

Review On: Chemical Kinetics And Reaction Mechanism

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ABSTRACT:

Chemical kinetics determines the overall order of the reaction, as well as the order of each of the reactants.^[1] Rates of chemical reactions are measured through chemical kinetics. Reactions proceed at different rates depending on the nature of its reactants, the concentration of the substances, the temperature of the substances, and the presence of catalysts. This study aims to cast light on the application of chemical kinetics: to determine the rate law of a reaction using initial rates method, to apply the Arrhenius equation in determining the activation energy (E_a) of a reaction, to examine a catalyzed reaction and identify the role of the catalyst, and to illustrate the effect of varying temperatures and concentrations on the reaction rate. The factors—concentration, temperature, and catalyst—that affect the speed of reaction are observed and analyzed to see how effectively each factor affects the results of the reactions. Data gathered from the experiment showed that the rates of reactions increased or speed up when there is larger concentration, increase in temperature, and presence of a catalyst. Knowing these would help us predict the behaviour of the chemical reaction and its efficiency.^[2]

KEYWORDS: Chemical kinetics, Factors affecting rate of reaction, Rate law, Order of Reaction, Units of rate constant k for different reaction orders.

INTRODUCTION:

Chemical kinetics is an important phenomenon in physical chemistry. The term **kinetics** is referred to as the **study of motion**. It is derived from the Greek word “**kinesis**”.

It is a study of chemical reaction with respect to reaction rates, effect of different variables such as temperature and concentration. It also describes about the formation and deformation of bonds and formation of products via intermediates or transition state.

Many properties like order of a chemical reaction, rate of the reaction, or concentration of the components can be easily calculated from the study of chemical kinetics.

Chemical kinetics explains the mechanism of a chemical reaction. It gives an idea about the activation energy of a chemical reaction.

For a chemical reaction,



rate of the chemical reaction can be expressed in terms of reactants or products

$$\text{rate} = -d[A]/dt = -d[B]/dt = d[C]/dt = d[D]/dt$$

[] = concentration symbol of the component and t = time

If the reaction will be n^{th} order, then $\text{rate} = kC^n$

Where, k = rate constant, C = concentration, and n = order of the reaction

According to Arrhenius equation, $k = Ae^{-E_a/RT}$

Where, A is pre-exponential factor, R is universal gas constant, and E_a is activation energy of the reaction.

Chemical kinetics explains the collision theory and gives proper idea about the reaction mechanism.^[3]

FACTORS AFFECTING RATE OF REACTION:

Factor	Affect on Reaction Rate
Temperature	increasing temperature increases reaction rate
Pressure	increasing pressure increases reaction rate
Concentration	in a solution, increasing the amount of reactants increases the reaction rate
state of matter	gases react more readily than liquids, which react more readily than solids
Catalysts	a catalyst lowers activation energy, increasing reaction rate
Mixing	mixing reactants improves reaction rate

Table 1: Factors which affects the rate of reaction [4]

OBJECTIVES:

- Rate of Reaction
- Average Rate and Instantaneous Rate
- Rate Law
- Order of Reaction
- Zero Order Reactions
- First Order Reactions[5]

The rate of a reaction can be expressed as:

1) average rate

2) instantaneous rate

AVERAGE RATE:

The change in molar concentration of either reactants or products in unit time is called as average rate.

$$\text{rate (r)} = \frac{\text{change in concentration}}{\text{time interval}}$$

INSTANTANEOUS RATE:

The change in molar concentration of either reactants or products at an instant of time (or in infinitesimally small interval of time) is called as instantaneous rate.

$$r = \lim_{\Delta t \rightarrow 0} -\frac{\Delta c}{\Delta t} = -\frac{dc}{dt}$$

or

$$r = \lim_{\Delta t \rightarrow 0} +\frac{\Delta x}{\Delta t} = +\frac{dx}{dt}$$

Where,

dc = change in the concentration of reactant in infinitesimally small interval of time 'dt'

dx = change in the concentration of product in infinitesimally small interval of time 'dt' [6]

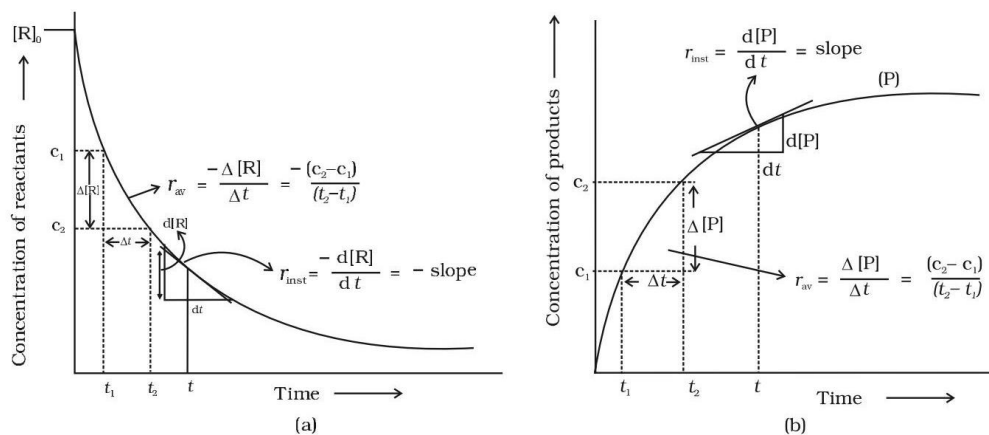


Figure 1: Instantaneous and average rate of a reaction: [7]

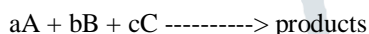
UNITS OF RATE OF A REACTION:

From equations (a) and (b), it is clear that units of rate are concentration time⁻¹. For example, if concentration is in mol L⁻¹ and time is in seconds then the units will be mol L⁻¹s⁻¹. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s⁻¹. [8]

RATE LAW:

The differential equation that describes the mathematical dependence of rate of reaction on the concentration terms of the reactants is called **rate law or rate expression or rate equation**.

For a general reaction,



the rate law can be written as:

$$\text{rate } (r) = k[A]^x[B]^y[C]^z$$

where,

k = rate constant or specific rate

x, y and z are the orders with respect to A, B and C respectively. [9]

ORDER OF REACTION:

Sum of the powers of the concentration terms in the rate equation is called overall **order of the reaction**.

Hence the order of above reaction = x + y + z [9]

CHARACTERISTICS OF ORDER OF REACTION:

- Order of reaction represents the number of atoms, ions and molecules whose concentration influence the rate of reaction.
- Order of the reaction is defined as the sum of the exponents to which the concentration terms in the rate law raised. Thus it is not dependent on the stoichiometric coefficients in a balanced chemical reaction.
- Values of x and y are determined experimentally. The values of x and y in the rate law are not necessarily equal to the stoichiometric coefficients of reactants. Thus the order of reaction can be decided by performing experiment only.
- Order of reaction is defined in terms of concentration of reactants only and not of products.
- Order of reaction may be integer, fraction or zero. [10]

Depending on the order of reaction, the chemical reactions can be divided into zero, first, second & third order reactions as follows. [9]

ZERO ORDER REACTION:

In a zero order reaction, the rate is independent of the concentration of the reactants. Thus, it means the sum of the powers of concentrations is zero. It can only be zero when the all the powers are zero. Consider a reaction, $R \rightarrow P$. Therefore, the rate law of this reaction is,

$$\text{Rate} \propto [R]^0$$

$$\therefore \text{Rate} = -d[R]/dt = k[R]^0 = k \times 1$$

$$\therefore \text{Rate} = -d[R]/dt = k$$

$$\therefore d[R] = -kdt$$

Integrating both sides, $[R] = -kt + I$(I)

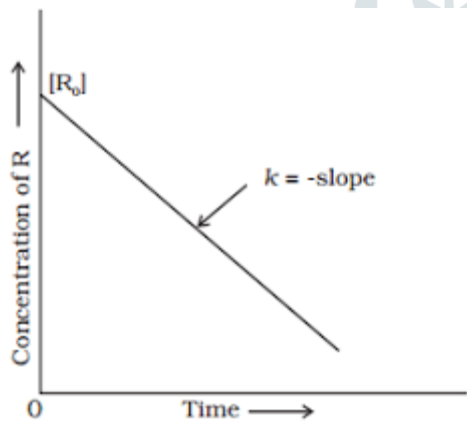
Where, I is the constant of integration. At $t = 0$, the concentration of the reactant $R = [R]_0$, where $[R]_0$ is the initial concentration of the reactant. Substituting this value in the equation I,

$$[R]_0 = -k \times 0 + I = I$$

Substituting this value of I in the equation (I), we get

$$[R] = -kt + [R]_0$$
(II)

Comparing equation II with the equation of a straight line $y = mx + c$, if we plot $[R]$ against t , we get a straight line with slope = $-k$ and intercept = $[R]_0$ [13]



Figure[2]: Graphic representation of time versus concentration of R[11]

Therefore, on simplifying equation II, we get

$$k = \{ [R]_0 - [R] \} / t$$
.....(III)

FIRST ORDER REACTION:

In this type of reaction, the sum of the powers of concentrations of reactants in rate law is equal to 1, that is the rate of the reaction is proportional to the first power of the concentration of the reactant. Consider the reaction $R \rightarrow P$ again. Therefore, the rate law for this reaction is,

Rate $\propto [R]$

We know that $[R] = -kt + [R]_0$ (from equation II). Taking log of both sides, we get

$$\ln[R] = -kt + \ln[R]_0 \dots\dots\dots(IV)$$

$$\therefore \ln[R]/[R]_0 = -kt \dots\dots\dots(V)$$

$$\therefore k = (1/t) \ln [R]_0/[R] \dots\dots\dots(VI)$$

Now, consider equation II again. At time t_1 and time t_2 , the equation II will be

$[R]_1 = -kt_1 + [R]_0$ and $[R]_2 = -kt_2 + [R]_0$ respectively, where $[R]_1$ and $[R]_2$ are concentrations of the reactants at time t_1 and t_2 respectively.

Subtracting second equation from first one, we get

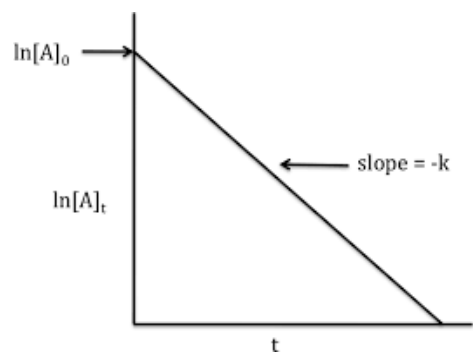
$$\ln [R]_1 - \ln[R]_2 = -kt_1 - (- kt_2)$$

$$\therefore \ln[R]_1 / [R]_2 = k (t_2 - t_1)$$

$$\therefore k = [1/(t_2 - t_1)] \ln[R]_1 / [R]_2$$

Now, taking antilog of both sides of equation V, we get $[R] = [R]_0 e^{-kt}$

Comparing this equation with equation of a straight line $y = mx + c$, if we plot $\ln [R]$ against t , we get a straight line with slope = $-k$ and intercept = $\ln[R]_0$ [13]



Figure[3]:Graphic representation of first order reaction[12]

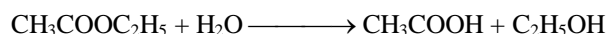
On removing natural logarithm from equation VI, the first-order reaction can also be written as,

$$k = 2.303/t \log[R]_0/[R] \dots\dots\dots(VII)$$

If we plot a graph of $\log[R]_0/[R]$ against t , we get slope = $k/2.303$

PSEUDO FIRST ORDER REACTION:

The order of a reaction is sometimes altered by conditions. Consider a chemical reaction between two substances when one reactant is present in large excess. During the hydrolysis of 0.01 mol of ethyl acetate with 10 mol of water, amounts of the various constituents at the beginning ($t = 0$) and completion (t) of the reaction are given as under. [14]



The concentration of water does not get altered much during the course of the reaction. So, in the rate equation

$$\text{Rate} = k' [\text{CH}_3\text{COOC}_2\text{H}_5] [\text{H}_2\text{O}]$$

The term $[\text{H}_2\text{O}]$ can be taken as constant. The equation, thus, becomes

$$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]$$

Where $k = k' [\text{H}_2\text{O}]$ and the reaction behaves as first order reaction. Such reactions are called pseudo first order reactions. [14]

Inversion of cane sugar is another pseudo first order reaction [14]



Cane sugar Glucose Fructose

$$\text{Rate} = k [\text{C}_{12}\text{H}_{22}\text{O}_{11}]$$

UNITS OF RATE OF A REACTION:

Table2: Units of rate constant k for different reaction orders [15]

Reaction	Order	Units of rate constant
Zero order reaction	0	$\text{Mol L}^{-1}\text{s}^{-1}$
First order reaction	1	s^{-1}
Second order reaction	2	$\text{Mol}^{-1}\text{L s}^{-1}$

CONCLUSION:

Chemical kinetics determines the overall order of the reaction, as well as the order of each of the reactants. Chemical kinetics is an important phenomenon in physical chemistry. Many properties like order of a chemical reaction, rate of the reaction, or concentration of the components can be easily calculated from the study of chemical kinetics. Chemical kinetics explains the mechanism of a chemical reaction. It gives an idea about the activation energy of a chemical reaction. The factors—concentration, temperature, and catalyst—that affect the speed of reaction are observed and analyzed to see how effectively each factor affects the results of the reactions. Order of reaction is defined in terms of concentration of reactants only and not of products. Order of reaction may be integer, fraction or zero. In a zero order reaction, the rate is independent of the concentration of the reactants. Thus, it means the sum of the powers of concentrations is zero. In first order of reaction, the sum of the powers of concentrations of reactants in rate law is equal to 1, that is the rate of the reaction is proportional to the first power of the concentration

of the reactant. The principles of chemical kinetics apply to purely physical processes as well as to chemical reactions. One reason for the importance of kinetics is that it provides evidence for the mechanisms of chemical processes. A chemical reaction is, by definition, one in which chemical substances are transformed into other substances, which means that chemical bonds are broken and formed so that there are changes in the relative positions of atoms in molecules.

ACKNOWLEDGMENT:

The author is gratefully acknowledge to The Department of Pharmacy, Ideal College of Pharmacy & Research, Kalyan, University of Mumbai, Maharashtra, India for providing the facility.

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