

UNIT -1

Basics of Reactor Design

BASIC REACTION THEORY

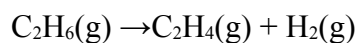
A chemical reaction is a process that leads to the transformation of one set of chemical substances to another. The substance (or substances) initially involved in a chemical reaction are called reactants or reagents. Chemical reactions are usually characterized by a chemical change and they yield one or more products which usually have properties different from the reactants. Reactions often consist of a sequence of individual sub-steps, the so-called elementary reactions, and the information on the precise course of action is part of the reaction mechanism. Chemical reactions are described with chemical equations which symbolically present the starting materials, end products, and sometimes intermediate products and reaction conditions.

Chemical reactions happen at a characteristic reaction rate at a given temperature and chemical concentration. Typically, reaction rates increase with increasing temperature because there is more thermal energy available to reach the activation energy necessary for breaking bonds between atoms.

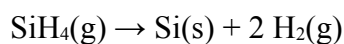
CLASSIFICATION OF REACTIONS

Reactions may be classified by (a) the number of phases involved, (b) the presence or absence of a catalyst, and (c) the nature of the overall reaction.

If all the reactants and products, and catalysts, if any, are in a single phase, the reaction is said to be homogeneous. An example is provided by the thermal cracking of ethane to ethylene

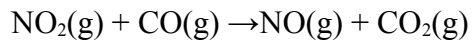


On the other hand, if more than one phase is involved, the reaction is said to be heterogeneous. An example is provided by the chemical vapour deposition (CVD) of Si on a substrate

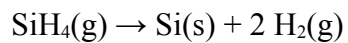


Thermal cracking of ethane to ethylene represents a non-catalytic reaction, whereas ammonia synthesis involves a solid catalyst. In some cases, a homogeneous catalyst may be involved. For

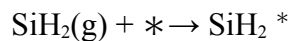
example, an enzyme called glucose isomerase catalyzes the isomerization of glucose to fructose in the liquid phase. It can be noted that this is the largest bioprocess in the chemical industry. As fructose is five times sweeter than glucose, the process is used to make high-fructose corn syrup for the soft drink industries. The overall reaction, as written, may represent either an elementary reaction or a non-elementary reaction. An example of the former is given by the gas-phase reaction



Here NO is formed by the collision between molecules of NO₂ and CO, and the rate expression conforms to the stoichiometry shown. On the other hand,



represents a non-elementary reaction, as it actually proceeds by the sequence of reactions shown below



Irreversible Reactions: Reactions that proceed unidirectionally under the conditions of interest

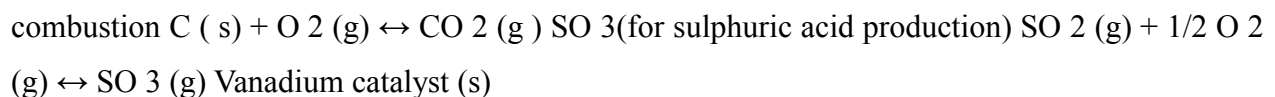
Reversible Reactions: Reactions that proceed in both forward and reverse directions under conditions of interest. $\text{SO}_2 + 0.5 \text{O}_2 \rightleftharpoons \text{SO}_3$ $\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}$ $\text{H}_2\text{S} \rightleftharpoons \text{H}_2 + 1/2 \text{S}_2$

Thermodynamics tells us that all reactions are reversible. However, in many cases the reactor is operated such that the rate of the reverse reaction can be considered negligible.

Homogeneous Reactions: reactions that occur in a single-phase (gas or liquid) NO_x formation



Heterogeneous Reactions: reactions that require the presence of two distinct phases Coal



Single and Multiple reactions:

Single reaction: When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, then it is said to be 'single reaction'. Multiple reactions: When more than one stoichiometric equation is chosen to represent the observed changes, then more than one kinetic expression is needed to follow the changing composition of all the reaction components, it is said to be 'multiple reactions'. Multiple reactions may be classified as; Series reactions, Parallel reactions, and SeriesParallel reactions.

Elementary and Non- Elementary reactions

The reactions in which the rate equation corresponds to a stoichiometric equation are called elementary reaction. The reactions in which there is no correspondence between stoichiometry and rate equation are known as Non-elementary reaction

Kinetic Models of Non- Elementary reactions

Free radicals, ions and polar substances, molecules, transition complexes are the various intermediates that can be formed in a non-elementary reaction.

In testing the kinetic models that involve a sequence of elementary reaction, we hypothesize the existence of two types of intermediates; Type-I: An unseen and unmeasured intermediate 'X' usually present at such small concentration that its rate of change in the mixture can be taken to be zero. Thus, we have $[X]$ is small and $d[X]/dt = 0$. This is called the '**steady-state approximation**'. Type-II: Where a homogeneous catalyst of initial concentration C_0 is present in two forms, either as free catalyst 'C' or combined in an appreciable extent to form the intermediate 'X', an accounting for the catalyst gives $[C_0] = [C] + [X]$. We then also assume that either $(dX/dt) = 0$ or that the intermediate is in equilibrium with its reactants. Using the above two types of approach, we can test the kinetic model or search a good mechanism; Trial and error procedure is involved in searching for a good mechanism.

REACTIONRATEANDKINETICS

Reactionrate

The rate expression provides information about the rate at which a reactant is consumed. Consider a single phase reaction $aA + bB \rightarrow rR + sS$. Rate of reaction is defined as number of moles of reactant disappearing per unit volume per unit time

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = \frac{\text{(amount of A disappearing)}}{\text{(volume) (time)}}, \quad \frac{\text{mol}}{\text{m}^3 \cdot \text{s}}$$

In addition, the rates of reaction of all materials are related by

$$-r_A = -\frac{1}{a} \frac{dN_A}{dt} = -\frac{1}{b} \frac{dN_B}{dt} = \frac{1}{c} \frac{dN_R}{dt} = \frac{1}{d} \frac{dN_S}{dt}$$

Rate constant k

When the rate expression for a homogeneous chemical reaction is written in the form

$$-r_A = kC_A^a C_B^b \dots C_D^d, \quad a+b+\dots+d = n$$

The dimensions of the rate constant k for the n th order reaction are

$$(\text{time})^{-1}(\text{concentration})^{1-n}$$

Which for a first order reaction becomes

(time)⁻¹

Factors affecting rate of reaction

Many variables affect the rate of reaction of a chemical reaction. In homogeneous systems the temperature, pressure, and composition are obvious variables. In heterogeneous systems, material may have to move from phase to phase during reaction; hence, the rate of mass transfer can be important. In addition, the rate of heat transfer may also become a factor. In short, the variables affecting the rate of the reaction are (1) temperature (2) Pressure and (3) Composition of materials involved.

Various forms of rate equation

Based on unit volume of the reaction mixture

$$r_i = \frac{1}{V} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid}) (\text{time})}$$

Based on unit mass in fluid-solid system

$$r'_i = \frac{1}{W} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid}) (\text{time})}$$

Based on unit surface of solid in fluid-solid system or unit interfacial area in two fluid systems

$$r''_i = \frac{1}{S} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface}) (\text{time})}$$

Based on unit volume of solid in fluid-solid system

$$r'''_i = \frac{1}{V_s} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid}) (\text{time})}$$

Based on unit volume of reactor when different from unit volume of the reaction mixture

$$r''''_i = \frac{1}{V_r} \frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor}) (\text{time})}$$

Rates defined on various basis are interchangeable and the following may be shown

$$\left(\frac{\text{volume}}{\text{of fluid}}\right) r_i = \left(\frac{\text{mass of}}{\text{solid}}\right) r_i' = \left(\frac{\text{surface}}{\text{of solid}}\right) r_i'' = \left(\frac{\text{volume}}{\text{of solid}}\right) r_i''' = \left(\frac{\text{volume}}{\text{of reactor}}\right) r_i''''$$

or

$$Vr_i = Wr_i' = Sr_i'' = Vr_i''' = V_r r_i''''$$

Power law kinetics is simply put rate is proportional to concentration of species 1 to the power q_1 concentration of species 2 to the power q_2 . So, products of all the, such C_1 raise to q_1 C_2 raise to q_2 , up to C_N raise to q_N . In a compact form, we can express this as rate equal to K , K is that proportionality constant, product of C_j raise to q_j , j going from 1 to N . So, q_j is the order of the reaction with respect to species A_j ; and this is the simplest form of form of power law power law kinetics. Now, we call this q_j as order with respect to A_j and if you sum up all these q_j s, we get q , what we call as overall overall order. reaction of hydrogen iodide getting decomposed to H_2 plus I_2 . Now, it turns out for this particular reaction, the rate of reaction is proportional to concentration of hydrogen iodide raise to power 2. So, clearly in this case, q is 2 there is only one species in the reactant side, so our q_j and q_r q_r are same. So, this is the this is the order of the reaction, so q can be integer. Let us take another example, decomposition of acetaldehyde to give us methane and carbon monoxide. Now, it turns out the rate of these reactions is proportional to concentration of acetaldehyde raise to power 3 by 2. So, q in this case is 3 by 2, or in other words, orders can be integers, they can be even fractions.

Molecularity

It is the number of molecules taking part in the reaction

e.g. $A \rightarrow C$: Unimolecular reaction

$A + B \rightarrow C$: Bimolecular reaction

Order

It is defined as the sum of the powers to which the concentration terms are raised. The overall kinetic order of a reaction is defined by how many concentrations appear on the right side of the rate expression. The order of the reaction with respect to a particular species is defined by whether that species appears one or more times. For example, if the right side of the rate law is $[A]^m[B]^n$, then the overall order of the reaction is $m+n$ and the reaction is m 'th order with respect to $[A]$ and n 'th order with respect to $[B]$. Zeroth order means that the reaction rate does not change as the concentration of a species is changed. There are no biochemical reactions that are zeroth order overall.

e.g. $A + B \rightarrow C$

$$-r_A = kC_A C_B$$

$$n(\text{order}) = 1+1=2$$

Concentration dependent term of rate equation

Rate of reaction is defined as number of moles of reactant disappearing per unit volume per unit time

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt}$$

If constant volume systems are considered, the rate of reaction is modified to

$$-r_A = -\frac{dC_A}{dt}$$

The definition of rate of a chemical reaction describing change in molar concentration with respect to time, i.e., is not general and valid only when the volume of the mixture

does not change during the course of the reaction. This may be only true for liquid phase reactions where volume changes are not significant. The volume of a gas also changes due to changes in operating conditions (temperature and pressure) in addition to changes in number of moles.

Rate equation in terms of partial pressure

For isothermal (elementary) gas reactions where the number of moles of material 'r' to the changes during reaction, the relation between the total pressure of the system 'P' changing concentration or partial pressure of any of the reaction component is $r R + s S + \dots a A + b B + \dots$ $p_A = C_A R T = p_{Ao} - [(a/ r) - n]$ (For the component 'A', $p_A = C_A R T = p_{Ao} - [(a/ r) - n]$) (For the component 'R', $p_R = C_R R T = p_{Ro} + [(r/ r) - n]$ And the rate of the reaction, for any component 'i', is given by $r_i = (1/RT) (dp_i/dt)$

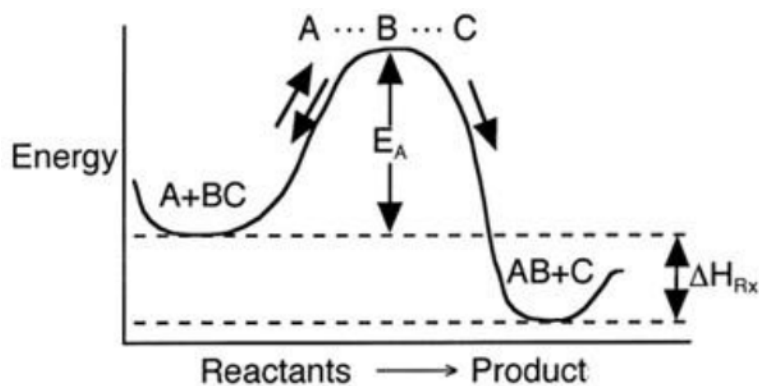
EFFECT OF TEMPERATURE ON REACTION

Temperature dependency from Arrhenius law

For many reactions and particularly elementary reactions, the rate expression can be written as a product of a temperature . The excess energy of the reactants required to dissociate into products is known as activation energy. The temperature dependency on the reaction rate constant is given by Arrhenius Law. That is, $k = k_0 e^{-E/RT}$ Where k = rate constant, k_0 = frequency factor, E = Activation energy The temperature dependence of the rate constant k is usually fitted by the **Arrhenius equation** . Arrhenius equation is frequently applied to approximate the temperature dependency of reaction rate and the rate constant or velocity constant, k , is related to temperature, T , by the following expression:

$$k = k_0 e^{-E/RT}$$

Where, k_0 = pre-exponential factor and has units similar to that of k . E_a = activation energy, $J \cdot mol^{-1}$.



where the pre-exponential factor k_0 and the activation energy E are treated as constants and T is the absolute temperature. If a plot of $\ln k$ versus $1/T$ shows a significant curvature, the rate constant k is a function of temperature

$$k = k_0 e^{-E_a/RT}$$

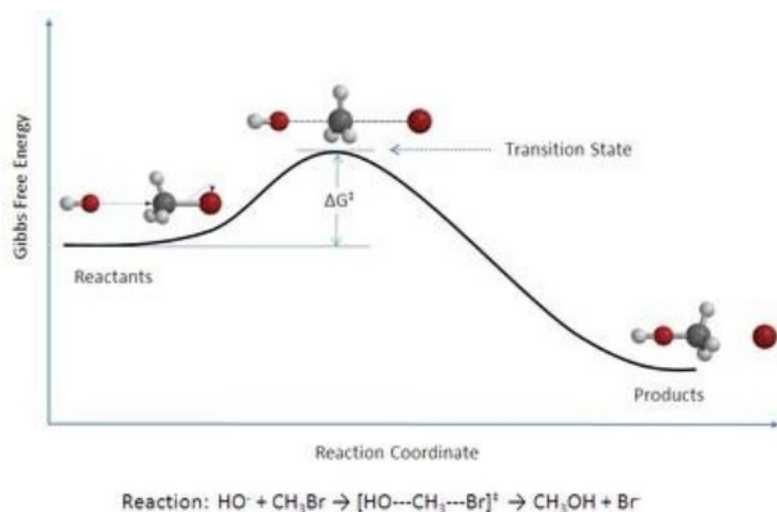
The higher the temperature the more molecules that have enough energy to make it over the barrier Arrhenius Plot $k = A \exp(-E_a/RT)$ $\ln k = \ln A - E_a/RT$ straight line plot $y = b + mx$ $y = \ln k$ $x = 1/T$ $b = \ln A$ $m = -E_a/R$ Plot $\ln k$ vs $1/T$, slope = $-E_a/R$ intercept = $\ln A$. A plot of $\ln k$ vs $1/T$ will be straight line, the slope of which is E_a/R . The units of the slope are K. A large slope of Arrhenius plot means large value of E_a and vice versa. Reactions having large value of E_a are more temperature sensitive while with low value of E_a are less temperature dependent.

Transition state theory

Transition state theory (TST) explains the reaction rates of elementary chemical reactions. The **theory** assumes a special type of chemical equilibrium (quasi-equilibrium) between reactants and activated **transition state** complexes. Describes the flow of systems from reactants-

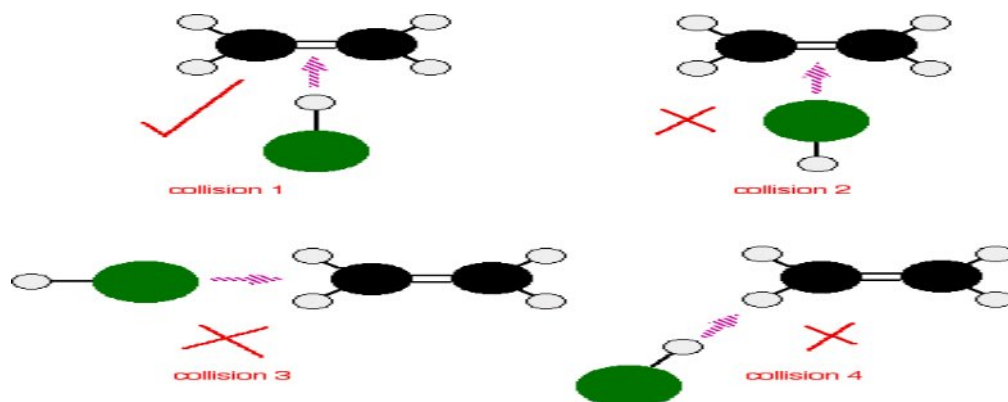
to-products over potential energy surfaces. Predicts the rate of an elementary equation in term of reactant concentration .

$$k = T A e^{-E_a/RT}$$



Collision theory This theory was proposed by Trautz (1916) and Lewis (1918) for gas phase reactions. It is based on the kinetic theory of dilute gases. Consider an elementary reaction of the form $\text{A}_1 + \text{A}_2 \rightarrow \text{products}$. The reaction rate, i.e the number of molecules of A_1 consumed per unit volume per unit time is assumed to be equal to the number of collisions per unit volume per unit time between molecules of A_1 and A_2 . The latter may be estimated as follows. Using the Maxwell-Boltzmann velocity distribution for each species, the activation energy can be found from

$$k = T^{1/2} A e^{-E_a/RT}$$



Constant volume reactions

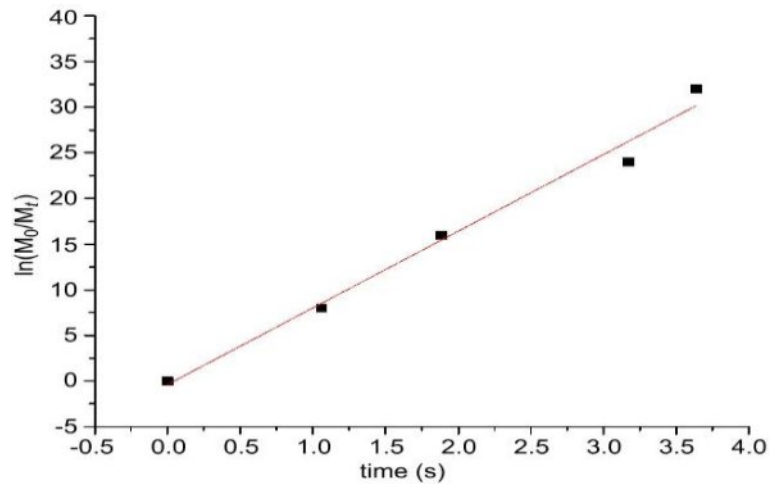
1. Integral method
2. Differential method

METHOD OF ANALYSIS OF DATA

Integral method

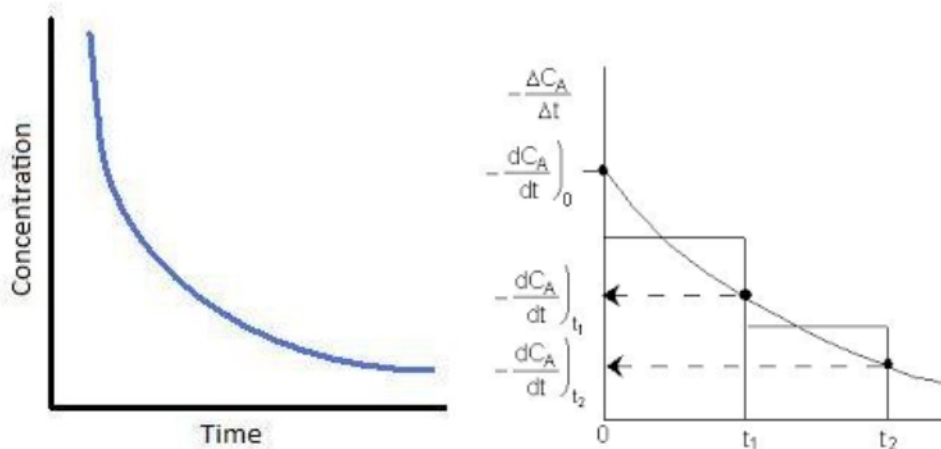
General Procedure

The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted C versus t curve with the experimental C versus t data. If the fit is unsatisfactory, another rate equation is guessed and tested. This procedure is shown in the figure. It should be noted that the integral method is especially useful for fitting simple reaction types corresponding to elementary reactions.



Differential method

Plot the concentration versus time data and then carefully draw a smooth curve to represent the data. This curve will most likely not pass through all experimental points. Determine the slope of the curve at suitably selected concentration values. These slopes are rates of the reactant at particular concentration. Search for a rate expression to represent this rate versus concentration data either by fitting and testing a particular rate equation or by trail and error method or by testing the nth order equation.



Irreversible Unimolecular-type first order reaction**First order (unimolecular) reaction:**

Suppose we wish to test the first-order rate equation of the following type, for this reaction.



Rate Law: $-d[A]/dt = k[A]$

Integrated solution: $\int d[A]/[A] = -k \int dt \ln [A] = -kt + \ln [A_0] \quad [A] = [A_0] e^{-kt}$

Separating and integrating we obtain a plot of $\ln (1 - X_A)$ or $\ln (C_A/C_{A0})$ vs. t , a straight line through the origin for this form of rate of equation. If the experimental data seems to be better fitted by a curve than by a straight line, try another rate form because the first-order reaction does not satisfactorily fit the data.

Fractional conversion X_A

Fractional conversion of a reactant A is defined as fractional reactant converted into product at any time. It is given by the equation, $X_A = (N_{A0} - N_A) / N_{A0}$ Where 'NAO' is the initial no. of moles of reactant 'A' at $t = 0$. 'NA' is the remaining no. of moles of reactant at any time 't' in the reaction.

Irreversible Unimolecular-type second order reaction**Second-order reaction (dimerization) (like molecules)**

Rate Law: $-d[A]/dt = k[A]^2$

Integrated solution: $\int d[A]/[A]^2 = -k \int dt \quad 1/[A] = k(t) + 1/[A_0] \quad [A] = A_0/(A_0kt + 1)$

The equation is a hyperbolic equation, and second-order, dimerization kinetics are often called hyperbolic kinetics.

Bimolecular reactions with different reactants: (unlike molecules)

Reaction: $A+B \rightarrow AB$

Rate Law: $-d[A]/dt = -d[B]/dt = k[A][B]$

Integrated solution:

$$-r_A = C_{AO} \frac{dX_A}{dt} = k(C_{AO} - C_{AO}X_A)(C_{BO} - C_{BO}X_A)$$

Let $M = C_{BO}/C_{AO}$ be the initial molar ratio of reactants, we obtain

$$-r_A = C_{AO} \frac{dX_A}{dt} = kC_{AO}^2 (1-X_A)(M-X_A)$$

after breakdown into partial fractions, integration and rearrangement, the final result in a number of different forms is

$$\ln(1-X_B/1-X_A) = \ln(M-X_A/M(1-X_A)) = \ln C_B C_{AO} / C_{BO} C_A = \ln C_B / M C_A = C_{AO} (M-1)kt = (C_{BO} - C_{AO})kt$$

$$M \neq 1$$

A linear plot will be obtained between the concentration function and time for this second order rate law.

Half life

The half-life ($t_{1/2}$) for a reaction is the time required for half of the reactants to convert to products.

For a first-order reaction, $t_{1/2}$ is a constant and can be calculated from the rate constant as:

$$t_{1/2} = -\ln(0.5)/k = 0.693/k$$

Pseudo First order reaction

A second order rate equation which follows the first order rate equation is defined as pseudo First order reaction. Example: Ester hydrolysis. $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$
(A) (B) (C) (D) When $C_{BO} \gg C_{AO}$, Concentration of H_2O is very large, $-r_A = -dC_A/dt = k' C_A$

Zero order reaction

When the rate of the reaction is independent of the concentration of the reactants, it is called as Zero order reaction. Example: Decomposition of HI

Third-order reaction

An irreversible trimolecular-type third-order reaction may fall on two categories; Products with corresponding rate equation(1) The reaction $A + B + D \rightarrow A + B + D$ $-r_A = - (dC_A/dt) = k C_A C_B C_D$. If C_{D0} is much greater than both C_{A0} and C_{B0} , the reaction becomes second order. Products with corresponding rate equation(2) The reaction $A + 2B \rightarrow A + 2B$ $-r_A = - (dC_A/dt) = k C_A C_B^2$.

nth order

The empirical rate equation of nth order, $-r_A = - dC_A/dt = k C_A^n$ (constant volume). Separating the variables and integrating, we get $C_A^{1-n} - C_{A0}^{1-n} = (n-1) k t$. Case i) $n > 1$, $C_{A0}^{1-n} = (1-n) k t$. The slope is $(1-n) k$ is negative Or the time decreases. Case ii) n

STEADY-STATE APPROXIMATION

The kinetics of reactions of this type can also be analyzed by writing the overall expression for the rate of change of B and setting this equal to 0. By doing this, we are making the assumption that the concentration of B rapidly reaches a constant, steady-state value that does not change appreciably during the reaction. $d[B]/dt = k_1[A] - k_{-1}[B] - k_2[B] = k_1[A] - (k_{-1} + k_2)[B] = 0$ $(k_{-1} + k_2)[B] = k_1[A]$ $[B] = (k_1)/(k_{-1} + k_2) [A]$ substituting into $d[C]/dt = k_2[B]$ gives: $d[C]/dt = (k_1 k_2)/(k_{-1} + k_2) [A]$ now if $k_{-1} \gg k_2$ $d[C]/dt \approx (k_1 k_2)/(k_{-1}) [A]$, if $k_2 \gg k_{-1}$ $d[C]/dt \approx (k_1 k_2)/(k_2) [A] = k_1[A]$

Limiting reactant

Usually in a reaction, one of the reactants is present in excess to that required stoichiometrically. If the reactants are added in stoichiometric amounts, there is no point using the concept of limiting reactant. The limiting reactant is the one which is consumed first and may be indicated by dividing the number of moles of each reactant in feed to the corresponding stoichiometric amount (from a balanced chemical equation) of the reactant. The reactant with the lowest ratio is the limiting reactant and will be the first to fully consumed in the reaction, if the reaction goes to completion.

Constant volume and Variable volume

Constant volume method: It refers to the volume of reaction mixture, and not the volume of reactor. It actually means a constant density reaction system, that is, the composition of reaction mixture is constant. Most of the liquid phase as well as gas phase reactions occurring in a constant volume bomb fall in this class. In a constant volume system, the measure of reaction rate of component 'i' (reactant or product) becomes $r_i = (1/V) (dN_i / dt) = dC_i / dt$. Conversion of reactant 'A' in this method is given by $X_A = 1 - (C_A/C_{A0})$. Variable volume method: It actually means the composition of reaction mixture varies with time by the presence of inerts. Gas phase reactions involving the presence of inerts or of impure reactants occurring in a reactor fall in this class. The measure of reaction rate of component 'i' (reactant or product), in this method, is $[d(\ln V) / dt]$. becomes $r_i = (C_{i0} / V_0) [d(\ln V) / dt]$. In variable volume system, the fractional change in volume of the system between the initial and final stage of the reaction will be accounted. Thus, conversion of reactant A (C_A/C_{A0}) . 'A' becomes $X_A = [1 - (C_A/C_{A0})] / [1 + \epsilon_A (C_A/C_{A0})]$

Reversible reaction

For the given, the rate of reaction is $-r_A = k_1 C_A^2 - k_2 C_R C_S$. At equilibrium, $-r_A = 0$. Then, $k_1 C_A^2 - k_2 C_R C_S = 0$ (or) $K_c = k_1 / k_2 = (C_R C_S) / C_A^2$.

Autocatalytic reaction

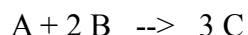
A reaction in which one of the products of reaction acts as a catalyst is called R+R autocatalytic reaction. Example: $A+R \rightarrow R+R$

Method of Isolation

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

Method of Initial Rates

The Method of Initial Rates involves measuring the rate of reaction, r , at very short times before any significant changes in concentration occur. Suppose one is studying a reaction with the following stoichiometry:



While the form of the differential rate law might be very complicated, many reactions have a rate law of the following form:

$$r = k [A]^a [B]^b$$

The initial concentrations of A and B are known; therefore, if the initial reaction rate is measured, the only unknowns in the rate law are the rate constant, k , and the exponents a and b . One typically measures the initial rate for several different sets of concentrations and then compares the initial rates.

Method of Excess

In this method the concentration of one reactant is made much larger i.e. in excess than the concentrations of the other reactants.

Runaway reaction

A runaway reaction is the consequence of the loss of control of the temperature of a chemical compound or a mixture, in an enclosure. This phenomenon is also called Thermal Runaway or thermal explosion. The consequences of the loss of control of the temperature are . An increase of the rate of the chemical reactions. . The occurrence of unwanted exothermic reactions which are not obtained in the normal process conditions. Most of the time these reactions are decomposition reactions of the reaction mixture. . A pressure rise due to two phenomena : An increase of the reaction mixture vapor pressure due to the temperature rise. The production of non condensable decomposition gasses. The pressure increase often causes the enclosure to burst. This explains the name thermal explosion .

This loss of containment results in the emission of a two phase mixture of gas and liquid to the outside giving an aerosol. If the reaction mixture is released in the open air, the aerosol can ignite due to the oxidation of the hot gasses and droplets with air, or possibly to the occurrence of electrostatic sparks. The ignition of the cloud gives a fire ball with a weak pressure effect at the ground level. If the reaction mixture is released in a housing, the mixture of the gasses, droplets and air can explode in this enclosed area. In this case a strong blast effect is produced causing the destruction of the building and secondary fires. Often the reaction vessel bursts with emission of projectiles to a distance of several hundred meters.

Most of the time, the occurrence of a runaway reaction is an unexpected event for those who are in charge of running the plants. For this reason it is of interest to describe the various process deviations which can cause a runaway reaction to happen, and to discuss the experimental information necessary for risk assessment, the choice of safe process and the mitigation of the consequences of the runaway.