

Chemical Kinetics

Objectives

At the end of the session you will understand the theoretical concepts pertaining to the chemical kinetics especially the rate of a reaction, rate law, and mechanism of a reaction. Further, you will also understand the thermodynamic dependence and catalysis.

1.0 Background

You may have heard two major phenomena that should be satisfied for a chemical reaction to be taken place; thermodynamic stability and kinetic stability. Understanding on these two phenomenon is very important in chemical industry. You can understand this with the help of two examples.

Do you know that among two forms of carbon, graphite and diamond, diamond form is the most stable form?

Graphite has a lower free energy compared to the diamond. Therefore, diamond is thermodynamically favorable to convert into graphite. However, this will never happen within your lifetime. For diamond \rightarrow graphite transformation, getting to the transition state probably involves, among other things, breaking all the carbon-carbon bonds in diamond. Breaking those bonds demand huge amount of energy, implying high activation energy. Transformation is thermodynamically favorable but kinetically unfavorable.

Under thermodynamics we will study the thermodynamic feasibility of a reaction and we will be able to answer the questions that will the chemical reaction occur? and then how far the reaction will take place? (ratio of reactants to products at equilibrium). In this section under the chemical kinetics we will answer the question that how fast the reaction will take place?

1.1 Chemical reaction and chemical equation

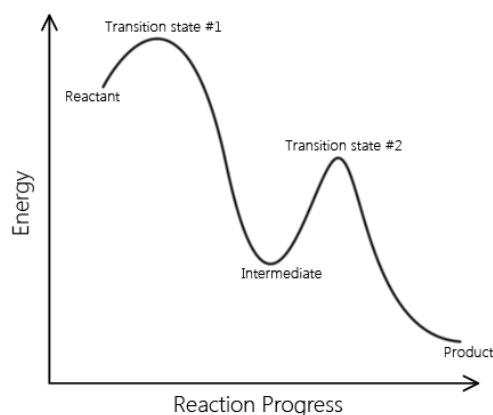
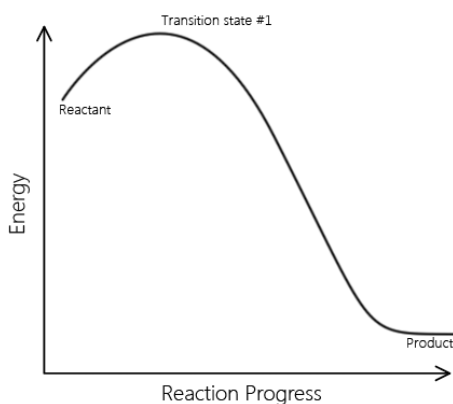
Chemical reaction is a process in transformation of reactants (a set of chemicals) to products (a set of another chemical). The chemical equation pertaining to this process is the symbolic representation of a chemical reaction with the stoichiometric relation between reactants and products. This transformation can be either a one step process or a sum of several steps. If a chemical reaction has one transition state and no intermediates it is called elementary reaction or elementary step, it is a one step process. Therefore in other word, chemical reaction can be either an elementary reaction or a sum of several elementary reactions called overall reaction. Overall reaction is a complex reaction. In summary,

Elementary reaction: has only one transition state
has no intermediates
cannot be broken down further into simpler reactions

Complex reaction: has two or more transition states
has one or more intermediate states
can be broken down further into simpler steps(elementary reactions)

Elementary reaction

Complex reaction



An elementary reaction expresses how actually molecules or ions react with each other. The equation in an elementary step represents the reaction at the molecular level, not the overall reaction. There are three kinds of elementary steps based on numbers of molecules involved in the elementary step. They are unimolecular process, bimolecular process, and trimolecular process.

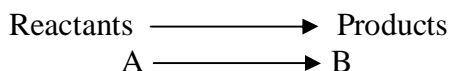
Unimolecular process: When a molecule or ion decomposes by itself, then it is a unimolecular process. A unimolecular step is always a first order reaction (see rate law and order of reaction below)

Bimolecular process: This involves two reacting molecules or ions. Bimolecular process is a second order reaction.

A **trimolecular process** involves the collision of three molecules. Trimolecular processes and higher order processes are less common because the chance of three or more molecules coming together with the right orientation is unlikely.

1.2 Rate, rate law and order of a reaction

Rate of a reaction is a change in the concentration of a reactant or a product with time, therefore unit of a rate of a reaction is always $\text{mol dm}^{-3} \text{s}^{-1}$. In measurement, we measure the change in concentration of a chemical species (a reactant or a product) in a given **time interval**. So, several such measurements throughout the reaction process would give the average rate of the reaction.



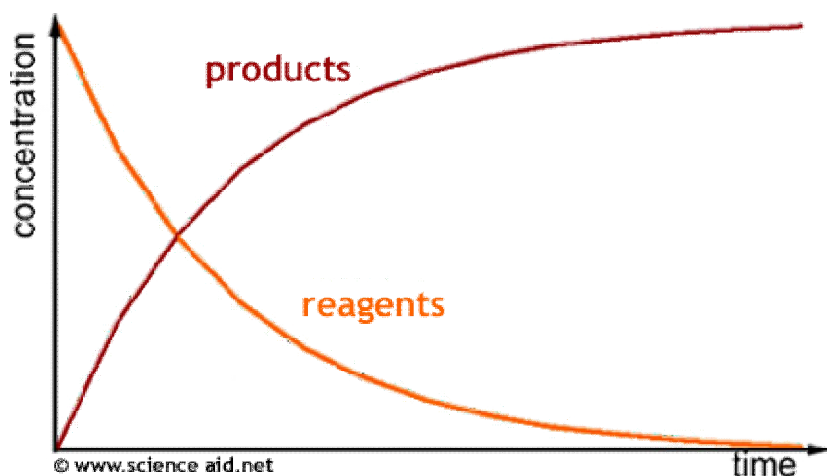
$$\text{Average rate} = \frac{\text{change in number of moles in B}}{\text{time interval}} = \frac{\Delta B}{\Delta t}$$

Since the disappearance of product occurs during the reaction,

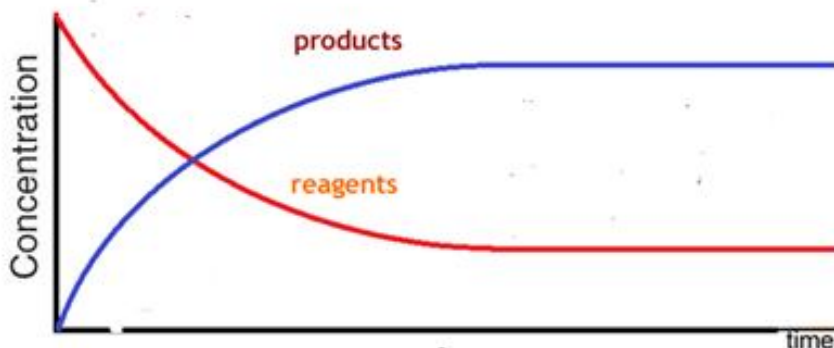
$$\text{Average rate} = -\frac{\Delta A}{\Delta t}$$

With the time, number of moles of product, B, increases and number of moles of reactant, A, decreases.

$$\text{Average rate of reaction} = -\frac{\Delta A}{\Delta t} = \frac{\Delta B}{\Delta t}$$



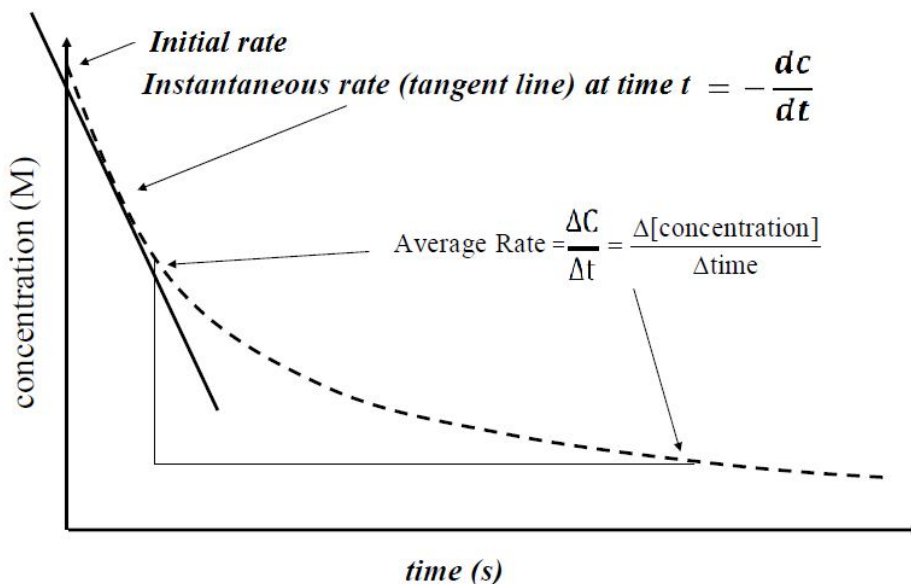
Note: This figure is only for a representation of a change in concentration of a reactant and product. In this case reactant has been completely converted to the product. It is not always in this way. As an example, in following figure, reactants are not completely converted to product.



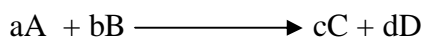
Instantaneous rate of a reaction is the rate of a reaction at a particular time considered (given time). If we consider infinitesimal change in concentration and time, the rate is given by

$$\text{Instantaneous rate} = -\frac{dA}{dt} = \frac{dB}{dt}$$

Initial rate of a reaction is the rate of a chemical reaction at the time of the reaction start, i.e. right after the reactants are mixed. It is the rate of a chemical reaction extrapolated back to the instant the reactants were mixed.



When the reaction involves two or more reactants, relationship of the rate of the reaction to the rate of disappearance or formation of each species gives according to the stoichiometry of the reaction.



$$\text{Rate} = -\frac{1}{a} \frac{\Delta A}{\Delta t} = -\frac{1}{b} \frac{\Delta B}{\Delta t} = -\frac{1}{c} \frac{\Delta C}{\Delta t} = -\frac{1}{d} \frac{\Delta D}{\Delta t}$$

a , b , c and d are stoichiometric coefficients.

Rate law of a reaction is the relation of the reaction rate to the concentrations of the reactant. For a general reaction, when each concentration is expressed with an order (exponent). Consider the general reaction,



$$\text{Rate} = k[A]^x[B]^y$$

Note that the x and y are not the stoichiometric coefficients of the reaction. k is the rate constant. x is the order of the reaction with respect to the species A and y is the order of the reaction with respect to the species B . This form of rate law is also called differential rate law, because it includes the first derivative of concentration of a species with respect to the time.

Overall order of the reaction is the sum of the individual orders, in this case,

overall order $n = x + y$

If the above reaction is an elementary reaction, each order (x and y) equals to the stoichiometric coefficients (a and b , respectively). In this case, the order of the reaction is called molecularity.

For an elementary reaction, $aA + bB \longrightarrow cC + dD$

$$\text{Rate} = k[A]^a[B]^b$$

x and y are determined experimentally. Note also that the order of a reaction can be either, positive, negative or half integers.

The units of rate are always $\text{mol dm}^{-3} \text{s}^{-1}$, therefore the units of a rate constant depend upon the overall order of the reaction. We can find the units of a rate constant for a particular rate law, by simply dividing the units of rate by the units of molarity in the concentration term of the rate law.

$$k = \frac{\text{Rate}}{[A]^x[B]^y} = \frac{\text{mol dm}^{-3} \text{s}^{-1}}{(\text{mol dm}^{-3})^n}$$

n is the overall order of the reaction

Relationship between rate law, order and the rate constant

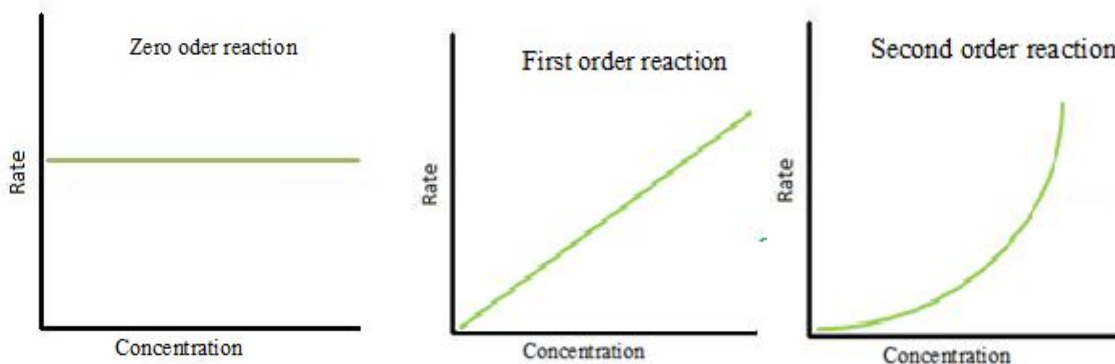
Rate law (differential)	Order	Example	Units of k
Rate = k_0	Zero order Doesn't depend on reactant concentration	$2\text{HI} \longrightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$	$\text{mol dm}^{-3} \text{s}^{-1}$
Rate = $k_1[A]$	First order reaction Radioactive decay reaction, unimolecular reaction	$\text{ArN}_2^+ + \text{X}^- \longrightarrow \text{ArX} + \text{N}_2$ $\text{N}_2\text{O}_4(\text{g}) \longrightarrow 2\text{NO}_2(\text{g})$	s^{-1}
Rate = $k_2[A]^2$ or = $k_2[A][B]$	Second order reaction Order with respect to A =1 Order with respect to B =1	$\text{NO}_2 + \text{CO} \longrightarrow \text{NO} + \text{CO}_2$ Rate = $k[\text{NO}_2]^2$ $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \longrightarrow 2\text{HI}$ Rate = $k[\text{H}_2][\text{I}_2]$	$\text{mol}^{-1}\text{dm}^3 \text{s}^{-1}$
Rate = $k_3[A]^2[B]$ Or other combination	Third order reaction Order with respect to A =2 Order with respect to B =1	$2\text{NO} + \text{O}_2 \longrightarrow 2\text{NO}_2$ Rate = $k[\text{NO}]^2[\text{O}_2]$	$\text{mol}^{-2}\text{dm}^6 \text{s}^{-1}$
Rate = $k[A]^{n/2}$	Order of the reaction is half integers (fractional order)	$\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$ Rate = $k[\text{CH}_3\text{CHO}]^{3/2}$	$\text{mol}^{-1/2}\text{dm}^{3/2}\text{s}^{-1}$
Rate = $k_1[A]^x + k_2[A]^y$	Mixed order reaction	$\text{H}_2 + \text{Br}_2 \longrightarrow 2\text{HBr}$ $\text{Rate} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + j[\text{HBr}][\text{Br}_2]}$	

2.0 Determination of rate law

One of the first steps in studying the kinetics of a chemical reaction is to determine the rate law for the reaction. There are two forms of a rate law for chemical kinetics, the **differential rate law** and the **integrated rate law**.

2.1 Differential rate law method.

The differential rate law relates the rate of reaction to the concentrations of the various species in the system (zero order, first order etc.) as we discussed above and it is a differential equation. In this method, one way of finding reaction rate to measure the change in concentration of a product or a reactant with time as the reaction progress and then plot the graph of concentration against the time. As shown in above graph, we can calculate the rate of the reaction at different points on the graph. The differential rate law and the rate constant are then determined for a reaction by examining how the rate of reaction varies with the reactant concentration. Concentration dependence of rate of each type, zero order, first order and second order, is given in graphs below.

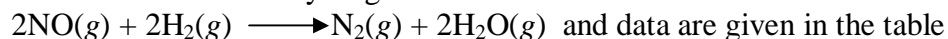


There are two major methods which used differential rate law (rate of the reaction); Initial rate methods and isolation method.

2.1.1 Initial rate method

The Initial rate method involves measuring the rate of reaction, r , at very short times before any significant changes in concentration occur. This method works well for slow reaction. We measure the initial rates for several different sets of concentrations of reactants and compare the initial rates. Let us consider following example.

The reaction of nitric oxide with hydrogen at 1280°C is:



Experiment	$[\text{NO}]_0$ / mol dm^{-3}	$[\text{H}_2]_0$ / mol dm^{-3}	Initial rate / $\text{mol dm}^{-3} \text{ min}^{-1}$
1	0.0100	0.0100	0.00600
2	0.0200	0.0300	0.144
3	0.0100	0.0200	0.0120

$$\text{Rate} = k[\text{NO}]^x[\text{H}_2]^y$$

$$\text{Rate} = k[\text{NO}]_0^x[\text{H}_2]^y$$

Using the experiments (1) and (3),

$$\frac{\text{Rate (1)}}{\text{Rate (3)}} = \frac{k[0.0100 \text{ mol dm}^{-3}]^x [0.0100 \text{ mol dm}^{-3}]^y}{k[0.0100 \text{ mol dm}^{-3}]^x [0.0200 \text{ mol dm}^{-3}]^y}$$

$$= \frac{0.006 \text{ mol dm}^{-3} \text{ min}^{-1}}{0.012 \text{ mol dm}^{-3} \text{ min}^{-1}}$$

$$\left(\frac{1}{2}\right)^y = \frac{1}{2}$$

Order of the reaction with respect to the $\text{H}_2 = y = 1$

Since now we know the y , we can calculate the x using experiments (1) and (2).

$$\frac{\text{Rate (1)}}{\text{Rate (2)}} = \frac{k[0.0100 \text{ mol dm}^{-3}]^x [0.0100 \text{ mol dm}^{-3}]^y}{k[0.0200 \text{ mol dm}^{-3}]^x [0.0300 \text{ mol dm}^{-3}]^y} = \frac{0.006 \text{ mol dm}^{-3} \text{ min}^{-1}}{0.144 \text{ mol dm}^{-3} \text{ min}^{-1}}$$

$$\left(\frac{1}{2}\right)^x \times \frac{1}{3} = \frac{1}{24}$$

$$\left(\frac{1}{2}\right)^x = \left(\frac{1}{2}\right)^3$$

Order of the reaction with respect to the $\text{NO} = x = 3$

Therefore overall order of the reaction is $1 + 3 = 4$

$$\text{Rate} = k[\text{NO}]^3[\text{H}_2]$$

We can find the rate constant by just substituting the data of any experiment to rate law.

Substituting data of experiment (1) to $\text{Rate} = k[\text{NO}]^3[\text{H}_2]$

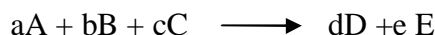
$$0.006 \text{ mol dm}^{-3} \text{ min}^{-1} = k(0.0100 \text{ mol dm}^{-3})^3(0.0100 \text{ mol dm}^{-3})$$

$$k = 6 \times 10^5 \text{ mol}^{-3} \text{ dm}^9 \text{ min}^{-1}$$

2.1.2 Isolation method

When a chemical reaction involves multiple reactants with the concentrations of several species changing simultaneously, it is difficult to determine the rate law. In such a case, all rate laws often do not follow the simple zero-, first-, and second-order rate laws. Even though in principle, the initial rate method can be used to determine the rate law, it poses serious experimental difficulties in accurately determining the initial rate.

In isolation method, the concentration of one reactant is made much smaller than the concentrations of the other reactants. Under this condition, except one, all reactant concentrations are essentially constant, and the simple zero-, first-, and second-order kinetic plots can usually be used to interpret the concentration-time data. Consider the following reactions with multiple reactants.



$$\text{Rate} = k[\text{A}]^x[\text{B}]^y[\text{C}]^z$$

We select one reactant (say A) at a time as a variable and others (B and C) are kept at higher concentration so that they remain as constants throughout the reaction process. In this way, selected reactant, A, becomes isolated. Then the product of concentration terms of others and rate constant k become a another constant called k_{obs}

$$\text{Rate} = k_{\text{obs}}[A]^x$$

Now this has become a simple reaction we can calculate the order and the pseudo-order rate constant, k_{obs} using the initial rate method or any other method.

$$k_{\text{obs}} = k[B]^y[C]^z$$

We can follow the same procedure separately for A and B and determine the y and z , respectively. Once we find the x , y and z , true rate constant k can be calculated.

2.2. Integrated rate law

Integration of differential rate law equation produces the corresponding **integrated rate law**, which relates the concentration to time. In differential methods, we have to determine the rate of a reaction from a concentration-time graph. It is the slope of such a graph and difficult to find accurately. Much better way is to determine the rate constant directly from a concentration-time plot. Integrated rate derived for each type gives a straight line (characteristic kinetic plot) in which slope and intercept show the rate parameters.

2.2.1. Zero order reaction

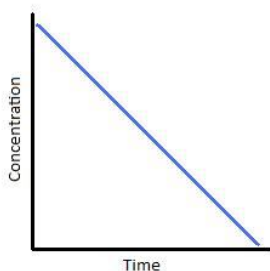


$$-\frac{dA}{dt} = k_0[A]^0 = k_0$$

If the initial concentration of A is $[A]_0$

$$\int_{[A]_0}^{[A]} dA = -k_0 \int_0^t dt$$

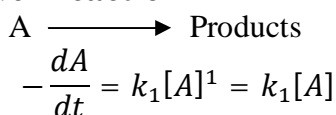
$$[A] = [A]_0 - k_0 t$$



If the concentration against the time plot is a straight line with negative slope, it is a zero order reaction and slope gives the rate constant k .

Zero-order reactions are only applicable for a very narrow region of time. Therefore, the linear graph shown in figure is only realistic over a limited time range.

2.2.2 First order reaction



If the initial concentration of A is $[A]_0$

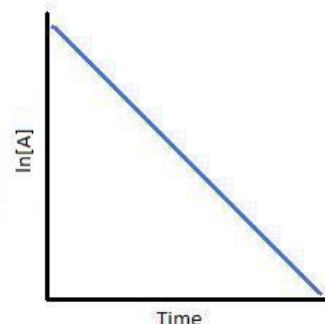
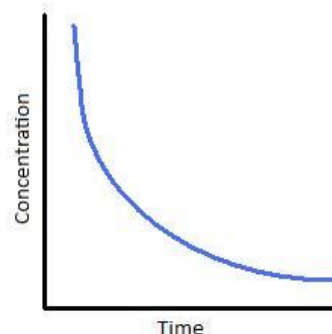
$$\int_{[A]_0}^{[A]} \frac{dA}{A} = -k_1 \int_0^t dt \quad \ln[A] - \ln[A]_0 = -k_1 t$$

$$\ln \frac{[A]}{[A]_0} = -k_1 t, \quad [A] = [A]_0 e^{-k_1 t}$$

Concentration of reactant decreases exponentially with time (when reaction progress) for first order reaction.

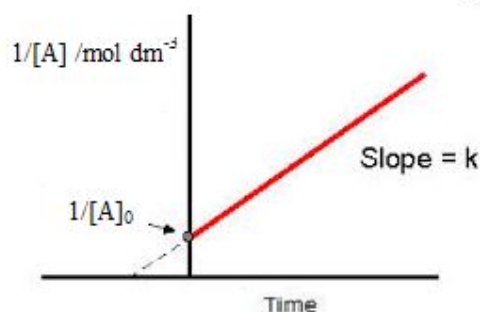
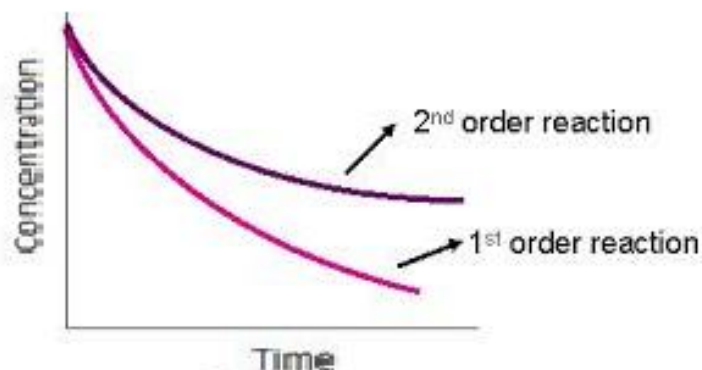
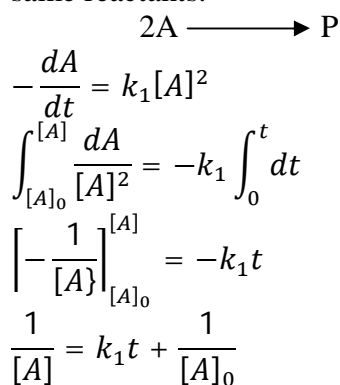
This is a test for first order reaction; we can also plot the natural logarithm of a reactant concentration versus time and see whether the graph is linear. If the graph is linear and has a negative slope, the reaction must be a first order reaction.

$$\ln[A] = \ln[A]_0 - k_1 t$$



2.2.3. Second order reaction

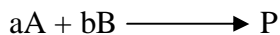
Second order reaction can either be due to two same reactants (A) or two dissimilar reactants (A and B). Let us first consider a single elementary reaction involving two same reactants.



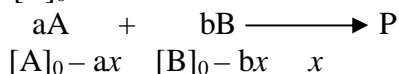
You can see that variation of concentration of reactant with the time shows an exponential decay similarly to a first order reaction. Only difference is that the second order reaction decays slowly compared to the first order reaction. Therefore we

cannot use it as a characteristic plot to test for second order reaction or first order reaction. But if we plot the $1/[A]$ against the time, it gives the characteristic linear graph with a intercept and positive slope as shown in the graph.

Now let us consider second order reaction involving two different reactants.



Let us take the concentration of the product at time t is x , and initial concentrations of A and B as $[A]_0$ and $[B]_0$.



$$Rate = -\frac{1}{a} \frac{dA}{dt} = \frac{dx}{dt} = k[A][B]$$

$$\frac{dx}{dt} = k([A]_0 - ax)([B]_0 - bx)$$

$$\int_0^x \frac{dx}{([A]_0 - ax)([B]_0 - bx)} = k \int_0^t dt$$

Using partial fractional method we can separate left term into simple form of integration.

$$\frac{1}{([A]_0 - ax)([B]_0 - bx)} = \frac{1}{(a[B]_0 - b[A]_0)} \left[\frac{a}{([A]_0 - ax)} - \frac{b}{([B]_0 - bx)} \right]$$

Then,

$$\begin{aligned} \int_0^x \frac{dx}{([A]_0 - ax)([B]_0 - bx)} &= \int_0^x \frac{1}{(a[B]_0 - b[A]_0)} \left[\frac{a}{([A]_0 - ax)} - \frac{b}{([B]_0 - bx)} \right] dx = k \int_0^t dt \\ &= \frac{1}{(a[B]_0 - b[A]_0)} \left[\int_0^x \frac{a}{([A]_0 - ax)} dx - \int_0^x \frac{b}{([B]_0 - bx)} dx \right] = kt \end{aligned}$$

$$\frac{1}{(a[B]_0 - b[A]_0)} [-\ln([A]_0 - ax) + \ln([B]_0 - bx)]_0^x = kt$$

$$\frac{1}{(a[B]_0 - b[A]_0)} \left[\ln \frac{([B]_0 - bx)^x}{([A]_0 - ax)} \right]_0^x = kt$$

$$\frac{1}{(a[B]_0 - b[A]_0)} \left[\ln \frac{([B]_0 - bx)^x}{([A]_0 - ax)} \right]_0^x = kt$$

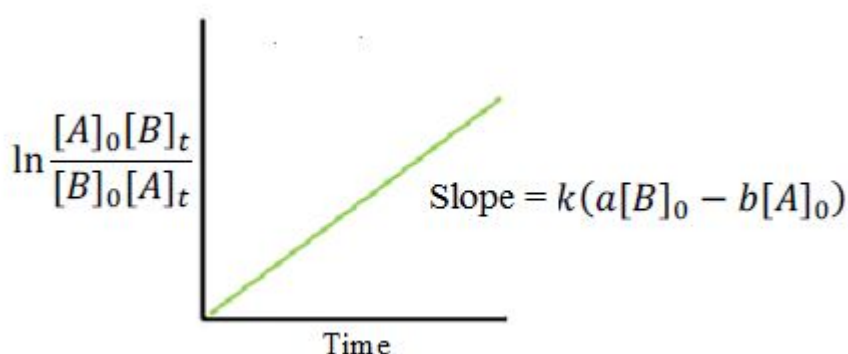
$$\frac{1}{(a[B]_0 - b[A]_0)} \ln \frac{[A]_0([B]_0 - bx)}{[B]_0([A]_0 - ax)} = kt$$

$([A]_0 - x)$ and $([B]_0 - x)$ are the concentration of A and B at time t , if we take the as $[A]_t$ and $[B]_t$, above equation can be written as,

$$\frac{1}{(a[B]_0 - b[A]_0)} \ln \frac{[A]_0[B]_t}{[B]_0[A]_t} = kt$$

$$\ln \frac{[A]_0[B]_t}{[B]_0[A]_t} = k(a[B]_0 - b[A]_0)t$$

This is a linear plot between $\ln \frac{[A]_0[B]_t}{[B]_0[A]_t}$ and time and also a characteristic of a second order reaction



3.0 Reaction Half –Life

Half-life is the time taken for the concentration of a reactant to drop to half of its original value. Therefore, the faster the reaction, the shorter the half-life, the rate of the reaction is proportional to the rate constant; thus the larger the rate constant, the shorter the half-life. Using the integrated rate law, we can express the half time of the reaction mathematically. This is also another method of determining the rate constant of a reaction.

$$\text{When } [A] = \frac{[A]_0}{2}, \text{ time } t = t_{1/2}$$

Zero order reaction:

Substituting the $[A] = \frac{[A]_0}{2}$, time $t = t_{1/2}$ for the integrated rate law equation, $[A] = [A]_0 - kt$

$$[A] = [A]_0 - kt \quad \rightarrow \quad \frac{[A]_0}{2} = [A]_0 - kt_{1/2}$$

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

You can see that half-life of zero order reaction depends on the initial concentration

First order reaction:

Integrated rate law reaction for a first order reaction is $\ln[A] = \ln[A]_0 - kt$

$$\ln[A] = \ln[A]_0 - kt \quad \rightarrow \quad kt = \ln[A]_0 - \ln[A]$$

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

$$k = \frac{2.302 \log 2}{t_{1/2}} = \frac{0.693}{t_{1/2}}$$

You can see that the half-life of a first order reaction remains constant throughout reaction and is independent of concentration. This applies to any fractional lifetime, though the half-life is the one most commonly used. The relaxation time is the other common fractional lifetime. The relaxation time is relevant only to first order reactions, and is a fractional lifetime

That is the time taken for concentration of a reactant to drop to 1/e of its original value.

$$[A] \rightarrow [A]_0/e \quad t \rightarrow \tau$$

$$\ln[A]_0 - \ln \frac{[A]_0}{e} = k\tau$$

$$\ln \frac{[A]_0}{\frac{[A]_0}{e}} = 1 = k\tau$$

$$\tau = \frac{1}{k}$$

Second order reaction:

Let us consider form of the integrated law for consider a single elementary reaction involving two same reactants. We cannot define half-life for when two reactants are different.

Integrated rate law for second order reaction is $\frac{1}{[A]} = kt + \frac{1}{[A]_0}$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0} \Rightarrow \frac{1}{[A]_{0/2}} = kt_{1/2} + \frac{1}{[A]_0}$$

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

4.0 Temperature dependence of the reaction rate

The rate of the most of the reactions increases with increase of temperature. Therefore, understanding how increase of temperature affects a reaction in molecular level is very important. On molecular level, before new products form, first relevant bonds must be broken and then new bonds should form between reactants. This means that as the reactant molecules should come together and should collide. This collision must have enough energy to initiate the bond breakage for the reaction to occur. Not all collisions will have this amount of energy. The collisions, that do not have sufficient energy to react, end up as elastic scattering. Not all collisions that have sufficient energy to react will react, because the geometry of the molecules may not be 'favorable' for reaction

Therefore we can summarize three major requirements that should be satisfied for a reaction to take place.

- 1) Collisions between reactants
- 2) Collisions with enough energy to initiate the reaction
- 3) Right orientation of colliding molecules favorable for reaction

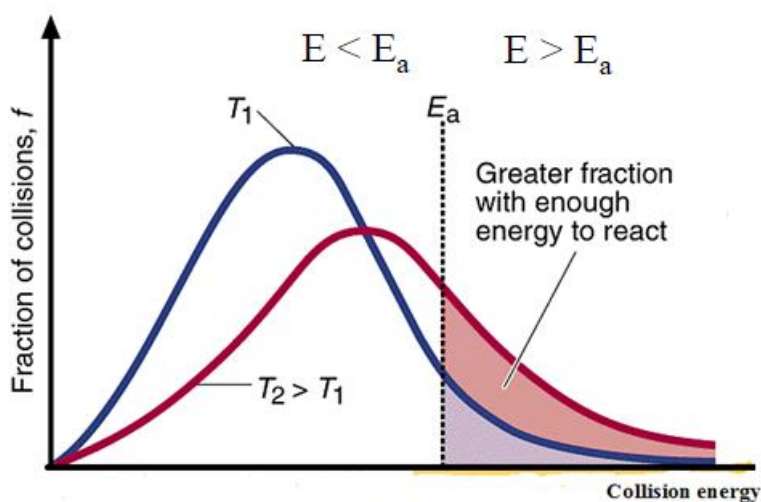
Collisions between reactants

In order for molecules to react they must collide. As temperature increases, the molecules move faster and the collision frequency increases. Therefore, the greater the number of collisions the faster the rate → reaction rate should increase with an increase in temperature.

If there are more molecules present, the probability of collision is greater → reaction rate should increase with an increase of concentration of reaction molecules.

Collisions with enough energy to initiate the reaction

Only collisions with enough energy react to form products. The energy of the system changes as the reactants approach each other. The critical amount of energy to make the reaction proceed is called the **Activation Energy, E_a** . In other words, The Activation energy is the minimum energy required to initiate a chemical reaction. This energy is used to break relevant bonds. This energy comes from thermal excitation of molecules (kinetic energy.) Molecules moving too slowly, with too little kinetic energy, don't react when they collide. According to kinetic molecular theory, at a given temperature, the molecules in any sample have a distribution of energies, with a well defined average. This energy distribution is the same distribution as the kinetic energy distribution in a gas. The energy distribution looks like following graph.



You can see when the temperature increases fraction with enough energy to react increases. The rate of the reaction should depend on the fraction of collisions that have energy in excess of this critical value (activation energy).

Right orientation of colliding molecules favorable for reaction

The orientation of a molecule during collision can have a profound effect on whether or not a reaction occurs. Not all collisions that have sufficient energy to react will react because the geometry of the molecules may not be 'favorable' for reaction. Some collisions do not lead to reaction even if there is sufficient energy.

Arrhenius Equation

Arrhenius discovered that most reaction-rate data obeyed an equation based on three factors discussed above.

- The number of collisions per unit time.
- The fraction of collisions that occur with the correct orientation.
- The fraction of the colliding molecules that have energy greater than or equal to E_a .

From these observations Arrhenius developed a mathematical expression called Arrhenius equation.

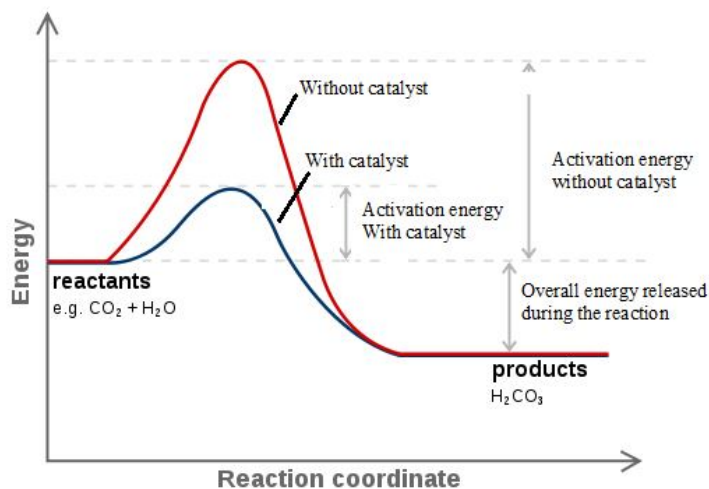
$$k \text{ (rate constant)} = Ae^{\frac{-E_a}{RT}}$$

k is the rate constant, E_a is the activation energy, R is the ideal-gas constant (8.314 J/K mol) and A is known as frequency or pre exponential factor. This frequency factor accounts for frequency of collisions and the orientation of a favorable collision probability. Both A and E_a are specific to a given reaction.

4.1 Effect of catalyst on reaction rates

A catalyst is a substance that speeds up a reaction without being consumed. Catalyst lowers the potential energy barrier between reactants and products (activation energy E_a) by providing alternative reaction mechanism (alternative pathway). In other words, catalyst forms an alternative path with lower activation energy. Catalysts increase the rate of a reaction by

- increasing the frequency factor A , or
- decreasing the activation energy, E_a (most dramatic effect) in Arrhenius Equation

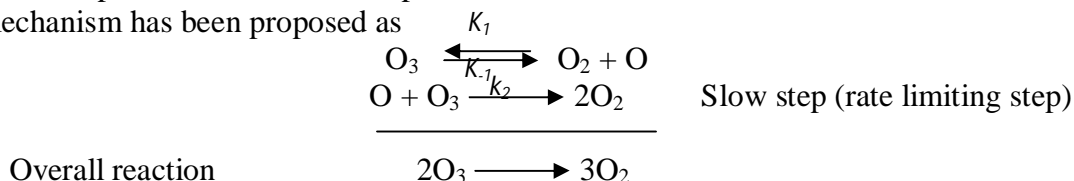


5.0 Reaction mechanism

A mechanism for a reaction is a collection of elementary processes that explains how the overall reaction proceeds. An elementary step is written to mean a single collision or molecular vibration that result in a chemical reaction. As described at the beginning of the note, molecularity says how many reactants are involved in the reaction. In general, there are three major properties that can be seen a reaction mechanism.

- 1) It exhibits a series of elementary reactions whose sum is the overall balanced equation
- 2) It may include reaction intermediates. Reaction intermediates are the chemical species that are both created and destroyed in the mechanism and cannot be seen in the overall reaction.
- 3) It includes a rate limiting step. That is an elementary reaction which is the slowest step. That means the rate of overall reaction is equal to the rate of the slowest step. Therefore this step determine the rate of the reaction and hence the rate law.

For example, consider the decomposition reaction of ozone, $2\text{O}_3 \longrightarrow 3\text{O}_2$. Reaction mechanism has been proposed as



First two reactions are elementary reactions and the overall reaction is the sum of them. O is a reaction intermediate and it is found that the second reaction is the rate determine step.

The Steady-State Approximation

The steady-state approximation states that the concentration of an intermediate is generally small and slowly varying. As a result, the rate of change of its concentration (the time dependence of its concentration) is approximated to be zero.

In above example, rate of the second reaction governs the rate of the overall reaction because it is the slowest step ($k_{-1} \gg k_2$). Then the rate law of the reaction is

$$\text{rate} = k_2[\text{O}_3][\text{O}]$$

O is an intermediate, according to the steady state approximation, rate of change of its concentration is zero;

$$\frac{d[\text{O}]}{dt} = k_1[\text{O}_3] - k_{-1}[\text{O}_2][\text{O}] - k_2[\text{O}][\text{O}_3] = 0$$

$$k_1[\text{O}_3] = (k_{-1}[\text{O}_2] + k_2[\text{O}_3])[\text{O}]$$

$$[\text{O}] = \frac{k_1[\text{O}_3]}{(k_{-1}[\text{O}_2] + k_2[\text{O}_3])}$$

Substituting this to the rate law equation above, we get the theoretical expression for rate law.

$$\text{rate} = \frac{k_2 k_1 [\text{O}_3]^2}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]}$$

Experimentally determined rate law, $\text{rate} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}$.

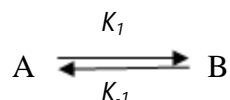
Above mechanism is proposed according to the observed rate law. We can obtained experimentally observed rate law by considering the fact that above equilibrium can take place only if $k_{-1} \gg k_2$.

$$\text{rate} = \frac{k_2 k_1 [\text{O}_3]^2}{k_{-1} [\text{O}_2] + k_2 [\text{O}_3]} = \frac{k_2 k_1 [\text{O}_3]^2}{k_{-1} [\text{O}_2]} = k \frac{[\text{O}_3]^2}{[\text{O}_2]}, \text{ where } k = \frac{k_1 k_2}{k_{-1}}$$

There are three major ways that the most of the complicated reactions can be break down into elementary reactions.

5.1 Opposing or reversible reaction

Products of the chemical reaction react together to form original reactant, because of the reversibility, this kind of reaction does not go to completion. Two steps, forward and backward are considered as elementary reaction in proposing reaction mechanism. Overall (or net reaction) rate eventually reach to zero as forward and backward reactions rate become equals at the equilibrium point.



k_1 is the rate constant for forward reaction and k_{-1} is the rate constant for backward reaction.

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

Let us consider that initial concentration of A = $[A]_0 = a$, and concentration of B after time t is x . Also the concentration of B at the equilibrium is x_e that is

Concentration at time	$t=0,$	a	0
Concentration at time	$t=t,$	$a-x$	x
Concentration at the equilibrium	$t=t_e$	$a-x_e$	x_e

At equilibrium, $-\frac{d[A]}{dt} = k_1(a - x_e) - k_{-1}(x_e) = 0$

$$k_{-1} = \frac{k_1(a - x_e)}{x_e}$$

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}x$$

$$\frac{dx}{dt} = k_1(a - x) - \frac{k_1(a - x_e)}{x_e}x$$

$$\frac{dx}{dt} = \frac{k_1a(x_e - x)}{x_e}$$

$$\int_0^x \frac{dx}{(x_e - x)} = \frac{k_1a}{x_e} \int_0^t dt$$

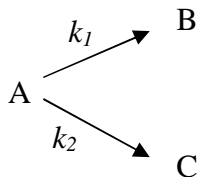
$$\ln \frac{x_e}{(x_e - x)} = \frac{k_1at}{x_e}$$

Examples for reversible reactions are



5.2 Parallel reaction (competing or side reaction)

A substance reacts or decomposes in two different ways forming two or more different products.



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

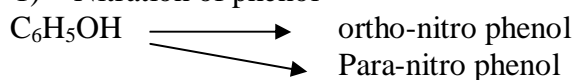
If the concentration of A at time $t = 0$ is a and $t = t$ is $(a-x)$

$$\begin{aligned}
 -\frac{d[A]}{dt} &= \frac{dx}{dt} = (k_1 + k_2)(a - x) \\
 \int_0^x (a - x)dx &= (k_1 + k_2) \int_0^t dt \\
 k &= (k_1 + k_2) = \frac{1}{t} \ln \frac{a}{a-x}
 \end{aligned}$$

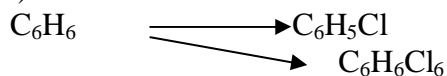
k can be determined by measuring the change in the concentration of A with time

Examples for parallel reactions

1) Nitration of phenol

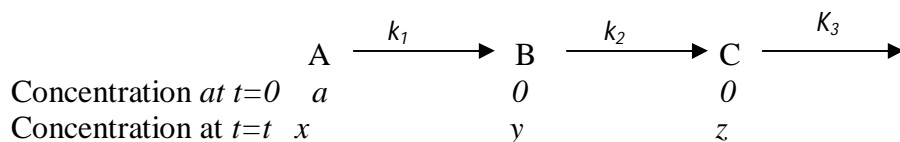


2) Combination of benzene with chlorine



6.3 Consecutive reaction

A consecutive reaction proceeds from reactant to final product through two or several intermediate stages. The overall reaction is a result of several consecutive steps (successive steps).



$$\begin{aligned}
 \text{Rate of disappearance of A, } -\frac{dx}{dt} &= k_1x \Rightarrow \int_a^x \frac{1}{x} dx = -k_1 \int_0^t dt \\
 \ln x/a &= -k_1t \text{ or } x = ae^{-k_1t}
 \end{aligned}$$

$$\text{Net rate of consumption of B, } -\frac{dy}{dt} = k_2y - k_1x$$

$$\text{Substituting value for } x, -\frac{dy}{dt} = k_2y - k_1ae^{-k_1t}$$

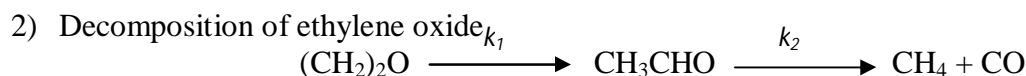
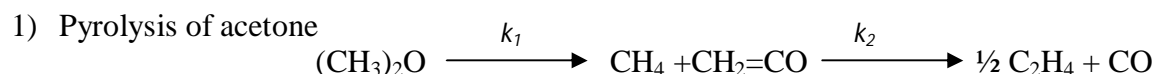
This is a linear equation of first order whose solution is

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

Since there is no net change in number of moles during the course of reaction, so sum the sum of moles A, B and C at time t .

$$\begin{aligned} x + y + z &= a \quad \rightarrow \quad z = a - (x + y) \\ z &= a - a e^{-k_1 t} - \frac{k_1 a}{(k_2 - k_1)} [e^{-k_1 t} - e^{-k_2 t}] \\ z &= a \left[1 - \frac{[k_2 e^{-k_1 t} - k_1 e^{-k_2 t}]}{(k_2 - k_1)} \right] \end{aligned}$$

Examples for consecutive reactions

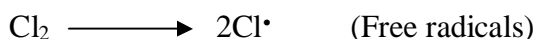


6.0 Chain reactions

Chain reaction is a chemical process in which the products of the reaction assist in promoting the process itself. Few examples for chain reactions are reaction between H_2 and Cl_2 in presence of light, dehydrogenation of ethane to ethane, addition polymerization reactions, atomic fission, etc. A chain reaction is mainly characterized by four steps, initiation, propagation, retardation and termination steps.

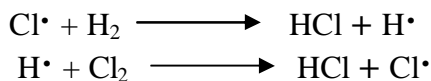
i) Initiation step

This is the first step in which reaction inter mediates are formed. These reaction intermediates are called chain carriers because they assist in propagation of chain reaction. Chain carriers may be radicals, ions or neutrons. There is an induction period in this step. In this period reaction is comparatively slow.



ii) Propagation step

The chain carriers produced in the initiation step attack other reactant molecules, thereby producing a new chain carrier in each attack.

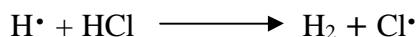


In some cases, each attack yield more than one chain carriers. This is known as branching step. An example is attack of oxygen atom having two unpaired electrons to H_2O .



iii) Retardation step

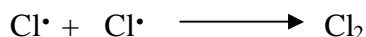
The chain carriers can attack product molecule also. Then it reduces the net rate of the formation of the product.



Not that the in retardation step it does not end the chain because as in this example it produces another chain carrier.

iv) Termination step

In this step, the chain carriers combine and end the chain

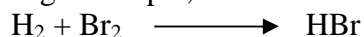


Features of chain reactions

- i) Every chain reaction involves initial slow step. In this period, it generates active intermediate species which facilitates the fast propagation steps.
- ii) In all non chain reaction, the rate is highest in the beginning but falls off with time but in chain reactions, initial rate is zero, then rises to maximum and finally decreases with time.
- iii) Chain reactions are highly influenced by pressure or concentrations of reactants.
- iv) Every chain reaction has an induction period

6.1 Stationary or non branching chain reaction

In this case there is only one chain carrier is produced in the propagation step for each free radical reacting. Example,



One may write the rate equation taking as second order kinetics, $\frac{d[\text{HBr}]}{dt} = k_2[\text{H}_2][\text{Br}_2]$ but experimentally it has been found that it has a more complicated form.

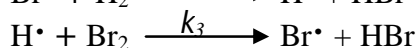
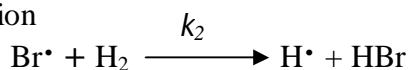
$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k' \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

Therefore it is proposed that this reaction follows a *radical chain mechanism*.

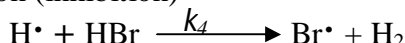
1 Initiation



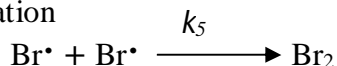
2 Propagation



3 Retardation (inhibition)



4 Termination



Reaction rate can be expressed by using the rate of change in production of HBr

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Br}_2] - k_4[\text{H}\cdot][\text{HBr}] \quad \text{-----(1)}$$

$\text{Br}\cdot$ and $\text{H}\cdot$ are intermediates. Rate of change of these species is zero (Steady state approximation).

$$\frac{d[\text{Br}\cdot]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}\cdot][\text{H}_2] + k_3[\text{H}\cdot][\text{Br}_2] + k_4[\text{H}\cdot][\text{HBr}] - 2k_5[\text{Br}\cdot]^2 \approx 0 \quad \text{-----(2)}$$

$$\frac{d[\text{H}\cdot]}{dt} = k_2[\text{Br}\cdot][\text{H}_2] - k_3[\text{H}\cdot][\text{Br}_2] - k_4[\text{H}\cdot][\text{HBr}] \approx 0 \quad \text{-----(3)}$$

Terms shown in equation (2) is zero according to the equation (3)

$$\text{Therefore, } 2k_1[Br_2] - 2k_5[Br\cdot]^2 = 0 \Rightarrow [Br\cdot] = \sqrt{\frac{k_1}{k_5}}[Br_2]$$

Substituting this into equation (3) then we can solve for $[H\cdot]$

$$[H\cdot] = \frac{k_2[Br\cdot][H_2]}{k_3[Br_2] + k_4[HBr]}$$

$$[H\cdot] = \frac{k_2[H_2]\sqrt{\frac{k_1}{k_5}}[Br_2]}{k_3[Br_2] + k_4[HBr]}$$

Then we can substitute these into equation (1) so that the rate equation becomes

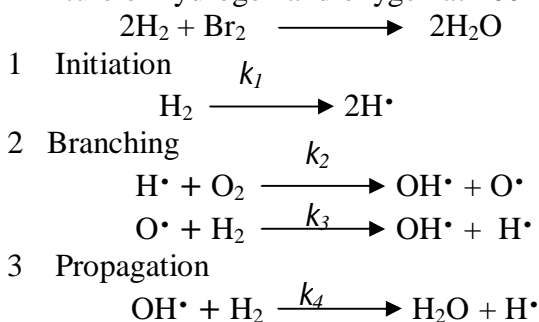
$$\frac{d[HBr]}{dt} = \frac{2k_2\sqrt{\frac{k_1}{k_5}}[H_2][Br_2]^{1/2}}{1 + \frac{k_4[HBr]}{k_3[Br_2]}}$$

$$2k_2\sqrt{\frac{k_1}{k_5}} = k \text{ and } \frac{k_4}{k_3} = k'$$

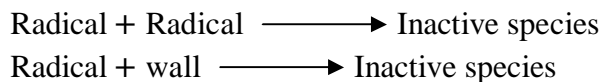
$$\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'\frac{[HBr]}{[Br_2]}}$$

6.2 Non-stationary or branching chain reaction

Each propagation step produces more than one chain carrier. This results in branching chains. Therefore number of chain carriers increases rapidly. A good example for this is combustion of 2: 1 mixture of hydrogen and oxygen at 460°C with increasing pressure.



7.0 Termination



Reference

- 1) Engineering Chemistry, 15th edition, T. Jain and J. Jain, Dhanpat Rai Publishing, New Delhi, 2006
- 2) Physical Chemistry, P. W. Atkins

Tutorial

- 1) In the reaction; $A + B \longrightarrow \text{product}$, the rate is doubled when the concentration of B is doubled and the rate increase by a factor of 8 when the concentrations of both the reactants are doubled. Find the order of the reaction with respect to each species.
- 2) The kinetics of the catalytic decomposition of hydrogen peroxide in aqueous solution has been studied. During the decomposition, H_2O_2 concentration was measured by titrating aliquot of the reaction sample with potassium permanganate in acidic medium. Show that the decomposition reaction follows the first order kinetic and calculate the first order rate constant.

Time/min	0	5	15	25	45
cm^3 of KMnO_4	37.0	29.8	19.6	12.3	5.0

- 3) In a second order reaction involving same reactants, half of the reactants consumed in 60 minutes. If the rate constant is $5.2 \times 10^{-3} \text{ mol}^{-1} \text{L minute}^{-1}$. What is the initial concentration?
- 4) Derive the integrated rate law equation, half life expression for a first order reaction and hence show that the time taken for 99.9% of the reaction to take place is about ten times that taken for half the reaction to take place.
- 5) When the initial concentration is changed from 0.50 to 1.0 mol dm^{-3} , the time of half-completion of a certain reaction is found to change from 50 s to 25s. Calculate the time taken for the concentration to be reduced to 20 percent of the initial value.
- 6) At 300 K, a first order reaction is 50 % completed in 20 minutes. At 350 K, the same reaction is 50 % completed in 5 minutes. Calculate the activation energy of the reaction.
- 7) The first order decomposition of N_2O_4 into NO_2 has a k value of $4.5 \times 10^3 \text{ s}^{-1}$ at 10C and activation energy of 58 kJ mol^{-1} . At what temperature is half-life would be $6.93 \times 10^{-5} \text{ s}$.
- 8) Consider a gaseous decomposition reaction, $A \longrightarrow \text{Products}$ at 500°C and at an initial pressure of 350 torr. The rate of the reaction was 1.07 torr s^{-1} when 5% of the decomposition was over and 0.76 torr s^{-1} , when 100% decomposition was over. Determine the order of the reaction.
- 9) For the reaction $2\text{NO} + \text{Cl}_2 \rightleftharpoons 2\text{NOCl}$, the following mechanism has been proposed.

Step 1 $\text{NO} + \text{Cl}_2 \xrightleftharpoons[k_{-1}]{k_1} \text{NOCl}_2$

Step 2 $\text{NO} + \text{NOCl}_2 \xrightarrow{k_2} 2\text{NOCl}$

Show that the overall rate of the reaction is $k[\text{NO}]^2[\text{Cl}_2]$