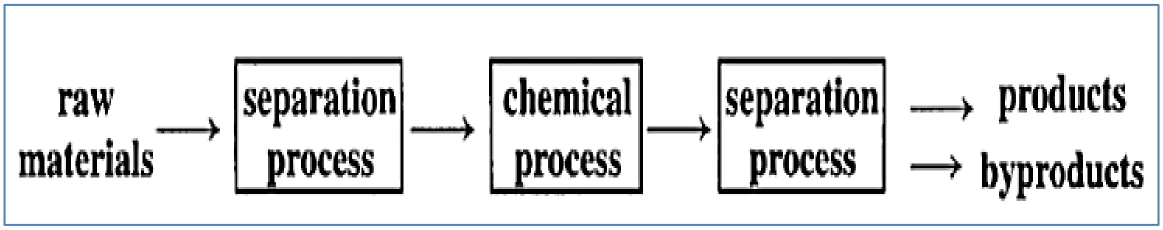
Chemical Reactor Design:

Introduction:

The Chemical industry is a branch of the industry that produces highly value-added chemicals from a variety of natural resources used as basic raw materials. Therefore the design and operation of chemical reactors as ways and means of realizing the chemical reaction, are so important that they may be said to be the key technology of the chemical industry while the efficient separation process ensured the savings in any process.

The chemical reactor converts inexpensive chemicals in to valuable products. While separation units, such as distillation columns, are required to purify materials before they enter the chemical reactor via physical treatment steps to put them in the form in which they can be reacted chemically. Then the products are purified after they leave the reactor undergoing further physical treatment-separations, purifications, etc. for the final desired product to be obtained.

Here is a very generic flow diagram of a chemical process.



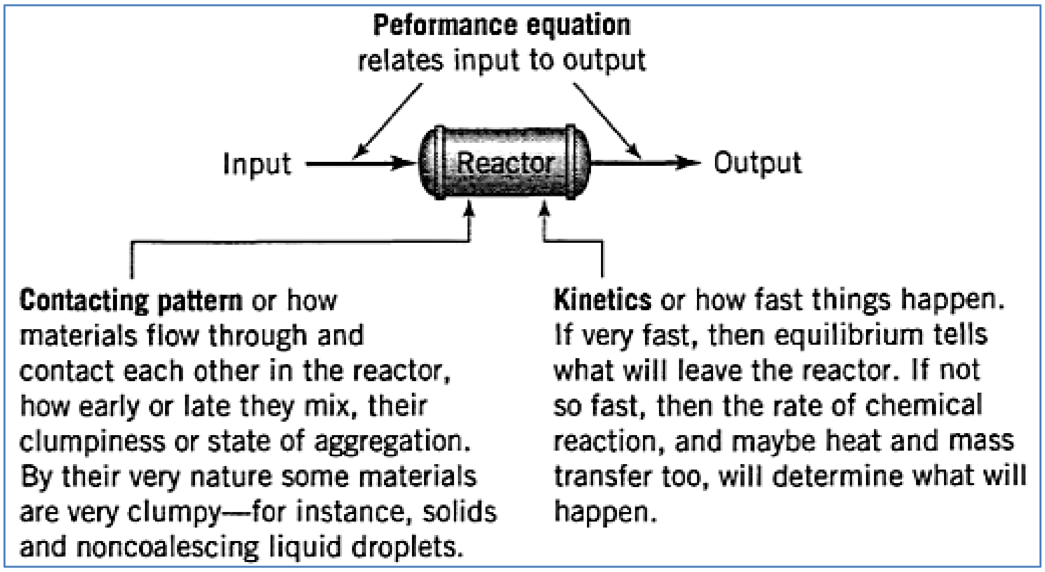
Raw materials from another chemical process or purchased externally must usually be purified to a suitable composition for the reactor to handle. After leaving the reactor, the unconverted reactants, any solvents, and all byproducts must be separated from the desired product before it is sold or used as a reactant in another chemical process.

One feature that distinguishes the chemical engineer from other types of engineers is the ability to analyze systems in which chemical reactions are occurring and to apply the results of his analysis in a manner that benefits society. Consequently, chemical engineers must be well acquainted with the fundamentals of chemical kinetics and the manner in which they are applied in chemical reactor design.

The performance of the chemical reactor:

This issue is totally controlling the cost and modes of operation of the expensive separation units that dominated the size. Therefore, the chemical reactor extremely controls the overall economics of most processes (See Fig. 1.)

In general, the capital and operating costs of a reactor equal 10 to 25 percent of the total cost of a typical chemical process. This process could be a petroleum refining, food processing, materials, fine chemicals, pharmaceuticals, etc.



Peformance equation relates input to output

Contacting pattern or how materials flow through and contact each other in the reactor, how early or late they mix, their clumpiness or state of aggregation. By their very nature some materials are very clumpy—for instance, solids and noncoalescing liquid droplets.

Kinetics or how fast things happen. If very fast, then equilibrium tells what will leave the reactor. If not so fast, then the rate of chemical reaction, and maybe heat and mass transfer too, will determine what will happen.

Fig. 1. The performance equation for a chemical reactor

Theory of chemical reaction:

Why and how does a chemical reaction take place? What factors govern the selectivity and the rate of reaction? The specific field of science dealing with these issues is termed as the theory of chemical reaction, which is comprised of chemical equilibrium, kinetics and mechanisms. The equilibrium of chemical reactions is discussed by chemical thermodynamics, which reveals whether a given chemical reaction will take place or not and if so, to what extent. In more detail, the change in standard free energy of formation accompanied by a chemical reaction gives an equilibrium constant at a given temperature, which provides the equilibrium conversion of reactants under their particular initial pressure and composition. In addition, chemical thermodynamics enables the calculation of the heat balance associated with a reaction which is either endothermic or exothermic. This thermodynamic information is indispensable for reactor design. The rate of chemical reaction is another critical factor in reactor design. The progress of rate theory, however, is so far behind meeting the need to predict precisely any particular rate of reaction that it has to be observed by experiment. Chemical kinetics deals with the rate of a chemical reaction to reach its equilibrium. It originated from careful observation of the rate of a chemical reaction through experiments, followed by a mathematical expression of the rate of the chemical reaction.

Analysis of chemical reactors:

The analysis of a chemical reactor is required various fields in the chemical engineering curriculum. It starts from the chemical reaction theory toward the optimum operation of the chemical reactor designed. Figure 2 reveals the main objectives that should be taken into consideration to ensure that the progress of designing the reactor is accurate.

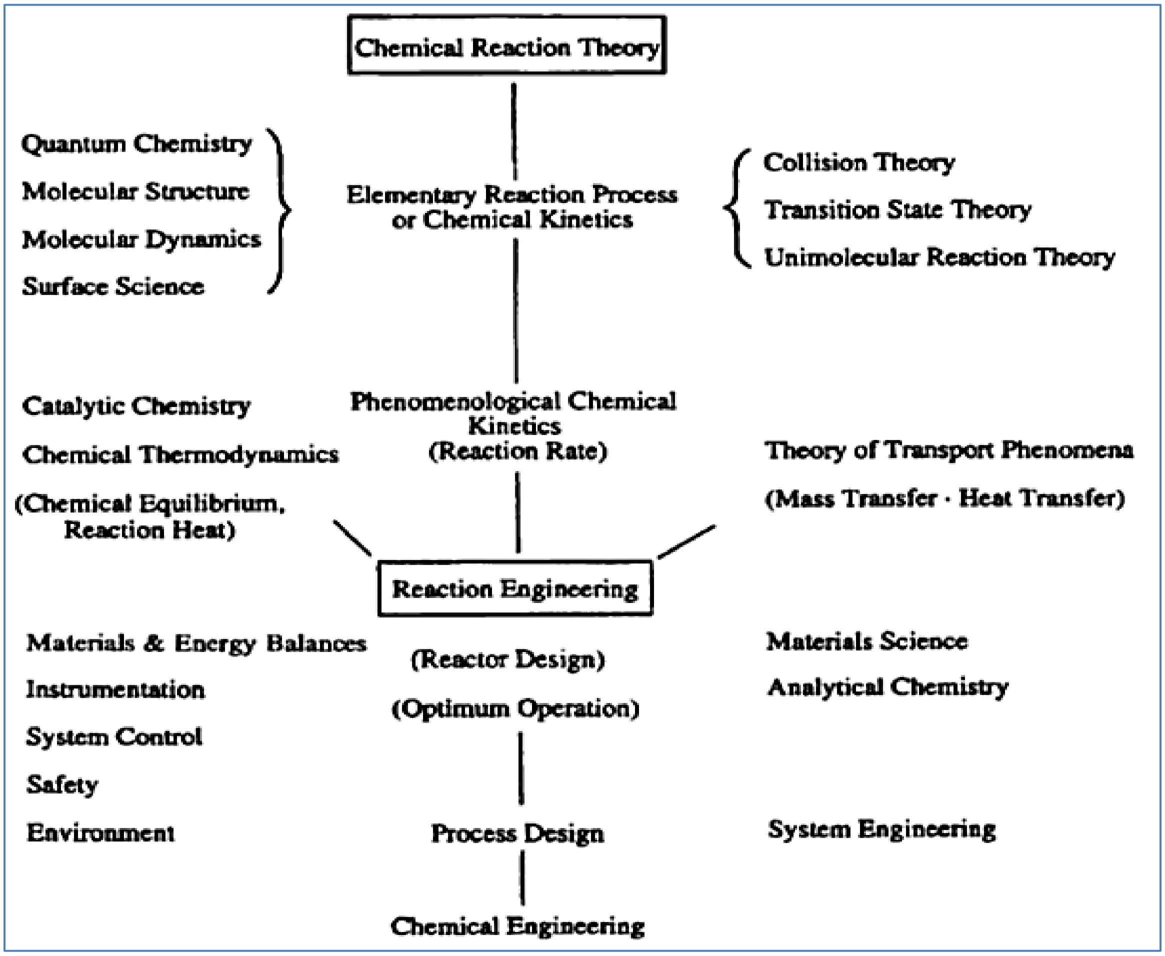


Fig. 2. Science and engineering related to reactor design

Logically, the subject of designing a chemical reactor for a given process might proceed as shown in the following sequence of steps.

bench-scale batch reactor ➔ *bench-scale continuous* ➔ *pilot plant* ➔ *operating plant*

The conversions, selectivities, and kinetics are ideally obtained in a small batch reactor, the operating conditions and catalyst formulation are determined from a bench-scale continuous reactor, the process is tested and optimized in a pilot plant, and finally the plant is constructed and operated. While this is the ideal sequence, it seldom proceeds in this way, and the chemical engineer must be prepared to consider all aspects simultaneously.

Real processes almost invariably involve multiple reactors. These may be simply reactors in series with different conversions, operating temperatures, or catalysts in each reactor. One example is the production of aspirin from natural gas. Current industrial technology involves the steps

natural gas ➔ *methane* ➔ *syngas* ➔ *methanol* ➔ *acetic acid* ➔ *acetylsalicylic acid*

Although a gas company would usually purify the natural gas, a chemical company would buy methane and convert it to acetic acid, and a pharmaceutical company would make and sell aspirin.

The objective of the study on chemical reaction engineering is to establish the practical methodology of reactor design and operation not only for simple but also for complex reaction systems, where mass and heat transfer have crucial effects on the rates of the chemical reaction. Examples of the reactors where mass transfer of reactants in heterogeneous phases plays an important role, include the ***bubbling column reactor*** in which a gas is blown into a liquid, and the ***catalytic reactor*** in which a gas passes through a porous granular catalyst bed. In the former case, the mass transfer on the gas/liquid interface, and in the latter case, the diffusion rate of gaseous molecules in the pores of the catalyst, respectively, govern the reaction rate and the product distribution significantly.

Examples of heat transfer-controlled reaction systems include ***high-temperature thermal cracking*** and ***partial oxidation of hydrocarbons***. Since the former case is accompanied by a large amount of heat absorption, the heat transfer rate through the reactor tube wall substantially governs the reaction rate, while in the latter case, elimination of the large amount of heat generated and control of the reaction temperature are the keys to the reactor design in order to minimize the side reaction, namely complete oxidation of hydrocarbons.

Classification of Reactions

In chemical reaction engineering probably the most useful scheme is the breakdown according to the number and types of phases involved, the big division being between the homogeneous and heterogeneous systems. A reaction is homogeneous if it takes place in one phase alone. A reaction is heterogeneous if it requires the presence of at least two phases to proceed at the rate that it does. It is unimportant whether the reaction takes place in one, two, or more phases; at an interface; or whether the reactants and products are distributed among the phases or are all contained within a single phase. All that counts is that at least two phases are necessary for the reaction to proceed as it does. In homogeneous systems the temperature, pressure, and composition are obvious variables. In heterogeneous systems more than one phase is involved; hence, the problem becomes more complex. Thus, heat and mass transfer may play important roles in determining the rates of heterogeneous reactions.

The catalytic reaction whose rate is altered by materials that are neither reactants nor products. These foreign materials, called catalysts, need not be present in large amounts. Catalysts act somehow as go-betweens, either hindering or accelerating the reaction process while being modified relatively slowly if at all.

H.W. 1.1*: Give three examples of industries containing reactors.*

Chemical Reactor Design:

Chemical kinetics:

It is extremely essential for any study or design of each type of reactors because they relates to the studies of the rates at which chemical processes occur, the factors on which these rates depend, and the molecular acts involved in reaction mechanisms. A description of a reaction in terms of its constituent molecular acts is known as the ***mechanism*** of the reaction. Therefore, chemical kinetics and reactor design are clearly important of producing all industrial chemicals. In general, chemical reactions could be classified into ***elementary reaction*** which corresponds to the stoichiometric equation and ***non-elementary reactions*** which are not corresponding to the stoichiometric equations.

1. Stoichiometric Coefficients

Consider the following general reaction.

$$bB + cC = sS + tT \qquad (1)$$

where ***b, c, s,*** and ***t*** are the stoichiometric coefficients of the species ***B,*** **C, S,** and **T**, respectively. The generalized stoichiometric coefficients v_i ***(nue)*** for the above reaction by rewriting it in the following manner.

$$0 = v_B B + v_C C + \ldots\ldots + v_S S + v_T T \qquad (2)$$

Where: $v_B = -b$; $v_C = -c$; $v_S = s$; $v_T = t$

Or the equation (2) could be written as follow where the sum is taken over all components A_i present in the system.:

$$0 = \sum_i v_i A_i \qquad (3)$$

The generalized stoichiometric coefficients are defined as positive quantities for the products of the reaction ($v_i > 0$) and as negative quantities for the reactants ($v_i < 0$). The coefficients of species that are neither produced nor consumed by the indicated reaction are taken to be zero.

Example: one could write the carbon monoxide oxidation reaction in our notation as

$$0 = 2CO_2 - 2CO - O_2$$

instead of in the more conventional form, which has the reactants on the left side and the products on the right side.

$$2CO + O_2 = 2CO_2$$

This second form is preferred, provided that one keeps the proper sign convention for the stoichiometric coefficients in mind.

$$v_{CO} = -2;\ v_{O2} = -1;\ v_{CO2} = 2$$

Alternatively, the reaction could be written as

$$0 = CO_2 - CO - (1/2)\ O_2$$

With: $v_{CO} = -1;\ v_{O2} = (-1/2);\ v_{CO2} = 1$

Since the reaction stoichiometry can be expressed in various ways, one must always write down a stoichiometric equation for the reaction under study during the initial stages of the analysis and base subsequent calculations on this reference equation.

2. Reaction Progress Variables

In order to measure the progress of a reaction, it is necessary to define a parameter, which is a measure of the degree of conversion of the reactants. We will find it convenient to use the concept of the ***extent*** of reaction. Consider a closed system (i.e., one in which there is no exchange of matter between the system and its surroundings) where a single chemical reaction may occur according to equation (3). Initially there are N_{io} moles of constituent A_i present in the system. At some later time there are N_i moles of species A_i present. At this time the molar extent of reaction is defined as:

$$\xi = \frac{N_i - N_{io}}{v_i} \qquad (4)$$

The molar extent of reaction ζ (***zeta***) is a time-dependent extensive variable that is measured in moles. Changes in the mole numbers of two species j and k can be related to one another by eliminating ζ between two expressions that may be derived from equation (4.)

$$N_k = N_{ko} + \left(\frac{v_k}{v_j}\right)(N_j - N_{jo}) \qquad (5)$$

If more than one chemical reaction is possible, an extent may be defined for each reaction. If ζ_k is the extent of the ***kth*** reaction, and v_{ki} the stoichiometric coefficient of species ***i*** in reaction ***k***, the total change in the number of moles of species $\boldsymbol{A_i}$ because of ***R*** reactions is given by:

$$N_i - N_{io} = \sum_{k=1}^{k=R} v_{ki}\xi_k \tag{6}$$

The fraction conversion $\boldsymbol{x}$ is an intensive measure of the progress of a reaction, and it is a variable that is simply related to the extent of reaction. The fraction conversion of a reactant $\boldsymbol{A_i}$ in a closed system in which only a single reaction is occurring is given by:

$$\boldsymbol{x = \frac{N_{io} - N_i}{N_{io}} = 1 - \frac{N_i}{N_{io}}} \tag{7}$$

H.W.: Relate the extent of reaction (ζ) to the fraction conversion ($\boldsymbol{x}$) for a substance ***i***.

For the ***irreversible*** reaction the ζ_e is approximately equal to $\boldsymbol{\zeta_{max}}$ where in these cases the equilibrium for the reaction highly favors formation of the products, and only an *extremely small* quantity of the limiting reagent remains in the system at equilibrium. Whereas, for the ***reversible*** reaction, the ζ_e differs measurably from $\boldsymbol{\zeta_{max}}$ **.** From a thermodynamic point of view, all reactions are reversible. However, when one is analyzing a reacting system, it is often convenient to neglect the reverse reaction in order to simplify the analysis. For "irreversible" reactions, one then arrives at a result that is an extremely good approximation to the correct answer.

3. The rate of reaction:

It is time-dependent issue of consuming such materials to generate new materials via three basic ways as follow:

1. Decomposition such as the conversion of cumene into benzene and propylene.
2. Combination such the formation of cumene from benzene and propylene.
3. Isomerization which is neither the first way or the second one mentioned above.

It is common practice to define the rate of reaction based on the unit volume. The reaction rate is expressed as the number of molecules reacting per unit volume in unit time. This unit volume is the basis of finding the concentration. If the probability of a molecule reacting per unit time has been determined, the number of molecules reacting per volume is proportional to the number of molecules per volume, i.e. the concentration.

The rate of elementary reactions is proportional to the concentration while the rate of catalytic reactions is proportional to the adsorption concentration. Let us consider a case in which a product is formed from two kinds of raw molecules A and B,

$$A + B \rightarrow C$$

The reaction rates of **A** and **B** are proportional to the concentrations of **A** and **B**, respectively. Thus, the rate of reaction to form **C** from **A** and **B** is

$$r = k[A][B] \qquad (8)$$

4. Factors governing the rate of reaction

A reaction rate is dependent on the concentration of the active molecules in all molecules which have energy sufficient for causing a reaction, and also on the frequency of reactions of the active molecules. The factors determining the fraction of active molecules and the frequency of reactions are the temperature for thermal reactions and the luminous intensity for photochemical reactions.

$$r = f(T, C_i) = f(T) \cdot f(C_i) = k\,C_i \qquad (9)$$

where k is the rate constant that could be found using several laws such as the ***Arrhenius equation***:

$$k = A \exp(-E/RT) \qquad (10)$$

where: ***A*** is the pre-exponential constant; ***E*** is the activation energy (J/mol); ***R*** is the gas constant; and ***T*** is the temperature in Kelvin.

The activation energy is obtained from (- ***E/ R***), the slope of the straight line as shown in the following figure (Fig. 1).

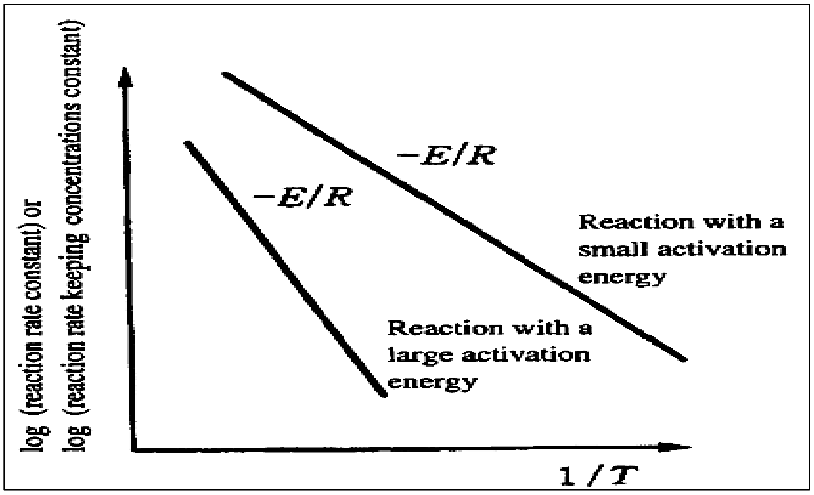


Fig. 1. Arrhenius plot

It is convenient to approach the concept of reaction rate by considering a closed, isothermal, constant pressure homogeneous system of uniform composition in which a single chemical reaction is taking place. In such a system the rate of the chemical reaction (r) is defined as:

$$r = \frac{1}{V}\frac{d\xi}{dt} \qquad \textbf{(11)}$$

Where: V is the system volume; ζ is the extent of reaction; and t is the time.

Since the extent of reaction is expressed in terms of moles, the reaction rate has the units of moles transformed per unit time per unit volume. Changes in the mole numbers *nt* of the various species involved in a reaction are related to the extent of reaction according to Equation (4). So the rate of reaction will be:

$$r = \frac{1}{v_i}\frac{1}{V}\frac{dN_i}{dt} \qquad \textbf{(12)}$$

If one defines the rate of increase of the moles of species i as:

$$r_i = \frac{1}{V}\frac{dN_i}{dt} \qquad \textbf{(13)}$$

Then: $r_i = v_i\, r$ **(14)**

Since the v_i are positive for products and negative for reactants, and since the reaction rate r is intrinsically positive, the various r_i will have the same sign as the corresponding v_i and dn_i/dt will have the appropriate sign (i.e., positive for products and negative for reactants).

In terms of molar concentrations, Ci = *ni/V*, Equation (12) becomes:

$$r = \frac{1}{v_i}\frac{dC_i}{dt} \qquad \textbf{(15)}$$

It refers that the rate of reaction at constant volume is thus proportional to the time derivative of the molar concentration.

Many reactions take place in heterogeneous systems rather than in a single homogeneous phase. In such cases it is appropriate to define the reaction rate in terms of the interfacial area (S) available for reaction.

$$r''_i = \frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface})\ (\text{time})} \qquad (16)$$

In many cases, however, the interfacial area is not known, particularly when one is dealing with a heterogeneous catalytic reaction involving a liquid phase and a solid catalyst. Consequently, the following definitions of the reaction rate are sometimes useful.

$$r_i' = \frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid})\,(\text{time})} \qquad (17)$$

$$r_i''' = \frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid})\,(\text{time})} \qquad (18)$$

Based on unit volume of reactor, if different from the rate based on unit volume of fluid:

$$r_i'''' = \frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor})\,(\text{time})} \qquad (19)$$

Note #1: You should know the difference between the species and elements items, for the following example the number of them are 3 and 2, respectively.

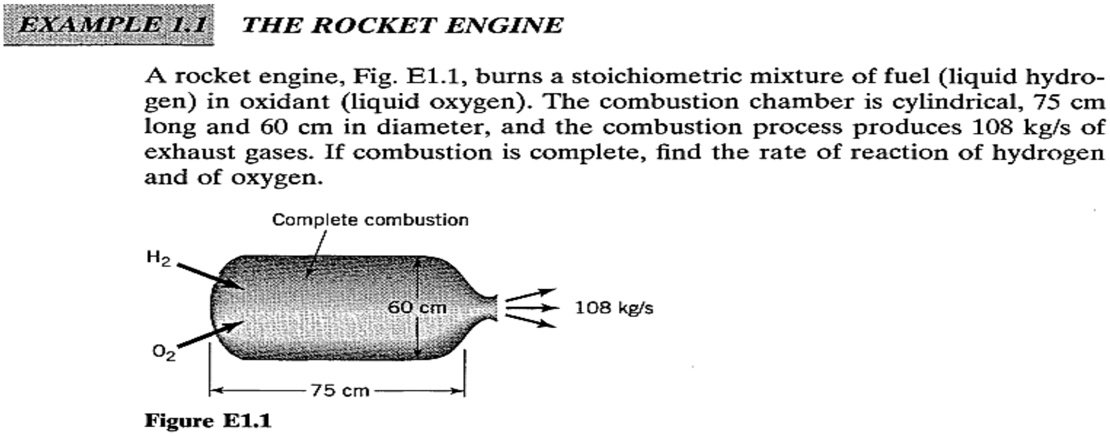
$$2\,SO_2 + O_2 = 2\,SO_3$$

$$SO_2 + (1/2)\,O_2 = SO_3$$

Note #2: You should know the difference between the elementary reaction and non-elementary reaction items. The former one requires that the chemical equation should be corresponded to the chemical reaction equation, for example:

$2\,A \rightarrow 2\,B$ $\quad -r_A = r_B = k\,C_A^2$: Elementary reaction

$A \rightarrow B$ $\quad -r_A = r_B = k\,C_A^{1/2}$: Non-elementary reaction



EXAMPLE 1.1 ***THE ROCKET ENGINE***

A rocket engine, Fig. E1.1, burns a stoichiometric mixture of fuel (liquid hydrogen) in oxidant (liquid oxygen). The combustion chamber is cylindrical, 75 cm long and 60 cm in diameter, and the combustion process produces 108 kg/s of exhaust gases. If combustion is complete, find the rate of reaction of hydrogen and of oxygen.

Figure E1.1

SOLUTION

We want to evaluate

$$-r_{H_2} = \frac{1}{V}\frac{dN_{H_2}}{dt} \quad \text{and} \quad -r_{O_2} = \frac{1}{V}\frac{dN_{O_2}}{dt}$$

Let us evaluate terms. The reactor volume and the volume in which reaction takes place are identical. Thus,

$$V = \frac{\pi}{4}(0.6)^2(0.75) = 0.2121\ \text{m}^3$$

Next, let us look at the reaction occurring.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O \qquad \textbf{(i)}$$

molecular weight: 2gm 16 gm 18 gm

Therefore,

$$H_2O\ \text{produced/s} = 108\ \text{kg/s}\left(\frac{1\ \text{kmol}}{18\ \text{kg}}\right) = 6\ \text{kmol/s}$$

So from Eq. (i)

$$H_2\ \text{used} = 6\ \text{kmol/s}$$
$$O_2\ \text{used} = 3\ \text{kmol/s}$$

and the rate of reaction is

$$\underline{\underline{-r_{H_2}}} = -\frac{1}{0.2121\ \text{m}^3}\cdot\frac{6\ \text{kmol}}{\text{s}} = \underline{\underline{2.829\times10^4\frac{\text{mol used}}{(\text{m}^3\ \text{of rocket})\cdot\text{s}}}}$$

$$\underline{\underline{-r_{O_2}}} = -\frac{1}{0.2121\ \text{m}^3}\cdot 3\frac{\text{kmol}}{\text{s}} = \underline{\underline{1.415\times10^4\frac{\text{mol}}{\text{m}^3\cdot\text{s}}}}$$

Note: Compare these rates with the values given in Figure 1.3.

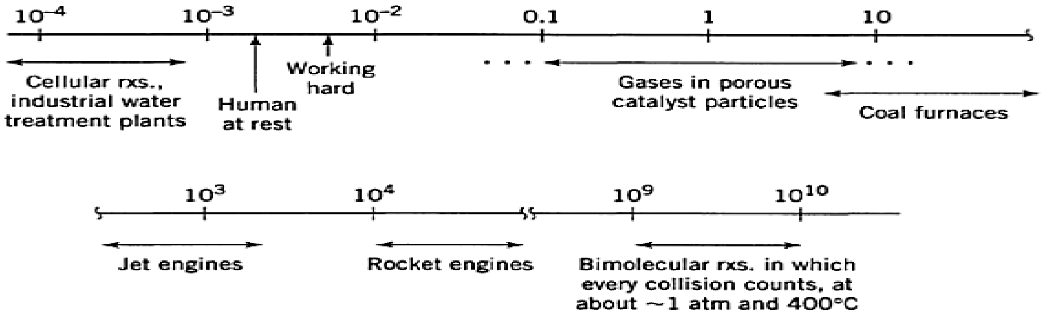


Figure 1.3 Rate of reactions $-r'''_A = \dfrac{\text{moles of A disappearing}}{\text{m}^3\ \text{of thing}\cdot\text{s}}$

H.W.: Solve the following problems (1.1 and 1.3)

Chemical Reactor Design:

Chemical kinetics:

There are other important aspects that should be taken into consideration in case of designing the chemical reactor which are as follows:

Yield:

In particular, the first step in determining the economic feasibility of producing a given material from a given reactant feed stock should be the determination of the product yield at equilibrium at the conditions of the reactor outlet which may equal or differ than the observed yield. For example, if the equilibrium yield of a given reactant system is 75%, and the observed yield from a given reactor is only 30%, it is obviously possible to obtain major improvements in the process yield. On the other hand, if the process yield were close to 75%, the potential improvement in the yield is minimal and additional efforts aimed at improving the yield may not be warranted. Without a knowledge of the equilibrium yield, one might be tempted to look for catalysts giving higher yields when, in fact, the present catalyst provides a sufficiently rapid approach to equilibrium.

The yield equals the ratio of moles of the desired product formed to the moles of the reactant consumed times of the stoichiometric factor of this reactant material. For the reaction ($aA \rightarrow bB$), yield equals:

$$\boldsymbol{Yield\ (Y) = \frac{moles\ of\ the\ product\ formed \times stoichiometric\ factor\ of\ the\ limiting\ reactant}{moles\ of\ the\ limiting\ reactant\ converted}}$$

So, for the above reaction:

$$\boldsymbol{Yield\ (Y) = \frac{N_b \times v_a}{N_a}}$$

Selectivity:

For commercial applications, selectivity is often more important than other aspects. In many cases selectivity considerations determine the processing mode, particularly when the reaction under study is accompanied by undesirable side reactions. It is the ratio of the desired product formed to the reactant consumed, it changes as the reaction proceeds. It could be ratio of moles, concentrations and conversion of the desired product formed to the limiting reactant really reacted. For the reaction ($aA \rightarrow bB$), selectivity equals:

$$\boldsymbol{Selectivity\ (S) = \frac{N_b formed}{N_a\ reacted} = \frac{N_b \times v_a}{N_a \times x_A} = \frac{C_B}{C_A} = \frac{x_B}{x_A}}$$

For multi-reactions, it could be obtained by relating one reaction to other such as the following example:

Example 3.1: Find the selectivity for a process if the following reactions had occurred at the same time were the first reaction is the desired one.

Reaction # 1: A + B → D ; $r_D = k_D C_A^2 C_B$ -------- (a)

Reaction # 2: A + B → V ; $r_V = k_V C_A C_B^2$ -------- (b)

Ans.: $Selectivity\ (S) = \frac{r_D}{r_V} = \frac{k_D\ C_A^2\ C_B}{k_V\ C_A C_B^2} = \frac{k_D C_A}{k_V C_B}$

H.W. 3.1*: Find the mathematical correlation between the yield and the selectivity.*

Limiting reactant:

It disappears first if a reaction proceeded to completion because it is present in less than its stoichiometric proportion relative to every other reactants. Therefore, We should refer our fractional conversions to this stoichiometrically limiting reactant if $\boldsymbol{x}$ is to lie between zero and unity. It is usual that the limiting reactant has selected as the basis for all material balance calculations.

Excess reactant:

If nonstoichiometric amounts of reactants are present in the initial system, the presence of excess reactants tends to increase the equilibrium fractional conversion of the limiting reactant above that which would be obtained with stoichiometric ratios of the reactants. The percentage of excess could be found from the following equation:

$$\boldsymbol{Excess\ \% = \frac{Q_{supplied} - Q_{stoich.}}{Q_{stoich.}} \times 100}$$

Example 3.2: For the reaction (2 A + B → 2 C), Specified which are of the following cases is the limiting reactant or the excess reactant.

Case #1: A= 200 mol; B= 100 mol

Case #2: A= 150 mol; B= 100 mol

Case #3: A= 250 mol; B= 100 mol

Ans.: *Case #1*: Stoichiometric; *Case #2*: The limiting reactant is ***A***; *Case #2*: The limiting reactant is ***B.***

Example 3.2: For the reaction (***A + 0.5 B → 0.3 C + 2.5 D***), calculate the theoretical Yield of the products.

Ans.: *The basis is (0.3 mol of C)*

$$Yield\ (Y_C) = \frac{0.3\ moles\ of\ C}{1\ moles\ of\ A} = 0.3\frac{moles\ of\ C}{moles\ of\ A}$$

$$Yield\ (Y_D) = \frac{2.5\ moles\ of\ D}{1\ moles\ of\ A} = 2.5\ \frac{moles\ of\ D}{moles\ of\ A}$$

Example 3.3: For the parallel reactions (***A → 2 B + 3 C***) and (***A → D + C***), find the selectivity of the product (***B***) relative to the product (***D***) if the collected values of the products are **3.5** and **0.5** moles of (***C***) and (***D***), respectively.

Ans.: *The basis is (3.5mol of C) for both reactions and (0.5mol of D) for the second reaction.*

Since the amount of (D) produced in the second reaction is 0.5 mol, so the amount of (C) produced in the same reaction is 0.5mol, stoichiometrically. Therefore, the amount of (C) produced in the first reaction equals: (3.5 - 0.5 = 3 mol)

So, the stoichiometric amount of (B) produced from the first reaction is:

$$\frac{N_B}{v_B} = \frac{N_C}{v_C} \rightarrow \frac{N_B}{2} = \frac{3}{3} \rightarrow N_B = 2\ mol$$

$$Selectivity\ (S_B) = \frac{moles\ of\ B}{moles\ of\ D} = \frac{2}{0.5} = 4\ \frac{moles\ of\ B}{moles\ of\ D}$$

Example 3.4: For the reaction ($N_2 + 3 H_2 \rightarrow 2 NH_3$), the feed of ($N_2$), ($H_2$) and ($NH_3$) are **100**, **50** and **5g**, respectively, and the product of (NH_3) is **90g**. Determine the extent of reaction and the quantities of reactants found the outlet.

Ans.: Let ***i,k*** and ***j*** denoted for NH_3, N_2 and H_2

$$\xi = \frac{N_i - N_{io}}{v_i} = \frac{N_k - N_{ko}}{v_k} = \frac{N_j - N_{jo}}{v_j}$$

$$N_{io} = \frac{5}{17} = 0.294\ mol\ NH_3$$

$$N_i = \frac{90}{17} = 5.294\ mol\ NH_3$$

So, the extent of reaction is: $\xi = \frac{5.294-0.294}{2} = 2.5$

$$N_{N_2} = \frac{100}{28} = 3.57\ mol\ N_2$$

$$N_{H_2} = \frac{50}{2} = 25\ mol\ H_2$$

For N_2: $N_k = N_{ko} + v_k \times \xi = 3.57 + (-1) \times 2.5 = 1.07 mol = 30 g\ N_2$

For H_2: $N_j = N_{jo} + v_j \times \xi = 25 + (-3) \times 2.5 = 17.5 mol = 35 g\ N_2$

Example 3.4: The following reactions ($C_2H_6 \rightarrow C_2H_4 + H_2$) and ($C_2H_6 + H_2 \rightarrow 2\ CH_4$) occurred in a continuous reactor. The feed contained 85mol% of (C_2H_6) and the balance is the inert (I). Calculate the molar composition of the product gas in case of the conversion of ethane is 50% and the yield of ethylene is 47%.

Ans.: *Basis 100mol feed*

Since we have two reactions, therefore, each reaction have an extent of reaction (ζ_i).

Components	Moles inlet	Reaction (1)	Reaction (2)	Moles outlet
C_2H_6	85	$-\zeta_1$	$-\zeta_2$	$85-\zeta_1-\zeta_2$
I	15	---	---	15
C_2H_4	---	ζ_1	---	ζ_1
H_2	---	ζ_1	$-\zeta_2$	$\zeta_1-\zeta_2$
CH_4	---	---	$2\zeta_2$	$2\zeta_2$

Moles of unconverted ethane = **0.5 x 85 = 42.5**

Moles outlet of ethane: **$85-\zeta_1-\zeta_2 = 42.5$**

$$Yield\ (Y) = \frac{N_{C_2H_4} \times v_{C_2H_6}}{N_{C_2H_6}} = \frac{N_{C_2H_4} \times 1}{85} = 0.47$$

$$N_{C_2H_4} = 0.47 \times 85 = 40\ mole = \zeta_1$$

$$\xi_2 = 85 - 42.5 - 40 = 2.6 mol$$

Components	Moles outlet	% moles
C_2H_6	42.5	30.3
I	15	10.7
C_2H_4	40	28.6
H_2	37.4	26.4
CH_4	5.2	3.7

H.W. 3.2: *For example 3.4, find the selectivity of ethylene to methane production for the same conversion and yield.*

H.W. 3.3: *For the reaction ($C_3H_6 + NH_3 + 1.5\ O_2 \rightarrow C_3H_3N + 3\ H_2O$), the feed to reactor contains 10, 12 and 78mol% of C_3H_6, NH_3 and air. The fractional conversion of the limiting reactant was 30%. Determine: (a) The limiting reactant, (b) The percentages of excess reactants, (c) The extent of reaction (d) The amount of products (in moles) in case of the above conversion.*

Chemical Reactor Design:

Kinetics of homogeneous reactor:

Chemical reactions are classified from various viewpoints with individual characteristics. Similarly, reactors can be classified on the basis of their kinetic behavior as follows and their basic concepts are shown in Fig. 1.

(1) *Batch type*.
(2) *Continuous flow type*: (a) Tubular reactor, plug flow; (b) Tank reactor, mixed flow.

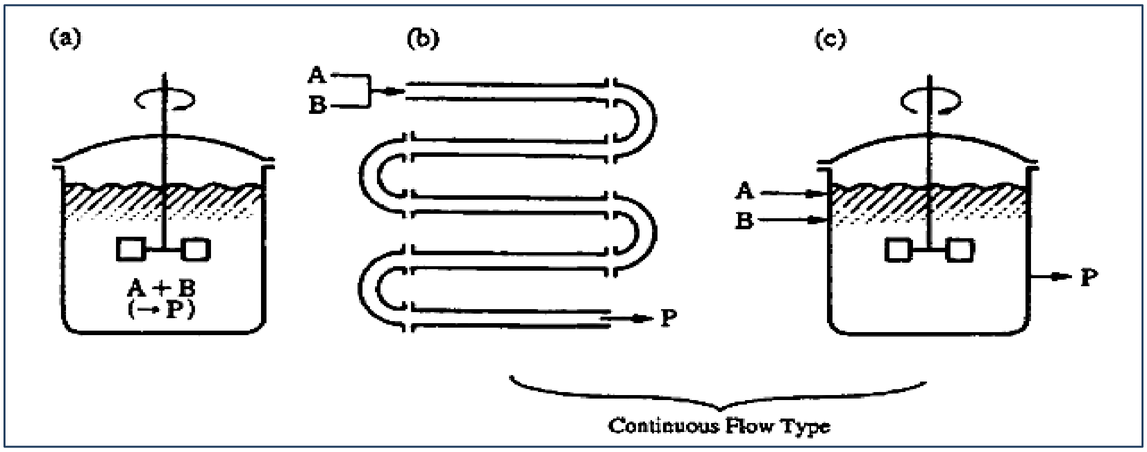


Fig. 1, Types of reactor. (a) Batch reactor. (b) Tubular reactor. (c) Continuous stirred tank reactor

So, in terms of the physical configurations encountered, there are basically only two types of reactors: the tank and the tube.

The *ideal tank reactor* is one in which stirring is so efficient that the contents are always uniform in composition and temperature throughout. The simple tank reactor may be operated in a variety of modes: batch, semibatch, and continuous flow. These modes are illustrated schematically in Fig. 2.

In the case of the batch type reactor, its operation starts by feeding the raw materials into the reaction vessel. In several hours or days of operation, the reaction proceeds nearly to completion, and it is terminated by cooling the reactor, if necessary, followed by the recovery of the product from the reactor. Batch reactors are often used for liquid phase reactions, particularly when the required production is small. They are seldom employed on a commercial scale for gas-phase reactions because the quantity of product that can be produced in reasonably sized reactors is small.

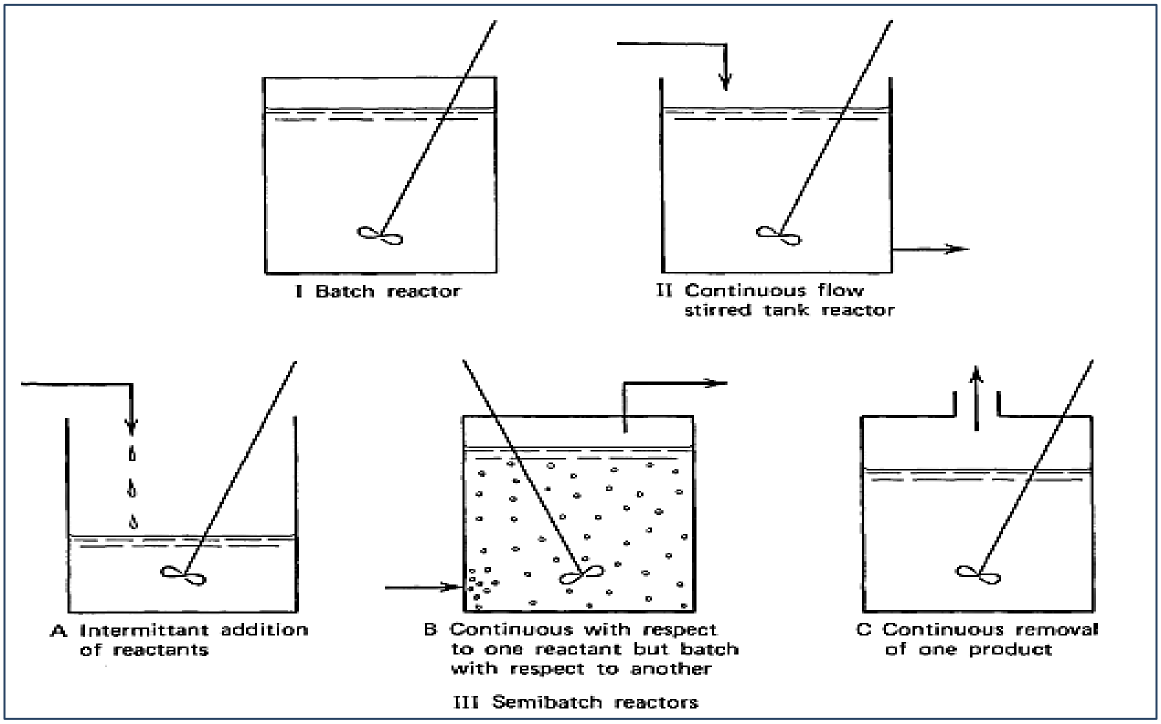


Fig. 2. Types of tank reactors.

The continuous flow type reactor, wherein raw materials are continuously fed and from where the product is taken out, is suitable for large-scale chemical processes with relatively high reaction rate at substantially constant operating conditions. In the case of the tubular reactor, the concentration of raw materials is highest at the inlet of the reactor tube and gradually decreases toward the outlet, while product concentration gradually increases along the reactor. In this type of reactor, there is no back-mixing or diffusion of reacting molecules along the direction of the material flow. Therefore, Continuous flow reactors are almost invariably preferred to batch reactors when the processing capacity required is large. Although the capital investment requirements will be higher, the operating costs per unit of product will be lower for continuous operation than for batch reaction. Table 1 shows a comparison of characteristics of reactors depending on their modes of flow. While table 2 summarizes the types of reactors, characteristics of chemical reactions, and major design considerations for such chemical processes. Reactors which handle reacting systems of a homogeneous phase such as gas or liquid are classified as homogeneous reactors.

Table 1. Comparison of characteristics of reactors

	Reactor / Comparison item	Batch	Continuous flow	
			Tubular type	Tank type
Ideal conditions	1. Temperature, pressure, composition in reactor	Uniform at each moment	• Concentration changes in the direction of flow • No gradient of reaction rate and temperature in radial direction • No mixing and diffusion in axial direction	• Complete mixing • Composition in the reactor is uniform and equal to that at the outlet
	2. Residence time distribution of reactant	None	None	Yes
Kinetic characteristics	1. Required reactor volume (Equal conversion basis)	Relatively small	Relatively small	Large
	2. Distribution of products (Consecutive reaction)	Large yield of intermediate product	Large yield of intermediate product	Small yield of intermediate product
	3. Probability of reaction with specific composition ratio	Impossible	Impossible	Possible
Features	1. Flexibility	Large	Small	Medium
	2. Application	Multi-purpose and small-scale production	Mass production	Medium

Table 2. Examples of industrial chemical processes

Process	Reactor	Chemical reaction	Design issues
Naphtha cracking	Vapour phase, homogeneous, tubular furnace	Endothermic, consecutive reaction	Product yield, rapid heating and cooling
Tubular steam reforming	Vapour solid phase, heterogeneous, fixed bed	Endothermic, reversible reaction chemical equilibrium	Heat balance, heat flux, catalyst
Epoxy resin production	Liquid phase, complete stirred tank reactor	Exothermic reaction polymerization	Heat removal, control of polymerization
Hydrotreating	Liquid and vapour phases, heterogeneous, fixed bed	Exothermic, high pressure reaction	Hydrogen consumption, heat removal, catalyst
Fluid catalytic cracking	Vapour-liquid-solid phases, heterogeneous, continuous fluidized bed	Endothermic, consecutive reaction	Product distribution, continuous catalyst regeneration
Wet-type flue gas desulphurization	Vapour-liquid-solid phases, heterogeneous, bubbling tank	Acid-base reaction	Mass transfer, saving power energy

Although homogeneous reactors are generally classified into tubular and stirred tank reactors as described above, there is another classification lying between the two as a column reactor with an aspect ratio of about 3-20. This reactor may often be placed horizontally. In this case it is called a lateral reactor. Generally, the distributor must be devised to allow uniform fluid feed. Since longitudinal mixing of the flow through the reactor is not negligible, perforated plates or packings may be set in place. Circulation in the reactor is sometimes preferred to control reacting conditions such as temperature and pH (Fig. 3).

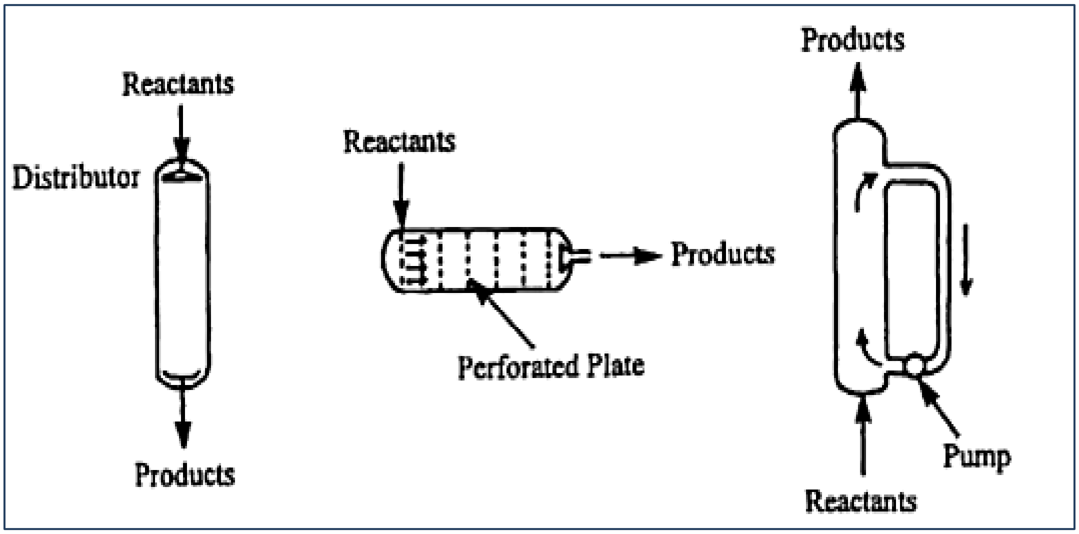


Fig. 3. (a) Column reactor. (b) Lateral reactor. (c) Column reactor with circulation

As explained before that the rate of reaction is extremely dependent on the concentration of materials whither are reactants or products and on the temperature of reaction occurred through in the reactor. Thus it could be designated as follows:

$$\overset{\frac{\text{mol}}{\text{m}^3\cdot\text{s}}}{-r_A} = f\begin{bmatrix}\text{temperature} & & \text{concentration}\\ \text{dependent} & , & \text{dependent}\\ \text{terms} & & \text{terms}\end{bmatrix} \overset{\text{as an}}{\underset{\text{example}}{=}} \overset{\left(\frac{\text{mol}}{\text{m}^3}\right)^{1-a}\text{s}^{-1}}{k}\underset{\text{reaction order}}{C_A^{a}} = k_0\underbrace{e^{-\overset{\text{activation energy}}{E}/RT}}_{\text{temperature dependent term}}C_A^{a}$$

Concentration-dependent term of a rate equation

Before we can find the form of the concentration term in a rate expression, we must distinguish between different types of reactions. This distinction is based on the form and number of kinetic equations used to describe the progress of reaction. Also, since we are concerned with the concentration-dependent term of the rate equation, we hold the temperature of the system constant.

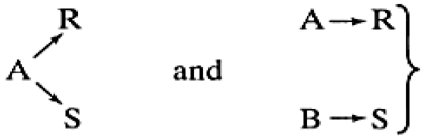
Single and Multiple Reactions

First of all, when materials react to form products it is usually easy to decide after examining the stoichiometry, preferably at more than one temperature, whether we should consider a single reaction or a number of reactions to be occurring. When a single stoichiometric equation and single rate equation are chosen to represent the progress of the reaction, we have a *single reaction.* 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, and we have *multiple reactions.* Multiple reactions may be classified as:

series reactions,

$$A \rightarrow R \rightarrow S$$

parallel reactions, which are of two types



competitive side by side

and more complicated schemes, an example of which is

$$A + B \rightarrow R$$
$$R + B \rightarrow S$$

Here, reaction proceeds in parallel with respect to B, but in series with respect to A, R, and S.

Elementary and nonelementary reactions

Consider a single reaction with stoichiometric equation such as occur when fast argon molecules collide with hydrogen molecules to decompose into hydrogen atoms which called as elementary reaction. However, it is very rare that a single reaction takes place independently. The mechanism of this reaction involves the collision or interaction of a single molecule of argon (A) with a single molecule of hydrogen (B) , then the number of collisions of molecules argon with hydrogen is proportional to the rate of reaction. But at a given temperature the number of collisions is proportional to the concentration of reactants in the mixture; hence, the rate of disappearance of (A) is given by ($-r_A = k\ C_A\ C_B$). Such reactions in which the rate equation corresponds to a stoichiometric equation, i.e. set of relations between reaction orders and stoichiometric coefficients, are called *elementary reactions.*

The number of chemical species involved in a single elementary reaction is referred to as the molecularity of that reaction. Molecularity is a theoretical concept, whereas stoichiometry and order are empirical concepts. Since an elementary reaction occurs on a molecular level exactly as it is written, its rate expression can be determined by inspection. A unimolecular reaction is first-order process, bimolecular reactions are second-order, and trimolecular processes are third-order. However, the converse statement is not true. Second-order rate expressions are not necessarily the result of an elementary bimolecular reaction.

When there is no direct correspondence between stoichiometry and rate, then we have *nonelementary reactions.* The classical example of a nonelementary reaction is that between hydrogen and bromine ($H_2 + Br_2 \rightarrow 2HBr$) which has a rate expression

$$r_{\mathrm{HBr}} = \frac{k_1[\mathrm{H_2}][\mathrm{Br_2}]^{1/2}}{k_2 + [\mathrm{HBr}]/[\mathrm{Br_2}]}$$

H.W. 4.1: *Give examples for elementary and nonelementary reactions (two examples for each type).*

Chemical Reactor Design:

Representation of an Elementary Reaction

In expressing a rate we may use any measure equivalent to concentration (for example, partial pressure), in which case

$$r_A = k\, p^a_A\, p^b_B \ldots .\, p^d_D$$

Whatever measure we use leaves the order unchanged; however, it will affect the rate constant k. For brevity, elementary reactions are often represented by an equation showing both the molecularity and the rate constant. For example,

$$2\mathrm{A} \xrightarrow{k_1} 2\mathrm{R} \tag{1}$$

represents a biomolecular irreversible reaction with second-order rate constant k_1, implying that the rate of reaction is

$$-r_\mathrm{A} = r_\mathrm{R} = k_1 C_\mathrm{A}^2$$

It would not be proper to write Eq. 1

$$\mathrm{A} \xrightarrow{k_1} \mathrm{R}$$

for this would imply that the rate expression is

$$-r_\mathrm{A} = r_\mathrm{R} = k_1 C_\mathrm{A}$$

Thus, we must be careful to distinguish between the one particular equation that represents the elementary reaction and the many possible representations of the stoichiometry. At times it may be necessary to specify the component in the reaction to which the rate constant is referred. For example, consider the reaction,

$$\mathbf{B + 2D \rightarrow 3T}$$

If the rate is measured in terms of B, the rate equation is

$$-r_\mathrm{B} = k_\mathrm{B} C_\mathrm{B} C_\mathrm{D}^2$$

If it refers to D, the rate equation is

$$-r_D = k_D C_B C_D^2$$

Or if it refers to the product T, then

$$r_T = k_T C_B C_D^2$$

But from the stoichiometry

$$-r_B = -\frac{1}{2} r_D = \frac{1}{3} r_T$$

hence,

$$k_B = \frac{1}{2} k_D = \frac{1}{3} k_T$$

Temperature-dependent term of a rate equation

Rate coefficients

We next consider the (k)s in the expressions of the rate of reaction. We will generally call these the rate coefficients (the coefficient of the concentration dependences in r). They are sometimes called rate constants; they are independent of concentrations, but rate coefficients are almost always strong functions of temperature. It is found empirically that these coefficients frequently depend on temperature as

$$k(T) = k_O \, EXP(-E/RT)$$

where E is called the activation energy for the reaction and k_O is called the pre-exponential factor (frequency factor- a temperature independent quantity) and the expression [***EXP(-E/RT)]*** called the *Boltzmann factor*. This relation is called the ***Arrhenius temperature dependence***.

The following figure (Fig. 1) described chemical reactions as the process of crossing a potential energy surface between reactants and products. This figure reveals that the activation energy for the forward reaction is E_f, for the back reaction E_b, and the heat of the reaction is ($\Delta H_R = E_f - E_b$). The curve at the left is for an endothermic reaction ($E_f > E_b$), while the curve at the right is for an exothermic reaction ($E_f < E_b$).

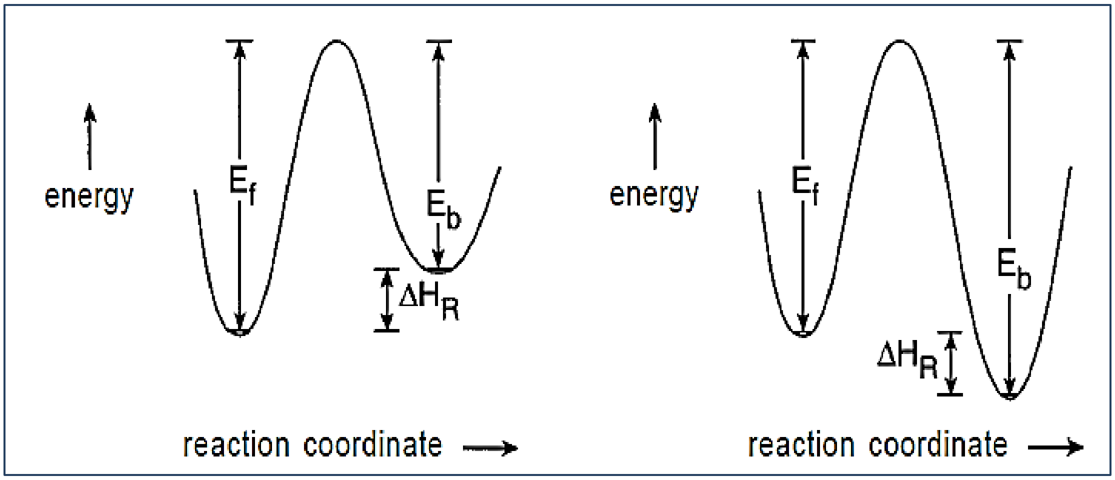


Fig. 1. Plot of energy of reactants and products in a chemical reaction versus the reaction coordinate

This functional form of ***k(T)*** predicts a very strong dependence of reaction rates on temperature, and this fact is central in describing the complexities of chemical reactions.

***Example 5.1*:** How much does a reaction rate with an activation energy of 15,000 Cal/mole vary when the temperature is increased from 300 to 310 K? From 300 to 400 K?

Ans.:

The ratio of the rate of this reaction at 310 K to that at 300 K,

$$\frac{k_{310}}{k_{300}} = \frac{e^{-E/RT_1}}{e^{-E/RT_2}} \quad \frac{\exp[-15,000/(2 \times 310)]}{\exp[-15,000/(2 \times 300)]} = 2.24$$

(We use the approximation of $R = 2$ cal/mole K). Between 300 and 400 K this ratio is very large,

$$\frac{k_{400}}{k_{300}} = \frac{e^{-E/RT_1}}{e^{-E/RT_2}} = \frac{\exp[-15,000/(2 \times 400)]}{\exp[-15,000/(2 \times 300)]} = 517$$

This shows that for this activation energy an increase of temperature by 10 K approximately doubles the rate and an increase of 100 K increases it by more than a factor of 500.

H.W. 5.1: *For example 5.1, how much does the reaction rate vary when the temperature is decreased from 300 to 200 K?*

The units of the rate constant will vary depending on the overall order of the reaction. Basically, we choose units to make the rate (in ***moles liter^{-1} time^{-1}***) dimensionally correct. For ***r*** = ***kC^{n}*, *k*** has units of ***liter $^{n-1}$ mole $^{1-n}$ time $^{-1}$***, which gives ***k(time^{-1})*** for ***n = 1***.

H.W. 5.2*: List a table containing the units of the reaction rate constant (k) for the orders (0.5, 1.5, 2 and 3) ?*

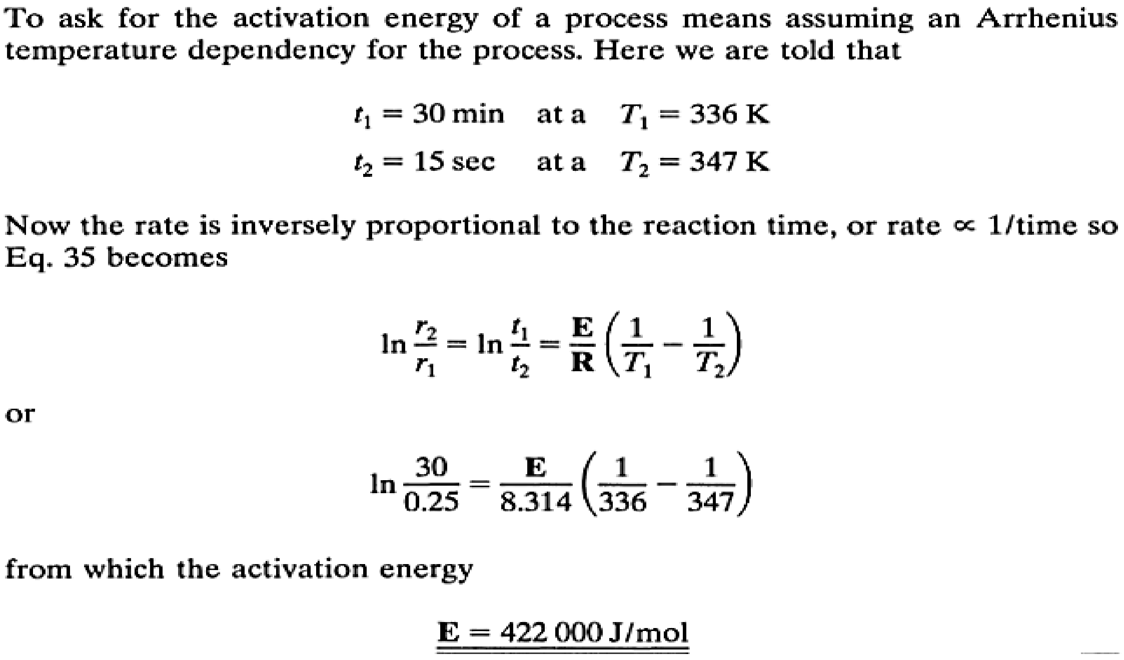
At the same concentration, but at two different temperatures, Arrhenius' law indicates that

$$\ln\frac{r_2}{r_1} = \ln\frac{k_2}{k_1} = \frac{\mathbf{E}}{\mathbf{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The temperature dependency of reactions is determined by the activation energy and temperature level of the reaction. Also, Reactions with high activation energies are very temperature-sensitive; reactions with low activation energies are relatively temperature-insensitive.

***Example 5.2*:** Milk is pasteurized if it is heated to 63^{o}C for 30 min, but if it is heated to 74°C it only needs 15 s for the same result. Find the activation energy of this sterilization process?

Ans.:



To ask for the activation energy of a process means assuming an Arrhenius temperature dependency for the process. Here we are told that

$$t_1 = 30 \text{ min} \quad \text{at a} \quad T_1 = 336 \text{ K}$$
$$t_2 = 15 \text{ sec} \quad \text{at a} \quad T_2 = 347 \text{ K}$$

Now the rate is inversely proportional to the reaction time, or rate ∝ 1/time so Eq. 35 becomes

$$\ln\frac{r_2}{r_1} = \ln\frac{t_1}{t_2} = \frac{\mathbf{E}}{\mathbf{R}}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

or

$$\ln\frac{30}{0.25} = \frac{\mathbf{E}}{8.314}\left(\frac{1}{336} - \frac{1}{347}\right)$$

from which the activation energy

$$\underline{\underline{\mathbf{E} = 422\,000 \text{ J/mol}}}$$

For multiple reactions a change in the observed activation energy with temperature indicates a shift in the controlling mechanism of reaction as shown in the following figure (Fig. 2).

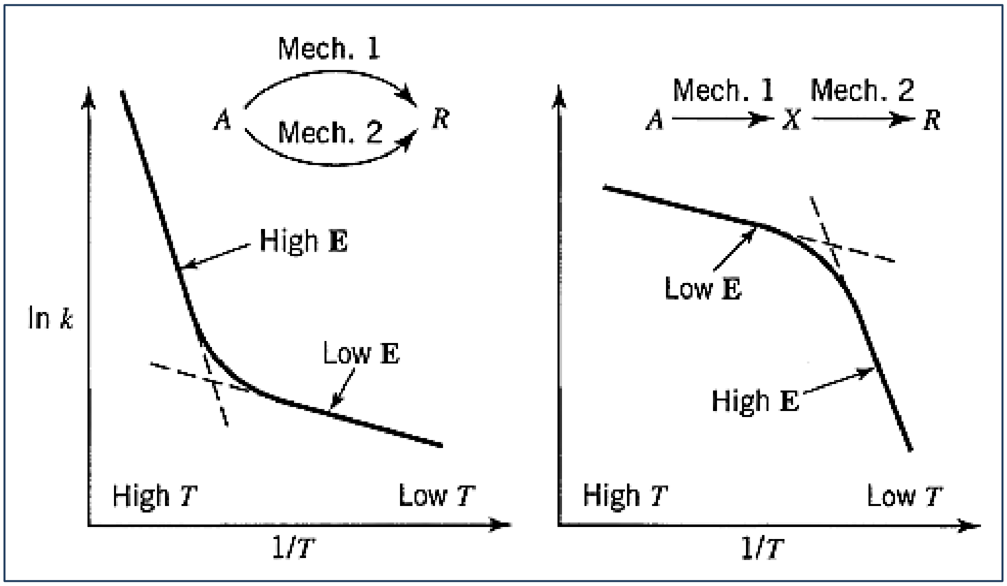


Fig. 2. A change in activation energy indicates a shift in controlling mechanism of reaction

H.W. *5.3: Solve the problems of Chapter 2 in the book (2.1 to 2.5)?*

Chemical Reactor Design:

Thermodynamics of chemical reactions

The science of chemical kinetics is concerned primarily with chemical changes and the energy and mass fluxes associated therewith. thermodynamics, on the other hand, is concerned with equilibrium systems . These systems are undergoing with no net change with time. Chemical thermodynamics enables the calculation of the heat balance associated with a reaction which is either endothermic or exothermic. This thermodynamic information is indispensable for reactor design. The basic criterion for the establishment of chemical reaction equilibrium is that

$$\sum_i v_i \mu_i = 0 \qquad (1)$$

where the $\boldsymbol{\mu_i}$ are the chemical potentials of the various species in the reaction mixture. If ***r*** reactions may occur in the system and equilibrium is established with respect to each of these reactions, it is required that

$$\sum_i v_{ki} \mu_i = 0 \qquad k = 1, 2, \dots, r \qquad (2)$$

These equations are equivalent to a requirement that the Gibbs free energy change for each reaction (ΔG) be zero at equilibrium.

$$\Delta G = \sum_i v_i \mu_i = 0 \text{ at equilibrium} \qquad (3)$$

The chemical potential of species ***i*** could be estimated from its value at standard state in addition to (RT) times its activity ($\boldsymbol{a_i}$) as follows:

$$\mu_i = \mu_i^0 + RT \ln a_i \qquad (4)$$

Where: ***R*** is the gas constant; ***T*** is the absolute temperature; $\boldsymbol{\mu_i^0}$ is the standard chemical potential of species ***i*** in a reference state where its activity is taken as unity.

In particular, standard states listed in Table 1 are used in calculations dealing with chemical reaction equilibrium. In all cases the temperature is the same as that of the reaction mixture.

Table 1: Standard States for Chemical Potential Calculations (for Use in Studies of Chemical Reaction Equilibrium)

State of Aggregation	**Standard state**
Gas	Pure gas at unit fugacity (for an ideal gas the fugacity is unity at 1 atm pressure; this is a valid approximation for most real gases).
Liquid	Pure liquid in the most stable form at 1 atm
Solid	Pure solid in the most stable form at 1 atm.

Once the standard states for the various species have been established, one can proceed to calculate a number of standard energy changes for processes involving a change from reactants, all in their respective standard states, to products, all in their respective standard states. For example, the Gibbs free energy change for this process is

$$\Delta G^0 = \sum_i v_i \mu_i^0 \tag{5}$$

where the superscript zero on $\Delta \boldsymbol{G}$ emphasizes the fact that this is a process involving standard states for both the final and initial conditions of the system. In a similar manner one can determine standard enthalpy ($\Delta \boldsymbol{H}^{0}$) and standard entropy changes ($\Delta \boldsymbol{S}^{0}$) for this process. Use of these symbols is restricted to the case where the extent of reaction (ζ) is ***1 mole*** for the reaction as written. Moreover, ***G*** and ***H*** are categorized as state functions, i.e. they are independent of whether the reaction takes place in one or in several steps.

Since chemical reactions involve the formation, destruction, or rearrangement of chemical bonds, they are invariably accompanied by changes in the enthalpy and Gibbs free energy of the system. It is also useful in determining the effect of temperature on the equilibrium constant of the reaction and thus on the reaction yield. The Gibbs free energy is useful in determining whether or not chemical equilibrium exists in the system being studied and in determining how changes in process variables can influence the yield of the reaction. In chemical kinetics there are two types of processes for which one calculates changes in these energy functions.

1. A chemical process whereby reactants, each in its standard state, are converted into products, each in its standard state, under conditions such that the initial temperature of the reactants is equal to the final temperature of the products.
2. An actual chemical process as it might occur under either equilibrium or non-equilibrium conditions in a chemical reactor.

The standard enthalpy change of a reaction that involves the formation of a compound from its elements is called the enthalpy (or heat) of formation of the compound and is denoted by the symbol ΔH_f^0, where ΔG_f^0 refers to the standard Gibbs free energy of formation. In more general form:

$$\Delta H^0 = \sum_i v_i \Delta H_{f,i}^0 \qquad (6)$$

$$\Delta G^0 = \sum_i v_i \Delta G_{f,i}^0 \qquad (7)$$

If ΔH^0 is negative, the reaction is said to be exothermic; if ΔH^0 is positive, the reaction is said to be endothermic.

***H.W. 6.1**: Write the standard entropy equation depending on the standard values of enthalpy and free energy?*

Cases of heat of reaction:

There are three important cases performed to evaluate the heat of reaction depending on the inlet and outlet conditions of the chemical reactor as follows:

Case 1: When the inlet and outlet streams having the same temperature at 25^0C, the heat of reaction $\Delta \boldsymbol{H_r}$ equals the difference of the standard heat of formation times moles of components between these streams (outlet-inlet) as follows:

$$\Delta H_r^0 = \sum_P v_i \Delta H_f^0 - \sum_R v_i \Delta H_f^0 \qquad \text{Hess's Law} \quad (8)$$

The symbol (ΔH_f^0) refers to the formation of a compound from its atomic constituents as they normally occurred in nature (e.g. O_2 rather than O atom). The values of ($\Delta \boldsymbol{H_f}$) for several compounds are found in tables.

Example 6.1. N_2 (g) +2H_2 (g) + 1.5O_2 → NH_4NO_3 (c) $\Delta H_r^0 = -365.14 \frac{kJ}{mol} = \Delta H_f^0$

6C (s) + 3H_2 (g) → C_6H_6 (l) $\Delta H_r^0 = +48.66 \frac{kJ}{mol} = \Delta H_f^0$

Example 6.2. Determine the standard heat of reaction for the following reaction:

$$C_5H_{12}\text{ (l)} + 8O_2\text{ (g)} \rightarrow 5CO_2\text{ (g)} + 6H_2O\text{ (l)}$$

Where ΔH_f^0 for C_5H_{12} (l) , CO_2 (g), and H_2O (l) are (-173, -393.5, and -285.84 kJ/mol) respectively.

Ans.: Using equation 8, the standard heat of reaction ΔH_r^0 could be obtained as follows:

$$\Delta H_r^0 = \sum_P \nu_i \Delta H_f^0 - \sum_R \nu_i \Delta H_f^0 = 5(-393.5) + 6(-285.84) - 1(-173) = -3509\ kJ/mol$$

Case 2: When the inlet and outlet streams having the same temperature but not 25^0C, the heat of reaction $\Delta \boldsymbol{H_r}$ equals the heat of reaction at (T_0=25^0C) in addition to the heat of reaction at this temperature (T) as follows:

$$\Delta H_{r,T} = \Delta H_{r,T_0} + \int_{T_0}^{T} \Delta C_p\, dT \qquad (9)$$

Where:

$$\Delta C_p = \sum_P n_i C_{P_i} - \sum_R n_i C_{P_i} \qquad (10)$$

Case 3: When the inlet and outlet streams having different temperatures and not 25^0C, the heat of reaction $\Delta \boldsymbol{H_r}$ will be:

$$\Delta H_{r,T} = \Delta H_{r,T_0} + \Delta H_P - \Delta H_R \qquad (11)$$

$$\Delta H_{r,T} = \Delta H_{r,T_0} + \sum_P \int_{T_0}^{T} n_i C_{P_i}\, dT - \sum_R \int_{T_0}^{T} n_i C_{P_i}\, dT \qquad (12)$$

Example 6.3. Explain the following reaction thermodynamically:

CaC_2 (s) + $2H_2O$ (l) → $Ca(OH)_2$ (s) + C_2H_2 (g) **ΔH_r = -125.4 kJ/mol (25^0C, 1 atm)**

Ans.: The heat of reaction given is mean:

$$\Delta H_{r,T} = \frac{-125.4\ kJ}{1\ mol\ CaC_2} \equiv \frac{-125.4\ kJ}{2\ mol\ H_2O} \equiv \frac{-125.4\ kJ}{1\ mol\ Ca(OH)_2} \equiv \frac{-125.4\ kJ}{1\ mol\ C_2H_2}$$

Example 6.4. Give examples showing that the heat of reaction (**ΔH_r**) is totally dependent on the state of material of both reactants and products.

Ans.: (1) CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (l) **ΔH_r = -890.3 kJ/mol (25^0C, 1 atm)**

(2) CH_4 (g) + $2O_2$ (g) → CO_2 (g) + $2H_2O$ (g) **ΔH_r = -802.3 kJ/mol (25^0C, 1 atm)**

H.W. 6.2. *For example 6.4., why the first case released more heat than the second case?*

Hint: The value of **ΔH_r** depends on how the stoichiometric equation is written. For example, the heat of reaction for (2A→2B) is a double of that for the reaction (A→B).

Example 6.5. Estimate the heat of cracking of propane to ethylene and methane at 900^0F

$$C_3H_8 \rightarrow C_2H_4 + CH_4$$

Where the heat of formation ($\Delta H^0_{f,64^0F}$) for C_3H_8, C_2H_4, and CH_4 are (-24820), (12496) and (-17889) cal/gmol, respectively, and the heat of capacity (C_p) for them are 41.0, 20.9, and 11.7 cal/gmol.K, respectively.

Ans.: Since the reaction had not occurred at standard condition (64^0F); therefore, case 2 should be applied as follows:

$$\Delta H_{r,T} = \Delta H_{r,T_0} + \int_{T_0}^{T} \Delta C_p\, dT$$

$$\Delta H^0_{r,64^0F} = \sum_P \nu_i \Delta H^0_f - \sum_R \nu_i \Delta H^0_f$$

= [12496 + (-17889)] – (-24820) = 19427 cal/gmol

$$\Delta H_{r,900^0F} = 19427 + \int_{64^0F=17.78\,K}^{900^0F=482.2\,K} [(20.9 + 11.7) - 41.0)]\, dT$$

$$\Delta H_{r,900^0F} = 15.525 \text{ cal/gmol}$$

H.W.6.3*: Relate the following parameters between each other:(T_K to T_C);(T_R to T_F);(T_F to T_C)?*

The heat of reaction could be estimated depending on the *heat of combustion* (ΔH^0_C) which it is the heat of reaction of that substance with oxygen to yield specified products with both reactants and products at standard conditions.

Example 6.6. C_2H_5OH (l) +3O_2 (g) → 2CO_2 (g) + 3H_2O (l) :$\Delta H^0_r = -13669 \frac{kJ}{mol} = \Delta H^0_C$

Hint: In general: (1) All carbon in the fuel → CO_2 (g)

(2) All Hydrogen in the fuel → H_2O (l)

(3) All Sulfur in the fuel → SO_2 (g)

(4) All Nitrogen → N_2 (g)

In the case of the heat of combustion, the heat of reaction at standard conditions is

$$\Delta H^0_{r,T^0} = \sum_R \nu_i \Delta H^0_C - \sum_P \nu_i \Delta H^0_C \qquad (13)$$

Moreover, the heat of combustion could be used to estimate the heat of formation for combustible substances such as (C_5H_{12}) which cannot be carried out in the laboratory:

5C (s) + 6H_2 (g) → C_5H_{12}

$$(\Delta H^0_f)_{C_5H_{12}(l)} = 5(\Delta H^0_C)_{C(s)} + 6(\Delta H^0_C)_{H_2(g)} - (\Delta H^0_C)_{C_5H_{12}(l)}$$

Chemical Reactor Design:

Thermodynamics of chemical reactions

As explained before that the Gibbs free energy is important in the analysis of chemical reactions. The change of this parameter is significant because of the associated chemical equilibrium for the reaction. If ΔG is negative, the thermodynamics for the reaction are favorable. On the other hand, if its value is highly positive, the thermodynamics are not favorable. For thermodynamic equilibrium, the following criteria is useful for quick screening of chemical reactions

$\Delta G_r < 0$ [kJ/mol]	Reaction favorable
$0 < \Delta G_r < 50$ [kJ/mol]	Reaction possibly favorable
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The correlation for Gibbs free energy of formation is

$$\Delta G_f = A + B\,T + C\,T^2 \qquad (1)$$

where the regression coefficients A, B, and C could be obtained from references. The chemical equilibrium for a reaction is associated with the change in Gibbs free energy ΔG_r for the reaction

$$\Delta G_r = \sum_P n_i \Delta G_f - \sum_R n_i \Delta G_f \qquad (2)$$

Example 7.1. Estimate the Gibbs free energy of formation of methane (CH_4) as a low-pressure gas at 500K.

Ans.: The value of ΔG_f could be estimated using Eq. 1; therefore, regression coefficients should be listed from references which are as follows:

A= -75.262; B= 0.07593; C= 1.87×10^{-5}

$\Delta G_f = A + B\,T + C\,T^2 = -75.262 + 0.07593\,(500) + 1.87\times10^{-5}\,(500)^2 = -32.63$ kJ/mol

H.W. 7.1*: Calculate the change in Gibbs free energy for the reaction of methanol and oxygen to produce formaldehyde and water at a reaction temperature of 600K? Then specify the criteria of reaction from the favorability view.*

$$CH_4O\ (g) + 0.5O_2\ (g) \rightarrow CH_2O\ (g) + H_2O\ (g)$$

Equilibrium rate constant

The rate constant had been estimated using Arrhenius equation studied before. Now, standard Gibbs free energy could be performed to evaluate the equilibrium rate constant as shown below:

$$\boldsymbol{\Delta G^0 = -R\,T\,lnK} \qquad (3)$$

Where: $\boldsymbol{R}$ is the gas constant; $\boldsymbol{T}$ is the absolute temperature (K); $\boldsymbol{K}$ is equilibrium constant.

The correlation that relate $\Delta \boldsymbol{G}$ to $\Delta \boldsymbol{H}$ and $\Delta \boldsymbol{S}$ at standard conditions is:

$$\boldsymbol{\Delta G^0 = \Delta H^0 - T\Delta S^0} \qquad (4)$$

The equilibrium rate constant could be estimated for fluids, i.e. liquids and gases, for both ideal and non-ideal cases. For example, the following reversible reaction occurred in a reactor:

$$\boldsymbol{aA + bB \Leftrightarrow cC + dD}$$

Where the foreword rate constant is assigned as $\boldsymbol{k_f}$ and the backward rate constant as $\boldsymbol{k_b}$. The equilibrium constant (K) equals ($\boldsymbol{k_f}$ / $\boldsymbol{k_b}$) in case of constant temperature and pressure.

- ***Non-Ideal gases***:

$$\boldsymbol{K = K_\alpha K_y P_T^{\Delta n}} \qquad (5)$$

Where:

$$K_\alpha = \frac{\alpha_C^c\ \alpha_D^d}{\alpha_A^a\ \alpha_B^b} \quad ; \ K_y = \frac{y_C^c\ y_D^d}{y_A^a\ y_B^b} \quad ; \ K_P = \frac{p_C^c\ p_D^d}{p_A^a\ p_B^b}$$

And; K_y is the equilibrium constant in case of mole fraction for gases, K_α is the equilibrium constant in case of fugacity coefficient, K_P is the equilibrium constant in case of partial pressure, P_T is the total pressure, and Δn is the difference of moles between the products and reactants **[**$\Delta n = d + c - (a + b)$]

Since;

$$K_P = K_y P_T^{\Delta n} \qquad (6)$$

Therefore, Eq. 5 will be

$$K = K_\alpha K_P \qquad (7)$$

- ***Ideal gases***: For ideal gases, $K_\alpha = 1$; therefore, Eq. 5 will be

$$K = K_y P_T^{\Delta n} \qquad (8)$$

- ***Non-Ideal solution***:

$$K = K_\gamma K_x \qquad (9)$$

Where:

$$K_x = \frac{X_C^c\ X_D^d}{X_A^a\ X_B^b} \quad ; \ K_\gamma = \frac{\gamma_C^c\ \gamma_D^d}{\gamma_A^a\ \gamma_B^b}$$

And; K_x is the equilibrium constant in case of mole fraction for liquids, and K_γ is the equilibrium constant in case of activity coefficients of components.

- ***Ideal solution***: For ideal liquids, $K_\gamma = 1$; therefore, Eq. 9 will be

$$K = K_x \qquad (10)$$

The effect of temperature on the chemical equilibrium constant could be estimated from *Vant Hoff equation* as follows:

$$\frac{d\ln K}{dT} = \frac{\Delta H_r^0}{RT^2} \qquad (11)$$

When the ΔH_r^0 is constant and independent on temperature, Eq. 11 will be

$$\ln\frac{K_2}{K_1} = \frac{\Delta H_r^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (12)$$

***H.W. 7.2**: Derive Eq. 12 from Eq. 11*

But, for variable ΔH_r^0 with temperature

$$\ln K = \frac{\Delta H_r^0}{RT} + \frac{\Delta a}{R}\ln T + \frac{\Delta b}{2R}T + \frac{\Delta C}{6R}T^2 + J \qquad (13)$$

Where ***a, b***, and ***c*** are the constants of C_p, and ***J*** is analytical coefficient

In general, For endothermic reaction, $T_2>T_1$ and $K_2>K_1$ which means that ***K*** increases as the temperature increased. Therefore, the reactor operates at the highest possible temperature to obtained a high conversion. But, for exothermic reaction, $T_2>T_1$ and $K_2<K_1$ which means that ***K*** decreases as the temperature increased. Here the temperature is kept high, and then decreased as equilibrium is approached. Therefore, an exothermic reaction must be performed at as a low temperature as possible to prevent the decreasing of the conversion.

Moreover, the equilibrium constant ***K*** is independent of pressure at standard state, but it will be extremely affected by the variation of pressure for gases. The following examples explain this topic.

Reaction	Δn	Pressure	Increasing	conversion
$N_2 + 3H_2 \Leftrightarrow 2NH_3$	-ve	Increased	Forward	increased
$C_2H_6 \Leftrightarrow C_2H_4 + H_2$	+ve	Increased	Backward	decreased
$I_2 + H_2 \Leftrightarrow 2HI$	Zero	No effect of pressure on conversion		

Example 7.2. A pure benzene is decomposed to form diphenyl at **1032K** and **1 atm** via the following gas phase reaction ($2C_6H_6 \Leftrightarrow C_{12}H_{10} + H_2$) where the equilibrium constant is 0.3. Find the conversion of benzene at equilibrium.

Ans.: Since the process occurred at 1 atm, so we could assumed that the process is as ideal gases; therefore, $\boldsymbol{K_\alpha = 1}$

$$\boldsymbol{K = K_y P_T^{\Delta n} = K_y (1)^{(1+1-2)} = 0.3} \quad ; \quad \text{So,} \qquad \boldsymbol{K_y = 0.3}$$

Take the basis as **1 mol** of benzene then rearrange the form of chemical equation to be:

$$C_6H_6 \Leftrightarrow 0.5C_{12}H_{10} + 0.5H_2$$

At initial conditions:	1	0	0
At equilibrium:	1-ζ	0.5 ζ	0.5 ζ

So, the total moles at equilibrium= (1-ζ) + 0.5 ζ + 0.5 ζ = 1 mol

The mole fractions of compounds at equilibrium are

$$y_{C_6H_6} = \frac{1-\zeta}{1} = 1-\zeta \ ; \ y_{C_{12}H_{10}} = \frac{0.5\ \zeta}{1} = 0.5\ \zeta \ ; \ y_{H_2} = \frac{0.5\ \zeta}{1} = 0.5\ \zeta$$

$$\boldsymbol{K_y = \frac{y_{H_2}^{0.5}\ y_{C_{12}H_{10}}^{0.5}}{y_{C_6H_6}^{1}}}$$

$$0.3 = \frac{(0.5\ \zeta)^{\mathbf{0.5}}(0.5\ \zeta)^{\mathbf{0.5}}}{1-\zeta}$$

After simplification, ζ= 0.523 mol

Therefore, the conversion of benzene = $\frac{Reacted}{inlet} = \frac{\zeta}{1} = \frac{0.523}{1} = 0.523$

Example 7.3. A feed consists of 95% of benzene and the balance is inert. Benzene had decomposed to form diphenyl at **1032K** and **1 atm** via the following gas phase reaction ($2C_6H_6 \Leftrightarrow C_{12}H_{10} + H_2$) where the equilibrium constant is 0.3. Find the conversion of benzene at equilibrium.

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Take the basis as **1 mol** of feed then rearrange the form of chemical equation to be:

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So, the feed contains (0.95*1= 0.95 mol) of benzene and (0.05*1=0.05 mol) of inert.

At initial conditions: 0.95 0 0

At equilibrium: 0.95-ζ 0.5 ζ 0.5 ζ

So, the total moles at equilibrium= (0.95-ζ) + 0.5 ζ + 0.5 ζ +0.05 = 1 mol

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$$\boldsymbol{K_y = \frac{y_{H_2}^{0.5}\, y_{C_{12}H_{10}}^{0.5}}{y_{C_6H_6}^{1}}}$$

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At equilibrium: 1-ζ 0.5 ζ 0.5 ζ

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$$\boldsymbol{K_y = \frac{y_{H_2}^{0.5}\, y_{C_{12}H_{10}}^{0.5}}{y_{C_6H_6}^{1}}}$$

$$0.3 = \frac{(0.5\ \zeta)^{\mathbf{0.5}}(0.5\ \zeta)^{\mathbf{0.5}}}{1-\zeta}$$

After simplification, ζ= 0.523 mol

Therefore, the conversion of benzene = $\frac{Reacted}{inlet} = \frac{\zeta}{1} = \frac{0.523}{1} = 0.523$

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Take the basis as **1 mol** of feed then rearrange the form of chemical equation to be:

$$C_6H_6 \Leftrightarrow 0.5C_{12}H_{10} + 0.5H_2$$

So, the feed contains (0.95*1= 0.95 mol) of benzene and (0.05*1=0.05 mol) of inert.

At initial conditions: 0.95 0 0

At equilibrium: 0.95-ζ 0.5 ζ 0.5 ζ

So, the total moles at equilibrium= (0.95-ζ) + 0.5 ζ + 0.5 ζ +0.05 = 1 mol

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$$\boldsymbol{K_y = \frac{y_{H_2}^{0.5}\ y_{C_{12}H_{10}}^{0.5}}{y_{C_6H_6}^{1}}}$$

$$0.3 = \frac{(0.5\ \zeta)^{\mathbf{0.5}}(0.5\ \zeta)^{\mathbf{0.5}}}{0.95 - \zeta}$$

After simplification, ζ= 0.496 mol

Therefore, the conversion of benzene = $\frac{Reacted}{inlet} = \frac{\zeta}{0.95} = \frac{0.496}{0.95} = 0.522$

Chemical Reactor Design:

Thermodynamics of chemical reactions

We have noted that the rate constant and/or the equilibrium constant could be evaluated depending on several methods such as *Arrhenius law* and *Vant Hoff equation*. Then we found that the thermodynamics parameters have a significant effect on the behavior of the chemical reaction then the performance of the chemical reactor consequently. The following examples are beneficial to explain the relation between these parameters.

Example 8.1. A chemical reaction [$H_2O\ (g) + C_2H_4\ (g) \Leftrightarrow C_2H_5OH\ (g)$] proceeds at 254^0C and 264atm. Find the equilibrium compositions and their mole fractions using the following data.

Compound	**Initial mol.%**	ΔG_f^o **(kCal)**	ΔH_f^o **(kCal)**	α_i
N_2	15	-	-	-
H_2O (g)	60	-54.636	-57.798	0.19
C_2H_4 (g)	25	16.282	12.496	0.885
C_2H_5OH (g)	-	-40.30	-56.24	0.28

Ans.: Basis equals 100mol of feed

In order to evaluate the equilibrium compositions, the equilibrium constant at 254^0C must be calculated using Vant Hoff equation. First we must calculate the equilibrium constant at standard case (298K) as follows:

$$\Delta G^0 = \sum_P \nu_i \Delta G_f^0 - \sum_R \nu_i \Delta G_f^0 = 1 \times (-40.3) - [1 \times 16.282 + (-1) \times (-54.636)] = -1.946\ kCal/mol$$

$$\Delta H_r^o = \sum_P v_i \Delta H_f^0 - \sum_R v_i \Delta H_f^0 = 1 \times (-56.24) - [1 \times 12.496 + (-1) \times (-57.798)]$$

$$= -10.938\ kCal/mol$$

$$\Delta G^0 = -R\,T\,lnK \quad \Rrightarrow \ -1.946 = -1.987 * 298 * \ln K_{298}$$

$$K_{298} = 3.28$$

Now, the equilibrium constant at 527K could be found using Vant Hoff equation as follows:

$$\frac{d\ ln\ K}{dT} = \frac{\Delta H_r^0}{RT^2} \quad \Rrightarrow ln\frac{K_2}{K_1} = \frac{\Delta H_r^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\Rrightarrow ln\frac{K_{527}}{3.28} = \frac{-10.938}{1.987}\left(\frac{1}{298} - \frac{1}{527}\right)$$

$$\Rrightarrow \ K_{527} = 8.74 \times 10^{-3}$$

Using the following equations to estimate the requirements

$$K = K_\alpha K_y P_T^{\Delta n}$$

Where:

$$K_\alpha = \frac{\alpha_C^c}{\alpha_A^a\ \alpha_B^b} \quad ; \ K_y = \frac{y_C^c}{y_A^a\ y_B^b}$$

$$K_{527} = \frac{\alpha_C^c}{\alpha_A^a\ \alpha_B^b}\ \frac{y_C^c}{y_A^a\ y_B^b}\ P_T^{\Delta n}$$

We have the values of fugacity coefficients but we must the relations of mole fractions using the following table

Compound	Initial moles	Moles at equilibrium
N_2	15	15
H_2O (g) [A]	60	60-ζ
C_2H_4 (g) [B]	25	25-ζ
C_2H_5OH (g) [C]	0	ζ
Total	**100**	**100-ζ**

$$8.74 \times 10^{-3} = \frac{0.28}{0.19 \times 0.885} \frac{\frac{\xi}{100-\xi}}{(\frac{60-\xi}{100-\xi})(\frac{25-\xi}{100-\xi})} 264^{(1-1-1)}$$

After simplification, **ζ = 10.8mol**

So the equilibrium compositions and the mole fractions of compounds are as follows:

Compound	Moles at equilibrium	Mole fractions
N_2	15	16.8
H_2O *(g)* [A]	49.2	55.2
C_2H_4 *(g)* [B]	14.2	15.9
C_2H_5OH *(g)*[C]	10.8	12.1
Total	**89.2**	**100**

H.W. 8.1*: For example 8.1., why the total moles was not 100mols at equilibrium?*

Example 8.2. For the synthesis of ammonia from hydrogen and nitrogen [$N_2\ (g) + 3H_2\ (g) \Leftrightarrow 2NH_3\ (g)$] which proceeds at 155^{0}C and 1 atm. Calculate the heat of reaction in case of (1) kCal/kmol of N_2 reacted, (2) kJ/kmol of H_2 reacted, and calculate the equilibrium constant using the following data.

Compound	ΔS^0 (kJ/kmol.K)	ΔS^0 (Cal/kmol.K)	ΔH_f^o (kCal/kmol)
N_2 (g)	191.9	45.87	0
H_2 (g)	130.9	31.29	0
NH_3 (g)	192.9	46.10	11020

The C_p Constants are:

Compound	**a**	**b**	**c**
N_2 (g)	6.457	1.39×10^{-3}	-0.069×10^{-6}
H_2 (g)	6.946	-0.196×10^{-3}	0.476×10^{-6}
NH_3 (g)	5.92	-8.963×10^{-3}	-1.764×10^{-6}

Ans.: By using Hess's law

$\Delta H_r^0 = \sum_P \nu_i \Delta H_f^0 - \sum_R \nu_i \Delta H_f^0$ = 2(11020)-[1(0)+3(0)]= -22040 kCal per kmol of N_2 reacted at standard state.

Now to find this parameter at 155^{0}C, we will use the following equation:

$$\Delta H_{r,T} = \Delta H_{r,T_0} + \int_{T_0}^{T} \Delta C_p\, dT$$

We must, at first, calculate the values of capacities variables using the following equation:

$$\Delta C_p = \Delta a + \Delta b\, T + \Delta c\, T^2$$

$$\Delta a = 2(5.92) - [1(6.457) + 3(6.946)] = -15.455$$

$$\Delta b = 2(-8.963 \times 10^{-3}) - [1(1.39 \times 10^{-3}) + 3(-0.196 \times 10^{-3})] = 17.124 \times 10^{-3}$$

$$\Delta c = 2(-1.764 \times 10^{-6}) - [1(-0.069 \times 10^{-6}) + 3(0.476 \times 10^{-6})] = -4.887 \times 10^{-6}$$

$$\Delta C_p = -15.455 + 17.124 \times 10^{-3}\, T + (-4.887 \times 10^{-6})\, T^2$$

$$\Delta H_{r,T} = \Delta H_{r,T_0} + \Delta a(T - T_{0)} + \frac{\Delta b}{2}(T^2 - T_0^2) + \frac{\Delta c}{3}(T^3 - T_0^3)$$

$$\Delta H_{r,428} = -22040 + (-15.455)(428 - 298) + \frac{(17.124 \times 10^{-3})}{2}(428^2 - 298^2) + \frac{(-4.887 \times 10^{-6})}{3}(428^3 - 298^3) = -23325.68\,\frac{kCal}{kmol\ N_2 reacted}$$

***H.W. 8.2**: Find its value in* $\frac{kJ}{kmol\ N_2 reacted}$ *?*

To find the heat of reaction based on H_2 reacted

$$\Delta H_{r,428} = \frac{1\ kmol\ N_2\ reacted}{3\ kmol\ H_2\ reacted}\left(\frac{kJ}{kmol\ N_2 reacted}\right) = ?$$

Now, to calculate the equilibrium constant, we could use the following equation:

$$\Delta G_{r,428} = -R\ T\ lnK = \Delta H_{r,428} - T\Delta S_{r,428}$$

$$\Delta H_{r,428} = -23325.68\,\frac{kCal}{kmol\ N_2 reacted}$$

$$\Delta S_{r,428} = \Delta S_{r,298} + \int_{298}^{428} \frac{\Delta C_p}{T}\, dT$$

$$\Delta S_{r,298} = \sum_P \nu_i \Delta S^0 - \sum_R \nu_i \Delta S^0 = 2(46.10) - [1(45.87) + 3(31.29)] = -47.54\,\frac{cal}{mol.K}$$

$$\Delta S_{r,428} = -47.54 + \int_{298}^{428} \left(\frac{-15.455}{T} + 17.124 \times 10^{-3} - 4.887 \times 10^{-6}\, T \right) dT$$

$$\Delta S_{r,428} = -51.14 \frac{cal}{mol_{N_2}.K}$$

$$lnK = \frac{-1}{R\,T}\left(\Delta H_{r,428} - T\Delta S_{r,428}\right)$$

$$= \frac{-1}{1.987 \times 428}(-23325.68 - 428 \times (-51.14)) = 1.69$$

So the equilibrium constant for this reaction: ***K*= 5.42**

Example 8.3. Calculate the heat that must be removed or provided for the gas phase reaction proceeding [CO_2 (g) + $4H_2$ (g) → $2H_2O$ (g) + CH_4 (g)] with 100% conversion and the gas entering at 450°C. The heat of formation at standard conditions and the specific heat capacities are shown below:

Compound	ΔH_f^o (J/mol)	a	$b \times 10^{-2}$	c$\times 10^{-5}$
CO_2 (g)	–393513	26.75	4.226	-1.425
H_2 (g)	0	26.88	0.435	-0.033
H_2O (g)	–241826	29.16	1.449	-0.202
CH_4 (g)	–74848	13.44	7.703	-1.874
Δ	-	-62.54	4.635	-0.721

Ans.: The heat of reaction at the standard state 298 K is:

$\Delta H_r^0 = \sum_P \nu_i \Delta H_f^0 - \sum_R \nu_i \Delta H_f^0$ = 2(–241826)+[1(–74848)]-1(–393513)= -164987 J per mol of CO_2

$$\Delta C_p = \Delta a + \Delta b\, T + \Delta c\, T^2$$

$$\Delta C_p = -62.54 + 4.635 \times 10^{-2}\, T + (-0.721 \times 10^{-5})\, T^2$$

$$\Delta H_{r,723} = \Delta H_{r,298} + \int_{298}^{723} \Delta C_p\, dT$$

$$\Delta H_{r,723} = -164987 + \int_{T_0}^{T} (-62.54 + 4.635 \times 10^{-2}\, T + (-0.721 \times 10^{-5})\, T^2)\, dT$$

$$\Delta H_{r,723} = -182355 \frac{J}{CO_2}$$

The result shows that –182355 J/mol CO_2 must be removed

Chemical Reactor Design:

Reaction orders

The manner in which the reaction rate varies with the concentrations of the reactants and products can be shown by the orders of the reaction. These are the powers to which the concentrations are raised and are expressed as:

$$-r_A = kC_A^{\alpha}C_B^{\beta} \qquad (1)$$

where α^{th} is the order with respect to component A, and β^{th} is the order with respect to component B. The overall order of the reaction n is:

$$n = \alpha + \beta \qquad (2)$$

The exponents α and β may be integers or fractions and may be both positive and negative values, as well as the value of zero. In some cases, the exponents are independent of temperature. Where the experimental data fit the expressions in the form of Equation 1, the exponents will vary slightly with temperature. In these cases, the observed correlation should be applied only in a restricted temperature interval. Not all reactions can be expressed to have a specific order. As mentioned before, The units of the reaction rate constant k vary with the overall order of the reaction. These units are those of a rate divided by the *n*th power of concentration as evident from Equations 1 and 2.

$$k = \frac{(-r_A)}{C^n} = \frac{\text{moles}/(\text{volume} - \text{time})}{(\text{moles}/\text{volume})^n}$$

or

$$k = \text{time}^{-1}(\text{moles})^{1-n}\frac{1}{(\text{volume})^{1-n}}$$

$$= \text{time}^{-1}\left(\frac{\text{moles}}{\text{volume}}\right)^{-n+1}$$

Consider a reaction involving a reactant such that ***A*** → ***products***. The rate equations corresponding to a zero, first, second, and third order reaction together with their corresponding units are:

1. Zero order (n = 0; k = moles/m^3-sec)

   $(-r_A) = kC_A^0$

2. First order (n = 1; k = 1/sec)

   $(-r_A) = kC_A$

3. Second order (n = 2; k = m^3/moles-sec)

   $(-r_A) = kC_A^2$

4. Third order (n = 3; k = (m^3/moles)^2•sec^{-1})

   $(-r_A) = kC_A^3$

Determining the order of reactions

There are two methods that could be used to obtain the order of reaction then the rate equation which are the integral method and the differential method. In case of Integral method for irreversible and isothermal reaction of a constant volume system.

- **Zero order reactions**

The rate of a chemical reaction is of a zero order if it is independent of the concentrations of the participating substances. The rate of reaction is determined by such limiting factors as:

1. In radiation chemistry, the energy, intensity, and nature of radiation.
2. In photochemistry, the intensity and wave length of light.
3. In catalyzed processes, the rates of diffusion of reactants and availability of surface sites.

If the rate of the reaction is independent of the concentration of the reacting substance ***A***, then the amount ***d***C_A by which the concentration of ***A*** decreases in any given unit of time ***dt*** is constant throughout the course of the reaction. The rate equation for a constant volume batch system (i.e., *constant density*) can be expressed as:

$$-r_A = -\frac{dC_A}{dt} = k \qquad (3)$$

Assuming that at time t_1 the concentration of A is C_{A0}, and at time t_2 the concentration is C_{Af}, integrating Equation 3 between these limits gives:

$$-\int_{C_{AO}}^{C_{Af}} dC_A = k\int_{t_1}^{t_2} dt$$

$$-(C_{Af}-C_{AO}) = k(t_2-t_1)$$

$$k = \frac{(C_{AO}-C_{Af})}{(t_2-t_1)}$$

If $t_1 = 0$ and $t_2 = t$, therefore

$$C_{A0} - C_{AF} = kt \qquad (4)$$

Plotting the concentration (C_A) versus time t gives a straight line, where C_{A0} is the intercept and k is the slope. The velocity constant k may include arbitrary constants resulting from various limiting factors such as *diffusion constants* (D_{AB}) and a fixed intensity of absorbed light (I). In terms of the fractional conversion X_A

$$C_{A0}\, X_A = kt \qquad \text{for } t < \frac{C_{A0}}{k} \qquad (5)$$

Examples of zero order reactions are the intensity of radiation within the vat for photochemical reactions or the surface available in certain solid catalyzed gas reactions. Figure 1 shows plots of the zero order rate equations.

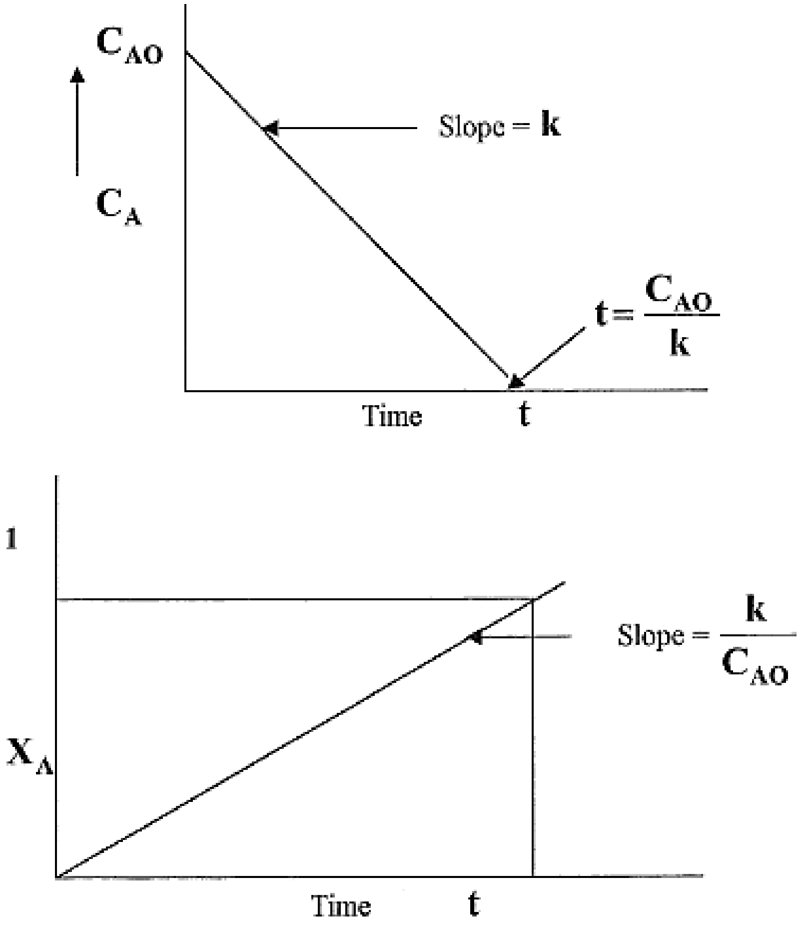


Fig. 1. Zero order reaction

***H.W. 10.1**. Derive the rate equation for (n= 0.25) order of isothermal reaction* $A \xrightarrow{k} B$ *proceeds in a constant volume batch system.*

- **First order reactions**

Consider the reaction $A \xrightarrow{k} B$. The rate of a first order reaction is proportional to the first power of the concentration of only one component. Assuming that there is no change in volume, temperature, or any other factor that may affect the reaction, the amount dC_A that undergoes a chemical change in the short time interval dt depends only on the amount of component A present at that instant. The rate for a first order reaction for a constant volume batch system (i.e., constant density) can be expressed as:

$$-r_A = -\frac{dC_A}{dt} = kC_A \qquad (6)$$

Rearranging and integrating Equation 6 between the limits gives

$$-\int_{C_{AO}}^{C_{Af}} \frac{dC_A}{C_A} = k\int_{t_1}^{t_2} dt$$

$$-\ln\left[\begin{matrix} C_{Af} \\ C_A \\ C_{AO} \end{matrix}\right] = k(t_2 - t_1)$$

$$-\ln\left[C_{Af} - C_{AO}\right] = k(t_2 - t_1)$$

$$-\ln\frac{C_{Af}}{C_{AO}} = k(t_2 - t_1)$$

If $t_1 = 0$ and $t_2 = t$, therefore

$$-ln\frac{C_{Af}}{C_{A0}} = kt \qquad (7)$$

In terms of the fractional conversion X_A

$$-ln\ (1 - X_{Af}) = kt \qquad (8)$$

A plot of $-ln(1 - X_A)$ or $-ln\ C_{Af}/C_{AO}$ versus t gives a straight line through the origin. The slope of the line is the rate constant k, as represented by Figure 2. The unit of the rate constant k is sec^{-1}.

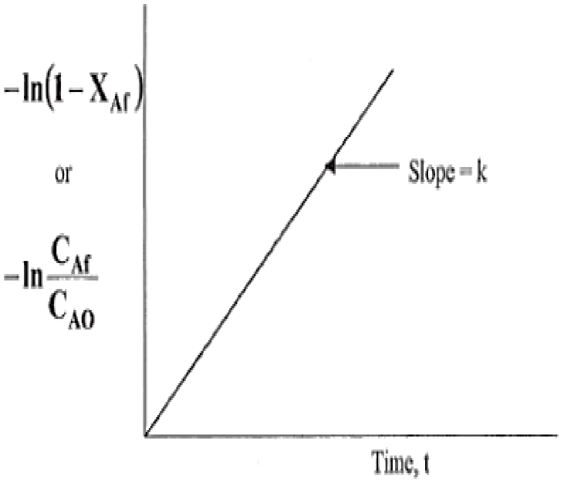


Fig. 2. First order reaction

Many reactions follow first order kinetics or pseudo-first order kinetics over certain ranges of experimental conditions. Examples are the cracking of butane, many pyrolysis reactions, the decomposition of nitrogen pentoxide (N_2O_5), and the radioactive disintegration of unstable nuclei.

- **Second order reactions**

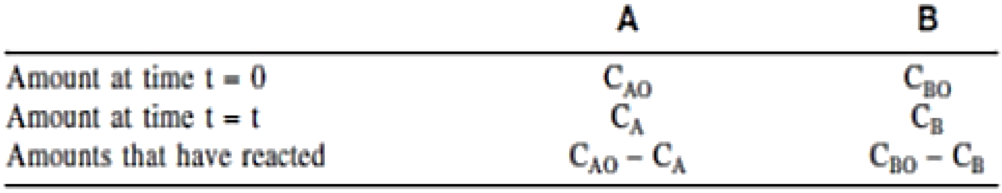
second order reaction occurs when two reactants A and B interact in such a way that the rate of reaction is proportional to the first power of the product of their concentrations. Another type of a second order reaction includes systems involving a single reactant. The rate at any instant is proportional to the square of the concentration of a single reacting species.

Case 1

Consider the reaction $\boldsymbol{A + B \overset{k}{\rightarrow} products}$. The rate of a The rate equation for a constant volume batch system (i.e., constant density) is:

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B \qquad (9)$$

The amount of ***A*** and ***B*** that have reacted at any time ***t*** can be described by the following mechanism and set of equations.



	A	B
Amount at time t = 0	C_{AO}	C_{BO}
Amount at time t = t	C_A	C_B
Amounts that have reacted	$C_{AO} - C_A$	$C_{BO} - C_B$

From stoichiometry:

$$C_B = C_{B0} - (C_{A0} - C_A) \qquad (10)$$

Substituting Equation 10 into Equation 9, rearranging and integrating between the limits gives

$$\int_{C_{AO}}^{C_A} \frac{-dC_A}{C_A\left[C_{BO}-\left(C_{AO}-C_A\right)\right]} = k\int_0^t dt \qquad (11)$$

Equation 11 is resolved into partial fractions as

$$\frac{1}{C_A\left[\left(C_{BO}-C_{AO}\right)+C_A\right]} = \frac{p}{C_A} + \frac{q}{\left[\left(C_{BO}-C_{AO}\right)+C_A\right]} \qquad (12)$$

$$1 \equiv p\left[\left(C_{BO}-C_{AO}\right)+C_A\right] + qC_A \qquad (13)$$

Equating the coefficients of C_A and the constant on both the right and left side of Equation 13 gives

“Const” $1 = p(C_{BO} - C_{AO})$

“C_A” $0 = p + q$

where

$p = 1/(C_{BO} - C_{AO})$

and

$q = -1/(C_{BO} - C_{AO})$

Substituting **p** and **q** into Equation 12 and integrating between the limits gives

$$-\left\{\int_{C_{AO}}^{C_A} \frac{dC_A}{\left(C_{BO}-C_{AO}\right)C_A} - \int_{C_{AO}}^{C_A} \frac{dC_A}{\left(C_{BO}-C_{AO}\right)\left[\left(C_{BO}-C_{AO}\right)+C_A\right]}\right]$$

$$= k\int_0^t dt$$

$$\frac{1}{\left(C_{BO}-C_{AO}\right)}\left\{\ln\frac{C_{AO}}{C_A} + \ln\left[\left\{\frac{\left(C_{BO}-C_{AO}\right)+C_A}{\left(C_{BO}-C_{AO}+C_{AO}\right)}\right\}\right]\right\} = kt$$

$$\ln\left\{\left(\frac{C_{AO}}{C_{BO}}\right)\left[\frac{\left(C_{BO}-C_{AO}\right)+C_A}{C_A}\right]\right\} = k\left(C_{BO}-C_{AO}\right)t \qquad (14)$$

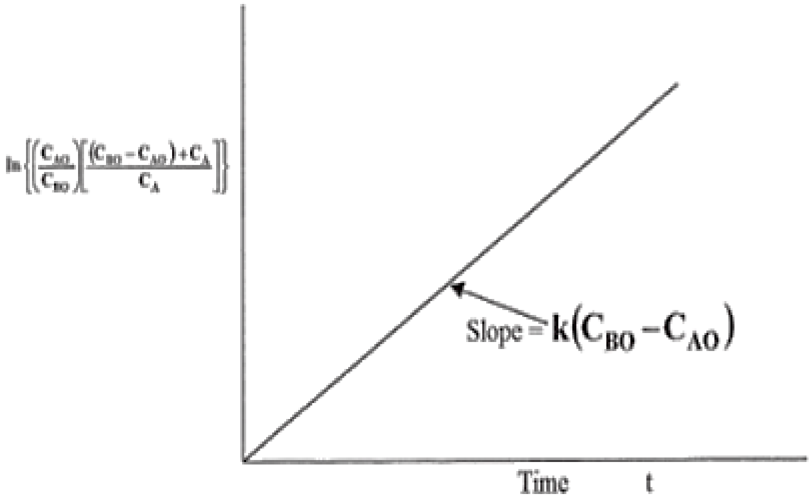


Fig. 3. Test for the reaction ***A*** + ***B*** → ***products***

If C_{B0} is much larger than C_{A0}, then the concentration of **B** remains approximately constant, and Equation 14 approaches Equations 7 or 8 for the first order reaction. Therefore, the second order reaction becomes a *pseudo-first order* reaction.

Case 2

This Case involves a system with a single reactant. In this case, the rate at any instant is proportional to the square of the concentration of A. The reaction mechanism is $2A \xrightarrow{k} products$. The rate expression for a constant volume batch system (i.e., constant density) is

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2 \qquad (15)$$

Rearranging Equation 15 and integrating between the limits yields

$$\int_{C_{AO}}^{C_A} \frac{-dC_A}{C_A^2} = k\int_0^t dt$$

$$\left[\frac{1}{C_A}\right]_{C_{AO}}^{C_A} = kt$$

$$\frac{1}{C_A} - \frac{1}{C_{AO}} = kt$$

or

$$\frac{1}{C_A} = \frac{1}{C_{AO}} + kt \qquad (16)$$

In terms of the fractional conversion, X_A

$$\frac{X_A}{(1-X_A)} = kC_{AO}t \qquad (17)$$

***H.W. 10.2**. Derive Equation 17.*

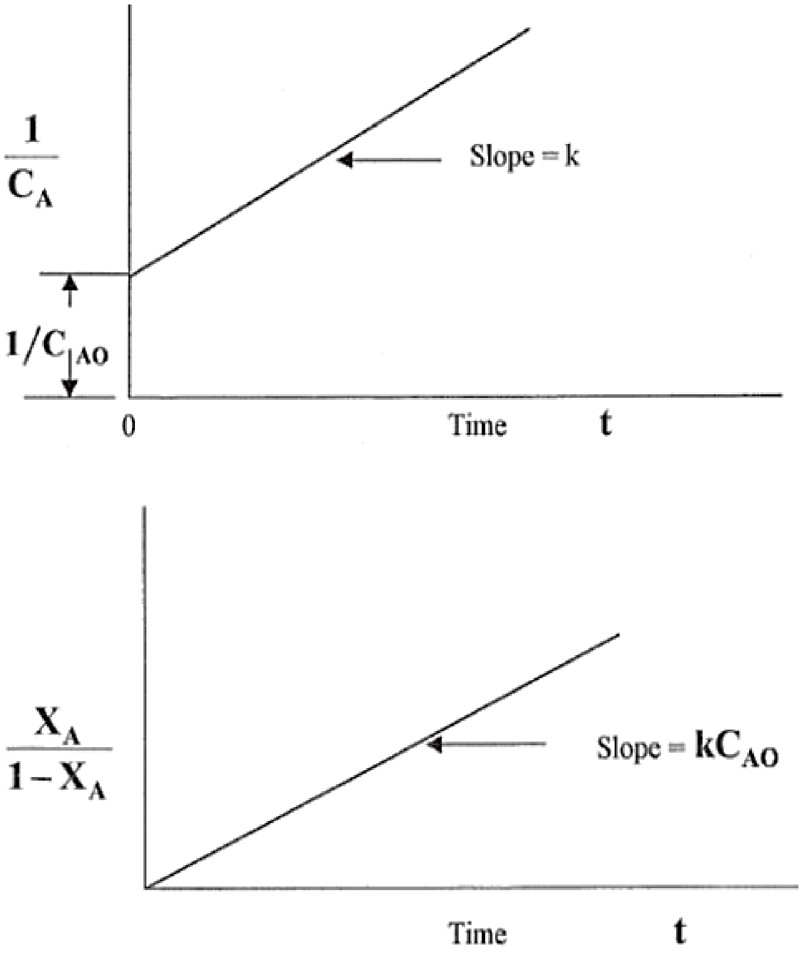


Fig. 3. Test for the reaction ***2A → products***

Consider the second order reaction $2A + B \xrightarrow{k} products$, which is first order with respect to both ***A*** and ***B***, and therefore second order overall. The rate equation is:

$$-r_A = -\frac{dC_A}{dt} = kC_AC_B \qquad (18)$$

The amount of ***A*** and ***B*** that have reacted at any time ***t*** can be described by the following mechanism and set of equations.

	A	**B**
Amount at time t = 0	C_{AO}	C_{BO}
Amount at time t = t	C_A	C_B
Amounts that have reacted	$C_{AO} - C_A$	$C_{BO} - C_B$

and from stoichiometry:

$$(C_{A0} - C_A) = 2(C_{B0} - C_B) \qquad (19)$$

Then

$$C_B = C_{BO} - \frac{1}{2}(C_{AO} - C_A) \qquad (20)$$

Substituting Equation 20 into Equation 18 gives

$$\int_{C_{AO}}^{C_A} \frac{-dC_A}{kC_A\left\{C_{BO} - \frac{1}{2}(C_{AO} - C_A)\right\}} = \int_0^t dt$$

$$-\int_{C_{AO}}^{C_A} \frac{dC_A}{C_A\left\{\left(C_{BO} - \frac{1}{2}C_{AO}\right) + \frac{1}{2}C_A\right\}} = k\int_0^t dt \qquad (21)$$

Taking the partial fractions of Equation 21 with ***α* = [*C_{B0}* – (1/2) *C_{A0}*]** gives

$$\frac{1}{C_A\left\{\alpha + \frac{1}{2}C_A\right\}} \equiv \frac{p}{C_A} + \frac{q}{\alpha + \frac{1}{2}C_A} \qquad (22)$$

"Const" $1 = \alpha p$

"C_A" $0 = \frac{1}{2}p + q$

$$p = \frac{1}{\alpha}$$

and

$$q = \frac{-1}{2}p = \frac{-1}{2\alpha}$$

After simplifying Equation 22, the final equation is

$$\ln\left(\frac{C_{AO}}{C_A} \bullet \frac{C_B}{C_{BO}}\right) = \alpha kt \qquad (23)$$

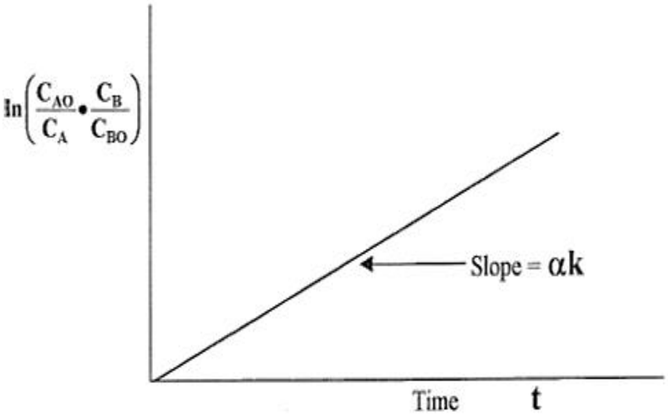


Fig. 4. Test for the reaction ***2A + B → products***

Chemical Reactor Design:

Reaction orders

Method of half-life $t_{1/2}$

The half-life of a reaction is defined as the time it takes for the concentration of the reactant to fall to half of its initial value. Determining the half-life of a reaction as a function of the initial concentration makes it possible to calculate the reaction order and its specific reaction rate. Consider the reaction $A \rightarrow products$. The rate equation in a constant volume batch reaction system gives

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \qquad (1)$$

Rearranging and integrating Equation 1 with the boundary conditions $t = 0$, $C_A = C_{A0}$ and $t = t$, $C_A = C_A$ gives

$$-\int_{C_{AO}}^{C_A} \frac{dC_A}{C_A^n} = \int_0^t dt$$

$$-\left\{\frac{C_A^{-n+1}}{-n+1}\right\}_{C_{AO}}^{C_A} = kt$$

$$\frac{1}{(n-1)}\left\{C_A^{1-n}\right\}_{C_{AO}}^{C_A} = kt$$

$$\left\{C_A^{1-n} - C_{AO}^{1-n}\right\} = kt(n-1) \qquad (2)$$

or

$$t = \frac{1}{k(n-1)}\left\{C_A^{1-n} - C_{AO}^{1-n}\right\} \qquad (3)$$

The half-life is defined as the time required for the concentration to drop to half of its initial value, that is, at $t = t_{1/2}$, $C_A = 1/2\ C_{A0}$. From Equation 2,

$$\left(2^{-1}C_{AO}\right)^{1-n} - C_{AO}^{1-n} = kt_{1/2}(n-1)$$

$$\left(2^{-1} \bullet 2^{n} - 1\right)C_{AO}^{1-n} = kt_{1/2}(n-1)$$

$$t_{1/2} = \frac{\left(2^{n-1}-1\right)C_{AO}^{1-n}}{k(n-1)} \qquad (4)$$

Similarly, the time required for the concentration to fall to ***1/p*** of its initial value gives

$$t_{1/p} = \frac{\left(p^{n-1}-1\right)C_{AO}^{1-n}}{k(n-1)} \qquad (5)$$

From Equation 4, the reaction rate constant **k** is

$$k = \frac{\left(2^{n-1}-1\right)\, C_{AO}^{1-n}}{(n-1)\; t_{1/2}} \qquad (6)$$

Taking the natural logarithm of both sides of Equation 4 gives

$$\ln t_{1/2} = \ln\left(2^{n-1}-1\right) + (1-n)\ln C_{AO} - \ln k - \ln(n-1)$$

$$\ln t_{1/2} = \ln\left\{\frac{2^{n-1}-1}{k(n-1)}\right\} + (1-n)\ln C_{AO} \qquad (7)$$

Plots of $\ln t_{1/2}$ versus $\ln C_{A0}$ from a series of half-life experiments are shown in Figure 1. This figure reveals that the half-life method requires data from several experiments, each at different initial concentration. The method shows that the fractional conversion in a given time rises with increased concentration for orders greater than one, drops with increased concentration for orders less than one, and is independent of the initial concentration for reactions of first order. This also applies to the reaction $A + B \rightarrow$ ***products*** when $C_{A0} = C_{B0}$.

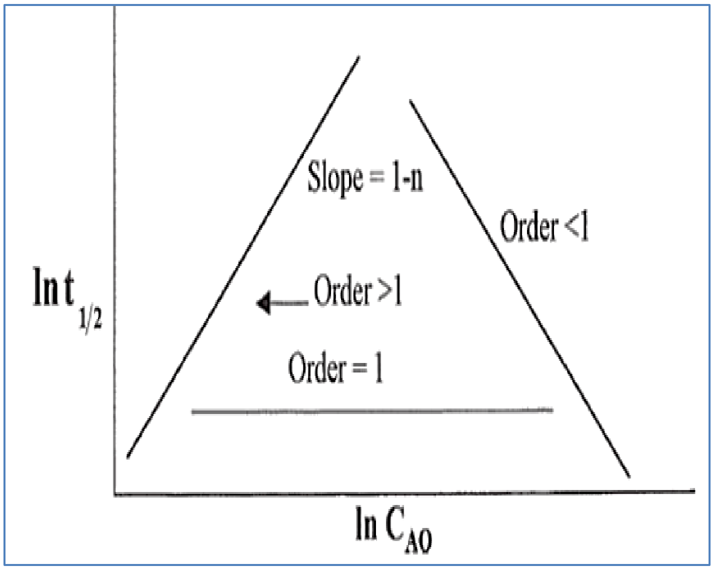


Fig. 1. Overall order of reaction from a series of half-life experiments each at different initial concentration of reactant.

H.W. 11.1. *Find the expression of half-life for (0, 1, 2, and 3) orders for single reaction substance (**A**) such as the reaction:* $\boldsymbol{A \xrightarrow{k} B}$ *which proceeds in a constant volume batch system.*

Irreversible reactions

As mentioned that the rate equation for irreversible reactions for a constant volume batch system (i.e., constant density), according to the boundary conditions: at $t = 0$, $C_A = C_{AO}$ and $t = t$, $C_A = C_A$ using ***Integrating method***, is

$$C_A^{1-n} - C_{AO}^{1-n} = (n-1)kt \qquad (8)$$

The value of n must be found by trial-and-error. In terms of the fractional conversion, X_A,

$$(-r_A) = C_{AO}\frac{dX_A}{dt} = kC_{AO}^n(1-X_A)^n \qquad (9)$$

The rate equation, according to the boundary conditions: at $t = 0$, $X_A = 0$ and $t = t$, $X_A = X_A$ using ***Integrating method***, is

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)^n} = kC_{AO}^{n-1}\int_0^t dt \qquad (10)$$

$$\left\{\frac{(1-X_A)^{-n+1}}{1-n}\right\}_0^{X_A} = kC_{AO}^{n-1}t \qquad (11)$$

$$(1-X_A)^{1-n} - 1 = kC_{AO}^{n-1}(1-n)t \qquad (12)$$

Parallel reactions

Consider elementary reactions $\boldsymbol{A \xrightarrow{k_1} B}$ and $\boldsymbol{A \xrightarrow{k_2} C}$. The rate equations for these reactions for a constant volume batch system (i.e., constant density) are

$$(-r_A) = \frac{-dC_A}{dt} = k_1C_A + k_2C_A = (k_1+k_2)C_A \qquad (13)$$

$$(+r_B) = \frac{dC_B}{dt} = k_1C_A \qquad (14)$$

$$(+r_C) = \frac{dC_C}{dt} = k_2C_A \qquad (15)$$

Rearranging and integration Equation 13 according to the boundary conditions: at ***t =0***, $\mathbf{C_A = C_{AO}}$ and **t = t**, $\mathbf{C_A = C_A}$ gives

$$-\int_{C_{AO}}^{C_A} \frac{dC_A}{C_A} = \int_0^t (k_1+k_2)dt \qquad (16)$$

$$-\ln\frac{C_A}{C_{AO}} = (k_1+k_2)t \qquad (17)$$

In terms of the fractional conversion

$$-\ln(1-X_A) = (k_1+k_2)t \qquad (18)$$

If $-\ln C_A/C_{A0}$ or $-\ln (1 - X_A)$ is plotted against time t, the slope of the line is ($k_1 + k_2$) (Fig. 2). Also, dividing Equation 14 by Equation 15 gives

$$\frac{r_B}{r_C} = \frac{dC_B}{dC_C} = \frac{k_1}{k_2} \tag{19}$$

Integrating Equation 19 between the limits yields

$$\frac{C_B - C_{BO}}{C_C - C_{CO}} = \frac{k_1}{k_2} \tag{20}$$

or $$C_B - C_{BO} = \frac{k_1}{k_2} C_C - \frac{k_1}{k_2} C_{CO} \tag{21}$$

Therefore, the slope of the linear plot C_B versus C_C gives the ratio k_1/k_2. Knowing the ($k_1 + k_2$) and k_1/k_2, the values of k_1 and k_2 can be determined as shown in Figure 2.

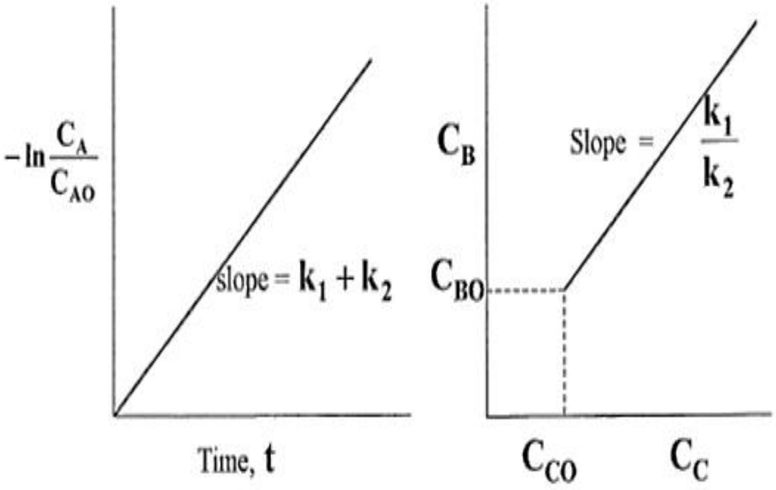


Fig. 2. Rate constants for two competing elementary first order reactions.

An example of parallel reactions involves the two modes of decomposition of an alcohol:

$C_2H_5OH = C_2H_4 + H_2O$

$C_2H_5OH = CH_3CHO + H_2$

Generally, these reactions occur simultaneously. The relative amount of ethylene and acetaldehyde obtained therefore depends on the relative speed of the two reactions competing with each other for the available alcohol. These speeds, in turn, are determined by the choice of catalyst and temperature.

Irreversible reactions in series

Consider a first order reaction in series as $A \overset{k_1}{\to} B \overset{k_2}{\to} C$ and . The rate equations for these reactions for a constant volume batch system (i.e., constant density) are

$$(-r_A) = -\frac{dC_A}{dt} = k_1 C_A \quad (22)$$

$$(-r_B)_{net} = -\frac{dC_B}{dt} = k_2 C_B - k_1 C_A \quad (23)$$

$$(+r_C) = \frac{dC_C}{dt} = k_2 C_B \quad (24)$$

The initial conditions are at time t = 0, C_A = C_{A0} and C_B = 0, C_C = 0. From stoichiometry:

	A	B	C
Amount at time t = 0	C_{AO}	0	0
Amount at time t = t	C_A	C_B	C_C
Amounts that have reacted	$C_{AO} - C_A$	C_B	C_C

and from stoichiometry $C_{A0} - C_A = C_B = C_C$. From Equation 22, the concentration of A is obtained by integration

$$\frac{dC_A}{dt} = -k_1 C_A \quad (25)$$

$$\int_{C_{AO}}^{C_A} \frac{dC_A}{dt} = -k_1 \int_0^t dt \quad (26)$$

$$\ln \frac{C_A}{C_{AO}} = -k_1 t$$

Therefore,

$$C_A = C_{AO} e^{-k_1 t} \quad (27)$$

The variation in concentration of ***B*** is obtained by substituting the concentration of ***A*** from Equation 27 into Equation 23:

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{AO} e^{-k_1 t} \quad (28)$$

Equation 28 is a first order linear differential equation of the form dy/dx + Py = Q. The integrating factor is IF = $e^{\int Pdx}$, and the solution is (y $e^{\int Pdx} = \int Q e^{\int Pdx} dx$ + Constant.) Applying this general procedure to Equation 28, the integrating factor is IF = $e^{\int k2dt}$. Multiplying Equation 28 by the integrating factor gives

$$e^{\int k_2 dt} \frac{dC_B}{dt} + k_2 C_B e^{\int k_2 dt} = k_1 C_A e^{\int k_2 dt} \quad (29)$$

$$\frac{d}{dt}\left(C_B e^{k_2 t}\right) = k_1 C_A e^{\int k_2 dt} \quad (30)$$

$$C_B e^{k_2 t} = \int k_1 C_A e^{\int k_2 dt} dt \ + \ \text{Const.} \quad (31)$$

where Const. = constant.

$$= k_1 C_{AO} \int e^{-k_1 t} \bullet e^{k_2 t} \, dt \ + \ \text{Const.} \quad (32)$$

$$= k_1 C_{AO} \int e^{(k_2 - k_1)t} \, dt \ + \ \text{Const.} \quad (33)$$

$$C_B e^{k_2 t} = \frac{k_1 C_{AO} e^{(k_2 - k_1)t}}{(k_2 - k_1)} \ + \ \text{Const.} \quad (34)$$

At time ***t* = 0**, the concentration of component ***B*** is ***C_B = 0***. Therefore, the constant *Const*. becomes

$$\text{Const.} = -\frac{k_1 C_{AO}}{(k_2 - k_1)} \quad (35)$$

Therefore, Equation 34 becomes

$$C_B = \frac{k_1 C_{AO}}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \qquad (36)$$

To obtain the maximum concentration of ***B***, differentiate Equation 36 with respect to time ***t***, which gives

$$\frac{dC_B}{dt} = \frac{k_1 C_{AO}}{k_2 - k_1}\left\{-k_1 e^{-k_1 t} + k_2 e^{-k_2 t}\right\} \qquad (37)$$

The values of k_1 and k_2 govern the location and maximum concentration of ***B***, and this occurs at $dC_B/dt = 0$, $t = t_{max}$. Equation 37 becomes:

$$0 = -\frac{k_1^2 C_{AO} e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 k_2 C_{AO} e^{-k_2 t}}{k_2 - k_1}$$

$$\frac{k_1^2 C_{AO} e^{-k_1 t}}{k_2 - k_1} = \frac{k_1 k_2 C_{AO} e^{-k_2 t}}{k_2 - k_1} \qquad (38)$$

$$e^{(k_2 - k_1)t_{max}} = \frac{k_2}{k_1}$$

$$t_{max}(k_2 - k_1) = \ln\frac{k_2}{k_1}$$

$$t_{max} = \frac{\ln\left(\frac{k_2}{k_1}\right)}{k_2 - k_1} \qquad (39)$$

At t_{max}

$$k_2 e^{-t_{max} k_2} = k_1 e^{-t_{max} k_1} \qquad (40)$$

From Equations 36 and 40,

$$\frac{C_{B_{max}}}{C_{AO}} = \frac{1}{(k_2 - k_1)}\left\{k_2 e^{-k_2 t_{max}} - k_1 e^{-k_2 t_{max}}\right\} = e^{-k_2 t_{max}} \qquad (41)$$

Then, from Equations 39 and 41

$$\frac{C_{B_{max}}}{C_{AO}} = e^{-k_2\left[\frac{\ln(k_2/k_1)}{k_2-k_1}\right]} \qquad (42)$$

Taking the natural logarithm gives

$$\ln\frac{C_{B_{max}}}{C_{AO}} = \left(-\frac{k_2}{k_2-k_1}\right)\ln\left(\frac{k_2}{k_1}\right) \qquad (43)$$

Treating $k_2/(k_2 - k_1)$ as an exponent and removing the natural logarithm gives

$$\frac{C_{B_{max}}}{C_{AO}} = \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2-k_1}\right)} \qquad (44)$$

This shows that C_{Bmax}/C_{AO} depends only on k_1 and k_2, and k_2 can be evaluated from C_{Bmax}/C_{AO} at t_{max} (Equation 41).

From stoichiometry: $A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$

	A	B	C
Amount at time t = 0	C_{AO}	0	0
Amount at time t = t	C_A	C_B	C_C

and from stoichiometry, $(C_{AO} - C_A) = (C_B + C_C)$. That is, $[C_C = (C_{AO} - C_A) - C_B]$. The concentration of C in terms of C_{AO}, k_1, and k_2 are:

$$\frac{C_C}{C_{AO}} = \left\{1 - e^{-k_1 t} - \left(\frac{k_1}{k_2-k_1}\right)\left(e^{-k_1 t} - e^{-k_2 t}\right)\right\}$$

$$= \left\{1 + \frac{k_1}{k_2-k_1}e^{-k_2 t} - \frac{k_2}{k_2-k_1}e^{-k_1 t}\right\} \qquad (45)$$

Important features of consecutive reactions occur in substitution processes. For example $CH_4 + Cl_2 = CH_3Cl + HCl$ and $CH_3Cl + Cl_2 = CH_2Cl_2 + HCl$, and so forth. They also occur frequently in oxidation processes, where the desired product may further oxidize to give an undesired product. An example is the oxidation of methanol, where the desired formaldehyde is readily degraded to carbon dioxide: $CH_3OH \rightarrow HCHO \rightarrow CO_2$. The formation of resins, tarry matter by consecutive reaction, is prevalent in organic reactions.

Figure 3a shows the time variations in the concentrations of **A, B**, and **C** as given by these equations. The concentration of **A** falls exponentially, while **B** goes through a maximum. Since the formation rate of **C** is proportional to the concentration of **B**, this rate is initially zero and is a maximum when **B** reaches its maximum value. Figure 3b shows plots of the exponentials e^{-k1t} and e^{-k2t} and of their difference.

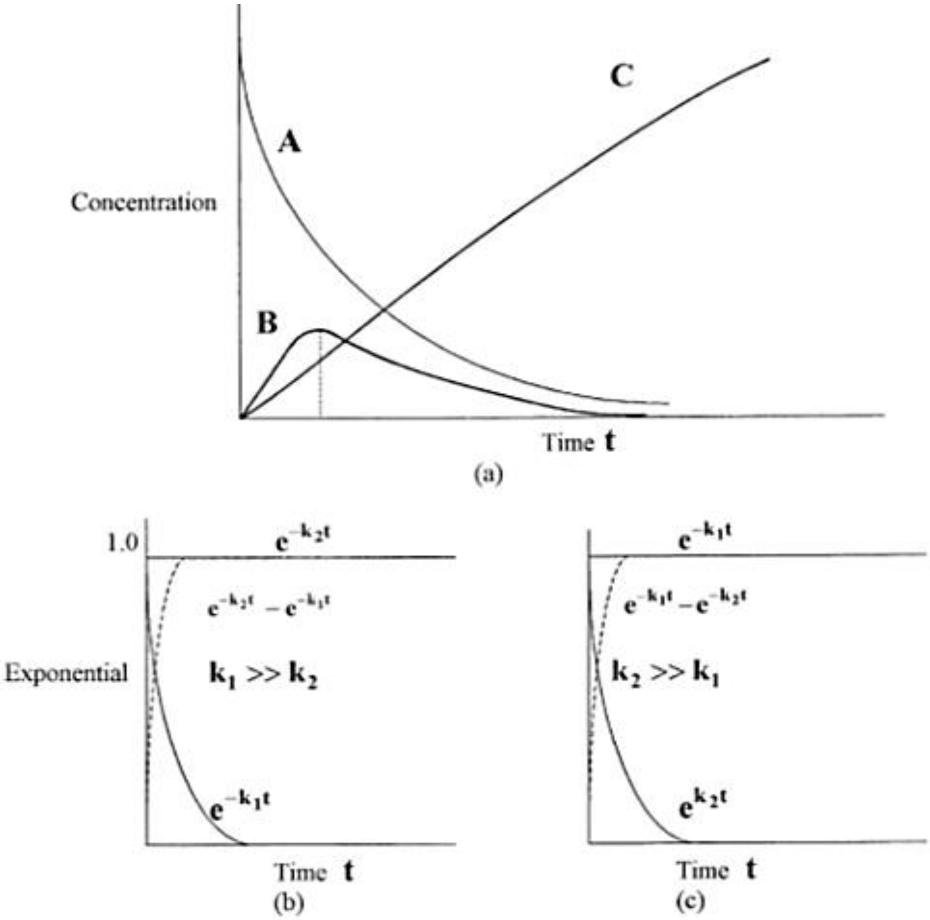


Fig. 3. (a) Variations in the concentrations of A, B, and C for a reaction occurring by the mechanism $A \overset{k_1}{\rightarrow} B \overset{k_2}{\rightarrow} C$ (b) Variations with time of the exponentials when $k_1 \gg k_2$. (c) Variations of the exponentials when $k_2 \ll k_1$.

Chemical Reactor Design:

Reaction orders

First order reversible reactions

Consider the reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$. The rate equation for a constant volume batch system is:

$$(-r_A) = -\frac{dC_A}{dt} = k_1 C_A - k_2 C_B \qquad (1)$$

From stoichiometry:

	A	B
Amount at time t = 0	C_{AO}	C_{BO}
Amount at time t = t	C_A	C_B
Amounts that have reacted	$C_{AO} - C_A$	$C_B - C_{BO}$

and the concentration of ***B*** is [$\mathbf{C_B = (C_{AO} - C_A) + C_{BO}}$]. Equation 1 will be:

$$\int_{C_{AO}}^{C_A} -\frac{dC_A}{k_1 C_A - k_2\{(C_{AO} - C_A) + C_{BO}\}} = \int_0^t dt$$

$$-\int_{C_{AO}}^{C_A} \frac{dC_A}{(k_1 + k_2)C_A - k_2(C_{AO} - C_{BO})} = \int_0^t dt$$

$$-\frac{1}{(k_1 + k_2)} \int_{C_{AO}}^{C_A} \frac{dC_A}{C_A - \left(\frac{k_2}{k_1 + k_2}\right)(C_{AO} - C_{BO})} = \int_0^t dt \qquad (2)$$

where

$$\alpha = \left(\frac{k_2}{k_1 + k_2}\right)(C_{AO} - C_{BO}) \qquad (3)$$

Substituting Equation 3 into Equation 2 becomes

$$-\frac{1}{k_1 + k_2} \int_{C_{AO}}^{C_A} \frac{dC_A}{C_A - \alpha} = \int_0^t dt \qquad (4)$$

Integrating Equation 3-161 between the boundary conditions $\boldsymbol{t = 0}$, $\mathbf{C_A = C_{AO}}$ and $\boldsymbol{t = t}$, $\mathbf{C_A = C_A}$ gives

$$-\frac{1}{k_1 + k_2}\ln\left[C_A - \alpha\right]_{C_{AO}}^{C_A} = t$$

That is:

$$-\frac{1}{k_1 + k_2}\left[\ln\left(C_A - \alpha\right) - \ln\left(C_{AO} - \alpha\right)\right] = t \qquad (5)$$

Substituting Equation 4 into Equation 5 gives

$$-\left\{\ln\left(C_A - \frac{k_2(C_{AO} - C_{BO})}{k_1 + k_2}\right)\right.$$

$$\left.-\ln\left(C_{AO} - \frac{k_2(C_{AO} - C_{BO})}{k_1 + k_2}\right)\right\} = (k_1 + k_2)t$$

$$-\left\{\ln\left[\frac{(k_1 + k_2)C_A - k_2C_{AO} + k_2C_{BO}}{(k_1 + k_2)}\right]\right.$$

$$\left.-\ln\left[\frac{k_1C_{AO} + k_2C_{AO} - k_2C_{AO} + k_2C_{BO}}{(k_1 + k_2)}\right]\right\} = (k_1 + k_2)t$$

$$-\left\{\ln\left[(k_1 + k_2)C_A - k_2(C_{AO} - C_{BO})\right]\right.$$

$$\left.-\ln\left[k_1C_{AO} + k_2C_{BO}\right]\right\} = (k_1 + k_2)t$$

or

$$-\ln\left\{\frac{\left(\frac{k_1}{k_2} + 1\right)C_A - (C_{AO} - C_{BO})}{\left(\frac{k_1}{k_2}C_{AO} + C_{BO}\right)}\right\} = (k_1 + k_2)t \qquad (6)$$

At equilibrium with concentrations of ***A*** and ***B*** as $\mathbf{C_{Ae}}$, $\mathbf{C_{Be}}$, respectively, then $\boldsymbol{k_1}\mathbf{C_{Ae}} = \boldsymbol{k_2}\mathbf{C_{Be}}$. Since $\mathbf{dC_A/dt = 0}$ at equilibrium

$$\frac{k_1}{k_2} = K = \frac{C_{Be}}{C_{Ae}} \qquad (7)$$

Substituting Equation 7 into Equation 6 gives

$$-\ln\left\{\frac{\left(\frac{C_{Be}}{C_{Ae}}+1\right)\bullet C_A-(C_{AO}-C_{BO})}{\left(\frac{C_{Be}}{C_{Ae}}\bullet C_{AO}+C_{BO}\right)}\right\}=(k_1+k_2)t \qquad (8)$$

Figure 1 shows a plot of the reversible first order reaction. From the slope and the equilibrium constant ***K***, ***k₁*** and ***k₂*** can be determined.

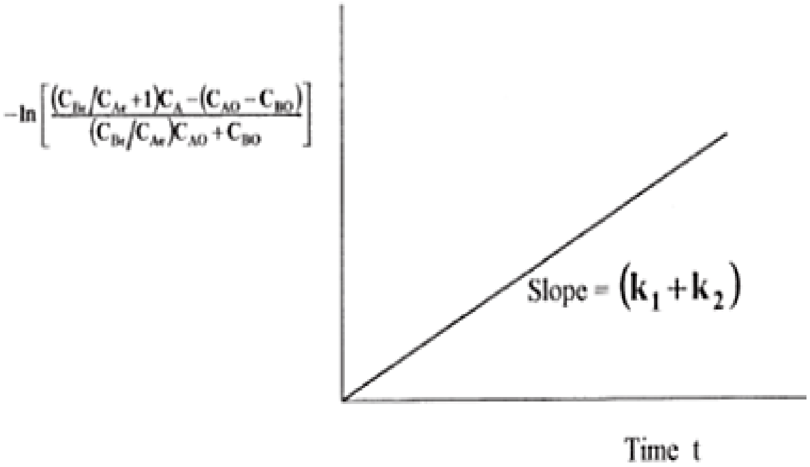


Fig. 1. First order reversible reaction

Examples of first-order reversible reactions are gas phase cis-trans isomerization, isomerizations in various types of hydrocarbon systems, and the racemization of α and β glucoses. An example of a catalytic reaction is the ortho-para hydrogen conversion on a nickel catalyst.

Second order reversible reactions

Bimolecular-type second order reactions are:

$$A+B\underset{k_2}{\overset{k_1}{\rightleftharpoons}}C+D \qquad (9)$$

$$2A\underset{k_2}{\overset{k_1}{\rightleftharpoons}}C+D \qquad (10)$$

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2C \qquad (11)$$

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2C \qquad (12)$$

With the restrictions that $\mathbf{C_{AO} = C_{BO}}$ and $\mathbf{C_{CO} = C_{DO} = 0}$ in Equation 9, the rate equation for a constant volume batch system becomes

$$(-r_A) = -\frac{dC_A}{dt} = C_{AO}\frac{dX_A}{dt} = k_1C_A^2 - k_2C_C^2 \qquad (13)$$

$$= k_1C_{AO}^2(1-X_A)^2 - \frac{k_2}{k_1}X_A^2 \qquad (14)$$

where the fractional conversion $\mathbf{X_A = 0}$ at $\mathbf{t = 0}$. At equilibrium, $\mathbf{dX_A/dt = 0}$ and the final solution is:

$$\ln\left\{\frac{X_{Ae}-(2X_{Ae}-1)X_A}{X_{Ae}-X_A}\right\} = 2k_1C_{AO}\left(\frac{1}{X_{Ae}}-1\right)t \qquad (15)$$

All other reversible second-order rate equations have the same solution with the boundary conditions assumed in Equation 15.

Integrating the rate equation is often difficult for orders greater than 1 or 2. Therefore, the differential method of analysis is used to search the form of the rate equation. If a complex equation of the type below fits the data, the rate equation is:

$$(-r_A) = -\frac{dC_A}{dt} = k_1\frac{C_A}{(1+k_2C_A)} \qquad (16)$$

Taking the reciprocals of Equation 16 gives

$$\frac{1}{(-r_A)} = \frac{1+k_2C_A}{k_1C_A} = \frac{1}{k_1C_A} + \frac{k_2}{k_1} \qquad (17)$$

Plotting $\mathbf{1/(-r_A)}$ versus $\mathbf{1/C_A}$ would give a straight line with the slope equal to $\mathbf{1/k_1}$ and an intercept of $\mathbf{k_2/k_1}$.

H.W. 12.1. *Another analysis method could be applied for Equation 17 then solving it for* $(-r_A)$*. What is it?*

Homogeneous Catalyzed Reactions

A catalyzed reaction can be expressed as

$$A \xrightarrow{k_1} P \quad \text{(uncatalyzed)} \qquad (18)$$

$$A + C \xrightarrow{k_2} P + C \quad \text{(catalyzed)} \qquad (19)$$

where C and P represent the catalyst and product respectively. The reaction rates for a constant volume batch system (i.e., constant density) are:

$$(-r_A) = -\left(\frac{dC_A}{dt}\right)_1 = k_1 C_A \qquad (20)$$

$$(-r_A) = -\left(\frac{dC_A}{dt}\right)_2 = k_2 C_A C_C \qquad (21)$$

The overall rate of disappearance of reactant ***A*** is:

$$-\frac{dC_A}{dt} = k_1 C_A + k_2 C_A C_C \qquad (22)$$

The catalyst concentration remains unchanged and integrating Equation 22 with the boundary conditions: **t = 0,** $\mathbf{C_A = C_{AO}}$ and **t = t**, $\mathbf{C_A = C_A}$

$$-\int_{C_{AO}}^{C_A} \frac{dC_A}{C_A} = \int_0^t (k_1 + k_2 C_C)\,dt \qquad (23)$$

$$-\ln\frac{C_A}{C_{AO}} = (k_1 + k_2 C_C)\,t = Kt \qquad (24)$$

where $K = k_1 + k_2 C_C$.

In this case, a series of experiments are performed with varying catalyst concentrations. A plot is made of $\boldsymbol{K = (k_1 + k_2 C_C)}$ versus $\boldsymbol{C_C}$. The slope of the straight line is $\boldsymbol{k_2}$ and the intercept is $\boldsymbol{k_1}$, as shown in Figure 2.

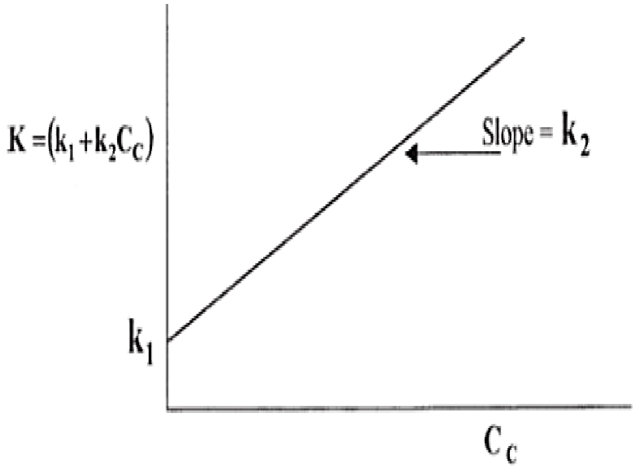


Fig. 2. Rate constants for a homogeneous catalyzed reaction from a series of experiments with different catalyst concentrations.

Autocatalytic Reactions

This type of reaction occurs when one of the products of the reactions acts as a catalyst, and is expressed by

$$A + B \xrightarrow{k} B + B \qquad (25)$$

The rate equation for a constant volume batch system is:

$$(-r_A) = -\frac{dC_A}{dt} = kC_AC_B \qquad (26)$$

When ***A*** is consumed, then the total moles of ***A*** and ***B*** remain unchanged at any time ***t*** and can be expressed as $\mathbf{C_0 = C_A + C_B = C_{AO} + C_{BO} = constant}$. Then the rate equation becomes

$$(-r_A) = -\frac{dC_A}{dt} = kC_A(C_O - C_A) \qquad (27)$$

Rearranging Equation 27 and integrating between the limits gives

$$\int_{C_{AO}}^{C_A} -\frac{dC_A}{C_A(C_O - C_A)} = \int_0^t kdt \qquad (28)$$

Integrating Equation 28 between the limits gives

$$-\left\{\int_{C_{AO}}^{C_A} \frac{1}{C_O}\frac{dC_A}{C_A} + \int_{C_{AO}}^{C_A} \frac{1}{C_O}\frac{dC_A}{(C_O - C_A)}\right\} = k\int_0^t dt \qquad (29)$$

$$-\left\{\frac{1}{C_O}\ln\frac{C_A}{C_{AO}}-\frac{1}{C_O}\ln\left(\frac{C_O-C_A}{C_O-C_{AO}}\right)\right\}=kt$$

$$\ln\left\{\frac{C_{AO}}{C_A}\left(\frac{C_O-C_A}{C_O-C_{AO}}\right)\right\}=\ln\frac{C_B/C_{BO}}{C_A/C_{AO}}=C_O kt \qquad (30)$$

The fractional conversion, X_A, and the initial reaction ratio, $\theta_B = C_{BO}/C_{AO}$, yields

$$\ln\frac{\theta_B+X_A}{\theta_B(1-X_A)}=C_{AO}(\theta_B+1)kt=(C_{AO}+C_{BO})kt \qquad (31)$$

For an autocatalytic reaction some product ***B*** must be present if the reaction is to proceed. Starting with a small concentration of ***B***, the rate rises as ***B*** is formed, and when ***A*** is used up, the rate must drop to zero. A plot of concentration versus time gives a straight line through the origin as shown in Figure 3.

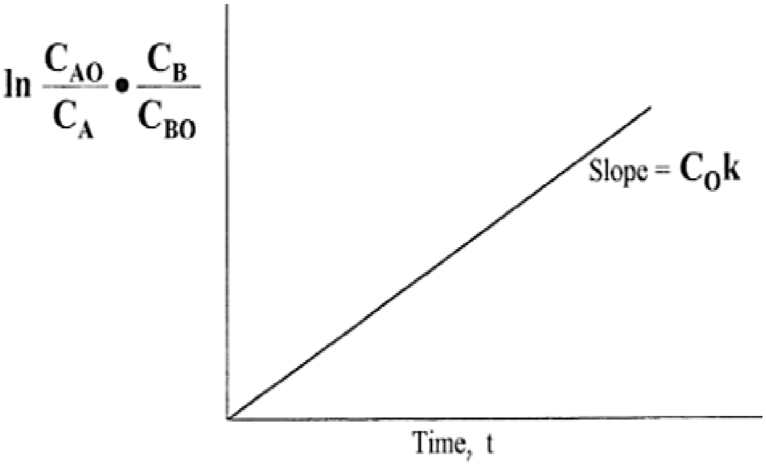


Fig. 3. Autocatalytic reaction

Chemical Reactor Design:

Examples

Example 13.1. An irreversible aqueous reaction gives 80% conversion in a batch reactor at 40^0C in 10 min. and required 3 min. for the same conversion but at 50^0C.

a) Assuming first order kinetics, find the rate constant at both cases of temperatures.
b) Estimate the activation energy for this reaction.
c) What will be the temperature at a conversion of 80% after 1 min.?
d) What will be the time required to achieve conversion of 99% at 40^0C and 50^0C in the case of half-order kinetics?
e) What will be the temperature at a conversion of 99% after 1 min. in the case of half-order kinetics?
f) What will be the time required to achieve conversion of 99% at 40^0C and 50^0C in the case of second-order kinetics?
g) What will be the temperature at a conversion of 99% after 1 min. in the case of second-order kinetics?

Ans.:

a) For first order reaction:

$$-ln\frac{C_{Af}}{C_{A0}} = kt \qquad \text{(7 - Lecture 10)}$$

$$-ln\ (1- X_{Af}) = kt \qquad \text{(8 - Lecture 10)}$$

At T= 40^0C; t= 10min.

$$-ln\ (1- 0.8) = 10\ k$$

$$k = 0.161\ \text{min}^{-1}$$

At T= 50^0C; t= 3min.

$$-ln\ (1- 0.8) = 3\ k$$

$$k = 0.536\ \text{min}^{-1}$$

***H.W. 13.1**. Plot the relation between **T**, **t**, and **k** obtained in this point and analyzed it.*

b) Using the modification of Arrhenius' law for two values of temperatures.

$$\ln\frac{r_2}{r_1}=\ln\frac{k_2}{k_1}=\frac{\mathbf{E}}{\mathbf{R}}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

Since the reaction rate is inversely proportional with time; therefore,

$$\ln\frac{r_2}{r_1}=\ln\frac{t_1}{t_2}=\frac{\mathbf{E}}{\mathbf{R}}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$ln\frac{10}{3}=\frac{E}{8.314}\left(\frac{1}{313}-\frac{1}{323}\right)$$

$$E=101198\frac{kJ}{kmol}$$

c) Using Arrhenius' law to find the required temperature

$$ln\frac{t_1}{t_2}=\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$$ln\frac{10}{1}=\frac{101198}{8.314}\left(\frac{1}{313}-\frac{1}{T_2}\right)$$

$$T_2=332\ K=59℃$$

***H.W. 13.2**. Plot the relation between **T** and **t** for points b and c then analyzed it.*

d) For half-order:

$$-r_A=-\frac{dC_A}{dt}=kC_A^{0.5}$$

Rearranging and integrating this equation between the limits (at ***t=0; C_A=C_{A0}*** and at ***t=t; C_A=C_{Af}***) gives:

$$C_{A0}^{0.5}\left[1-\left(\frac{C_{Af}}{C_{A0}}\right)^{0.5}\right]=0.5\ kt$$

In terms of the fractional conversion X_A

$$C_{A0}^{0.5}[1-(1-X_A)^{0.5}]=0.5\ kt$$

At T= 40^{0}C; t= 10 min. ; X_A= 0.80

$$C_{A0}^{0.5}[1-(1-0.80)^{0.5}] = 0.5 \times 10\, k$$
$$k = 0.111\, C_{A0}^{0.5}$$

At T= 40^{0}C; t= ? min. ; X_A= 0.99

$$C_{A0}^{0.5}[1-(1-0.99)^{0.5}] = 0.5 \times 0.111\, C_{A0}^{0.5} \times t$$
$$t = 16.2\, min.$$

At T= 50^{0}C; t= 3 min. ; X_A= 0.80

$$C_{A0}^{0.5}[1-(1-0.80)^{0.5}] = 0.5 \times 3\, k$$
$$k = 0.369\, C_{A0}^{0.5}$$

At T= 50^{0}C; t= ? min. ; X_A= 0.99

$$C_{A0}^{0.5}[1-(1-0.99)^{0.5}] = 0.5 \times 0.369\, C_{A0}^{0.5} \times t$$
$$t = 4.88\, min.$$

***H.W. 13.3**. Plot the relation between **T**, **t**, and **X_A** obtained for half-order kinetics in this point and analyzed it.*

e) To find the required temperature for the half-order reaction in the case of the first temperature was 40^{0}C and 99%:

$$ln\frac{t_1}{t_2} = \frac{E}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$
$$ln\frac{16.2}{1} = \frac{101198}{8.314}(\frac{1}{313} - \frac{1}{T_2})$$

$$T_2 = 337\, K = 64°\text{C}$$

***H.W. 13.4**. Find the required temperature for the half-order reaction in the case of the first temperature was 50^{0}C and 99%.*

f) The information given before could be used to find a relation for the rate constant using the second-order kinetics assuming that reaction obeys (Case 2- Lecture 10):

$$\frac{X_A}{1-X_A} = kC_{A0}t \qquad (17-Lecture\ 10)$$

At T= 40^0C; t= 10 min. ; X_A= 0.80

$$\frac{0.80}{1-0.80} = 10\ kC_{A0}$$
$$kC_{A0} = 0.4$$

At T= 40^0C; t= ? min. ; X_A= 0.99

$$\frac{0.99}{1-0.99} = 0.4\ t$$
$$t = 247.5\ min.$$

At T= 50^0C; t= 3 min. ; X_A= 0.80

$$\frac{0.80}{1-0.80} = 3\ kC_{A0}$$
$$kC_{A0} = {}^{4}/_{3}$$

At T= 50^0C; t= ? min. ; X_A= 0.99

$$\frac{0.99}{1-0.99} = {}^{4}/_{3}\ t$$
$$t = 74.3\ min.$$

***H.W. 13.5**. Plot the relation between **T**, **t**, and $\mathbf{X_A}$ obtained in this point for second-order kinetics and analyzed it.*

g) To find the required temperature for the second-order reaction in the case of the first temperature was 40^0C and 99%:

$$ln\frac{t_1}{t_2} = \frac{E}{R}(\frac{1}{T_1} - \frac{1}{T_2})$$

$$ln\frac{247.5}{1} = \frac{101198}{8.314}(\frac{1}{313} - \frac{1}{T_2})$$

$$T_2 = 365\ K = 92℃$$

***H.W. 13.6**. Find the required temperature for the second-order reaction in the case of the first temperature was 50^0C and 99%.*

***H.W. 13.7**. Find the value of (k_1/k_2) in case of 80% conversion for three cases of kinetics, i.e. half, first, and second-orders, plot the findings and analyzed it.*

Example 13.2. The first order reversible liquid phase reaction $\mathbf{A} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathbf{B}$ .The initial concentrations of ***A*** and ***B*** are 0.5 gmol/lit and 0, respectively. The conversion of ***A*** attained 33.3% after 8 min. while the equilibrium conversion was 66.7%. Find the rate equation for this reaction.

Ans.: Depending on the following equations:

$$\frac{k_1}{k_2} = K = \frac{C_{Be}}{C_{Ae}} \qquad \text{(7 - Lecture 12)}$$

$$-\ln\left\{\frac{\left(\frac{C_{Be}}{C_{Ae}}+1\right)\bullet C_A - (C_{AO}-C_{BO})}{\left(\frac{C_{Be}}{C_{Ae}}\bullet C_{AO}+C_{BO}\right)}\right\} = (k_1+k_2)t \qquad \text{(8 - Lecture 12)}$$

$$C_{Ae} = C_{A0}\,(1 - X_{Ae});\; C_{Be} = C_{B0} + \frac{b}{a}C_{A0}\,X_{Ae} \qquad (1)$$

Substituting Eq. (1) in Equation (8 - Lecture 12) gives:

$$ln\frac{X_{Ae}}{X_{Ae}-X_A} = (k_1+k_2)t$$

Or:

$$C_{Ae} = 0.5\,(1 - 0.667) = 0.167\frac{gmol}{lit}$$

$$C_{Be} = 0 + \frac{1}{1}0.5 \times 0.667 = 0.334\frac{gmol}{lit}$$

$$C_A = C_{A0}\,(1 - X_A) = 0.5\,(1 - 0.333) = 0.334\frac{gmol}{lit} = C_{Be}$$

$$K_{eq} = \frac{C_{Be}}{C_{Ae}} = \frac{k_1}{k_2} = \frac{0.334}{0.167} = 2 \qquad (2)$$

Substituting these data in Equation (8 - Lecture 12) gives:

$$k_1 + k_2 = 0.087 \qquad (3)$$

From Eqs. (2) and (3):

$$k_1 = 0.058\, min^{-1}$$

$$k_2 = 0.029\, min^{-1}$$

$$(-r_A) = -\frac{dC_A}{dt} = k_1C_A - k_2C_B \qquad (1 - \text{Lecture } 12)$$

$$-r_A = 0.058C_A - 0.029\, C_B$$

Example 13.3. Starting with pure ***A***, a reversible reaction liquid phase reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$ occurred at constant temperature and volume where the initial concentrations of ***B*** is **C_{B0}=0**.

Time (hr)	0	0.744	1.990	3.050	4.620	∞
C_A (gmol/lit)	3.00	2.60	2.10	1.80	1.50	1.00

Determine the reaction rate equation.

Ans.: Here the order of this reaction is not given; therefore, we will starting with the assumption of first order reaction depending on Eq. (8 - Lecture 12)

$$ln\frac{C_{A0} - C_{Ae}}{C_A - C_{Ae}} = (k_1 + k_2)t \qquad (4)$$

According to the table, the initial concentration of $\boldsymbol{C_{A0} = 3\,\frac{gmol}{lit}}$ and the final (equilibrium) concentration $\boldsymbol{C_{Ae} = 1.0\,\frac{gmol}{lit}}$

Time (hr)	0.744	1.990	3.050	4.620
C_A (gmol/lit)	2.60	2.10	1.80	1.50
$\boldsymbol{(k_1 + k_2)\ hr^{-1}}$	0.300	0.300	0.300	0.300

Since the value of $\boldsymbol{(k_1 + k_2)}$ not varied; therefore, the assumption of first-order is correct.

$$C_{Ae} = C_{A0}\,(1 - X_{Ae});\ C_{Be} = C_{B0} + \frac{b}{a}C_{A0}\,X_{Ae}$$

$$C_{Ae} = 1;\ C_{Be} = 0 + \frac{1}{1}C_{A0}\,\frac{(C_{A0} - C_{Ae})}{C_{A0}} = (C_{A0} - C_{Ae})$$

$$K_{eq} = \frac{k_1}{k_2} = \frac{C_{Be}}{C_{Ae}} = \frac{C_{A0} - C_{Ae}}{C_{Ae}} = \frac{3-1}{1} = 2 \qquad (5)$$

And

$$k_1 + k_2 = 0.300 \qquad (6)$$

From Eqs. (5) and (6):

$$k_1 = 0.2\ hr^{-1}$$

$$k_2 = 0.1\ hr^{-1}$$

$$(-r_A) = -\frac{dC_A}{dt} = k_1 C_A - k_2 C_B \qquad (1 – \text{Lecture } 12)$$

$$-r_A = 0.20\ C_A - 0.10\ C_B$$

Chemical Reactor Design:

Gaseous Reactions:

In gaseous reactions, the composition term in the rate equation is often expressed as the partial pressure of the reacting species. These pressures are then transformed to concentration. Consider the reaction $\boldsymbol{A \rightarrow products}$. The rate equation is:

$$-r_A = k_p p_A^n = kC_A^n \qquad (1)$$

Where

$$(-r_A) = \frac{\text{mol}}{\text{m}^3 \bullet \text{s}} \qquad \left(\frac{\text{mol}}{\text{l} \bullet \text{s}}\right)$$

$$k_p = \frac{\text{mol}}{\text{m}^3 \bullet \text{Pa}^n \bullet \text{s}} \qquad \left(\frac{\text{mol}}{\text{l} \bullet \text{atm}^n \bullet \text{s}}\right)$$

$$p_A^n = \text{Pa}^n \qquad \left(\text{atm}^n\right)$$

$$k = \left(\frac{\text{mol}}{\text{m}^3}\right)^{1-n} \text{s}^{-1} \qquad \left(\frac{\text{mol}}{\text{l} \bullet \text{s}}\right)^{1-n} \text{s}^{-1}$$

For ideal gases, the partial pressure is expressed as:

$$p_A = C_A RT \qquad (2)$$

Where

$$p_A = \text{Pascal, Pa} \qquad (\text{atm})$$

$$C_A = \frac{\text{mol}}{\text{m}^3} \qquad \left(\frac{\text{mol}}{\text{l}}\right)$$

$$R = 8.314 \frac{\text{m}^3\text{Pa}}{\text{mol} \bullet \text{K}} \quad \text{or} \quad 0.082 \bullet \frac{\text{l} \bullet \text{atm}}{\text{mol} \bullet \text{K}}$$

From the reaction stoichiometry and measurements of the total pressure as a function of time, it is possible to determine the extent of the reaction and the partial pressure or concentrations of the reactant and product species at the time of measurement.

Consider the following gaseous reaction $aA + bB \rightarrow cC + dD$. Pressure and concentration are related, and for a constant volume reactor with changing number of moles during reaction, the total pressure (π) changes with time, t. For an ideal gas, with any reactant ***A*** or ***B***, the partial pressure is expressed as:

$$p_A = C_A RT = p_{AO} + \frac{a}{\Delta n}(\pi_O - \pi) \qquad \textbf{(3)}$$

where

$$\Delta n = (c + d) - (a + b) \qquad \textbf{(4)}$$

For any product C or D, the partial pressure is expressed as:

$$p_C = C_C RT = p_{CO} - \frac{c}{\Delta n}(\pi_O - \pi) \qquad \textbf{(5)}$$

For an ideal gas at both constant temperature and pressure, but with changing number of moles during reaction

$$V = V_O(1 + \varepsilon_A X_A) \qquad \textbf{(6)}$$

where

$$\varepsilon_A = \frac{V_{\text{all A reacted}} - V_{\text{no reaction}}}{V_{\text{no reaction}}} = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \qquad \textbf{(7)}$$

Or

$$\boldsymbol{\varepsilon_A = (\frac{\Delta n}{a}) y_{A0}}$$

Where: a: moles of limiting reactant A; y_{A0}: mole fraction of A in the feed.

Example 14.1. For the following reaction (3A+2B→ R), the feed consists of 20% A, 50% B, and 30% inert. Find $\boldsymbol{\varepsilon_A}$**?**

Ans.:

$$\boldsymbol{\varepsilon_A = \left(\frac{\Delta n}{a}\right) y_{A0} = \left(\frac{1-5}{3}\right) \times 0.2 = -0.267}$$

Case 1: Constant Density Systems

This case includes most liquid reactions and also those gas reactions that operate at both constant temperature and pressure with no change in the number of moles during reaction. The relationship between concentration $\mathbf{C_A}$ and fractional conversion $\mathbf{X_A}$ is as follows:

$$X_A = 1 - \frac{C_A}{C_{AO}} \quad \text{and} \quad dX_A = -\frac{dC_A}{C_{AO}}$$

$$\frac{C_A}{C_{AO}} = 1 - X_A \quad \text{and} \quad dC_A = -C_{AO} dX_A$$

where $\varepsilon_A = 0$. The changes in B and C to A are

$$\frac{C_{AO} - C_A}{a} = \frac{C_{BO} - C_B}{b} = \frac{C_C - C_{CO}}{c} \qquad \textbf{(8)}$$

or

$$\frac{C_{AO} X_A}{a} = \frac{C_{BO} X_B}{b} \qquad \textbf{(9)}$$

Case 2: Changing Density Gases

This case involves constant temperature $\boldsymbol{T}$ and total pressure $\boldsymbol{\pi}$. In this case, the density changes since the number of moles change during the reaction, and the volume of a fluid element changes linearly with conversion or $\boldsymbol{V = V_O(1 + \varepsilon_A X_A)}$. The relationship between $\mathbf{C_A}$ and $\mathbf{X_A}$ is as follows:

$$X_A = \frac{C_{AO} - C_A}{C_{AO} + \varepsilon_A C_A} \quad \text{and} \quad dX_A = \frac{-C_{AO}(1+\varepsilon_A)dC_A}{(1+\varepsilon_A C_A)^2} \qquad \mathbf{(10)}$$

$$\frac{y_A}{y_{AO}} = \frac{C_A}{C_{AO}} = \frac{1-X_A}{1+\varepsilon_A X_A} \quad \text{and} \quad \frac{dC_A}{C_{AO}} = \frac{-1+\varepsilon_A}{(1+\varepsilon_A X_A)^2} dX_A \qquad \mathbf{(11)}$$

for $\varepsilon_A \neq 0$, where y_A = mole fraction of component A. The changes between the reactants are:

$$\varepsilon_A X_A = \varepsilon_B X_B \qquad \mathbf{(12)}$$

$$\frac{a\varepsilon_A}{C_{AO}} = \frac{b\varepsilon_B}{C_{BO}} \qquad \mathbf{(13)}$$

and for the products and inerts:

$$\frac{y_C}{y_{AO}} = \frac{C_C}{C_{AO}} = \frac{(c/a)X_A + C_{CO}/C_{AO}}{1+\varepsilon_A X_A} \qquad \mathbf{(14)}$$

$$\frac{y_I}{y_{IO}} = \frac{C_I}{C_{IO}} = \frac{1}{1+\varepsilon_A X_A} \qquad \mathbf{(15)}$$

$$\boldsymbol{N_A = N_{A0}(1 - X_A)} \qquad (16)$$

$$\boldsymbol{C_A = \frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X_A)} = \frac{C_{A0}(1 - X_A)}{(1 + \varepsilon_A X_A)}} \qquad (17)$$

The percent increase or decrease in volume could be obtained as follows:

$$\boldsymbol{Percent\ change\ in\ volume = \frac{\Delta V}{V^0} \times 100\% = \frac{V - V^0}{V^0} \times 100\%} \qquad \mathbf{(18)}$$

$$\boldsymbol{V = V_0(1 + \varepsilon_A X_A)}$$

$$\boldsymbol{\frac{V}{V_0} = (1 + \varepsilon_A X_A) \quad \rightarrow \quad \frac{V}{V_0} - 1 = \varepsilon_A X_A}$$

The fraction increase or decrease in volume:

$$\boldsymbol{\frac{\Delta V}{V^0} = \varepsilon_A X_A}$$

$$\boldsymbol{X_A = \frac{\Delta V}{\varepsilon_A V^0}} \qquad (19)$$

The following table summarized the status of the system depending on the above parameters.

Δn	ε_A	$\Delta V/V^0$	*Volume*	*Example*
-ve	*-ve*	*-ve*	*Decreased*	*(gaseous phase) 2A→B*
+ve	*+ve*	*+ve*	*Increased*	*(gaseous phase) A→2B*
zero	*Zero*	*Zero*	*Constant*	*(gaseous phase) A→B*

Using integral method for variable volume of reaction mixture, the following represents the rate equation for zero, first, and second orders.

Zero-order:

$$\frac{C_{A0}}{\varepsilon_A} ln \frac{V}{V^0} = kt \qquad (20)$$

First-order:

$$-ln\,(1-\frac{\Delta V}{\varepsilon_A V^0}) = kt \qquad (21)$$

Second-order:

$$\frac{(1+\varepsilon_A)X_A}{1-X_A} + \varepsilon_A ln\,(1-X_A) = kC_{0A}t \qquad (22)$$

Or

$$\frac{(1+\varepsilon_A)\Delta V}{\varepsilon_A V^0 - \Delta V} + \varepsilon_A ln\,(1-\frac{\Delta V}{\varepsilon_A V^0}) = kC_{0A}t \qquad (23)$$

Case 3: Gases With Varying Density, Temperature, and Total Pressure

Consider the following reaction: $aA + bB \rightarrow cC;\ a + b \neq c$. For an ideal gas behavior with reactant A as the key component, the relationship between concentration $\mathbf{C_A}$, $\mathbf{C_B}$, $\mathbf{C_C}$, and X_A are as follows:

$$X_A = \frac{1 - \frac{C_A}{C_{AO}}\left(\frac{T\pi_O}{T_O\pi}\right)}{1 + \varepsilon_A \frac{C_A}{C_{AO}}\left(\frac{T\pi_O}{T_O\pi}\right)} \quad \text{or} \quad \frac{C_A}{C_{AO}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}\left(\frac{T_O\pi}{T\pi_O}\right) \qquad \textbf{(24)}$$

$$X_A = \frac{\frac{C_{BO}}{C_{AO}} - \frac{C_B}{C_{AO}}\left(\frac{T\pi_O}{T\pi}\right)}{\frac{b}{a} + \varepsilon_A \frac{C_B}{C_{AO}}\left(\frac{T\pi_O}{T_O\pi}\right)} \quad \text{or} \quad \frac{C_B}{C_{AO}} = \frac{\frac{C_{BO}}{C_{AO}} - \frac{b}{a}X_A}{1 + \varepsilon_A X_A}\left(\frac{T_O\pi}{T\pi_O}\right) \qquad \textbf{(25)}$$

$$X_A = \frac{\frac{C_C}{C_{AO}}\left(\frac{T\pi_O}{T_O\pi}\right) - \frac{C_{CO}}{C_{AO}}}{\frac{c}{a} - \varepsilon_A \frac{C_C}{C_{AO}}\left(\frac{T\pi_O}{T_O\pi}\right)} \quad \text{or} \quad \frac{C_C}{C_{AO}} = \frac{\frac{C_{CO}}{C_{AO}} + \frac{c}{a}X_A}{1 + \varepsilon_A X_A}\left(\frac{T_O\pi}{T\pi_O}\right) \qquad \textbf{(26)}$$

where ε_A is evaluated from stoichiometry at constant temperature **T** and total pressure **π**. For a high-pressure non-ideal gas behavior, the term ($\mathbf{T_O\pi/T\pi_O}$) is replaced by ($\mathbf{Z_OT_O\pi/ZT\pi_O}$), where **Z** is the compressibility factor. To change to another key reactant **B**, then

$$\frac{a\varepsilon_A}{C_{AO}} = \frac{b\varepsilon_B}{C_{BO}} \quad \text{and} \quad \frac{C_{AO}X_A}{a} = \frac{C_{BO}X_B}{b} \qquad \textbf{(27)}$$

For liquids or isothermal gases with no change in pressure and density, $\varepsilon_A \rightarrow 0$ and $(T_O\pi/T\pi_O) \rightarrow 1$

Example 14.2. A zero-order reaction (***A→2B***) with respect to ***A*** is carried out in a constant volume reactor with pure ***A***. The pressure rises from ***1*** to ***1.5atm*** in **5 min**. If the same reaction takes place at constant pressure batch reactor (variable volume). Find (a) The time required for the same conversion. (b) The fraction increase in volume at that time.

Ans.: **a)** For *Zero-order* and constant volume:

$$C_{A0} - C_A = kt \quad \rightarrow \quad \frac{p_{A0}}{RT} - \frac{p_A}{RT} = kt$$

$$p_{A0} - p_A = RTkt$$

At t=5min.

$$p_{A0} - p_A = 5RTk$$

$$p_A = C_A RT = p_{A0} + \frac{a}{\Delta n}(\pi_0 - \pi)$$

For pure $\boldsymbol{A}$:

$$p_{A0} = \pi_0 \ ; \ y_{A0} = 1; \ \Delta n = (2-1) = 1$$

$$p_A = \pi_0 + (\pi_0 - \pi) = 2\pi_0 - \pi$$

At t=0; $\pi = \pi_0 = 1\ atm$

At t=5min; $\pi = 1.5\ atm$

$$p_A = 2 \times 1 - 1.5 = 0.5\ atm$$

$$k = \frac{p_{A0} - p_A}{5RT} = \frac{1-0.5}{5RT} = \frac{0.1}{RT}$$

$$\varepsilon_A = \left(\frac{\Delta n}{a}\right) y_{A0} = \left(\frac{2-1}{1}\right) \times 1.0 = 1$$

$$X_A = \frac{p_{A0} - p_A}{p_{A0} + \varepsilon_A p_A} = \frac{1-0.5}{1+1\times 0.5} = 0.333$$

$$\frac{V}{V_0} = (1 + \varepsilon_A X_A) = 1 + 1 \times 0.333 = 1.333$$

$$\frac{C_{A0}}{\varepsilon_A} ln\ \frac{V}{V^0} = kt \qquad \rightarrow \qquad \frac{p_{A0}}{RT\varepsilon_A} ln\ \frac{V}{V^0} = kt$$

$$\frac{p_{A0}}{RT\varepsilon_A} ln\ \frac{V}{V^0} = \frac{0.1}{RT} t$$

$$\frac{p_{A0}}{RT\varepsilon_A} ln \ \frac{V}{V^0} = \frac{0.1}{RT} t$$

$$\frac{1}{1} ln \ (1.333) = 0.1 \ t$$

$$t = 2.87 \ min$$

b) The fraction increase in volume at 5min.:

$$\frac{\Delta V}{V^0} = \varepsilon_A X_A = 1 \times 0.333 = 0.333 \equiv 33.3\%$$

Chemical Reactor Design:

Basic Concepts in Reactor Design and Ideal Reactor Models

Chemical reactors are the most important features of a chemical process. A reactor is a piece of equipment in which the feedstock is converted to the desired product and is thus the single irreplaceable component of the process. The following question must be answered:

1. What is the composition of the feedstock and under what conditions is it available? Are any purification procedures necessary?
2. What is the scale of the process? What capacity is required?
3. Is a catalyst necessary or desirable? If a catalyst is employed, what are the ramifications with respect to product distribution, operating conditions, most desirable type of reactor, process economics, and other pertinent questions raised below?
4. What operating conditions (temperature, pressure, degree of agitation, etc.) are required for most economic operation?
5. Is it necessary or desirable to add inerts or other materials to the feedstock to enhance yields of desired products, to moderate thermal effects, or to prolong the useful life of any catalysts that may be employed?
6. Should the process be continuous or intermittent? Would batch or semibatch operation be advantageous?
7. What type of reactor best meets the process requirements? Are there advantages associated with the use of a combination of reactor types, or with multiple reactors in parallel or series?
8. What size and shape reactor(s) should be used?
9. How are the energy transfer requirements for the process best accomplished? Should one operate isothermally, adiabatically, or in accord with an alternative temperature protocol?
10. Is single pass operation best, or is recycle needed to achieve the desired degree of conversion of the raw feedstock?
11. What facilities are required for catalyst supply, activation, and regeneration?

12. What are the reactor effluent composition and conditions? Are any chemical separation steps or physical operations required in order to bring the effluent to a point where it is satisfactory for the desired end use?
13. Are there any special materials requirements imposed by the process conditions? Are the process fluids corrosive? Are extremely high temperatures or pressures required?

Various factors are considered in selecting chemical reactors for specific tasks:

- Economic costs.
- Highest yields and purity.
- Minimize pollution.
- Maximize profit.
- Meet the requirements imposed by the reaction mechanisms, rate expressions, and the required production capacity.
- Reaction heat.
- Reaction rate constant.
- Heat transfer coefficient.
- Reactor size.
- Temperature of the heat transfer medium. Temperature of the inlet reaction mixture.
- Inlet composition.
- Instantaneous temperature of the reaction mixture.
- The mode of operation involves either an isothermal (i.e., constant temperature) or an adiabatic (i.e., heat does not exchange with the surroundings) condition, whether a single pass operation is best, or whether recycling is needed to achieve the desired degree of conversion of the raw feedstock.

Stirred Tank Reactors:

The stirred tank reactor is a mixing tank with perfectly mixed flow. The liquid phase is normally used in this reactor. The reactor is operated with a batch or continuous process, or semi-continuous process (also called the fed batch) in which reactants are continuously fed in and products are discharged batchwise.

In combination with separation, reactants are fed by batch, while products can be discharged continuously. There are slight differences in stirred tank structure depending on the heat exchange method, stirring method and size of the reactor. A mixing blade must be carefully designed when the reactants contain solid particles, when solids are formed by reactions, or when the viscosity of the materials is increased.

Figure 1 shows typical types of systems using these stirred tank reactors. Due to its good mixing performance and high capacity, this type of reactor is best suited to regulate reactions for the careful control of reacting conditions. These reactors are used for neutralization, hydrolysis, esterification, amide formation, chelate formation etc. They are also applied to polymerization, in which case the baffle plate, mixing blade and heating element must be simple in structure because of increased viscosity.

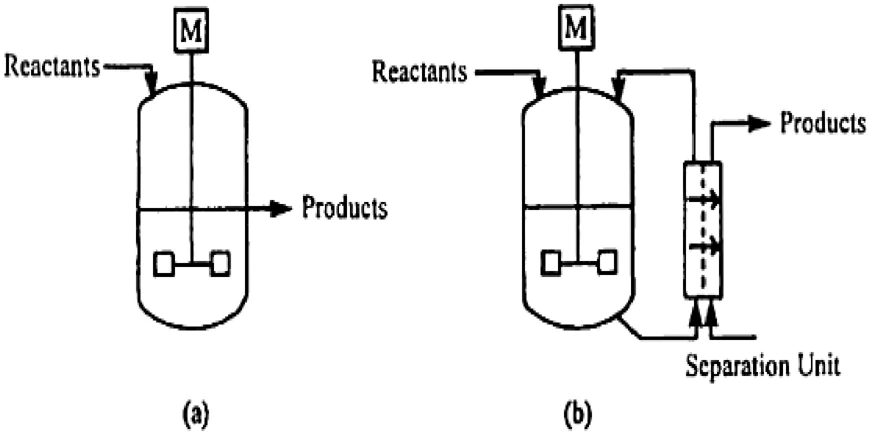


Fig. 1. Typical types of systems using stirred tank reactors. (a) Continuous stirred tank reactor. (b) Stirred tank reactor combined with separation unit.

Batch Reactors (Stirred Tanks).

Batch reactors are usually cylindrical tanks and the orientation of such tanks is usually vertical. The horizontal orientation may also be preferable when the reactor contents are quite viscous or take the form of a slurry. Batch reactors may be fabricated from ordinary or stainless steel, but there are often advantages to using glass or polymer coatings on interior surfaces in order to minimize corrosion or sanitation problems.

Cylindrical vessels are employed because they are easier to fabricate and clean than other geometries and because the construction costs for high-pressure units are considerably less than for alternative configurations. For simple stirred vertical batch reactors, the depth of liquid is usually comparable to the diameter of the reactor. For greater liquid height to diameter ratios more complex agitation equipment is necessary. Agitation can be supplied by stirrer blades of various shapes or by forced circulation with an external or built-in pump. The concept of a batch reactor assumes that the reaction is instantaneously charged (i.e., filled) and perfectly homogenized in the reactor (Fig. 2). The process is stopped as soon as the degree of conversion is achieved.

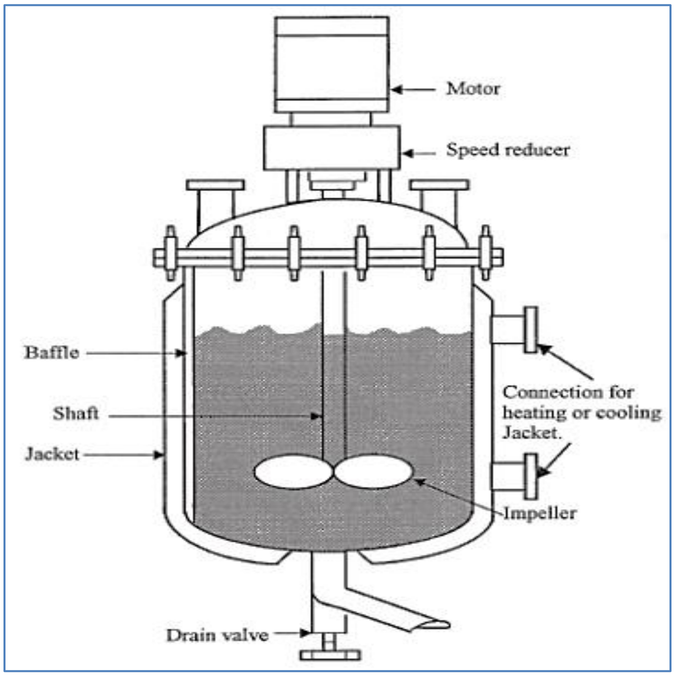


Fig. 2. A batch homogeneous-type reactor

The choice of a batch reaction over a continuous system is often a result of special considerations. The size of batch reactors range from (19 Liter) in small industrial pilot plants to (38,000–76,000 Liter) in large plants. When larger sizes are required, the design may include multiple units of batch reactors arranged in parallel. In small industrial pilot plants, a batch system may be employed for preliminary information. Also, batch reactors can be used in these plants to obtain small quantities of the new product for further evaluations such as purity, yield, and sales. At the industrial level, batch reactors are used in the pharmaceutical, biochemical, or multi-product plants as in the dye industry. These reactors require suitable access for inserting agitators, coils, or other internal devices and for cleaning. For example, a 450 Liter steam-jacketed for processing organic chemicals at 14 MPa and 150°C. The advantages of a batch reactor are:

- Simple in construction.
- Small instrumentation and cost.
- Flexibility of operation.

The principal disadvantage of a batch reactor is in the labor cost. Labor cost includes the time it takes to fill the reactor, heat it to reaction temperature, cool it after completion of the reaction, discharge the reactor contents, and clean the reactor for the next batch. These procedures increase the overall labor costs per unit of production. Another disadvantage involves the difficulty to control heat transfer and product quality. Chemical reaction rates usually increase with temperature and with more sufficient contact between reactants.

Mechanical agitation promotes the flow of heat by forcing convection of the mass and by reducing the film resistance at the vessel wall. Additionally, agitation breaks up agglomerated solids thereby increasing the contact surface and the rate at which reacting species come into close proximity. An important purpose of agitation or mixing is to bring a number of materials together in a physically homogeneous mixture. Two or more fluids are either blended or dispersed as emulsions; fluids and finely divided solids are dispersed as suspensions, gases dispersed as fluids, or soluble substances dissolved.

Because of the large energy effects that often accompany chemical reaction, it is usually necessary to provide for heat transfer to or from the reactor contents. Heating or cooling may be accomplished using jacketed walls, internal coils, or internal tubes filled with a heat transfer fluid that is circulated through an external heat exchanger. Energy may also be supplied by electrical heating or direct firing.

If the process fluid is noncorrosive and readily and safely pumped, it may be preferable to employ an external heat exchanger and circulation pump. Good temperature control can be achieved using an external reflux condenser for cases where appreciable vapor is given off. The selection of either internal or external heat transfer equipment is governed by the required area, the susceptibility of the heat transfer surface to fouling, the temperature and pressure requirements imposed by the heat transfer medium, and the potential adverse effects that might occur if the process fluid and the heat transfer medium come in direct contact through leakage.

For high-pressure operation, safety considerations are extremely important and care must be taken to ensure proper mechanical design.

***H.W. 15.1**. Give two examples of chemical industries used batch reactors.*

Chemical Reactor Design:

Thermodynamics of chemical reactions

$\Delta G_r < 0$ [kJ/mol]	Reaction favorable
$0 < \Delta G_r < 50$ [kJ/mol]	Reaction possibly favorable
$\Delta G_r > 50$ [kJ/mol]	Reaction not favorable

The correlation for Gibbs free energy of formation is

$$\Delta G_f = A + B\,T + C\,T^2 \qquad (1)$$

where the regression coefficients A, B, and C could be obtained from references. The chemical equilibrium for a reaction is associated with the change in Gibbs free energy ΔG_r for the reaction

$$\Delta G_r = \sum_P n_i \Delta G_f - \sum_R n_i \Delta G_f \qquad (2)$$

Equilibrium rate constant

$$\Delta G^0 = -R\,T\,lnK \qquad (3)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (4)$$

- ***Non-Ideal gases***:

$$K = K_\alpha K_y P_T^{\Delta n} \qquad (5)$$

Where:

$$K_\alpha = \frac{\alpha_C^c\ \alpha_D^d}{\alpha_A^a\ \alpha_B^b} \quad ; \quad K_y = \frac{y_C^c\ y_D^d}{y_A^a\ y_B^b} \quad ; \quad K_P = \frac{p_C^c\ p_D^d}{p_A^a\ p_B^b}$$

- ***Ideal gases***: For ideal gases, $K_\alpha = 1$; therefore, Eq. 5 will be

$$K = K_y P_T^{\Delta n} \qquad (6)$$

- ***Non-Ideal solution***:

$$K = K_{\gamma} K_{x} \qquad (7)$$

Where:

$$K_{x} = \frac{X_C^c \; X_D^d}{X_A^a \; X_B^b} \quad ; \quad K_{\gamma} = \frac{\gamma_C^c \; \gamma_D^d}{\gamma_A^a \; \gamma_B^b}$$

- ***Ideal solution***: For ideal liquids, $K_{\gamma} = 1$; therefore,

$$K = K_{x} \qquad (8)$$

Vant Hoff equation as follows:

$$\frac{d \ln K}{dT} = \frac{\Delta H_r^0}{RT^2} \qquad (9)$$

When the ΔH_r^0 is constant and independent on temperature, Eq. 11 will be

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r^0}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (10)$$

But, for variable ΔH_r^0 with temperature

$$\ln K = \frac{\Delta H_r^0}{RT} + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{2R} T + \frac{\Delta C}{6R} T^2 + J \qquad (11)$$

Reaction	**Δn**	**Pressure**	**Increasing**	**conversion**
$N_2 + 3H_2 \Leftrightarrow 2NH_3$	-ve	Increased	Forward	increased
$C_2H_6 \Leftrightarrow C_2H_4 + H_2$	+ve	Increased	Backward	decreased
$I_2 + H_2 \Leftrightarrow 2HI$	Zero	No effect of pressure on conversion		

Reaction orders

$$-r_A = kC_A^{\alpha}C_B^{\beta} \qquad (12)$$

$$n = \alpha + \beta \qquad (13)$$

$$k = \frac{(-r_A)}{C^n} = \frac{\text{moles}/(\text{volume} - \text{time})}{(\text{moles}/\text{volume})^n}$$

or

$$k = \text{time}^{-1}(\text{moles})^{1-n}\frac{1}{(\text{volume})^{1-n}}$$

$$= \text{time}^{-1}\left(\frac{\text{moles}}{\text{volume}}\right)^{-n+1}$$

1. Zero order ($n = 0$; $k = \text{moles/m}^3\text{-sec}$)

   $(-r_A) = kC_A^0$

2. First order ($n = 1$; $k = 1/\text{sec}$)

   $(-r_A) = kC_A$

3. Second order ($n = 2$; $k = \text{m}^3/\text{moles-sec}$)

   $(-r_A) = kC_A^2$

4. Third order ($n = 3$; $k = (\text{m}^3/\text{moles})^2 \bullet \text{sec}^{-1}$)

   $(-r_A) = kC_A^3$

Determining the order of reactions

- **Zero order reactions**

$$-r_A = -\frac{dC_A}{dt} = k \qquad (14)$$

$$C_{A0} - C_{AF} = kt \qquad (15)$$

In terms of the fractional conversion X_A

$$C_{A0} X_A = kt \qquad \text{for } t < \frac{C_{A0}}{k} \qquad (16)$$

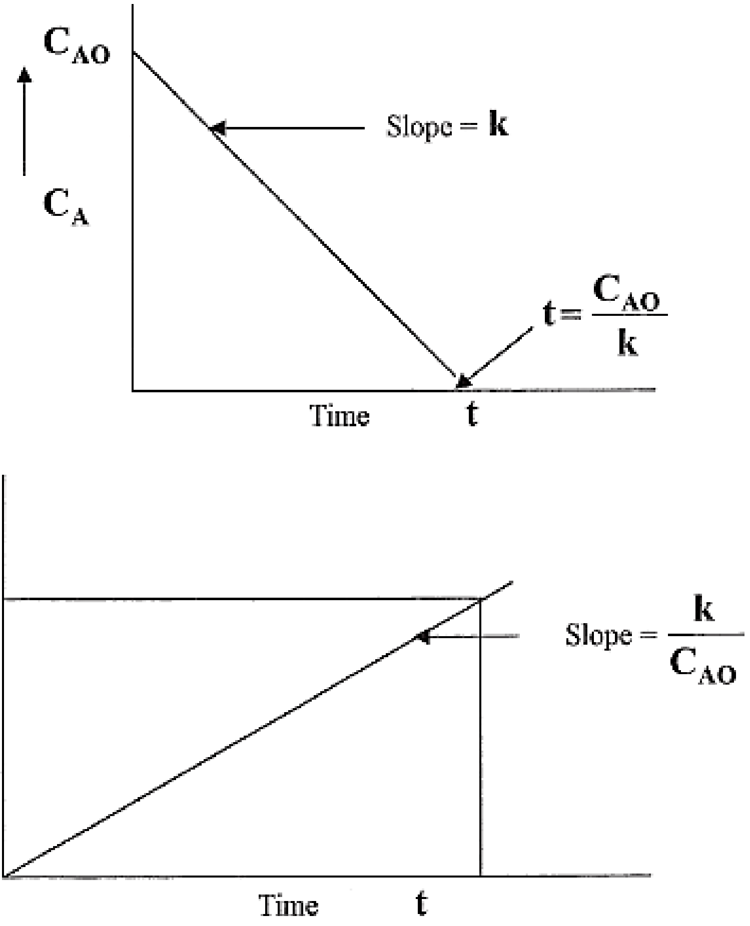


Fig. 1. Zero order reaction

- **First order reactions**

$$-r_A = -\frac{dC_A}{dt} = kC_A \qquad (17)$$

$$-\ln\frac{C_{Af}}{C_{A0}} = kt \qquad (18)$$

In terms of the fractional conversion X_A

$$-\ln(1 - X_{Af}) = kt \qquad (19)$$

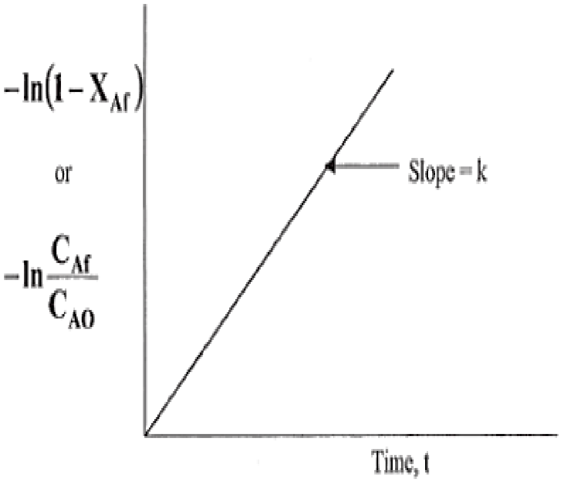


Fig. 2. First order reaction

- **Second order reactions**

Case 1

Consider the reaction $\boldsymbol{A+B\overset{k}{\rightarrow}products}$. The rate of a The rate equation for a constant volume batch system (i.e., constant density) is:

$$-r_A=-\frac{dC_A}{dt}=-\frac{dC_B}{dt}=kC_AC_B \qquad (20)$$

	A	B
Amount at time t = 0	C_{AO}	C_{BO}
Amount at time t = t	C_A	C_B
Amounts that have reacted	$C_{AO}-C_A$	$C_{BO}-C_B$

From stoichiometry:

$$C_B=C_{B0}-(C_{A0}-C_A) \qquad (21)$$

$$\ln\left\{\left(\frac{C_{AO}}{C_{BO}}\right)\left[\frac{(C_{BO}-C_{AO})+C_A}{C_A}\right]\right\}=k(C_{BO}-C_{AO})t \qquad (22)$$

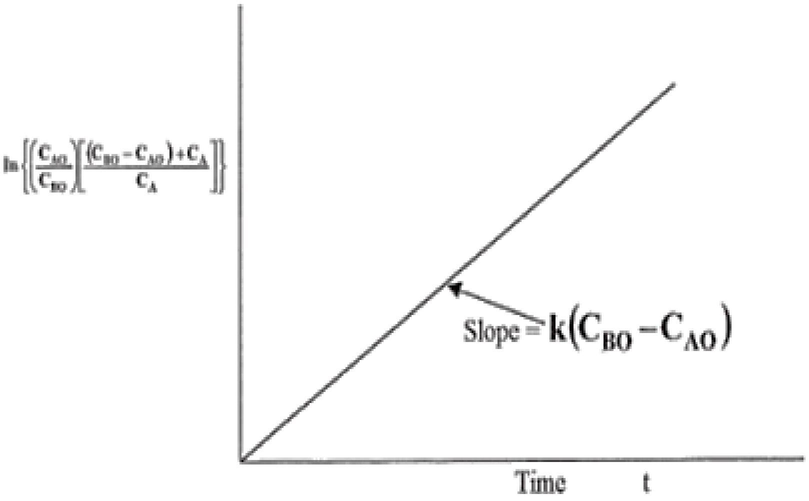


Fig. 3. Test for the reaction ***A* + *B* → *products***

Case 2

The reaction mechanism is $\boldsymbol{2A \overset{k}{\rightarrow} products}$. The rate expression for a constant volume batch system (i.e., constant density) is

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2 \qquad (23)$$

$$\frac{1}{C_A} - \frac{1}{C_{AO}} = kt$$

or

$$\frac{1}{C_A} = \frac{1}{C_{AO}} + kt \qquad (24)$$

In terms of the fractional conversion, X_A

$$\frac{X_A}{(1-X_A)} = kC_{AO}t \qquad (25)$$

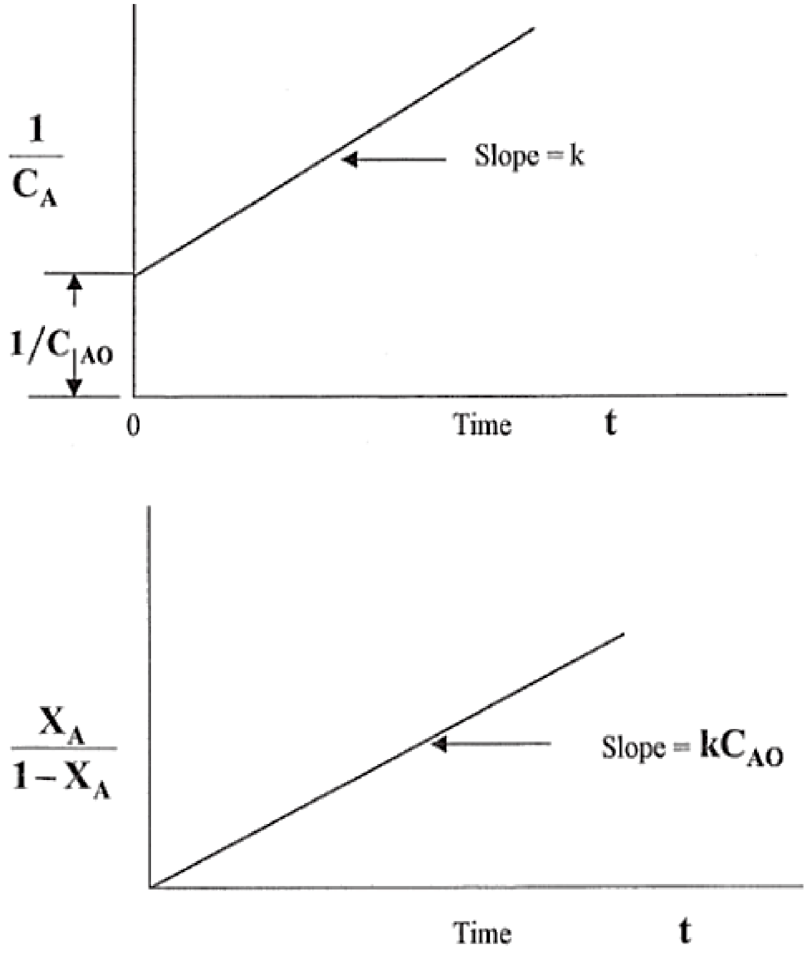


Fig. 4. Test for the reaction ***2A → products***

Method of half-life $t_{1/2}$

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \qquad (26)$$

$$t = \frac{1}{k(n-1)}\left\{C_A^{1-n} - C_{AO}^{1-n}\right\} \qquad (27)$$

$$t_{1/2} = \frac{\left(2^{n-1}-1\right)C_{AO}^{1-n}}{k(n-1)} \qquad (28)$$

$$t_{1/p} = \frac{\left(p^{n-1}-1\right)C_{AO}^{1-n}}{k(n-1)} \qquad (29)$$

$$k = \frac{\left(2^{n-1}-1\right) C_{AO}^{1-n}}{(n-1)\, t_{1/2}} \qquad (30)$$

$$\ln t_{1/2} = \ln\left\{\frac{2^{n-1}-1}{k(n-1)}\right\} + (1-n)\ln C_{AO} \qquad (31)$$

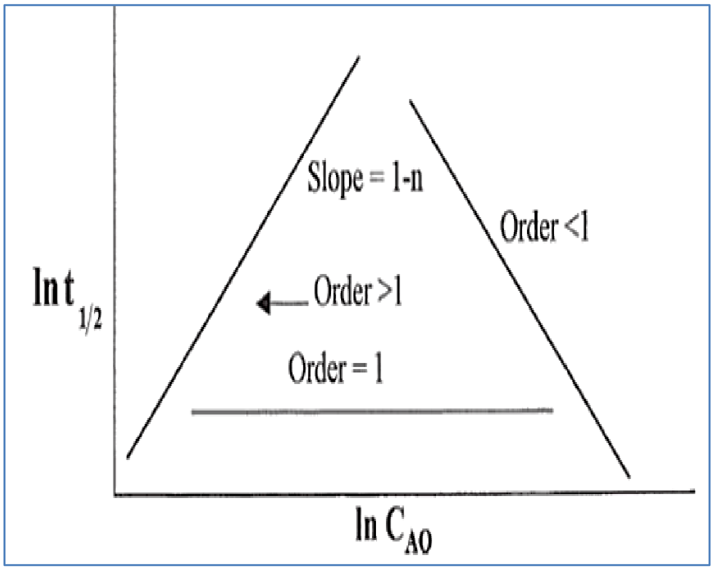


Fig. 5. Overall order of reaction from a series of half-life experiments each at different initial concentration of reactant.

Irreversible reactions

$$C_A^{1-n} - C_{AO}^{1-n} = (n-1)kt \qquad (32)$$

$$\left(1-X_A\right)^{1-n} - 1 = kC_{AO}^{n-1}(1-n)t \qquad (33)$$

Parallel reactions

Consider elementary reactions $\boldsymbol{A \overset{k_1}{\rightarrow} B}$ and $\boldsymbol{A \overset{k_2}{\rightarrow} C}$. The rate equations for these reactions for a constant volume batch system (i.e., constant density) are

$$(-r_A) = \frac{-dC_A}{dt} = k_1C_A + k_2C_A = (k_1 + k_2)C_A \tag{34}$$

$$(+r_B) = \frac{dC_B}{dt} = k_1C_A \tag{35}$$

$$(+r_C) = \frac{dC_C}{dt} = k_2C_A \tag{36}$$

$$-\int_{C_{AO}}^{C_A} \frac{dC_A}{C_A} = \int_0^t (k_1 + k_2)dt \tag{37}$$

$$-\ln\frac{C_A}{C_{AO}} = (k_1 + k_2)t \tag{38}$$

In terms of the fractional conversion

$$-\ln(1 - X_A) = (k_1 + k_2)t \tag{39}$$

$$\frac{r_B}{r_C} = \frac{dC_B}{dC_C} = \frac{k_1}{k_2} \tag{40}$$

Integrating Equation 19 between the limits yields

$$\frac{C_B - C_{BO}}{C_C - C_{CO}} = \frac{k_1}{k_2} \tag{41}$$

or $$C_B - C_{BO} = \frac{k_1}{k_2}C_C - \frac{k_1}{k_2}C_{CO} \tag{42}$$

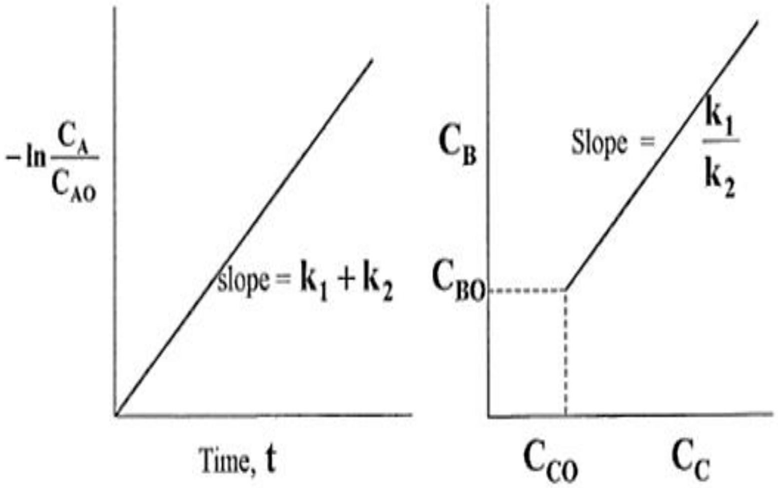


Fig. 6. Rate constants for two competing elementary first order reactions.

Irreversible reactions in series

Consider a first order reaction in series as $A \xrightarrow{k_1} B \xrightarrow{k_2} C$ and . The rate equations for these reactions for a constant volume batch system (i.e., constant density) are

$$(-r_A) = -\frac{dC_A}{dt} = k_1 C_A \qquad (43)$$

$$(-r_B)_{net} = -\frac{dC_B}{dt} = k_2 C_B - k_1 C_A \qquad (44)$$

$$(+r_C) = \frac{dC_C}{dt} = k_2 C_B \qquad (45)$$

	A	B	C
Amount at time t = 0	C_{AO}	0	0
Amount at time t = t	C_A	C_B	C_C
Amounts that have reacted	$C_{AO} - C_A$	C_B	C_C

$$C_A = C_{AO} e^{-k_1 t} \qquad (46)$$

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{AO} e^{-k_1 t} \qquad (47)$$

$$C_B = \frac{k_1 C_{AO}}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \qquad (48)$$

$$t_{max} = \frac{\ln\left(\frac{k_2}{k_1}\right)}{k_2 - k_1} \qquad (49)$$

At t_{max}

$$k_2 e^{-t_{max} k_2} = k_1 e^{-t_{max} k_1} \qquad (50)$$

$$\frac{C_{B_{max}}}{C_{AO}} = e^{-k_2\left[\frac{\ln(k_2/k_1)}{k_2 - k_1}\right]} \qquad (51)$$

Taking the natural logarithm gives

$$\ln\frac{C_{B_{max}}}{C_{AO}} = \left(-\frac{k_2}{k_2 - k_1}\right)\ln\left(\frac{k_2}{k_1}\right) \qquad (52)$$

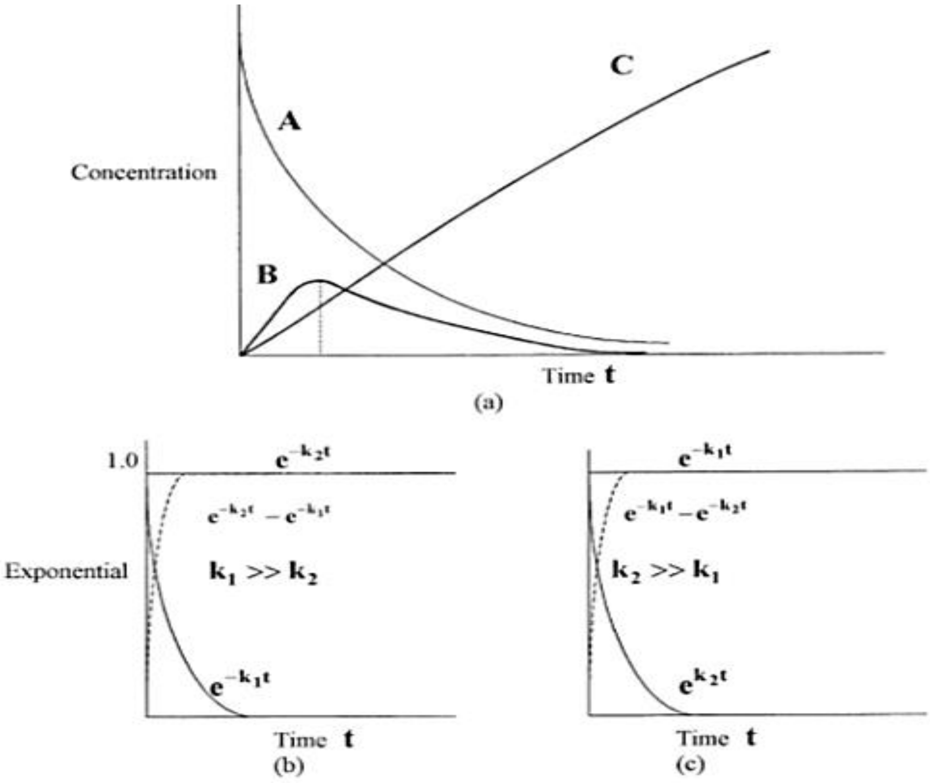


Fig. 7. (a) Variations in the concentrations of A, B, and C for a reaction occurring by the mechanism $\boldsymbol{A} \xrightarrow{k_1} \boldsymbol{B} \xrightarrow{k_2} \boldsymbol{C}$ (b) Variations with time of the exponentials when $k_1 \gg k_2$. (c) Variations of the exponentials when $k_2 \ll k_1$.

Chemical Reactor Design:

Basic Concepts in Reactor Design and Ideal Reactor Models

Stirred Tank Reactors:

Semi-batch or Semi-flow Reactors.

Semi-batch or semi-flow operations usually take place in a single stirred tank using equipment extremely similar to that described for batch operations (Fig. 1).

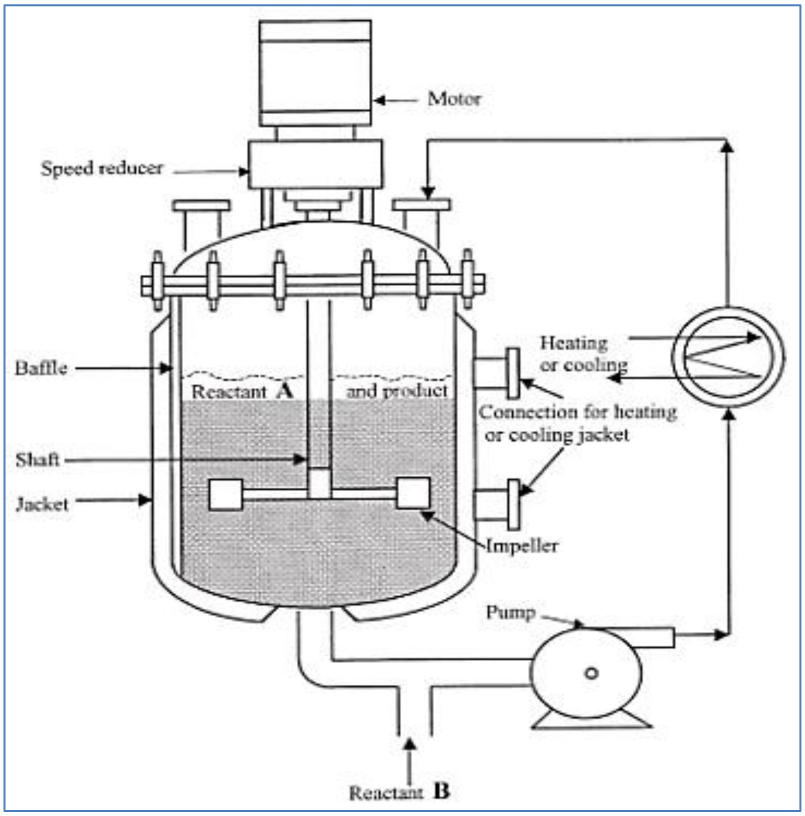


Fig. 1. semi-batch reactor with outside circulation

One common mode of operation involves loading some of the reactants into a stirred tank as a single charge and then feeding in the remaining material gradually. No product is withdrawn until the entire reagent has been added and the reaction has proceeded to the required extent.

As an example, consider the reaction A + B → C , where the reactor is first charged with reagent A and later reagent B is added continuously until the reaction is complete. Examples of this reaction process are:

- Reaction of a gas with a liquid where the gas bubbles through the liquid.
- Reaction of a highly reactive substance with a relatively inert substance where the reactive substance, if present in large amounts at the beginning of the reaction, either polymerize or decompose.

A semi-batch reactor has the same disadvantages as the batch reactor. However, it has the advantages of good temperature control and the capability of minimizing unwanted side reactions by maintaining a low concentration of one of the reactants. Semi-batch reactors are also of value when parallel reactions of different orders occur, where it may be more profitable to use semi-batch rather than batch operations. In many applications semi-batch reactors involve a substantial increase in the volume of reaction mixture during a processing cycle (i.e., emulsion polymerization).

This mode of operation is advantageous when large heat effects accompany the reaction. Exothermic reactions may be slowed down and temperature control maintained by regulating the rate at which one of the reactants is fed. Another mode of semibatch operation involves the use of a purge stream to remove continuously one or more of the products of a reversible reaction. For example, water may be removed in esterification reactions by the use of a purge stream or by distillation of the reacting mixture. Continuous removal of product(s) increases the net reaction rate by slowing down the reverse reaction.

Semibatch or semiflow processes are among the most difficult to analyze from the viewpoint of reactor design because one must deal with an open system under nonsteady-state conditions. Hence the differential equations governing energy and mass conservation are more complex than they would be for the same reaction carried out batchwise or in a continuous flow reactor operating at steady state.

Continuous Flow Reactors - Stirred Tanks.

The continuous flow stirred tank reactor is used extensively in chemical process industries. In many respects the mechanical and heat transfer aspects of these reactors closely resemble the stirred tank batch reactors treated in the previous subsection. However, in the present case, one must also provide for continuous addition of reactants and continuous withdrawal of the product stream. Both single tanks and batteries of tanks connected in series are used (Fig. 2).

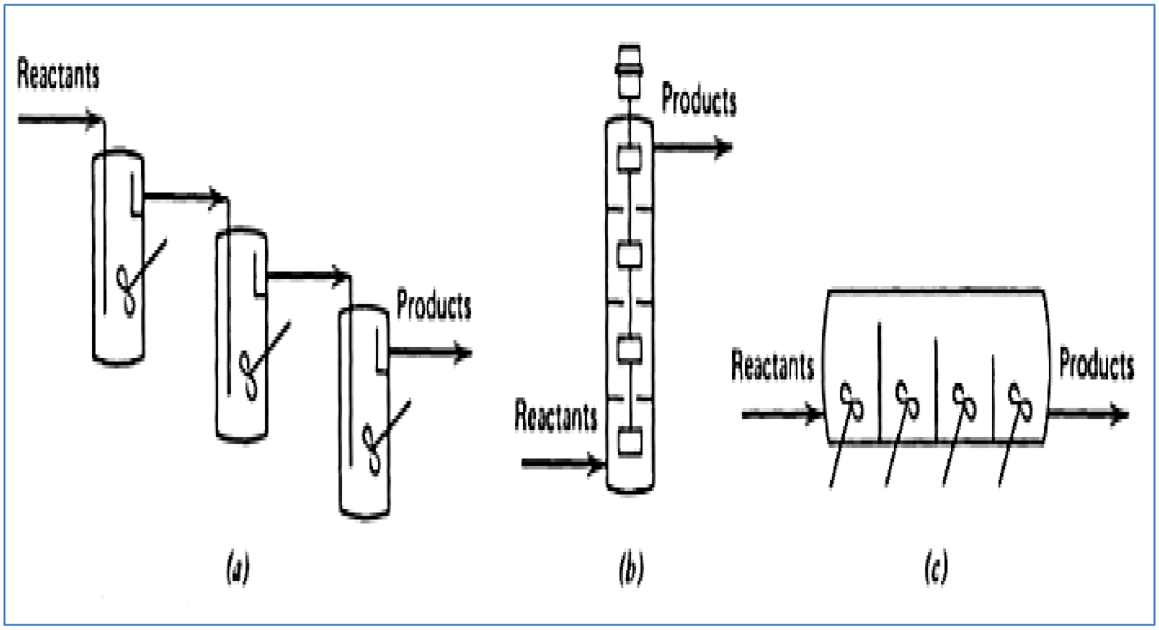


Fig. 2. Types of staged reactors, (a) Reactor battery, (b) Vertically staged, (c) Compartmented.

It is possible to employ either multiple individual tanks in series or units containing multiple stages within a single shell. Multiple tanks are more expensive, but provide more flexibility in use, since they are more readily altered if process requirements change. Therefore, very large reactors in series are needed to achieve high conversions (Fig. 3) . For example, the first reactor could be run to give a 50% conversion, yielding a high rate of reaction and subsequently reducing the total reactor volume. The next reactor might run from 50%–80% conversion and the third from 80%–90% until the desired conversion is reached. The effect of this process is a continuous reaction system that has a much lower volume, but has more equipment items because of the reactor vessels required.

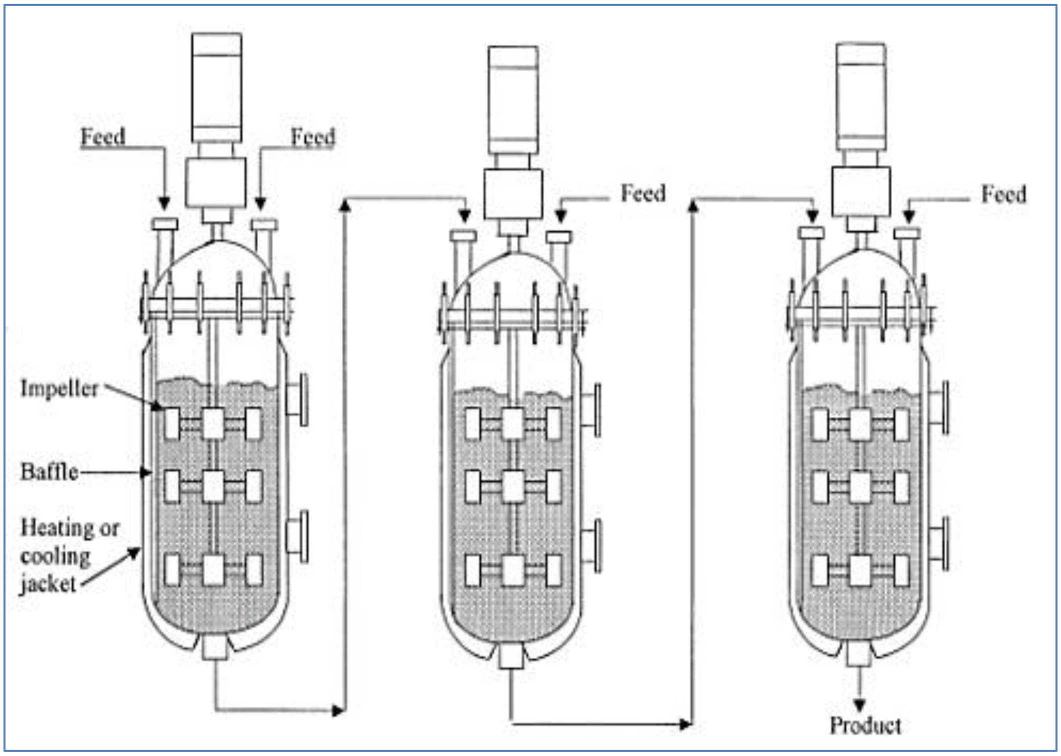


Fig. 3. A battery of continuous flow stirred tank reactors

In order to minimize pump requirements and maintenance, one often chooses to allow for gravity flow between stages. When the reactants are of limited miscibility, but differ in density, the vertical staged shell lends itself to countercurrent operation. This approach is useful when dealing with reversible reactions between immiscible fluids.

All that is required is that the time necessary to distribute an entering element of fluid uniformly throughout the tank be very small compared to the average residence time in the tank.

Because of the dilution that results from the mixing of entering fluid elements with the reactor contents, the average reaction rate in a stirred tank reactor will usually be less than it would be in a tubular reactor of equal volume and temperature supplied with an identical feed stream. Consequently, in order to achieve the same production capacity and conversion level, a continuous flow stirred tank reactor or even a battery of several stirred tank reactors must be much larger than a tubular reactor.

In many cases, however, the greater volume requirement is a relatively unimportant economic factor, particularly when one operates at ambient pressure in tanks constructed of inexpensive materials such as mild steel. In addition to lower construction costs, a continuous flow stirred tank reactor possesses other advantages relative to a tubular flow reactor, such as the facilitation of temperature control.

Efficient stirring of the reactor contents insures uniform temperature and the elimination of local hot spots.

The large heat capacity of the reactor contents also acts as a heat sink to moderate temperature excursions when changes occur in process conditions.

The physical configuration of cylindrical tanks provides a large heat transfer area on the external surface of the tank and permits augmentation of this area through the use of submerged coils within the tank. However, the rate of heat transfer per unit volume of reaction mixture is generally lower in a conventional stirred tank reactor than in conventional tubular reactors because of the lower ratio of heat transfer surface area to volume in the tank reactor. Consequently, tubular reactors are preferred for fast reactions when energy transfer requirements are very large.

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Selectivity considerations may also dictate the use of stirred tank reactors. They are preferred if undesirable side reactions predominate at high reactant concentrations, and they are also useful when one desires to "skip" certain concentration or temperature ranges where byproduct formation may be excessive.

Stirred tank reactors are employed when it is necessary to handle gas bubbles, solids, or a second liquid suspended in a continuous liquid phase. One often finds that the rates of such reactions are strongly dependent on the degree of dispersion of the second phase, which in turn depends on the level of agitation. Large stirred tank reactors are generally not suited for use at high pressures because of mechanical strength limitations. *They are used mainly for liquid phase reaction systems at low or medium pressures when appreciable residence times are required*.

Industrial reactors operate in the steady state with the volume, concentration, and temperature of the reaction mixture being constant with time. It is approximated that a steady state operation is reached when about five to ten times the reactor volume of the reaction mixture has passed through the reactor.

In the continuously flow stirred tank reactor, the reaction takes place at the temperature and the degree of conversion of the outlet stream. This gives the reactor its characteristic features from either the batch or semi-batch reactor.

Figure 4 is a variation of the continuous homogeneous reactor (baffled tank) in which backmixing has a considerable effect. The advantage of this type of reactor is its low cost per unit volume. It is often used when a long holding time would require a tubular reactor that is too long or too expensive. Agitation is not required and a high degree of backmixing is not harmful to the yield.

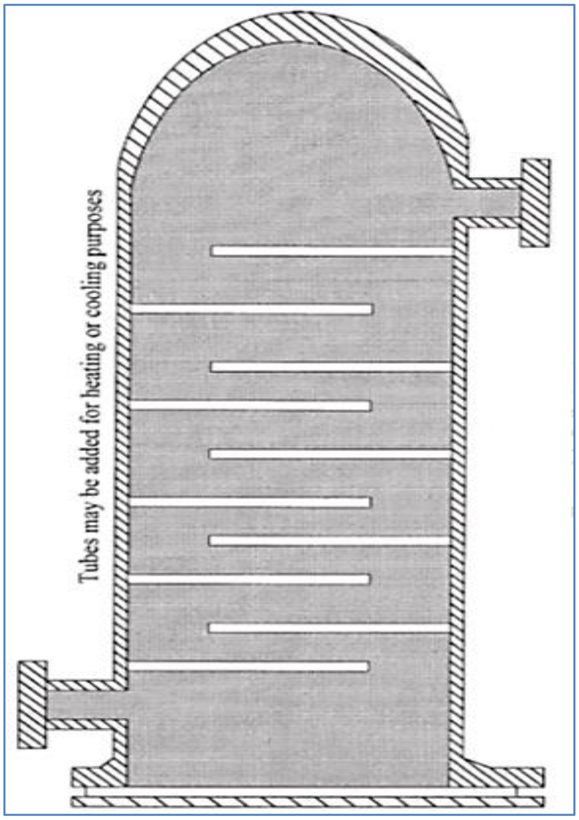

Fig. 4. Baffled tank reactor

H.W. 17.1. *Give two examples of chemical industries used semi-batch reactors.*

Chemical Reactor Design:

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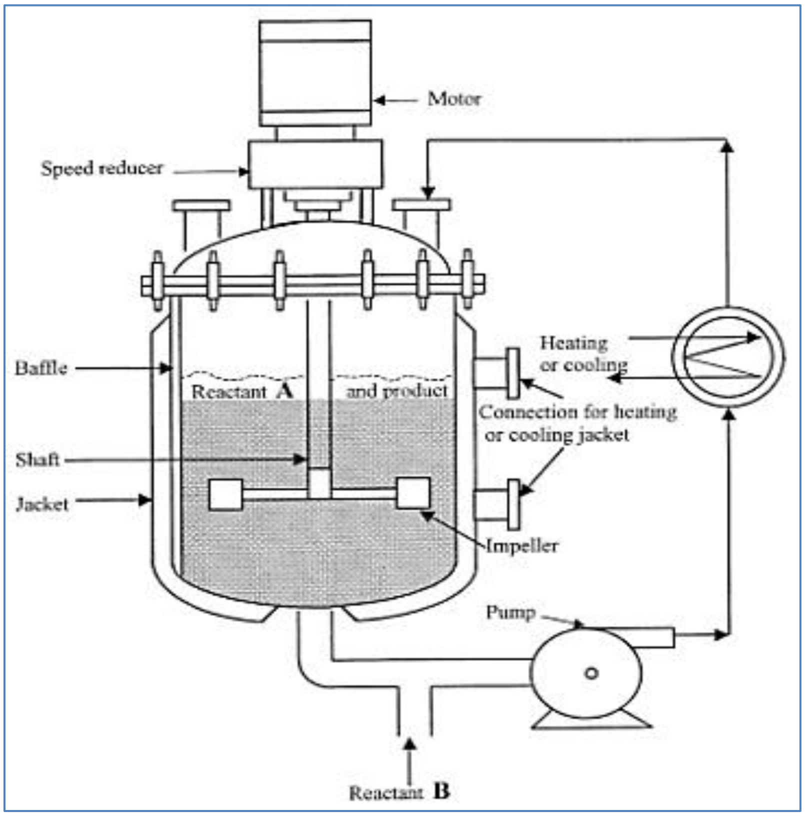

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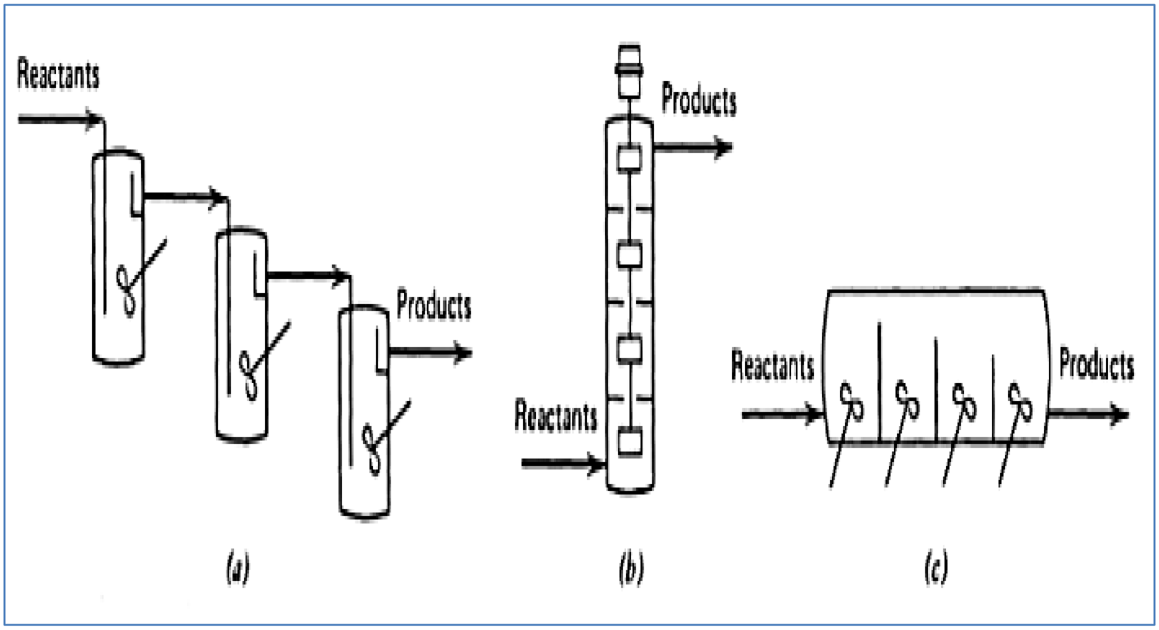

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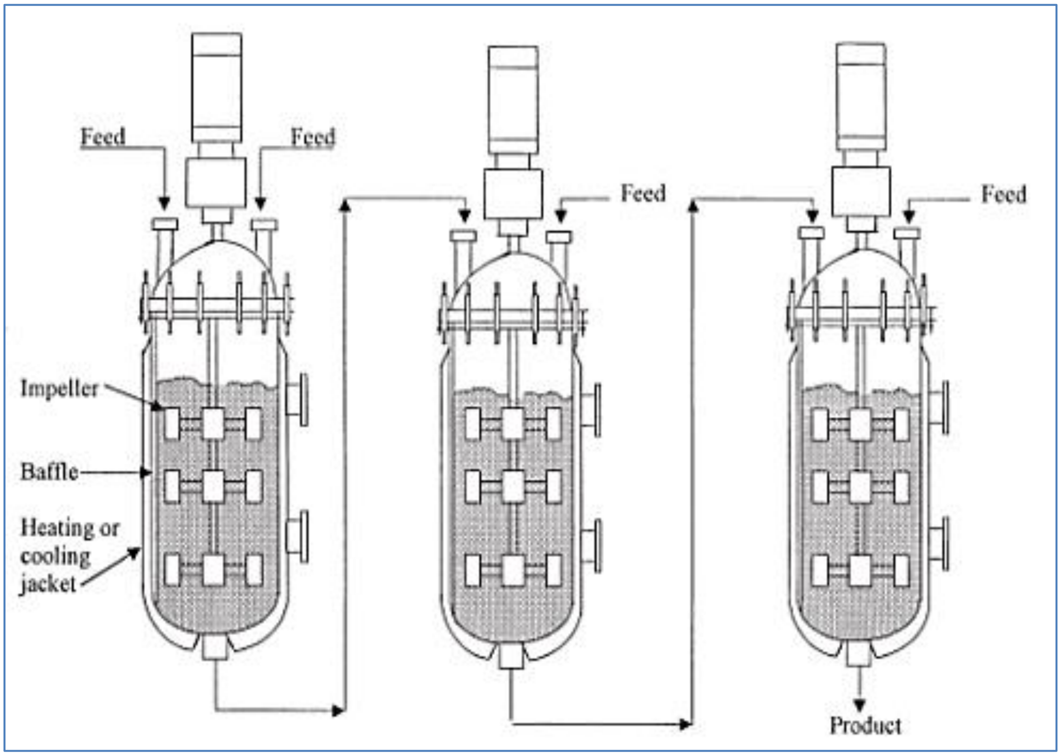

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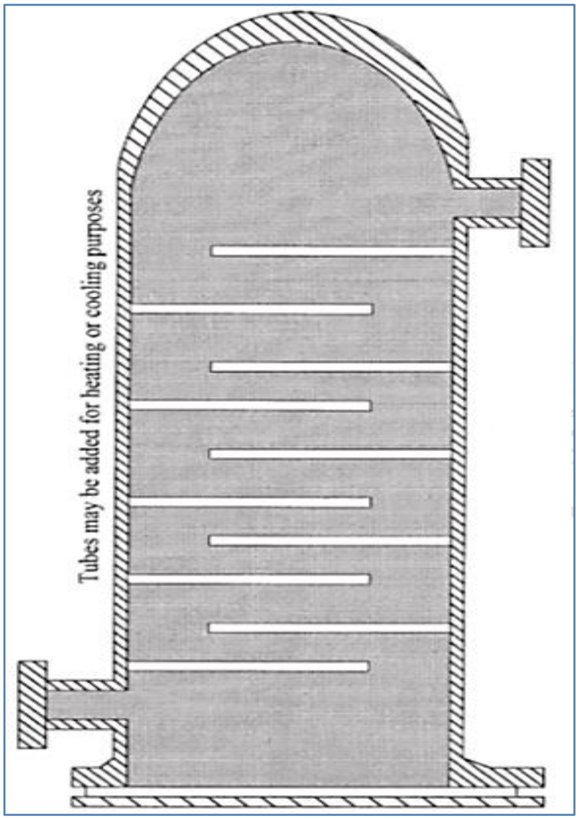


Fig. 4. Baffled tank reactor

H.W. 17.1*. Give two examples of chemical industries used semi-batch reactors.*

Chemical Reactor Design:

Basic Concepts in Reactor Design and Ideal Reactor Models

Continuous Flow Reactors - Tubular Reactors.

The tubular reactor is so named because the physical configuration of the reactor is normally such that the reaction takes place within a tube or length of pipe. The idealized model of this type of reactor assumes that an entering fluid element moves through the reactor as a plug of material that completely fills the reactor cross section. All particles that enter the reactor at the same time must leave simultaneously which mean that all fluid elements take the same length of time to move from the reactor inlet to the outlet.

Thus the terms piston flow or plug flow reactor (PFR) are often employed to describe the idealized model. The contents of a given elemental plug are presumed to be uniform in temperature and composition and pressure thus can be assumed that radial mixing is infinitely rapid. This model may be used to treat both the case where the tube is packed with a solid catalyst and the case where the fluid phase alone is present.

H.W. 18.1. *What is the difference between tube and pipe?*

The majority of tubular reactors may be classified in terms of three major categories:

1. Single-jacketed tubes.
2. Shell-and-tube heat exchangers.
3. Tube furnaces, in which the tubes are exposed to thermal radiation and heat transfer from combustion gases.

The single-jacketed tube reactor is the simplest type of tubular reactor to conceptualize and to fabricate. It may be used only when the heat transfer requirements are minimal because of the low surface area to volume ratio characteristic of these reactors.

When the shell-and-tube configuration is utilized, the reaction may take place on either the tube side or the shell side. The shell-and-tube tubular reactor has a much greater area for heat transfer per unit of effective reactor volume than the single-jacketed tube. Consequently, it may be used for reactions where the energy transfer requirements are large. On occasion the reaction zone may be packed with granular solids to promote increased turbulence or better contacting of heterogeneous fluid phases or to act as a thermal sink to facilitate control of the reactor. In many cases energy economies can be achieved using countercurrent flow of a hot product stream to preheat an incoming reactant stream to the temperature where the reaction occurs at an appreciable rate. Two commercial scale processes that employ this technique are the synthesis of ammonia from its elements and the oxidation of sulfur dioxide to sulfur trioxide. Tubular furnaces are used only when it is necessary to carry out endothermic reactions at fairly high temperatures on very large quantities of feedstock. Thermal reforming reactions and other reactions used to increase the yield of gasoline from petroleum-based feed stocks are commercial scale processes that employ this type of reactor. A tubular furnace is basically a combustion chamber with reactor tubes mounted on its walls and ceiling. Tube dimensions are typically 3 to 6 in. in diameter with lengths ranging from 20 to 40 ft. As many as several hundred tubes may be used, with either series or parallel connections possible depending on the required residence time.

Because there is no back-mixing of fluid elements along the direction of flow in a tubular reactor, there is a continuous gradient in reactant concentration in this direction. One does not encounter the step changes characteristic of multiple stirred tank reactors. Consequently, for the same feed composition and reaction temperature, the average reaction rate will generally be significantly higher in a plug flow reactor than it would be in a single stirred tank or a battery of stirred tanks with a total volume equal to that of the tubular reactor. The more efficient utilization of reactor volume is an advantage of the tubular reactor that permits one to use it in processes which demand very large capacity. Because variations in temperature and composition may occur in the axial direction in tubular reactors, these systems may be somewhat more difficult to control than continuous flow stirred tank reactors. However, the problems are usually not insurmountable, and one can normally obtain steady-state operating conditions which give rise to uniform product quality. Other advantages of the tubular reactor relative to stirred tanks include suitability for use at higher pressures and temperatures, and the fact that severe energy transfer constraints may be readily surmounted using this configuration.

The tubular reactor is usually employed for liquid phase reactions when relatively short residence times are needed to effect the desired chemical transformation. It is the reactor of choice for continuous gas phase operations.

The disadvantages are:

- Expensive instrumentation.
- High operating cost (maintenance, cleaning).
- Non-uniform heat flux of the radiant section of furnace.

The principal disadvantage of the tubular reactor is the difficulty in controlling the temperature within the reactor. This often results in hot spots especially when the reaction is exothermic.

Continuous Flow Reactors – Heterogeneous Reactors.

Figure 1 shows a continuous reactor used for bubbling gaseous reactants through a liquid catalyst. This reactor allows for close temperature control. The fixed-bed (packed-bed) reactor is a tubular reactor that is packed with solid catalyst particles. The catalyst of the reactor may be placed in one or more fixed beds (i.e., layers across the reactor) or may be distributed in a series of parallel long tubes. The latter type of fixed-bed reactor is widely used in industry (e.g., ammonia synthesis) and offers several advantages over other forms of fixed beds.

The type of reactor shown in Figure 2 is used in a heterogeneous reaction system involving catalyzed gas reactions. The fixed-bed reactor gives less chance for back-mixing, but channeling of the gas flow through the catalyst bed causes ineffective use of parts of the reactor bed. An advantage of the fixed-bed reactor is that for most reactions, it gives the highest conversion per weight of catalyst of any catalytic reactor. Another advantage is it provides large volumes of processed reactants. The disadvantages are:

- The catalysts are highly prone to deactivation.
- The catalysts often require regeneration after a relatively short period of operation. This may incur additional cost.
- It is difficult to control the heat-transfer in the catalyst bed.

- Some part of the catalyst surface remains unused as a result of the reaction system and the rate-controlling step.

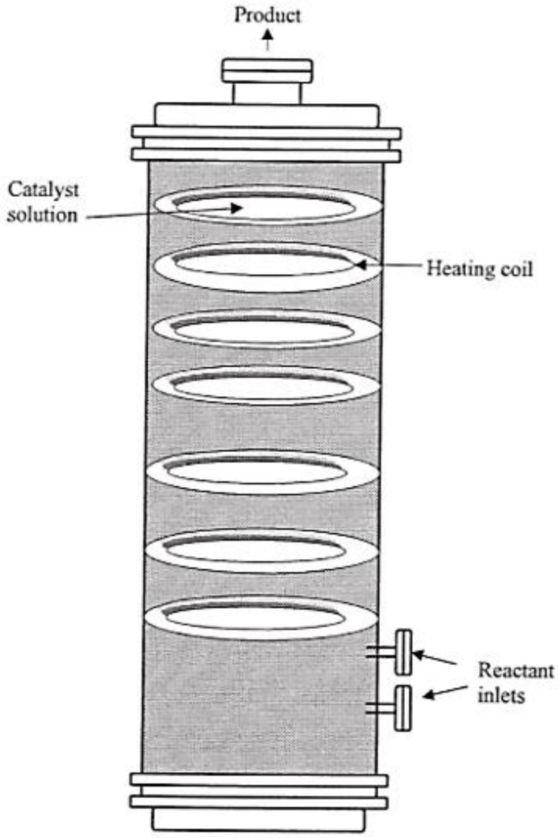


Fig. 1. Heterogeneous continuous reactor

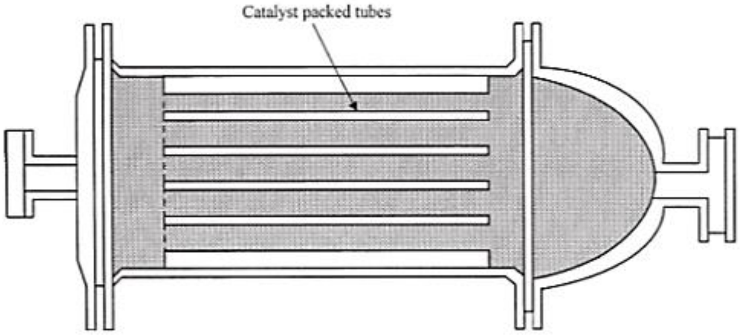


Fig. 2. Longitudinal catalytic fixed-bed reactor

Fluidized Bed System

The fluidized bed in Figure 3 is another common type of catalytic reactor. The fluidized bed is analogous to the CSTR in that its contents though heterogeneous are well mixed, resulting in an even temperature distribution throughout the bed. In a fluidized bed reactor, the solid material in the form of fine particles is contained in a vertical cylindrical vessel. The fluid stream is passed up through the particles at a rate strong enough for them to lift and not fall back into the fluidized phase above its free surface by carryover in the fluid stream. The bed of particles in this state shows the appearance of boiling. In heterogeneous catalytic reactions, the catalyst loses its activity with operating time.

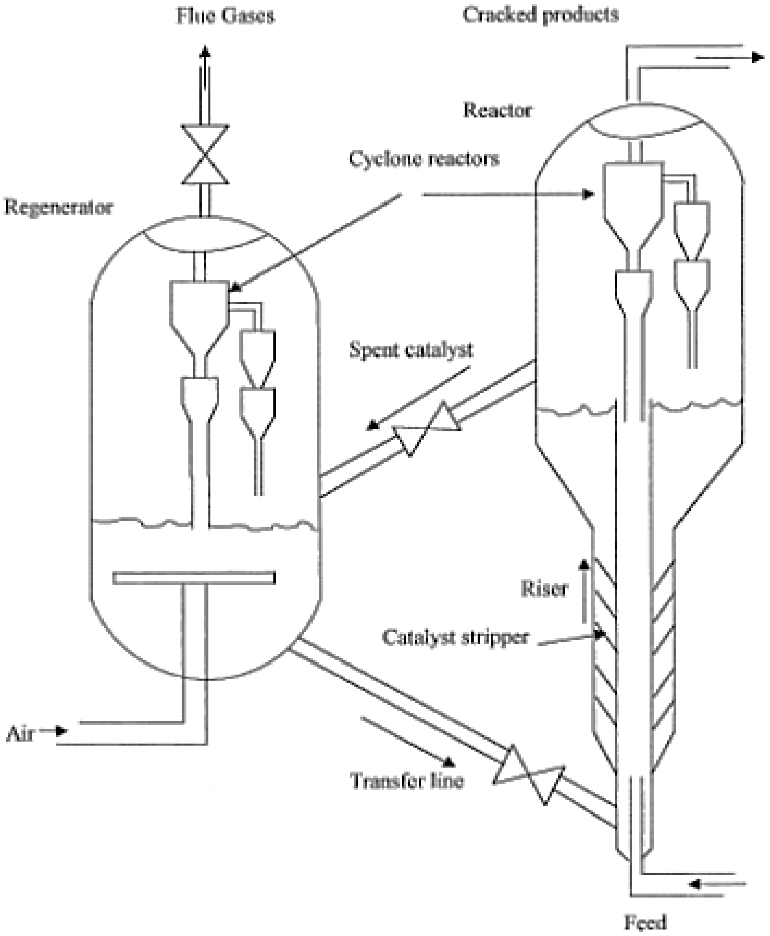


Fig. 3. Fluid catalytic cracking unit

The fluid catalytic cracking (FCC) process converts straight-run atmospheric gas oil, vacuum gas oils, and heavy stocks recovered from other operations into high-octane gasoline, light fuel oils, slurry oil, and olefin-rich light gases. The catalysts used are mixtures of crystalline alumina silicates (known as zeolites), active alumina, silica-alumina, clay, and rare earth oxides. In the FCC, an oil feed composed of heavy hydrocarbon molecules is mixed with catalyst and enters a fluidized bed reactor. The long molecules react on the surface of the catalyst and are cracked into lighter product molecules (e.g., gasoline), which leave the reactor from the top. During the cracking process, carbon and other heavy uncracked organic materials are deposited on the surface of the catalyst resulting in its deactivation. it operates at nearly constant temperature and is, therefore, easy to control. Also, there is no opportunity for hot spots. The catalyst is then taken into a regenerator where the deposited surface material is burned with air. The regenerated catalyst returns to the reactor after it has been mixed with fresh feed. The activity of the newer catalysts is so intense that much of the cracking takes place in the line returning the regenerated catalyst to the reactor. This process is referred to as the transfer line cracking. The advantages of the fluidized bed are:

- Savings in operating expenses due to heat recovery in the reaction regeneration steps.
- Rapid mixing of reactants-solids and high heat transfer rates.
- Easy to control both the heat transfer and the fluid flow system.

The disadvantages are:

- Backmixing due to particle distribution in dense and dilute phases.
- Inefficient contacting due to solids movement and the bypassing of solids by bubbles.
- Possible channeling, slugging, and attrition of catalyst.
- Possible agglomeration and sintering of fine particles in the dilute phase under certain conditions (e.g., high temperature).

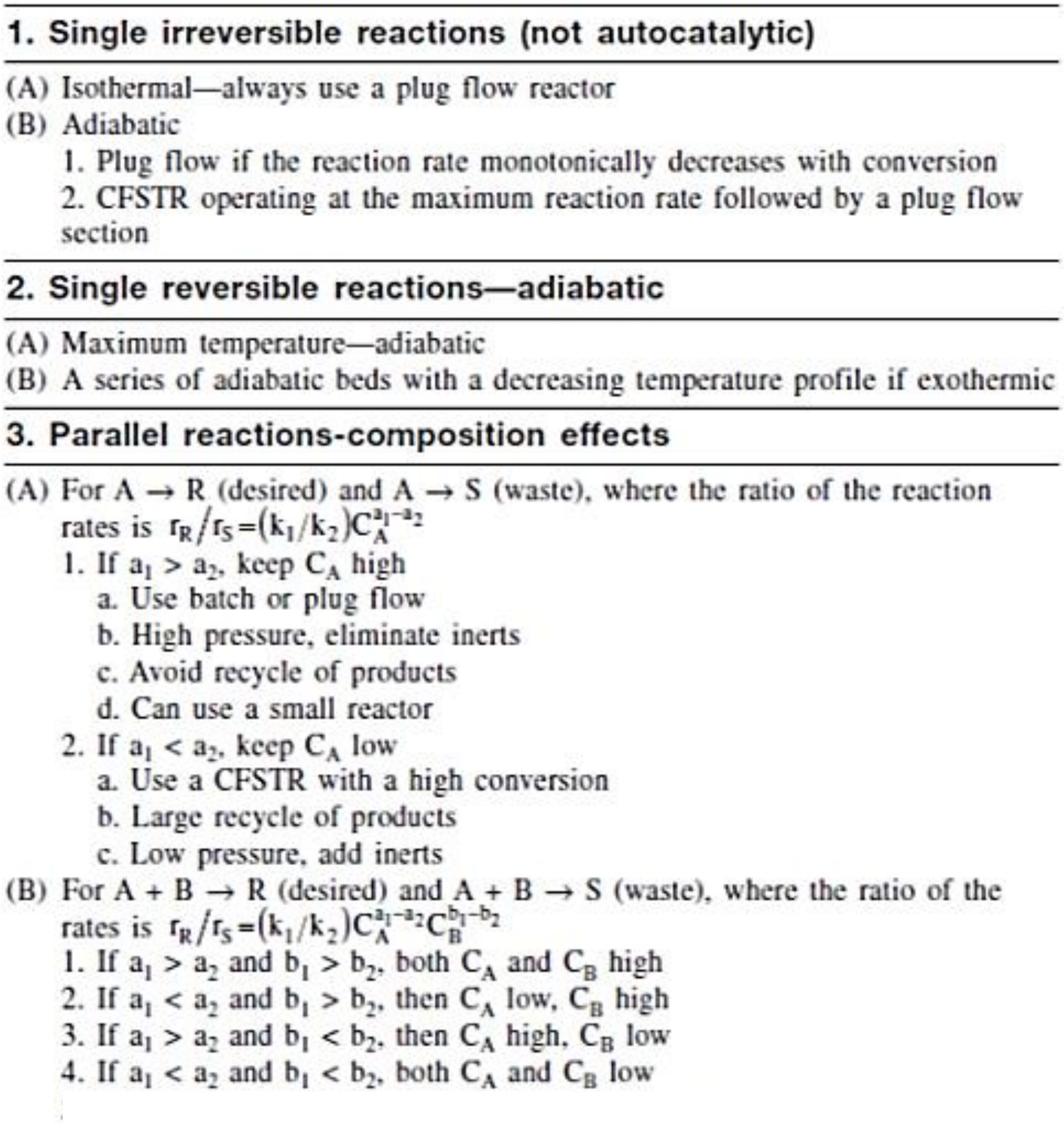
The advantages of the ease of catalyst replacement or regeneration are offset by the high cost of the reactor and catalyst regeneration equipment.

Other reactors are employed such as:

- Straight-Through Transport Reactors.
- Recirculating Transport Reactors.
- Pulse Reactors.
- Loop Reactors.
- Electrochemical Reactors.

Table 1 gives various guidelines for the design of reactors and Figure 4 illustrates various reactor configurations.

Table 1. Design guidelines for reactors



1. Single irreversible reactions (not autocatalytic)

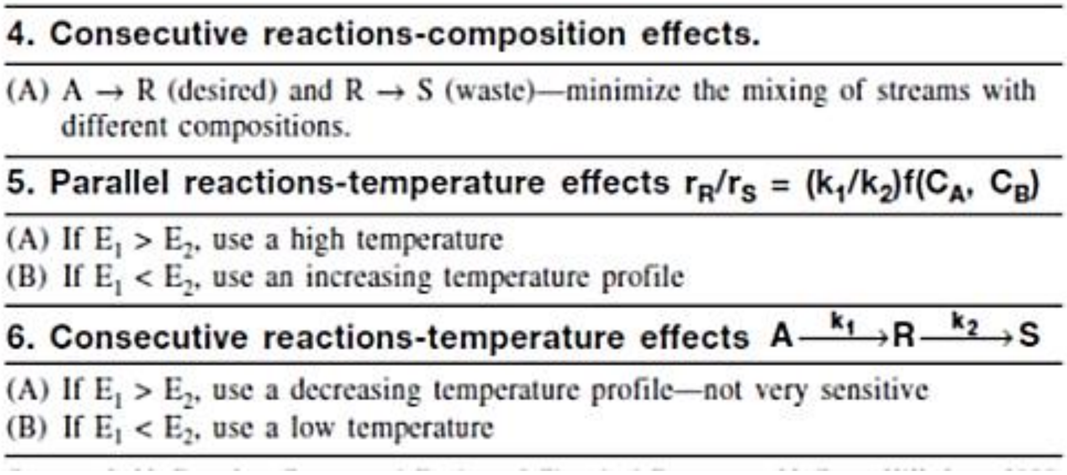
(A) Isothermal—always use a plug flow reactor
(B) Adiabatic
  1. Plug flow if the reaction rate monotonically decreases with conversion
  2. CFSTR operating at the maximum reaction rate followed by a plug flow section

2. Single reversible reactions—adiabatic

(A) Maximum temperature—adiabatic
(B) A series of adiabatic beds with a decreasing temperature profile if exothermic

3. Parallel reactions-composition effects

(A) For A → R (desired) and A → S (waste), where the ratio of the reaction rates is $r_R/r_S=(k_1/k_2)C_A^{a_1-a_2}$
  1. If $a_1 > a_2$, keep C_A high
    a. Use batch or plug flow
    b. High pressure, eliminate inerts
    c. Avoid recycle of products
    d. Can use a small reactor
  2. If $a_1 < a_2$, keep C_A low
    a. Use a CFSTR with a high conversion
    b. Large recycle of products
    c. Low pressure, add inerts
(B) For A + B → R (desired) and A + B → S (waste), where the ratio of the rates is $r_R/r_S=(k_1/k_2)C_A^{a_1-a_2}C_B^{b_1-b_2}$
  1. If $a_1 > a_2$ and $b_1 > b_2$, both C_A and C_B high
  2. If $a_1 < a_2$ and $b_1 > b_2$, then C_A low, C_B high
  3. If $a_1 > a_2$ and $b_1 < b_2$, then C_A high, C_B low
  4. If $a_1 < a_2$ and $b_1 < b_2$, both C_A and C_B low



4. Consecutive reactions-composition effects.

(A) A → R (desired) and R → S (waste)—minimize the mixing of streams with different compositions.

5. Parallel reactions-temperature effects $r_R/r_S = (k_1/k_2)f(C_A, C_B)$

(A) If $E_1 > E_2$, use a high temperature
(B) If $E_1 < E_2$, use an increasing temperature profile

6. Consecutive reactions-temperature effects $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

(A) If $E_1 > E_2$, use a decreasing temperature profile—not very sensitive
(B) If $E_1 < E_2$, use a low temperature

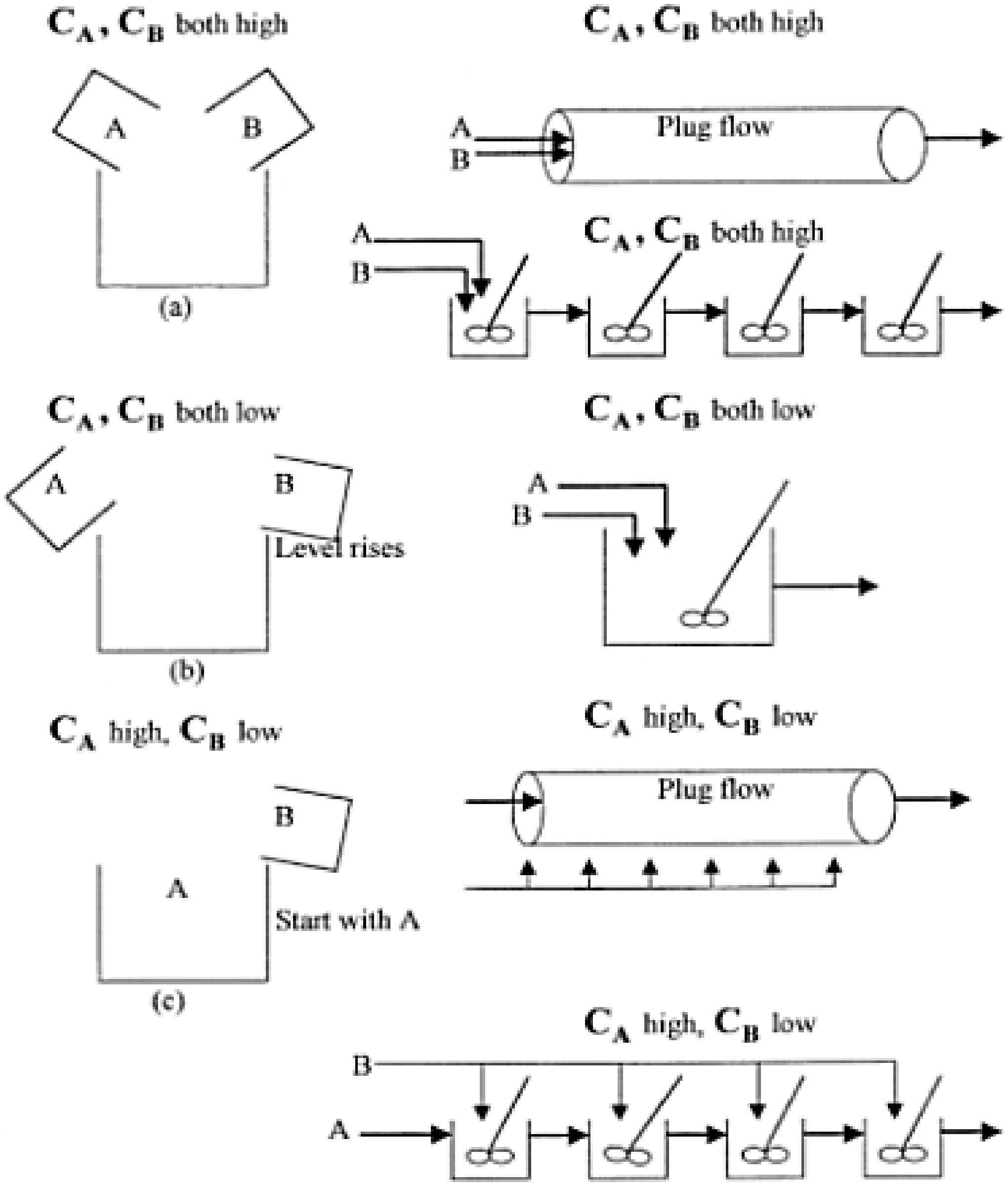


Fig. 4. Parallel reactions

Chemical Reactor Design:

Catalysts

The reforming catalyst, one of the most important factors in reactor design, must be durable enough for severe reacting conditions. A decrease in the catalytic activity is due to a reduction of the surface area caused by nickel sintering. This is prevented by providing the catalysts, which are made of porous carriers impregnated with nickel, with a suitable pore distribution and sufficient thermal resistance. The catalyst particle size and shape should be optimized to achieve maximum activity and maximum heat transfer, while minimizing the pressure drop. The high mass velocities in steam reforming reactor necessitate a relatively large catalyst particle size to obtain a low pressure drop across the catalyst bed; but the particle size is limited by another requirement for effective packing. The pressure drop depends strongly on the void fraction of the packed bed and decreases with the size of the packed particle.

Fig. 1. Industrial Catalyst Types

Fig. 1. Shows some types industrial catalyst where the internal surface areas are 10^7-10^9 m^{-1} for industrial catalysts. The choice of catalyst porosity is, therefore, very important. A high internal surface area is desirable to give high local reaction rates, but if, in achieving the high surface area, the pore size is reduced to the point where diffusion rates are hindered, then the overall performance will suffer.

The amount of catalyst used is that which will give the residence time needed for the reactants to be sufficiently converted at the operating temperature and pressure. In addition, carbon deposition on the catalyst surface can be a serious problem, thus its prevention is essential. Carbon tends to be formed under high temperatures and low hydrogen partial pressures. Unless the product gas is recycled, no hydrogen exists in the reacting gas at the inlet of the reactor. This raises the technical issue of what inlet temperature should be set to prevent carbon deposition. The problem can be solved by consideration based on chemical thermodynamics.

Hydrotreating is one of the key technologies in petroleum refining, covering a series of processes with different objectives. The process is commonly employed to reduce or saturate organic compounds. Various petroleum fractions are treated with hydrogen in the presence of catalyst (Fig. 2), to decompose and eliminate unfavourable impurities such as sulphur, nitrogen and metals in order to produce clean fuel oil or feed stock for fluid catalytic cracking or to hydrogenate olefin and aromatics into saturated hydrocarbons. Commercial hydrogenation catalysts are generally composed of cobaltmolybdenum supported on alumina, and if larger hydrogenation activity is required, then nickel is employed instead of cobalt.

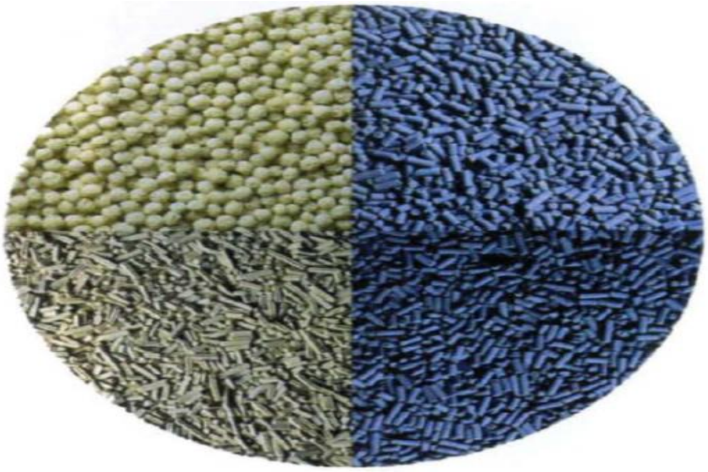


Fig. 2. Catalysts for Hydroprocessing

There are a large number of commercial catalysts available for hydrotreating. Typically, the supports are extruded alumina cylinders. Some, as shown on Fig. 3, are 'shaped', to give extended surfaces.

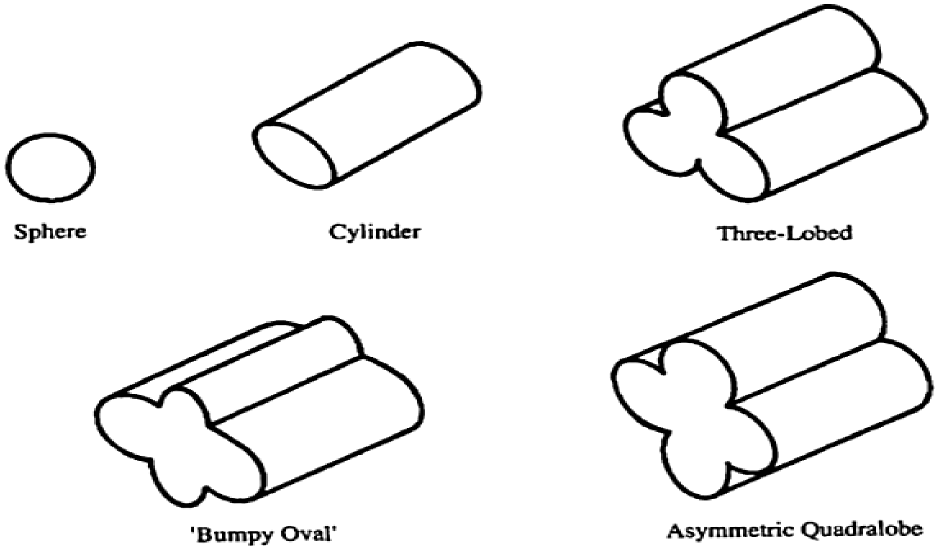


Fig. 3. Common catalyst shapes

In addition to the above metal oxides (sulphides in practical usage) as active components, control of pore diameter and acidity of the alumina as carrier are the important factors for preparation of the catalyst with excellent performance. The catalyst activity degrades gradually during the operating time because of metals and carbon produced from the heavy ends in the feed. to supplement its activity loss, the reactor is operated at temperatures which are increased gradually, and finally shut down either for replacement of the catalyst or regeneration of the catalyst while holding it within the reactor (in situ). Catalyst regeneration is carried out by adding air little by little into the inert gas which is charged into the reactor to burn (carefully) the carbon deposited on the catalyst. Catalysts do not change before or after a reaction, and neither give energy to raw molecules, but reduce the value of the activation energy. Since the activation energy is fed as heat, catalytic reactions are a kind of thermal reaction. The list of examples of catalytic reactions is endless: hydrogenation of the unsaturated hydrocarbons using palladium as a catalyst; synthesis of polymers from olefins using the Ziegler-Natta catalyst; and production of gasoline by zeolite (Fig. 4). It is more likely that catalysts are used in the majority of industrial reaction processes.

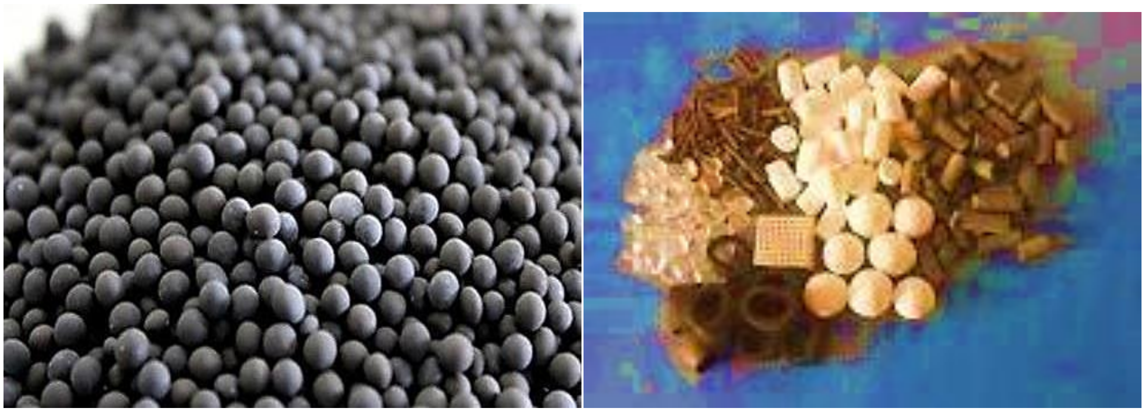


Fig. 4. Palladium and zeolite catalyst

Enzymes are also a kind of catalyst (Enzymes are protein as well as a catalyst existing in a living body). In the process that converts cane sugar into glucose through hydrolysis, either sulphuric acid or an enzyme called Alpha-amylase is available for accelerating the reaction; thus processes using either of them as a catalyst become widespread in industrial applications.

Diameters of the catalyst particles can vary from 0.8 mm to 5.0 mm. Small diameter catalysts have a larger external surface area per unit volume when compared to large diameter catalysts. However, there are limitations. Very small diameter catalysts can have two serious problems. One is crushing strength, an important catalyst property. Pressure drop through a bed of small diameter catalyst will be greater than that through larger diameter particles, and if too great, can exceed the mechanical strength of the supports. Larger diameter catalysts have greater strength and can resist the crushing effects of pressure drop. The other problem with very small diameter catalysts is their filtering ability, i.e., any discrete solid particles, such as scale, entering the catalyst bed will be trapped at the top of the bed by the fine catalyst. This, in turn, can raise pressure drop over the catalyst bed causing either catalyst crushing or increased operating costs. If scale is a serious problem it can be alleviated by using larger diameter catalyst in the top bed and smaller diameter in the lower bed or beds. Also, external filters are sometimes used on raw feed to remove particulate matter, especially when the stock comes from tankage. Although the actual composition of commercial hydrotreating catalysts is proprietary information, it can be said that a typical CoMo catalyst will contain about 2-5 wt% Co and 4-8 wt% Mo. A typical NiMo catalyst will contain about 2-5 wt% Ni and 4-8 wt% Mo. These compositions can vary widely depending on the selectivity desired in the hydrotreating process. One chemical reaction can be encouraged and another discouraged by changes in catalyst components. The products must meet certain specifications, but exceeding them may consume valuable hydrogen that could be used elsewhere in the refinery. Selectivity can be influenced both by variations in catalyst properties and by variations in operating conditions.

Reactor internal arrangements will vary depending on the reactant phases, catalyst and type of operation. Fig. 5. shows typical reactor internals for hydroprocessing units.

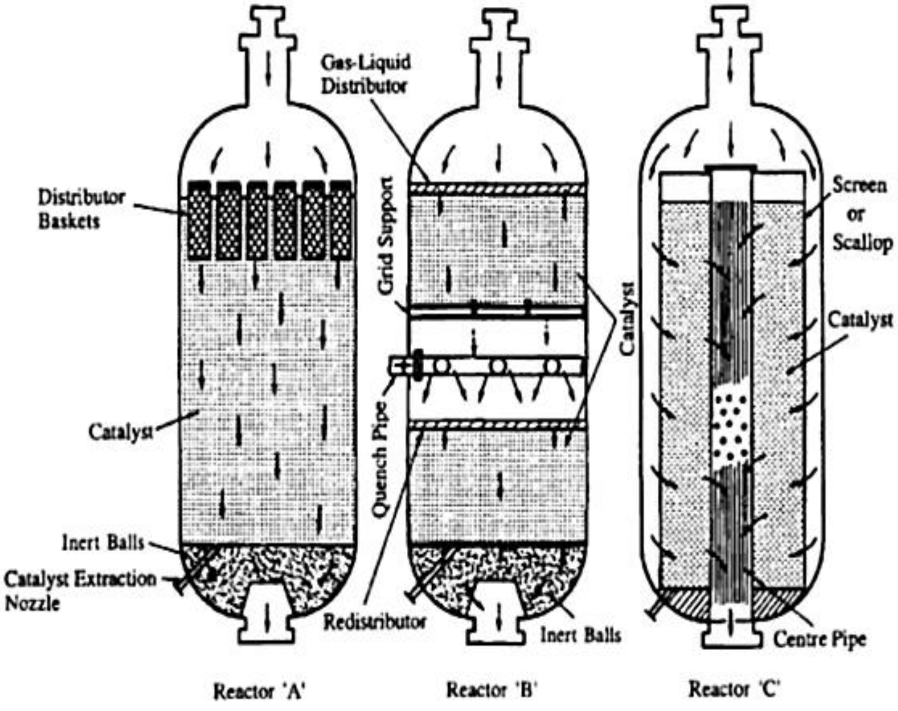


Fig. 5. Reactor internals

(I) Reactor A with distributor baskets at the catalyst top is used for both single-phase and two-phase operations. The purpose of the baskets is to give uniform distribution of the phase and/or to collect any particulate matter present in the feed which would otherwise clog the top of the catalyst bed and cause increasing pressure drop.

(2) Reactor B has multiple beds, each requiring support grids. Multiple beds are used to redistribute the liquid phase, and are needed when (1) pressure drop across a single bed would be excessive, or (2), as shown, where a cold quench stream must be introduced to control temperature. Multiple beds are used in hydrotreating units because the exothermic heat of reaction is high. Quench streams are inserted between beds to limit temperature rise. Temperature rise is usually limited to about 25^0C.

(3) Reactor C is used only for vapour-phase reactions, particularly where a low pressure drop is desired (which is typical in catalytic reforming units). The reactants distribute over the outer periphery of the catalyst bed (which is contained by a cylindrical screen or perforated sheet metal), then flow radially through a shallow bed into a perforated centre pipe and then out of the reactor bottom.

Catalysts are usually applied in fixed beds where there are several types of fixed bed reactors as shown in Fig. 6. The fixed bed reactors are most commonly used as catalytic reactors.

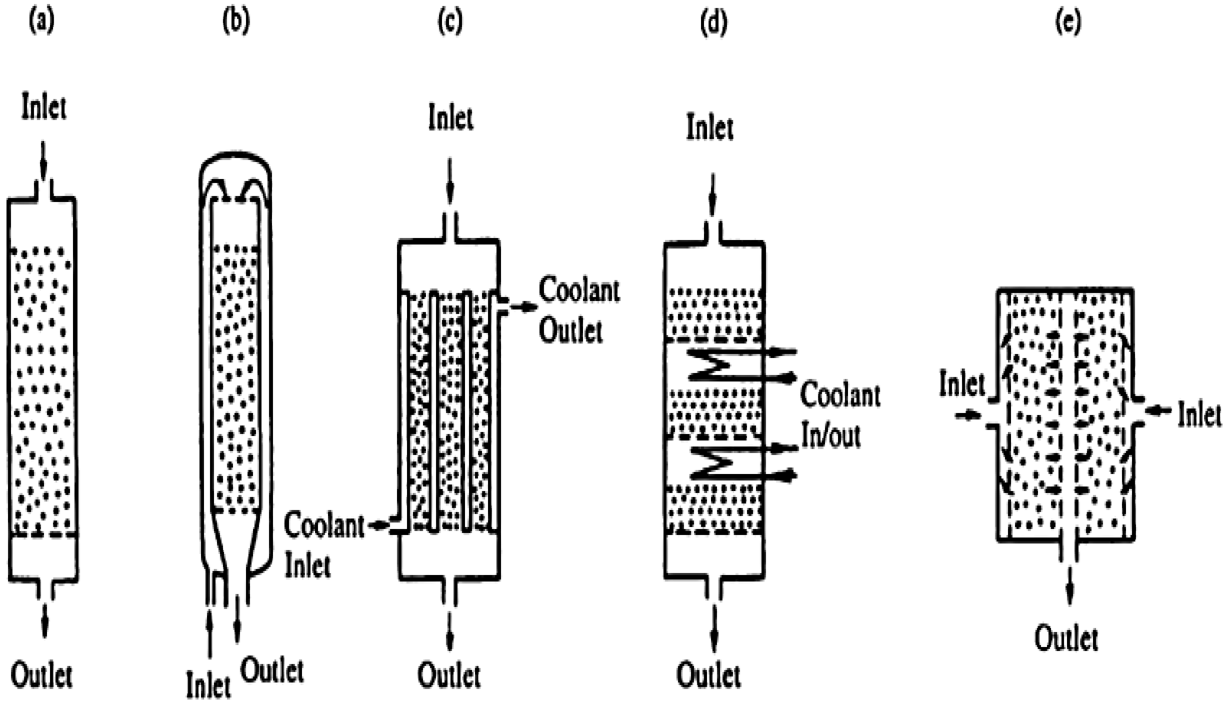


Fig. 6. Several types of fixed bed reactors. (a) Down flow type. (b) Self-thermal-exchange Type. (c) Cooling Type. (d) Intermediate Cooling Type. (e) Radial Flow Type.