_m = \frac{k_{-1}+k_2}{k_1}$ is called Michaelis Menton constant.

Equation 13 reveals that the rate depends on the concentration of the enzyme and that of the substrate.

(b) Based on the relative values of [S] and k_m, two possibilities can be ascertained.

(i) In the first case, $[S] >> k_m$ and the rate equation become, $Rate = k_2[E_0]$. This is a zero-order reaction because $[E_0]$ is constant.

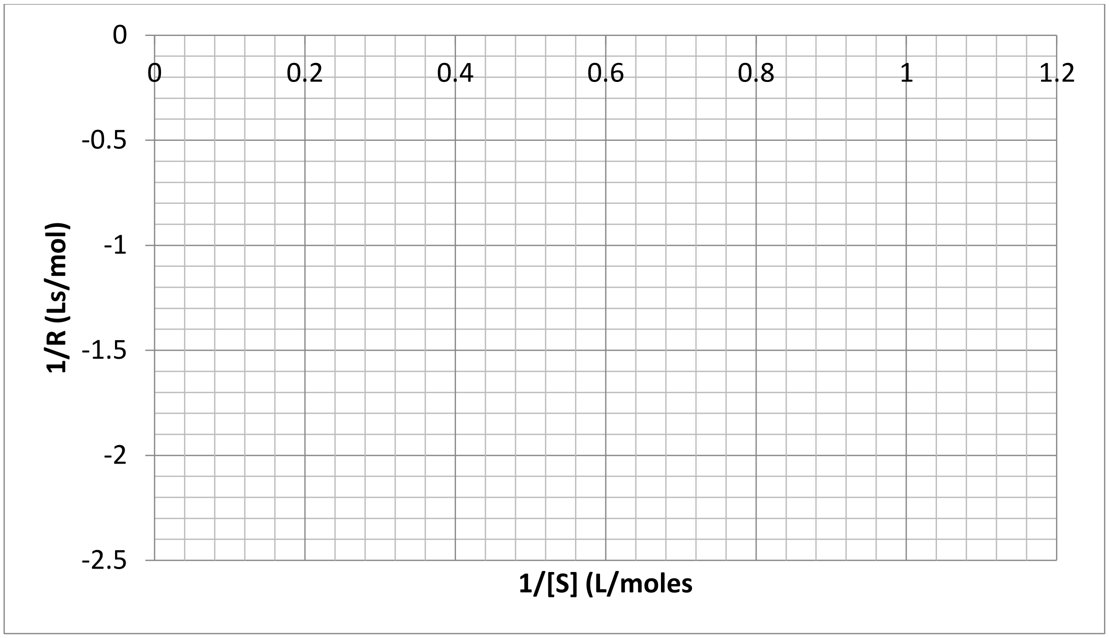
(ii) the second case is if $k_m >> [S]$, then the rate becomes, $Rate = k_{eff}[E_0][S]$. This is a first order reaction.

(c) An interesting method of using the Michaelis Menton equation is the graphical method. The rate equation, $rate = \frac{k_1k_2[E_0][S]}{k_{-1}+k_2+k_1[S]}$ (equation 213) can be converted into equation of a straight line by taking the reciprocal of the equation. That is

$$\frac{1}{Rate} = \frac{(k_{-1}+k_2)}{k_1k_2[E_0][S]} + \frac{1}{k_2[E_0]}$$

From equation 1, a plot of reciprocal of the rate against the reciprocal of the substrate concentration is a straight line, with intercept and slope equal to $\frac{1}{k_2[E_0]}$ and $\frac{(k_{-1}+k_2)}{k_1k_2[E_0]}$ respectively. This type of plot is called Lineweaver Burk plot

(d) The line-weaver Burk plot for the given data is presented below,



(i) From the graph, intercept and slope are 38.42. Therefore,

$$\frac{1}{k_2[E_0]} = 38.42$$

$$\frac{1}{k_2 0.0025} = 38.42$$

$$k_2 = \frac{1}{38.42(0.0025)} = 10.41$$

The catalytic rate constant, $k_2 = 10.41$

(ii) The slope = 39.87. therefore,

$$\frac{(k_{-1} + k_2)}{k_1 k_2 [E_0]} = 39.87$$

$$k_m = \frac{(k_{-1} + k_2)}{k_1)} = 39.87x\ (10.41x\ 0.0025) = 1.038$$

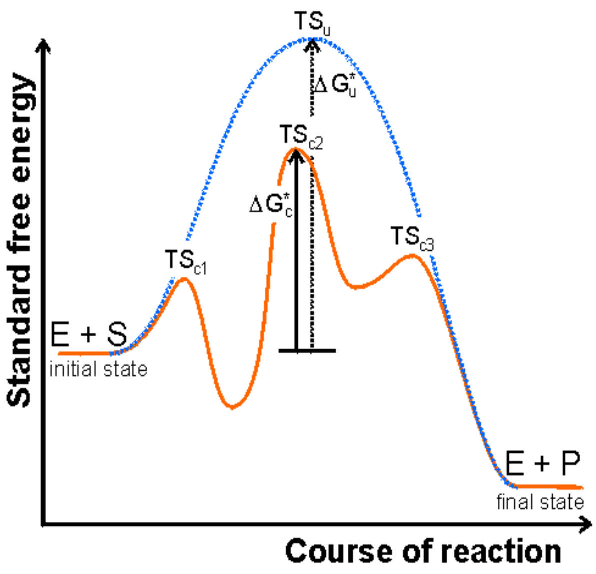
(iii) The catalytic efficiency = k_2/k_m = 10.41/1.038 = 10.03.

Question 22

Given that an enzyme, E react with a substrate, S to form enzyme-substrate (ES) and enzyme product (EP) complexes and subsequent product. Sketch a pattern of plot expected for the variation of standard free energy with the course of the reaction during an enzyme catalysed reaction. Explain the various transition state expected for the catalysed and uncatalysed reaction.

Solution

The expected sketch is shown below



The catalyzed reaction pathway goes through the transition states TS$_{c1}$, TS$_{c2}$ and TS$_{c3}$, with standard free energy of activation ΔG$_c^*$, whereas the uncatalyzed reaction goes through the transition state TS$_u$ with standard free energy of activation.

3.6 Acid catalysis

There are several reactions that are catalysed by acids and bases indicating that the acids and the bases involved are not consumed at the end of the reaction. Acids and bases include Arrhenius substances that ionize to produce hydrogen and hydroxyl ions respectively; the Bronsted acid and base donate or accept proton respectively; the Lewis acid and base that donate or accept electron respectively.

Acid or base catalysis is said to be general if the acid or the base affect the rate of the reaction. This implies that the acid or base take part in the rate determining step. Specific acid or base catalysis is defined when the catalysis reaction rate depends on a specific acid or base and not on the other acid that is present in the solution.

If the rate of disappearance of the substrate of the catalytic reaction is first order, then the rate of the reaction will be given as, $-d[S]/dt = k_1[S]$. The first order rate constant of this system, may be a linear function of $[H^+]$, $[OH^-]$, [HA] and $[A^-]$ (HA is the weak acid whose corresponding ion is A)$^-$. Therefore, the rate constant can be written as the summation of the various rate constant that contributes to the reaction,

$$k_1 = k_0 + k_{H^+}[H^+] + k_{OH^-}[OH^-] + k_{HA}[HA] + k_{A^-}[A^-] \qquad 5.15$$

K_0 is the first order rate constant at significantly low concentrations of all the catalytic species. k_{H^+}, k_{OH^-}, k_{HA} and k_{A^-} are catalytic coefficients. If only $k_{H^+}[H^+]$ is important, the reaction is said to be hydrogen ion catalysis, If only $k_{HA}[HA]$is significant, then the reaction is general acid catalysis, if only $k_{A^-}[A^-]$ is significant, the reaction is general base catalysis and if only $k_{OH^-}[OH^-]$ is significant, the reaction is said to be hydroxyl ion catalysis.

Te mechanism and kinetic of acid base catalysis can take several forms but the major and first step is the transfer of proton from acid to the substrate:

$$S + AH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^* + A^-$$

The above reaction will be succeeded by one of the following processes:

i. Protolytic mechanism, involving proton transfer to the solvent and the subsequent reaction to produce the product

$$SH^* + H_2O \xrightarrow{k_2} P + H_3O^+$$

ii. Prototrophic mechanism, which involves proton transfer to the base leading to the formation of the product, P and regeneration of the acid:

$$SH^* + A^- \xrightarrow{k_2} P + AH$$

The rate of reaction for the protolytic mechanism is given as,

$$-\frac{d[S]}{dt} = \frac{dP}{dt} = k_2[SH^*] \qquad 5.16$$

However, the rate of formation of the intermediate is given as,

$$\frac{d[SH^*]}{dt} = k_1[S][AH] - k_{-1}[SH^*][A^-] - k_2[SH^*] \qquad 5.17$$

Applying the steady state approximation to equation 218 implies that $\frac{d[SH^*]}{dt} = 0$.Therefore,

$$k_1[S][AH] - k_{-1}[SH^*][A^-] - k_2[SH^*] = 0$$

$$k_1[S][AH] = k_{-1}[SH^*][A^-] + k_2[SH^*]$$

$$k_1[S][AH] = [SH^*](k_{-1}[A^-] + k_2)$$

$$[SH^*] = \frac{k_1[S][AH]}{k_{-1}[A^-] + k_2} \qquad 5.18$$

From equation 217, the rate of the reaction is given as $-\frac{d[S]}{dt} = \frac{d[P]}{dt} = k_2[SH^*]$, therefore,

$$\frac{d[P]}{dt} = \frac{k_1 k_2[S][AH]}{k_{-1}[A^-] + k_2} \qquad 5.19$$

From the above rate equation, if $k_{-1}[A^-] >> k_2$, the rate equation becomes,

$$\frac{d[P]}{dt} = \frac{k_1 k_2[S][AH]}{k_{-1}[A^-]} \qquad 5.20$$

An acid, AH can ionize in water to produce H_3O^+ and A^-. i.e. $AH + H_2O = H_3O^+ + A^-$. The equilibrium constant for the ionization is given as $K = [H_3O^+] [A^-]/[AH]$. This implies that $[AH] = [H_3O^+] [A^-]/K$. Substituting for [AH] in equation 221, we have,

$$\frac{d[P]}{dt} = \frac{k_1 k_2[S][H_3O^+][A^-]}{k_{-1}[A^-]} = \frac{k_1 k_2}{k_{-1}}[S][H_3O^+] \qquad 5.21$$

Equation 222 implies that the derived rate is a function of the concentration of the substrate and that of H_3O^+ and because H_3O^+ appears in the final rate equation, the catalysis is said to be specific. On the other hand, when $k_2 \gg k_{-1}[A^-]$, equation 220 becomes,

$$\frac{d[P]}{dt} = k_1[S][AH] \qquad 5.22$$

From equation 5.22, it is evident that when $k_2 \gg k_{-1}[A^-]$, the catalysis is controlled by the specie, AH and is said to be general acid catalysis.

The prototrophic mechanism is achieved through the following mechanism,

$$S + AH \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} SH^* + A^-$$

$$SH^* + A^- \xrightarrow{k_2} P + AH$$

Therefore,

$$-\frac{d[S]}{dt} = \frac{d[P]}{dt} = k_2[SH^*][A^-] \qquad 5.23$$

However, the concentration of the intermediate can be defined in terms of the rate of formation of the intermediate thus,

$$\frac{d[SH^*]}{dt} = k_1[S][AH] - k_{-1}[SH^*][A^-] - k_2[SH^*][A^-] \qquad 5.24$$

Application of the steady state approximation implies that equation 225 can be written as,

$$k_1[S][AH] - k_{-1}[SH^*][A^-] - k_2[SH^*][A^-] = 0$$

$$k_1[S][AH] = [SH^*](k_{-1}[A^-] - k_2[A^-])$$

$$[SH^*] = \frac{k_1[S][AH]}{k_{-1}[A^-] - k_2[A^-]} \qquad 5.25$$

Substituting for [SH*] in equation 5.23, the rate of reaction becomes,

$$-\frac{d[S]}{dt} = \frac{d[P]}{dt} = \frac{k_1k_2[S][AH][A^-]}{k_{-1}[A^-] - k_2[A^-]} = \frac{k_1k_2[S][AH]}{k_{-1} - k_2} \qquad 5.26$$

The two possibilities that follow equation 227 is $k_{-1} \gg k_2$ or $k_2 \gg k_{-1}$. However, in either case, the reaction will be general acid catalysis since [AH] appears in the rate determining step in either case.

3.7 Theories on catalysis

There are two theories describing catalysis. These are intermediate compound formation theory.

3.7.1 Intermediate compound formation theory

The intermediate compound formation theory proposed that the catalyst reacts with one of the reactants to form an unstable intermediate compound. The formation of this intermediate compound requires less energy than needed for the actual reaction. Consequently, the intermediate compound formed is unstable and combines with the other reactant to form the final product while the catalyst is regenerated. The implication of this theory is that a catalyst creates alternative reaction pathways for the reaction. The new reaction pathway has lower activation energy that the original reaction pathway.

The intermediate compound formation theory has been found to offer good explanation for some catalytic reaction and also explain why catalysts remain chemically unchanged at the end of the reaction.

3.7.2 The adsorption theory

The adsorption theory is most applicable to heterogeneous reactions especially, gas solid reaction. The theory proposed that when the catalyst is in solid state and the reactants are in gaseous state or in solutions, the molecules of the reactants are adsorbed on the surface of the catalyst. Adsorption being an exothermic process, the heat of adsorption is taken up by the surface of catalyst, which is utilized on enhancing the chemical activity of reacting molecules.

The modern adsorption theory is the combination of intermediate compound formation theory and the old adsorption theory. Consequently, the following facts are applicable to the modern adsorption theory

The catalytic activity is located on the surface of the catalyst. The mechanism involves five steps

i. Diffusion of reactant on the surface of catalyst
ii. Adsorption of reactant molecules on the surface of catalyst
iii. Occurrence of chemical reaction on the catalyst surface through formation of intermediates
iv. Desorption of reaction products away from the catalyst surface
v. Diffusion of reactant products away from the catalyst surface

3.8 Activity of catalysts

Activity of a catalyst is the ability of catalyst to accelerate a chemical reaction. The degree of acceleration can be as high as 10^{10} times in certain reactions. For example, reaction between H_2 and O_2 to form H_2O in presence of platinum as catalyst takes place with explosion but without the catalyst, both gases can be stored together without any reaction. Selectivity of a catalyst is its ability to direct a reaction to yield particular product (excluding other)

For example:

$$CO(g) + 2H_2(g) \overset{Ni}{\rightarrow} CH_4(g) + H_2O(l)$$

$$CO(g) + 2H_2(g) \overset{Ca/ZnO-Cr_2O_3}{\rightarrow} CH_3OH(g)$$

$$CO(g) + 2H_2(g) \overset{Cu}{\rightarrow} HCHO(g)$$

3.8.1 Shape-Selective Catalysis by Zeolites

The catalytic reaction that depends upon the structure of pores of the catalyst and the size of the reactant and product molecules are called shape/selective catalysis. Zeolites are good shape/selective catalysts because of their honeycomb-like structures. Zeolites are aluminosilicates i.e., three-dimensional network silicates in which some silicon atoms are replaced by aluminum atoms. They are found in nature as well as synthesized for catalytic selectivity. Zeolites, before using as catalysts, are heated in vacuum so that the water of hydration is lost. As a result, zeolite becomes porous i.e., the cavities in the cage-like structure which were occupied by the water molecules become vacant. The size of the pores is generally 260 pm to 740 pm, because of which only those molecules can be adsorbed in these pores whose size is small enough to enter these cavities and also leave easily.

The reactions taking place in zeolites depend upon the size and shape of reactant and product molecules as well as upon the pores and cavities of the zeolites. That is why these types of reactions are called 'shape-selective catalysis' reactions.

4.0 Self Assessment Questions and Answers

1.(a) Use the adsorption theory to outline the five steps involves in mechanism of catalysis.

(b) Define the term, selectivity of a catalyst. Hence show that the reaction between CO and H_2 can yield different products depending on the catalyst

(c) Write short note on the activity of a catalyst. Provide an example to support your statement.

2. (a) Highlight four industrial processes that uses catalyst.

(b) In a Tabular form, present four differences between homogenous and heterogenous catalysis

4.(a) State five general characteristic of a catalyst.

(b) Using the reaction of sodium thiosulphate as an example, write short note on induced catalysis. (write suitable equations)

Answers to Self Assessment Questions

1(a) The catalytic activity is located on the surface of the catalyst. The mechanism involves five steps

vi. Diffusion of reactant on the surface of catalyst

vii. Adsorption of reactant molecules on the surface of catalyst

viii. Occurrence of chemical reaction on the catalyst surface through formation of intermediates

ix. Desorption of reaction products away from the catalyst surface

x. Diffusion of reactant products away from the catalyst surface

(b) Selectivity of a catalyst is its ability to direct a reaction to yield particular product (excluding other)

For example:

$$CO(g) + 2H_2(g) \overset{Ni}{\rightarrow} CH_4(g) + H_2O(l)$$

$$CO(g) + 2H_2(g) \overset{Ca/ZnO-Cr_2O_3}{\rightarrow} CH_3OH(g)$$

$$CO(g) + 2H_2(g) \overset{Cu}{\rightarrow} HCHO(g)$$

(c) Activity of a catalyst is the ability of catalyst to accelerate a chemical reaction. The degree of acceleration can be as high as 10 ^{10} times in certain reactions. For example, reaction between H_2 and O_2 to form H_2O in presence of platinum as catalyst takes place with explosion but without the catalyst, both gases can be stored together without any reaction.

x. 2.(a) The Haber process: This is the process for the production of ammonia in commercial quantity. The catalyst used in this process is reduced iron.

$$N_{2(g)} \; + \; 3H_{2(g)} \xrightarrow{Fe(s)} 2NH_{3(g)}$$

xi. The contact process uses vanadium (V) oxide or platinum catalyst for the commercial production of SO_3, which dissolves in water to form H_2SO_4,

$$SO_{2(g)} \; + \; O_{2(g)} \xrightarrow{Pt(s)} 2SO_{3(g)}$$

xii. The fermentation process for the conversion of sugar to alcohol uses zymase as a catalyst

$$C_6H_{12}O_{6(aq)} \xrightarrow{zymase} 2C_2H_5OH_{(aq)} \; + \; 2CO_2$$

xiii. In the manufacturing of nitric acid by oxidation of ammonia using a mixture of ferric oxide and bismuth oxide

$$4NH_3 \; + \; 5O_2 \xrightarrow{Fe_2O_3/Bi_2O_3} 4NO \; + \; 6H_2O$$

(b)

Homogeneous catalysis	Heterogeneous catalysis
Homogenous catalyst is found mostly in liquid or gaseous state	Found in liquid, gas and even solid phases
Operative temperature for homogeneous catalysis is generally low except under high pressure	Required significant high operative temperature

Diffusion in homogenous catalysis is usually high because the reactant and the catalyst are in the same phase	Since the catalyst are in different phases, diffusivity and absorbance are usually low
There is usually large heat transfer because the catalyst and the reactant are in the same phase	The heat transfer is relatively low because the reactant molecules and catalysts are in different phase

3.(a)

i. A catalyst alters the rate of a chemical reaction by creating new reaction pathway but does not affect the thermodynamic properties of the system

ii. A catalyst will catalyse a chemical reaction, even when present in a minute concentration.

iii. A given catalyst is specific in action in that it may not catalyse other reactions.

iv. A catalyst is sensitive to temperature and pH. This implies that a given catalyst has an optimum pH and temperature ranges in which its functions best. At a temperature and pH, outside its range of sensitivity, a catalyst may be denatured or render inactive.

v. A catalyst remains chemically unchanged at the end of the reaction. However, the physical state of the catalyst may change.

(b) Induced catalysis involves the use of one reactant to speed up the rate of a reaction, which will not occur ordinary. Such a catalyst is called an induced catalyst. For example, sodium thiosulphite oxidizes readily in air to give sodium thiosulphate but sodium arsenite does not oxidize in air. However, when air is passed through a mixture of sodium thiosulphite and sodium arsenite, the sodium arsenite oxidizes readily. Therefore, sodium thiosulphite is an induced catalyst for the oxidation of sodium arsenite, as the following equations present.

$$Na_2SO_3 \xrightarrow{air} Na_2SO_4$$

$$Na_2AsO_3 \xrightarrow{air} \quad No\ reaction$$

$$Na_2SO_3 + Na_2AsO_3 \xrightarrow{air} Na_2SO_4 + Na_2AsO_4$$

(ii) Class Activity

(i) Identify some industrial reactions that uses catalyst. Compare the reaction rate in the absence and presence of the respective catalyst.

(ii) State some reactions that requires negative catalysis before they can be usefully harnessed

5.0 Conclusion

Several reactions that progresses for days, weeks and even years indicating that if the usefulness of such reactions have to be harnessed, time is of essence. The use of catalyst to increase the rate of such reactions has offered significant economic advantages by accelerating or promoting the expected reactions to come to an end. Also, some reactions are very fast such that their usefulness can only be harnessed by using negative catalyst. Catalysis therefore enhance production rate and offer economic value for most reactions.

6.0 Summary

Catalysis is most industrial processes. Variation in the choice of a give catalyst depends on the expected product, selectivity of the catalyst, reaction conditions, expected mechanism of reaction, cost, availability of the catalyst and environmental requirements. Depending on bases for classification, catalysis can be acid, base, acid-base, enzyme, heterogeneous, homogenous, hydrolytic.ed.etc. Catalysts are needed in several industrial reactions, which wouldn't be possible at all. It is evident that the use of catalyst increase productivity, save time, reduces cost and risk (in some cases). The chemistry of catalysis deals with the choice of catalyst, selectivity, sensitivity and improvement of reaction conditions. Much is still available for research in catalysis.

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MODULE 3

STUDY UNIT 2: PHOTOCHEMISTRY

1.0 Introduction

Photochemistry is the study of chemical interaction of electromagnetic radiation (wave of electric and magnetic component travelling at right angle to each other) that leads to physical or chemical change. That means the interaction of light can lead to chemical change (light induced change) or chemical reaction (chemiluminescence). Light is an electromagnetic radiation spreading in quanta.

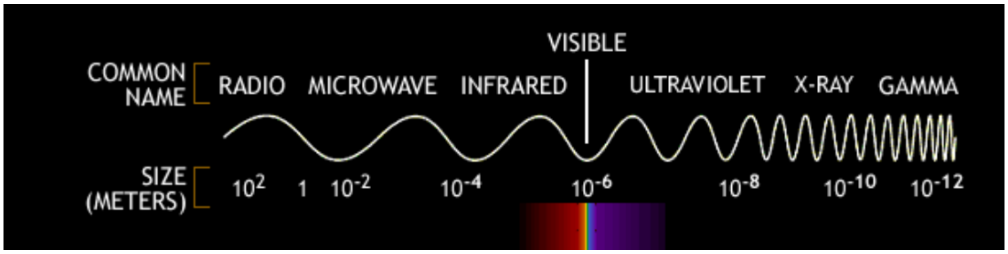
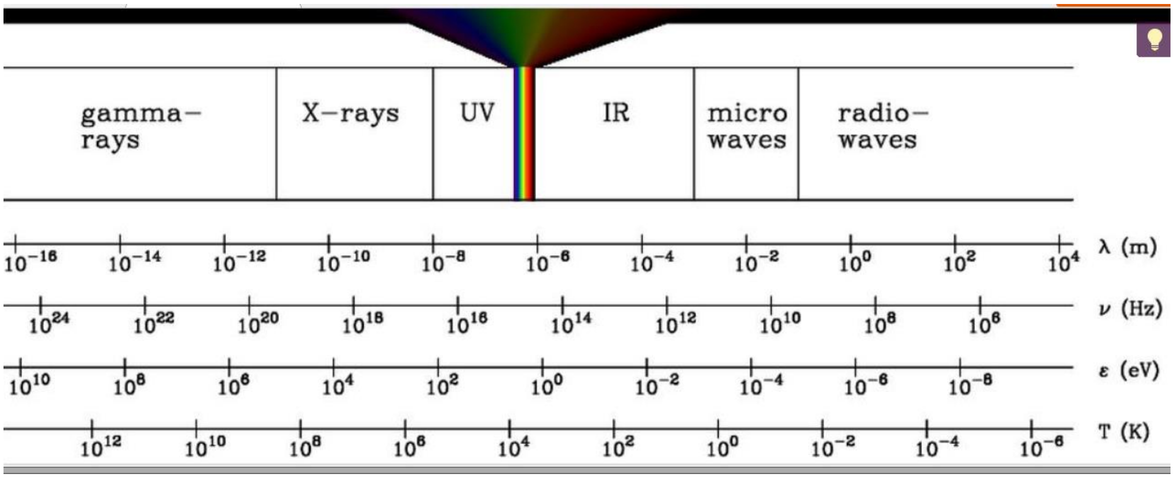


Fig. Electromagnetic spectrum



The study of photochemistry is important because it plays important role in atmospheric processes. The sun is the major source if photochemical energy. Normally, the ratio of atomic weight to the sum of the number of neutron and proton should be equal to unity for atoms but this is observed to be untrue for most atoms. The consequence is due to the binding energy of the atom. Therefore, nuclear energy can be expressed as

$$Nuclearenergy = neutron + proton - Bindingenergy$$

Therefore, the greater the binding energy, the lower the ratio, AW/(N+P). If two light nuclei join to form a heavier nucleus with higher binding energy, the extra energy is released as radiation. This gives rise to nuclear fusion. Nuclear fusion is a thermonuclear reaction that need to be activated by large amount of temperature. For example, the fusion of two atoms of deuterium occurs as follows,

$${}^{2}_{1}H \; + \; {}^{2}_{1}H \rightarrow {}^{4}_{2}He \; + \; Energy \qquad 6.1$$

The temperature needed to sustain the above reaction is in the range of 25, 000, 000 °C. This is the temperature in the sun interior. However, the temperature on the surface of the sum can be estimated using the steady state assumption, which states that the heat flow from interior is equal to the heat loss from the surface. Therefore,

$$\frac{dT}{dt} = C_1 M_s T_{interior} = C_2 (S.A)_s T_{surface} = 0 \qquad 6.2$$

$$\frac{4}{3} R^3 C_1 T_{interior} = \frac{4}{3} R^2 C_2 T_{surface} \qquad 6.3$$

$$T_{surface} = CRT_{interior} \approx 6000\, K \qquad 6.4$$

The energy of radiation can be estimated using the Einstein equation. Therefore, the energy per photon is given by

$$E = h\nu = \frac{hc}{\lambda} \qquad 6.5$$

where h is the Planck constant which is numerically equal to 6.6 x 10^{-34} J/s, c is the speed of light, numerically equal to 3.0 x 10^{8} m/s, λ is the wavelength and ν is the frequency. If we are interested in the energy per mole, then the above equation will be multiplied by the Avogadro's number, which is numerically equal to 6.02 x 10^{23}. If we substitute all numerical constants, the Einstein equation becomes,

$$E = h\nu = \frac{1.1925 \times 10^{5}}{\lambda} kJ/mole \qquad 6.6$$

Therefore, the smaller the wave length, the higher the energy. For example, wavelength of 10 nm will generate 290 kCal/mole. This is a large amount of energy, when compare to the energies of some chemical bonds. For example, a very strong bond in N-N (223 kcal/mol), strong bond in O-O (120 kcal/mol), intermediate bond in C-Cl (75 kcal/mol) and weak bonds in O-O_2 (35 kcal/mol) and HO-H (5 kcal/mol). Generally, chemical bond energies ranged from 100 to 1000 kJ/mol. Ultra violet radiation has a wavelength in the range of 200 nm to 400 nm, which is capable of generating Einstein energy ranging from 604 to 302 kJ/mol. Visible light has frequency ranging from 400 to 800 nm, which gives Einstein energy in the range of 302 to 151 kJ/mol while IR wavelength is 800 nm and can generates Einstein energy approximating to 151 nm. Therefore, UV and visible light can induce chemical reactions in most chemical systems.

Worked example 1

is. Write an equation to show the fusion reaction that generate high temperature in the range of 25, 000, 000 °C in the sun interior.

i. Derive an equation that can be used to estimate the interior temperature of the sun

ii. Use Einstein law to show that the energy of radiation can be written as $E = \frac{1.1925 \times 10^{5}}{\lambda} kJ/mole$. Hence Calculate the energy that can be generated by a radiation whose wavelength is 10 nm

iii. State the two major laws of photochemistry

Solution

1.i. $^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{4}_{2}He + Energy$

ii. The temperature on the surface of the sum can be estimated using the steady state assumption, which states that the heat flow from interior is equal to the heat loss from the surface. Therefore,

$$\frac{dT}{dt} = C_1 M_s T_{interior} = C_2 (S.A)_s T_{surface} = 0$$

$$\frac{4}{3} R^3 C_1 T_{interior} = \frac{4}{3} R^2 C_2 T_{surface} \qquad T_{surface} = CRT_{interior} \approx$$

$$6000\ K$$

iii. The energy of radiation can be estimated using the Einstein equation. Therefore, the energy per photon is given by

$$E = h\nu = \frac{hc}{\lambda}$$

where h is the Planck constant which is numerically equal to 6.6 x 10^{-34} J/s, c is the speed of light, numerically equal to 3.0 x 10^{8} m/s, λ is the wavelength and ν is the frequency

If we are interested in the energy per mole, then the above equation will be multiplied by the Avogadro's number, which is numerically equal to 6.02 x 10^{23}. If we substitute all numerical constants, the Einstein equation becomes,

$$E = h\nu = \frac{1.1925 \times 10^5}{\lambda} kJ/mole$$

When the wavelength is 10 nm, the energy will be,

E = 1.1925 x 10^{5}/10 x $10^{9\,=\,(}$kJ/mole)

The laws are:

i. Grotthus –Draper law". This law states that only light that is absorbed can produce photochemical change. The only exception to this law is in inelastic scattering of X-or γ-rays (electronic and Raman effects)

Stark-Einstein law: This law states that a molecule absorbs a single quantum of light is becoming excited. The exception to this law is in two-photon or multi-photon absorption (i.e. lasers)

2.0 Intended Learning Outcomes

When you have studied this session, you should be able to:

- (i) know what is photochemistry and the photochemical reactions
- (ii) comprehends the basic laws of photochemistry
- (iii) know and differentiate between photochemical and photochemical processes
- (iv) understand quantum yield as a measure of efficiency of photochemical reaction
- (v) know the theory of fluorescence and phosphorescence
- (vi) use Jablonski diagram to explain fluorescence and phosphorescence processes
- (vii) derive kinetic equations for photochemical reactions
- (viii) solve various problems in photochemistry

3.0 Main Content

3.1 Laws of Photochemistry

There are two basic laws of photochemistry and are summarised below,

3.1.1 Grotthus –Draper law". This law states that only light that is absorbed can produce photochemical change. The only exception to this law is in inelastic scattering of X-or γ-rays (electronic and Raman effects)

3.1.2 Stark-Einstein law: This law states that if a molecule radiation, then one particle is excited for each quantum of radiation absorbed. The exception to this law is in two-photon or multi-photon absorption (i.e. lasers)

The implication of Stark-Einstein law is that one particle of a chemical specie can absorbed only one photon of the light beam, whose energy is expressed as,

$$\Delta E = hv = \frac{hc}{\lambda} = \frac{(6.6 \times 10^{-23}\, Js^{-1})(3 \times 10^{8}\, ms^{-1})}{\lambda} = \frac{2 \times 10^{-16}\, J}{\lambda}$$

Consequently, the following relationships are true

- i. One mole is equivalent to hv = one Einstein
- ii. One photo is equivalent to one quantum and one molecule is also equivalent to one photon
- iii. One mole of a substance containing 6.023 x 10^{23} molecules is equivalent to one quanta mole of quanta or 6.023 x 10^{23} quanta of light or one Einstein

3.1.3 Lambert law

When monochromatic light passes through a medium, decrease in the intensity of the light with the thickness of the medium is proportional to the intensity of the light. If we denote the thickness with x, then according to Lambert's law,

$$-\frac{dI}{x} = kI$$

The above equation can be re-arranging and integrated as follow

$$-\frac{dI}{I} = kx$$

$$-\int_{I_0}^{I} \frac{dI}{I} = \int_{0}^{x} kxdx$$

$$-(lnI - lnI_0 = kx$$

$$ln\left(\frac{I}{I_0}\right) = -kx$$

$$I = I_0 e^{-kx}$$

I_0 is the intensity of the incident radiation and I is the intensity of the transmitted radiation while k is the absorption coefficient.

3.1.4 Beer's law and Beer-Lambert law

The law states that when monochromatic light passes through a solution, the decrease in intensity of the light with the concentration of the specie is directly proportional to the concentration. The consequence of this law also respects the following equations

$$-\frac{dI}{I} = kC$$

$$-\int_{I_0}^{I} \frac{dI}{I} = \int_{0}^{C} \varepsilon C dC$$

$$-(lnI - lnI_0 = \varepsilon C$$

$$ln\left(\frac{I}{I_0}\right) = -\varepsilon C$$

$$I = I_0 e^{-\varepsilon C}$$

ε is called molar absorption coefficient. Combination of Beer and Lambert laws leads to Beer-Lambert law of absorption, which can be expressed as follow,

$$I = I_0 e^{-\varepsilon x C}$$

$$A = ln\left(\frac{I_0}{I}\right) = \varepsilon x C$$

Worked example 2

A solution displays a transmittance of 20 % when taken in a cell of 2.5 cm thickness. Calculate its concentration if the molar absorption coefficient is 12, 000 dm^3/mol.cm.

Given

%T = 20 %, T = 20/100 = 0.20, x = 2,5 cm, $\varepsilon = 12\ 000\ dm^3/mol.cm$

It is known that, T = (I/I$_0$). Therefore, A = -logT consequently,

$$-logT = \varepsilon xC$$

$$C = -\frac{logT}{\varepsilon x} == -\frac{\log(0.20)}{12000\ \ x\ 24} = 2.33\ \times\ 10^{-5}\ moldm^3$$

3.2 Types of photochemical reactions

Photochemical reaction takes place in the presence of photons which implies that there must be absorption of light. The rate of such reaction is independent on temperature but on the intensity of the photon. The free energy change can be positive or negative, unlike normal chemical reaction such as thermochemical reaction. The general scheme for photochemical reaction involves excitation by absorption of photon, formation of intermediate and then conversion of intermediate to stable products. This can be represented by the following equation,

$$A\ \overset{h\nu}{\rightarrow}\ A^*\ \ \rightarrow intermediate\ \rightarrow Stable\ product$$

the quantum yield (Φ) is a measure of the efficiency of photon emission as defined by the ratio of the number of photons emitted to the number of photons absorbed. Primary quantum yield of a photochemical reaction is the number of photophysical or photochemical events that leads to primary products divided by the number of photons absorbed by the molecule in the same interval of time. This can be expressed as follows

$$\varphi = \frac{Number\ of\ photons\ emmited}{Number\ of\ photons\ absorbed}$$

Quantum yield can also be expressed as

$$\varphi = \frac{Rate\ of\ chemical\ reaction}{Intensity\ of\ light\ absorbed}$$

The sum of primary quantum yield for all photophysical and photochemical events must be equal to 1, i.e.

$$\sum_i \varphi_i = \sum_i \frac{v_i}{I_{abs}} = 1$$

where vi is the rate of reaction and I_{abs} is the intensity of light absorbed or quanta absorbed per second. Consequently, primary quantum yield can be obtained from the experimental rate of all the photophysical and photochemical processes that deactivate the excited state

$$\varphi_i = \frac{v_i}{\sum v_i}$$

The different types of photochemical reactions are

i. Photodissociation reaction
ii. photosynthesis reaction
iii. photosensitized reaction

3.2.1 Photodissociation: In photodissociation, the molecule absorbs dissociating heat from the energy of the photons. For example,

$$X_2 \overset{h\nu}{\rightarrow} X + X \qquad 6.7$$

A typical example of photodissociation reaction is the photolysis of HBr, which can be represented by the following reactions

$$HBr \overset{h\nu}{\rightarrow} H + Br \qquad 6.8$$

$$H + HBr \rightarrow H_2 + Br \qquad 6.9$$

$$Br + Br \rightarrow Br_2 \qquad 6.10$$

Equation 8 represents photochemical reactions while equations 6.9 and 6.10 constitute the dark reactions. The overall reaction can be written according to equation 6.11,

$$2HBr \overset{h\nu}{\rightarrow} H_2 + Br_2 \qquad 6.11$$

From equation 11, it can be deduced that one photon absorbs 2 molecules of HBr. At this juncture, we can define the term quantum yield as the ratio of the number of molecules undergoing the process to the number of quanta absorbed. That is,

$$\Phi = \frac{Number\ of\ molecule\ undergoing\ photochemical\ process}{Number\ of\ quanta\ absorbed} \qquad 6.12$$

Therefore, the quantum yield for photochemical reaction of HBr is 2. Another example of photodissociation is the formation of ozone in the lower atmosphere, which occurs approximately around the altitude of 25 km. The reactions can be represented by the following equations,

$$O_2 \overset{h\nu}{\rightarrow} \quad O + O \tag{6.13}$$

$$O_2 + 2O + energy \rightarrow 2O_3 + energy \tag{6.14}$$

The photochemical dissociation reaction involves wavelength in the range of < 240 nm, which implies that the photo energy generated will be greater than 4.968 x 10^{11} kJ/mol. The quantum yield for this reaction is 2. The ozone produced in the photochemical reaction offers protection to the earth by absorbing the dangerous ray of ultra violet radiation (equation 15). The ozone is in the process converted to oxygen molecule (equation 6.16)

$$O_3 \overset{h\nu}{\rightarrow} O_2 + O \tag{6.15}$$

$$O + O_3 \overset{h\nu}{\rightarrow} 2O_2 \tag{6.16}$$

3.2.2 Photosynthesis reaction: This involves the formation of a larger molecule from simple ones. An example of photosynthesis is the photosynthesis of HCl.

$$H_2 + Cl_2 \overset{h\nu}{\rightarrow} \quad 2HCl \tag{6.17}$$

The mechanism of photosynthesis of HCl can be broken into several steps as shown in equations 6.18 to 6.22

$$Cl_2 \xrightarrow{h\nu, <500\,nm} 2Cl \tag{6.18}$$

$$Cl_2 + H_2 \rightarrow HCl + H \tag{6.19}$$

$$H + Cl_2 \rightarrow HCl + Cl \tag{6.20}$$

$$H + H + M \rightarrow H_2 + M^* \tag{6.21}$$

$$Cl + Cl + M \rightarrow Cl_2 + M^* \tag{6.22}$$

Equation 6.18 represent photochemical initiation step (i.e. the production of free radicals), equation 6.19 and 6.20 represent propagation step, which are dark reaction, while equation 6.21 and 6.22 represent chain termination, through recombination of free radicals. It has been found that the quantum yield for this photosynthesis reaction is about 10^6, which is typical for explosion reaction.

Perhaps the most essential and significant photosynthesis reaction is the one connected with plant, which leads to the synthesis of carbohydrate in plant through the absorption of photons by chlorophyll. This reaction can be represented as follows,

$$6CO_2 + 6H_2O \xrightarrow{chlorophyl,hv} C_5H_{12}O_6 + 6O_6 \qquad 6.23$$

3.2.3 Photosensitized reactions: In photosensitized reactions, a photo excited molecule supplies activation energy to the reactant. The most significant example of photosensitized reaction is in photography. A photographic film is a colloidal suspension of finely powdered silver halogenide in gelatine, which when exposed to light, the AgBr granule becomes activated as follows,

$$AgBr \overset{hv}{\rightarrow} AgBr^* \qquad 6.24$$

Development of the film is achieved by treating it with a reducing agent, which accelerate the reduction to a black metallic silver, according to equation 6.25

$$AgBr^* \xrightarrow{Developer,reduction} Ag^0 \text{ (black)} \qquad 6.25$$

During this development, the unactivated granule will not change but becomes photosensitive and is removed during fixation (fixation involves treatment of the unactivated granuli of AgBr with thiotrioxosulphate compound, in order to remove it from the developed film) according to equation 6.26

$$AgBr + 2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-} + Br^- \qquad 6.26$$

Another example is the hydrogen gas containing trace concentration of mercury during the synthesis of formaldehyde as shown in the following equations,

$$H + CO \rightarrow HCO$$

$$H_s + HCO \rightarrow HCHO + H$$

$$HCO + HCO \rightarrow HCHO + CO$$

The above equation forms the basis for photodynamic therapy

Worked example 3

i. List the three basic types of photochemical reactions that you know.

ii. Write a general equation that represent photodissociation of X_2 molecule.

iv. Photolysis of HBr is known to be characterised with two sets of reaction. Name the reaction and write suitable equations for each. Hence write the overall reaction.

v. Write an equation that can be used to calculate the quantum yield of a photochemical reaction. Hence calculate the quantum yield for photolysis of HBr.

vi. With suitable equations, explain the photochemical reactions that leads to the formation of ozone in the lower atmosphere (at approximately 25 km). Hence calculate the quantum yield for the reaction.

vii. What is the major function of ozone in the atmosphere. Hence write the photochemical equations that represent the conversion of ozone into molecular oxygen

Solution

(i) The different types of photochemical reactions are

i. Photodissociation reaction
ii. photosynthesis reaction
iii. Photosensitized reaction

(ii) $X_2 \overset{h\nu}{\rightarrow} X + X$

(iii) A typical example of photodissociation reaction is the photolysis of HBr, which can be represented by the following reactions

$$HBr \overset{h\nu}{\rightarrow} H + Br \qquad (1)$$

$$H + HBr \rightarrow H_2 + Br \qquad (2)$$

$$Br + Br \rightarrow Br_2 \qquad (3)$$

Equation 1 represents photochemical reactions while equations 2 and 3 constitute the dark reactions.

The overall reaction can be written as follows

$$2HBr \overset{h\nu}{\rightarrow} H_2 + Br_2 \qquad (4)$$

(iv) Quantum yield is the ratio of the number of molecules undergoing the process to the number of quanta absorbed. That is,

$$\Phi = \frac{Numberofmoleculeundergoingphotochemicalprocess}{Numberofquantaabsorbed}$$

From equation 4, it can be deduced that one photon absorbs 2 molecules of HBr. Therefore, the quantum yield for photochemical reaction of HBr is 2.

(v) The formation of ozone in the lower atmosphere occurs approximately around the altitude of 25 km. The reactions can be represented by the following equations,

$$O_2 \overset{h\nu}{\rightarrow} O + O \qquad (1)$$

$$O_2 + 2O + energy \rightarrow 2O_3 + energy \qquad (2)$$

The photochemical dissociation reaction (equation 2) involves wavelength in the range of < 240 nm, which implies that the photo energy generated will be greater than 4.968 x 10^{11} kJ/mol. The quantum yield for this reaction is 2.

(vi) The ozone produced in the photochemical reaction offers protection to the earth by absorbing the dangerous ray of ultra violet radiation (equation 1). The ozone is in the process converted to oxygen molecule (equation 2)

$$O_3 \overset{h\nu}{\rightarrow} O_2 + O \qquad (1)$$

$$O + O_3 \overset{h\nu}{\rightarrow} 2O_2 \qquad (2)$$

Worked example 4

i. Write the mechanism of photosynthesis of HCl given that the photochemical reaction can be written as, $H_2 + Cl_2 \overset{hv}{\rightarrow} 2HCl.$

ii. Identify the three major stages associated with the mechanism presented in ‘i’above and give reason for your answer.

iii. Do you expect the photochemical reaction of HCl to lead to explosion? Give reason for your answer.

iv. With the aid of suitable equation, highlight the essential features of the photochemical reaction that leads to the production of carbohydrate in plants.

v. Highlight the mechanism involve in photosensitization in photography films towards the production of photographic films. Suitable equations must be provided.

Solution

(i) The mechanism of photosynthesis of HCl can be broken into several steps as shown in equations 18 to 22

$$Cl_2 \xrightarrow{h\nu,<500\ nm} 2Cl \qquad (1)$$

$$Cl_2 \ + \ H_2 \rightarrow HCl \ + \ H \qquad (2)$$

$$H \ + \ Cl_2 \rightarrow HCl \ + Cl \qquad (3)$$

$$H \ + \ H \ + \ M \rightarrow H_2 \ + \ M^* \qquad (4)$$

$$Cl \ + \ Cl \ + \ M \rightarrow Cl_2 \ + \ M^* \qquad (5)$$

(ii) Equation 1 represent photochemical initiation step (i.e. the production of free radicals), equation 2 and 3 represent propagation step, which are dark reaction, while equation 4 and 5 represent chain termination, through recombination of free radicals.

(iii) It has been found that the quantum yield for this photosynthesis reaction is about 10^6, which is typical for explosion reaction. Therefore, the above photochemical reaction will lead to explosion.

(iv) Perhaps the most essential and significant photosynthesis reaction is the one connected with plant, which leads to the synthesis of carbohydrate in plant through the absorption of photons by chlorophyll.

This reaction can be represented as follows,

$$6CO_2 \ + \ 6H_2O \xrightarrow{chlorophyl,h\nu} C_5H_{12}O_6 \ + \ 6O_6$$

(v) In photosensitized reactions, a photo excited molecule supplies activation energy to the reactant. The most significant example of photosensitized reaction is in photography. A photographic film is a colloidal suspension of finely powdered silver halogenide in gelatine, which when exposed to light, the AgBr granuli becomes activated as follows, (1 mark)

$$AgBr \overset{h\nu}{\rightarrow} AgBr^*$$

Development of the film is achieved by treating it with a reducing agent, which accelerate the reduction to a black metallic silver, according to the following equation

$$AgBr^* \xrightarrow{Developer,reduction} Ag^0 \text{ (black)}$$

During this development, the unactivated granuli will not change but becomes photosensitive and is removed during fixation (fixation involves treatment of the unactivated granuli of AgBr with thiotrioxosulphate compound, in order to remove it from the developed film) according to the following equation

$AgBr\ +\ 2S_2O_3^{2-} \rightarrow [Ag(S_2O_3)_2]^{3-}\ +\ Br^-$

Worked example 5

A sample of 4-heptane was irradiated for 100s with 313 nm radiation, having a power output of 50 W under conditions of total absorption. 2.8 mmol C_2H_4 was formed. Calculate the quantum yield for the formation of ethylene

Solution

Number of photons generated is

$$N_{photon} = \frac{P\Delta t\lambda}{hc} = \frac{(50\,W)(100s)(313 \times 10^{-9}\,m)}{(6.6260 \times 10^{-23}\,m^2kgs^{-1})(3 \times 10^8\,ms^{-1})}$$

$$\Phi = \frac{n_{C_2H_4}N_A}{N} = \frac{(2.8 \times 0.001\,mol)(6.022 \times 10^{23}\,mol^{-1})}{N_{photon}} = 0.21$$

3.4 Consequence of Absorption of Light

When a substance absorbs light, one or more of the underlisted processes will occur:

Dissociation/photolysis: Involves breaking the chemical bond in the molecule such that AB* = A + B*. For a chemical bond in a molecule to be broken, the energy must be greater than the bond energy. Generally, energy with wave length in the range of 10 to 1000 nm is sufficient to break most chemical bonds.

Ionization: Ionization is the removal of electron such that AB = AB^+ + e^-. generally, ionization energy is greater than chemical bond strength. Ionization energy is the energy needed to remove loosely bound electron from an atom.

Luminescence: Luminescence is the re-emission of photons. i.e. AB* = AB + hν. In atom, the energy of the excited and emitted photon is the same such that $\lambda_{excited} = \lambda_{emitted}$. But in molecules, the energy of the emitted photon may be less than that of the excited photon and as such, $\lambda_{excited} > \lambda_{emitted}$. There are two major type of tumescence, namely fluorescence and phosphorescence. Fluorescence is a visible wavelength while phosphorescence is a non visible wavelength.

Fluorescence is fast (10^{-8}s) and occur when there is a transition between states of the same spin ($\Delta S=0$). e.g. many aromatic hydrocarbons and dyes as vapours, in solution, or as solids, at room temperature. On the other hand, phosphorescence is slow (10^{-3}s) and it occurs when there is a transition between states of different spin multiplicities, e.g. triplet to singlet ($\Delta S \neq 0$). e.g. aromatic hydrocarbons, ketones, heterocyclic compounds in solid matrices at liquid nitrogen temperature. The major exception to phosphorescence is in heavy atom compounds (e.g. I_2) the strong spin-orbit coupling makes the distinction between singlets and triplets invalid. in other words, spin-orbit coupling makes spin changing transitions relatively allowed.

In chemiluminescence, an excited state is created via a chemical reaction. The light emission tracks the kinetic progress of the underlying chemical reaction. The excited state will then transfer to a dye molecule, also known as a sensitizer or fluorophor, and subsequently fluoresce back to the ground state.

Intra molecular energy transfer: This involves the conversion of the absorbed energy to several forms of lower energy (such as vibration, rotation and eventually to heat). Intra molecular energy transfer is typical for large molecules. i.e. $AB^* = AB^S$

Inter molecular energy transfer: In this case, the excited molecule transfers its energy to another molecule such as $AB^* + CD = AB + CD^*$

Quenching: In quenching, the activated molecule, loses its energy part of it may be lost as kinetic energy. This can be represented by the following equation, $AB^* + M = AB + M$ (KE)

Chemical reactions: This involves conversion to more active state, which may lead to selective chemical reactions. This can be represented as $AB^* + CD =$ different chemical species

Worked example 6

Highlight three mechanism for bimolecular quenching of fluorescence

Solution

The mechanisms are

(i0 Collisional deactivation

$$S^* + Q \rightarrow S + Q$$

This mechanism is most efficient when the quencher, Q is a heavy atom such as iodide ion

(ii) Resonance energy transfer: In this case, the energy is transferred to the quencher, Q as shown below,

$$S^* + Q \rightarrow S + Q^*$$

(iii) Electron transfer: Electron may be transfer from the quencher to the activated specie or from the activated specie to the quencher according to the following equations

$$S^{*} + Q \rightarrow S^{+} + Q^{-}$$

$$S^{*} + Q \rightarrow Q^{+} + S^{-}$$

Worked example 7

Highlight the basic concepts of Forster theory of energy transfer. Hence write the expression for the efficiency of energy transfer

Solution

Forster theory states that energy transfer is more efficient if,

(i) The energy donor and acceptor are separated by a short distance in the nanometer scale.

(ii) Photons emitted by the excited state of the donor can be absorbed directly by the acceptor

The efficiency of energy transfer can be written as,

$$E_T = ! + \frac{\Phi_F}{\Phi_{F,O}} = \frac{R_0^6}{R_0^6 + R^6}$$

Where Ris the distant between the acceptor and the donor while R_0 is a parameter that characterize each donor-acceptor pair

Worked example 8

Enumerate the basics of Marcus theory of electron transfer reactions

Solution

The Marcus theory can be summarised as follows,

(i) Distance between donor and acceptor: Electron transfer become more efficient as the distance between donor and acceptor decreases

(ii) The reaction Gibb energy: Electron transfer becomes more efficient as the reaction becomes more exergonic

(iii) Electron transfer become more efficient as the reorganizational energy matches the Gibb energy more closely. Reorganization energy is the energy cost incurred by molecular rearrangement of donor, acceptor and medium during electron transfer.

Worked example 9

(a) What is photosensitizer and photosensitization. Give at least three examples for atomic and two for molecular photosensitizers.

(b) Briefly explain how dissociation of hydrogen molecule can be achieved using photons generated by UV radiation. Provide useful equations to support your answer

Solution

(a) Photosensitization is a process of initiating a photochemical reaction on a substance that was unable to undergoes the reaction. The foreign substances use to sensitize the photochemical unreactive specie is called photosensitizer. Example of atomic photosensitizers are mercury vapour, cadmium and zinc while examples of molecular photosensitizers are benzophenone and sulphur dioxide

(b) Hydrogen molecule do not absorb UV radiation therefore the dissociation cannot be achieved directly. However, if minute concentration of mercury vapour is added, the mercury absorbs photons from the UV radiation and photo-sensitised the hydrogen molecule to undergoes dissociation. The equations for the process are as follows,

$$Hg + hv \rightarrow Hg^*$$

$$Hg^* + H_2 \rightarrow Hg + H_2^*$$

$$H_2^* \rightarrow 2H$$

In this process, the mercury acts as a photosensitizer

3.5 Fluorescence

Fluorescence is a spontaneous emission of light by a substance that has absorbed light or other electromagnetic radiation. In fluorescence the emission is independent on the number of photons present, which implies that the emitted light may have energy lower (higher wave length) lower than the excitation source. For example, if the source of excitation is in the visible UV region, the emitted light may be in the visible region and will give the fluorescence a distinct colour.

Fluorescence and phosphorescence differ in that in fluorescence, the emitted light ceases once the source of excitation is removed but in phosphorescence, the emission will continue even after excitation source has been turned off. This suggest that fluorescence is involved in immediate conversion of absorbed light into re-emitted energy while phosphorescence is concern with the storage of energy in a reservoir from which it slowly leaks.

3.5.1 Theory of fluorescence

Molecules have various states referred to as energy levels. Fluorescence spectroscopy is primarily concerned with electronic and vibrational states. Generally, the species being examined has a ground electronic state (a low energy state) and an excited electronic state of higher energy. Within each of these electronic states, there are various vibrational states. For fluorescence to occur, the molecule will absorb photon and become excited to a higher energy level. The excited molecule is subjected to collision with the surrounding molecule and as it gives off energy, it steps down the ladder of the vibrational levels. The surrounding molecules may not be able to absorb the energy needed to bring the molecule to its ground state. However, it might survive long enough to undergo spontaneous emission and consequently emits radiation called fluorescence. The downward electronic transition is vertical, in accordance with the Frank

3.5.2 Condon principle

In fluorescence spectroscopy, the species is first excited, by absorbing a photon, from its ground electronic state to one of the various vibrational states in the excited electronic state. Collisions with other molecules cause the excited molecule to lose vibrational energy until it reaches the lowest vibrational state of the excited electronic state.

The molecule then drops down to one of the various vibrational levels of the ground electronic state again, emitting a photon in the process. As molecules may drop down into any of several vibrational levels in the ground state, the emitted photons will have different energies, and thus frequencies from the first emission. Emission intensity in fluorescent spectroscopy, along with their relative intensities, the structure of the different vibrational levels can be determined. The schemes that lead to fluorescence emission is shown in Jablonski diagram (Fig. 6.1) below. When the orbital electron of a molecule, atom or nanostructure in its ground state absorbed photons and moved to excited singlet state (the transition is $S_0 + h\nu_{excited} \rightarrow S_1$). Similarly, the emission transition can be represented as $S_1 \rightarrow S_0 + h\nu_{emission}$. S_0 is called the ground state of the fluorophore (fluorescent molecule) and S_1 is the first electronically excited state. Once the molecule is excited to S_1, it will undergo relaxation which can occur in one of the following ways

i. Non radiative relaxation: the excited state is dissipated as heat (vibration) to the solvent

ii. Conversion to a triplet state and subsequent relaxation via phosphorescence

iii. Secondary non radiative relaxation

iv. Relaxation from S_1 can also occur through interaction with a second molecule through fluorescence quenching. For example, molecular oxygen is an efficient quencher of fluorescence because of its unusual triplet ground state.

Since fluorescence emission occurs at a longer wave length and therefore lower energy than the absorbed radiation, the phenomenon is known as **Stokes shift**. However, with intense electromagnetic radiation, one electron may absorb two photons, which could lead to the emission of a radiation with the wave length shorter than the source or emission of radiation with wave length similar to that of the source (Resonance fluorescence). It is also possible for molecules that are unable to emit fluorescence to be photosensitized to do so. In this case, molecules that are excited through light absorption or through a different process (e.g. as the product of a reaction) can transfer energy to a second 'sensitized' molecule, which is converted to its excited state and can then fluoresce.

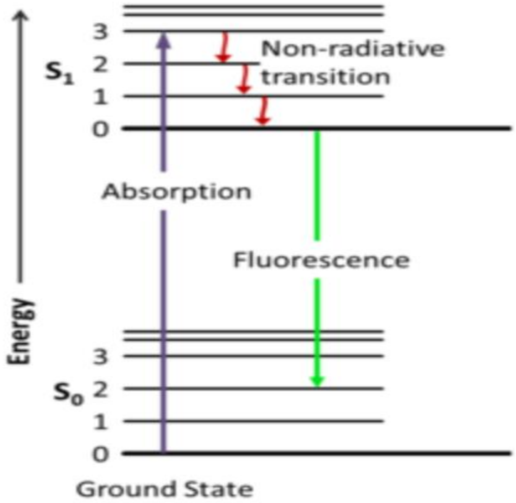


Fig. 6.1: Jablonski diagram showing scheme for fluorescence emission

(Source: https://en.wikipedia.org/wiki/Fluorescence)

A more detailed diagram that explain the phenomena of fluorescence and phosphorescence is also presented in Fig.6. 2

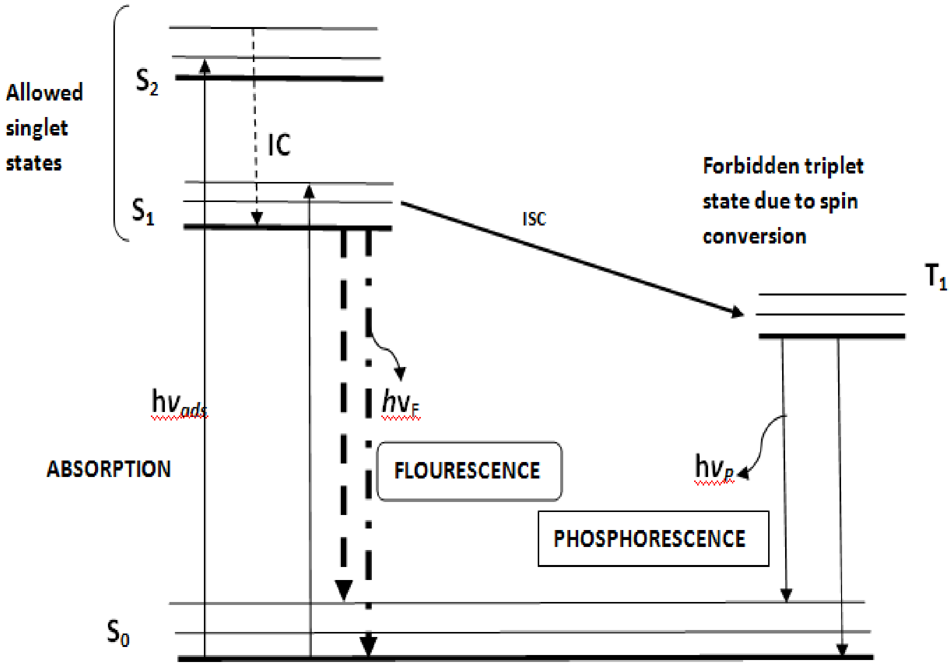
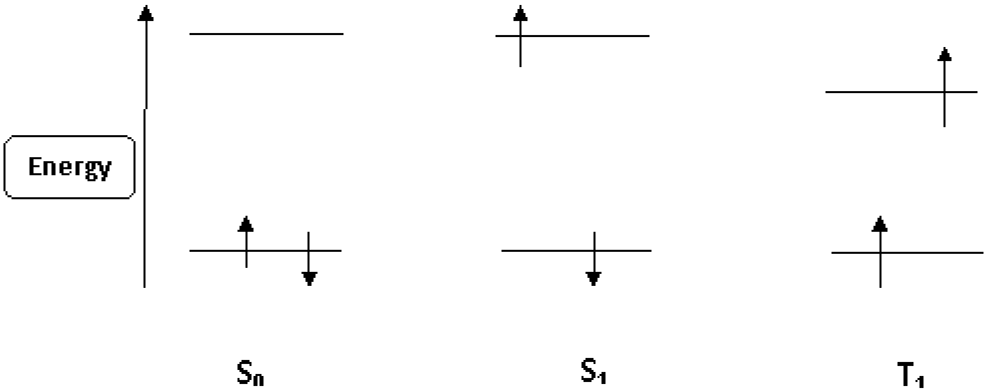


Fig. 6.2: Jabloski diagram for fluorescence and phosphorescence

(IC = Internal conversion, ISC = intersystem crossing, S_1= first excited singlet state, S_2 = second excited singlet state, T_1 = triplet state)

The path of excitation can be from singlet ground state to singlet excited state (fluorescence) or from singlet excited state to Triplet state (Phosphorescence). A singlet ground state (**S_0**) is a state with pair of electrons in the same orbital. A singlet excited state (**S_1**) is a pair of electrons with opposite spin in different orbital while a triplet excited state (**T_1**) is a pair of electrons with parallel spin in different orbital. The diagram below illustrates the three states



It is seen from the diagram that in S_0, one orbital is occupied, in S_1 and T_1 two orbitals are occupied. Also in S_1 and S_0 electron spin is opposed while in T_1, electron spin is parallel. The energy of the excited triplet state is lower than that of singlet excited state, which implies better stability for the T_1. It should also be stated that once in the excited state, the electron may returns to the ground state through one of the following process,

i. Emission of fluorescence
ii. Emission of phosphorescence
iii. Internal conversion follows by fluorescence emission
iv. Internal conversion follows by intersystem conversion and by phosphorescence emission.
v. Vibrational relaxation from one of the excited state vibrational level to another
vi. Non radiative decay from singlet or triplet excited state to ground state without emission of fluorescence or phosphorescence

The time scale through which the various transition occurs is usually short but differs for each process as shown in the Table 6.2 below

Table 6.2 : Time scale for some fluorescence and phosphorescence processes

Process	**Transition**	**Time scale (s)**
Excitation (light absorption)	$S_0 \rightarrow S_n$ (n = 1,2..)	10^{-15} (instantaneous)
Internal conversion (IC)	$S_n \rightarrow S_0$	10^{-14} to 10^{-11}
Vibrational relaxation	$S_n^* \rightarrow S_n$	10^{-12} to 10^{-10}
Intersystem crossing (ISC)	$S_1 \rightarrow T_1$	10^{-11} to 10^{-6}
Fluorescence	$S_1 \rightarrow S_0$	10^{-9} to 10^{-6}
Phosphorescence	$T_1 \rightarrow S_0$	10^{-3} to 100
Non radiative decay	S_1 to S_0 T_1 to T_0	10^{-7} to 10^{-5} 10^{-3} to 100

The steps involve in fluorescence are

i. Absorption of photon by the molecule and excitation from ground state (S_0) to excited state (S_2)

ii. Transition from higher excited state to lower excited state (S_2 to S_1), which is called internal conversion (IC), a non radiative process

iii. The molecule may lose all the energy and the entire process become non radiative

iv. If all the energy is not lost, some molecule will undergo radiative transition from S_1 to S_0 leading to fluorescence

v. Part of the energy maybe transfer to the triplet state (T_1). This is called inter system crossing (ISC)

vi. The molecule in the T_1 will undergoes transition to S_0 leading to phosphorescence emission

vii. Examples of fluorescence materials are sodium vapour, iodine vapour mercury vapour and some organic dyes such as eosin and fluorescein while example of phosphorescence materials are zinc sulphide, sulphide and sulphate of barium, strontium and caesium.

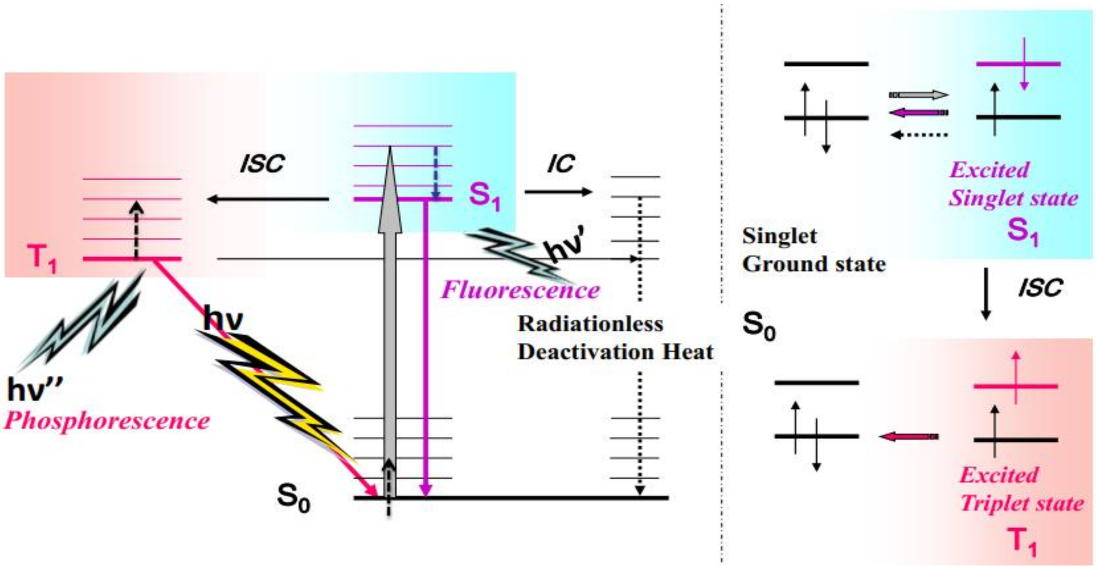


Fig. 6.3 Summary of scheme for absorption and loss of radiation

Fluorescence can be differentiated from phosphorescence in the following ways,

i. Fluorescence ceases once the source of excitation is removed but phosphorescence persist
ii. Fluorescence involves transition from excited singlet state to ground singlet state while phosphorescence involves transition from excited triplet state to singlet ground state.
iii. The transition that leads to fluorescence transition (S_1 to S_0) is allowed transition while the transition that leads to phosphorescence (T_1 to S_0) is forbidden transition.
iv. Transition for fluorescence is faster than that of phosphorescence
v. Efficiency of fluorescence is lower than that of phosphorescence
vi. Fluorescence is less selective and less sensitive than phosphorescence.
vii. Fluorescence does not occur in solution but phosphorescence can occur in solution.

Production of light by method, rather than heat is called luminescence while chemiluminescence is the production of radiation as a result of chemical reaction taking place at room temperature.

3.6 Kinetic of Decay of Excited Singlet State

The decay mechanism of excited singlet state can be summarised as follows,

i. Absorption: $S + h\nu_{abs} \rightarrow S^*$,. The rate = I_{ads}
ii. Fluorescence : $S^* \rightarrow S + h\nu_{abs}$ Rate = $k_F[S^*]$

iii. Internal conversion: S* → S, Rate = k_{IC}[S*]

iv. Intersystem crossing: S → T*, Rate = k_{ISC}[S*]

Therefore, the rate of decay would be given as,

$$\frac{d[S^*]}{dt} = -k_F[S^*] - k_{IC}[S^*] - k_{ISC}[S^*] \qquad 6.27$$

Rearranging the above equation, we have,

$$\frac{d[S^*]}{dt} = -[S^*](k_F - k_{IC} - k_{ISC}) \qquad 6.28$$

$$-\frac{d[S^*]}{[S^*]} = (k_F - k_{IC} - k_{ISC})dt \qquad 6.29$$

Integrating the equation from $[S^*]$ to $[S^*]_0$ and from t=0 to t=t, we have,

$$\int_{[S^*]_0}^{[S^*]} \frac{d[S^*]}{[S^*]} = -\int_0^t (k_F - k_{IC} - k_{ISC})dt \qquad 6.30$$

$$ln\left(\frac{[S^*]}{[S^*]_0}\right) = -(k_F - k_{IC} - k_{ISC})t \qquad 6.31$$

$$\frac{[S^*]}{[[S^*]_0]} = e^{-t((k_F - k_{IC} - k_{ISC})} \qquad 6.32$$

$$[S^*] = [S^*]_0 e^{-t((k_F - k_{IC} - k_{ISC})} \qquad 6.33$$

$$[S^*] = [S^*]_0 e^{-t/\tau_0} \qquad 6.34$$

where $\tau_0 = \frac{1}{(k_F - k_{IC} - k_{ISC}}$

3.6.1 Quantum yield of fluorescence emission

The efficiency of a fluorescence emission is expressed in terms of its quantum yield, which is defined as the ratio of the number of photons emitted to the number of photons absorbed.

$$\Phi = \frac{\text{Number of photons emitted}}{\text{Number of photons absorbed}}$$

From the above expression, the maximum value of Φ is unity (100 %), in this case, all the absorbed photons are emitted. It has been found that compounds with quantum yield ranging from 0.10 and above are fluorescence. Φ can also be defined in terms of the rate of excited state decay, thus,

$$\Phi = \frac{k_f}{\sum k_i} \qquad 6.35$$

where k_f is the rate constant of spontaneous emission of radiation and $\sum k_i$is the sum of all rates of excited state decay. Other rates of excited state decay are caused by mechanisms other than photon emission and are, therefore, often called "non-radiative rates", which can include: dynamic collisional quenching, near-field dipole-dipole interaction (or resonance energy transfer), internal conversion, and inter system crossing. Thus, if the rate of any pathway changes, both the excited state lifetime and the fluorescence quantum yield will be affected. Normally, fluorescence quantum yields are measured by comparison to a standard. The quinine salt *quinine sulphate* in a tetraoxosulphate (VI) acid solution is a common fluorescence standard.

Considering that the decay mechanism of exited singlet state consists of four steps and associated rate constants, the quantum yield of fluorescence emission can be derived using the rate of decay, thus,

$$\frac{d[S^*]}{dt} = -k_F[S^*] - k_{IC}[S^*] - k_{ISC}[S^*]$$

Invoking the steady state approximation, the equation becomes,

$$-k_F[S^*] - k_{IC}[S^*] - k_{ISC}[S^*] = 0$$

The rate of absorption was given as $I_{abs,}$ then,

$$I_{abs} - k_F[S^*] - k_{IC}[S^*] - k_{ISC}[S^*] = 0 \qquad 6.36$$

$$I_{abs} = k_F[S^*] + k_{IC}[S^*] + k_{ISC}[S^*] \qquad 6.37$$

Consequently, the expression for the quantum yield of fluorescence becomes,

$$\Phi_F = \frac{\text{Rate of fluorescence decay}}{\text{Overall rate}} = \frac{k_F[S^*]}{I_{abs}}$$

$$\Phi_F = \frac{k_F[S^*]}{= k_F[S^*] + k_{IC}[S^*] + k_{ISC}[S^*]} \qquad 6.38$$

$$\Phi_F = \frac{k_F}{k_F + k_{IC} + k_{ISC}} \qquad 6.39$$

In the presence of quencher, Q, additional process involving, $S^* + Q = S + Q$, whose rate is given as, $k_Q[Q][S^*]$, hence, the equation 6.36 becomes,

$$I_{abs} = k_F[S^*] + k_{IC}[S^*] + k_{ISC}[S^*] + k_Q[S^*][Q] \qquad 6.40$$

Hence, fluorescence quantum yield in the presence of quencher becomes,

$$\Phi_{F,Q} = \frac{k_F}{k_F + k_{IC} + k_{ISC} + k_Q[Q]} \qquad 6.41$$

The ratio $\frac{\Phi_{F,Q}}{\Phi_F}$ is expressed as,

$$\frac{\Phi_{F,Q}}{\Phi_F} = \frac{k_F}{k_F + k_{IC} + k_{ISC} + k_Q[Q]} \times \frac{k_F + k_{IC} + k_{ISC}}{k_F}$$

$$\frac{\Phi_{F,Q}}{\Phi_F} = \frac{k_F + k_{IC} + k_{ISC}}{k_F + k_{IC} + k_{ISC} + k_Q[Q]}$$

$$= \frac{\tau_0}{\tau_0 + \frac{1}{k_Q[Q]}} \quad \left(\tau_0 = \frac{1}{k_F + k_{IC} + k_{ISC}}\right) \qquad 6.42$$

Therefore, multiplying the denominator and the numerator of equation 36 by τ_0, we have

$$\frac{\Phi_{\mathrm{F,Q}}}{\Phi_{\mathrm{F}}} = \frac{1}{1 + \frac{1}{\tau_0 k_Q[Q]}} = 1 + \tau_0 k_Q[Q]$$

$$\frac{\Phi_{\mathrm{F,Q}}}{\Phi_{\mathrm{F}}} = 1 + \tau_0 k_Q[Q] \qquad 6.43$$

Equation 37 is the Stern-Volmer equation, which implies that a plot of $\frac{\Phi_{\mathrm{F,Q}}}{\Phi_{\mathrm{F}}}$ versus [Q} should be linear with slope equal to $\tau_0 k_Q[$ and intercept equal to unity. A plot of this nature is called Stern-Volmer plot.

3.6.2 Fluorescence lifetime

Fluorescence process is mostly known to follow a first order kinetics. Its lifetime is therefore the average time the molecule stays in its excited state before emitting a photon and can be expressed as,

$$[S^*] = [S^*]_0 e^{-t/\tau_0}$$

where $\tau_0 = \frac{1}{(k_F - k_{IC} - k_{ISC}}$, $[S^*]$ is the concentration of excited state molecules at time, t and $[S1]_0$ is the initial concentration. This is an instance of exponential. Various radiative and non-radiative processes can de-populate the excited state. In such case the total decay rate is the sum over all rates:

$$\Gamma_{Total} = \Gamma_{Radiative} + \Gamma_{Nonradiative}$$

where Γ_{Total} is the total decay rate, $\Gamma_{Radiative}$ the radiative decay rate and $\Gamma_{Nonradiative}$ the non-radiative decay rate. It is similar to a first-order chemical reaction in which the first-order rate constant is the sum of all of the rates (a parallel kinetic model). If the rate of spontaneous emission, or any of the other rates are fast, the lifetime is short Typical decay time for most fluorescent excited by radiations ranging from UV to near IR are in the range of 0.5 to 20 nanoseconds.

3.6.2 Theoretical rules for fluorescence

There are several rules that can serve as a guide to the direction or nature of fluorescence emission. Although some of these rules have some exception, they are generally applicable to cases where one electron absorbs one photon and not to two photon absorption. The following rules are highlighted in this section,

i. Kasha-Vavilove rule

ii. Frank Condon principle

iii. Stooke's shift

Kasha-Vavilove rule states that the quantum yield of luminescence is independent of the wavelength of exciting radiation. Kasha-Vavilove rule is simplifies if we consider the fact that the excited molecule must decay to the lowest vibrational level of the excited state before fluorescence can occur and that the emitted fluorescence often has higher wave length and lower energy that the excitation source. Modification of Kasha-Vavilove rule leads to the statement that the quantum of fluorescence spectrum has little dependence on the wavelength of the exciting radiation.

Frank-Condon (mirror image) rule simply states that electronic transitions are vertical and can be represented by Jablonski diagram. It has been found that for most fluorescence emission, the absorption spectrum is mirror image of the emission spectrum and is known as mirror image. One of the major implications of Frank Condon rules is that the nucleus does not move and the vibration levels of the excited state resemble the vibration levels of the ground state.

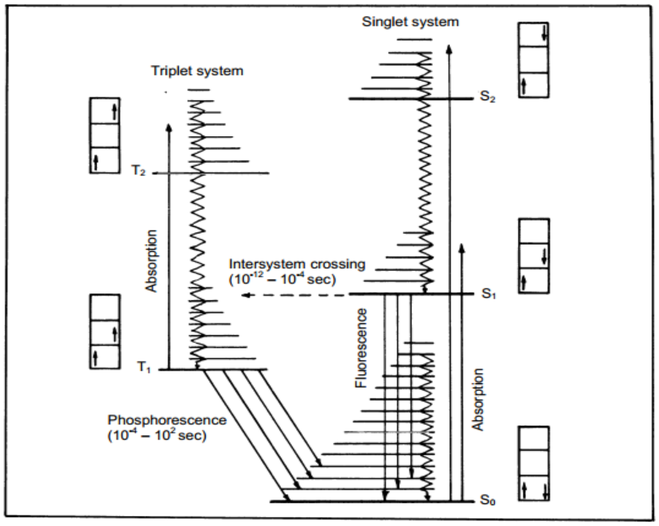
According to Stokes shift the emitted fluorescent light has a longer wavelength and lower energy than the absorbed light. Stokes shift is due to loss of energy between the time a photon is absorbed and when it emits fluorescence. Some of the causes of Stokes shift are non-radiative decay and that the emission of fluorescence leaves the molecule in a higher vibrational level of the ground state.

6.7 Phosphorescence

The steps leading to phosphorescence is the same as that of fluorescence except that there is an introduction of a triplet state in between singlet states. A triplet state is the state where the spin of electron is parallel. The singlet state can become a triplet state if a favourable mechanism for impairing electron exists. In this case, the molecule may undergo intersystem crossing. Phosphorescence occurs when an excited molecule crosses into a triplet state. In this case, it will continue to deposit energy into the surrounding and steps down the vibrational ladder (the triplet ladder) and becomes trapped as it descends to the lowest vibrational ladder of the triplet state. At this stage, it will be difficult for the solvent to extract large quantum of electronically excitation energy and the molecule cannot radiate its energy because transition to ground state is spin forbidden. However, the radiative transition is not totally forbidden because the selection rule is broken by spin-orbit coupling, which initiated intersystem crossing. Under this condition, the molecule is able to emits phosphorescence and the emission will continue for some time. Therefore, slower time scales of the re-emission are associated with forbidden energy state transition.

Most photoluminescent processes (i.e. process in which a chemical substrate absorbs and then re-emits a photon of light), are fast and take place within 10 nanoseconds. In this case, light is absorbed and emitted at these fast time scales when the energy of the photons involved matches the available energy states and allowed transitions of the substrate. However, in phosphorescence, the absorbed photon energy undergoes inter system crossing (ISC) into an energy state of higher spin multiplicity (usually a triplet state). The consequence is that energy can become trapped in the triplet state leaving only the forbidden transition available to return to the molecule to the lower energy state. These transitions, although "forbidden", will still occur in quantum mechanics but are kinetically unfavoured and thus progress at significantly slower time scales. The transition route that produces phosphorescence can be written as $S_0 + h\nu \rightarrow S_1 \rightarrow T_1 \rightarrow S_0 + h\nu$.

Most phosphorescent compounds are still relatively fast emitters, with triplet lifetimes on the order of milliseconds. However, some compounds have triplet lifetimes up to minutes or even hours, allowing these substances to effectively store light energy in the form of very slowly degrading excited electron states. If the phosphorescent quantum yield is high, these substances will release significant amounts of light over long time scales, creating so-called "glow-in-the-dark" materials.



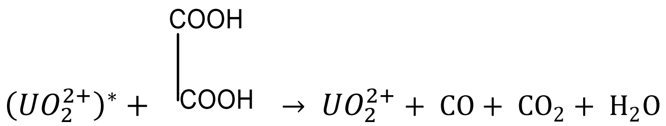
In the production of excited states by promotion of an electron into a higher orbital, the direction of the spin of the electron is preserved. Since most molecules have an even number of electrons and these are normally arranged in pairs of opposite spin, the promotion of an electron does not disturb this parity. However, it is possible for the spin of the promoted electron to be reversed so that it is no longer paired and the molecule has two independent electrons of the same spin in different orbitals. Quantum theory predicts that such a molecule can exist in three forms of very slightly differing, but normally indistinguishable energy, and the molecule is said to exist in a triplet state. The indirect process of conversion from the excited state produced by absorption of energy, the singlet state, to a triplet state, is known as intersystem crossing (Figure 3) and can occur in many substances when the lowest vibrational level of the excited singlet state, S1, has the same energy level as an upper vibrational level of the triplet state.

Direct transition from the ground state, usually a singlet state, for a molecule with an even number of electrons, to an excited triplet state is theoretically forbidden, which means that the reverse transition from triplet to ground state will be difficult. Thus, while the transition from an excited singlet state, for example, S1, to the ground state with the emission of fluorescence can take place easily and within 10^{-9}- 10^{-6}seconds, the transition from an excited triplet state to the ground state with the emission of phosphorescence requires at least 10^{-4}seconds and may take as long as 10^{2}seconds. This delay was once used as the characterisation of phosphorescence, but a more precise definition requires that phosphorescence be derived from transitions directly from the triplet state to the ground state.

3.8 Measuring the amount of radiation absorbed

Chemical actinometer is a device, used to measure the amount of radiation absorbed and rate of photochemical reaction. Uranyl oxalate actinometer is a commonly used It consists of 0.05 M oxalic acid and 0.01 M Uranyl sulphate in water. When it is exposed to radiation, Oxalic acid undergoes decomposition to give CO_2, CO and H_2O.

$$UO_2^{2+} + hv \rightarrow (UO_2^{2+})^*$$



$$(UO_2^{2+})^* + \begin{matrix}\mathrm{COOH}\\ |\\ \mathrm{COOH}\end{matrix} \rightarrow UO_2^{2+} + \mathrm{CO} + \mathrm{CO_2} + \mathrm{H_2O}$$

The residual concentration of oxalic acid can be found out by titrating with standard $KMnO_4$. The amount of oxalic acid consumed is a measure of the intensity of radiation. The process involves measuring of the total incident energy. This is done by filling the empty cell with the solvent and then exposing it to radiation before taking the reading. The cell is filled with the reactant and the reading is taken (i.e. residual energy). Finally, total energy absorbed by the reactant = total incident energy = residual energy

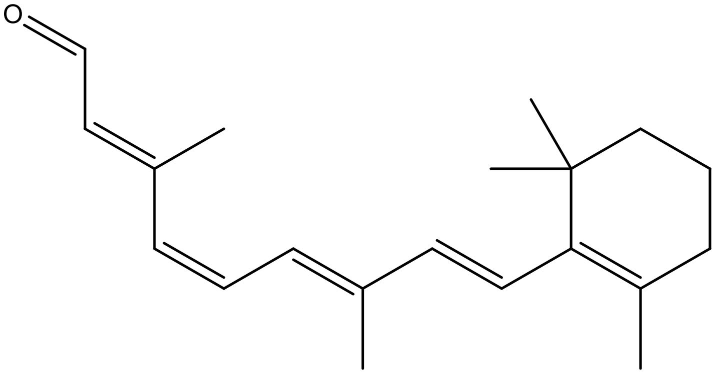
3.9 Photochemistry of vision

Vision is a process in which light is absorbed by a pigment in a photoreceptor cell (by a dye in the eye) and the photochemistry that ensues ultimately produces a transient electrical signal that is transmitted to the brain and interpreted as a visual image. There is much that is not fully understood about this process, but we shall discuss briefly the chemistry involved.

The eye is an extraordinarily sensitive instrument whose wavelength response is constricted to 400-800 nm. However, the eye has a very high degree of sensitivity. Diagram of the eye is shown in the diagram below

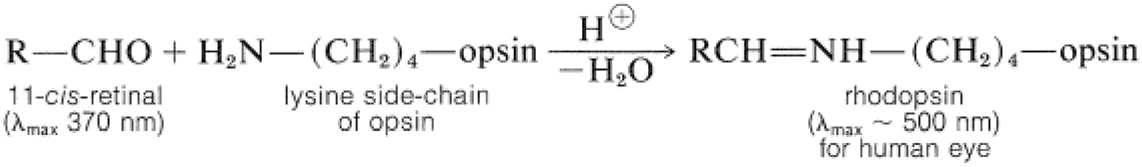
The retina consists of two kinds of light-sensitive (i.e., photoreceptor) cells, known as rods and cones. The rods are the more sensitive and are responsible for vision in dim light. The cones are much fewer in number than the rods and provide detail and color vision in good light. The part of the retina that corresponds to the center of the visual field contains only cones. A red pigment called **rhodopsin** is the photosensitive substance in the rod cells of the retina. It absorbs most strongly in the blue-green region of the visible spectrum (λ_{max} = 500nm) but unaffected by the far-red end of the spectrum. Cone vision appears to involve a different pigment called **iodopsin**, which absorbs farther toward the red than does rhodopsin.

Rhodopsin is a combination of a protein called **opsin**, and the highly conjugated aldehyde, 11-*cis*-retinal (λ_{max} = 370 nm)



11-cis-retinal

Little is known about the structure of opsin but 11-cis retinal (its prosthetic group) is bonded to opsin through an imine (Schiff base) function formed between the aldehyde group of the retinal and the side-chain amino function of a lysine unit of opsin:

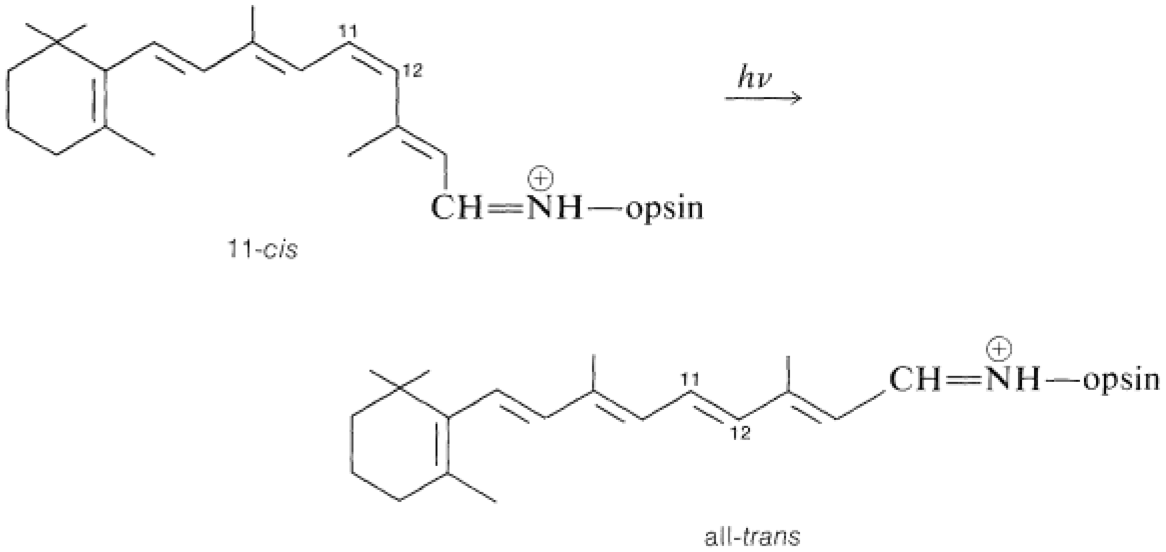


$$\mathrm{R{-}CHO + H_2N{-}(CH_2)_4{-}opsin \xrightarrow[-H_2O]{H^{\oplus}} RCH{=}NH{-}(CH_2)_4{-}opsin}$$

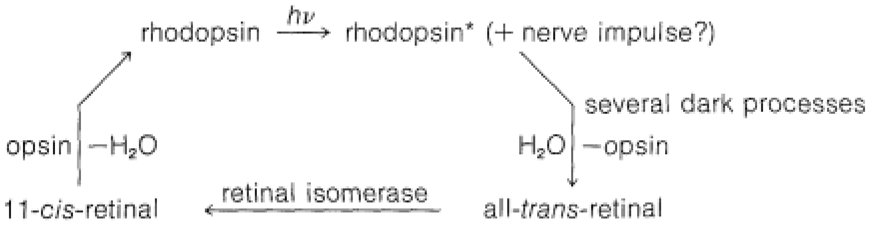
Opsin itself is colorless but 11-*cis*-retinal absorbs strongly at 370nm. It has been found that combination of opsin with 11-*cis*-retinal produces a remarkable shift of λmax to longer wavelengths (430nm to 620nm, depending on the species). Similar shifts in wavelength for 11-*cis*-retinal in combination with simple amines are observed only up to λmax of 440nm

Also, the chromophore in rhodopsin is believed to be protonated and to be profoundly modified by the structure of the opsin.

Light striking the retina changes the color of rhodopsin from red to yellow. The primary photochemical event in this process was established by G. Wald (Nobel Laureate in Physiology and Medicine, 1967), who showed that light absorption led to a change of configuration about the C11-C12 double bond of the retinal chromophore from *cis* to *trans* as shown below



There ensues a series of dark reactions or conformational changes that have the effect of greatly activating the imine linkage of the all-*trans*-rhodopsin towards hydrolysis. On hydrolysis, all-*trans*-retinal is released and is unable to recombine with opsin until it is reconverted to the 11-*cis* isomer. The *trans*-to-*cis* rearrangement is a thermal rather than a photochemical reaction and is catalyzed by the enzyme *retinal isomerase*. The cycle of reactions is summarized in Figure 28-13.



Schematic representation of the retinal cycle.

The exact point at which the nerve impulse is transmitted is not established with certainty, but is it believe to occur before the hydrolysis step because hydrolysis is too slow to account for the nerve impulse. One theory suggests that an electrical signal is generated at the instant of light absorption by electron transfer to a $\pi \rightarrow \pi*$ singlet excited state that has substantially charged carbon atoms

4.0 (i) Self Assessment Exercise and Answers

1. (a) Differentiate between primary and secondary photochemical reaction. Give example for each

(b) Give four reasons that may be responsible for higher values of quantum yield in some photochemical reactions.

2 (a) Identify primary and secondary photochemical steps involves in the following reactions

(i) Decomposition of HI

(ii) Formation of HCl

What is the expected quantum yield for both reactions?

(b) State four reasons that may lead to low quantum yield

3. Explain why the theoretical and experimental quantum yield for dimerization of anthracene differs significantly from each other. Provide chemical equations

4. Calculate spin multiplicity for

(i) Excited singlet state (S_1)

(ii) Excited triplet state (T_1)

5. The quenching of tryptophan fluorescence by dissolve oxygen was monitored by measuring emission lifetimes at 348 nm in aqueous solutions. Determine the quenching rate constant for this process, given the data below

$[O_2](10^{-2}M)$	0	2.3	5.5	8	10.8
$\tau_0\ (10^{-9}s)$	2.6	1.5	0.92	0.71	0.57

Answers to Self Assessment Questions

1. (a) In primary photochemical reaction, the molecule absorbed photon and become excited while secondary photochemical process involves further reaction of the excited molecule to give product of higher quantum yield.

Primary process: A + hν = A*, and Secondary process: A* = Product.

(b)

(1) When the absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions

(2) Formation of intermediate products which act as a catalyst

(3) If the reactions are exothermic, the heat evolved may activate other molecules

(4) The active molecules may collide with other molecules and activate them

2. (a)

(1) **Decomposition of HI**

primary reaction,

one HI molecule absorbs a photon and dissociated to produce one H and one I.

$$HI + h\nu \rightarrow H^* + I^*$$

secondary reaction

$$H^* + HI \rightarrow H_2 + I^*$$

$$I^* + I^* \rightarrow I_2$$

Overall reaction**:** $2HI + h\nu \rightarrow H_2 + I_2$

The overall reaction shows that the two HI are decomposed for one photon (hν).

Thus, the quantum yield (ϕ) = 2/1 = 2

(ii) **Formation of HCl**

Primary reaction**:** $Cl_2 + h\nu \rightarrow 2Cl^*$

Secondary reaction: $Cl^* + H_2 \rightarrow HCl + H^*$

$H^* + Cl_2 \rightarrow HCl + Cl^*$

The Cl atom consumed in the first step is regenerated. This will propagate the chain reaction.

The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.

H* + Cl* → HCl

Cl* + Cl* → Cl_2

Thus the quantum yield varies from 10^4 to 10^6

(b) Reasons for low quantum yield

(1) Deactivation of the intermediate before product formation

(2) Lost of energy by excited molecule through collision with unexcited molecule

(3) If the molecule does not receive sufficient energy to enhance reaction

(4) Recombination of dissociated fragment will result in low quantum yield

3. The equation for dimerization of anthracene is given as

$$2C_{14}H_{10} + hv \rightarrow C_{28}H_{20}$$

The theoretical quantum yield is 2 but the experimental quantum yield is 0.5. This is due to the reversibility of the reaction, that is

$$C_{28}H_{20} \rightarrow 2C_{14}H_{10}$$

4. Spin multiplicity can be calculated using the equation,

$$Spin\ multiplicity = 2S + 1$$

(i) For excited singlet state, S_1 has opposed electron spin. Therefore, a value of ½ will be assigned to one and –½ to the other

$$S = \left(\frac{1}{2}\right) + \left(-\frac{1}{2}\right) = 0$$

Therefore, $Spin\ multiplicity = 2(0) + 1 = 1$

(i) For excited singlet state, T_1 has two parallel electron spin, therefore, each of them will be assigned a value of ½

$$S = \left(\frac{1}{2}\right) + \left(\frac{1}{2}\right) = 1$$

Therefore, $Spin\ multiplicity = 2(1) + 1 = 3$

5. In purely collisional quenching (i.e. dynamic quenching) equation 37 can be written as,

$$\frac{\Phi_{F,Q}}{\Phi_F} = \frac{I_0}{I} = \frac{\tau_0}{\tau} = 1 + \tau_0 k_Q[Q]$$

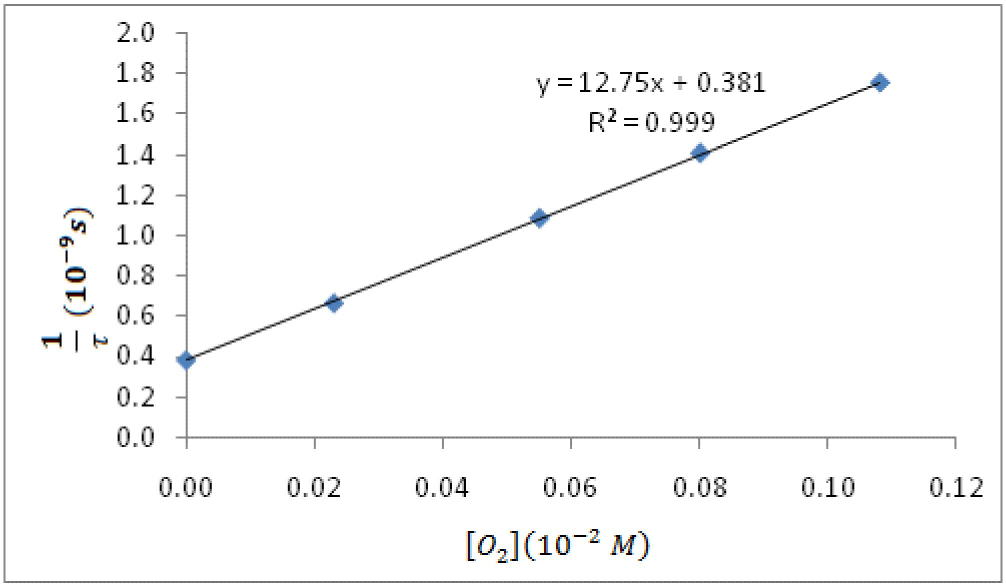
Consequently using $\frac{\tau_0}{\tau} = 1 + \tau_0 k_Q[Q]$, which fits the given data. Simplification of this equation by dividing the numerator and the denominator by τ_0 gives

$$\frac{1}{\tau} = \frac{1}{\tau_0} + k_Q[Q]$$

From the above equation, plotting of $\frac{1}{\tau}$ against [Q] should be linear with slope equal to k_Q and intercept equal to $\frac{1}{\tau_0}$. The Table of values used for the plot (and the plot) are shown below,

$[O_2](10^{-2}M)$	$\tau\ (\mathbf{10^{-9}}\boldsymbol{s})$	$\frac{\mathbf{1}}{\tau}\ (\mathbf{10^{-9}}\boldsymbol{s})$
0	2.6	0.3846
0.023	1.5	0.6667
0.055	0.92	1.0870
0.08	0.71	1.4085
0.108	0.57	1.7544

From the plot, the slope is equal to 12.75 which indicate that the rate constant for the quenching reaction is 12.75 $M^{-1}s^{-1}$ while τ_0 is the inverse of the intercept equal to 1/0.381 = 2.6247 s



(ii) Class Activity

(1) Look around yourself, your environment and the laboratory. Identify the various processes that uses the science of photochemistry

(2) In what ways can photochemistry be applied to correct eye defect.

5.0 Summary

The role of light in effecting chemical change has been recognized for many years. Indeed, the connection between solar energy and the biosynthesis of plant carbohydrates from carbon dioxide and water was known by the early 1800's. Yet organic photochemistry was slow to develop as a well-understood and manageable science. Progress only became rapid following the development of spectroscopy and spectroscopic techniques for structure determination and the detection of transient species. For this reason, photochemistry for many years was the domain of physical and theoretical chemists. Their work laid the foundation for modern organic photochemistry, which correlates the nature of excited electronic states of molecules with the reactions they undergo.

Most photochemical reactions can be considered to occur in three stages: (1) Absorption of electromagnetic radiation to produce electronically excited states. (2) Primary photochemical reactions involving excited electronic states. (3) Secondary or dark reactions whereby the products of the primary photochemical reactions are converted to stable products.

6.0 Conclusion

Photochemistry is the study of interaction of light and matter and their consequences. They are useful in several life encounters covering natural and artificial processes, which indicates that the study of photochemistry is vital in understanding several life processes.

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APPENDIX: MORE TRIAL QUESTIONS

1. Calculate the Einstein energy associated with ultra violet, visible and IR radiation. Given that their wave length are in the ranges, 200 to 400, 400 to 800 and 151 -160 nm respectively.
2. With suitable equations, discuss five consequences of light absorption by a substance.
3. Use the Jablonski diagram to explain the schemes that leads to fluorescence emission as a consequence of transition.
4. State the four ways that a molecule can relax prior to fluorescence emission
5. What is the technical meaning of Stoke's shift in fluorometry?
6. Under what condition can we have characterised fluorescence emission as resonance fluorescence?
7. What is the major difference between fluorescence and phosphorescence?
8. What is the difference between photophysical and photochemical process? How can photophysical process affects the rate of photochemical reaction.
9. Use mathematical equations to define quantum yield of fluorescence or phosphorescence emission in terms of absorbed/emitted spectrum and in terms of the rate of radiative decay respectively.
10. Calculate the concentration of an excited state molecule undergoing fluorescence if the initial concentration of the substance and the decay rate at 60 second are 20 moles/dm^3 and 0.2 respectively.
11. What are the processes that can de-populate the excited states of fluorescence? Hence write equation to show how the kinetic of such de-population can be compared with that of a first order reaction.
12. Given that an incident photon with intensity, I_0, passes through a medium containing a photochemical active substance. If the intensity of the transmitted photon is I_t. Derive from first principle, Beer-Lambert equation.
13. Derive expression for prototrophic mechanism of acid catalysis. Hence compare the magnitude of the two major rate constants (or rate constant and its coefficient) to derive expression for the expected order
14. Derive expression for protolytic mechanism of acid catalysis. Hence compare the magnitude of the two major rate constants (or rate constant and its coefficient) to derive expression for the expected order.

15 What is the general mechanism for enzyme catalysis

16. What is the selectivity of a catalyst. Hence write equations for selectivity of three catalyst that can catalyse the reaction between H_2O and CO

17. How does zeolite catalyst achieve its selectivity?

18. Outline the two theories on catalysis. Which of them is most widely accepted theory?

19. What is autocatalysis? Derive integrated rate law for autocatalysis

20. State five general properties of catalysts

21. State five industrial processes that rely on catalysis

22. State with the aid of suitable equations, a simple reaction that is not spontaneous but explosive in the present of a catalyst.

23. State one enzyme and explain its roles in a biological system

24. Does the production of beer require a catalyst? Justify