

When we see chemical reactions happening around us several questions come to our mind. How can we predict whether or not a reaction will take place? Once started, how fast does the reaction proceed? How far will the reaction go before it stops?

The laws of thermodynamics help us answer the first question. The current lesson, chemical kinetics provides answer to the question about the speed of a reaction and the last question is one of the many questions answered by the study of chemical equilibrium.

In this lesson, we will look closely at the relationships and laws that govern rates of chemical reactions. This lesson also covers the factors that affect the rate of the reaction; Determination of Rates of chemical reactions; Order of reactions; Rate constant; First order reactions; Temperature dependence of rate constant (Arrhenius equation).

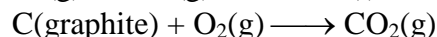
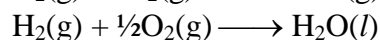
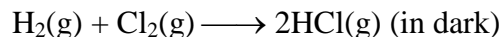
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1. Reaction Rate

Reactions can have wide difference in speeds. On one extreme, we have reactions, which proceed with very fast speeds so that the reaction appears to be instantaneous, e.g., reaction between a strong acid and a strong base. On the other extreme, reactions are known which proceed at very slow speeds so that virtually no visible changes are observed. Examples of very slow reactions include



Between these two extremes, there are many reactions, which proceed with measurable speeds. Examples include the decomposition of dinitrogen pentoxide dissolved in carbon tetrachloride, the hydrolysis of an ester, the reaction between persulphate and iodide ions and the hydrolysis of sugars. Rate of such reactions is estimated by estimating either the rate of consumption of reactants or the rate of formation of products.

The term “**rate of consumption of reactants**” means the rate of decrease in concentration of a reactant while “**rate of formation of products**” means the rate of increase in concentration of a product occurring in a given interval of time. It has the units of $\text{mol L}^{-1} \text{s}^{-1}$. Consider, for example, a simple reaction,



It is obvious that the amount of A will decrease whereas that of B will increase as the reaction proceeds. Fig (1a) displays typical behaviour of the change of the amounts of reactant and product as the chemical reaction shown above progresses.

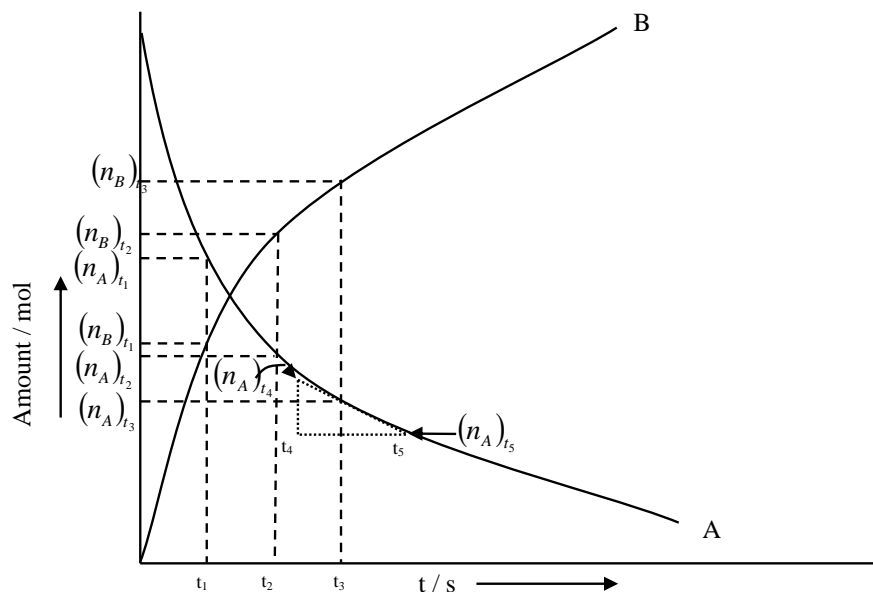


Fig (1a). The variations of amounts of A & B with time for the reaction $\text{A} \longrightarrow \text{B}$

Let $(n_A)_{t_1}$ and $(n_A)_{t_2}$ are the amounts of A at times t_1 and t_2 respectively. The change in the amount of A in the time interval $(t_2 - t_1)$ is equal to $[(n_A)_{t_2} - (n_A)_{t_1}]$. Therefore, rate of consumption of reactant A in unit time interval becomes

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$$R_{av} = \left[\frac{(n_A)_{t_1} - (n_A)_{t_2}}{(t_2 - t_1)} \right] = - \left[\frac{(n_A)_{t_2} - (n_A)_{t_1}}{(t_2 - t_1)} \right] = - \frac{\Delta n_A}{\Delta t} \quad \dots\dots(1b)$$

The term $\Delta n_A/\Delta t$ will be negative because A is being consumed and is decreasing with time but the rate is positive as -ve sign has appeared before the term of rate of change of concentration of reactant. We will see shortly that the rate expressed by Eq.(1b) changes during the course of a reaction. In general, the rate in the beginning is fast and it decreases as the reaction proceeds. Hence, the rate represented by Eq.(1b) is an average rate over the time interval $(t_2 - t_1)$. It is for this reason that the subscript 'av' has been added to the symbol R. Note that R_{av} is a positive quantity.

If $(n_B)_{t_1}$ and $(n_B)_{t_2}$ are the amounts of B at times t_1 and t_2 , respectively, the change in the amount of B (which we represent by Δn_B) in the time interval $(t_2 - t_1)$ ($=\Delta t$) is equal to $[(n_B)_{t_2} - (n_B)_{t_1}]$. Hence, the average rate of change of the amount of B (or average rate of formation of B) over the time interval t_1 to t_2 is

$$R'_{av} = \frac{\Delta n_B}{\Delta t} = \left[\frac{(n_B)_{t_2} - (n_B)_{t_1}}{(t_2 - t_1)} \right] \quad \dots\dots(1c)$$

Note the positive sign in $\Delta n_B/\Delta t$ as Δn_B is positive. From equation (1a) it follows that the decrease in the amount of A will be equal to the increase in the amount of B and thus, we have

$$R_{av} = R'_{av} \quad \dots\dots(1d)$$

1.1 Instantaneous Rate of Change of Reactant/Product Amount

In chemical kinetics, the rate at any particular instant of time rather than the average rate over a time interval has much more practical application and importance. This rate is known as the instantaneous rate (R_{ins}) and is defined as

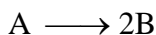
$$R_{ins} = \lim_{\Delta t \rightarrow 0} \left(\frac{-\Delta n_A}{\Delta t} \right) = - \frac{dn_A}{dt} \quad \dots\dots (1.1a)$$

$$\text{or} \quad R_{ins} = \lim_{\Delta t \rightarrow 0} \left(\frac{\Delta n_B}{\Delta t} \right) = \frac{dn_B}{dt} \quad \dots\dots (1.1b)$$

Therefore, the instantaneous rate at a given time may be determined by finding out the slope of either reactant or product curve at the given time. For example, at time t_3 , R_{ins} determined from Figure 1a is given by

$$R_{ins, t_3} = - \left(\frac{dn_A}{dt} \right)_{t_3} = - \left[\frac{(n_A)_4 - (n_A)_5}{(t_4 - t_5)} \right] \quad \dots\dots(1.1c)$$

Now consider another reaction,



here 1 mol of A on disappearing produces 2 mol of B, i.e., the amount of B will increase twice as fast as the decrease in amount of A. Therefore, the quantity dn_B/dt will be twice as large as $-dn_A/dt$. Obviously, we cannot write

$$- \frac{dn_A}{dt} = \frac{dn_B}{dt} \quad \dots\dots(1.1d)$$

but we can write as

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$$-\frac{dn_A}{dt} = \frac{1}{2} \frac{dn_B}{dt} \quad \dots (1.1e)$$

or as $-2 \frac{dn_A}{dt} = \frac{dn_B}{dt} \quad \dots (1.1f)$

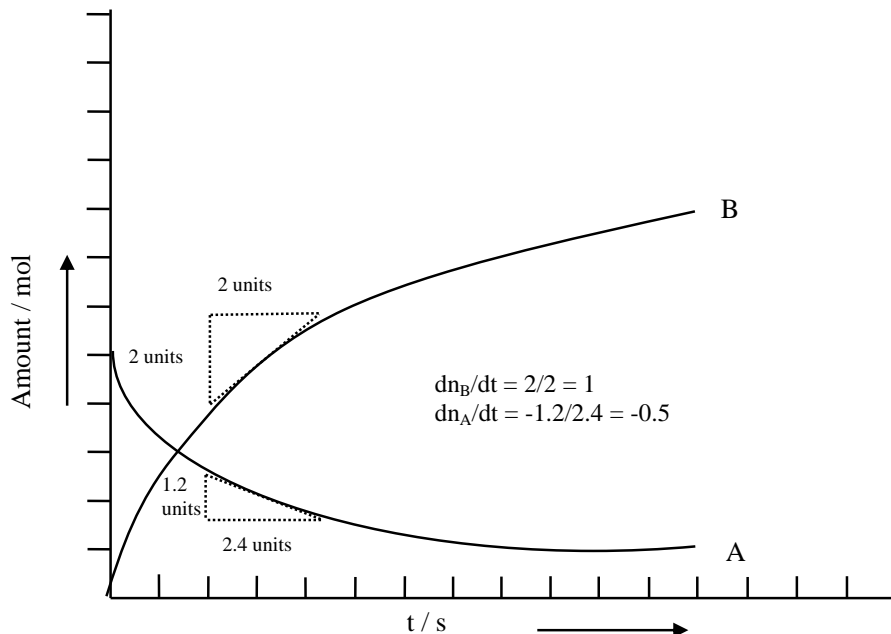


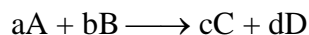
Fig (1.1a). The variations in the amounts of A & B with time for the reaction $A \rightarrow 2B$

In Figure 1.1a where the changes in amounts of A and B during the course of reaction are displayed, the above expressions may be verified. For example, for the indicated slope, we find that the slopes of A and B curves are -0.5 mol s^{-1} and 1.0 mol s^{-1} , respectively and hence,

$$-\frac{dn_A}{dt} = \frac{1}{2} \frac{dn_B}{dt} = 0.5 \text{ mol s}^{-1} \text{ and } -2 \frac{dn_A}{dt} = \frac{dn_B}{dt} = 1.0 \text{ mol s}^{-1}$$

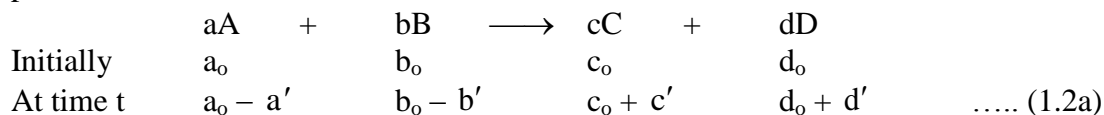
1.2 Generalized Expression of Rate of Reaction

Consider a reaction of the type



where a, b, c & d are the stoichiometric coefficients of reactants A & B and products C & D respectively. Let the initial mole of A, B, C and D be a_0 , b_0 , c_0 and d_0 respectively.

Let a' & b' are the mole of A and B reacting in time t and c' & d' are the mole of C and D produced in the same time interval.



For A: If the stoichiometric coefficients of A in the reaction is a then the amount of A reacting is a' . If the stoichiometric coefficient of A in the reaction is 1, then the amount of A reacting would be a'/a . Let $a'/a = x$. Then x is the amount of A reacting in time t if its

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coefficient in the reaction were 1. We know from the earlier discussion that the amount of A reacting in a certain time is the rate of the reaction if its coefficient were 1.

$$\therefore \text{rate of reaction} = \frac{dx}{dt} \quad \dots (1.2b)$$

(We are always interested in the instantaneous rate)

For B: If the stoichiometric coefficient of B in the reaction is b then the amount of B reacting is b'. If the stoichiometric coefficient of B in the reaction is 1, then the amount of B reacting would be b'/b. Let b'/b = x'. Then x' is the amount of B reacting in time t if its coefficient in the reaction were 1.

$$\therefore \text{rate of reaction} = \frac{dx'}{dt} \quad \dots (1.2c)$$

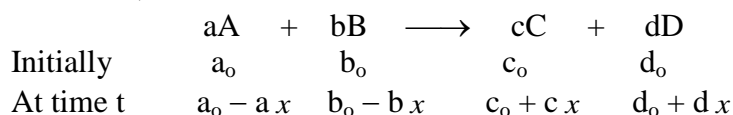
Comparing equation (1.2b) and (1.2c), we get

$$x' = x$$

Similarly it can be concluded that

$$\frac{c'}{c} = \frac{d'}{d} = x$$

Therefore,



The disappearance of amounts of reactants and appearance of amounts of products is given by

$$\begin{aligned} -\frac{dn_A}{dt} &= -\frac{d}{dt}[a_o - ax - a_o] = a \frac{dx}{dt} \\ -\frac{dn_B}{dt} &= -\frac{d}{dt}[b_o - bx - b_o] = b \frac{dx}{dt} \\ \frac{dn_C}{dt} &= \frac{d}{dt}[c_o + cx - c_o] = c \frac{dx}{dt} \\ \frac{dn_D}{dt} &= \frac{d}{dt}[d_o + dx - d_o] = d \frac{dx}{dt} \end{aligned}$$

From the above expressions, it follows that rate of reaction

$$= \frac{dx}{dt} = -\frac{1}{a} \frac{dn_A}{dt} = -\frac{1}{b} \frac{dn_B}{dt} = \frac{1}{c} \frac{dn_C}{dt} = \frac{1}{d} \frac{dn_D}{dt}.$$

If we divide the expressions by volume, the rate of the reaction becomes

$$\frac{dx}{dt} \left(\frac{1}{V} \right) = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}.$$

Thus, the rate of a reaction has the unit $\text{mol l}^{-1} \text{s}^{-1}$.

We can, therefore, conclude that “Rate of the reaction can be in general defined as the rate of consumption of any reactant or rate of formation of any product divided by the stoichiometric coefficient of that reactant or product”.

2. Order of A Reaction

Generally, the speed of a chemical reaction depends on the concentration of reacting species of the reaction. An early generalization in this regard is due to Gulberg and Waage. This generalization is known as law of mass action and is stated as follows.

According to law of mass action, the rate of a chemical reaction is proportional to the product of active masses of the reacting species. Active mass of a substance is not mass but its concentration raised to a power that is equal to the corresponding stoichiometric number of the substance appearing in the chemical reaction.

For a reaction $A + B \longrightarrow \text{Product}$

$$\text{Rate} \propto [A] [B]$$

For another reaction $A + A \longrightarrow \text{Product}$ or $2A \longrightarrow \text{Product}$

$$\text{Rate} \propto [A] [A] \quad \text{or} \quad \text{Rate} \propto [A]^2$$

Similarly, for a reaction $A + A + B \longrightarrow \text{Product}$ or $2A + B \longrightarrow \text{Product}$

$$\text{Rate} \propto [A] [A] [B] \quad \text{or} \quad \text{Rate} \propto [A]^2 [B]$$

Therefore, for a general reaction $aA + bB \longrightarrow cC + dD$

We have

$$r \propto [A]^a [B]^b$$

or $r = k [A]^a [B]^b$ here k is the constant of proportionality.

If the rate of a reaction is determined experimentally, it is found that above equation is not always applicable. However, the experimental results can be fitted to satisfy a relation of the type of above equation where the exponents may or may not be equal to the respective stoichiometric coefficients. The experimentally determined expression that relates actual rate of a reaction to the concentration of reactants is generally written as

$$r = k [A]^x [B]^y$$

Here the dimensionless exponents x & y may or may not be equal to a & b respectively. The constants x & y may have integral or fractional values or zero value. The constant x is known as the order of the reaction with respect to A, y as the order of the reaction with respect to B and so on. The sum (x + y) is known as the overall order (n) of the reaction (which does not have much of significance). If n = 1, the reaction is said to be of first-order; if n = 2, the reaction is said to be second-order and so on. The dependence of reaction rate on concentration is of great use as it helps in proposing the mechanism of a reaction.

The constant k, which appears in above rate equation is known as rate constant or more formally, the specific rate, since it is numerically equal to the rate of the reaction when all concentrations are unity (Specific concentration). Each reaction is characterized by its own reaction rate constant. From rate equation, we find that the units of k is $(\text{mole L}^{-1})^{1-n} \text{ s}^{-1}$ where $n = (x + y)$ and is called overall order of the reaction.

The expression that relates the rate of reaction, with the concentrations of reacting species is known as the differential rate law.

It may be emphasized once again here that the rate equation with its rate constant and order of various reacting species is an experimental finding and cannot be predicted from the stoichiometry of the balanced reaction.

Moreover the overall order of the reaction can have positive, negative, integral, and fractional or zero value. However, one must remember that order with respect to any reactant can never be

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negative. Overall order sometime may be negative due to inclusion of concentration terms of products.

Although many reactions obey general rate law expression, there are numerous others whose rate expressions are not of such simple form. A few such reactions are listed in following table.

Table: Examples of reactions obeying complicated Rate Laws

<i>Overall reaction</i>	<i>Experimentally determined rate laws</i>
$\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$	$\frac{1}{2} \frac{d[\text{HI}]}{dt} = k_1 [\text{H}_2][\text{I}_2] - k_{-1} [\text{HI}]^2$
$\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$	$\frac{1}{2} \frac{d[\text{HBr}]}{dt} = \frac{k [\text{H}_2][\text{Br}_2]^{1/2}}{1 + k' \frac{[\text{HBr}]}{[\text{Br}_2]}}$
$\text{OCl}^- + \text{I}^- \xrightarrow{\text{OH}^-} \text{OI}^- + \text{Cl}^-$	$\frac{d[\text{Cl}^-]}{dt} = k \frac{[\text{OCl}^-][\text{I}^-]}{[\text{OH}^-]}$
$\text{CH}_3\text{COCH}_3 + \text{I}_2 \xrightarrow{\text{H}^+} \text{CH}_3\text{COCH}_2\text{I} + \text{HI}$	$-\frac{d[\text{I}_2]}{dt} = k [\text{CH}_3\text{COCH}_3][\text{H}^+]$

Above table reveals the following facts.

1. The rate law may not have a simple relationship to the stoichiometric equation.
2. The rate law may not depend on the concentration of every reactant of the reaction.
3. The rate law may depend on the concentration of products as well as species (e.g., catalysts) which do not appear in the equation for the overall reaction.

These facts clearly indicate that the rate equation cannot be predicted from the form of the stoichiometric equation for the overall reaction. Hence, the rate equation must be determined experimentally. In some cases, the order of the reaction is meaningless. For example, for the hydrogen–bromine reaction, the reaction is of first–order with respect to hydrogen gas but it is impossible to assign the order with respect to bromine and to hydrogen bromide. Thus, the concept of order of reaction has no meaning if a rate law does not have the form as given in general rate law expression.

In the reaction between hypochlorite and iodide ions, though OH^- does not appear in the overall reaction, yet it appears in the denominator of the rate law. This indicates that OH^- acts as an inhibitor. Similarly, the reaction between acetone and iodine does not involve H^+ in the overall reaction, but it appears in the numerator of the rate law. This indicates that H^+ acts as an accelerator or a catalyst.

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3. Molecularity of Elementary Reactions

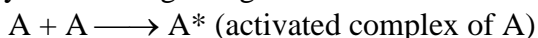
Most chemical reactions proceed through a series of elementary reactions. An elementary reaction is one that is taking place in a single step. These elementary steps are classified according to the number of molecules, which they involve. A process in which only one molecule is involved is known as unimolecular process. One involving two molecules is called bimolecular and so on. It is well known that in elementary reactions, the products are formed when the reactant molecules come close to each other and collide together. Since the collisions in which more than three particles come together simultaneously are very rare, the elementary process with molecularity greater than three are not usually observed and such reactions occur in a series of elementary steps.

If a reaction involves more than one step, the overall reaction is obtained by adding these elementary steps. In such a case, it is incorrect to assign molecularity to the overall reaction on the basis of its stoichiometry and rate law equation.

It was stated earlier that the order of a reaction, in general, cannot be predicted from the stoichiometry of the overall reaction. However, the order of an elementary step can be predicted from its molecularity. In fact, the order of an elementary step is always equal to its molecularity. This can be understood from the following analysis.

3.1 Unimolecular Elementary Process

In this process, a single reactant gives a product, $\text{A} \longrightarrow \text{B}$. This is achieved when A molecules collide to form an activated complex (an activated complex is the one whose energy is quite high) by transferring energies. The activated complex further decomposes independently.



It is obvious that the number of activated complexes produced would depend on the number or concentration of A molecules.

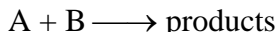
$$\begin{aligned} \text{A}^* &\longrightarrow \text{B} \\ r &= -\frac{d[\text{A}]}{dt} = k [\text{A}] \end{aligned}$$

Hence, the unimolecular elementary process is necessarily a first order reaction.

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3.2 Bimolecular Elementary Process

Let the elementary process be represented as



Now, for a molecule of A to react with a molecule of B it should come close to A and collide with it. The rate at which collisions between A & B molecules occur is directly proportional to the concentrations of A and B. Thus, the rate of the reaction will be given as

$$r = k [A] [B]$$

which is the expression of the second-order process. Hence, a bimolecular elementary process is necessary a second-order reaction.

The above arguments can be extended to a termolecular reaction. Hence a termolecular elementary process will follow third order rate law.

For all these arguments it has been assumed that the reactants are not pure solids or pure liquids and that none of the reactants are in excess. This is because the concentration of pure solids and pure liquids are always constants. This can be proved as follows

$$\text{Concentration} = \frac{\text{no. of mole}}{\text{volume}} = \frac{\frac{\text{mass}}{\text{density}}}{\frac{\text{molecular weight}}{\text{density}}} = \frac{\text{density}}{\text{molecular weight}} = \text{constant}$$

If A is a pure solid or a pure liquid, then its concentration will be a constant. Then experiment would give us a rate law as

$$r = k' [B] \text{ where } k' = k [A]$$

Therefore, the order with respect to A may be interpreted as zero. For the same reason, none of the reactants should be in large excess. If, for example, A is in large excess, then the change in the amount of A would be very small compared to the initial amount. And if the experiment is not very sensitive, then the concentration of A might appear as a constant.

Illustration 1

From the following data for the reaction between A and B, calculate the order of the reaction with respect to A and with respect to B.

[A]/mol L ⁻¹	[B]/mol L ⁻¹	Initial rate/mole L ⁻¹ s ⁻¹
2.5 × 10 ⁻⁴	3.0 × 10 ⁻⁵	5.0 × 10 ⁻⁴
5.0 × 10 ⁻⁴	6.0 × 10 ⁻⁵	4.0 × 10 ⁻³
1.0 × 10 ⁻³	6.0 × 10 ⁻⁵	1.6 × 10 ⁻²

Solution:

Let the order of reaction with respect to A and B are “x” and “y” respectively. The rate law would then be represented as Rate = k [A]^x[B]^y.

Therefore first data from the table gives

$$5.0 \times 10^{-4} = k [2.5 \times 10^{-4}]^x [3.0 \times 10^{-5}]^y \quad \dots(i)$$

Using second data, gives

$$4.0 \times 10^{-3} = k [5.0 \times 10^{-4}]^x [6.0 \times 10^{-5}]^y \quad \dots(ii)$$

and using third data, gives

$$1.6 \times 10^{-2} = k [1.0 \times 10^{-3}]^x [6.0 \times 10^{-5}]^y \quad \dots(iii)$$

Dividing equation (i) with (ii),

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$$\frac{4.0 \times 10^{-3}}{5.0 \times 10^{-4}} = \frac{k [5.0 \times 10^{-4}]^x [6.0 \times 10^{-5}]^y}{k [2.5 \times 10^{-4}]^x [3.0 \times 10^{-5}]^y}$$
$$8 = (2)^{x+y} \quad \text{or} \quad 2^3 = 2^{x+y}$$

$$\therefore x + y = 3$$

Similarly, dividing equation (iii) with (ii),

$$\frac{4.0 \times 10^{-3}}{1.6 \times 10^{-2}} = \frac{k [5.0 \times 10^{-4}]^x [6.0 \times 10^{-5}]^y}{k [1.0 \times 10^{-3}]^x [6.0 \times 10^{-5}]^y}$$
$$\frac{1}{4} = \left(\frac{1}{2}\right)^x \quad \text{or,} \quad 4 = 2^2 = 2^x$$

So, order with respect to A is two and with respect to B is one.

4. Integrated Rate Law of First-Order Reaction

The differential rate law shows how the rate of a reaction depends on the concentrations of reacting species. It is also useful to know how the concentrations of these species change with time. This information can be derived by integrating the differential rate law. In this section we derive the integrated rate law for reactions having first order and also derive their main characteristics.

In first order reactions, the rate expression generally depends on the concentration of one species only.

Thus, if the reaction $aA + bB \longrightarrow \text{products}$ is first order with respect to A and zero order with respect to B, we have

$$r = -\frac{1}{a} \frac{d[A]}{dt} = k[A]$$

$$\text{or} \quad -\frac{d[A]}{dt} = a k [A]$$

$$\text{Separating the variables give } -\frac{d[A]}{[A]} = a k dt \quad \dots (4a)$$

Integrating equation (4a) within the limits, we have

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = a k \int_0^t dt$$

$$\text{or } \ln \frac{[A]_0}{[A]_t} = a k t \quad \dots (4b)$$

$$\text{or } \ln \left(\frac{[A]_0}{[A]_0 - ax} \right) = a k t \quad \dots (4c)$$

For most of the simple first order reactions $a = 1$ and thus equation (4c) is given as

$$\ln \left(\frac{[A]_0}{[A]_0 - x} \right) = k t \quad \dots (4d)$$

From equation (4d), it follows that

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$$\ln \left(\frac{[A]_0 - x_{t_1}}{[A]_0 - x_{t_2}} \right) = k(t_2 - t_1) \quad \dots (4e)$$

Since the left hand side of equation (4d) and (4e) is a pure number, it follows that units of k are s^{-1} .

4.1. CHARACTERISTICS OF FIRST ORDER REACTIONS

Equation (4d) may be written as

$$\begin{aligned} \ln [A]_0 - \ln ([A]_0 - x) &= k t \\ \log ([A]_0 - x) &= \log [A]_0 - \frac{k t}{2.303} \end{aligned} \quad \dots (4.1a)$$

Equation (4d) may also be written as $[A]_t = [A]_0 e^{-kt}$ (4.1b)

Equation (4.1b), known as Wilhelmy's equation, indicates that the concentration of A decreases exponentially with time. The decrease is such that the time required for a definite fraction of the reaction to occur is independent of the initial concentration of the reactant.

Half-life, $t_{1/2}$, of a reaction is the time required for consumption of half of the reactant i.e concentration of the reactant decreases by half, i.e., $[A]_t = \frac{1}{2} [A]_0$.

Substituting the above relation in equation (4d) we get $\ln \frac{[A]_0}{[A]_0/2} = k t_{1/2}$

$$\begin{aligned} 2.303 \log 2 &= k t_{1/2} & t_{1/2} &= \frac{2.303 \times 0.3010}{k} & \dots (4.1c) \\ t_{1/2} &= \frac{0.693}{k} \end{aligned}$$

This relation indicates that $t_{1/2}$ is independent of initial concentration.

Figure 4.1a displays the typical variations of concentration of reactant exhibiting first order kinetics. It may be noted that though the major portion of the first-order kinetics may be over in a finite time, but the reaction will be completed in infinite time. Even though it is logical that there would be some value of time for completion of the reaction, it cannot be calculated based on equation (4.1a) because it ceases to be of use when the number of reactant molecules becomes very small.

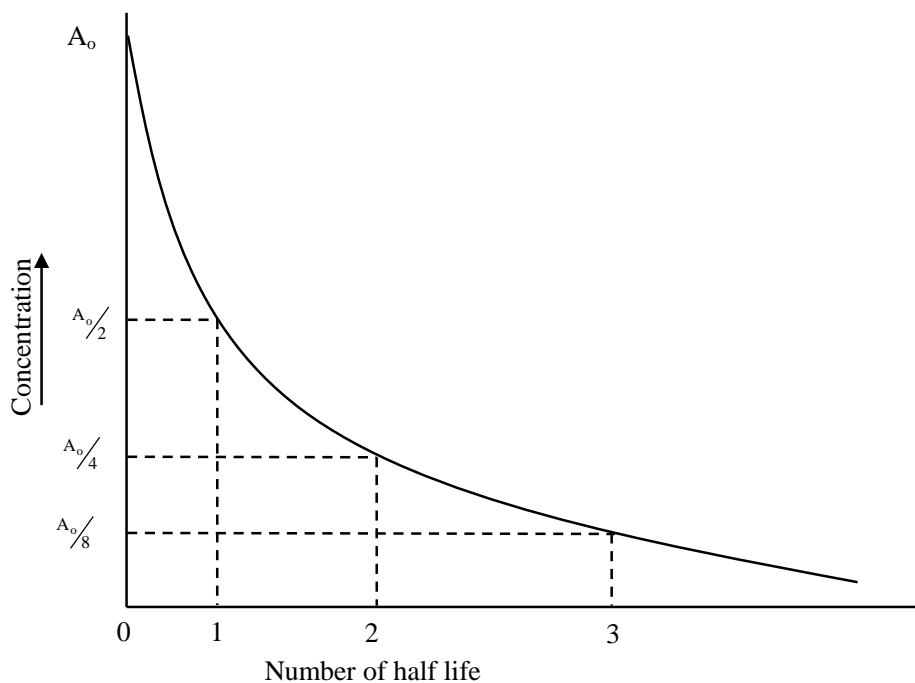
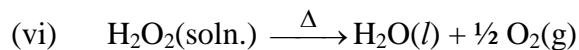
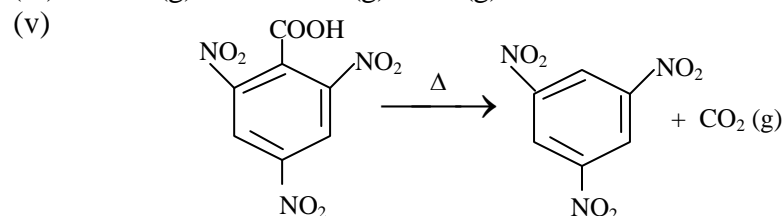
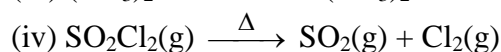
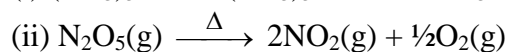
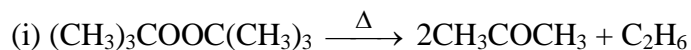


Fig (1.4a).

Variation of concentration of reactant exhibiting

4.2 Examples of First Order Reactions

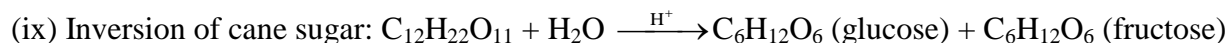
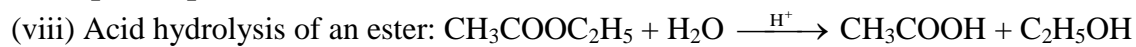
A large number of reactions exhibiting first order kinetics are known. A few examples are listed below.



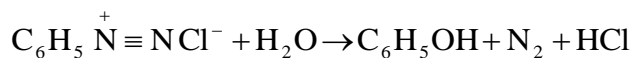
(vii) All radioactive decays.

There are reactions in which several species are involved in the rate determining step, but the order of the reaction is one. Such reactions are known as pseudo-unimolecular reactions and they involve solvent molecules or a catalyst as one of the reacting species.

Examples of pseudo-unimolecular reactions are:

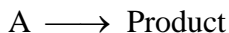


(x) Decomposition of benzene diazonium chloride:



5. Half-Life for n^{th} Order Reaction

Let us consider a reaction for finding the half-life of any n^{th} order reaction.



$$-\frac{d[\text{A}]}{dt} = k_n [\text{A}]^n$$

On separating the variables,

$$-\frac{d[\text{A}]}{[\text{A}]^n} = k_n dt$$

Integrating within the limits 0 and $t_{1/2}$, when the concentrations of reactant are $[\text{A}]_0$ and $\frac{[\text{A}]_0}{2}$ respectively.

$$\begin{aligned} -\int_{[\text{A}]_0}^{[\text{A}]_0/2} \frac{d[\text{A}]}{[\text{A}]^n} &= k_n \int_0^{t_{1/2}} dt \\ \int_{[\text{A}]_0/2}^{[\text{A}]_0} [\text{A}]^{-n} d[\text{A}] &= k_n \int_0^{t_{1/2}} dt \end{aligned}$$

On integration, we get

$$\begin{aligned} \left[\frac{[\text{A}]^{1-n}}{1-n} \right]_{[\text{A}]_0/2}^{[\text{A}]_0} &= k_n t_{1/2} \\ \frac{1}{(1-n)} \left[[\text{A}]_0^{1-n} - \left(\frac{[\text{A}]_0}{2} \right)^{1-n} \right] &= k_n t_{1/2} \\ \frac{[\text{A}]_0^{1-n}}{(1-n)} \left[1 - \left(\frac{1}{2} \right)^{1-n} \right] &= k_n t_{1/2} \\ \frac{(1-2^{n-1})}{(1-n)[\text{A}]_0^{n-1}} &= k_n t_{1/2} \\ t_{1/2} &= \frac{(2^{n-1}-1)}{(n-1)[\text{A}]_0^{n-1} k_n} \end{aligned}$$

Since n and k_n are constants, thus the half-life for n^{th} order reaction is inversely proportional to the initial concentration raised to the power $(n-1)$.

$$\therefore t_{1/2} \propto \frac{1}{[\text{A}]_0^{n-1}}$$

Thus, there will be different $t_{1/2}$'s for two different initial concentrations for all reactions other than first order reactions.

$$\therefore \frac{(t_{1/2})_2}{(t_{1/2})_1} = \left[\frac{[A_0]_1}{[A]_2} \right]^{n-1}$$

Using this relation, order of the reaction 'n' can be easily determined.

6. Replacement of Concentrations by Other Quantities in First Order Integrated Rate Law

It is evident that to determine the rate constant for a first order reaction, it is necessary to determine the ratio of the concentrations at two different times. However, most of the times during experiments, other quantities (proportional to the concentration) are being measured. Therefore, it will be useful to get integrated rate equations in terms of these quantities directly. We describe below a few typical cases where concentration terms are replaced by other easily measurable quantities (say X).

$$k = \frac{1}{t} \ln \frac{X_\infty - X_0}{X_\infty - X_t}$$

Here, X_0 , X_t and X_∞ represent the values of measured quantity at the beginning, at t time and after long time (end of the reaction). It must be remembered that X can include any measurable quantity that is regular function of time. It must however, not include a quantity that is not a regular function of time.

CASE – I:

Let us consider a first order reaction of the type, $A \longrightarrow B + C$. Let us further assume that all the three species are gases. We are required to calculate the value of rate constant based on the following data.

Time	0	t	∞
Partial pressure of A	P_0	P_t	—

STRATEGY:

We know integrated rate law for a first order reaction is $k = \frac{1}{t} \ln \frac{A_0}{A_t}$

At $t = 0$, the partial pressure of A is P_0 and at time t , it is P_t . According to the ideal gas law

$$P = \frac{n}{V} R T \quad \text{or} \quad \frac{n}{V} = \frac{P}{R T}$$

$$\left(\frac{n}{V} \right)_{t=0} = \frac{P_0}{R T}; \quad \left(\frac{n}{V} \right)_{t=t} = \frac{P_t}{R T}$$

$$\therefore \frac{\left(\frac{n}{V} \right)_{t=0}}{\left(\frac{n}{V} \right)_{t=t}} = \frac{A_0}{A_t} = \frac{P_0}{P_t} \quad \therefore k = \frac{1}{t} \ln \frac{P_0}{P_t}$$

CHEMICAL KINETICS

Alternatively, we could have got above expression directly from $k = \frac{1}{t} \ln \frac{X_{\infty} - X_0}{X_{\infty} - X_t}$ by

putting $X_{\infty} = 0$, $X_0 = P_0$ and $X_t = P_t$ where X represents partial pressure of A only.

$$k = \frac{1}{t} \ln \frac{0 - P_0}{0 - P_t} \quad \text{or} \quad k = \frac{1}{t} \ln \frac{P_0}{P_t}$$

CASE – II :

Let us consider first order reaction, $A \longrightarrow B + C$. Let us assume all three are gases. We are required to calculate the value of rate constant based on the following data

Time	0	t	∞
Total pressure	P_0	P_t	—

Calculate the expression of rate constant.

STRATEGY:

Total Pressure means the sum of partial pressures of all the gaseous species present in the system.

	A(g)	\longrightarrow	B(g)	+	C(g)	
At time = 0	P_0		0		0	
At time = t	$P_0 - x$		x		x	
At time = ∞	0		P_0		P_0	$P_{\infty} = 2P_0$

Since at $t = 0$ the total pressure is P_0 , it must also be the partial pressure of A at $t = 0$, since in the beginning only the reactant will be present. Let the decrease in pressure of A due to reaction till time t be x . Thus, at time t , the total pressure would be

$$(P_0 - x) + x + x = P_0 + x$$

$$P_0 + x = P_t \quad \Rightarrow \quad x = P_t - P_0$$

$$(P_0 - x) = P_0 - (P_t - P_0) = 2P_0 - P_t$$

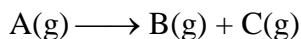
$$k = \frac{1}{t} \ln \frac{P_0}{2P_0 - P_t}$$

Alternatively, we could have got above expression directly from $k = \frac{1}{t} \ln \frac{X_{\infty} - X_0}{X_{\infty} - X_t}$ by

putting $X_{\infty} = 2P_0$, $X_0 = P_0$ and $X_t = P_t$ where X represents total pressure.

$$k = \frac{1}{t} \ln \frac{2P_0 - P_0}{2P_0 - P_t} \quad \text{or} \quad k = \frac{1}{t} \ln \frac{P_0}{2P_0 - P_t}$$

CASE – III:



Time	0	t	∞
Partial pressure of A + B + C	—	P_t	P_{∞}

Calculate the expression of rate constant.

STRATEGY:

Let the initial pressure of A be P_0 and the pressure of A reacted till time t are x .

	A(g)	\longrightarrow	B(g)	+	C(g)	
At time = 0	P_0		0		0	
At time = t	$P_0 - x$		x		x	
At time = ∞	0		P_0		P_0	$P_{\infty} = 2P_0$

CHEMICAL KINETICS

∞ is the time when the reaction is complete.

At time = t, the total pressure will be

$$(P_0 - x) + x + x = P_t$$

$$P_0 + x = P_t$$

$$x = P_t - P_0$$

At time = ∞ , the total pressure will be

$$P_\infty = 0 + P_0 + P_0 = 2P_0; 2P_0 = P_\infty ; P_0 = \frac{P_\infty}{2}$$

$$x = P_t - P_0 = P_t - \frac{P_\infty}{2}$$

$$(P_0 - x) = \frac{P_\infty}{2} - \left(P_t - \frac{P_\infty}{2} \right) = P_\infty - P_t$$

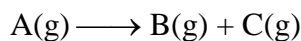
$$k = \frac{1}{t} \ln \frac{P_\infty}{2(P_\infty - P_t)}$$

Alternatively, we could have got above expression directly from $k = \frac{1}{t} \ln \frac{X_\infty - X_0}{X_\infty - X_t}$ by

putting $X_\infty = P_\infty$, $X_0 = P_0 = \frac{P_\infty}{2}$ and $X_t = P_t$ where X represents total pressure.

$$k = \frac{1}{t} \ln \frac{P_\infty - \frac{P_\infty}{2}}{P_\infty - P_t} \quad \text{or} \quad k = \frac{1}{t} \ln \frac{P_\infty}{2(P_\infty - P_t)}$$

CASE – IV:

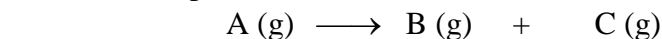


Time	0	T	∞
Total pressure of B + C	–	P_t	P_∞

Calculate the expression of rate constant.

STRATEGY:

Let the initial pressure of A be P_0 and the amount of pressure reacted till time t be x.



$$\text{At time} = 0 \quad P_0 \quad 0 \quad 0$$

$$\text{At time} = t \quad P_0 - x \quad x \quad x$$

$$\text{At time} = \infty \quad 0 \quad P_0 \quad P_0$$

At time infinity, the total pressure of B and C will be

$$P_0 + P_0 = 2P_0 = P_\infty$$

$$P_0 = \frac{P_\infty}{2}$$

At time t, the total pressure of B and C will be $x + x = 2x = P_t$

$$x = \frac{P_t}{2}$$

Putting the values of P_0 and x in the expression $k = \frac{1}{t} \ln \frac{P_0}{P_0 - x}$

CHEMICAL KINETICS

$$k = \frac{1}{t} \ln \frac{P_{\infty} / 2}{P_{\infty} / 2 - P_t / 2}$$

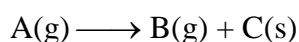
$$k = \frac{1}{t} \ln \frac{P_{\infty}}{P_{\infty} - P_t}$$

Alternatively, we could have got above expression directly from $k = \frac{1}{t} \ln \frac{X_{\infty} - X_0}{X_{\infty} - X_t}$ by

putting $X_{\infty} = P_{\infty}$, $X_0 = 0$ and $X_t = 2x = P_t$ where X represents combined pressure of only B and C.

$$k = \frac{1}{t} \ln \frac{P_{\infty} - 0}{P_{\infty} - P_t} \quad \text{or} \quad k = \frac{1}{t} \ln \frac{P_{\infty}}{P_{\infty} - P_t}$$

CASE – V:

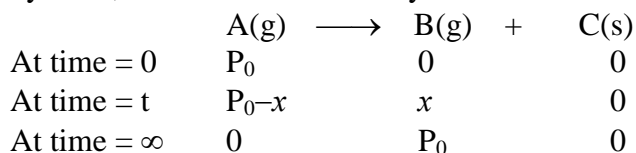


Time	0	t	∞
Total pressure of B	–	P_t	P_{∞}

Calculate the expression of rate constant.

STRATEGY:

Let the initial pressure of A was P_0 and the decrease in pressure due to reaction till time t was x . Solids do not exert any appreciable pressure with respect to gas. So, pressure exerted by solid, C would be zero at any time.



At time t , pressure of B is x .

$$\therefore x = P_t$$

At time ∞ , the pressure of B is P_0 .

$$\therefore P_0 = P_{\infty}$$

$$\therefore k = \frac{1}{t} \ln \frac{P_{\infty}}{P_{\infty} - P_t}$$

Alternatively, we could have got above expression directly from $k = \frac{1}{t} \ln \frac{X_{\infty} - X_0}{X_{\infty} - X_t}$ by

putting $X_{\infty} = P_{\infty}$, $X_0 = 0$ and $X_t = P_t$ where X represents partial pressure of only B.

$$k = \frac{1}{t} \ln \frac{P_{\infty} - 0}{P_{\infty} - P_t} \quad \text{or} \quad k = \frac{1}{t} \ln \frac{P_{\infty}}{P_{\infty} - P_t}$$

Illustration 2.

The gaseous reaction, $A(g) \longrightarrow 2B(g) + C(g)$ is observed to be the first order. On starting with pure A, it is found that at the end of 10 min, the total pressure of the system is 176 mm of Hg and after a long time, it is 270 mm of Hg. Calculate (a) the initial pressure of A (b) the partial pressure of A after 10 min, and (c) the rate constant of the reaction.

CHEMICAL KINETICS

Solution:

(a) Let the initial pressure of A be P_0 mm of Hg and the pressure of A decreased in 10 minute be a .

	$A(g)$	\longrightarrow	$2B(g)$	$+ C(g)$
Initially	P_0		0	0
At time 10 min.	$P_0 - a$		$2a$	a
At ∞ time	0		$2P_0$	P_0

After long time interval, $P_\infty = 0 + 2P_0 + P_0 = 3P_0$

$$\therefore P_0 = \frac{P_\infty}{3} = \frac{270}{3} = \mathbf{90 \text{ mm of Hg.}}$$

(b) After 10 minutes, $P_t = P_0 - a + 2a + a = P_0 + 2a$

$$176 = 90 + 2a$$

$$\therefore a = 43 \text{ mm of Hg.}$$

\therefore Partial pressure of A after 10 min = $P_0 - a = 90 - 43 = \mathbf{47 \text{ mm of Hg.}}$

(c) For a first-order reaction, the rate constant expression would be

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - a}$$

$$k = \frac{2.303}{10} \log \frac{90}{47} = \mathbf{0.0649 \text{ min}^{-1}.}$$

CASE – VI:

Let the reaction be unknown, there is only one reactant and it is a gas. Some or all products are gases.

Time	0	t	∞
Total pressure	P_0	P_t	P_∞

Calculate the expression of rate constant.

STRATEGY:

Let the change in the number of mole of gases in the reaction be Δn (number of mole of gaseous product – number of mole of gaseous reactant) based on the stoichiometric coefficients.

Let the initial pressure of the reactant be P_0 and x be the pressure reacted till time t .

$$k = \frac{1}{t} \ln \frac{P_0}{P_0 - x}$$

The stoichiometric coefficient of A (the reactant) in the reaction be a and let that of each of the gaseous products be b, c, d, \dots

At time t , the total pressure would be,

$$P_0 - x + \frac{b}{a}x + \frac{c}{a}x + \dots = P_t$$

$$P_0 + x \left[-1 + \frac{b}{a} + \frac{c}{a} + \dots \right] = P_t$$

$$P_0 + \frac{\Delta n x}{a} = P_t \quad \dots\dots\dots(\text{vi-a})$$

CHEMICAL KINETICS

At time = ∞ , the total pressure would be

$$\begin{aligned}\frac{b}{a}P_0 + \frac{c}{a}P_0 + \dots &= P_\infty \\ P_0\left(\frac{b}{a} + \frac{c}{a} + \dots\right) &= P_\infty \\ \left(\frac{\Delta n}{a} + 1\right)P_0 &= P_\infty \\ \frac{\Delta n}{a} &= \left(\frac{P_\infty}{P_0} - 1\right) = \frac{P_\infty - P_0}{P_0}\end{aligned}$$

\therefore From equation (vi-a), we get

$$x = \frac{P_t - P_0}{\Delta n/a} = \frac{P_t - P_0}{P_\infty - P_0} \times P_0$$

$$\therefore (P_0 - x) = P_0 - \frac{P_t - P_0}{P_\infty - P_0} \times P_0$$

$$= P_0 \left(1 - \frac{P_t - P_0}{P_\infty - P_0}\right)$$

$$= P_0 \left(\frac{P_\infty - P_t}{P_\infty - P_0}\right)$$

$$\therefore k = \frac{1}{t} \ln \frac{P_0}{P_0 \left(\frac{P_\infty - P_t}{P_\infty - P_0}\right)}$$

$$k = \frac{1}{t} \ln \frac{P_\infty - P_0}{P_\infty - P_t}$$

Alternatively, we could have got above expression directly from $k = \frac{1}{t} \ln \frac{X_\infty - X_0}{X_\infty - X_t}$ by

putting $X_\infty = P_\infty$, $X_0 = P_0$ and $X_t = P_t$ where X represents total pressure in the vessel.

$$k = \frac{1}{t} \ln \frac{P_\infty - P_0}{P_\infty - P_t}$$

CASE – VII:

Now, let us assume a first-order reaction, $A \longrightarrow B + C$, such that A, B and C are in solution. At time zero, a small amount of the solution is taken, cooled (to stop the reaction from proceeding) and titrated with a suitable reagent. Let us assume that the reagent reacts only with A and not with B and C. The same process is repeated at time t.

Time	0	t
Volume of reagent	V_0	V_t

Calculate the expression of rate constant.

CHEMICAL KINETICS

STRATEGY:

The volume of the reagent would be directly proportional to the concentration of A since reagent reacts with A only.

$$V_0 \propto A_0$$

$$V_t \propto A_t$$

$$\therefore k = \frac{1}{t} \ln \frac{V_0}{V_t}$$

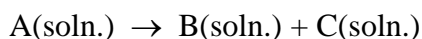
CASE – VIII:

For the same first-order reaction, $A \longrightarrow B + C$, occurring in solution phase, now let us assume that the reagent reacts with all the species A, B and C. The 'n' factor of A, B and C with the reagent is α , β and γ respectively and that of the reagent with A, B and C is a, b and c.

Time	0	t
Volume of reagent	V_0	V_t

Calculate the expression of rate constant.

STRATEGY:

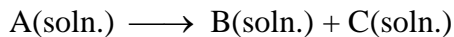


At time = 0 V_0 0 0

At time t, let us assume x mole of A reacts to give x mole of B and x mole of C. The equivalents of A reacted with respect to the reagent is αx and that B and C produced is βx and γx . If y is that volume of the reagent, which decreases for A at time t due to the reaction of A, then the equivalents of the reagent in y volume units of the reagent would be αx . Therefore the mole of the reagent in y volume units of the reagent would be $\alpha x / a$. This

gives the volume units of the reagent containing βx and γx equivalents as $\frac{a\beta}{b\alpha} y$ and $\frac{a\gamma}{c\alpha} y$.

So it follows that,



At time = 0 V_0 0 0

At time = t $V_0 - y$ $\frac{a\beta}{b\alpha} y$ $\frac{a\gamma}{c\alpha} y$

At time t, the total volume of the reagent used up is

$$V_0 - y + \frac{a\beta}{b\alpha} y + \frac{a\gamma}{c\alpha} y = V_t$$

$$y = \frac{V_t - V_0}{\left(\frac{a\beta}{b\alpha} + \frac{a\gamma}{c\alpha} - 1 \right)} = \frac{V_t - V_0}{\frac{a\beta c + a\gamma b - bc\alpha}{bc\alpha}}$$

$$y = \frac{bc\alpha (V_t - V_0)}{a\beta c + a\gamma b - bc\alpha}$$

$$\therefore (V_0 - y) = V_0 - \left(\frac{bc\alpha (V_t - V_0)}{a\beta c + a\gamma b - bc\alpha} \right)$$

CHEMICAL KINETICS

$$\begin{aligned}
 &= \frac{(a\beta c + a\gamma b - bc\alpha) V_0 - bc\alpha (V_t - V_0)}{a\beta c + a\gamma b - bc\alpha} \\
 &= \frac{(a\beta c + a\gamma b) V_0 - (bc\alpha) V_t}{a\beta c + a\gamma b - bc\alpha} \\
 k &= \frac{1}{t} \ln \frac{V_0}{V_0 - y} = \frac{1}{t} \ln \frac{V_0}{\frac{(a\beta c + a\gamma b) V_0 - (bc\alpha) V_t}{a\beta c + a\gamma b - bc\alpha}} \\
 \therefore k &= \frac{1}{t} \ln \frac{(a\beta c + a\gamma b - bc\alpha) V_0}{(a\beta c + a\gamma b) V_0 - (bc\alpha) V_t}
 \end{aligned}$$

If $a = b = c$ ('n' factor of reagent is same for A, B and C)

and $\alpha = \beta = \gamma$ ('n' factor of A, B and C are same for the reagent).

Then $k = \frac{1}{t} \ln \frac{V_0}{2V_0 - V_t}$ which is similar to the expression derived in case II.

CASE -IX:

$A(\text{soln.}) \longrightarrow B(\text{soln.}) + C(\text{soln.})$

Reagent reacts with all species A, B and C.

Time	0	t	∞
Volume of reagent	V_0	V_t	V_∞

The n factor of A, B and C with the reagent and that of the reagent with A, B and C are not known. Calculate the expression of rate constant.

STRATEGY:

Since 'n' factors are not mentioned, let us consider them to be same as in case VIII.

$A(\text{soln.}) \rightarrow B(\text{soln.}) + C(\text{soln.})$

At time = 0	V_0	0	0
At time = t	$V_0 - y$	$\frac{a\beta}{b\alpha} y$	$\frac{a\gamma}{c\alpha} y$
At time = ∞	0	$\frac{a\beta}{b\alpha} V_0$	$\frac{a\gamma}{c\alpha} V_0$

We know that $k = \frac{1}{t} \ln \frac{V_0}{V_0 - y}$

At time t, the total volume of the reagent used is,

$$V_0 - y + \frac{a\beta}{b\alpha} y + \frac{a\gamma}{c\alpha} y = V_t$$

$$y = \frac{V_t - V_0}{\left(\frac{a\beta}{b\alpha} + \frac{a\gamma}{c\alpha} - 1 \right)} \quad \dots\dots(\text{ix-a})$$

At time = ∞ , the total volume of the reagent used up is,

$$\frac{a\beta}{b\alpha} V_0 + \frac{a\gamma}{c\alpha} V_0 = V_\infty$$

CHEMICAL KINETICS

$$\frac{a\beta}{b\alpha} + \frac{a\gamma}{c\alpha} = \frac{V_{\infty}}{V_0}$$

Substituting this in equation (ix-a), we get

$$y = \frac{V_t - V_0}{\left(\frac{V_{\infty}}{V_0} - 1\right)} = \frac{V_t - V_0}{\left(\frac{V_{\infty} - V_0}{V_0}\right)} = V_0 \left(\frac{V_t - V_0}{V_{\infty} - V_0} \right)$$

$$(V_0 - y) = V_0 - V_0 \left(\frac{V_t - V_0}{V_{\infty} - V_0} \right) = V_0 \left[1 - \frac{(V_t - V_0)}{(V_{\infty} - V_0)} \right] = V_0 \left[\frac{V_{\infty} - V_t}{V_{\infty} - V_0} \right]$$

$$k = \frac{1}{t} \ln \frac{V_0}{V_0 \left(\frac{V_{\infty} - V_t}{V_{\infty} - V_0} \right)} = \frac{1}{t} \ln \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

Alternatively, let the initial moles of A be 'a' and the moles of A reacted in time be x. Let the normality of the reagent be N. Then, at time zero,

Initial equivalents of A = Equivalents of reagent

$$a \alpha = NV_0 \quad \dots \quad (\text{ix-b})$$

at time t,

Equivalents of A + Equivalents of B + Equivalents of C = Equivalents of reagent.

$$\begin{aligned} \therefore (a - x) \alpha + x\beta + x\gamma &= NV_t \\ a\alpha - x\alpha + x\beta + x\gamma &= NV_t \\ x(\beta + \gamma - \alpha) &= NV_t - NV_0 \\ x &= \frac{N(V_t - V_0)}{(\beta + \gamma - \alpha)} \quad \dots \quad (\text{ix-c}) \end{aligned}$$

At ∞ time,

Equivalents of B + Equivalents of C = Equivalents of reagent.

$$a\beta + a\gamma = NV_{\infty} \quad \dots \quad (\text{ix-d})$$

Subtracting equation (ix-b) from (ix-d), we get

$$a(\beta + \gamma - \alpha) = N(V_{\infty} - V_0)$$

$$\therefore a = \frac{N(V_{\infty} - V_0)}{(\beta + \gamma - \alpha)} \quad \dots \quad (\text{ix-e})$$

$$\therefore a - x = \frac{N(V_{\infty} - V_t)}{(\beta + \gamma - \alpha)} \quad \dots \quad (\text{ix-f})$$

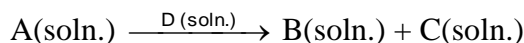
Dividing equation (ix-e) by (ix-f) gives

$$\frac{a}{a - x} = \frac{N(V_{\infty} - V_0) \times (\beta + \gamma - \alpha)}{(\beta + \gamma - \alpha) \times N(V_{\infty} - V_t)} = \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

$$\therefore k = \frac{1}{t} \ln \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

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CASE –X:



D is a catalyst present in the solution whose n-factor is not known. Catalyst has a constant concentration throughout the reaction.

Time	0	t	∞
Volume of reagent	V_0	V_t	V_∞

Calculate the expression of rate constant.

STRATEGY:

Let V_A be the volume of the reagent used for A at time zero and y be the volume of the reagent decreased for A due to the reaction of A. Let V_D be the volume of the reagent used for D.

	A (soln.)	$\xrightarrow{D(\text{soln.})}$	B (soln.)	+	C (soln.)
At time = 0	V_A	V_D	0		0
At time = t	$V_A - y$	V_D	$\frac{a\beta}{b\alpha} y$		$\frac{a\gamma}{c\alpha} y$
At time = ∞	0	V_D	$\frac{a\beta}{b\alpha} V_A$		$\frac{a\gamma}{c\alpha} V_A$

$$V_0 = V_A + V_D \quad \dots\dots(x-a)$$

$$V_t = V_A - y + \frac{a\beta}{b\alpha} y + \frac{a\gamma}{c\alpha} y + V_D \quad \dots\dots (x-b)$$

$$V_\infty = V_D + \frac{a\beta}{b\alpha} V_A + \frac{a\gamma}{c\alpha} V_A \quad \dots\dots(x-c)$$

Subtracting equation (x-c) from equation (x-a)

$$\frac{V_0 - V_\infty}{\left(1 - \frac{a\beta}{b\alpha} - \frac{a\gamma}{c\alpha}\right)} = V_A$$

Subtracting equation (x-c) from equation (x-b)

$$(V_t - V_\infty) = V_A \left(1 - \frac{a\beta}{b\alpha} - \frac{a\gamma}{c\alpha}\right) - y \left(1 - \frac{a\beta}{b\alpha} - \frac{a\gamma}{c\alpha}\right)$$

$$(V_t - V_\infty) = (V_A - y) \left(1 - \frac{a\beta}{b\alpha} - \frac{a\gamma}{c\alpha}\right)$$

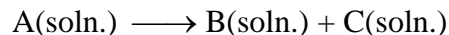
$$(V_A - y) = \frac{V_t - V_\infty}{\left(1 - \frac{a\beta}{b\alpha} - \frac{a\gamma}{c\alpha}\right)}$$

$$\therefore k = \frac{1}{t} \ln \frac{V_0 - V_\infty}{V_t - V_\infty}$$

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CASE XI:

Now, let us assume that A, B and C are optically active compounds, which rotate the plane polarized light in the clockwise or anticlockwise direction.



Time	0	t	∞
Total rotation in degrees	r_0	r_t	r_∞

Calculate the expression of rate constant.

STRATEGY:

Let the rotations of A, B and C per unit concentration be r_a , r_b and r_c (including +ve or -ve).
Let the initial concentration of A be a and the decrease in concentration till time t be x .

	A (soln.) \longrightarrow B (soln.) + C (soln.)		
At time = 0	a	0	0
At time = t	$a - x$	x	x
At time = ∞	0	a	a

Such that $k = \frac{1}{t} \ln \frac{a}{a-x}$

Optical rotation at time = 0, $r_a a = r_0$ (xi-a)

Optical rotation at time = t , $r_a (a - x) + x r_b + x r_c = r_t$

$$r_a a + x (r_b + r_c - r_a) = r_t$$

$$r_0 + x (r_b + r_c - r_a) = r_t \quad \text{.....(xi-b)}$$

Optical rotation at time = ∞ , $a (r_b + r_c) = r_\infty$ (xi-c)

From equation (xi-b) we get $x = \frac{r_t - r_0}{(r_b + r_c - r_a)}$ (xi-d)

Since constant involved in x is $\frac{1}{(r_b + r_c - r_a)}$, the same constant must appear in the expression of a . Thus, subtracting equation (xi-a) from equation (xi-d), we get

$$a = \frac{r_\infty - r_0}{(r_b + r_c - r_a)} \quad \text{.....(xi-e)}$$

Subtracting equation (xi-d) from equation (xi-e)

$$a - x = \frac{r_\infty - r_t}{(r_b + r_c - r_a)} \quad \therefore k = \frac{1}{t} \ln \frac{r_\infty - r_0}{r_\infty - r_t}$$

Important Note:

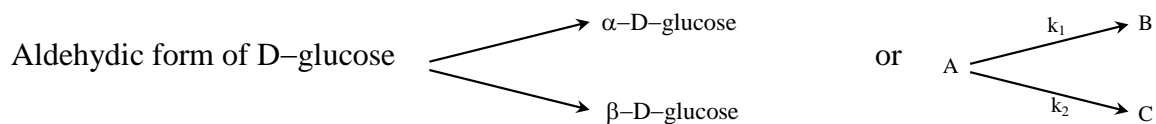
For any first order reaction, the general integrated rate law can be written as

$$\therefore k = \frac{1}{t} \ln \frac{X_\infty - X_0}{X_\infty - X_t}$$

Here X_0 , X_t and X_∞ represent value of any property, that is regular function of time, at the beginning, after time t and after long time i.e. after completion of the reaction. This property must not include any component that is not a regular function of time (like pressure due to vapours of liquid because if the value reaches equal to vapour pressure, it will not increase further and will then become constant).

7. Parallel (or Simultaneous) Reactions

Reactions leading to the formation of two products from same set of reactant(s) by different paths are called parallel or simultaneous reactions. For example, α -D-glucose and β -D-glucose are formed in solution from the aldehydic (acyclic) form of D-glucose following different paths as:



The various differential rate laws are

$$-\frac{d[A]}{dt} = k_1 [A] + k_2 [A] = (k_1 + k_2) [A] \quad \text{.....(7a)}$$

$$\frac{d[B]}{dt} = k_1 [A] \quad \text{.....(7b)}$$

$$\frac{d[C]}{dt} = k_2 [A] \quad \text{.....(7c)}$$

Now, let us imagine that at $t = 0$, only A was present. After a very small time, say 2 second, x mole/l of B and y mole/l of C was formed.

Then $\frac{d[B]}{dt} = \frac{x}{2}$ and $\frac{d[C]}{dt} = \frac{y}{2}$

$$\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{x}{y}$$

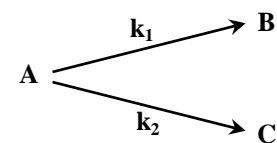
From equation (7b) and (7c),

$$\frac{\frac{d[B]}{dt}}{\frac{d[C]}{dt}} = \frac{k_1}{k_2}$$
$$\therefore \frac{x}{y} = \frac{k_1}{k_2}$$

This means that at any given instant of time, the ratio of amount of B formed to that of C formed till that instant is a constant.

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Illustration 3



$$k_1 = a \text{ hr}^{-1} \quad ; \quad k_1 : k_2 = 1 : 10$$

Calculate $\frac{[C]}{[A]}$ after one hour from the start of the reaction, assuming only A was present in the beginning.

Solution:

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

Separating the variables give

$$\frac{-d[A]}{[A]} = (k_1 + k_2) dt \quad \dots\dots(7d)$$

Integrating equation (7d) within limits,

$$-\int_{A_0}^{A_t} \frac{d[A]}{[A]} = (k_1 + k_2) \int_0^t dt$$

$$\ln \frac{[A_0]}{[A_t]} = (k_1 + k_2) t$$

$$\frac{[B]}{[C]} = \frac{1}{10}, \quad \text{since } k_1 = a \text{ hr}^{-1} \text{ and } k_2 = 10 a \text{ hr}^{-1}$$

We can write, $[A_0] = [A_t] + [B] + [C]$

$$\ln \frac{[A_t] + [B] + [C]}{[A_t]} = (k_1 + k_2) t$$

$$\ln \left(1 + \frac{\frac{[C]}{10} + [C]}{[A_t]} \right) = 11 a$$

$$\left[\because \frac{[B]}{[C]} = \frac{1}{10}; k_1 = a \text{ hr}^{-1}, k_2 = 10a \text{ hr}^{-1}, t = 1 \text{ hr} \right]$$

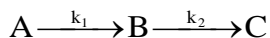
$$\ln \left(1 + \frac{11 [C]}{10 [A_t]} \right) = 11 a$$

The equation can be written as

$$\frac{[C]}{[A]_t} = \frac{10}{11} (e^{11a} - 1)$$

8. Sequential or Serial or Consecutive Reaction

Reactions in which a reactant gives product, which further goes to give another product, are called sequential or consecutive reaction.



The differential rate equations are

$$\text{Rate of disappearance of A, } \frac{-d[A]}{dt} = k_1 [A] \quad \dots(8a)$$

$$\text{Rate of change of B, } \frac{d[B]}{dt} = k_1 [A] - k_2 [B] \quad \dots(8b)$$

$$\text{Rate of formation of C, } \frac{d[C]}{dt} = k_2 [B] \quad \dots(8c)$$

Concentration of A:

Integrating equation (8a) within the limits we get,

$$[A]_t = [A]_0 e^{-k_1 t} \quad \dots(8d)$$

Concentration of B:

In order to get the value of B at any instant of time, we need to integrate equation (8b). Since this is a differential equation, we integrate it in the following manner.

First bringing $k_2[B]$ to the left side of the equation

$$\frac{d[B]}{dt} + k_2 [B] = k_1 [A] \quad \dots(8e)$$

From equation (8e), we get

$$\frac{d[B]}{dt} + k_2 [B] = k_1 [A]_0 e^{-k_1 t}$$

Integration of this equation is not possible as we are unable to separate the two variables, $[B]$ and t . Thus, the equation is to be multiplied on both sides by an integrating factor $e^{k_2 t}$.

$$\begin{aligned} e^{k_2 t} \left(\frac{d[B]}{dt} + k_2 [B] \right) &= k_1 [A]_0 e^{(k_2 - k_1)t} \\ e^{k_2 t} \frac{d[B]}{dt} + k_2 [B] e^{k_2 t} &= k_1 [A]_0 e^{(k_2 - k_1)t} \quad \dots(8f) \end{aligned}$$

Left hand side of the equation (8f) is equal to $\frac{d}{dt} ([B]e^{k_2 t})$ (a differential of $[B]e^{k_2 t}$).

$$\begin{aligned} \frac{d}{dt} ([B]e^{k_2 t}) &= k_1 [A]_0 e^{(k_2 - k_1)t} \\ d([B]e^{k_2 t}) &= k_1 [A]_0 e^{(k_2 - k_1)t} dt \quad \dots(8g) \end{aligned}$$

Integrating equation (8g) within the limits, 0 and t ,

$$\begin{aligned} \int_0^t d([B]e^{k_2 t}) &= k_1 [A]_0 \int_0^t e^{(k_2 - k_1)t} dt \\ [B]e^{k_2 t} &= k_1 [A]_0 \left[\frac{e^{(k_2 - k_1)t}}{k_2 - k_1} \right]_0^t = \frac{k_1}{(k_2 - k_1)} [A]_0 [e^{(k_2 - k_1)t} - 1] \end{aligned}$$

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$$[B] = \frac{k_1}{(k_2 - k_1)} [A]_0 e^{-k_2 t} \left[e^{(k_2 - k_1)t} - 1 \right]$$

$$[B] = \frac{k_1}{(k_2 - k_1)} [A]_0 \left[e^{-k_1 t} - e^{-k_2 t} \right] \quad \dots(8h)$$

In general, the concentration of A decreases exponentially, the concentration of B initially increases up to a maximum and thereafter decreases, and the concentration of C increases steadily with time.

Time when [B] becomes maximum:

$$\frac{d[B]}{dt} = k_1 [A] - k_2 [B] = 0$$

$$k_1 [A] = k_2 [B]$$

Substituting equation (8d) and equation (8h), we get

$$k_1 [A]_0 e^{-k_1 t} = \frac{k_2 k_1}{(k_2 - k_1)} [A]_0 \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

Rearranging further, we get

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

$$1 - \frac{k_1}{k_2} = 1 - e^{(k_1 - k_2)t}$$

$$t_{\max} = \frac{1}{(k_1 - k_2)} \ln \frac{k_1}{k_2} \quad \dots(8i)$$

Maximum concentration of B:

$$[B] = \frac{k_1}{(k_2 - k_1)} [A]_0 \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

$$[B] = \frac{k_1}{(k_2 - k_1)} [A]_0 \left[e^{\frac{-k_1}{(k_1 - k_2)} \ln \frac{k_1}{k_2}} - e^{\frac{-k_2}{(k_1 - k_2)} \ln \frac{k_1}{k_2}} \right]$$

$$[B] = \frac{k_1}{(k_2 - k_1)} [A]_0 \left[e^{\ln \left(\frac{k_2}{k_1} \right)^{\frac{k_1}{(k_1 - k_2)}}} - e^{\ln \left(\frac{k_2}{k_1} \right)^{\frac{k_2}{(k_1 - k_2)}}} \right]$$

$$[B]_{\max} = \frac{k_1}{(k_2 - k_1)} [A]_0 \left[\left(\frac{k_2}{k_1} \right)^{\frac{k_1}{(k_1 - k_2)}} - \left(\frac{k_2}{k_1} \right)^{\frac{k_2}{(k_1 - k_2)}} \right] \quad \dots(8j)$$

Concentration of C:

In order to get the concentration of [C], we substitute [B] from equation (8h) to (8c) and then integrate within the limits.

$$\frac{d[C]}{dt} = k_2 [B] = \frac{k_2 k_1}{(k_2 - k_1)} [A]_0 \left[e^{-k_1 t} - e^{-k_2 t} \right]$$

$$d[C] = \frac{k_2 k_1}{(k_2 - k_1)} [A]_0 [e^{-k_1 t} - e^{-k_2 t}] dt$$

Upon integrating within the limits, 0 to t,

$$\int_0^t d[C] = \frac{k_2 k_1}{(k_2 - k_1)} [A]_0 \int_0^t [e^{-k_1 t} - e^{-k_2 t}] dt$$

$$[C] = \frac{k_2 k_1}{(k_2 - k_1)} [A]_0 \left[\frac{e^{-k_1 t}}{-k_1} - \frac{e^{-k_2 t}}{-k_2} \right]_0^t$$

$$[C] = \frac{k_2 k_1}{(k_2 - k_1)} [A]_0 \left[\left(\frac{e^{-k_1 t} - 1}{-k_1} \right) - \left(\frac{e^{-k_2 t} - 1}{-k_2} \right) \right]$$

$$[C] = \frac{k_2 k_1}{(k_2 - k_1)} [A]_0 \left[\left(\frac{1 - e^{-k_1 t}}{k_1} \right) - \left(\frac{1 - e^{-k_2 t}}{k_2} \right) \right]$$

$$[C] = \frac{[A]_0}{(k_2 - k_1)} [k_2(1 - e^{-k_1 t}) - k_1(1 - e^{-k_2 t})] \quad \dots\dots(8k)$$

9. Temperature Dependency of Reaction Rate

It was observed that for most of the reactions (except nuclear reactions), rate increases with the increase of temperature. For most of the reactions, it was found that the rate of the reaction increases approximately two to three fold with the increase of 10°C temperature. This increase in rate was defined by temperature coefficient.

Temperature coefficient is the ratio of rate constants of a chemical reaction at two temperatures differing by 10°C. The value of temperature coefficient for most of the reactions lies between two and three.

$$\therefore \text{Temperature coefficient} = \frac{k_{T+10}}{k_T} \approx 2 \text{ to } 3.$$

The actual dependence of rate constant on temperature is represented by the Arrhenius equation,

$$k = A e^{-E_a / RT} \quad \dots\dots (9a)$$

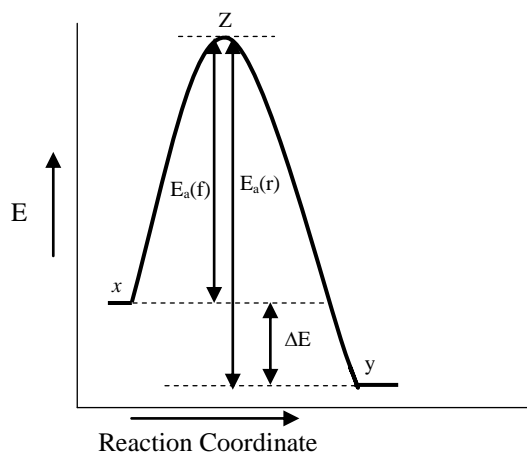
According to this equation, the rate constant increases exponentially with temperature. The constant A is frequently referred to as the Arrhenius constant, pre-exponential factor or frequency factor.

The constant E_a in equation (9a) is known as the energy of activation. Its significance may be explained as follows:

It has been stated before that the products are formed only when the reactant molecules come close and collide together at one and the same time. During the collision the molecular rearrangement takes place which leads to the formation of products. The molecular rearrangement usually involves breaking of some bonds and making others. The molecular rearrangement can take place only when the colliding molecules have energy equal to or greater than the minimum energy (threshold energy) required for the said rearrangement. If the energy of colliding molecules is less than this minimum energy it is obvious that molecular rearrangement will not take place and thus the molecules will remain unchanged after the collision, i.e., no product will be formed. Thus all collisions will not lead to the formation of products but only

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those collisions, which involve sufficient energy, are expected to form products. The difference between the minimum energy required to bring about molecular rearrangement and the average energy of reactant molecules is identified with the constant E_a and is known as energy of activation.



Above Figure illustrates the activation energies of forward and backward reactions of a reversible reaction. State X represents the average energy of the reactants, state Y represents that of products and state Z represents the minimum energy which the reactants or products must possess in order to react. Molecules in state Z are said to be activated or to be in an activated state. From figure 9(a), it is obvious that

$$E_{a(f)} = E_z - E_x$$

$$E_{a(r)} = E_z - E_y$$

$$\text{Thus, } E_{a(f)} - E_{a(r)} = (E_z - E_x) - (E_z - E_y) = E_y - E_x = \Delta H$$

When temperature is changed, the average energy of reactants also changes. This changes the activation energy. But for the small range of temperatures, the activation energy can be assumed to be constant.

Constant A is defined as the number of effective collisions occurring per unit time for unit concentration (or per unit concentration per unit time etc.). When two molecules collide, the chances of formation of products also depend on orientation of the colliding molecules. This implies that no random collision of the reactant molecules can lead to the formation of products.

9.1 Interpretation of Arrhenius Equation

The factor $e^{-E_a/RT}$ refers to the fraction of collisions (also effective collisions) that have the sufficient activation energy to collide and form products. A is the number of effective collision per unit time per unit concentration. Therefore the product of A and $e^{-E_a/RT}$ is the number of collisions that actually lead to the formation of products.

9.2 Determination of Activation Energy

Method I:

Taking natural logarithm of both the sides of equation (9a),

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

Converting natural log to common log,

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$$\log k = \log A - \frac{E_a}{2.303 RT} \quad \dots(9.2a)$$

The equation (9.2a) can be rearranged as

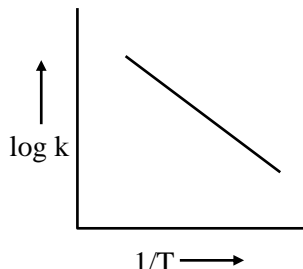
$$\log k = - \frac{E_a}{2.303 R} \left[\frac{1}{T} \right] + \log A$$

This is nothing but equation of straight line,

$y = mx + c$. If $\log k$ is plotted against $\frac{1}{T}$, a straight line is

obtained, the slope of which is given by

$$- \left(\frac{E_a}{2.303 R} \right).$$



Thus, if the slope is known, the activation energy, E_a can be calculated. The intercept of the line will give the value of $\log A$.

Method II:

Equation (9.2a) for two different temperatures (with small difference), T_1 and T_2 K is written as

$$\log k_1 = \log A - \frac{E_a}{2.303 RT_1} \quad \dots(9.2b)$$

$$\log k_2 = \log A - \frac{E_a}{2.303 RT_2} \quad \dots(9.2c)$$

Here it is assumed that with the change of temperature from T_1 to T_2 K, A and E_a remain constant. Subtracting equation (9.2b) from (9.2c) gives

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

$$\text{or } \log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

where k_1 and k_2 are rate constants at temperatures T_1 and T_2 K, respectively. Knowing these values, E_a can be calculated. Care must be taken to insert the value of R in a unit in which E_a (activation Energy) is desired.

9.3 Main Characteristics of Arrhenius Equation

- (i) Larger the activation energy of a reaction, smaller is the value of rate constant.
- (ii) Larger the activation energy of a reaction, greater is the influence of change in temperature on rate constant.
- (iii) For lower temperature range, increase in temperature causes more change in the value of k than the same increase in temperature for high temperature range.

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Illustration 4

The time required for 10% completion of a first-order reaction at 298 K is equal to the time required for its 25% completion at 308 K. If the pre-exponential factor for the reaction is $3.56 \times 10^9 \text{ sec}^{-1}$, calculate its rate constant at 318 K and also the energy of activation.

Solution:

For a first-order reaction, the rate constant expression is

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

$$\text{At } 298 \text{ K, } t_{298} = \frac{2.303}{k_{298}} \log \frac{[A]_0}{0.9[A]_0}$$

$$\text{At } 308 \text{ K, } t_{308} = \frac{2.303}{k_{308}} \log \frac{[A]_0}{0.75[A]_0}$$

The time taken at 298 K (for completion of 10% of reaction) and at 308 K (for completion of 25% of reaction) are same.

$$\begin{aligned} \therefore \frac{2.303}{k_{298}} \log \frac{[A]_0}{0.9[A]_0} &= \frac{2.303}{k_{308}} \log \frac{[A]_0}{0.75[A]_0} \\ \frac{k_{308}}{k_{298}} &= \frac{0.1249}{0.0457} = 2.73 \end{aligned}$$

Activation energy of the reaction can be calculated using

$$\begin{aligned} \log \frac{k_{308}}{k_{298}} &= \frac{E_a}{2.303 R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \\ \log 2.73 &= \frac{E_a}{2.303 \times 8.314} \left[\frac{308 - 298}{298 \times 308} \right] \\ \therefore E_a &= 76651 \text{ J mol}^{-1} = \mathbf{76.65 \text{ kJ mol}^{-1}} \end{aligned}$$

Rate constant at 318 K can be calculated using

$$\begin{aligned} k_{318} &= A e^{-E_a/RT} = 3.56 \times 10^9 e^{-\left(\frac{76.65}{8.314 \times 10^{-3} \times 318}\right)} \\ k_{318} &= \mathbf{9.13 \times 10^{-4} \text{ s}^{-1}} \end{aligned}$$

10. Catalysts

Sometimes, the rate of a chemical reaction is much higher in the presence of a substance called the catalyst. A catalyst increases the rate of reaction either by increasing A or by decreasing E_a or by doing both. Though catalyst is involved in the reaction, it does not appear in the overall reaction. Thus, its concentration remains constant throughout the chemical reaction. Broadly, two types of catalysts are known, namely homogenous or reactant catalyst and heterogeneous or surface catalyst.

A homogenous or reactant catalyst is basically a reactant. The only difference with an ordinary reactant is that it gets regenerated at later stage when products are formed. Therefore, it does not figure in the reaction. But its concentration will have an impact on the rate of reaction and thus it appears in the rate law.

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On the other hand, a heterogeneous or a surface catalyst generally adsorbs one or more reactants on the surface, which facilitates the collision between reactants. Such catalysts do not appear in the rate law.

Examples of homogenous catalysts are acid catalyzed hydrolysis of an ester and saponification of an ester etc. Examples of heterogeneous catalysts are decomposition of NH_3 on tungsten, decomposition of N_2O on gold, hydrogenation of alkenes and alkynes on platinum etc.

11. Radioactivity

All radioactive decay follows first order kinetics. The only difference from chemical reactions is that temperature does not influence the rate of radioactive decay.

In radioactive decay the term used for identifying the reaction rate is the number of nuclei rather than concentration.

$$\begin{aligned} \text{A} &\longrightarrow \text{B} \\ \frac{-dN_A}{dt} &= \lambda N_A \end{aligned} \quad \text{.....(11a)}$$

λ is similar to k in chemical reactions and is known as *decay constant or disintegration constant* and N_A is the number of nuclei of A at a given instant of time.

Following first order kinetics,

$$\ln \frac{N_0}{N_t} = \lambda t ; \quad N_t = N_0 e^{-\lambda t} \quad \text{.....(11b)}$$

$$t_{1/2} = \frac{0.693}{\lambda}$$

A term called average life time is introduced here which is given by $1/\lambda$.

$$\therefore t_{av} = \frac{1}{\lambda}$$

Average lifetime means the life time of a single nuclei. If $N_A = 1$, and this nuclei decays in one second, then according to the equation (11a), $\frac{-dN_A}{dt} = \lambda$.

If a nucleus of A decays after 2 seconds, then $\frac{-dN_A}{dt} = \frac{1}{2} = \lambda$. The average lifetime of the nucleus is therefore $1/\lambda$.

$$t_{av} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44 t_{1/2}$$

Activity of a radioactive element is the rate at which it decays and is given by λN .

$$A = \lambda N$$

Since according to equation (11b)

$$N_t = N_0 e^{-\lambda t}$$

Multiplying by λ , we get

$$\begin{aligned} \lambda N_t &= \lambda N_0 e^{-\lambda t} \\ A_t &= A_0 e^{-\lambda t}, \end{aligned}$$

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$\frac{-dN_A}{dt}$ describes the rate of change while A describes the rate of decay. They are equal, only when A is decaying and not produced. This means that if the radioactive element is also produced at a constant rate q , then,

$$\frac{-dN_A}{dt} = q - A = q - \lambda N \quad \left(\frac{-dN_A}{dt} \text{ and } A \text{ will not be equal} \right)$$

Specific activity is the activity of a unit mass of a radioactive substance.

Units of radioactivity

$$1 \text{ curie} = 3.7 \times 10^{10} \text{ disintegrations per second (dps)} = 3.7 \times 10^{10} \text{ Bq.}$$

$$1 \text{ Becquerel} = 1 \text{ disintegrations per second (dps)}$$

Amount of radioactive substance left after n half lives:

Let us start with the amount of radioactive substance in the beginning as A_0 .

$$\text{Then, amount of radioactive substance after first half life} = \frac{A_0}{2^1}.$$

$$\text{Amount of radioactive substance after second half life} = \frac{A_0}{2^2}$$

$$\text{And amount of radioactive substance after } n \text{ half lives} = \frac{A_0}{2^n}.$$