PHYSICAL CHEMISTRY

CHEMICAL KINETICS

This chapter introduces the principles of chemical kinetics, the study of reaction rates,by showing how the rates of reactions may be measured and interpreted.

The rate of a chemical reaction might depend on variables under our control, such as the pressure, the temperature,and the presence of a catalyst, and we may be able to optimize the rate by the appropriate choice of conditions. The study of reaction rates also leads to an understanding of the mechanisms of reactions, their analysis into a sequence of elementary steps

1- Order of a Reaction

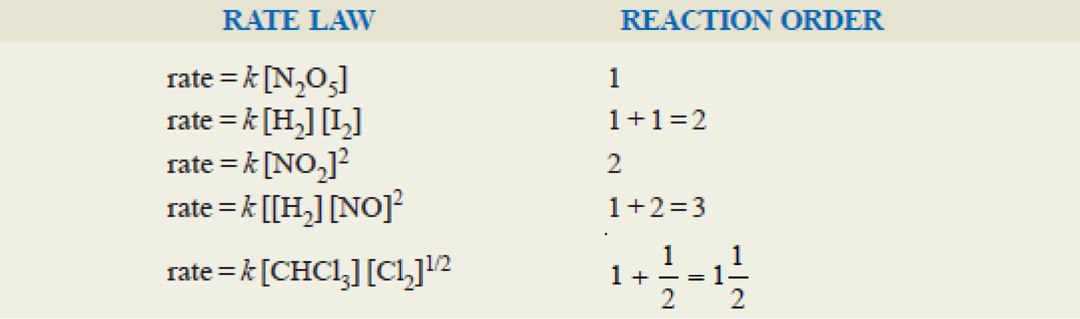
The order of a reaction is defined as the sum of the powers of concentrations in the rate law.

Let us consider the example of a reaction which has the rate law

rate = k $[A]^m$ $[B]^n$ ...(1)

The order of such a reaction is (m + n).

The order of a reaction can also be defined with respect to a single reactant. Thus the reaction order with respect to A is m and with respect to B it is n. The overall order of reaction (m + n) may range from 1 to 3 and can be fractional



RATE LAW	REACTION ORDER
$\text{rate} = k[N_2O_5]$	1
$\text{rate} = k[H_2][I_2]$	$1 + 1 = 2$
$\text{rate} = k[NO_2]^2$	2
$\text{rate} = k[[H_2][NO]^2$	$1 + 2 = 3$
$\text{rate} = k[CHCl_3][Cl_2]^{1/2}$	$1 + \frac{1}{2} = 1\frac{1}{2}$

2- Molecularity of a Reaction

Chemical reactions may be classed into two types :

(a) Elementary reactions

(b) Complex reactions

An elementary reaction is a simple reaction which occurs in a single step.

A complex reaction is that which occurs in two or more steps.

2-1 Molecularity of an Elementary Reaction

The molecularity of an elementary reaction is defined as : the number of reactant molecules involved in a reaction.

Thus the molecularity of an elementary reaction is 1, 2, 3, etc., according as one, two or three reactant molecules are participating in the reaction. The elementary reactions having molecularity 1, 2 and 3 are called unimolecular, bimolecular and termolecular respectively. Thus we have :

(a) Unimolecular reactions : (molecularity = 1)

$A \longrightarrow$ product

Examples are : (i) $Br_2 \longrightarrow 2Br$

(b) Bimolecular reactions : (molecularity = 2)

$A + B \longrightarrow$ products

$2A \longrightarrow$ products

Examples are :

(i) $CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

(ii) $2HI \longrightarrow H_2 + I_2$

(c) Termolecular reactions : (molecularity = 3)

$A + B + C \longrightarrow$ products

Examples are :

$2NO + O_2 \longrightarrow 2NO_2$

$2NO + Cl_2 \longrightarrow 2NOCl$

2-2 Molecularity of a Complex Reaction

Most chemical reactions are complex reactions. These occur in a series of steps. Each step is an elementary reaction. The stepwise sequence of elementary reactions that convert reactions to products is called the mechanism of the reaction. In any mechanism, some of the steps will be fast, others will be slow. A reaction can proceed no faster than its slowest step. Thus the slowest step is the ratedetermining step of the reaction.

The decomposition of N_2O_5,

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

is an example of a complex reaction. It occurs by the following steps :

Step 1 $2N_2O_5 \longrightarrow 2NO_2 + 2NO_3$ (slow)

Step 2 $NO_2 + NO_3 \longrightarrow NO + NO_2 + O_2$ (slow)

Step 3 $O + NO_3 \longrightarrow 2NO_2$ (fast)

Overall reaction $2N_2O_5 \longrightarrow 4NO_2 + O_2$

Each elementary reaction has its own molecularity equal to the number of molecules or atoms participating in it. It is meaningless to give the molecularity of the overall reaction because it is made of several elementary reactions, each, perhaps with a different molecularity. At best could be thought of as : the number of molecules or atoms taking part in the rate-determining step.

Thus step 2 in the above mechanism is rate-determining and has molecularity ‘2’ which could be considered as the molecularity of the decomposition reaction of N_2O_5.

3- Empirical chemical kinetics

The first steps in the kinetic analysis of reactions are to establish the stoichiometry of the reaction and identify any side reactions. The basic data of chemical kinetics are then the concentrations of the reactants and products at different times after a reaction has been initiated. The rates of most chemical reactions are sensitive to the temperature, so in conventional experiments the temperature of the reaction mixture must be held constant throughout the course of the reaction. This requirement puts severe demands on the design of an experiment. Gas-phase reactions, for instance, are often carried out in a vessel held in contact with a substantial block of metal.

Liquid-phase reactions, including flow reactions, must be carried out in an efficient thermostat. Special efforts have to be made to study reactions at low temperatures, as in the study of the kinds of reactions that take place in interstellar clouds

3-1 Experimental techniques

The method used to monitor concentrations depends on the species involved and the rapidity with which their concentrations change. Many reactions reach equilibrium over periods of minutes or hours, and several techniques may then be used to follow the changing concentrations

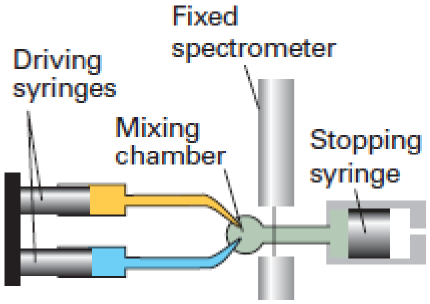
3-1-1-Monitoring the progress of a reaction

A reaction in which at least one component is a gas might result in an overall change in pressure in a system of constant volume, so its progress may be followed by recording the variation of pressure with time.

Spectrophotometry, the measurement of absorption of radiation in a particular spectral region, is widely applicable, and is especially useful when one substance in the reaction mixture has a strong characteristic absorption in a conveniently accessible region of the electromagnetic spectrum .Other methods of determining composition include emission spectroscopy, mass spectrometry, gas chromatography, nuclear magnetic resonance, and electron paramagnetic resonance

3-1-2-Flow method

In a real-time analysis the composition of the system is analysed while the reaction is in progress. Either a small sample is withdrawn or the bulk solution is monitored. In the flow method the reactants are mixed as they flow together in a chamber (Fig. 1).The reaction continues as the thoroughly mixed solutions flow through the outlet tube, and observation of the composition at different positions along the tube is equivalent to the observation of the reaction mixture at different times after mixing. The disadvantage of conventional flow techniques is that a large volume of reactant solution is necessary. This makes the study of fast reactions particularly difficult because tospread the reaction over a length of tube the flow must be rapid. This disadvantage is avoided by the stopped-flow technique, in which the reagents are mixed very quickly in a small chamber fitted with a syringe instead of an outlet tube



The flow ceases when the plunger of the syringe reaches a stop, and the reaction continues in the mixed solutions. Observations, commonly using spectroscopic techniques such as ultraviolet–visible absorption, circular dichroism, and fluorescence emission, are made on the sample as a function of time. The technique allows for the study of reactions that occur on the millisecond to second timescale. The suitability of the stopped flow method to the study of small samples means that it is appropriate for many biochemical reactions.

3-1-3-Flash photolysis

Very fast reactions can be studied by flash photolysis, in which the sample is exposed to a brief flash of light that initiates the reaction and then the contents of the reaction chamber are monitored. Most work is now done with lasers with photolysis pulse widths that range from femtoseconds to nanoseconds . The apparatus used for flash photolysis studies is based on the experimental design for time-resolved spectroscopy . Reactions occurring on a picosecond or femtosecond timescale may be monitored by using electronic absorption or emission, infrared absorption, or Raman scattering. The spectra are recorded at a series of times following laser excitation. The laser pulse can initiate the reaction by forming a reactive species, such as an excited electronic state of a molecule, a radical, or an ion

Rates of reactions

Reaction rates depend on the composition and the temperature of the reaction mixture. Consider a reaction of the form **A + 2 B →3 C + D**, in which at some instant the molar concentration of a participant J is [J] and the volume of the system is constant. The instantaneous rate of consumption of one of the reactants at a given time is **–d[R]/dt**, where R is A or B. The rate of formation of one of the products (C or D, which we denote P) is **d[P]/dt** (note the difference in sign). This rate is also positive. It follows from the stoichiometry for the reaction

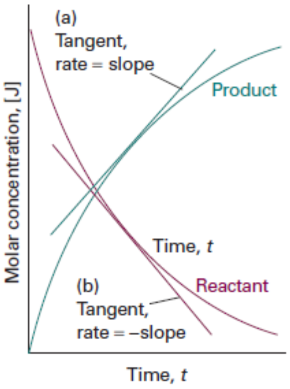
A + 2 B →3 C + D

That

Rate of reaction = rate of disappearance of A

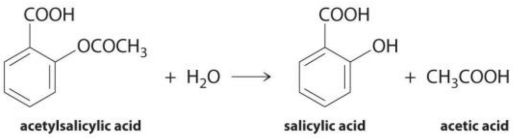
= rate of appearance of B

$$\frac{d[D]}{dt}=\frac{1}{3}\frac{d[C]}{dt}=-\frac{d[A]}{dt}=-\frac{1}{2}\frac{d[B]}{dt}$$



reaction rates of homogeneous reactions are reported in moles per cubic decimetre per second **(mol dm^{-3} s^{-1})** or related units

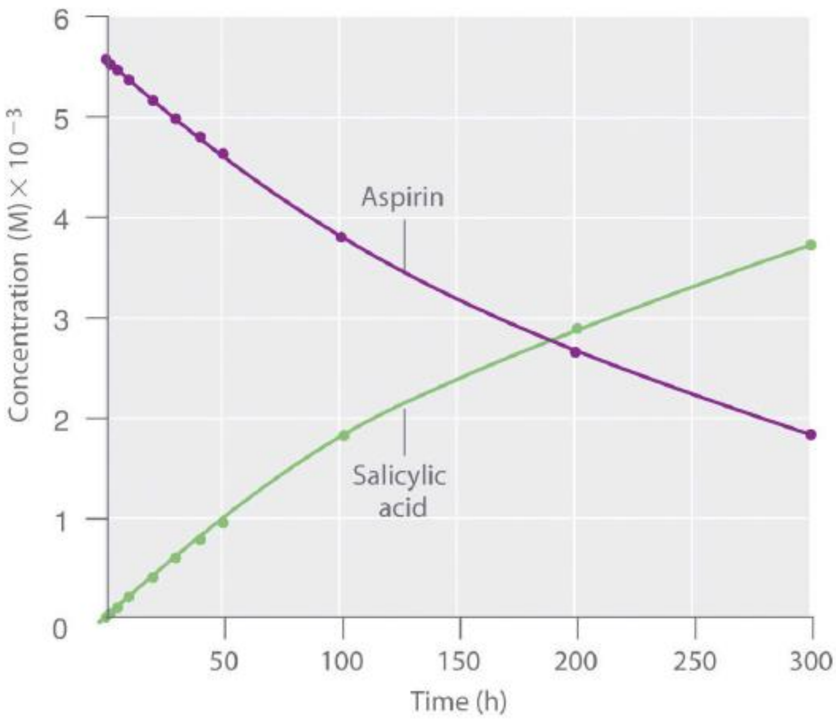
Example/Determining the Reaction Rate of Hydrolysis of Aspirin



Data for the hydrolysis of a sample of aspirin are in the Table below

Time (h)	[Aspirin] (M)	[Salicylic Acid] (M)
0	5.55×10^{-3}	0
2.0	5.51×10^{-3}	0.040×10^{-3}
5.0	5.45×10^{-3}	0.10×10^{-3}
10	5.35×10^{-3}	0.20×10^{-3}
20	5.15×10^{-3}	0.40×10^{-3}
30	4.96×10^{-3}	0.59×10^{-3}
40	4.78×10^{-3}	0.77×10^{-3}
50	4.61×10^{-3}	0.94×10^{-3}
100	3.83×10^{-3}	1.72×10^{-3}
200	2.64×10^{-3}	2.91×10^{-3}
300	1.82×10^{-3}	3.73×10^{-3}

The graph shows the concentrations of aspirin and salicylic acid as a function of time, based on the hydrolysis data In the Table



Rate laws and rate constants

The rate of reaction is often found to be proportional to the concentrations of the reactants raised to a power. For example, the rate of a reaction may be proportional to the molar concentrations of two reactants A and B, so we write

$$v = k[A][B]$$

with each concentration raised to the first power. The coefficient **k** is called the **rate constant** for the reaction. An experimentally determined equation of this kind is called the **rate law** of the reaction

A **rate law** is an equation that expresses the rate of reaction as a function of the concentrations of all the species present in the overall chemical equation for the reaction.

4- Reaction order

Many reactions are found to have rate laws of the form

$$v = k[A]^a[B]^b \qquad \cdots (5\text{-}1)$$

The power to which the concentration of a species is raised in a rate law of this kind is the **order** of the reaction with respect to that species. A reaction with the rate law in eqn 5-1 is first-order in A and first-order in B. The overall order of a reaction with a rate law like that in eqn 5-1 is the sum of the individual orders, $a + b + \cdots$. The rate law in eqn 5-1 is therefore second-order overall.

5- PSEUDO–ORDER REACTIONS

A reaction in which one of the reactants is present in a large excess shows an order different from the actual order. The experimental order which is not the actual one is referred to as the pseudo order. Since for elementary reactions molecularity and order are identical, pseudo-order reactions may also be called pseudo molecular reactions.

Let us consider a reaction

$$A + B \longrightarrow \text{products}$$

in which the reactant B is present in a large excess. Since it is an elementary reaction, its rate law can be written as

$$\text{rate} = k\,[A]\,[B]$$

As B is present in large excess, its concentration remains practically constant in the course of reaction. Thus the rate law can be written as

rate = k′ [A]

where the new rate constant k′ = k [B]. Thus the actual order of the reaction is second-order but in practice it will be first-order. Therefore, the reaction is said to have a pseudo-first order.

Example of Pseudo-order Reactions:

Hydrolysis of an ester. For example, ethyl acetate upon hydrolysis in aqueous solution using a mineral acid as catalyst forms acetic acid and ethyl alcohol.

$CH_3COOC_2H_5 + H_2O \longrightarrow CH_3COOH + C_2H_5OH$

ethyl acetate (excess) acetic acid ethyl alcohol

Here a large excess of water is used and the rate law can be written as

rate = k $[CH_3COOH]$ [H2O]

= k′ [CH3COOH]

The reaction is actually second-order but in practice it is found to be first-order. Thus it is a pseudo-first order reaction.

6- Integrated rate laws

Because rate laws are differential equations, we must integrate them if we want to find the concentrations as a function of time. A number of simple cases analytical solutions are easily obtained, and prove to be very useful. We examine a few of these simple cases here.

(A)Zero-order Reaction

A reactant whose concentration does not affect the reaction rate is not included in the rate law. In effect, the concentration of such a reactant has the power 0. Thus $\mathbf{[A]^0 = 1}$. A zero order reaction is one whose rate is independent of concentration.

A ⟶ Products

Rate of reaction = $-\,d\,[A]/dt = k$

This expression can be integrated directly because k is a constant independent of t. Initially (at t = 0) the concentration of A is $[A]_0$, and at a later time t it is [A], so we make these values the limits of the integrals and write

$$\int_{[A]0}^{[A]} d[A] = \int_{t=0}^{t} dt$$

Integration of the expression gives:

$$[A] - [A]_0 = -k_0 \ t \qquad ......7\text{-}1$$

Half-lives time :

A useful indication of the rate of a first-order chemical reaction is the half-life, t1/2, of a substance, the time taken for the concentration of a reactant to fall to half its initial value. The time for [A] to decrease from $[A]_0$ to 1/2 $[A]_0$ in a first-order reaction is given by eqn. 7-1 as :

$$1/2[A]_0 - [A]_0 = -k_0 \ t$$

Hence:

$$\mathbf{t_{\frac{1}{2}} = \frac{[A]0}{2K}}$$

(B) First-order reactions

For the reaction

A ⟶ products

The rate low

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

This expression can be integrated directly because k is a constant independent of t. Initially (at t = 0) the concentration of A is [A]0, and at a later time t it is [A], so we make these values the limits of the integrals and write

$$\int_{[A]0}^{[A]} d[A]/[A] = K \int_{t=0}^{t} dt$$

Integration of the expression gives:

$$\boldsymbol{ln\frac{[A]}{[A]0} = -Kt} \quad \textbf{or} \quad \textbf{[A] = [A]}_0\, \boldsymbol{e^{-Kt}} \qquad \text{...... 7-2}$$

the concentration of A is a moles litre^{-1}. after time t, x moles of A have changed, the concentration of A is a – x , eq. (1) will be

$$\ln\frac{a}{a-x} = kt$$

Half-lives time :

$$kt_{1/2} = -\ln\left(\frac{\frac{1}{2}[\mathrm{A}]_0}{[\mathrm{A}]_0}\right) = -\ln\tfrac{1}{2} = \ln 2$$

Hence:

$$t_{1/2} = \frac{\ln 2}{k}$$

(ln 2 = 0.693.)

(B) Second-order reactions

1- For the reaction

A ⟶ products

The rate low:

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

The concentration of A is [A$_0$] at t = 0 and [A] at a general time t later. Therefore,

$$-\int_{[A]0}^{[A]} d[A]/[A]^2 = \int_{t=0}^{t} K\, dt$$

is either of the following two forms:

Because the integral of $1/x^2$ is $-1/x$

.

$$\frac{1}{[A]}-\frac{1}{[A]_0}=Kt \qquad \text{........(7-3)}$$

Or

$$[A]=\frac{[A]_0}{1+Kt\,[A]_0}$$

The units for **K** for second order reactions are **(mol^{-1} L $time^{-1}$)**, in some references Eq. (7-3) will be

$$\frac{1}{a-x}-\frac{1}{a}=Kt$$

The half-life for this reaction:

$$t_{1/2}=\frac{1}{k[A]_0}$$

B) A reaction that occurs in solution that is first order in two reactants is second order overall.

$$d[A]/dt=-k[A][B] \qquad \text{------- (7-4)}$$

If the reaction has the stoichiometry

$$a\,A + b\,B \rightarrow P$$

$[A]_0$: Initial conc. of A, $[B]_0$: Initial conc. of A

a : no. of moles of A, b : no. of moles of B

X : No. of reactant moles, the conc. Of **A** after t time

$$[A] = [A]_0 - x \qquad \text{------ (7-5)}$$

The no. of moles of **B** after t time will proportional with $X(\frac{b}{a})$ will be:

$$[B] = [B]_0 - x\left(\frac{b}{a}\right) \qquad \text{------- (7-6)}$$

$X = [A]_0 \_ [A]$ from eq. (7-5), by substitution of x in eq. (7-6)

$$[B] = [B]_0 \_ ba^{-1}([A]_0 - [A])$$

For this type of reactions the integrated rate equation is:

$$\frac{1}{a[B]_0 - b[A]_0} \ln \frac{[B]/[B]_0}{[A]/[A]_0} = Kt \qquad \text{--------(7-7)}$$

Example:

The decomposition of nitrous oxide at 565 °C

$2\ N_2O \rightarrow 2\ N_2 + O_2$

is second order in N_2O with a rate constant of $1.10 \times 10^{-3}\ M^{-1}s^{-1}$. If the reaction is initiated with $[N_2O]$ equal to 0.108 M, what will its concentration be after 1250 s have elapsed?

Solution

Because the reaction is first order, we use the first order integrated rate equation.

$$\frac{1}{[A]_t} - \frac{1}{[A]_o} = kt$$

We know $[N_2O]_o$, k, and t. We solve for $[N_2O]_t$.

$$\frac{1}{[N_2O]_t} - \frac{1}{0.108M} = \left(1.10 \times 10^{-3} M^{-1} s^{-1}\right)\ 1250\ \text{s}$$

$$\frac{1}{[N_2O]_t} = 9.26M^{-1} + 1.38M^{-1}$$

$[N_2O]_t = 0.940\ M$

(C) Third -order reactions:

1- Let us consider a simple third order reaction of the type

A ⟶ products

$d\,[A]/\,dt = K\,[A]^{3}$

$$\int_{A0}^{A} \frac{d[A]}{[A]^{3}} = -\int_{t=0}^{t} K\,dt$$

The integrated rate equation is:

$$\frac{1}{[A]^{2}} - \frac{1}{[A]_{0}^{2}\;\;{}_{0}^{2}} = 2Kt \qquad \text{--------(7-8)}$$

The unit of K **($mol^{-2}\ L^{-2}\ Min.^{-1}$)**

The $t_{1/2}$ for this reaction :

$$t_{1/2} = \frac{3}{2\,[A]_{0}^{2}\;\;K}$$

2- For the reaction:

aA + bB ⟶ P

The rate low

$-d\,[A]/\,dt = K\,[A]^{2}\,[B]$

The integrated rate equation is:

$$\frac{1}{a[B]_{0}\;\; - b[A]_{0}}\left(\frac{1}{[A]_{0}} - \frac{1}{[A]} + \frac{b}{a[B]_{0}\;\; - b[A]_{0}}\ln\;\; \frac{[B]/[B]_{0}}{[A]/A]_{0}}\right) = K\,t \text{ ------(7-9)}$$

8-How to determine the order of a reaction

There are at least four different methods to determine the order of a reaction.

(1) Using integrated rate equations

The reaction under study is performed by taking different initial concentrations of the reactant $[A]_0$ and noting the concentration [A] after regular time intervals (t). The experimental values of A_0, A and t are then substituted into the integrated rate equations for the first, second and third order reactions. **The rate equation which yields a constant value of k corresponds to the correct order of the reaction**. This method of ascertaining the order of a reaction is essentially a method of hit-and-trial but was the first to be employed. It is still used extensively to find the order of simple reactions.

(2) Graphical method

For reactions of the type

A → products

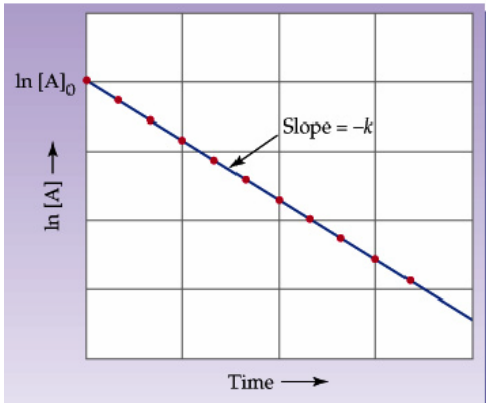
we can determine the reaction order by seeing whether a graph of the data fits one of the integrated rate equations.

In case of First order

We have already derived the integrated rate equation for first order as

$$ln\frac{[A]}{[A]0} = -Kt$$

$$\ln[A] = \ln[A]_o - k \times t$$

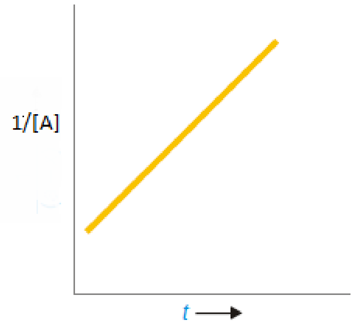


Hence, if 1n [A] is plotted against t and straight line results , the corresponding reaction is of the first order. However, if a curve is obtained, the reaction is not first order, so we tried the other orders equation.

In case of Second order

We have already shown that second order rate equation can be written as

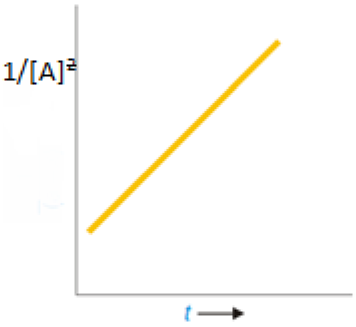
$$\frac{1}{[A]} - \frac{1}{[A]_0} = Kt$$



, if straight line obtain , the corresponding reaction is of the SECOND order. However, if a curve is obtained, we tried the other orders equation.

In case of third -order

We have already shown that third order rate equation can be written as



3-The Differential method

This method was suggested by van't Hoff and, therefore, it is also called van't Hoff's differential method. According to it, the rate of a reaction of the nth order is proportional to the nth power of concentration.

$$-\frac{dC}{dt} = k\,C^n$$

where C = concentration at any instant. In two experiments performed with different initial concentrations, we can write:

$$-\frac{dC_1}{\mathrm{dt}} = k\,C_1^n \qquad \text{...(1)}$$

$$-\frac{dC_2}{\mathrm{dt}} = k\,C_2^n \qquad \text{...(2)}$$

Taking logs of the expression (1) and (2)

$$\log\left(-\frac{dC_1}{dt}\right) = \log k + n\,\log C_1 \qquad \text{...(3)}$$

$$\log\left(-\frac{dC_2}{dt}\right) = \log k + n\,\log C_2 \qquad \text{...(4)}$$

On substracting (4) from (3), we get

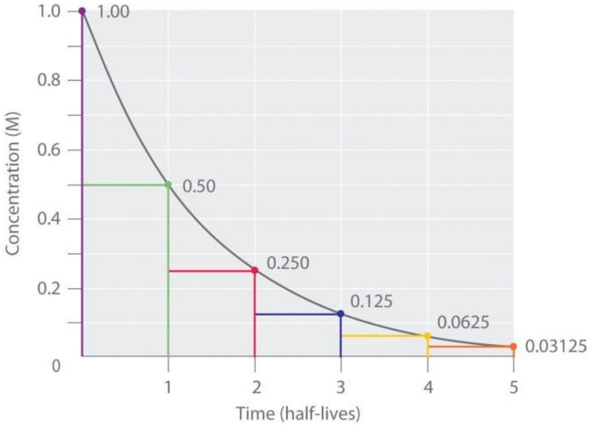
$$n = \frac{\log\left(-\frac{dC_1}{dt}\right) - \left(-\frac{dC_2}{dt}\right)}{\log C_1 - \log C_2} \qquad \text{...(5)}$$

To find n,(-dc/dt) in the two experiments is determined by plotting concentrations against time (t).

Using the values of slopes, ($-dc_1/dt$) and ($-dc_2/dt$), in the eq.5 , n can be determined

4-Half lives method

Another way of determining the reaction order is to investigate the behaviour of the half life as the reaction proceeds. Specifically, we can measure a series of successive half lives. t = 0 is used as the start time from which to measure the first half life, $t_{1/2}(1)$. Then $t_{1/2}(1)$ is used as the start time from which to measure the second half life, $t_{1/2}(2)$, and so on.



From the general half live eq.

$$t_{\frac{1}{2}} = \frac{(2)^{n-1} - 1}{(n-1)k(a)^{n-1}} \qquad \mathbf{(n \neq 1)}$$

Taking natural logs of each side of the eq.

$$\log t_{\frac{1}{2}} = \log \frac{2^{(n-1)} - 1}{(n-1)k_n}\left(\frac{1}{[A]_0^{(n-1)}}\right)$$

$$\log t_{\frac{1}{2}} = \log\left(\frac{2^{(n-1)} - 1}{(n-1)k_n}\right) + \log\left(\frac{1}{[A]_0^{(n-1)}}\right)$$

$$\log t_{\frac{1}{2}} = \log\left(\frac{2^{(n-1)} - 1}{(n-1)k_n}\right) - (n-1)\log[A]_0$$

n, is determined by plotting Log $t_{1/2}$ against Log $[A]_0$.The slope,(1-n) is measured to determine the order of the reaction

5-Isolation method

This method is employed in determining the order of complicated reactions by 'isolating' one of the reactants so far as its influence on the rate of reaction is concerned. Suppose the reaction under consideration is :

$A + B + C \longrightarrow$ products

The order of the reaction with respect to A, B and C is determined. For the determination of the order of reaction with respect to A, B and C are taken in a large excess so that their concentrations are not affected during the reaction. The order of the reaction is then determined by using any of the methods described earlier. Likewise, the order of the reaction with respect to B and C is determined. If nA, nB and nC are the orders of the reaction with respect to A, B and C respectively, the order of the reaction n is given by the expression.

$n = nA + nB + nC$

9. The kinetics of Complex reactions

In kinetics, a 'complex reaction' simply means a reaction whose mechanism comprises more than one elementary step. In the previous sections we have looked at experimental methods for measuring reaction rates to provide kinetic data that may be compared with the predictions of theory.

9-1 Consecutive reactions

The simplest complex reaction consists of two consecutive, irreversible elementary steps e.g.

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

An example of such a process is radioactive decay. This is one of the few kinetic schemes in which it is fairly straightforward to solve the rate equations analytically, so we will look at this example in some detail. We can see immediately that the following initial conditions hold.

at $t = 0$, $[A] = [A]_0$
$[B] = 0$
$[C] = 0$

with at all times $[A]+[B]+[C] = [A]_0$.

Using this information, we can set up the rate equations for the process and solve them to determine the concentrations of [A], [B], and [C] as a function of time. The rate equations for the concentrations of A, B, and C are:

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

$$(2)\qquad \frac{d[B]}{dt} = k_1[A] - k_2[B]$$

$$(3)\qquad \frac{d[C]}{dt} = -\,k_2[B]$$

Integrating (1) gives

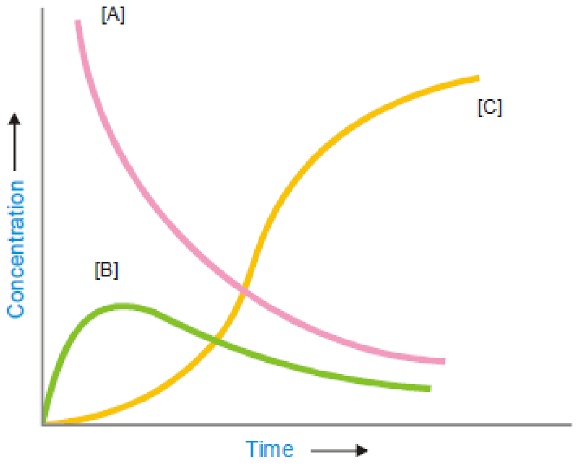
$$[A] = [A]_0 \exp(-k_1 t).$$

Substituting this into (2) gives $\frac{d[B]}{dt} + k_2[B] = k_1[A]_0 \exp(-k_1 t)$, a differential equation with the solution

$$[B] = \frac{k_1}{k_2 - k_1}\{\exp(-k_1 t) - \exp(-k_2 t)\}\,[A]_0$$

Finally, since $[C] = [A]_0 – [B] – [A]$, we find

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

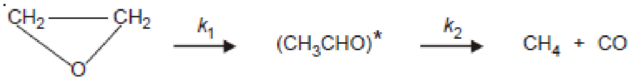


Examples of First Order Consecutive Reactions

(*a*) Decomposition of dimethyl ether is gaseous phase

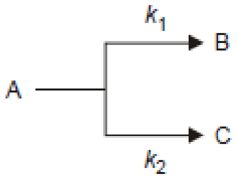
$$CH_3COCH_3 \xrightarrow{k_1} CH_4 + HCHO \xrightarrow{k_2} H_2 + CO$$

(*b*) Decomposition of Ethylene oxide



9-2 Parallel or Side Reactions:

In these reactions the reacting substance follows two or more paths to give two or more products. The preferential rate of such may be changed by varying the conditions like pressure, temperature or catalyst. The reaction in which the maximum yield of the products is obtained is called the main or major reaction while the other reaction (or reactions) are called side or parallel reactions. For example,



$$r_1 = \frac{-d[\mathrm{A}]}{dT} = k_1[\mathrm{A}] \qquad \text{...}(i)$$

and

$$r_2 = \frac{-d[\mathrm{A}]}{dT} = k_2[\mathrm{A}] \qquad \text{...}(ii)$$

The total rate of disappearance of A is given by

$$\frac{-d[\mathrm{A}]}{dT} = r_1 + r_2 = k_1[\mathrm{A}] + k_2[\mathrm{A}]$$

$$= (k_1 + k_2)[\mathrm{A}]$$

$$= k'[\mathrm{A}] \qquad \text{...}(iii)$$

where k' is the first order rate constant. It is equal to the sum of the two constants k_1 and k_2 of two side reactions.

Integrating equation (*iii*), we get

$$\int \frac{-d[\mathrm{A}]}{dT} = \int k'[\mathrm{A}]$$

applying the limits $[\mathrm{A}_0]$ & $[\mathrm{A}]_t$ and 0 & t, we have

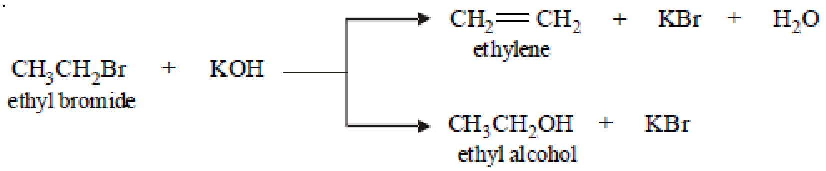
$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_t} \frac{-d[\mathrm{A}]}{dt} = k' \int_0^t dt$$

$$\ln \frac{[\mathrm{A}]_0}{[\mathrm{A}]_t} = k't + (k_1 + k_2)t \qquad \text{...}(iv)$$

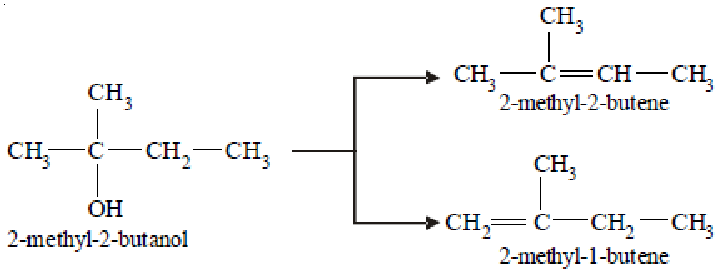
where $[\mathrm{A}]_0$ is the initial concentration of the reactant A and $[\mathrm{A}]_t$ is concentration of A at time t.

Examples of Parallel or Side Reactions

(*a*) Reaction of ethyl bromide with potassium hydroxide



(*b*) Dehydration of 2-methyl–2–butanol



9-3 Reversible or Opposing Reactions

In reversible or opposing reactions the products formed also react to give back the reactants. Initially, we sagest that b the rate of forward reaction and the rate of backward or reverse reaction is first- order A reaction of this type maybe represented as

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$\frac{d[A]}{dt} = -K_f[A] + K_b[B]$$

$[A]_0$ = initial con. of A substance at t=0, at this time the conc. Of B =0, So

$[A]_0 = [A] + [B]$ at t time

$$\frac{d[A]}{dt} = -K_f[A] + K_b([A]_0 - [A])$$

$$= -(K_f + K_B)[A] + K_f[A]_0$$

Integration of the expression gives:

$$[A] = [A]_0\left(\frac{K_b + K_f - exp.(K_f + K_b)t}{K_f + K_b}\right)$$

If the reaction is irreversible K_b =0 and the conc. Of a will be

$$[A] = [A]_0\, e^{-Kt}$$

As t→∞, the concentrations reach their equilibrium values, It follows that the equilibrium constant of the reaction is

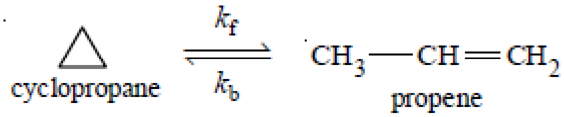
$$\mathbf{K} = \left(\frac{[B]}{[A]}\right)_{eq} = \frac{[B]_\infty}{[A]_\infty} = \frac{K_f}{K_b}$$

Examples of Opposing Reactions

(*a*) Dissociation of hydrogen iodides

$$2HI \underset{k_b}{\overset{k_f}{\rightleftharpoons}} H_2 + I_2$$

(*b*) Isomerisation of cyclopropane into propene



10- **Reaction mechanism**

The rate equations for virtually all complex reaction mechanisms generally comprise a complicated system of coupled differential equations that cannot be solved analytically. Very good approximate solutions may often be obtained by making simple assumptions about the nature of reactive intermediates.

1- rate-determining step:

In multiple-step reactions

A- The reaction mechanism include one or more reversible(fast) steps

B- one of the elementary reactions in the sequence is often slower than the rest , It therefore determines the rate of reaction.

Example/ the overall reaction $2\ NO_2 + O_2 \longrightarrow 2\ NO_2$

The mechanism

$$2\,NO \underset{K_R}{\overset{K_F}{\rightleftarrows}} N_2O_2 \qquad \text{(fast)}$$

$$N_2O_2 + O_2 \xrightarrow{K_2} 2NO_2 \qquad \text{(slow)}$$

$[N_2O_2]$: intermediate substance

Rate= Rate of slow step

$$r = k_2[N_2O_2][O_2]$$

Note: the intermediate should not be included in the rate low

From the reversible step:

$$\boldsymbol{Keq} = \frac{\boldsymbol{K}_{\boldsymbol{F}}}{\boldsymbol{K}_{\boldsymbol{R}}} = \frac{[\boldsymbol{N}_2\boldsymbol{O}_2]}{[\boldsymbol{NO}]^2}$$

$$[N_2O_2] = (k_f / k_r)[NO]^2$$

So the rate :

$$\text{rate} = k_2[N_2O_2][O_2] = k_2(k_f / k_r)[NO]^2[O_2]$$
$$= k_2 K_{eq}[NO]^2[O_2]$$

2- Steady state approximation:

The steady-state approximation assumes that, after an initial induction period, an interval during which the concentrations of intermediates, R, rise from zero, and during the major part of the reaction, the rates of change of concentrations of all reaction intermediates are negligibly small.

If a reactive intermediate R is present at low and constant concentration throughout (most of) the course of the reaction, then we can set

d[R]/dt = 0

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

We can apply the steady state approximation (SSA) to C, to obtain

$$\frac{d[C]}{dt} = 0 = k_1[A][B] - k_{-1}[C] - k_2[C]$$

This may be solved to give [C] in terms of the reactant concentrations [A] and [B].

$$[C] = \frac{k_1}{k_{-1} + k_2}[A][B]$$

The overall rate is the rate of formation of the product, D, giving

$$\nu = \frac{d[D]}{dt} = k_2[C] = \frac{k_1 k_2}{k_{-1} + k_2}[A][B]$$

11-Chain reactions:

In a chain reaction, a reaction intermediate produced in one step generates an intermediate in a subsequent step, then that intermediate generates another intermediate, and so on. The intermediates in a chain reaction are called chain carriers. In a radical chain reaction the chain carriers are radicals.

A chain reaction can have a simple rate law. As a first example, consider the pyrolysis, or thermal decomposition in the absence of air, of acetaldehyde (ethanal, CH_3CHO),which is found to be three-halves order in CH_3CHO:

$CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ $v = k[CH3CHO]^{3/2}$ -------(1)

Some ethane is also detected. The mechanism for this reaction is as follows

Initiation: $CH_3CHO \rightarrow \cdot CH_3 + \cdot CHO$ $v = k_i$ [CH3CHO]

Propagation: $CH_3CHO + \cdot CH_3 \rightarrow CH_3CO\cdot + CH_4$ $v = k_p$ [CH3CHO][·CH3]

Propagation: $CH_3CO\cdot \rightarrow \cdot CH_3 + CO$ $v = k'_p$ [CH3CO·]

Termination: $\cdot CH_3 + \cdot CH_3 \rightarrow CH_3CH_3$ $v = k_t$ [·CH3]

The chain carriers ·CH3 and ·CHO are formed initially in the **initiation step**. To simplify the treatment, we shall ignore the subsequent reactions of ·CHO. The chain carrier $\cdot CH_3$ attacks other reactant molecules in the **propagation steps**, and each attack gives rise to a new carrier. Radicals combine and end the chain in the **termination step**. To test the proposed mechanism we need to show that it leads to the observed rate law. According to the steady-state approximation, the net rate of change of the intermediates ($\cdot CH_3$ and $CH_3CO\cdot$) may be set equal to zero:

$$\frac{d[\cdot CH_3]}{dt} = k_i[CH_3CHO] - k_p[\cdot CH_3][CH_3CHO] + k'_p[CH_3CO\cdot] - 2k_t[\cdot CH_3]^2 = 0$$

$$\frac{d[CH_3CO\cdot]}{dt} = k_p[\cdot CH_3][CH_3CHO] - k'_p[CH_3CO\cdot] = 0$$

The sum of the two equations is

$$k_i[CH_3CHO] - 2k_t[\cdot CH_3]^2 = 0$$

which shows that the steady-state approximation also implies that the rate of chain initiation is equal to the rate of chain termination. The steady-state concentration of ·CH3 radicals is

$$[\cdot CH_3] = \left(\frac{k_i}{2k_t}\right)^{1/2} [CH_3CHO]^{1/2}$$

It follows that the rate of formation of CH_4 is

$$\frac{d[CH_4]}{dt} = k_p[\cdot CH_3][CH_3CHO] = k_p\left(\frac{k_i}{2k_t}\right)^{1/2} [CH_3CHO]^{3/2}$$

which is in agreement with the three-halves order observed experimentally in eq. (1) .

11-1 Explosions

A thermal explosion is a very rapid reaction arising from a rapid increase of reaction rate with increasing temperature. The temperature of the system rises if the energy released by an exothermic reaction cannot escape, and the reaction goes faster. The acceleration of the rate results in an even faster rise of temperature, so the reaction becomes catastrophically fast. A chain-branching explosion occurs when the number of chain centres grows exponentially. An example of both types of explosion is the reaction between hydrogen and oxygen:

$2\ H_2(g) + O_2(g) \rightarrow 2\ H_2O(g)$

Although the net reaction is very simple, the mechanism is very complex and has not yet been fully elucidated. A chain reaction is involved, and the chain carriers include $H\cdot$, $\cdot O\cdot$, and $\cdot OH$. Some steps involving $H\cdot$ are:

Initiation: $H2 \rightarrow H\cdot + H\cdot$

Propagation: $H2 + \cdot OH \rightarrow \cdot H + H2O$ $v = kp[H2][\cdot OH]$

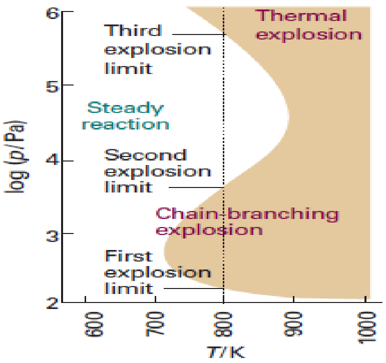
Branching: $\cdot O2\cdot + \cdot H \rightarrow \cdot O\cdot + \cdot OH$ $v = kb[\cdot O2\cdot][H\cdot]$

$\cdot O\cdot + H2 \rightarrow \cdot OH + \cdot H$ $v = k'b[\cdot O\cdot][H2]$

Termination: $H\cdot + \text{wall} \rightarrow 1\text{–}2\ H2$ $v = kt[H\cdot]$

$H\cdot + O2 + M \rightarrow HO2\cdot + M^*$ $v = k't[H\cdot][O2][M]$

A branching step is an elementary reaction that produces more than one chain carrier. The occurrence of an explosion depends on the temperature and pressure of the system, and the explosion regions for the reaction, the conditions under which explosion occurs, are shown in the Fig. below.



At very low pressures the system is outside the explosion region and the mixture reacts smoothly. At these pressures the chain carriers produced in the branching steps can reach the walls of the container where they combine. Increasing the pressure along a vertical line in the illustration takes the system through the first explosion limit (provided the temperature is greater than about 730 K). The chain carriers react before reaching the walls and the branching reactions are explosively efficient. The reaction is smooth when the pressure is above the second explosion limit. The concentration of third-body M molecules is then so high compared to the concentrations of chain carriers that the combination of $H\cdot$ atoms with O_2 molecules to form relatively unreactive $HO_2\cdot$ molecules becomes faster than the branching reaction between $H\cdot$ atoms and O_2 molecules. These long-lived $HO_2\cdot$ molecules then diffuse to the walls and are removed there, in what amounts to another termination step. When the pressure is increased to above the third explosion limit, diffusion of $HO_2\cdot$ molecules to the walls becomes so slow that they can react with H_2 molecules (now at very high concentrations) to regenerate H atoms and H_2O_2 molecules.