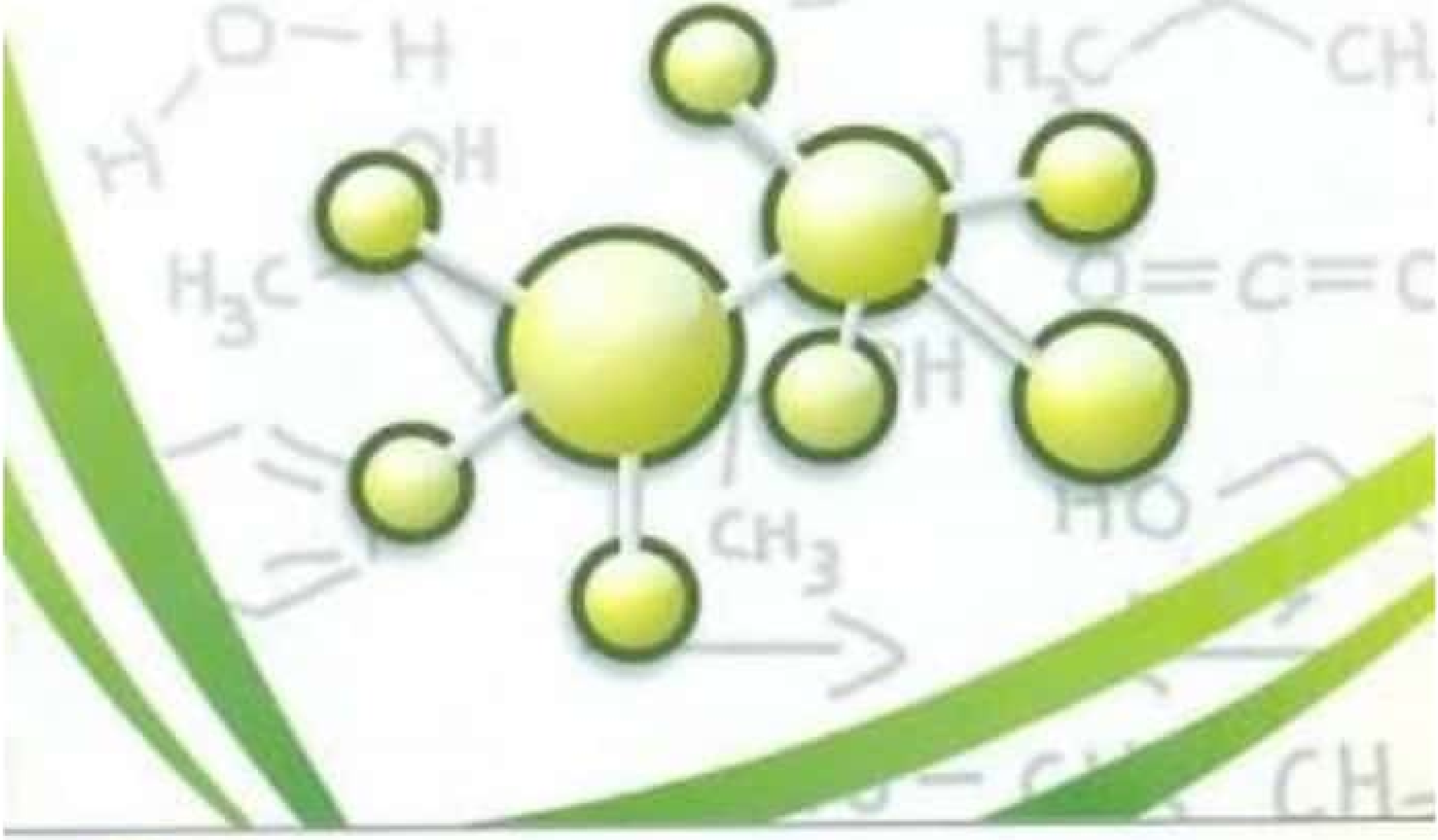
CHEMICAL REACTION ENGINEERING-I

KA GAVHANE



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KINETICS OF HOMOGENEOUS REACTIONS

Every industrial chemical process is aimed at production of a desired product economically from given raw materials. Such chemical process can be thought of as the sum of unit operations and unit processes (that are performed on materials in correct sequence) as it involves a series of physical and chemical treatment steps in proper sequence starting from feed material to product. It is the chemical step – (unit process such as oxidation, sulphonation, nitration) – the step in which raw materials are converted into product-that decides largely the economics of the overall process. So it is the heart of the process and maximum attention is given to this step during the development stage. A piece of equipment in which the reactants are converted into useful product is referred to as a chemical reactor. Design of a chemical reactor properly for given reactions and given process conditions is the aim of this subject matter and this design activity makes use of information, knowledge, and experience from areas such as thermodynamics, chemical kinetics, fluid flow, heat transfer, mass transfer and economics.

When new molecules are formed by the rearrangement or redistribution of the constituent atoms, a chemical reaction is said to occur. For example : $CO + 2\ H_2 \rightarrow CH_3OH$. A chemical engineer wishes to know primarily two important things about a chemical reaction : (i) can it go ? and (ii) how long will it take ? – whether a reaction is feasible or not and if feasible, what is the maximum possible extent of a reaction and time required for a given reaction for a specific extent of reaction. The first question is concerned with the thermodynamics (i.e. answered by thermodynamics) and second one with the chemical kinetics.

Chemical kinetics is a study of rates at which chemical reactions occur and effect of parameters such as temperature, pressure, and reactant concentration/composition on the reaction rates. The chemical kinetics provides us information about reaction mechanism, speed of a chemical reaction and type of rate equation (that represents satisfactorily a given chemical reaction) which is to be used in design of reactor.

Thermodynamics provides us information about feasibility of a reaction, (i.e. whether the reaction will occur or not under given set of conditions), heat absorbed or liberated during course of reaction i.e. heat of a reaction and maximum possible extent of a reaction. We need the information from thermodynamics and chemical kinetics in design of a chemical reactor.

Now we will deal with the classification of chemical reactions.

Classification of Chemical Reactions :

(1) Chemical reactions may be classified depending upon number of phases involved as homogeneous and heterogeneous reactions.

- A homogeneous reaction is one which takes place in only one phase, i.e. all the reacting materials, products and catalyst (if any) will all be present within a same phase (one phase).

Examples :

(i) Oxidation of nitrogen oxide to nitrogen dioxide with air, is a gas phase reaction.

$$NO + \frac{1}{2} O_2 \rightarrow NO_2$$

(ii) Formation of esters from organic acids and alcohols in presence of sulphuric acid is a liquid phase reaction.

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{acetic acid}}{CH_3COOH} \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

→A heterogeneous reaction is one which involves presence of more than one phase i.e. in heterogeneous reactions at least one of the reactants, catalyst or products is present in phase different from the remaining components of the reacting system.

Examples :

Oxidation of sulfur dioxide to sulfur trioxide using vanadium pentaoxide catalyst is a heterogeneous reaction as SO_2, O_2 and SO_3 are gaseous while V_2O_5 is a solid material.

$$SO_2 + \frac{1}{2} O_2 \xrightarrow{V_2O_5} SO_3$$

(2) The reactions may be classified as catalytic and non-catalytic reactions.

Catalytic reactions are those reactions which involve the use of catalyst to enhance the rate of a reaction/speed of a reaction.

Example : $$\underset{\text{ethylene}}{C_2H_4} + H_2 \xrightarrow[\text{Heat}]{Ni} \underset{\text{ethane}}{C_2H_6}$$

Hydrogenation of ethylene is a catalytic reaction which makes use of nickel catalyst.

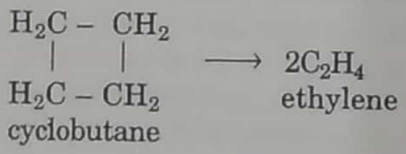
Non-catalytic reactions are those reactions which does not involve use of catalyst.

Oxidation of NO to NO_2 is a non-catalytic reaction.

$$NO + \frac{1}{2} O_2 \rightarrow NO_2$$

(3) The reactions may be classified based upon the molecularity of a reaction i.e. based upon the number of molecules that take part in the reaction (in rate determining step) as : unimolecular, bimolecular and termolecular reactions.

Examples : (i) Decomposition of cyclobutane is a unimolecular reaction.



(ii) Decomposition of hydrogen iodide is a bimolecular reaction which involves collision of two molecules.

$$2\,HI\,(g) \rightarrow I_2\,(g) + H_2\,(g)$$

(iii) Oxidation of NO to NO_2 is a trimolecular/termolecular reaction which involves collision of three molecules.

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

(4) The reactions may be classified based upon the heat effect (i.e. according as they give off or absorb heat to or from the surroundings) as exothermic and endothermic reactions.

Exothermic reaction is the one in which heat is evolved.

The reaction between CO and H_2 to produce methanol is exothermic reaction.

$$CO + 2H_2 \xrightarrow{Cu} CH_3OH + \text{Heat}$$

Endothermic reaction is the one in which heat is absorbed (heat will be supplied to reacting system from surroundings for reaction to take place).

Dehydration of ethyl alcohol to produce ethylene is a endothermic reaction.

$$\underset{\text{ethyl alcohol}}{C_2H_5OH} \xrightarrow{Al_2O_3} \underset{\text{ethylene}}{C_2H_4} + H_2O - \text{Heat}$$

(5) The reactions may be classified based upon the order of a reaction as first orde reaction, second order reaction, third order reaction, etc.

A reaction of which overall order of reaction is one (i.e. sum of orders with respect t participants in reaction is unity) is called first order reaction.

Decomposition of nitrogen pentaoxide is a first order reaction.

$$N_2O_5 \rightarrow NO_2 + \frac{3}{2} O_2$$

A reaction of which the sum of orders with respect to reactants participated in reaction is two, is called second order reaction.

Saponification of ester is a second order reaction.

$$\underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + NaOH \longrightarrow \underset{\text{sodium acetate}}{CH_3COONa} + C_2H_5OH$$

Example of third order reaction is

$$2\,NO\,(g) + H_2\,(g) \longrightarrow N_2O\,(g) + H_2O\,(g)$$

(6) The reactions are also classified as reversible and irreversible reactions base upon whether they proceed in one or both the directions.

Reversible reactions are those in which the forward and reverse reactions take plac simultaneously.

Example : Esterification reaction is a reversible reaction.

$$\underset{\text{ethanol}}{C_2H_5OH} + \underset{\text{acetic acid}}{CH_3COOH} \overset{H^+}{\rightleftharpoons} \underset{\text{ethyl acetate}}{CH_3COOC_2H_5} + H_2O$$

Irreversible reactions are those which can proceed only in one direction.

Example : Nitration of benzene is a irreversible reaction.

$$\underset{\text{benzene}}{C_6H_6} + HNO_3 \xrightarrow{H^+} \underset{\text{nitrobenzene}}{C_6H_5NO_2} + H_2O$$

Rate of a Chemical Reaction :

The rate of a chemical reaction may vary from a large value (instantaneous reaction to essentially zero. In ionic reactions, such as those that occur on photographic film, or in high temperature combustion reactions, the rate is extremely fast. The rate of combination o hydrogen and oxygen in the absence of a catalyst at room temperature is immeasurably slow Most industrially important reactions occur at rates between these extremes.

There are number of ways of defining the rate of reaction, say for example based on un volume of a reacting fluid.

The rate of reaction can be defined in number of ways, based on unit volume of reacting fluid in case of homogeneous system, based on unit mass of solid in case of fluid-solid systems and so on.

In homogeneous systems, the rate of reaction is defined based on unit volume of reacting fluid.

So for homogeneous systems, the rate of reaction is defined as the change in moles of reactant or product due to reaction per unit time per unit volume of reacting fluid/reaction mixture.

The rate of reaction may be expressed either as the rate of disappearance of a certain reactant or rate of formation of a certain product. It is a positive quantity and tells us how the concentration of reactant or product changes with time during the course of reaction.

[In this book grammoles and kilogram moles will be specified as mol and kmol respectively.]

Consider an irreversible reaction of the type

$$aA + bB \rightarrow rR$$

As per the above reaction, A and B are disappearing due to reaction i.e. reacting and R is being produced. So A and B are the reactants and R is the product.

The rate of reaction with respect to reactant A i.e. rate of disappearance of reactant A is given by

$$-r_A = -\frac{1}{V}\left(\frac{dN_A}{dt}\right) = \frac{(\text{amount in moles of A disappearing})}{(\text{volume of fluid}) \times (\text{time})}, \frac{\text{mol}}{l.\text{s}} \quad \ldots (1.1)$$

where N_A is the moles of component A.

For constant volume reaction systems, V is constant, so

$$-r_A = -\frac{d\,(N_A/V)}{dt}$$

We have, $C_A = \frac{N_A}{V}$

$$\therefore \quad -r_A = -\frac{dC_A}{dt} \quad \ldots (1.2)$$

So for such systems, the rate of chemical reaction may be expressed as the rate of change of concentration of any reactant or product of a chemical reaction.

$$-r_B = -\frac{1}{V}\left(\frac{dN_B}{dt}\right) = -\frac{dC_B}{dt}$$

$$r_R = \frac{1}{V}\left(\frac{dN_R}{dt}\right) = \frac{dC_R}{dt}$$

The negative sign in case of reactants A and B implies that the concentration of reactants is decreasing with time and the rate becomes positive in either case.

The relation between the rates of participants in a chemical reaction from a stoichiometry of a reaction is

$$\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_R}{r} \quad \ldots (1.3)$$

From the stoichiometry of a reaction for the reaction $A + 3B \rightarrow 2R$, we have

$$\frac{-r_A}{1} = \frac{-r_B}{3} = \frac{r_R}{2}$$

i.e. rate of disappearance of B is three times the rate of disappearance of A and the rate of formation of R is twice the rate of disappearance of A.

Factors affecting the rate of reaction :

(i) Nature of reactants and products.

(ii) Concentration of reactants.

(iii) Temperature of a system.

(iv) Pressure of a system.

(v) Nature of catalyst if present.

(vi) Surface area of reactants.

(vii) Rates of the heat and mass transfer.

For homogeneous systems, the possible factors that affect the rate of reaction are temperature, pressure, and composition. These are interdependent factors and pressure is determined given the temperature and composition of a phase. So for homogeneous systems, we can write rate of reaction as a function of temperature and composition.

$$-r_A = f\left[\begin{matrix}\text{temperature} \\ \text{dependent} \\ \text{terms}\end{matrix} , \begin{matrix}\text{concentration} \\ \text{dependent} \\ \text{terms}\end{matrix}\right], \frac{\text{mol}}{l.\text{s}} \qquad \ldots (1.4)$$

As an example, for $A \rightarrow R$

$$-r_A = k \cdot C_A^{\alpha}$$

$$-r_A = k_o \cdot e^{-E/RT} \cdot C_A^{\alpha} \qquad \ldots (1.5)$$

where, $k_o\, e^{-E/RT}$ – temperature dependent term

C_A^{α} – concentration dependent term

E – activation energy

α – order of reaction with respect to A.

Concentration-Dependent term of a Rate Equation :

When single stoichiometric equation and single rate expression is needed to represent the progress of a chemical reaction, we have a single reaction ($A \rightarrow R$). When more than one stoichiometric equation and hence more than one kinetic expression (rate equation) is needed to follow the progress of reaction i.e. to follow the changing composition of all the reacting components, we have multiple reactions ($A \rightarrow R$, $A \rightarrow S$).

Consider a irreversible reaction

$$aA + bB + \ldots\ldots \rightarrow rR + sS + \ldots\ldots$$

In describing the rate of reaction, hence-forth we will take for basis of calculation a species A, which is one of the reactants that is disappearing as a result of reaction. The limiting reactant is usually taken as a basis of calculation. The rate of disappearance of A, $-r_A$ depends upon temperature and composition. For many reactions it can be written as the product of a reaction rate constant and function of concentrations of various species involved in the reaction

$$-r_A = \text{rate of reaction w.r.t. A} = k\, f(C_A, C_B, \ldots)$$

f is the mathematical function of C_A, C_B ... which are concentrations of A, B, ... However, from the kinetic study, the dependence of rate of reaction on the concentrations of the reactants for many reactions has been found to be

$$-r_A = k\, C_A^{n_A} \cdot C_B^{n_B} \ldots \qquad \ldots (1.6)$$

where k is reaction rate constant. n_A, n_B ... are the powers (exponents) of concentrations of reactants A, B, ... on which the rate of reaction depends. It is not necessary that $n_A = a$, $n_B = b$ and so on.

The algebraic equation that relates $-r_A$ to the concentrations of species participating in a reaction is called the kinetic expression, rate law or rate equation. Hence the rate expression/rate law gives the relationship between reaction rate and concentration.

Rate constant :

6 The rate constant of a chemical reaction is a measure of the rate of reaction when all the reactants are at unit concentration. Hence,

$$\text{Rate of reaction} = k \times (\text{function of concentration of reactants})$$

If we assume that the concentrations are equal to unity, then

$$\text{Rate of reaction} = k$$

where k is rate constant. It is also called as specific rate constant. The rate constant (k) depends upon the temperature. It increases with temperature. The unit of k depends upon the units of concentration and time. If we use units mol/l for concentration and seconds (s) for time then unit of k will be

$$\frac{\text{mol}/(l.\text{s})}{(\text{mol}/l)^n} = (\text{s})^{-1}\,(\text{mol}/l)^{1-n} \quad \text{from } -r_A = k\,C_A^n$$

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

where n = order of reaction. For a first order reaction, n = 1. Therefore the unit of k is s^{-1}. For second order reaction, n = 2. Therefore units of k would be $l \cdot (\text{mol})^{-1} \cdot (\text{s})^{-1}$ if time is in seconds.

The rate constant (k) for a reaction is simply a numerical measure of how fast a reaction can occur if the reactants are brought together at unit concentration.

Reaction mechanism : It refers to the step or series of steps by which the initial reactants interact in the process of forming products.

A reaction usually does not occur in the single step which may be represented by the overall stoichiometric equation but rather takes place in a series of steps which add up to the overall equation. These steps are the mechanism of the reaction.

For example, the reaction

$$2A + B \rightarrow R + S$$

might take place as follows :

Step 1 : $A + B \rightarrow AB$

Step 2 : $A + AB \rightarrow A_2B$

Step 3 : $A_2B \rightarrow AB + R$

Step 4 : $AB \rightarrow S$

$$2A + B \rightarrow R + S$$

The slowest step controls the rate of a chemical reaction and also determines the form of overall rate equation.

Elementary and Nonelementary Reactions :

Chemical reaction rarely proceed in one step. In conventional single step writing of the stoichiometric equation of a chemical reaction only initial and final states of the reaction system are indicated. In case of multistep reactions, the rate of overall reaction is determined primarily by the slowest step.

It is customary in chemical kinetics to class all reactions as elementary and nonelementary reactions.

The reactions in which the formation of product from the original reactants occurs through a series of reaction steps are called as nonelementary reactions. The individual reaction steps which contribute to the overall reaction (i.e. to the reaction mechanism) are termed as elementary reactions.

For nonelementary reactions there is difference between order and stoichiometric coefficients (in other words, the order and stoichiometry does not agree) due to the fact that what we observe as a single reaction is in reality the overall effect of a series of elementary reactions. We observe nonelementary reaction as a single reaction rather than elementary reactions in series because the amount of the intermediates formed is negligibly small and cannot be detected. In other words,(the stoichiometric equation for nonelementary reaction reflects only the initial and final states of the reaction system involved and failed to describe the mechanism of a reaction in details and so there is no direct relation between the order of reaction and reaction stoichiometry for nonelementary reaction)

The reaction in which the molecules react exactly as the stoichiometric equation written for a reaction, is called as an elementary reaction. For example, $H_2O_2 + H_2 \rightarrow 2\,H_2O$ occurs by reacting one molecule of H_2O_2 with one molecule of hydrogen. For such reactions, order with respect to a particular reactant is equal to its stoichiometric coefficient in stoichiometric equation. This is a single step reaction.

For irreversible elementary reaction

$$aA + bB \rightarrow rR$$

the rate equation is

$$-r_A = k\,C_A^a \cdot C_B^b$$

For nonelementary reaction

$$aA + bB \rightarrow rR$$

the rate equation (rate law), by analogy with a true simple (or elementary) reaction may be written as

$$-r_A = k\,C_A^\alpha \cdot C_B^\beta$$

where α and β are orders with respect to A and B and are found by the experiment and $\alpha \neq a$ and $\beta \neq b$.

Difference between elementary and nonelementary reactions :

(i) Elementary reactions are single step reactions whereas nonelementary reactions are multistep reactions i.e. such reactions occur by series of reaction steps.

(ii) Elementary reactions are simple in nature whereas the nonelementary reactions are complex in nature.

(iii) For elementary reaction the order agrees with stoichiometry (i.e. order is equal to stoichiometric coefficient of participant) whereas for nonelementary reaction the order does not agrees with stoichiometry (i.e. there is difference between order and stoichiometric coefficients).

(iv) For elementary reaction the order of reaction must have integer value whereas for nonelementary reaction, the order of a reaction may have integer or fractional value.

(v) For elementary reaction $2A \rightarrow R$, the rate law is $-r_A = k\,C_A^2$ whereas for nonelementary reaction $2B \rightarrow S$, the rate law may be $-r_B = k\,C_B^\alpha$ where $\alpha \neq 2$.

(vi) Examples of an elementary reaction :

$C_2H_5OH + CH_3COOH \rightarrow CH_3COOC_2H_5 + H_2O$ ✓

Examples of nonelementary reaction :

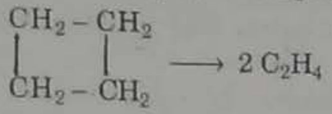
(i) $H_2 + Br_2 \rightarrow 2\,HBr$

(ii) $CH_3CHO \rightarrow CH_4 + CO$

Molecularity of Reaction

Many chemical reactions proceed through a number of steps and each of the individual step is called as an elementary step (elementary reaction). The rate of reaction is determined by the slowest step and hence it is known as the rate determining step. **Molecularity** is the number of reacting species (molecules, atoms, or ions) which collide simultaneously to bring about a chemical reaction in an elementary reaction step.

If one molecule is transformed in an elementary process, the reaction is called unimolecular. For example, decomposition of cyclobutane is unimolecular in nature.



In bimolecular reactions, the two reacting molecules (same or different) participate to cause a chemical change. In trimolecular / termolecular reaction, there will be collision of three molecules.

bimolecular : $2\,HI_{(g)} \rightarrow H_{2\,(g)} + I_{2\,(g)}$

termolecular : $2\,NO + O_2 \rightarrow 2\,NO_2$

It may be noted that reactions involving a molecularity of three or more are uncommon. This is because such reactions require the simultaneous collision of three or more molecules which is rare.

In case of complex reactions the overall chemical reaction does not provide any clue to the number of molecules colliding (except in single step reactions). Hence, molecularity has no meaning for overall reaction. It is concerned with each elementary step or reaction which proceed through one step only.

Molecularity of a reaction must be whole number and never be zero or a fraction.

Molecularity of a reaction is a theoretical quantity.

Order of Reaction :

Based upon the assumption that only molecules which collide can react, the rate of reaction is proportional to the number of collisions. At a given temperature, the number of collisions is directly proportional to number of molecules. Therefore, the rate of a chemical reaction should be proportional to the concentration of the reactants.

Hence, for the reaction of the type

$$aA + bB + \dots\dots\dots \rightarrow rR + sS + \dots$$

the rate of disappearance of reactant A is given by

$$\text{Rate of reaction} = -r_A = -\frac{dC_A}{dt} = k\,C_A^{n_1} \cdot C_B^{n_2} \qquad \dots (1.7)$$

$-r_A$ is the rate of reaction with respect to reactant A.

$$-r_A = -\frac{dC_A}{dt} = k\,C_A^{n_1} \cdot C_B^{n_2}$$

The mathematical expression giving the functional relation between the rate of reaction and concentration of the reactants is referred to as rate law, rate equation or rate expression.

So from equation (1.7) it is clear that rate of reaction is directly proportional to n_1 power of the concentration of A, n_2 power of concentration of reactant B and so on. Therefore, the reaction is n_1 order with respect to A, n_2 order with respect to B. The overall order of reaction is $n = n_1 + n_2 + \dots$

Order of a reaction may be given with respect to any one of the reactants or with respect to all of the participating reactants in which case it is called as overall order of reaction or simply order of reaction.

Order of a reaction (or overall order of reaction) in above case is

$$n = n_1 + n_2 + \ldots$$

Order of reaction is defined as the sum of the exponents of the concentration terms in the rate expression/rate law.

Order of reaction with respect to a particular reactant is the exponent of the concentration of that reactant in the rate equation. In above case, order of reaction with respect to A is n_1.

For bimolecular reaction of the type

$$A + B \rightarrow R$$

if the rate is given as

$$-r_A = -dC_A/dt = k\,C_A^{1/2} \cdot C_B$$

then molecularity is 2 and the order of reaction is 1/2 + 1 = 1.5.

(It is not necessary that n_1, n_2 ... be whole numbers, these can be fraction as well i.e. order of reaction may be whole number, zero or can have fractional values.)

(The order of reaction is not determined by the molecularity (i.e. by theory) but it is entirely experimental quantity (i.e. determined experimentally). The order of reaction is obtained from the experimental kinetic data collected in the laboratory.)

For liquid phase reaction,

$$A + B \rightarrow R$$

The data of concentration of A as a function of time collected in laboratory by carrying above reaction in a glass flask is the kinetic data of the said reaction.

It may be noted that there is no correspondence between stoichiometric coefficients a, b, ... and orders with respect to reactants n_1, n_2 ... for complex reactions.

The order of reaction agrees with the molecularity only for simple reactions/elementary reactions. In such cases, the rate expression can be written directly from the stoichiometric equation as it describes the true mechanism. Example is the decomposition of nitrosyl chloride.

$$2\,NOCl \rightarrow 2\,NO + Cl_2$$

Decomposition of hydrogen peroxide

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}\,O_2$$

is found to follow the rate law

$$-\frac{dC_{H_2O_2}}{dt} = k\,C_{H_2O_2}$$

Then, this is first order reaction since the concentration term of H_2O_2 i.e. $C_{H_2O_2}$ is raised to unity.

Difference between Molecularity and Order of Reaction :

The molecularity is defined as the number of molecules, atoms or ions participating in the rate determining step.

The order of reaction is defined as the sum of the exponents of the concentration terms in the rate law equation.

Molecularity of a reaction is a theoretical quantity to satisfy the experimental findings whereas the order of reaction is entirely an experimental quantity.

Molecularity of a reaction must be a whole number and never be zero or a fraction, but the order of a reaction may be whole number, zero or a fraction.

Representation of an elementary reaction :

While writing a rate equation we may use any measure equivalent to concentration e.g. partial pressure of the reacting materials in case of gas phase reaction in which case the rate is given by

$$-r_A = k\, p_A^{n_1}\, p_B^{n_2} \qquad \text{... (1.8)}$$

Remember that order with respect to reacting component remains same/unchanged though we use any measure equivalent to concentration only thing is that it will change the numerical value and units of k.

Elementary reactions are represented by an equation showing the molecularity and the rate equation.

For example,

$$2A \xrightarrow{k_1} 2S \qquad \text{... (1.9)}$$

represents a irreversible bimolecular second order reaction implying that the rate of reaction is

$$-r_A = r_S = k_1 C_A^2$$

k_1 is the second order rate constant.

It would not be proper to write equation (1.9) as

$$A \xrightarrow{k_1} S$$

For this, it would imply that the rate equation is

$$-r_A = r_R = k\, C_A$$

and this is incorrect as reaction is second order with respect to A.

So one must be careful to distinguish between one particular equation that represents the elementary reaction and many possible representations of the stoichiometry.

There are many possible representations of stoichiometry but there is a single representation of rate of reaction.

While writing the elementary reaction with rate constant (i.e. while writing the rate equation) so as to avoid any confusion, it is necessary to specify the component in the reaction to which the rate constant is referred.

For example, consider the reaction

$$B + 2D \rightarrow 3R \qquad \text{... (1.10)}$$

If we measure the rate of reaction in terms of B, the rate equation is

$$-r_B = k_B\, C_B\, C_D^2 \qquad \text{... (1.11)}$$

If the rate of reaction is based on component D, the rate equation is

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

If the rate of reaction refers to product T then

$$r_T = k_T\, C_B\, C_D^2$$

From the stoichiometry of reaction we have rate of formation R is three times the rate of disappearance of B and rate of disappearance of D is two times the rate of disappearance of B. Therefore,

$$\frac{-r_B}{1} = \frac{-r_D}{2} = \frac{r_T}{3} \quad \text{... (1.12)}$$

hence,

$$\frac{k_B}{1} = \frac{k_D}{2} = \frac{k_T}{3} \quad \text{... (1.13)}$$

So when stoichiometry of reaction involves different numbers of molecules of the participating components, while writing the rate constant in rate equation, one must specify the component being considered.

Representation of a nonelementary reaction :

A non-elementary reaction is one whose stoichiometry does not match with its kinetics (i.e. for such reaction there is no direct correspondence between reaction order and stoichiometry).

For example,

Stoichiometry : $H_2 + Br_2 \rightarrow 2\,HBr$

Rate : $$r_{HBr} = \frac{k_1 C_{H_2} \cdot C_{Br_2}^{1/2}}{k_2 + (C_{HBr}/C_{Br_2})} \quad \text{... (1.14)}$$

So this non-correspondance indicates that we must develop a multistep reaction scheme/ model to explain its kinetics.

Kinetic Models for Nonelementary Reactions :

To explain the kinetics of nonelementary reactions, we assume that the overall reaction is the result of a series of nonelementary reactions that involve the formation and subsequent reaction of the intermediate species. (We cannot measure and observe the intermediates formed as they are present in very minute quantities and thus left undetected.) Now we will see how to develop a kinetic model (reaction mechanism) to explain kinetics of nonelementary reactions and how to test the kinetic model. In testing of kinetic model all that we have to do is : assume the model, obtain the kinetic expression and see whether the predicted rate expression corresponds to the experiment i.e. see whether the predicted rate expression is similar in form to the experimentally found rate expression, if not, assume new model.

Let us see first the types of intermediates.

The types of intermediates that can be formed are :

(i) Free radicals : Free atoms or larger fragments of stable molecules that contain one or more unpaired electrons are called free radicals. The unpaired electron is designated by a dot in the chemical formula of a substance. Examples : $H^{\bullet}$, $CH_3^{\bullet}$, $C_2H_5^{\bullet}$, etc.

(ii) Ionic intermediates : Electrically charged atoms, molecules, or fragments of molecules such as Na^+, OH^-, NH_4^+ are called ions.

(iii) Molecules : Molecule R in series reaction A → R → S. In such reaction if the molecule R is highly reactive, its mean life time is very small and its concentration in the reaction mixture is too small to measure. In such situation R may not be observed and thus can be considered as reactive intermediate.

(iv) Transition complexes : Unstable forms of molecules, unstable association of molecules which decompose to give products or by further collision return to the molecules in the normal states, such unstables formed are called transition complexes.

Now we will see the reaction schemes involving above mentioned kinds of intermediates.

The suggested schemes can be of two types – (i) non-chain reactions and (ii) chain reactions.

Non-chain reactions : In case of non-chain reaction, the intermediate is formed in the first reaction and then disappears as it reacts further to yield the product(s).

$$\text{Reactants} \rightarrow (\text{Intermediates})^*$$

$$(\text{Intermediates})^* \rightarrow \text{products.}$$

Chain reactions : In case of chain reaction the intermediate is formed in chain initiation step (first reaction). It is then combined with reactant to yield product and more intermediate in the chain propagation step and finally it gets destroyed in the chain termination step.

$$\text{Reactant} \rightarrow (\text{Intermediate})^* \ \ldots \text{ initiation}$$

$$(\text{Intermediate})^* + \text{reactant} \rightarrow (\text{Intermediate})^* + \text{product} \ \ldots \text{ propagation}$$

$$(\text{Intermediate})^* \rightarrow \text{product} \ \ldots\ldots\ldots \text{ termination}$$

Consider chlorination of propane (PrH) :

$$Cl_2 \rightarrow 2\,Cl \ \ldots\ldots \text{ initiation}$$

$$Cl + PrH \rightarrow Pr + HCl$$

$$Pr + Cl_2 \rightarrow PrCl + Cl \ \ldots\ldots \text{ propagation}$$

$$Cl + Cl \rightarrow Cl_2 \ \ldots\ldots \text{ termination}$$

$$Pr + Cl \rightarrow PrCl$$

The essential feature of the chain reaction is the propagation step, as in this step, the intermediate is not consumed but acts as catalyst for converting reactant into product. Hence, the intermediate before getting destroyed can catalyse the long chain of reactions.

Examples of mechanisms of various kinds :

(i) Free radicals, chain reaction mechanism :

The experiment shows that the reaction

$$H_2 + Br_2 \rightarrow 2\,HBr$$

proceeds with rate

$$r_{HBr} = \frac{k_1\, C_{H_2}\, C_{Br_2}^{1/2}}{k_2 + C_{HBr} \cdot C_{Br_2}}$$

This reaction can be explained by the following scheme (reaction mechanism).

$$Br_2 \rightleftharpoons 2\,Br^\bullet \quad \text{initiation and termination}$$

$$Br^\bullet + H_2 \rightleftharpoons HBr + H^\bullet \quad \text{propagation}$$

$$H^\bullet + Br_2 \rightarrow HBr + H^\bullet \quad \text{propagation}$$

(ii) Molecular intermediates, non-chain mechanism :

Enzyme catalysed fermentation reactions

$$A \xrightarrow{\text{enzyme}} R$$

with experimental rate

$$r_R = \frac{k\, C_A \cdot C_{Eo}}{M + C_A}$$

where M is Michaelis constant and C_{Eo} – initial enzyme concentration. It can be explained by following scheme with (A. enzyme)* as an intermediate.

$$A + E \rightleftharpoons (A \cdot E)^*$$

$$(A \cdot E)^* \rightarrow R + E \quad \text{where } E = \text{enzyme}$$

In fermentation reaction carried out in aqueous solution, water is in large excess and the concentration of water is therefore considered constant.

(iii) Transition complexes, non-chain mechanism :

The reaction such as decomposition of azomethane

$$(CH_3)_2 N_2 \rightarrow C_2H_6 + N_2 \quad \text{or } A \rightarrow R + S$$

proceeds with rate

$$r_{N_2} = \frac{k\, C_A^2}{1 + k'\, C_A}$$

This reaction exhibits first order, second order, or intermediate kinetics under various conditions. It is first order in A at high concentration (at high pressure) and is second order in A at low concentration (at low pressure).

Such type of behaviour can be explained by postulating the existence of an energized and unstable form (active intermediate) for the reactant, A^*.

So the reaction is viewed to proceed by the following scheme :

$A + A \rightarrow A^* + A$ formation of energized molecule

$A^* + A \rightarrow A + A$ return to stable form by collision

$A^* \rightarrow R + S$ spontaneous decomposition into products

Above scheme can also be written as

$$A + A \rightleftharpoons A^* + A$$

$$A^* \rightarrow R + S$$

Testing Kinetic Model

Now we will deal with how to test the correspondence between experiment and a proposed mechanism. i.e. How to obtain a mechanism that gives a rate expression similar in form to the experimentally found expression.

In matching the predicted rate expression with the experimentally found, we rely on the following rules :

(i) If any component i takes part in more than one reaction then its net rate of change is equal to sum of the rates of change of component i in each of the elementary reactions in which it is participated.

$$r_{i,\text{net}} = \sum_{\substack{\text{all elementary}\\ \text{reactions}\\ \text{participated}}} r_i \qquad \dots (1.15)$$

(ii) As the intermediates are highly reactive they have very short life time and they are present in a very small quantities; hence their net rate of formation is taken as zero. (net rate of formation of A^* = rate of formation of A^* – rate of disappearance of A^*)

$$\therefore \quad r_{A}^{*} = 0 \qquad \dots (1.16)$$

This is called the steady state approximation.

In elementary reaction scheme we hypothesize the presence of two types of intermediates.

Type 1 : An unobserved and unmeasured intermediate X^* usually present at such a low concentration that its rate of change in the reaction system is taken as zero.

Hence, if we assume C_X^* small,

$$\frac{dC_X^*}{dt} = 0$$

Type 2 : Whenever homogeneous catalyst with initial concentration C_o is present in two forms – (i) as a free catalyst C and (ii) in combination with reactant to form active intermediate X^* then accounting for catalyst gives

$$[C_o] = [C] + [X^*]$$

We can assume either

$$\frac{dX^*}{dt} = 0$$

or the intermediate is in equilibrium with the reactants.

$$\underset{\text{(reactant)}}{A} + \underset{\text{(catalyst)}}{C} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\text{(intermediate)}}{X}$$

$$\text{With } K = \frac{k_1}{k_2} = \frac{[X]}{[A]\,[C]}$$

Note that trial-and-error procedure is required in searching mechanism that yields the rate expression that corresponds the experiment.

Temperature-Dependent Term of a Rate Equation :

For many reactions, and particularly elementary reactions the rate of reaction can be written as the product of concentration-dependent term and the temperature-dependent term.

$$\begin{aligned} r_i &= f_1\,(\text{temperature}) \cdot f_2\,(\text{composition}) \\ &= k\,f_2\,(\text{composition}) \end{aligned}$$

It is the rate constant of the chemical reaction that depends upon the temperature. Now we will see the dependence of rate of reaction on temperature through rate constant of a chemical reaction.

✓ **Temperature dependency from Arrhenius law :** LQ

Under normal conditions the number of collision between the molecules of gases and liquids is so high that if any collision between reactant molecules led to the formation of the reaction product, all reactions would proceed virtually instantaneously. But it is not the case in actual practice. For a reaction to occur, it is first necessary to break or weaken the bonds between atoms and molecules of the reactants which require a definite amount of energy. If the colliding molecules do not possess this energy, a collision between them does not result in the formation of new molecule.

The minimum amount of energy which the colliding molecules must have in order to bring about a reaction is known as **activation energy** (or the energy barrier that the molecules must overcome when the reaction system passes from one state to another.)

Lower the value of activation energy higher will be rate at which reaction will proceed (as considerable part of collisions between the molecules result in a reaction) and higher the value of activation energy lower will be the rate at which the reaction proceeds.

For many reactions, and particularly elementary reactions, the temperature dependence of reaction rate constant, k, can be correlated by an equation of the type

$$k = k_o e^{-E/RT} \qquad \dots (1.17)$$

where, k_o ≡ pre exponential factor or frequency factor
E ≡ activation energy, J/mol or cal/mol
R ≡ gas constant = 8.314 J/(mol.K) = 1.987 cal/(mol.K)
T ≡ absolute temperature, K

Equation (1.17) is known as Arrhenius equation/Arrhenius law. It has been verified empirically to give the temperature behaviour of most reaction rate constants within the experimental accuracy over fairly large temperature ranges.

The activation energy is the minimum energy that must be possessed by reacting molecules before the reaction will occur i.e. energy possessed by reacting molecules for getting them converted into products. From the kinetic theory of gases, the factor $e^{E/RT}$ gives the fraction of the collision between molecules that together have this minimum energy (i.e. fraction of the collisions that are effective/that brings about a chemical reaction).

The activation energy is determined experimentally by carrying out the reaction at several different temperatures.

Taking the natural logarithm of equation (1.17), we get

$$\ln k = \ln k_o - \frac{E}{RT} \qquad \dots (1.18)$$

It follows from equation (1.18) that a plot of ln k v/s 1/T should give a straight line with slope equal to –E/R.

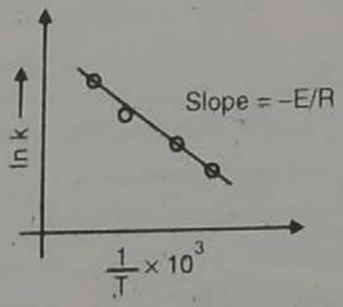


Fig. 1.1 : Temperature dependency of reaction rate constant and hence rate

So one must have data of reaction rate constant as a function of temperature for getting E known.

Alternatively, energy of activation can also be obtained by measuring the rate constants k_1 and k_2 at temperatures T_1 and T_2 respectively.

$$\ln k_1 = \ln k_o - \frac{E}{RT_1}$$

$$\ln k_2 = \ln k_o - \frac{E}{RT_2}$$

$$\ln k_2 - \ln k_1 = \frac{-E}{RT_2} + \frac{E}{RT_1}$$

$$\therefore \quad \ln (k_2/k_1) = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln (k_2/k_1) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \dots (1.19)$$

If the concentration dependency of the rate of reaction is not known but rate of reaction v/s temperature data is available for concentrations, E can be obtained from the plot of ln r v/s 1/T.

A rule of thumb is that the rate of reaction doubles for every 10 °C rise in temperature. However, this is true only for a specific combination of activation energy and temperature. For example, if the activation energy is 147000 J/cal, the rate will double only if the temperature is raised from 500 K (227 °C) to 510 K (237 °C).

Consider that the rate of reaction is given by

$$r = k\, C_A^{\alpha}\, C_B^{\beta}$$

$$r = k_0 \cdot e^{-E/RT}\; C_A^{\alpha}\, C_B^{\beta} \qquad \ldots (1.20)$$

Equation (1.20) provides a description of the rate of reaction in terms of the measurable variables, concentration and temperature.

Consider equation (1.20). The concentration function $C_A^{\alpha}\, C_B^{\beta}$ would be constant for constant concentrations. Hence, it could be combined with k_0 to give a new constant k_o'.

Then, equation (1.20) becomes

$$r = k_o'\, e^{-E/RT} \qquad \ldots (1.21)$$

$$\ln r = -\frac{E}{R}\left(\frac{1}{T}\right) + \ln k_o' \qquad \ldots (1.22)$$

From equation (1.22) it is clear that plot of ln r v/s 1/T yields a straight line with slope equal to – E/R and hence we can calculate E.

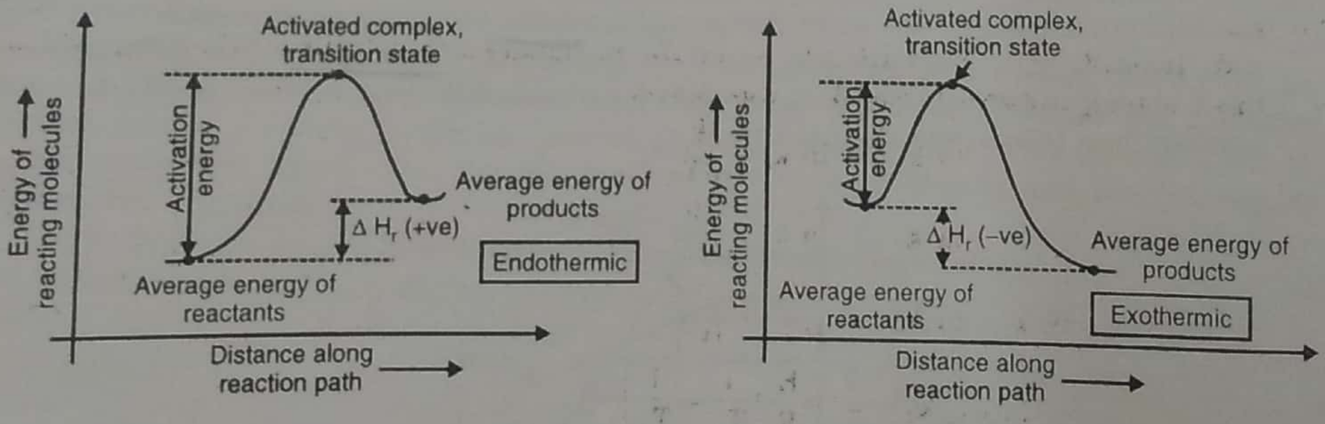
If rate is known at two different temperatures T_1 and T_2 then we can calculate E with equation (1.23).

$$\ln \frac{r_2}{r_1} = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \ldots (1.23)$$

Activation energy is usually reported in cal/mol or J/mol. In all above equations we have to use T in K and R = 1.987 cal/(mol.K) or 8.314 J/(mol.K).

Activation energy significance :

According to Arrhenius, the reacting molecules must acquire discrete minimum energy



(a) (b)

Fig. 1.2 (a) and (b) : Sketch of energies involved in the process of transformation of reactants into products for elementary reactions

before the end products are formed. Thus the reactants must pass through the energy rich or activated state before they can react. The quantity of energy required by the reactants to overcome this activated state or energy barrier is known as activation energy. The difference between the energies of reactants and products is the heat of reaction. This may be made clear through Fig. 1.2 (a) and (b).

In Fig. 1.2 (a) and (b) the abscissa (reaction coordinate showing progress of the reaction) in a reaction energy diagram is a measure of interatomic distances when the reactants approach one another to form the activated complex and its disintegration into products. When the molecules come together, physical variations (such as structural orientations, intermolecular distances etc.) occur which causes energy changes in the system. The change in energy is continued till an intermediate configuration corresponding to the maximum energy i. e. the activated complex is formed.

Hence, we find that energy of activation for any reaction is the difference between the energy of activated complex and energy of the reactants as evident from Fig. 1.2 (a) and (b).

Activation energy and temperature dependency : LD

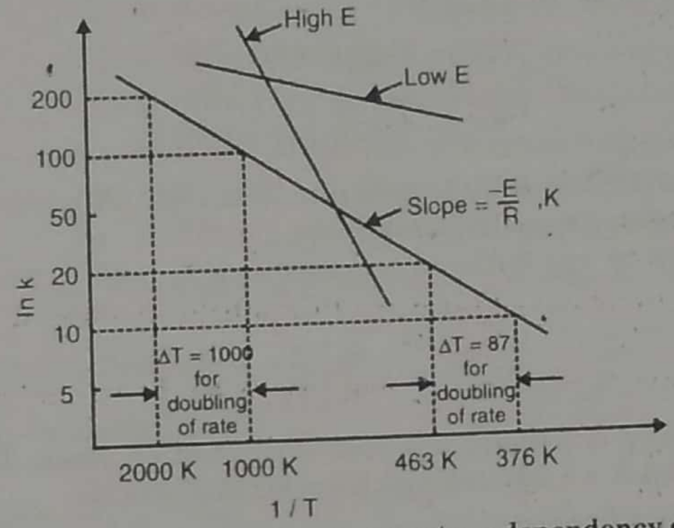
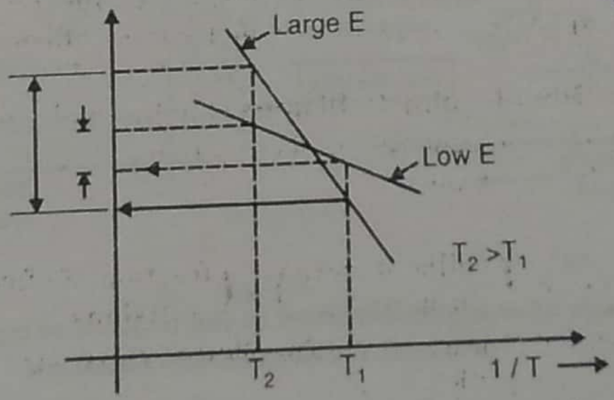


Fig. 1.3 : Sketch showing temperature dependency of rate

(i) From Fig. 1.3 it is clear that plot of ln k v/s 1/T gives large slope for large E and small slope for small E.

(ii) Reactions with high activation energies are very temperature sensitive, i.e. larger the activation energy, the more temperature sensitive is the rate of reaction. The reactions with low activation energies are relatively temperature insensitive, (i.e. for reactions with low E change in temperature does not give remarkable difference in reaction rate, so the rate of reaction does not change very much).

C_A $\frac{p_A}{RT}$



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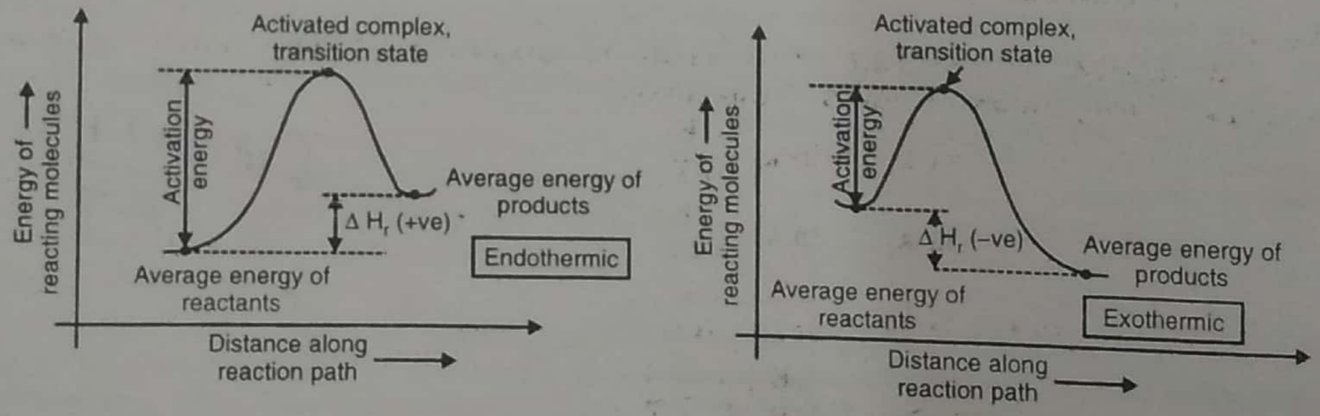

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Fig. 1.2 (a) and (b) : Sketch of energies involved in the process of transformation of reactants into products for elementary reactions

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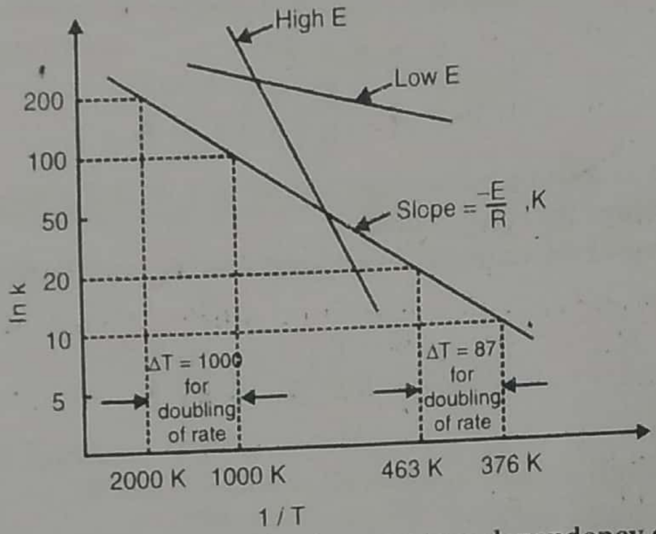
Activation energy and temperature dependency :



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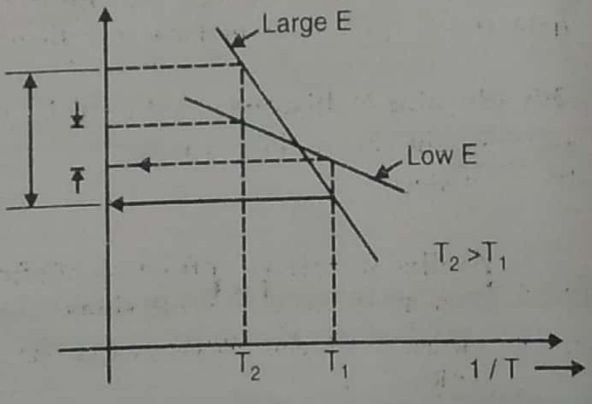

Fig. 1.4 : Sketch showing temperature dependency of rate

Change in temperature from T_1 to T_2 ($T_2 > T_1$) results in small change in lnk for low E indicating that the reaction with low E is relatively temperature insensitive.

For large E, the change in temperature from T_1 to T_2 results in large change in lnk indicating that the reaction with large E is very temperature sensitive.

(iii) A given reaction is much more temperature sensitive at low temperature than at high temperature. In other words, the reaction rate changes more rapidly at low temperature compared to the change in reaction at high temperature for a given temperature change. So from Fig. 1.4 it is clear that for doubling the rate of reaction $\Delta T = 87$ K (°C) at low temperature and at high temperature for doubling the reaction rate, ΔT required is 1000 K (°C).

The Arrhenius equation was originally derived from thermodynamics.

The variation of equilibrium constant with temperature for reversible reaction of the type

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$$

is given by the Van't Hoff equation :

$$\frac{d\ln K}{dT} = \frac{\Delta H_R}{RT^2} \quad \text{...(1.24)}$$

$$K = K_C = k_1/k_2$$

$$\therefore \quad \frac{d\ln (k_1/k_2)}{dT} = \frac{\Delta H_R}{RT^2}$$

$$\frac{d\ln k_1}{dT} - \frac{d\ln k_2}{dT} = \frac{\Delta H_R}{RT^2} \quad \text{...(1.25)}$$

If the RHS of above equation is divided into two enthalpy changes ΔH_1 and ΔH_2 such that

$$\Delta H_R = \Delta H_1 - \Delta H_2$$

then equation (1.25) can be divided into two equations one for the forward reaction and other for reverse reaction.

$$\frac{d\ln k_1}{dT} = \frac{\Delta H_1}{RT^2}$$

$$\frac{d\ln k_2}{dT} = \frac{\Delta H_2}{RT^2}$$

Integrating either of the equation and setting the integration constant equal to lnk_o gives a result of the form of the Arrhenius equation [equation (1.17)].

$$k = k_o e^{-\Delta H/RT} \quad \text{...(1.26)}$$

Temperature Dependency from the Collision Theory : LO

The collision theory is based on the concept that before molecules react, there must be collision between the reactant molecules and only those collisions in which the colliding molecules possess a certain minimum amount of energy are effective. This concept leads to the rate expression based upon the frequency of molecular collisions and the fraction of collisions that are effective.

Let us first consider the **Bimolecular Collisions** of unlike molecules :

According to the collision theory, the rate of the reaction

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

is given by

$$-r_A = \begin{pmatrix} \text{collision rate} \\ \text{in mol/}(l.\text{s}) \end{pmatrix} \times \begin{pmatrix} \text{fraction of effective} \\ \text{collisions} \end{pmatrix} \quad \text{...(1.27)}$$

Fraction of effective collision = fraction of collisions releasing energy equal to or greater than E

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

The collision rate of molecules in a gas can be found from the kinetic theory of gases. For bimolecular collisions of unlike molecules in a mixture of A and B from kinetic theory of gases, we have

$$Z_{AB} = \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 n_A n_B \left[8\pi k_B T\left(\frac{1}{M_A} + \frac{1}{M_B}\right)\right]^{1/2}$$

$$= \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \frac{N^2}{10^6} \left[8\pi k_B T\left(\frac{1}{M_A} + \frac{1}{M_B}\right)\right]^{1/2} C_A C_B.$$

where,

σ_A, σ_B = molecular diameters of molecules A and B respectively in cm

$\sigma_{AB} = \frac{\sigma_A + \sigma_B}{2}$ = average molecular diameter (collision diameter), cm

M = (molecular weight)/N, mass of a molecule, g

M_A = (molecular weight of A)/N, mass of a molecule A, g

C_A = concentration of A, mol/l

C_B = concentration of B, mol/l

M_B = (molecular weight of B)/N, mass of molecule B, g

$N = 6.023 \times 10^{23}$ molecules/mol, Avogadro's number

$n_A = NC_A/10^3$, number of molecules of A/cm^3

$n_B = NC_B/10^3$, number of molecules of B/cm^3

$k_B = R/N = 1.30 \times 10^{-16}$ erg/K, Boltzmann constant

$$Z_{AB} = \frac{\text{number of collisions of A with B}}{(\text{s})\ (\text{cm}^3)}$$

Collision rate in molecules/(s.cm^3) = Z_{AB}

$\therefore$ Collision rate in mol/(l.s) = $\dfrac{Z_{AB} \times 10^3}{N}$

$\therefore$ Rate of reaction, $-r_A = \dfrac{Z_{AB} \times 10^3}{N} \cdot e^{-E/RT}$

$$= \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \frac{N^2}{10^6} \left[8\pi k_B T\left(\frac{1}{M_A} + \frac{1}{M_B}\right)\right]^{1/2} C_A C_B \times \frac{10^3}{N} \times e^{-E/RT}$$

$$= \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \frac{N}{10^3} \left[8\pi k_B T\left(\frac{1}{M_B} + \frac{1}{M_B}\right)\right]^{1/2} \cdot e^{-E/RT} \cdot C_A C_B \quad \text{... (1.28)}$$

Rate of bimolecular type reaction is given by

$$-r_A = k\, C_A C_B \quad \text{... (1.29)}$$

So equating equations (1.28) and (1.29), we get,

$$k = \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \frac{N}{10^3} \left[8\pi k_B T\left(\frac{1}{M_A} + \frac{1}{M_B}\right)\right]^{1/2} \cdot e^{-E/RT}$$

$$k = k_o' \cdot T^{1/2} \cdot e^{-E/RT} \quad \text{... (1.30)}$$

where,

$$k_o' = \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \frac{N}{10^3} \left[8\pi k_B \left(\frac{1}{M_A} + \frac{1}{M_B}\right)\right]^{1/2}$$

Equation (1.30) describes the temperature dependency of the reaction rate constant from the collision theory.

Taking logarithm of equation (1.30), we get,

$$\ln k = \ln k_o^{'} + \frac{1}{2} \ln T - \frac{E}{RT} \qquad \text{... (1.31)}$$

Differentiating above equation with respect to T, we get,

$$\frac{d \ln k}{dT} = \frac{1}{2T} + \frac{E}{RT^2}$$

In most cases, the term 1/2T is small compared to E/RT². So neglecting 1/2T we get

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \qquad \text{... (1.32)}$$

Equation (1.32) is an equation originally proposed by Arrhenius.

For bimolecular collisions of like molecules/identical molecules

$$A + A \rightarrow \text{products}$$

we have,

$$Z_{AA} = \sigma_A^2 n_A^2 \left(\frac{8\pi k_B T}{M_A}\right) = \sigma_A^2 \frac{N^2}{10^6} \left(\frac{8\pi k_B T}{M_A}\right)^{1/2} \cdot C_A^2$$

$$-r_A = \begin{pmatrix}\text{collision rate} \\ \text{in mol/}(l.\text{s})\end{pmatrix} \times \text{fraction of effective collisions}$$

$$-r_A = \frac{Z_{AA} \times 10^3}{N} \cdot e^{-E/RT}$$

$$= \sigma_A^2 \frac{N}{10^3} \left(\frac{8\pi k_B T}{M_A}\right)^{1/2} \cdot e^{-E/RT} \cdot C_A^2$$

$$\therefore \quad k = \sigma_A^2 \frac{N}{10^3} \left[\frac{8\pi k_B T}{M_A}\right]^{1/2} \cdot e^{-E/RT}$$

$$k_o^{''} = \sigma_A^2 \frac{N}{10^3} \left[\frac{8\pi k_B}{M_A}\right]^{1/2}$$

$$\therefore \quad k = k_o^{''} \, T^{1/2} \cdot e^{-E/RT} \qquad \text{... (1.33)}$$

So for all bimolecular reactions, equations (1.30) and (1.33) show that the temperature dependency of the reaction rate constant is given by

$$k \propto T^{1/2} \cdot e^{-E/RT} \qquad \text{... (1.34)}$$

The collision theory is found to be satisfactory (i.e. give results in good agreement with the experimental data) for number of bimolecular gas phase reactions as well as for many reactions in solution involving simple ions. The collision theory apparently fails with unimolecular reactions.

There are cases where the actual rates of reactions differ to a marked extent from the rates calculated from theory. So as to take in account this deviation from the collision theory, the probability factor P (also called the steric factor) has to be introduced into equations.

The steric factor is referred to as the ratio of observed rate constant to that calculated from the collision theory.

$$P = \frac{k_{\text{observed}}}{k_{\text{theory}}} \qquad \text{... (1.35)}$$

$$k_{\text{observed}} = P \cdot k_{\text{theory}}$$

Temperature Dependency from Transition State Theory :

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Transition state theory also called absolute reaction rate theory gives more detailed explanation for the transformation of reactants into products. The fundamental postulate of the theory is that (i) the reacting molecules must form unstable intermediate called activated complex before being converted (i.e. there is formation of activated complex from the reactants which subsequently get decomposed to products) to products, and (ii) there exists an equilibrium between the activated complex and reactants at all times, and that the rate of decomposition of complex is the same for all reactions and is given by k_BT/h where k_B is the Boltzmann constant (1.380×10^{-16} erg/K) and h is the Planck constant (6.024×10^{-27} erg.s).

The activated complex is a molecule in the process of breaking or forming bonds. In the activated complex, the atoms are linked together with loose valence bonds. The activated complex has only a transient existence.

The bimolecular reaction between a molecules of A and B can be written as :

$$\underset{\text{Reactants}}{A + B} \longrightarrow \underset{\substack{\text{Activated complex}\\ \text{or transition state}}}{AB^*} \longrightarrow \text{Products}$$

The energy variation along the reaction path is shown in Fig. 1.5.

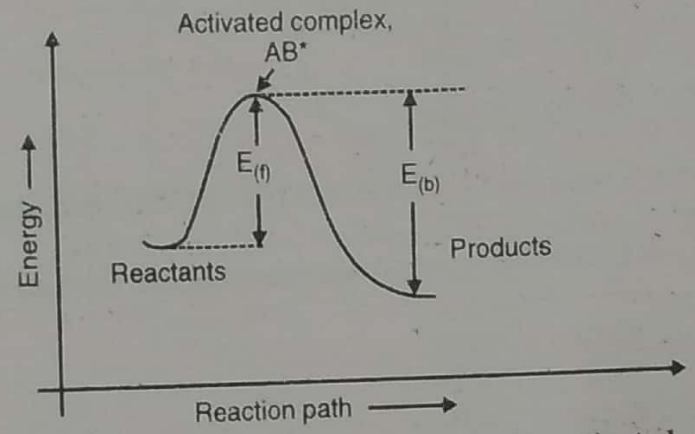

Fig. 1.5 : Energy variation along the reaction path in the activated complex theory

The rate of reaction is equal to the product of the concentration of the activated complex and the frequency (rate) of the decomposition of activated complex.

$$\text{Rate} = \begin{matrix}\text{Concentration of}\\ \text{activated complex}\end{matrix} \times \begin{matrix}\text{Frequency of decomposition}\\ \text{of activated complex}\end{matrix}$$

$$= C_{AB^*} \times \frac{k_BT}{h} \qquad \text{... (1.36)}$$

If C_A, C_B and C_{AB^*} represent the concentrations of A, B and AB* at time t, then equilibrium constant K_C^* for formation of the activated complex may be written as

$$K_C^* = \frac{C_{AB^*}}{C_A C_B} \qquad \text{... (1.37)}$$

$$C_{AB^*} = K_C^* \,.\, C_A . C_B$$

Equation (1.36) becomes

$$\text{Rate} = \frac{k_BT}{h} K_C^* \cdot C_A C_B \qquad \text{... (1.38)}$$

The equilibrium constant K_C^* can be expressed in thermodynamic terms.

Thus,

$$\Delta G^* = -RT \ln K_C^* = \Delta H^* - T\,\Delta S^*$$

$$\therefore \quad \ln K_C^* = (T\,\Delta S^* - \Delta H^*)/RT$$

$$K_C^* = e^{(\Delta S^*/R - \Delta H^*/RT)} = e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \qquad \ldots (1.39)$$

where ΔG^*, ΔH^* and ΔS^* are the changes in free energy, enthalpy and entropy of activation.

Equation (1.38) becomes

$$\text{Rate} = \frac{k_B T}{h} \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \cdot C_A\, C_B \qquad \ldots (1.40)$$

If k is the velocity constant (reaction rate constant) of the reaction, the experimentally obtained rate law -

$$\text{Rate} = k\, C_A\, C_B \qquad \ldots (1.41)$$

Comparing equations (1.40) and (1.41) we get

$$k = \frac{k_B T}{h} \cdot e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT} \qquad \ldots (1.42)$$

Equation (1.42) is the fundamental relation of the transition state theory.

In above equation, the term $e^{\Delta S^*/R}$ is so much less temperature sensitive that we may take it to be constant.

Relationship between ΔH^* and the Arrhenius activation energy E for liquids and solids is

$$E = \Delta H^* - RT$$

Relationship between ΔH^* and E for gases is given by following equation:

$$E = \Delta H^* - (\text{molecularity} - 1)\, RT$$

With these relationships the difference between E and ΔH^* is small and of the order of RT; hence transition state theory predicts approximately that

$$k \propto T\, e^{-E/RT} \qquad \ldots (1.43)$$

Equation (1.43) describes the temperature dependency of reaction rate (through k) from the transition state theory.

Comparison of Theories with collision theory. LP

Prediction of reaction rates from a transition state theory agrees more closely with experiment whereas reaction rates predicted with collision theory does not agree more closely with experiment. Transition state theory is based on statistical mechanics whereas collision theory is based on kinetic theory of gases.

Consider A and B are colliding and forming an unstable intermediate which then decomposes into product.

$$A + B \rightarrow AB^* \rightarrow \text{product}$$

Transition state theory views that the formation of activated complex is very rapid whereas collision theory views that the decomposition of activated complex is very rapid.

Transition state theory views that decomposition of activated complex is slow and rate determining whereas collision theory views that formation of activated complex is slow and rate controlling.

Transition state theory approximately predicts the temperature dependency of reaction rate as :

$$k \propto T \cdot e^{-E/RT}$$

Collision theory approximately predicts the temperature dependency of reaction rate as

$$k \propto T^{1/2} \cdot e^{-E/RT}$$

Comparison of Theories with Arrhenius Law :

According to theories given, we have

$$k \propto T^m \cdot e^{-E/RT}$$

$$= k_o' T^m \cdot e^{-E/RT}, \; 0 \le m \le 1 \qquad \dots (1.44)$$

Above equation is a simpler version of these theories for the temperature dependency of rate constant. As the exponential term is so much temperature sensitive than T^m, the variation of k caused by the latter is effectively masked and we have in effect.

$$k \propto e^{-E/RT}$$

$$k = k_o' \cdot e^{-E/RT}$$

This can be shown in another way, for this take logarithms of equation (1.44) and differentiate with respect to T.

$$d \ln k = \ln k_0' + \ln T^m + (-E/RT)$$

$$\frac{d \ln k}{dT} = \frac{m}{T} + \frac{E}{RT^2}$$

$$\frac{d \ln k}{dT} = \frac{mRT + E}{RT}$$

As mRT << E for most reactions we may delete the mRT term and may write

$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \qquad \dots (1.45)$$

or

$$k \propto e^{-E/RT}$$

Hence, this discussion shows that Arrhenius law/ equation is a good approximation to the temperature dependency of both collision and transition state theories.

Temperature Dependency from Thermodynamics :

The temperature of the equilibrium constant (i.e. variation of the equilibrium constant with temperature) of the elementary reversible reaction of the type

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R, \; \Delta H_R$$

is given by the Van't Hoff equation

$$\frac{d \ln K}{dT} = \frac{\Delta H_R}{RT^2} \qquad \dots (1.46)$$

We have for a reversible reaction

$$K = K_C = C_{Re}/C_{Ae} = k_1/k_2$$

$$\therefore \quad \frac{d \ln (k_1/k_2)}{dT} = \frac{\Delta H_R}{RT^2}$$

$$\frac{d \ln k_1}{dT} - \frac{d \ln k_2}{dT} = \frac{\Delta H_R}{RT^2}$$

The difference in derivatives equal to $\Delta H_R/RT^2$ may suggest that each derivative alone is equal to a term of that kind. So splitting above equation into two equations one for the forward reaction and another for the reverse reaction, we can have

$$\frac{d \ln k_1}{dT} = \frac{E_1}{RT^2}$$

and

$$\frac{d \ln k_2}{dT} = \frac{E_2}{RT^2} \qquad \dots (1.47)$$

where

$$\Delta H_R = E_1 - E_2$$

We will see how the Van't Hoff equation can be obtained :

The relationship between the thermodynamic equilibrium constant and ΔG is given by

$$\Delta G = -RT \ln K \quad \ldots (1.48)$$

$$\Delta G = \Delta H - T\Delta S$$

$$G = H - TS$$

$$dU = dQ - PdV$$

and $$dQ = TdS$$

$\therefore$ $$dU = TdS - PdV$$

$$H = U + PV$$

$\therefore$ $$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

$$G = H - TS$$

$$dG = dH - TdS - SdT$$

$\therefore$ $$dG = TdS + VdP - TdS - SdT$$

$\therefore$ $$dG = VdP - SdT$$

$\therefore$ $$(dG/dT)_P = -S$$

$\therefore$ $$G = H + T\,(dG/dT)$$

$$T\,(dG/dT) = G - H$$

$$\frac{d\,(G/T)}{dT} = \frac{T\,dG/dT - G}{T^2}$$

$\therefore$ $$\frac{d\,(G/T)}{dT} = \frac{(G-H) - G}{T^2}$$

$$\frac{d\,(G/T)}{dT} = -\frac{H}{T^2}$$

$\therefore$ $$\frac{d\,(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2}$$

We have, $$\Delta G = -RT \ln K$$

$\therefore$ $$\frac{\Delta G}{T} = -R \ln K$$

$$\frac{d\,(-R \ln K)}{dT} = -\frac{\Delta H}{T^2}$$

$\therefore$ $$-R\frac{d \ln K}{dT} = -\frac{\Delta H}{T^2}$$

$\therefore$ $$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2}$$

This is the Van't Hoff equation.

SOLVED EXAMPLES

Ex. 1.1 : A reaction has the stoichiometric equation A + 2B → 2R. What is the order of reaction ?

Solution : $A + 2B \rightarrow 2R$.

Order of reaction is a experimental quantity and their is no direct correspondance between order of reaction and stoichiometry of reaction. So it is not possible to predict order of this reaction.

... **Ans.**

Ex. 1.2 : Given the reaction $2\,NO_2 + \frac{1}{2}\,O_2 \rightarrow N_2O_5$. What is the relation between the rate of formation and disappearance of these three components ?

Solution : $2\,NO_2 + \frac{1}{2}\,O_2 \rightarrow N_2O_5$

The relationship between the rate of disappearance of NO_2 and O_2 and the rate of formation of N_2O_5 is :

$$\frac{-r_{NO_2}}{2} = \frac{-r_{O_2}}{1/2} = \frac{r_{N_2O_5}}{1}$$

Ex. 1.3 : A reaction with stoichiometric equation $1/2\,A + B \rightarrow R + \frac{1}{2}\,S$ has the following rate equation :

$$-r_A = 2\,C_A^{0.5}\,C_B$$

What is the rate expression for this reaction if the stoichiometric equation is written as

$$A + 2B \rightarrow 2R + S\,?$$

Solution : Order of an reaction is the experimental quantity. It does not change with the stoichiometry of reaction, so the rate law/equation for

$A + 2B \rightarrow 2R + S$ is also $-r_A = k\,C_A^{0.5}\,C_B$ ... **Ans.**

Ex. 1.4 : A certain reaction has a rate given by :

$$-r_A = 0.005\,C_A^2\,, \quad mol/(cm^3.min)$$

If the concentration is expressed in mol/l and time in hours, what would be the value and units of rate constant ?

Solution :

$$-r_A = 0.005\,C_A^2, \quad mol/(cm^3.min)$$

$$-r_A = 0.005\left(\frac{cm^3}{mol.min}\right) C_A^2\left(\frac{mol}{cm^3}\right)^2, \quad \frac{mol}{cm^3.min}$$

$$\therefore \quad k = 0.005\,\frac{cm^3}{mol.min}$$

$$1000\,cm^3 = 1\,l$$

$$\therefore \quad 1\,cm^3 = \left(\frac{1}{1000}\right) l$$

$$60\,min = 1\,h$$

$$\therefore \quad 1\,min = \frac{1}{60}\,h$$

$$k = \frac{0.005\ \text{cm}^3 \times \left(\frac{1}{1000}\right)\left(\frac{l}{\text{cm}^3}\right)}{\text{mol.min}\left(\frac{1}{60}\right)\left(\frac{\text{h}}{\text{min}}\right)}$$

$$= 3 \times 10^{-4}\left(\frac{l}{\text{mol.h}}\right)$$

Value of k $= 3 \times 10^{-4}$

Units of k $= l/(\text{mol.h})$ ... **Ans.**

Ex. 1.5 : On doubling the concentration of reactant, the rate of reaction triples. Find the reaction order.

Solution : $-r_A = k\,C_A^n$

At C_{A1}, the rate is

$$-r_{A1} = k\,C_{A1}^n$$

At C_{A2}, the rate is

$$-r_{A2} = k\,C_{A2}^n$$

If $C_{A2} = 2\,C_{A1}$, we have

$$-r_{A2} = 3\,(-r_{A1})$$

$$\frac{-r_{A2}}{-r_{A1}} = \frac{k\,C_{A2}^n}{k\,C_{A1}^n}$$

$$\frac{-r_{A2}}{-r_{A1}} = \frac{C_{A2}^n}{C_{A1}^n}$$

CA2 = 2CA1
rA2 = 3rA1

$$\therefore \quad \frac{3\,(-r_{A1})}{-r_{A1}} = \frac{(2\,C_{A1})^n}{(C_{A1})^n}$$

$$3 = 2^n$$

$$\ln 3 = n \ln 2$$

$$1.0986 = n\,(0.693)$$

$$n = 1.58$$

$$= \cancel{1.6}$$ ... **Ans.**

*

Ex. 1.6 : For a gas reaction at 400 K the rate is reported as

$$\rightarrow p_A \quad \frac{-dp_A}{dt} = 3.66\,p_A^2, \quad \text{atm/h}$$

(a) What are the units of rate constant ?

(b) What is the value of the rate constant for this reaction if the rate equation is written as

(i) $-r_A = \frac{-1}{V}\frac{dN_A}{dt} = k\,C_A^2$, mol/(l.h)

(ii) $-r_A = k\,C_A^2$, mol/(m³.s)

Solution : A gas phase reaction at 400 K.

The rate is given as

$$-\frac{dp_A}{dt} = 3.66\,p_A^2, \ \text{atm/h}$$

$$-\frac{dp_A}{dt} = k\,p_A^2$$

$$-\frac{dp_A}{dt} = 3.66\left(\frac{1}{\text{atm.h}}\right) p_A^2 \ (\text{atm})^2, \quad \text{atm/h}$$

$$\therefore \quad k = 3.66\left(\frac{1}{\text{atm.h}}\right)$$

$$= 3.66 \ (\text{atm.h})^{-1}$$

Units of k are $(\text{atm.h})^{-1}$. ... **Ans.**

For gases :

$$C_A = p_A/RT$$

$$\therefore \quad p_A = C_A RT$$

$$\frac{dp_A}{dt} = RT\frac{dC_A}{dt}$$

$$-\frac{dp_A}{dt} = k' \, p_A^2$$

$$-RT\frac{dC_A}{dt} = k' (C_A RT)^2$$

$$-\frac{dC_A}{dt} = (RT) \, k' \, C_A^2, \quad \text{mol}/(l.\text{h})$$

$$-\frac{dC_A}{dt} = k \, C_A^2$$

$$\therefore \quad k = (RT) \ k'$$

$$= 0.08206\left(\frac{l.\text{atm}}{\text{mol.K}}\right) \times (400 \text{ K}) \times 3.66\left(\frac{1}{\text{atm.h}}\right)$$

$$= 0.08206 \times 400 \times 3.66\left(\frac{l}{\text{mol.h}}\right)$$

$$= 120.13 \ l/(\text{mol.h})$$

∴ Value of rate constant is 120.13 with units $l/(\text{mol.h})$. ... **Ans.**

If rate is in $\text{mol}/(\text{m}^3.\text{s})$ then k is

$$k = 120.13 \ l/(\text{mol.h})$$

$$= \frac{120.13 \times 10^{-3} \text{ m}^3}{(\text{mol}) \ (3600 \text{ s})}$$

$$= 3.34 \times 10^{-5} \ \text{m}^3/(\text{mol.s})$$ ... **Ans.**

Ex. 1.7 : Phosphine decomposes when heated according to following reaction :

$$4 \, PH_{3\,(g)} \rightarrow P_{4\,(g)} + 6 \, H_{2\,(g)}$$

At a given instant, the rate at which phosphine decomposes is 2.4×10^{-3} mol/(l.s).

(a) Express the rate in three different ways, using differential notation and show the relationship between them.

(b) What is the rate of formation of (i) P_4 and (ii) H_2 ?

Solution : $4 \, PH_{3\,(g)} \rightarrow P_{4\,(g)} + 6 \, H_{2\,(g)}$

From stoichiometry the rate of decomposition of PH_3, formation of P_4 and H_2 are related as given below :

$$-\frac{dC_{PH_3}/dt}{4} = \frac{dC_{P_4}/dt}{1} = \frac{dC_{H_2}/dt}{6}$$

$$\frac{-dC_{PH_3}}{dt} = 4\frac{dC_{P_4}}{dt} = \frac{2}{3}\frac{dC_{H_2}}{dt}$$ ... **Ans. (a)**

From above relation we have,

$$\text{Rate of formation of } P_4 = \frac{1}{4} \text{ (rate of decomposition of } PH_3)$$

$$= \frac{1}{4} [2.4 \times 10^{-3}] = 0.006 = 6.0 \times 10^{-4} \text{ mol/(}l\text{.s)} \quad \text{... Ans.}$$

$$\text{Rate of formation of } H_2 = \frac{6}{4} \text{ (rate of decomposition of } PH_3)$$

$$= \frac{3}{2} [2.4 \times 10^{-3}] = 3.6 \times 10^{-3} \text{ mol/(}l\text{.s)} \quad \text{... Ans.}$$

Ex. 1.8 : The following table shows how the concentration of reactant A varied with time in a particular experiment.

Time (min)	Concentration of A (mol/l)
0	2.77×10^{-4}
18	2.32×10^{-4}
31	2.05×10^{-4}
55	1.59×10^{-4}
79	1.26×10^{-4}
157	0.58×10^{-4}
∞	0.00

(a) Plot a graph of concentration of A against time.

(b) Draw tangents to the curves at 10, 50, 100 and 150 minutes and calculate their slopes.

(c) Plot a graph of rate of reaction against concentration of A

(i) Find if the line passes through origin. Explain.

(ii) With the help of graph, state the relationship between the rate of reaction and concentration of reactant both in words and mathematically.

(iii) Find the value of rate constant from graph.

(iv) What is the order of reaction ?

Solution : (a) Plot a graph of concentration v/s time by taking concentration of reactant A along the vertical axis and time along horizontal axis.

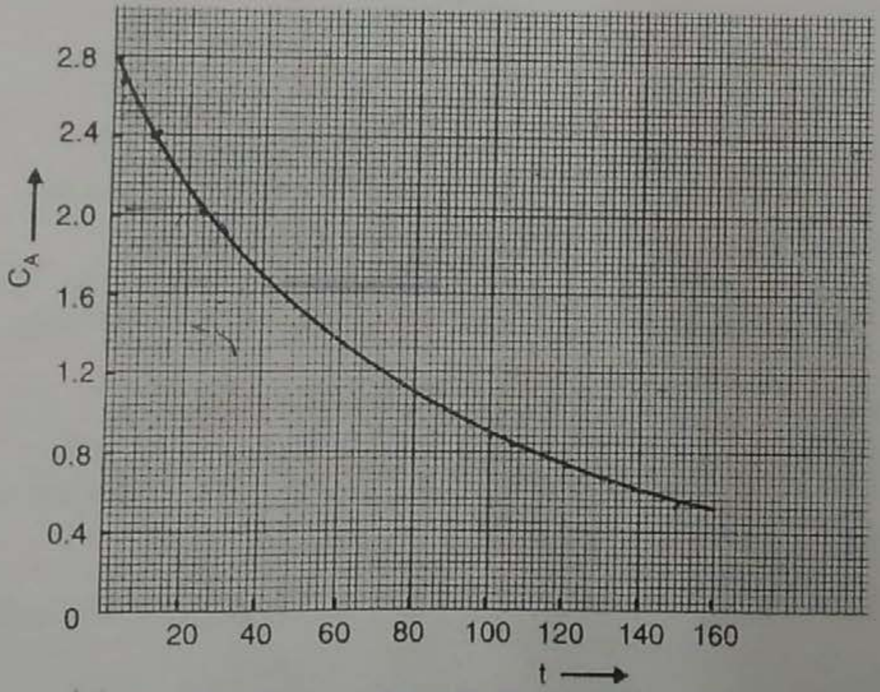

Fig. E. 1.8 (1) : Concentration v/s time

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(b)

Time	Concentration mol/l	Slope mol/(l.min)	Rate mol/(l.min)
10	2.50×10^{-4}	$-2.74 \times 10^{-4}/112.5$	2.44×10^{-6}
50	1.66×10^{-4}	$-2.49 \times 10^{-4}/151.5$	1.64×10^{-6}
100	1.04×10^{-4}	$-2.04 \times 10^{-4}/199.5$	1.02×10^{-6}
105	0.63×10^{-4}	$-1.58 \times 10^{-4}/249$	0.635×10^{-6}

(c) Plot a graph of rate v/s concentration by taking rate on vertical axis an concentration on horizontal axis.

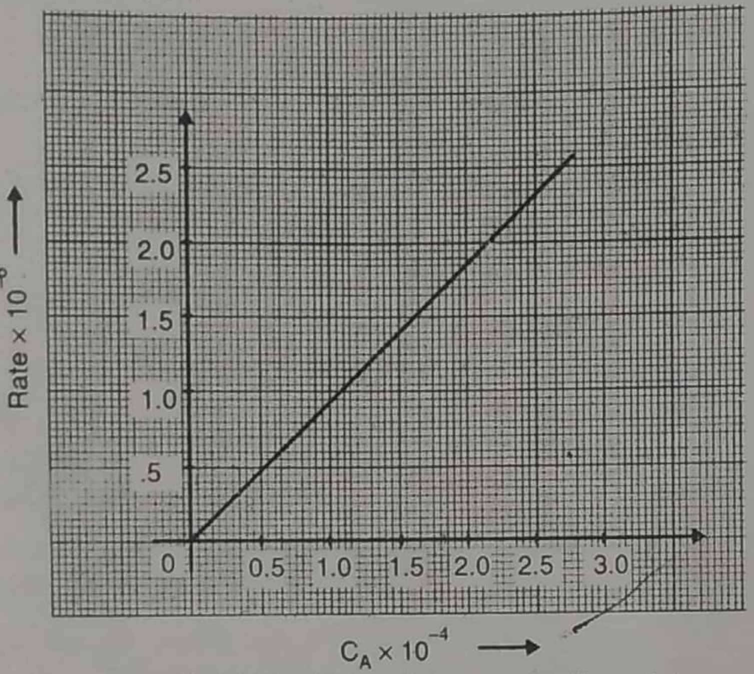

Fig. E. 1.8 (2) : Rate v/s concentration of A

(i) Line passes through the origin. At the origin, the rate of reaction is zero as the concentration of reactant is also zero.

(ii) From the graph it is clear that the rate of reaction is proportional to concentration of the reactant.

$$\text{Rate} \propto C_A$$

$$\therefore \quad \text{Rate} = k\,C_A \qquad \text{... An}$$

(iii) The graph of rate v/s concentration is a straight line with slope equal to k.

$$\therefore \quad k = \text{slope} = \frac{\Delta\,\text{rate}}{\Delta\,\text{concentration}}$$

$$= \frac{2.44 \times 10^{-6}\ \text{mol/}(l\text{.min})}{2.50 \times 10^{-4}\ \text{mol/}l}$$

$$= 9.76 \times 10^{-3}\ (\text{min})^{-1} \qquad \text{... Ans}$$

(iv) The reaction is first order with respect to A, as the rate is proportional to the firs power of concentration of A.

Ex. 1.9 : Concentration - rate data for the decomposition of N_2O_5 at 67 K is given below :

$$2\,N_2O_{5\,(g)} \longrightarrow 4\,NO_{2\,(g)} + O_{2\,(g)}$$

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Concentration, mol/l	0.113	0.080	0.056	0.040
Rate, mol/(l.min)	0.039	0.028	0.020	0.014

Plot a graph of rate against the concentration of N_2O_5 and answer the following :

(i) What is the rate expression for the reaction ?

(ii) Calculate the value of rate constant.

Solution : $2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$

From the data given, plot a graph of rate v/s concentration.

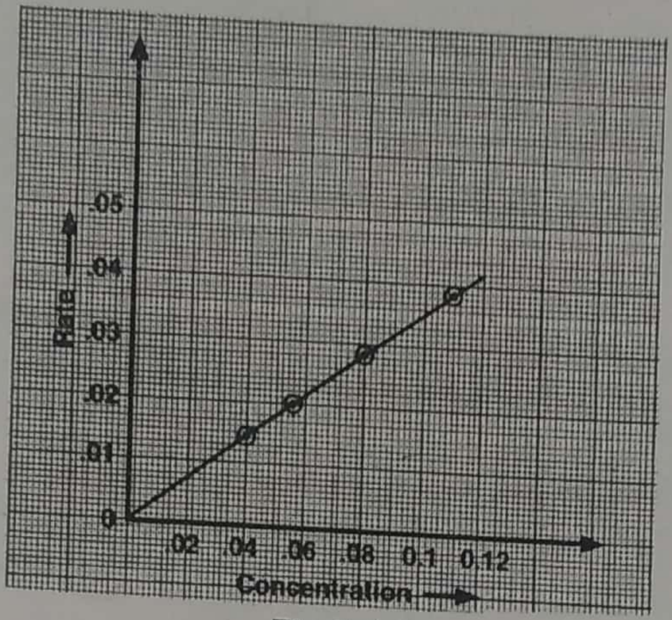

Fig. E. 1.9

Draw the line joining the points located on graph. It is a straight line passing through the origin. Therefore, rate is directly proportional to concentration.

$$\text{Rate} \propto C_{N_2O_5}$$

$$\text{Rate} = k\,C_{N_2O_5} \qquad \text{... Ans. (i)}$$

From graph,

$$k = \text{slope}$$

$$= \frac{0.035\ \text{mol}/(l.\text{min})}{0.10\ \text{mol}/l} = \left[\frac{0.035-0}{0.10-0}\right]$$

$$= 0.35\ (\text{min})^{-1} \qquad \text{... Ans. (ii)}$$

Ex. 1.10 : Concentration v/s time data for the reactions is given below :

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

Time (h)	Concentration of A, mol/l	Concentration of R, mol/l
0	0.100	0.00
2	0.050	0.050

Time (h)	Concentration of B, mol/l	Concentration of S, mol/l
0	0.10	0.00
2	0.075	0.025

(a) Which reaction proceed at the greatest rate ?

(b) What are the rates of formation of R and S ?

Solution :

$$A \rightarrow R$$

Rate of reaction-1 :

$$\text{Rate - 1} = -\frac{dC_A}{dt} = -\left[\frac{C_A - C_{A0}}{t - t_o}\right]$$

$$C_A = 0.05 \text{ mol}/l,\ t = 2\text{ h}$$
$$C_{Ao} = 0.10 \text{ mol}/l,\ t_o = 0\text{ h}$$
$$\text{Rate - 1} = -\frac{[0.05 - 0.10]}{[2-0]}$$
$$= \frac{0.10 - 0.05}{2}$$
$$= 0.025 \text{ mol}/(l.\text{h})$$
$$B \rightarrow S$$

Rate of reaction-2 : $$\text{Rate - 2} = -\left[\frac{C_B - C_{Bo}}{t - t_o}\right]$$

$$C_B = 0.075 \text{ mol}/l,\ t = 2\text{ h}$$
$$C_{Bo} = 0.10 \text{ mol}/l,\ t_o = 0\text{ h}$$
$$\text{Rate - 2} = -\frac{[0.075 - 0.10]}{[2-0]}$$
$$= \frac{0.1 - 0.075}{2}$$
$$= 0.0125 \text{ mol}/(l.\text{h})$$

As rate of reaction-1 is greater than reaction-2, reaction A → R proceeds at a greater rate.
... **Ans. (a)**

$$\text{Rate of formation of R} = \frac{dC_R}{dt}$$
$$= \frac{0.05 - 0.0}{2-0}$$
$$= 0.025 \text{ mol}/(l.\text{h})$$
... **Ans. (b)**

$$\text{Rate of formation of S} = \frac{dC_S}{dt}$$
$$= \frac{0.025 - 0.0}{2-0}$$
$$= 0.0125 \text{ mol}/(l.\text{h})$$
... **Ans. (b)**

Q D3

T **Ex. 1.11 :** The pyrolysis of ethane proceeds with an activation energy of about 75000 cal How much faster is the decomposition at 650 °C than at 500 °C ?

Solution : $$C_2H_6 \longrightarrow \text{Product}$$
$$E = 75000 \text{ cal/mol}$$

Let k_1 be the rate constant at T_1 and k_2 be the rate constant at T_2.

$T_1 = 500\ °C = 773$ K; $T_2 = 650\ °C = 923$ K

$$\ln\frac{r_2}{r_1} = \ln(k_2/k_1) = -\frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$
$$R = 1.987 \text{ cal/mol.K}$$
$$\ln(k_2/k_1) = \frac{75000}{1.987}\left[\frac{1}{773} - \frac{1}{923}\right]$$
$$\ln(k_2/k_1) = 7.951$$
$$k_2/k_1 = 2838$$
$$\therefore\ k_2 = 2838\, k_1$$

∴ At 650 °C, the decomposition is faster by a factor 2838 than at 500 °C.

Ex. 1.12 : The activation energy of a bimolecular reaction is about 9150 cal/mol. How much faster is this reaction takes place at 500 K than at 400 K ?

Solution :

$$2A \rightarrow \text{Products}$$

$$E = 9150 \text{ cal/mol}$$

Let k_1 be the rate constant at T_1 and k_2 be the rate constant at T_2.

$$T_1 = 400 \text{ K}, \quad T_2 = 500 \text{ K}$$

$$\ln (k_2/k_1) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] = \frac{9150}{1.987}\left[\frac{1}{400} - \frac{1}{500}\right]$$

$$\therefore \quad k_2/k_1 = 10$$

$\therefore$ The reaction is 10 times faster at 500 K than at 400 K.

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Ex. 1.13 : At 500 K the rate of a bimolecular reaction is ten times the rate at 400 K. Find the activation energy for this reaction (a) from Arrhenius law, (b) from collision theory, (c) what is the percentage difference in rate of reaction at 600 K predicted by these two methods ?

r2 r1 r3

Solution :

(a) We have :

$$\ln (r) = -E/RT + \ln k_0$$

$$\therefore \quad \ln (r_2/r_1) = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln (r_2/r_1) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

r1 → r2 → r3

600 500

500 400

We have : $r_2 = 10\, r_1$, $T_1 = 400$ K, $T_2 = 500$ K

$$R = 1.987 \text{ cal/(mol.K)}$$

$$\ln (10\, r_1/r_1) = \frac{E}{1.987}\left[\frac{1}{400} - \frac{1}{500}\right]$$

$$\therefore \quad E = 9150 \text{ cal/mol}$$

... **Ans.**

(b) From Collision theory :

$$k \propto T^{1/2} \cdot e^{-E/RT}$$

$$r = k_0' \, T^{1/2} \cdot e^{-E/RT}$$

$$\ln r = -\frac{E}{R}\left(\frac{1}{T}\right) + \ln T^{1/2} + \ln k_0'$$

$$\ln r_1 = -\frac{E}{R}\left(\frac{1}{T_1}\right) + \ln T_1^{1/2} + \ln k_0'$$

$$\ln r_2 = -\frac{E}{R}\left(\frac{1}{T_2}\right) + \ln T_2^{1/2} + \ln k_0'$$

$$\ln (r_2/r_1) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] + \ln\left(\frac{T_2^{1/2}}{T_1^{1/2}}\right)$$

$$T_1 = 400 \text{ K}, \; T_2 = 500 \text{ K}, \; r_2 = 10\, r_1$$

$$\ln (10\, r_1/r_1) = \frac{E}{1.987}\left[\frac{1}{400} - \frac{1}{500}\right] + \ln\left[(500)^{1/2}/(400)^{1/2}\right]$$

$$\therefore \quad E = 8707 \text{ cal/mol}$$

... **Ans.**

(c) From Arrhenius law :

$$\ln(r_3/r_2) = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_3}\right], T_3 = 600\text{ K}, T_2 = 500\text{ K}$$

$$\ln(r_3/r_2) = \frac{9150}{1.987}\left[\frac{1}{500} - \frac{1}{600}\right]$$

$$r_3/r_2 = 4.64 \quad \therefore \quad r_3 = 4.64\, r_2$$

From Collision theory :

$$\ln(r_3/r_2) = \frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_3}\right] + \ln\left(\frac{T_3^{1/2}}{T_2^{1/2}}\right)$$

$$\ln(r_3/r_2) = \frac{8707}{1.987}\left[\frac{1}{500} - \frac{1}{600}\right] + \ln\left[(600)^{1/2}/(500)^{1/2}\right]$$

$$r_3/r_2 = 4.72$$

$$r_3 = 4.72\, r_2$$

From Arrhenius law, $r_3 = 4.64\, r_2$

From Collision theory, $r_3 = 4.72\, r_2$

$\therefore$ The % difference in rates $= \frac{(4.72 - 4.64)\, r_2}{4.72\, r_2} \times 100$

$= 1.7\ \%$ ... **Ans.**

The rate of reaction from Collision theory is 1.7% more than it is given by Arrhenius law.

Ex. 1.14 : The rate constants of a certain reaction are 1.6×10^{-3} and $1.625 \times 10^{-2} (s)^{-1}$ at 10 °C and 30 °C. Calculate the activation energy.

Solution : $k_1 = 1.6 \times 10^{-3}$ at $T_1 = 10\ ^\circ C = 283\text{ K}$

$k_2 = 1.625 \times 10^{-2}$ at $T_2 = 30\ ^\circ C = 303\text{ K}$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln(k_2/k_1) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$R = 1.987 \text{ cal/(mol.K)}$$

$$\ln\left(\frac{1.625 \times 10^{-2}}{1.6 \times 10^{-3}}\right) = \frac{E}{1.987}\left[\frac{1}{283} - \frac{1}{303}\right]$$

$$E = 19500 \text{ cal/mol}$$

... **Ans.**

Ex. 1.15 : Decomposition of a acetone dicarboxylic acid is a first order reaction :

$$CO(CH_2COOH)_2 \rightarrow CO(CH_3)_2 + 2\, CO_2$$

Following is the data for the same :

T, K	273	293	313	333
k, $(s)^{-1}$	2.46×10^5	47.5×10^5	576×10^5	5480×10^5

Find out the energy of activation for this reaction graphically.

Solution :

$$\ln k = \frac{-E}{RT} + C$$

Plot of ln k (on y-axis) v/s 1/T on x - axis yields a straight line with slope equal to – E/R. Once we know the slope we can get value of E (activation energy) in cal/mol as R = 1.987 cal/(mol.K).

From data given, tabulate ln k and 1/T.

T, K	1/T	k	ln k
273	3.63×10^{-3}	$2.46 \times 10^{+5}$	12.41
293	3.41×10^{-3}	$47.5 \times 10^{+5}$	15.37
313	3.195×10^{-3}	$576 \times 10^{+5}$	17.87
333	3.003×10^{-3}	$5480 \times 10^{+5}$	20.12

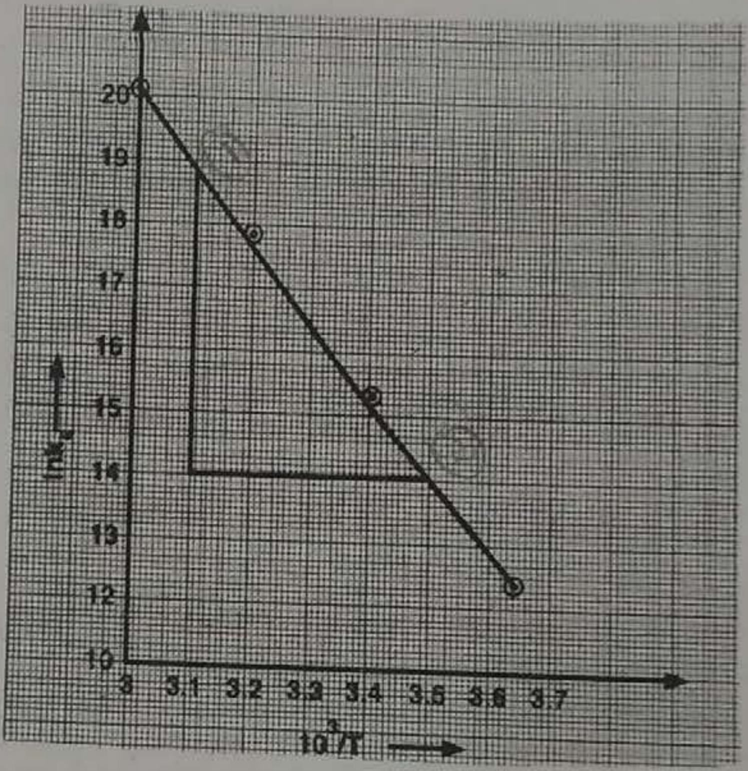

Fig. E. 1.15

From graph,

$$\text{Slope} = -\frac{E}{R}$$

$$= \frac{-(18.9-14)}{(3.5-3.1)\,10^{-3}}$$

$$= -12250$$

$$\therefore \quad -\frac{E}{R} = -12250$$

$$E = 12250 \times 1.987 = 24341 \text{ cal/mol}$$

... **Ans.**

Ex. 1.16 : A reaction $2\,HI_{(g)} \rightarrow H_{2\,(g)} + I_{2\,(g)}$ is studied over a range of temperatures. The results obtained are tabulated below.

Temperature, K	633	666	697	715	781
Rate constant k, l/(mol.s)	1.7×10^{-5}	1.07×10^{-4}	5.01×10^{-4}	1.05×10^{-3}	1.51×10^{-3}

(i) Find out the value of activation energy graphically using the given data

(ii) Determine by what factor the rate increases when temperature rises from 300 K to 310 K.

Solution :
$$\ln k = -\frac{E}{R}\left(\frac{1}{T}\right) + C$$

$$\log k = \frac{-E}{2.303\ R}\left(\frac{1}{T}\right) + C$$

(i) Plot log k v/s $(1/T) \times 10^3$ and from slope, obtain E. For this prepare table as given below :

T, K	$1/T \times 10^{-3}$	k, l/(mol.s)	log k
633	1.58	1.78×10^{-5}	– 4.75
666	1.50	1.07×10^{-4}	–3.97
697	1.43	5.01×10^{-4}	– 3.30
715	1.40	1.05×10^{-3}	– 2.98
781	1.28	1.51×10^{-3}	– 1.82

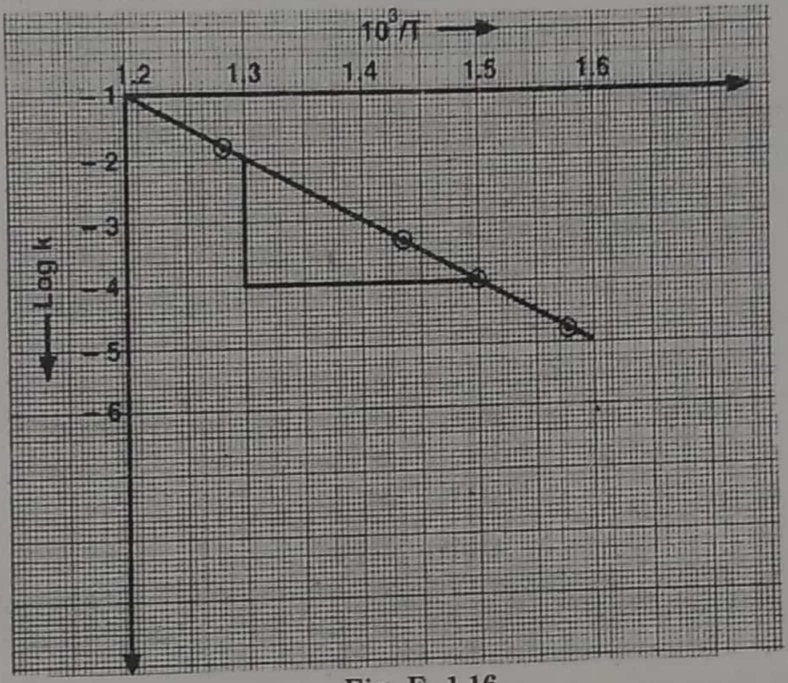

Fig. E. 1.16

$$\text{Slope} = -\frac{E}{2.303\ R}$$

But,
$$\text{Slope} = \frac{-4-(-2)}{(1.5-1.3)\times 10^{-3}} = -10\times 10^3$$

$$\therefore \quad E = -2.303\ R \times \text{Slope} = -2.303 \times 1.987 \times (-10 \times 10^3)$$
$$= 45761 \text{ cal/mol} \quad \ldots \textbf{Ans. (i)}$$

We can plot ln k v/s $(1/T) \times 10^3$ instead of log k v/s $(1/T) \times 10^3$.

(ii)
$$\ln\frac{k_2}{k_1} = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

k_1 = rate constant at $T_1 = 300$ K

k_2 = rate constant at $T_2 = 310$ K

$$\ln\frac{k_2}{k_1} = \frac{-45761}{1.987}\left[\frac{1}{310} - \frac{1}{300}\right]$$

$$\therefore \quad \frac{k_2}{k_1} = 24.77 \quad \ldots \textbf{Ans. (ii)}$$

∴ Rate increases by factor 24.77.

Ex. 1.17 : At 500 K, the rate of a bimolecular reactions is ten times the rate at 400 K. Find the activation energy of this reaction from Arrhenius law.

Solution :

$$\ln \frac{r_2}{r_1} = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln \frac{r_2}{r_1} = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

r_1 = rate constant at 400 K, $T_1 = 400$ K

r_2 = rate constant at 500 K, $T_2 = 500$ K

$R = 1.987$ cal/(mol.K)

At $T = T_2$, $r_2 = 10\, r_1$

$$\therefore \quad \ln\left(\frac{10\, r_1}{r_1}\right) = \frac{E}{1.987}\left[\frac{1}{400} - \frac{1}{500}\right]$$

$$E = 9150.5 \text{ cal/mol}$$

... **Ans.**

KJ = 8.318
cal = 1.987
lit atm = 0.082
$T_1 = 500$
$T = 400$
~~K2 = 10K1~~
$r_2 = 10 r_1$

Ex. 1.18 : A common rule of temperature is that the rate of a reaction doubles for each 10 °C rise in temperature. What activation energy would this suggest at a temperature of 25 °C ?

Solution :

$$\ln r = -\frac{E}{RT} + C$$

$$\ln \frac{r_2}{r_1} = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$r = r_1$ at $T = T_1 = 15 + 273 = 288$ K

$r = r_2$ at $T = T_2 = 25 + 273 = 298$ K

$r_2 = 2\, r_1$, $R = 1.987$ cal/(mol.K)

$$\ln (2) = \frac{E}{1.987}\left[\frac{1}{288} - \frac{1}{298}\right]$$

Solving we get, $E = 11820$ cal/mol

... **Ans.**

Ex. 1.19 : The activation energy of a chemical reaction is 17982 cal/mol in the absence of a catalyst, and 11980 cal/mol with a catalyst. By how many times will the rate of the reaction will grow in the presence of a catalyst, if a reaction proceeds at 25 °C ?

Solution : Let E_1 be the activation energy of a reaction without catalyst (17982 cal/mol).

E_2 be the activation energy of a reaction with catalyst (11980 cal/mol).

We have,

$$k = k_o\, e^{-E/RT}$$

k_1 be the rate constant of a reaction (uncatalysed)

k_2 be the rate constant of a reaction (catalysed)

$$k_1 = k_o \cdot e^{-E_1/RT}$$

$$k_2 = k_o \cdot e^{-E_2/RT}$$

$$\frac{k_2}{k_1} = \frac{e^{-E_2/RT}}{e^{-E_1/RT}}$$

$$\frac{k_2}{k_1} = e^{(E_1 - E_2)/RT} = \exp\cdot\left(\frac{E_1 - E_2}{RT}\right) = \exp\cdot\left(\frac{17982 - 11980}{1.987 \times 298}\right)$$

$$= 2.52 \times 10^4$$

$$k_2 = 2.52 \times 10^4\, k_1$$

$\therefore$ In presence of catalyst, the rate of reaction will grow by 2.52×10^4 times (the rate for uncatalysed reaction).

... **Ans.**

Ex. 1.20 : The pyrolysis of ethane proceeds with an activation energy of about 300 kJ/mol. How much faster is the decomposition at 650 °C than at 500 °C ?

Solution :

$$E = 300 \text{ kJ/mol} = 300 \times 10^3 \text{ J/mol}$$

$$T_1 = 500\ ^\circ\text{C} = 773,\ T_2 = 650\ ^\circ\text{C} = 923 \text{ K}$$

$$R = 8.314 \text{ J/(mol.K)}$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$= \frac{300 \times 10^3}{8.314}\left[\frac{1}{773} - \frac{1}{923}\right]$$

$$= 7.587$$

$$k_2/k_1 = e^{7.587}$$

$$= 1972.4$$

$$k_2 = 1972.4\ k_1$$

So the decomposition at 650 °C is 1972.4 times faster the one at 500 °C. ... **Ans.**

Ex. 1.21 : A 1100 K n-nonane thermally cracks 20 times as rapidly as at 1000 K. Estimate the activation energy for this decomposition.

Solution :

$$T_2 = 1100 \text{ K}, \qquad r = r_2$$

$$T_1 = 1000 \text{ K}, \qquad r = r_1$$

We have,

$$r_2 = 20\, r_1$$

$$\ln (r_2/r_1) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln (20 r_1/r_1) = \frac{E}{8.314}\left[\frac{1}{1000} - \frac{1}{1100}\right]$$

$$\therefore \quad E = 273973 \text{ J/mol}$$

$$= 274 \text{ kJ/mol}$$

... **Ans.**

Ex. 1.22 : The rule of thumb that the rate of reaction doubles for a 10 °C increase in temperature occurs only at a specific temperature for a given activation energy (i.e. for specific combination of temperature and activation energy). Show that the relationship between activation energy and temperature for which the rule holds is

$$T = \left[\frac{10\,(K)\,E}{R \ln 2}\right]^{1/2}$$

Solution : We have,

$$k = k_o \cdot e^{-E/RT}$$

$$-r = k\, C_A^\alpha = k_o \cdot C_A^\alpha \cdot e^{-E/RT}$$

For constant concentration, the term C_A^α is constant, and can be coupled with k_o

$$-r = k_o^{'}\, e^{-E/RT}$$

valid for estimation of E from rate v/s temperature data at constant concentration.

$$\ln (-r) = \ln k_o^{'} - \frac{E}{RT}$$

$$\ln (-r_1) = \ln k_o^{'} - \frac{E}{RT_1}$$

$$\ln(-r_2) = \ln k_o' - \frac{E}{RT_2}$$

$$\ln\left(\frac{-r_2}{-r_1}\right) = -\frac{E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln\left(\frac{-r_2}{-r_1}\right) = \frac{E}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln\left(\frac{-r_2}{-r_1}\right) = \frac{E}{R}\left[\frac{T_2 - T_1}{T_1\,T_2}\right]$$

At T_1 the rate is $-r_1$

At T_2 the rate is $-r_2$

$T_2 > T_1$ by 10 °C

At T_2,

$$(-r_2) = 2\,(-r_1)$$

$$(T_1 - T_2)\ ^{\circ}C = [(T_1 + 273) - (T_2 + 273)]\ K$$

∴ temperature difference in °C = temperature difference in K

difference of 10 °C in temperatures = difference of 10 K in temperatures

∴

$$T_2 - T_1 = 10\ K$$

∴

$$\ln\left[\frac{-2r_1}{-r_1}\right] = \frac{E}{R}\left[\frac{10\ (K)}{T_1\,T_2}\right]$$

$$T_1\,T_2 = \frac{10\ (K)\cdot E}{R \ln 2}$$

$$T_1\,T_2 = T^2$$

∴

$$T^2 = \frac{10\ (K)\ E}{R \ln 2}$$

$$T = \left[\frac{10\ (K)\ E}{R \ln 2}\right]^{1/2}$$

If $T = 300$ K for doubling rate E is

$$(300)^2 = \frac{10\ E}{1.987 \times \ln 2}$$

$$E = 12395.5\ \text{cal/mol} = 12.4\ \text{kcal/mol}$$

$$= 51.99\ \text{kJ/mol}$$

So the rate will double only.

If the activation energy is 51.99 kJ/mol (12395.5 cal/mol), the rate will double only if the temperature is raised from 300 K to 310 K.

Ex. 1.23 : The rate constant at 27°C for a reaction is $1.3 \times 10^{-3}\ (s)^{-1}$ and its frequency factor is $2.785 \times 10^{6}\ (s)^{-1}$. Determine its entropy of activation and enthalpy of activation.

Solution : We have

$$k = \frac{k_B T}{h}\, e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT}$$

∴

$$k_o = \frac{k_B T}{h}\, e^{\Delta S^*/R}$$

$$\log k_o = \log \frac{k_B T}{h} + \frac{\Delta S^*}{2.303\ R}$$

$k_o = 2.785 \times 10^6 \, (s)^{-1}$, $k = 1.3 \times 10^{-3} \, (s)^{-1}$, $T = 273 + 27 = 300$ K

$h = 6.62 \times 10^{-27}$ erg·s, $R = 1.987$ cal/(mol.K)

$$\log 2.785 \times 10^6 = \log \frac{1.38 \times 10^{-3} \times 300}{6.62 \times 10^{-27}} + \frac{\Delta S^*}{1.987 \times 2.303}$$

$$6.4448 = 12.7963 + \frac{\Delta S^*}{1.987 \times 2.303}$$

$$\Delta S^* = -29.06 \text{ e. u.}$$ ... **Ans.**

Now,

$$k = \frac{k_B T}{h} e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT}$$

$$= k_o \, e^{-\Delta H^*/RT}$$

$$\log k = \log k_o - \frac{\Delta H^*}{2.303 \, RT}$$

$$\log 1.3 \times 10^{-3} = \log 2.785 \times 10^6 - \frac{\Delta H^*}{2.303 \times 1.987 \times 300}$$

Solving, we get,

$$\Delta H^* = 12.8 \text{ kcal/mol}$$ ... **Ans.**

Ex. 1.24 : The rate constant of a reaction at 27°C is $1.3 \times 10^{-3} \, (s)^{-1}$. Determine the frequency factor. Take E (energy of activation) = 128170 cal/mol.

Solution : The Arrhenius equation is

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

where

$k = 1.3 \times 10^{-3} \, (s)^{-1}$, $E = 128170$ cal/mol

$R = 1.987$ cal/(mol.K), $T = 27 + 273 = 300$ K

k_0 = frequency factor

$$\ln k = \ln k_0 - \frac{E}{RT}$$

$$\ln k_o = \ln k + \frac{E}{RT} = \ln (1.3 \times 10^{-3}) + \frac{128170}{1.987 \times 300}$$

$$\therefore \quad k_0 = 2.79 \times 10^6 \, (s)^{-1}$$

In Ex. 1.25 to 1.33, [A] represents the concentration of A (wherever applicable).

Ex. 1.25 : Experimental analysis shows that the homogeneous decomposition of ozone proceeds with a rate

$$-r_{O_3} = k \, [O_3]^2 \, [O_2]^{-1}$$

i.e.

$$-r_{O_3} = k \, C_{O_3}^2 / C_{O_2}$$

(i) Suggest a two-step mechanism to explain this rate.

(ii) What is the overall order of reaction ?

Solution : The homogeneous decomposition of ozone proceeds as

$$2 \, O_3 \rightarrow 2 \, O_2$$

and follows the rate law

$$-r_{O_3} = k \, [O_3]^2 \, [O_2]^{-1}$$

The two-step mechanism, consistent with the rate, suggested is

Step 1: $O_3 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} O_2 + O$ (fast, at equilibrium)

Step 2: $O + O_3 \xrightarrow{k_3} 2 \, O_2$ (slow)

The step 2 is the slower, rate determining step and accordingly, the reaction rate is given by

$$-r_{O_3} = \frac{-d[O_3]}{dt} = k_3 [O_3] [O] \qquad \dots (1)$$

The step 1 is fast and reversible. For this equilibrium step, we have

$$K = \frac{k_1}{k_2} = \frac{[O_2][O]}{[O_3]}$$

$$\therefore \quad [O] = K [O_3] / [O_2] \qquad \dots (2)$$

Putting value of [O] from equation (2) into equation (1), we get,

$$-r_{O_3} = \frac{-d[O_3]}{dt} = k_3 \cdot K [O_3]^2 / [O_2]$$

Let

$$k = k_3 K$$

$$\therefore \quad -r_{O_3} = k [O_3]^2 [O_2]^{-1} \qquad \dots \textbf{Ans.}$$

Overall order of reaction is 2 – 1 = 1 ... **Ans.**

Ex. 1.26 : The reaction between nitric oxide and oxygen

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

follows the rate law

$$\frac{-d[O_2]}{dt} = k [NO]^2 [O_2]$$

Suggest a reaction mechanism which is consistent with the rate law.

Solution : The reaction between nitric oxide and oxygen

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

follows the rate law

$$\frac{-d[O_2]}{dt} = k [NO]^2 [O_2]$$

The following mechanism consistent with the rate law is suggested as :

Step 1: $NO + NO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_2$ (fast, at equilibrium)

Step 2: $N_2O_2 + O_2 \xrightarrow{k_3} 2\,NO_2$ (slow)

The second step is slow and rate determining, so the rate of reaction is given by

$$-r_{O_2} = \frac{-d[O_2]}{dt} = k_3 [N_2O_2] [O_2] \qquad \dots (1)$$

From step 1, which is fast at equilibrium,

$$K = \frac{k_1}{k_2} = [N_2O_2] / [NO]^2$$

$$\therefore \quad [N_2O_2] = K [NO]^2 \qquad \dots (2)$$

Combining equations (1) and (2),

$$\frac{-d[O_2]}{dt} = k_3 K [NO]^2 [O_2]$$

Let

$$k = k_3 K$$

$$\therefore \quad \frac{-d[O_2]}{dt} = k [NO]^2 [O_2] \qquad \dots \textbf{Ans.}$$

Ex. 1.27 : Experiments show that reaction between H_2 (g) and I (g) to produce HI (g) proceeds with a rate

$$\frac{1}{2}\frac{d[HI]}{dt} = k[H_2][I_2]$$

Suggest a two-step mechanism which is consistent with this rate.

Solution : The reaction between H_2 (g) and I_2 (g) is

$$H_2(g) + I_2(g) \rightarrow 2HI(g)$$

is consistent with the rate

$$\frac{1}{2}\frac{d[HI]}{dt} = k[H_2][I_2]$$

A two-step mechanism suggested is :

Step 1: $I_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2I$ (fast, at equilibrium)

Step 2: $H_2 + 2I \xrightarrow{k_3} 2HI$ (slow)

The step 2 is low and rate determining, therefore

$$\frac{1}{2}\frac{d[HI]}{dt} = k_3[H_2][I]^2 \quad \text{... (1)}$$

$$\left[\text{as } \frac{-r_{H_2}}{1} = \frac{r_{HI}}{2}\right]$$

From the equilibrium step

$$K = \frac{k_1}{k_2} = \frac{[I]^2}{[I_2]}$$

$$\therefore \quad [I]^2 = K[I_2] \quad \text{... (2)}$$

Combining equations (1) and (2), we get ,

$$\frac{1}{2}\frac{d[HI]}{dt} = k_3[H_2]\cdot K[I_2]$$

Let $k = k_2 K$

$$\therefore \quad \frac{1}{2}\frac{d[HI]}{dt} = k[H_2][I_2] \quad \text{... Ans.}$$

Ex. 1.28 : The reaction between CO and NO_2 at low temperatures proceeds with rate :

$$-r_{NO_2} = k[NO_2]^2$$

Suggest a mechanism to explain this rate.

Solution : The reaction between CO and NO_2 at low temperatures

$$CO + NO_2 \xrightarrow{k_1} NO + CO_2$$

proceeds with a rate

$$-r_{NO_2} = k[NO_2]^2$$

It is clear from the rate expression that the concentration of CO is not involved in the rate determining step. The mechanism thus suggested is :

Step 1: $NO_2 + NO_2 \xrightarrow{k_1} NO_3 + NO$ (slow)

Step 2: $NO_3 + CO \xrightarrow{k_2} NO_2 + CO_2$ (fast)

As the first step is slow and the rate determining one,

$$\frac{-d[NO_2]}{dt} = -r_{NO_2} = k_1\,[NO_2]^2$$

Applying the steady state approximation to NO_3 we get

$$\frac{d[NO_3]}{dt} = 0 = k_1\,[NO_2]\,[NO_2] - k_2\,[NO_3]\,[CO]$$

$$\therefore \quad k_1\,[NO_2]^2 = k_2\,[NO_3]\,[CO] \qquad \ldots (1)$$

The overall rate of disappearance of NO_2 is given by

$$\frac{-d[NO_2]}{dt} = 2\,k_1\,[NO_2]^2 - k_2\,[NO_3]\,[CO] \qquad \ldots (2)$$

Combining equations (1) and (2), we get

$$\frac{-d[NO_2]}{dt} = 2\,k_1\,[NO_2]^2 - k_1\,[NO_2]^2$$

$$= k_1\,[NO_2]^2$$

Let $k = k_1$

$$\therefore \quad -r_{NO_2} = k\,[NO_2]^2 \qquad \ldots \textbf{Ans.}$$

Ex. 1.29 : Show that the following scheme :

$$N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NO_2 + NO_3^*$$

$$NO_2 + NO_3^* \xrightarrow{k_3} NO_2 + O_2 + NO^*$$

$$NO^* + NO_3^* \xrightarrow{k_4} 2\,NO_2$$

proposed by Ogg is consistent with, and can explain the observed first order decomposition of N_2O_5.

Solution : The gas phase decomposition of N_2O_5

$$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$$

has the rate expression

$$r = -\frac{1}{2}\,\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt} = k\,[N_2O_5]$$

The suggested mechanism is :

Step 1: $N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftarrows}} NO_2 + NO_3^*$ (fast, at equilibrium)

Step 2: $NO_2 + NO_3^* \xrightarrow{k_3} NO_2 + O_2 + NO^*$ (slow)

Step 3: $NO^* + NO_3^* \xrightarrow{k_4} 2\,NO_2$ (fast)

The step 2 is slow, so the rate of reaction is given by the rate of formation of oxygen, hence

$$r = -\frac{1}{2}\,\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt} = k_3\,[NO_2]\,[NO_3^*] \qquad \ldots (1)$$

Both NO^* and NO_3^* are intermediates. Their concentrations can be calculated by steady state (or stationary state) approximation. The concentrations of reactive intermediates are very low and are effectively remain constant compared to the reactant concentration. So the rate of change of concentration of intermediate with time is assumed to be zero.

$$\frac{d\,[NO_3^*]}{dt} = 0 = k_1\,[N_2O_5] - k_2\,[NO_2]\,[NO_3^*]$$

$$- k_3\,[NO_2]\,[NO_3^*] - k_4\,[NO^*]\,[NO_3^*]$$

$$\therefore \quad [NO_3^*] = \frac{k_1\,[N_2O_5]}{k_2\,[NO_2] + k_3\,[NO_2] + k_4\,[NO^*]} \qquad \ldots (2)$$

$$\frac{d\,[NO^*]}{dt} = 0 = k_3\,[NO_2]\,[NO_3^*] - k_4\,[NO^*]\,[NO_3^*]$$

$$\therefore \quad [NO^*] = \frac{k_3}{k_4}\,[NO_2] \qquad \ldots (3)$$

$$[NO_3^*] = \frac{k_1\,[N_2O_5]}{k_2\,[NO_2] + k_3\,[NO_2] + k_4 \cdot \frac{k_3}{k_4}\,[NO_2]}$$

$$= \frac{k_1\,[N_2O_5]}{k_2\,[NO_2] + 2\,k_3\,[NO_2]}$$

$$[NO_3^*] = \frac{k_1\,[N_2O_5]}{(k_2 + 2\,k_3)\,[NO_2]} \qquad \ldots (4)$$

Putting value of $[NO_3^*]$ from equation (4) into equation (1), we get,

$$r = -\frac{1}{2}\,\frac{d\,[N_2O_5]}{dt} = \frac{d\,[O_2]}{dt} = \frac{k_3\,[NO_2]\,k_1\,[N_2O_5]}{(k_2 + 2\,k_3)\,[NO_2]}$$

$$r = \left(\frac{k_3}{k_2 + 2\,k_3}\right)[N_2O_5]$$

$$k = \frac{k_3}{(k_2 + 2\,k_3)}$$

$$\therefore \quad r = k\,[N_2O_5] \qquad \ldots (A)$$

So the mechanism suggested is consistent with observed first order **decomposition** of N_2O_5.

Ex. 1.30 : Show that the following scheme

$$N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3^*$$

$$NO_2 + NO_3^* \xrightarrow{k_3} NO_2 + O_2 + NO^*$$

$$NO^* + NO_3^* \xrightarrow{k_4} 2\,NO_2$$

proposed by Ogg is consistent with, and can explain the observed first order decomposition of N_2O_5.

Solution : The gas phase decomposition of N_2O_5

$$2\,N_2O_5 \rightarrow 4\,NO_2 + O_2$$

has the rate expression

$$r = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt} = k\,[N_2O_5]$$

The suggested mechanism is :

Step 1 : $N_2O_5 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3^*$ (fast, at equilibrium)

Step 2 : $NO_2 + NO_3^* \xrightarrow{k_3} NO_2 + O_2 + NO^*$ (slow)

Step 3 : $NO^* + NO_3^* \xrightarrow{k_4} 2\,NO_2$ (fast)

As the step-2 is slower than the others (i.e. it occurs at a much slower rate than the others), this step will determine the rate of the overall reaction (it is rate controlling step).

So the rate of reaction is given by rate of formation of O_2.

$$r = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt} = k_3\,[NO_2]\,[NO_3^*] \qquad \dots (1)$$

As the concentration of NO^* does not appear in this rate equation, the step-3 has to be fast with respect to step-2.

The step-1 is fast and reversible. So we can relate the concentrations of the three species by equilibrium equation :

$$K = \frac{k_1}{k_2} = \frac{[NO_2]\,[NO_3^*]}{[N_2O_5]}$$

$$\therefore \quad [NO_3^*] = \frac{K\,[N_2O_5]}{[NO_2]} \qquad \dots (2)$$

where K is the equilibrium constant for step-1. Combining equations (1) and (2), we get,

$$r = -\frac{1}{2}\frac{d\,[N_2O_5]}{dt} = \frac{d[O_2]}{dt} = \frac{k_3\,[NO_2]\cdot K\,[N_2O_5]}{[NO_2]}$$

Let

$$k = k_3 \cdot K$$

$$\therefore \quad r = k\,[N_2O_5]$$

... **Ans.**

So we have shown the rate to be first order in N_2O_5 by using the assumption that the kinetics is controlled by one step in the mechanism (i.e. by using rate controlling method).

Ex. 1.31 : The formation and decomposition of phosgene proceeds as

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$$CO + Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} COCl_2$$

Forward reaction : $r_{COCl_2} = k_1\,C_{Cl_2}^{3/2} \cdot C_{CO}$

Reverse reaction : $-r_{COCl_2} = k_2\,C_{Cl_2}^{1/2} \cdot C_{COCl_2}$

Two mechanisms have been suggested.

Mechanism I :

$$Cl_2 \rightleftharpoons 2\,Cl^* \qquad \text{fast, at equilibrium}$$

$$Cl^* + CO \rightleftharpoons COCl^* \qquad \text{fast, at equilibrium}$$

$$COCl^* + Cl_2 \rightleftharpoons COCl_2 + Cl^* \qquad \text{slow and rate controlling}$$

Mechanism II :

$$Cl_2 \rightleftharpoons 2\,Cl^* \qquad \text{fast, at equilibrium}$$

$$Cl^* + Cl_2 \rightleftharpoons Cl_3^* \qquad \text{fast, at equilibrium}$$

$$Cl_3^* + CO \rightleftharpoons COCl_2 + Cl^* \quad \text{slow and rate controlling}$$

Determine which of above mechanisms is consistent with the given experimental rates.

Solution : The formation of phosgene proceeds as

$$CO + Cl_2 \xrightarrow{k_1} COCl_2$$

with the rate equation

$$r_{COCl_2} = \frac{dC_{COCl_2}}{dt} = k_1\, C_{CO}\, C_{Cl_2}^{3/2}$$

Let us try the mechanism-I :

Step 1: $$Cl_2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} 2\,Cl^* \qquad \text{(fast, at equilibrium)}$$

Step 2: $$Cl^* + CO \underset{k_6}{\overset{k_5}{\rightleftharpoons}} COCl^* \qquad \text{(fast, at equilibrium)}$$

Step 3: $$COCl^* + Cl_2 \underset{k_8}{\overset{k_7}{\rightleftharpoons}} COCl_2 + Cl^* \quad \text{(slow, rate controlling)}$$

As the step-3 is slow, it is rate determining step i.e. step-3 gives the rate of overall reaction So the rate of formation/production of $COCl_2$ is given as

$$COCl^* + Cl_2 \xrightarrow{k_7} COCl_2 + Cl^*$$

$$r_{COCl_2} = \frac{dC_{COCl_2}}{dt} = k_7\, C_{COCl^*} \cdot C_{Cl_2} \qquad \text{... (1}$$

Since the step-1 and step-2 are fast at equilibrium, we can write equilibrium constants i terms of concentrations of species involved as :

For step-1, $$K_1 = \frac{k_3}{k_4} = \frac{C_{Cl^*}^2}{C_{Cl_2}}$$

$$\therefore \quad C_{Cl^*}^2 = \frac{k_3}{k_4} \cdot C_{Cl_2}$$

$$C_{Cl^*} = (k_3/k_4 \cdot C_{Cl_2})^{1/2} \qquad \text{... (2)}$$

For step-2, $$\frac{k_5}{k_6} = \frac{C_{COCl^*}}{C_{CO} \cdot C_{Cl^*}}$$

$$\therefore \quad C_{COCl^*} = \frac{k_5}{k_6} \cdot C_{CO} \cdot C_{Cl^*} \qquad \text{... (}$$

Putting value of C_{Cl^*} from equation (2) into equation (3), we get,

$$C_{COCl^*} = \frac{k_5}{k_6}\, C_{CO} \left(\frac{k_3}{k_4} \cdot C_{Cl_2}\right)^{1/2}$$

$$C_{COCl^*} = \frac{k_5}{k_6} \left(\frac{k_3}{k_4}\right)^{1/2} \cdot C_{CO}\, C_{Cl_2}^{1/2} \qquad \text{...}$$

Putting value of $C_{COCl}{}^{*}$ from equation (4) into equation (1), we get,

$$r_{COCl_2} = \frac{d\,C_{COCl_2}}{dt} = k_7 \cdot \frac{k_5}{k_6} \cdot \left(\frac{k_3}{k_4}\right)^{1/2} \cdot C_{CO} \cdot C_{Cl_2}^{1/2} \cdot C_{Cl_2}$$

Let $$k_1 = k_7 \cdot \frac{k_5}{k_6} \cdot \left(\frac{k_3}{k_4}\right)^{1/2}$$

$\therefore$ $$r_{COCl_2} = k_1\, C_{CO} \cdot C_{Cl_2}^{3/2} \qquad \text{... Ans.}$$

So the mechanism-I agrees with given experimental forward reaction rate.

$$CO + Cl_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} COCl_2 \quad \text{(given reaction)}$$

can be written as (as it involves two elementary reactions)

(A) $CO + Cl_2 \xrightarrow{k_1} COCl_2$ (formation of phosgene)

(B) $COCl_2 \xrightarrow{k_2} CO + Cl_2$ (decomposition of phosgene)

Now we will derive the rate equation for decomposition of phosgene i.e. for reverse reaction (B).

As the step-3 is rate determining one, the rate of decomposition of $COCl_2$ is given as :

Step 3 : Reverse reaction :

$$COCl_2 + Cl^{*} \xrightarrow{k_8} COCl^{*} + Cl_2$$

$$-r_{COCl_2} = \frac{-dC_{COCl_2}}{dt} = k_8 \cdot C_{COCl_2} \cdot C_{Cl}{}^{*} \qquad \text{... (5)}$$

We have, $$C_{Cl}{}^{*} = \left(\frac{k_3}{k_4} \cdot C_{Cl_2}\right)^{1/2}$$

Putting value of $C_{Cl}{}^{*}$ into equation (5), we get

$$-r_{COCl_2} = \frac{-dC_{COCl_2}}{dt} = k_8\; C_{COCl_2} \cdot \left(\frac{k_3}{k_4} \cdot C_{Cl_2}\right)^{1/2}$$

Let $$k_2 = k_8\,(k_3/k_4)^{1/2}$$

$$-r_{COCl_2} = k_2 \cdot C_{COCl_2} \cdot C_{Cl_2}^{1/2} \qquad \text{... Ans.}$$

Hence, mechanism suggested agrees with given reverse reaction rates, so the mechanism-I is consistent with the given experimental rates.

Ex. 1.32 : The gas phase decomposition of azomethane

$$(CH_3)_2\,N_2 \rightarrow C_2H_6 + N_2$$

proceeds with rate

$$r_{N_2} = \frac{k_1\, C_{AZO}^2}{1 + k'\, C_{AZO}}, \quad \text{where AZO} \equiv \text{azomethane}$$

Devise a mechanism to explain this rate.

Solution : $(CH_3)_2\,N_2 \rightarrow C_2H_6 + N_2$, gas phase reaction

follows the rate law

$$r_{N_2} = \frac{k_1\, C_{AZO}^2}{1 + k'\, C_{AZO}}, \quad \text{where AZO} \equiv \text{azomethane}$$

The suggested mechanism is :

Step 1 : $(CH_3)_2\,N_2 + (CH_3)_2\,N_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (CH_3)_2\,N_2 + (CH_3)_2\,N_2^*$

Step 2 : $(CH_3)_2\,N_2^* \xrightarrow{k_3} C_2H_6 + N_2$

$$AZO + AZO \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AZO + AZO^*$$

$$AZO^* \xrightarrow{k_3} C_2H_6 + N_2$$

In decomposition of azomethane, the active intermediate (activated complex) is formed by the reaction

$$AZO + AZO \xrightarrow{k_1} AZO + AZO^*$$

The activated complex after being form follows two paths.

In one path, the activated molecule become deactivated through collision with other molecule,

$$AZO^* + AZO \xrightarrow{k_2} AZO + AZO$$

This reaction is reverse of reaction by which activated molecule is formed.

In second path, the active intermediate decomposes spontaneously to form ethane and nitrogen.

$$AZO^* \xrightarrow{k_3} C_2H_6 + N_2$$

The rate of formation of N_2 is given by

$$r_{N_2} = k_3\,C_{AZO^*} \qquad \dots (1)$$

According to steady state approximation, the net rate of formation of active intermediate is zero.

$$\therefore \quad \frac{dC_{AZO^*}}{dt} = 0 = k_1\,C_{AZO}^2 - k_2\,C_{AZO} \cdot C_{AZO^*} - k_3\,C_{AZO^*} \qquad \dots (2)$$

(AZO is formed by forward reaction, disappears by reverse reaction and spontaneous decomposition reaction) Equation (2) yields

$$k_1\,C_{AZO}^2 = C_{AZO^*}\,[k_2\,C_{AZO} + k_3]$$

$$C_{AZO^*} = \frac{k_1\,C_{AZO}^2}{[k_3 + k_2\,C_{AZO}]} \qquad \dots (3)$$

Putting value of C_{AZO^*} from equation (3) into equation (1), we get,

$$r_{N_2} = \frac{k_3 \cdot k_1\,C_{AZO}^2}{[k_3 + k_2\,C_{AZO}]}$$

$$r_{N_2} = \frac{k_1\,C_{AZO}^2}{1 + (k_2/k_3)\,C_{AZO}}$$

Let $\quad k' = k_2/k_3$

$$r_{N_2} = \frac{k_1\,C_{AZO}^2}{1 + k'\,C_{AZO}} \qquad \dots \textbf{Ans.}$$

So the suggested mechanism agrees with the observed rate/experimental rate.

We have,

$$r_{N_2} = \frac{k_1 k_3 C^2_{AZO}}{(k_3 + k_2 C_{AZO})}$$

At low concentration,

$$k_2 C_{AZO} << k_3$$

$$\therefore \quad r_{NO_2} = k_1 C^2_{AZO}$$

So the reaction follows second order kinetics.

At high concentration,

$$k_2 C_{AZO} >> k_3$$

$$\therefore \quad r_{N_2} = \frac{k_1 k_3}{k_2} C_{AZO} = k C_{AZO}$$

So the reaction follows first order kinetics.

In describing reaction order for this decomposition, one would say that at high concentrations of azomethane, the reaction is apparent first order and at low concentrations of azomethane, the reaction is apparent second order with respect to azomethane.

Ex. 1.33 : The primary reaction occurring in the homogeneous decomposition of nitrous oxide is found to be

$$N_2O \rightarrow N_2 + \frac{1}{2} O_2$$

with rate

$$-r_{N_2O} = \frac{k_1 [N_2O]^2}{1 + k' [N_2O]}$$

Devise a mechanism to explain this observed rate.

Solution : The gas phase decomposition of N_2O proceeds as

$$N_2O \rightarrow N_2 + \frac{1}{2} O_2$$

with rate

$$-r_{N_2O} = \frac{k_1 [N_2O]^2}{1 + k_2 [N_2O]}$$

The proposed mechanism is :

Step 1: $N_2O + N_2O \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O + N_2O^*$

Step 2: $N_2O^* \xrightarrow{k_3} N_2 + \frac{1}{2} O_2$

The rate of reaction is given rate of formation of N_2.

$$\therefore \quad r_{N_2} = k_3 [N_2O^*] \qquad \dots (1)$$

As per steady state approximation, the net rate of formation of active intermediate $[N_2O^*]$ is zero.

$$\therefore \quad r_{N_2O^*} = \frac{d [N_2O^*]}{dt} = k_1 [N_2O]^2 - k_2 [N_2O] [N_2O^*] - k_3 [N_2O^*]$$

$$= 0$$

$$\therefore \quad k_1 [N_2O]^2 - k_2 [N_2O] [N_2O^*] - k_3 [N_2O^*] = 0$$

$$k_2 [N_2O] [N_2O^*] + k_3 [N_2O^*] = k_1 [N_2O]^2$$

$$\therefore \quad [N_2O^*] = \frac{k_1 [N_2O]^2}{k_3 + k_2 [N_2O]} \qquad \ldots (2)$$

Putting the value of $[N_2O^*]$ from equation (2) in equation (1), we get,

$$r_{N_2} = \frac{k_3 \cdot k_1 [N_2O]^2}{k_3 + k_2 [N_2O]}$$

We have,

$$r_{N_2} = -r_{N_2O}$$

$$\therefore \quad -r_{N_2O} = r_{N_2} = \frac{k_1 [N_2O]^2}{1 + \left(\frac{k_2}{k_3}\right) [N_2O]}$$

Let

$$k' = k_2/k_3$$

$$-r_{N_2O} = r_{N_2} = \frac{k_1 [N_2O]^2}{1 + k' [N_2O]}$$

$$-r_{N_2O} = r_{N_2} = \frac{k_1 [N_2O]^2}{1 + k' [N_2O]} \qquad \ldots \textbf{Ans.}$$

So the suggested mechanism is consistent with the observed rate.

At low concentrations of N_2O,

$$k' [N_2O] << 1$$

$$\therefore \quad -r_{N_2O} = k_1 [N_2O]^2$$

The rate follows second order kinetics i.e. the rate is second order with respect to N_2O.

At high N_2O concentrations,

$$k' [N_2O] >> 1$$

$$\therefore \quad -r_{N_2O} = r_{N_2} = k [N_2O]$$

where

$$k = k_1/k'$$

∴ The rate is first order with respect to N_2O. ... **Ans.**

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Chapter ... ❷

INTERPRETATION OF BATCH REACTOR DATA

In order to obtain a size of a chemical reactor by making use of appropriate design equation, one must know the rate equation/rate law for a specific reaction as the term–rate of reaction is involved in the design equation of a reactor.

The determination of complete rate equation involves two steps : (1) finding of concentration dependency at fixed temperature and (2) finding of temperature dependency of rate constants.

Suppose the irreversible reaction

$$aA + bB \rightarrow \text{products}$$

has the rate equation/expression of the form

$$-r_A = k\, C_A^{\alpha}\, C_B^{\beta} \qquad \text{... (2.1)}$$

For making use of this equation in design equation, one must know the value of constants k, α and β. For any isothermal reaction system, for knowing the rate equation, one must know the value of constants k, α and β of the rate equation. In any case the value of constants of the equation can only be found by experiments. So we have to carry reaction runs, collect the kinetic data, and analyse the data.

In this chapter we will deal with ways of obtaining and analysing reaction rate data to obtain the rate equation/rate law for a specific reaction.

In this chapter, in particular, we will deal with the batch reactor for obtaining rate data/kinetic data. The batch reactor is simply a container to hold the contents while they react. The experimental batch reactor is usually operated isothermally and is used primarily for obtaining homogeneous kinetic data i.e. for collecting data of homogeneous reactions.

By performing the experiments what is to be determined is the extent of reaction at various times and this can be done by carrying out a chemical reaction in experimental batch reactor and by measuring and recording :

(i) concentration of a given component at different times during the course of reaction (i.e. data is collected by following concentration of a given component);

(ii) total pressure of a reaction system at different times during the course of reaction;

(iii) volume of a reaction system at different times during the course of reaction;

(iv) physical property of a fluid such as the electrical conductivity or refractive index at different times during the course of reaction.

So depending upon the situation, we carry out a chemical reaction in a experimental batch reactor. We have to collect the data of either concentration of a given component as a function of time, total pressure of constant volume system as a function of time or volume of reacting system as a function of time of constant pressure system. The last two ways are generally adopted in case of gas phase reaction with changing number of moles or wherein one of the components of the system is a gas. The experiments so performed are called the kinetic runs and data thus obtained is also called the kinetic data.

The data is tabulated as :

C_{A1}	C_{A2}	C_{A3}	C_{A4}	C_{A5}	C_{A6}	...
t_1	t_2	t_3	t_4	t_5	t_6	...

P_1	P_2	P_3	P_4	P_5	...
t_1	t_2	t_3	t_4	t_5	...

V_1	V_2	V_3	V_4	V_5	...
t_1	t_2	t_3	t_4	t_5	...

This way, one can obtain the rate data.

The data is then used to find the rate equation that satisfactorily fits the data. There are various methods available for analysing the rate data. i.e. for interpretation of data. The **methods used to analyse the kinetic data/rate data** (or to determine order of a reaction) are :

(i) Integral method.
(ii) Differential method.
(iii) Initial rate method.
(iv) Half-life method.
(v) Ostwald's isolation method.

To find out the specific reaction rate (rate constant) and reaction order with respect to one of the reactants, integral and differential methods of (rate) analysis require only one experiment. On the other hand, the methods of half-life and initial rates require many experiments at different initial conditions to determine rate constant and the reaction order.

Integral v/s differential method :

In case of integral method of analysis of rate data, we assume a particular form of rate equation, do the integration and mathematical manipulations, and then finally see that the plot of certain concentration function v/s time yields a straight line or not. After plotting data if we obtain a reasonably good straight line then we surely say that the rate equation (assumed) satisfactorily fits the data.

In case of differential method of analysis, we assume a particular form of rate equation and test the fit of the rate equation to the data directly, and without any integration. Here we have to first find out $\frac{1}{V}$ (dN/dt) from the data, as the rate equation is differential equation before attempting the fitting procedure.

Integral method is easy to use (to test the fit of the data).

Differential method is not that much easy. It is cumbersome one.

Integral method is useful for testing relatively simple rate equations/expressions.

Differential method is useful for testing more complicated rate expressions.

Integral method can be used when also the scattered data is available.

Differential method is used only when more accurate and large amount of data are available.

Integral method can only test this or that particular form of rate equation.

Differential method can be used to develop the rate equation to fit the data.

In general, it is suggested that, first make use of (try with) the integral method of analysis and if not successful then try the differential method of analysing the kinetic data.

These methods will be discussed in detail latter.

Constant-Volume Batch Reactor :

The term constant-volume batch reactor means a constant volume reaction system, as when we mention the constant-volume batch reactor, we are really referring to the volume of the reaction system (reaction mixture) and not the volume of a reactor. The reaction systems that undergo no change in volume as the reaction progresses are called as constant-volume or constant density systems. For such systems, there is invarience of either volume or density during the reaction process or during the course of reaction.

The examples of constant-volume systems :

In case of gas phase reaction with changing number of moles carried out in batch reactor, the reactor is usually a sealed vessel (closed vessel) provided with appropriate instruments to measure pressure and temperature within the reactor. The volume of the reaction mixture within this vessel is fixed and will not change, and is therefore a constant-volume system. The gas mixture within the vessel occupies volume of the vessel and though the number of moles are say increasing, as the reaction proceeds, they will occupy the same volume which results in compression of gas and increase in the pressure in the vessel. The laboratory bomb reactor is a constant-volume batch reactor.

The gas phase reaction process yielding number of moles of product equal to number of moles of reactants consumed (i.e. a gas phase reaction with no change in number of moles e.g. $A + 2B \rightarrow 3R$) is a constant-volume system.

Consider a reaction

$$CO + H_2O = CO_2 + H_2$$

In this reaction, two moles of products are formed from two moles of reactants. Whenever the number of product molecules produced are equal to the number of reactant molecules reacted by reaction at a given temperature and pressure then the volume of the reacting mixture/reaction system will not change. So this is also a constant-volume system.

Almost all liquid phase reaction systems are constant-volume systems as the density change with reaction is usually small and can be neglected. Most liquid phase organic reactions do not undergo change in density sufficiently during the reaction. In case of liquid phase reactions taking place in solution, the changes in density of the solute during reaction do not affect the overall density of the solution as the solvent usually dominates the situation. So these are constant-volume reaction systems.

The rate of reaction of any component i is given by

$$r_i = \frac{1}{V} \cdot \frac{dN_i}{dt} \qquad \text{... (2.2)}$$

For **constant-volume system** as the volume is constant, we can take V inside the differential and write the rate of reaction in terms of concentration of i :

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{d\,(N_i/V)}{dt} = \frac{dC_i}{dt}, \quad \text{as } C_i = N_i/V \qquad \text{... (2.3)}$$

If A is the reactant that is disappearing during the course of reaction then the rate of disappearance of A i.e. $-r_A$ is given by

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

Alternatively, $$r_i = \frac{1}{V}\frac{dN_i}{dt}$$

We have, $$N_i = C_iV$$

$$r_i = \frac{1}{V}\left[\frac{d\,(C_iV)}{dt}\right]$$

$$= \frac{1}{V}\left[V\frac{dC_i}{dt} + C_i\frac{dV}{dt}\right]$$

For constant-volume system, $dV/dt = 0$ as $V = V_o$

vol. [illegible] fie

pre [illegible] vol.

$$\therefore \quad r_i = \frac{1}{V}\left[V\frac{dC_i}{dt}\right] = \frac{dC_i}{dt}$$

For reacting component A,

$$(-r_A) = \frac{-dC_A}{dt} \tag{2.4}$$

If A is a gaseous material for which ideal gas law is applicable, then

$$C_A = N_A/V = p_A/RT$$

$$\therefore \quad (-r_A) = \frac{-dC_A}{dt} = \frac{-d\,(p_A/RT)}{dt}$$

$$(-r_A) = \frac{-1}{RT}\,\frac{dp_A}{dt} \tag{2.5}$$

For any component,

$$r_i = \frac{1}{RT}\,\frac{dp_i}{dt} \tag{2.6}$$

Relation of concentration and conversion for constant-volume batch system :

The concentration of A is the number of moles of A per unit volume.

$$C_A = \frac{N_A}{V} \tag{2.7}$$

where C_A is concentration and N_A is the moles of A remained (unreacted) at any time t during the course of reaction.

If X_A is the fractional conversion of A

$$X_A = \frac{\text{moles of A reacted}}{\text{initial moles of A}}$$

$$N_{Ao} = \text{initial moles of A}$$

$$N_{Ao}X_A = \text{moles of A reacted}$$

Material balance of A : A unreacted = A initially – A reacted

$$N_A = N_{Ao} - N_{Ao}X_A$$

$$N_A = N_{Ao}(1 - X_A)$$

$$\therefore \quad C_A = \frac{N_A}{V} = \frac{N_{Ao}(1 - X_A)}{V}$$

For constant-volume system, $V = V_o$

$$\therefore \quad C_A = \frac{N_{Ao}(1 - X_A)}{V_o}$$

$$N_{Ao}/V_o = C_{Ao}$$

$$\therefore \quad \boxed{C_A = C_{Ao}(1 - X_A)} \tag{2.7 a}$$

The above equation relates concentration of A at any time t to initial concentration of A through the fractional conversion of A for constant-volume system.

Finding concentrations of B, C and D :

Consider a chemical reaction :

$$aA + bB \rightarrow cC + dD$$

Let there be N_{Ao} moles of A and N_{Bo} moles of B in the reactor. Let X_A be the fractional conversion of A. Then moles of A reacted/consumed = $N_{Ao}X_A$ mole.

$$\text{Moles of A remaining} = N_A = N_{Ao}(1 - X_A)$$

$$A + b/a\,B \rightarrow c/a\,C + d/a\,D$$

From reaction it is clear that for every mole of A reacted, b/a moles of B must react.

$$\therefore \quad \text{Moles of B reacted} = \frac{b}{a} \times \text{moles of A reacted}$$

$$= \left(\frac{b}{a}\right) N_{Ao} X_A$$

Moles of B remaining at any time t are

$$N_B = N_{Bo} - \left(\frac{b}{a}\right) N_{Ao} X_A$$

Concentration of B at any time t is given by

$$C_B = \frac{N_B}{V} = \frac{N_{Bo} - (b/a)\, N_{Ao}\, X_A}{V}$$

For constant-volume batch systems,

$$C_B = \frac{N_{Bo} - (b/a)\, N_{Ao}\, X_A}{V_o}$$

$$\boxed{C_B = C_{Bo} - \left(\frac{b}{a}\right) C_{Ao}\, X_A} \qquad \text{... (2.8)}$$

If b = a, then

$$C_B = C_{Bo} - C_{Ao} X_A$$

$$C_B = C_{Bo} (1 - X_B)$$

$$X_B = \frac{\text{moles B reacted}}{\text{moles B initially}}$$

$$N_{Bo} X_B = (b/a)\, N_{Ao} X_A$$

$$\frac{N_{Bo} X_B}{V_o} = (b/a) \frac{N_{Ao} X_A}{V_o}$$

$$C_{Bo} X_B = (b/a)\, C_{Ao} X_A$$

For b = a,

$$C_{Bo} X_B = C_{Ao} X_A$$

Similarly,

$$C_C = \frac{N_C}{V} = \frac{N_{Co} + (c/a)\, N_{Ao}\, X_A}{V}$$

For $V = V_o$,

$$\boxed{C_C = C_{Co} + (c/a)\, C_{Ao}\, X_A} \qquad \text{... (2.9)}$$

and

$$\boxed{C_D = C_{Do} + (d/a)\, C_{Ao}\, X_A} \qquad \text{... (2.10)}$$

For flow systems :

For flow system, the concentration of A at a given point is given by

$$C_A = F_A/v \qquad \text{... (2.11)}$$

where v is the volumetric flow rate at that time. If F_{Ao} is entering flow rate to the reactor in moles/time and X_A is a conversion of A, then

change in moles of A within the reactor = $-F_{Ao}\, X_A$

Molal flow rate of A from reactor = $F_A = F_{Ao}\,(1 - X_A)$

For liquids, volume change with reaction is negligible. So we can take

$$v = v_o$$

$$\therefore \quad C_A = \frac{F_A}{V} = \frac{F_{Ao}(1-X_A)}{v_o} \quad \text{... (2.12)}$$

$$C_A = C_{Ao}(1-X_A) \text{ (for constant-volume system)} \quad \text{... (2.13)}$$

However, for gas phase reaction the volumetric flow rate most often changes during the course of reaction due to change in number of moles or temperature or pressure.

Similarly, for component B,

$$C_B = \frac{F_B}{v} = \frac{F_{Bo}-(b/a)\,F_{Ao}\,X_A}{v} \quad \text{... (2.14)}$$

For $v = v_o$

$$C_B = \frac{F_{Bo}-(b/a)\,F_{Ao}\,X_A}{v_o}$$

$$C_B = C_{Bo}-(b/a)\,C_{Ao}\,X_A \quad \text{... (2.15)}$$

Analysis of Total Pressure Data obtained in a Constant-volume System :

The data–total pressure as a function of time of a reacting system during the course of a reaction at a given temperature is generally collected in a laboratory bomb reactor in case of gas phase reaction with change in number of moles.

Now we will develop a general expression which relates the changing total pressure P of the reacting system to the changing partial pressure or concentration of any of the reaction components of a gas phase reaction involving change in number of moles carried out isothermally for a given initial condition and for any reaction stoichiometry.

With the help of developed expressions between P and partial pressure of components of reaction system, the total pressure data may be converted into partial pressure or concentration data or same may be used directly in rate equation in terms of partial pressure or concentration by making use of these developed expressions for analysing/interpreting the data.

Consider isothermal gas phase reaction of the type

$$aA + bB + \ldots \rightarrow rR + sS + \ldots$$

Let, at time t = 0,

$N_{Ao}, N_{Bo}, \ldots N_{Ro}, N_{So} \ldots, N_{inert}$ be the moles of A, B, ..., R, S, ..., and inerts respectively present in the reaction system. Let P_o be the initial total pressure of the system (i.e. total pressure at t = 0).

Let x be the moles of A reacted within the time period t. Then at any time t,

$$\text{Moles of A unreacted} = \text{initial moles of A} - \text{moles of A reacted}$$

$$= N_{Ao} - x$$

$$\therefore \quad \text{Moles of A at time t} = N_{Ao} - x$$

From reaction, we have :

$$a \text{ moles of A} \equiv b \text{ moles of B}$$

i.e. for a moles of A reacted, b moles of B must react.

$$\frac{a}{a} \text{ moles of A} \equiv \frac{b}{a} \text{ moles of B}$$

i.e. for every mole of A reacted, b/a moles of B must react.

$$\therefore \quad \text{Moles of B reacted} = \frac{b/a}{1} \times x = \frac{b}{a}\,x \text{ mol}$$

$$\text{Moles of B unreacted} = N_{Bo} - \frac{b}{a}\,x \text{ mol}$$

$$\text{Moles of B at time t} = N_{Bo} - \frac{b}{a}\,x$$

Similarly, for products R and S :

$$\text{Moles of R at time t} = \text{Initial moles + Moles of R produced at t by reaction}$$

$$= N_{Ro} + \frac{r}{a}\,x$$

$$\text{Moles of S at time t} = N_{So} + \frac{s}{a}\,x$$

$$\text{Moles of inerts at time t} = \text{Moles of inerts at } (t = 0) = N_{inerts}$$

(as moles of inerts remain unchanged during reaction.)

Let N_o be the initial total moles of reaction system.

$$\therefore \quad N_o = N_{Ao} + N_{Bo} + \ldots + N_{Ro} + N_{So} + \ldots + N_{inert}$$

Let N be the moles of system at any time t.

$$\therefore \quad N = (N_{Ao} - x) + (N_{Bo} - b/a \cdot x) + \ldots + \left(N_{Ro} + \frac{r}{a}\,x\right) + \left(N_{So} + \frac{s}{a}\,x\right) + \ldots + N_{inerts}$$

$$= (N_{Ao} + N_{Bo} + \ldots + N_{Ro} + N_{So} + \ldots + N_{inerts}) - x - \frac{b}{a}x \;\ldots + \frac{r}{a}\;x + \frac{r}{s}\,x + \ldots$$

$$N = N_o + \frac{r}{a} + \frac{s}{a} + \;\ldots\ldots - x - \frac{b}{a}\,x \ldots\ldots$$

$$N = N_o + \frac{x}{a}\,[r + s + \ldots - a - b - \ldots]$$

$$N = N_o + \frac{x}{a}\,[\Delta n]$$

where $\Delta n = [r + s + \ldots - a - b - \ldots]$

$$\therefore \quad x = \frac{a\,(N - N_o)}{\Delta n} \qquad \ldots (2.16)$$

Assume that ideal gas law is applicable.

For reactant A, we have

$$C_A = \frac{N_A}{V}$$

and

$$p_A V = N_A R T$$

$$\therefore \quad \frac{p_A}{RT} = C_A = \frac{N_A}{V}$$

C_A is concentration of A, p_A is the partial pressure of A, and N_A is the moles of A remained at any time t.

$$\therefore \quad N_A = N_{Ao} - x$$

$$\therefore \quad p_A = C_A RT = \left(\frac{N_{Ao} - x}{V}\right) RT \qquad \ldots (2.17)$$

Combining equations (2.16) and (2.17), we get

$$p_A = C_A RT = \frac{\left[N_{Ao} - \frac{a(N - N_o)}{\Delta n}\right] RT}{V}$$

$$= \frac{N_{Ao}}{V} RT - \frac{a}{\Delta n} \frac{(N - N_o) RT}{V}$$

$$= \frac{N_{Ao} RT}{V} - \frac{a}{\Delta n}\left[\frac{N}{V} RT - \frac{N_o}{V} RT\right]$$

For constant-volume, $V = V_o$

$$\therefore \quad p_A = \frac{N_{Ao} RT}{V_o} - \frac{a}{\Delta n}\left[\frac{N}{V} RT - \frac{N_o RT}{V_o}\right]$$

We have $\quad PV = NRT$

$$\therefore \quad p_A = C_A RT = p_{Ao} - \frac{a}{\Delta n} [P - P_o] \qquad \text{... (2.18)}$$

where P_o is the initial total pressure of reaction system, P is the total pressure of reaction system at any time t, and p_{Ao} is the initial partial pressure of A.

Similarly, for B,

$$p_B = C_B RT = p_{Bo} - \frac{b}{\Delta n} [P - P_o] \qquad \text{... (2.19)}$$

$$p_R = C_R RT = \frac{N_R}{V} RT = \left[\frac{N_{Ro} + \frac{r}{a} x}{V}\right] RT$$

$$p_R = C_R RT = \frac{N_{Ro} RT}{V} + \frac{\left[\frac{r}{a} \cdot \frac{a(N - N_o)}{\Delta n}\right] RT}{V}$$

We have, $\quad V = V_o$

$$p_R = C_R RT = p_{Ro} + \frac{r}{\Delta n} [P - P_o] \qquad \text{... (2.20)}$$

Equation (2.18) relates the concentration or partial pressure of reactant A to the total pressure P at any time t, initial partial pressure of A, and initial total pressure of the system P_o. So the equation (2.18) gives C_A or p_A of component A as a function of P, p_{Ao} and P_o.

The equations (2.18) and (2.20) are the desired relationships between the total pressure of the system and partial pressure of the reacting materials.

Consider a gas phase reactions :

(i) $\quad N_2O_4 \rightarrow 2NO_2 \quad$ i.e. $\quad A \rightarrow 2R$

$$a = 1, \quad \Delta n = 2 - 1 = 1$$

$$\therefore \quad p_A = p_{Ao} - \frac{1}{1}(P - P_o), \text{ desired relationship}$$

$$p_A = p_{Ao} - (P - P_o)$$

For pure N_2O_4, initially, we have $p_{Ao} = P_o$

$$\therefore \quad p_A = P_o - (P - P_o) = (2P_o - P)$$

$$p_A = (2P_o - P), \text{ desired relationship}$$

(ii)
$$N_2O \rightarrow N_2 + \frac{1}{2} O_2$$

i.e.
$$A \rightarrow R + \frac{1}{2} S$$

$$a = 1, \quad \Delta n = 1.5 - 1 = 0.5$$

$$p_A = p_{Ao} - \frac{1}{0.5} (P - P_o)$$

$$p_A = p_{Ao} - 2 (P - P_o)$$

For pure N_2O, initially, $p_{Ao} = P_o$

$\therefore$
$$p_A = P_o - 2 (P - P_o)$$
$$p_A = (3 P_o - 2 P)$$

(iii) For reaction :

$$N_2O_5 \rightarrow N_2O_4 + \frac{1}{2} O_2$$

With 60 mole % N_2O_5 and 40 mole % inerts initially,

$$A \rightarrow R + \frac{1}{2} S$$

$\therefore$ $p_A = p_{Ao} - 2 (P - P_o)$ as a = 1 and $\Delta n = 1.5 - 1 = 0.5$

$p_{Ao} = 0.60 \ P_o$ as initially N_2O_5 is 60 mole %

$\therefore$ $p_A = 0.6 \ P_o - 2 (P - P_o)$

$p_A = (2.6 \ P_o - 2 \ P)$

This way we can generate the relationship between p_A and P, P_o for pure gas or for gas with inerts.

Use of ideal gas law to calculate C_{Ao}:

Suppose that the gas mixture containing 50 mole % A and 50 mole % inerts is there in a closed vessel at pressure of 10 atm and temperature of 150 °C.

Partial pressure of A = molefraction of A × total pressure

$$p_{Ao} = \left(\frac{\text{mole \%}}{100}\right) P_o$$

$$= \frac{50}{100} \times 10 = 5 \text{ atm}$$

$\int x^n = \frac{x^{n+1}}{n+1}$ $n \neq 1$

$n = -1$

$$C_{Ao} = \frac{p_{Ao}}{RT}$$

$$T = 150\,^{\circ}C = 423 \text{ K}$$

$$R = 0.08206 \ l\cdot\text{atm/(mol}\cdot\text{K)}$$

$$C_{Ao} = \frac{5}{0.08206 \times 423}$$

$$= 0.144 \text{ mol}/l \text{ or mol/dm}^3 \text{ or kmol/m}^3$$

Integral Method of Analysis of Rate Data : LD

For determining the order of reaction, order by the integral method, we assume the reaction order and integrate the differential equation. For order we assume to be correct, the plot of concentration function v/s time has to be linear. If plot is not linear, assumed value for reaction order is incorrect and new value of it should be tried. The integral method uses a trial-and-error procedure to determine the reaction order. This method is often used to evaluate rate constants at different temperatures to determine the activation energy when reaction order is known.

The general step-wise procedure of analysis of kinetic data by integral method is given below :

(i) Assume a particular form of rate equation. In constant-volume system, the equation for the disappearance of A (reacting component) is of the form :

$$-r_A = \frac{-dC_A}{dt} = kf(C) \qquad \text{... (2.21)}$$

[e.g. for A → R, if we assume disappearance of A to be second order then $-r_A = -dC_A/dt = k\,C_A^2$]

(ii) Rearrange the rate equation to get in the form

$$\frac{-dC_A}{f(C)} = k\,dt \qquad \text{... (2.22)}$$

Here f(C) only involves concentration of reacting materials, which may be expressed in terms of C_A. Hence equation (2.22) may be integrated analytically or graphically to give

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{f(C)} = k\int_0^t dt = kt \qquad \text{... (2.23)}$$

(iii) From the experimental concentration versus time data, determine the numerical values of the integral of equation (2.23) and plot the concentration function. i.e. integral of equation (2.23) against time. As the concentration function (so obtained) is proportional to time, the plot yields a straight line with slope equal to k.

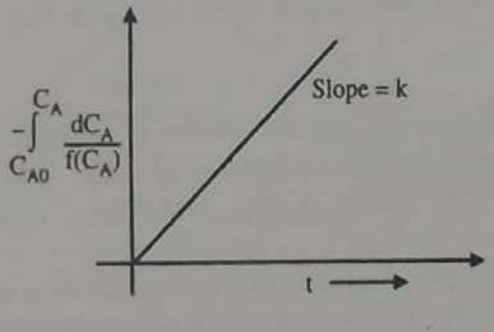


Fig. 2.1 : Test of rate equation by the integral method of analysis

(iv) If the above plot yields a straight line passing through the origin then it may be said that the assumed rate equation (being tested) satisfactorily fits the data i. e. assumed order of reaction with respect to the reactant is correct. The slope of such plot gives us the value of rate constant. If we do not get a straight line then the assumed rate equation (i.e. order of reaction) is rejected as it being incorrect and another rate equation is tried.

In integral method of analysis of rate data, we must know the appropriate concentration function corresponding to a particular rate equation that is proportional to the time (i.e. linear with time). One must be thoroughly familiar with the methods of obtaining linear plots for first, second, etc. order reactions.

Integrated Rate Equations for Different Order Reactions :

Irreversible Unimolecular-Type First-Order Reactions

When the rate of reaction is directly proportional to the concentration of only one reactant, the reaction is said to be of first order.

Consider the reaction

$$A \rightarrow \text{Products} \qquad \ldots (2.24\ a)$$

The rate of disappearance of A is given by

$$-r_A = \frac{-dC_A}{dt} = kC_A \qquad \ldots (2.24\ b)$$

Rearranging, we get,

$$-\frac{dC_A}{C_A} = k\,dt$$

Integrating the above equation within the limits

$$C_A = C_{A0} \text{ at time } 0$$

and

$$C_A = C_A \text{ at time } t$$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k \int_0^t dt$$

$$-[\ln C_A]_{C_{A0}}^{C_A} = k\,[t]_0^t$$

$$-\ln\left[\frac{C_A}{C_{A0}}\right] = kt \qquad \ldots (2.25)$$

$$\therefore \qquad k = \frac{1}{t}\ln\frac{C_{A0}}{C_A} \qquad \ldots (2.26)$$

Equation (2.25) is the integrated rate equation for first order reaction in terms of concentration.

Characteristics

It is followed from the expression (2.26) that k depends only on the ratio of concentrations C_{A0}/C_A, and has the dimensions of reciprocal of time, (t^{-1}). Hence, rate constant of the first order reaction will be expressed in s^{-1}, min^{-1} etc. and is independent of the units of concentration.

A plot of $-\ln C_A/C_{A0}$ versus t would give a straight line showing that the reaction is of first order. The value of first order rate constant is equal to the slop of line.

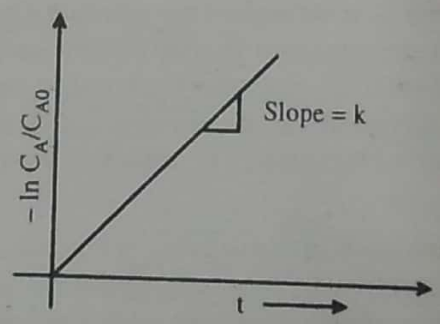


Fig. 2.2 : Test for irreversible first order reaction

An important characteristic of the first order kinetics is that the *half life* i. e. *the time required to reduce the concentration of the reactant to half of its original value*, is independent of the initial concentration of the reactant.

$$-\ln\frac{C_A}{C_{Ao}} = kt$$

$$\therefore \quad t = \frac{1}{k}\ln\frac{C_{Ao}}{C_A}$$

$$= \frac{2.303}{k}\log C_{Ao}/C_A$$

Substituting the condition that when $t = t_{1/2}$, $C_A = C_{Ao/2}$ in above equation, we get

$$t_{1/2} = \frac{2.303}{k}\log 2$$

$$t_{1/2} = \frac{0.693}{k} \qquad \text{... (2.27)}$$

Equation (2.27) gives a direct relation between half-life and rate constant.

Decomposition of nitrogen pentaoxide in the gas phase as well as in organic solvent like CCl_4, hydrolysis of methyl acetate and inversion of cane sugar are some examples of first order kinetics.

Now we will develop the integrated rate expression for first order reaction in terms of conversion.

Fractional conversion (or simply conversion) is a convenient variable often used in place of concentration in engineering work; therefore most of the results which follow will be presented in terms of both C_A and X_A.

The fractional conversion X_A of a given reactant A is defined as the fraction of reactant converted to product.

Let N_{Ao} and N_A be the moles of A at t = 0 and t = t respectively then,

$$X_A = \frac{\text{moles A reacted}}{\text{initial moles of A}}$$

$$= \frac{N_{Ao} - N_A}{N_{Ao}}$$

$$= \frac{N_{Ao}/V - N_A/V}{N_{Ao}/V}$$

$$\frac{C_{Ao} - C_A}{C_{Ao}}$$

$$X_A = 1 - \frac{N_A}{N_{Ao}}$$

$$\frac{N_A}{N_{Ao}} = 1 - X_A$$

$$N_A = N_{Ao}(1 - X_A)$$

For first order reaction of the type

$$A \rightarrow \text{Products}$$

we have,

$$-r_A = -\frac{dC_A}{dt} = k\,.\,C_A \qquad \text{... (2.28)}$$

$$C_A = \frac{N_A}{V} = \frac{N_{Ao}(1 - X_A)}{V} = C_{Ao}(1 - X_A)$$

$$\therefore \quad dC_A = -C_{Ao}\,dX_A$$

$$-dC_A = C_{Ao}\,dX_A$$

Putting values of dC_A and C_A in equation (2.28), we get

$$C_{Ao}\frac{dX_A}{dt} = k\,.\,C_{Ao}(1 - X_A)$$

Rearranging and integrating, it gives

$$\int_0^{X_A} \frac{dX_A}{1-X_A} = k\int_0^t dt$$

$$-\ln(1-X_A) = kt \qquad \ldots(2.29)$$

Plot of $-\ln(1-X_A)$ versus t yields a straight line passing through origin with slope equal to k.

Equation (2.29) is the integrated rate equation for first order reaction in terms of conversion.

Integral.

Irreversible Bimolecular-Type Second Order Reactions :

1D — [illegible]

When the rate of reaction is directly proportional to the concentrations raised to power unity of two different reactants or to the square of concentration of one reactant, the reaction is said to be of second order.

For reaction $2A \rightarrow$ Products ... (2.30 a)

OR

For reaction $A + B \rightarrow$ Products, with equal concentrations of A and B, the rate expression can be given as :

$$-r_A = \frac{-dC_A}{dt} = kC_A^2 \qquad \ldots(2.30\text{ b})$$

$$-\frac{dC_A}{C_A^2} = k\,dt$$

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A^2} = k\int_0^t dt$$

$$-\left[\frac{-1}{C_A}\right]_{C_{A0}}^{C_A} = kt$$

$$\therefore \quad \left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right] = kt \qquad \ldots(2.31)$$

$kt = \frac{1}{c_A} - \frac{1}{c_{A0}}$

$$t = \frac{1}{k}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right] \qquad \ldots(2.32)$$

Equation (2.31) is the integrated rate expression for second order reaction in terms of concentration.

Now we will develop integrated rate expression in terms of conversion.

For reaction $2A \rightarrow$ Products

$$-r_A = -\frac{dC_A}{dt} = kC_A^2$$

$$C_A = C_{A0}(1-X_A),$$

$$dC_A = -C_{A0}\,dX_A$$

$$-dC_A = C_{A0}\,dX_A$$

$$\therefore \quad C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1-X_A)^2$$

Rearranging, we get,

$$\frac{dX_A}{(1-X_A)^2} = k\, C_{Ao}\, dt$$

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)^2)} = k\, C_{Ao} \int_0^{t} dt$$

$$1 - X_A = Y$$

$$-\, dX_A = dY$$

At $X_A = 0,\ Y = 1,$ and at $X_A = X_A,\ Y = 1 - X_A$

$$-\int_1^{1-X_A} \frac{dY}{Y^2} = k\, C_{Ao}\, t$$

$$[1/Y]_1^{1-X_A} = k\, C_{Ao}\, t$$

$$\frac{1}{(1-X_A)} - 1 = k\, C_{Ao}\, t$$

$$\frac{X_A}{1-X_A} = k\, C_{Ao}\, t$$

$$\frac{1}{C_{Ao}}\left[\frac{X_A}{(1-X_A)}\right] = k\,t \qquad \ldots (2.33)$$

Equation (2.33) is the integrated rate equation for second order reaction in terms of conversion.

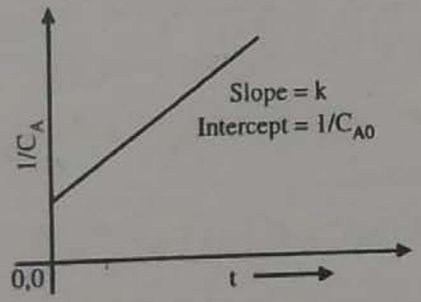


Fig. 2.3

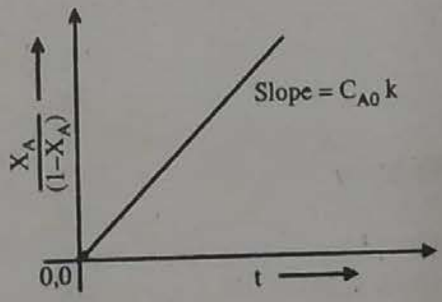


Fig. 2.4

Characteristics :

The plot of $1/C_A$ v/s t should yield a straight line with slope equal to k and intercept equal to $1/C_{Ao}$. The plot of $X_A/(1-X_A)$ v/s t should yield n straight lines with slope equal to C_{Ao} k.

It is evident from equations (2.31) and (2.33) that the dimensions of a second order rate constant of a reaction are (molar concentration × time)$^{-1}$. It is customary to express the second order rate constant in units *l*/(mol.s).

Integrated form for – 2 A → product is

$$\frac{1}{C_A} - \frac{1}{C_{Ao}} = k\,t$$

The half life i. e. the time required to reduce the concentration of the reactant to half of its original value can be found by employing the condition $C_A = C_{Ao}/2$ at the half life time $t = t_{1/2}$ in above equation.

$$\frac{1}{C_{Ao}/2} - \frac{1}{C_{Ao}} = k\,t_{1/2}$$

$$t_{1/2} = \frac{1}{kC_{Ao}} \qquad \ldots (2.34)$$

$$t_{1/2} \propto 1/C_{Ao} \qquad \ldots (2.35)$$

Thus half life for a second order reaction is inversely proportional to the first power of initial concentration. The half life method cannot be used with reactions where the concentrations of A and B are different, since A and B will have different times for half reaction.

Consider the reaction of the type

$$A + B \rightarrow \text{Products} \qquad \ldots (2.36\text{ a})$$

The corresponding rate equation is

$$-r_A = -\frac{d\,C_A}{dt} = k.\,C_A\,.\,C_B \qquad \ldots (2.36\text{ b})$$

Let C_{Ao} and C_{Bo} be the initial concentrations of A and B respectively.

Let $M = C_{Bo}/C_{Ao}$ be the initial molar ratio of reactants.

Let C_A and C_B be the concentrations of A and B at any time t.

Let X_A and X_B be the fractional conversions of A and B respectively.

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao}} \qquad \therefore \text{ Amount of A reacted} = X_A C_{Ao}.$$

$$X_B = \frac{C_{Bo} - C_B}{C_{Bo}} \qquad \therefore \text{ Amount of B reacted} = X_B C_{Bo}.$$

The amounts of A and B which have reacted at any time t are equal and given by

$$X_A.C_{Ao} = X_B.C_{Bo}$$

$$C_A = C_{Ao}\,(1 - X_A)$$

$$-dC_A = C_{Ao}.\,dX_A$$

$$\therefore \qquad -r_A = C_{Ao}\frac{dX_A}{dt} = k\,C_{Ao}\,(1 - X_A)\,C_{Bo}\,(1 - X_B)$$

$$= k\;C_{Ao}\,(1 - X_A)\,(C_{Bo} - C_{Bo}\,X_B)$$

$$C_{Ao}\frac{dX_A}{dt} = k\,C_{Ao}\,(1 - X_A)\,(C_{Bo} - C_{Ao}\,X_A)$$

We have :

$$C_{Bo} = M\,C_{Ao}$$

$$C_{Ao}\frac{dX_A}{dt} = k\,C_{Ao}\,(1 - X_A)\,(M\,C_{Ao} - C_{Ao}.\,X_A)$$

$$C_{Ao}\frac{dX_A}{dt} = k\,C_{Ao}^2\,(1 - X_A)\,(M - X_A)$$

Rearranging, we get,

$$\frac{dX_A}{(1 - X_A)\,(M - X_A)} = k\,C_{Ao}\,dt$$

Integrating above equation within the limits

At $t = 0$, $X_A = 0$

At $t = t$, $X_A = X_A$

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)\,(M - X_A)} = k\,C_{Ao}\int_0^t dt$$

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)\,(M - X_A)} = k\,C_{Ao}\,t$$

Break the L.H.S. of above equation into partial fraction and then integrate it.

$$\frac{A}{1-X_A}+\frac{B}{M-X_A} = \frac{1}{(1-X_A)(M-X_A)}$$

$$\frac{A(M-X_A)+B(1-X_A)}{(1-X_A)(M-X_A)} = \frac{1}{(1-X_A)(M-X_A)}$$

$A(M-X_A)+B(1-X_A)=1$

Putting $X_A = 1$, we get $A(M-1)=1 \quad \therefore \; A = 1/M-1$

Putting $X_A = M$, we get $B = -1/M-1$

$$\int_0^{x_A}\frac{dx}{(ax-b)} = \frac{1}{a}\ln(ax-b)$$
$$= \frac{1}{m}\ln(m-x_A$$

$$\frac{1}{(M-1)}\left[\int_0^{X_A}\frac{dX_A}{(1-X_A)} - \int_0^{X_A}\frac{dX_A}{(M-X_A)}\right] = k.C_{Ao}\,t$$

$$\frac{1}{(M-1)}\left[-\ln(1-X_A)+\ln\frac{(M-X_A)}{M}\right] = k.C_{Ao}\,t$$

$$\frac{1}{(M-1)}\ln\frac{(M-X_A)}{M(1-X_A)} = k\,C_{Ao}\,t$$

$$\therefore \quad \boxed{\ln\left[\frac{(M-X_A)}{M(1-X_A)}\right] = C_{Ao}(M-1)\,k\,t}\,,\; M \neq 1 \qquad \ldots(2.37)$$

Equation (2.37) is the desired integrated rate equation for second order reaction with $C_{Ao} \neq C_{Bo}$ in terms of conversion.

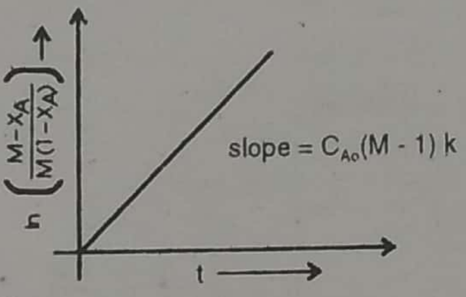


Fig. 2.5

We can write, $\quad M-X_A = M-M\,X_B$

$$(M-X_A) = M(1-X_B)$$

$$\therefore \quad \ln\left[\frac{1-X_B}{1-X_A}\right] = C_{Ao}(M-1)\,k\,t, \qquad M \neq 1$$

We have, $\quad 1-X_B = \dfrac{C_B}{C_{Bo}}$

and $\quad 1-X_A = \dfrac{C_A}{C_{Ao}},\; M = \dfrac{C_{Bo}}{C_{Ao}}$

$$\therefore \quad \ln\left[\frac{C_B\,.\,C_{Ao}}{C_{Bo}\,.\,C_A}\right] = (C_{Bo}-C_{Ao})\,k\,.\,t$$

Rearranging, we get,

$$\ln C_B/C_A = (C_{Bo} - C_{Ao})\,k\,t + \ln C_{Bo}/C_{Ao} \qquad \text{... (2.38)}$$

$$\therefore \quad k = \frac{1}{t\,(C_{Bo} - C_{Ao})} \ln\left[\frac{C_B \,.\, C_{Ao}}{C_{Bo} \,.\, C_A}\right] \qquad \text{... (2.39)}$$

Equation (2.38) is the integrated rate equation for second order reaction when $C_{Ao} \neq C_{Bo}$ in terms of concentration.

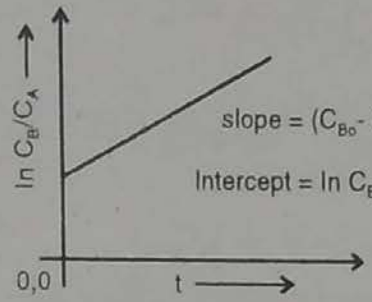


Fig. 2.6

A number of bimolecular reactions have been studied that obey the second order kinetics. Saponification of an ester is a second order reaction.

$$CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

Reaction between ethylene bromide and potassium iodide in 99% methanol is a second order reaction.

$$C_2H_4Br_2 + 3\,KI \rightarrow C_2H_4 + 2\,KBr + KI_3$$

Zero-Order Reactions : 10

A reaction is of zero order when the rate of reaction is independent of the concentration of the reactant.

A reaction of zero order is represented as

$$A \rightarrow \text{product} \qquad \text{... (2.40 a)}$$

$$-r_A = -\frac{dC_A}{dt} = k\,C_A^{o} \qquad \text{... (2.40 b)}$$

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

$$-\int_{C_{Ao}}^{C_A} dC_A = k \int_0^1 dt$$

$$C_{Ao} - C_A = kt \qquad \text{... (2.41)}$$

The equation (2.36) is the integrated rate equation for zero order reaction in terms of concentration.

We have

$$C_A = C_{Ao}(1 - X_A)$$

$$C_{Ao} - C_A = C_{Ao}\,X_A$$

$$\therefore \quad C_{Ao}\,X_A = kt \qquad \text{... (2.42)}$$

The equation (2.42) is the integrated rate equation in terms of conversion.

Characteristics :-

The equation (2.41) is a integrated rate expression for zero order reaction. The dimensions of specific rate constant are concentration/time.

[illegible]

A plot of $C_{A_0} - C_A$ against t yields a straight line passing through origin with slope equal to k.

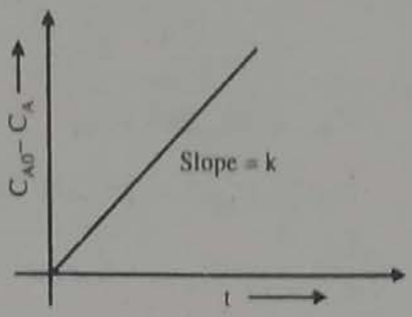


Fig. 2.7

The important characteristic of zero order kinetic is the half life which is proportional to the initial concentration of the reactant. **Half life** is defined as *the time required to reduce the concentration of reactant A to half of its original value.*

Substituting the condition $t = t_{1/2}$ when $C_A = C_{A_0}/2$, in equation (2.41), we get

$$\frac{C_{A_0}}{2} = k\, t_{1/2}$$

$$t_{1/2} = \frac{C_{A_0}}{2\,k} \qquad \ldots (2.43)$$

i. e.

$$t_{1/2} \propto C_{A_0} \qquad \ldots (2.44)$$

where C_{A_0} is the initial concentration of the reactant. Hence the half life of the zero order reaction is directly proportional to the initial concentration of reactant.

Some heterogeneous reactions of zero order occurring on surfaces are given below :

$$2\,N_2O \xrightarrow[\text{wire}]{\text{hot Pt}} 2\,N_2 + O_2$$

✓

$$2\,NH_3 \xrightarrow{\text{tungsten}} N_2 + 3\,H_2$$

$$2\,HI \xrightarrow{\text{Gold}} H_2 + I_2$$

✓

In all these cases, the reaction occurs only on the surface of catalyst. When the surface becomes saturated, the amount of adsorbed gas is constant and further increase in pressure cannot change the surface concentration. Thus the rate of reaction is independent of the concentration of the reactant in gas phase.

The integrated rate equation depends on the stoichiometry as well as the kinetics. Let us explain it by considering the reaction

$$A + 2B \rightarrow \text{products}$$

which is first order with respect to both A and B (hence second order overall).

$$-r_A = \frac{-dC_A}{dt} = k\,C_A\,C_B = C_{A_0}^2\,(1 - X_A)\,(M - 2\,X_A)$$

$$C_A = C_{A_0}(1 - X_A)$$

$$C_B = \frac{N_{B_0} - (b/a)\,N_{A_0}\,X_A}{V}$$

$$V = V_0$$

$$C_B = \frac{N_{Bo}}{V_o} - (2/1)\frac{N_{Ao}}{V_o} X_A$$

$$C_B = C_{Bo} - 2\,C_{Ao} X_A$$

$$= C_{Ao}\left[\frac{C_{Bo}}{C_{Ao}} - 2\,X_A\right]$$

$$C_B = C_{Ao}\,[M - 2\,X_A]$$

$$\therefore \quad -r_A = \frac{-dC_A}{dt} = k\,C_{Ao}(1-X_A)\cdot C_{Ao}(M - 2\,X_A)$$

$$\frac{-dC_A}{dt} = k\,C_{Ao}^2\,(1-X_A)(M-2\,X_A)$$

which on integration yields

$$\ln\left(\frac{C_B \cdot C_{Ao}}{C_{Bo}\,C_A}\right) = \ln\left[\frac{M - 2\,X_A}{M\,(1-X_A)}\right] = C_{Ao}\,(M-2)\,kt \quad \text{for} \quad M \neq 2 \qquad \dots(2.45)$$

with a stoichiometric reactant ratio

$$M = \frac{C_{Bo}}{C_{Ao}} = 2 \quad \therefore\ C_{Bo} = 2\,C_{Ao}$$

$$\therefore \quad C_B = C_{Bo} - 2\,C_{Ao}X_A = 2\,C_{Ao} - 2\,C_{Ao}X_A = 2\,C_{Ao}(1-X_A)$$

$$\therefore \quad \frac{-dC_A}{dt} = k\,C_{Ao}(1-X_A)\cdot 2\;C_{Ao}(1-X_A)$$

$$\frac{-dC_A}{dt} = 2\,k\,C_{Ao}^2\,(1-X_A)^2$$

which on integration yields

$$\frac{1}{C_A} - \frac{1}{C_{Ao}} = \frac{1}{C_{Ao}}\left[\frac{X_A}{1-X_A}\right] = 2\,kt,\ \ M = 2 \qquad \dots(2.46)$$

Irreversible Third Order Reactions

Third and higher order reactions are quite rare. This is due to the fact that the probability of a collision between three molecules having sufficient energy is very slight in comparison to bimolecular collisions.

A simple third order reaction can be given as :

$$A + B + C \rightarrow \text{products}$$

$$3A \rightarrow \text{products}$$

If all the reactants are at the same concentration, then

$$-r_A = -\frac{dC_A}{dt} = k\,C_A\,C_B\,C_C$$

$$C_A = C_{Ao}\,(1-X_A)$$

$$-\,dC_A = C_{Ao}\,dX_A$$

$$C_{Ao}\frac{dX_A}{dt} = k\,C_{Ao}^3\,(1-X_A)^3, \text{ for same concentration.}$$

Rearranging, we get,

$$\frac{dX_A}{(1-X_A)^3} = k\;C_{Ao}^2\,dt$$

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)^3} = k\,C_{Ao}^2 \int_0^t dt$$

$1-X_A = Y \quad \therefore \quad dX_A = -dY$

At $X_A = 0,\ y = 1$, At $X_A = X_A,\ Y = 1-X_A$

$$-\int_1^{1-X_A} \frac{dY}{Y^3} = k\,C_{Ao}^2 \,.\, t$$

$$\frac{1}{2}\left[\frac{1}{Y^2}\right]_1^{1-X_A} = k\,C_{Ao}^2 \,.\, t$$

$$\frac{1}{2}\,[(1-X_A)^{-2} - 1] = k\,C_{Ao}^2 \,.\, t \qquad \ldots (2.47)$$

Equation (2.47) is the integrated form of third order kinetics in terms of conversion.

$$-r_A = -\frac{dC_A}{dt} = k\,.\,C_A^3$$

$$-\frac{dC_A}{C_A^3} = k.dt$$

$$-\int_{C_{Ao}}^{C_A} \frac{dC_A}{C_A^3} = k \int_0^t dt$$

$$\frac{1}{2}\,[1/C_A^2]_{C_{Ao}}^{C_A} = k\,t$$

$$\therefore \quad \frac{1}{2}\left[\frac{1}{C_A^2} - \frac{1}{C_{Ao}^2}\right] = k\,t \qquad \ldots (2.48)$$

$$k = \frac{1}{2t}\left[\frac{1}{C_A^2} - \frac{1}{C_{Ao}^2}\right]$$

Equation (2.48) is the integrated rate equation for third order reaction, with same concentrations of all reactants, in terms of concentration.

Most of the reactions of third kinetics which have been studied are of the type

$$2A + B \rightarrow \text{Products.} \qquad \ldots (2.49\ a)$$

Rate of disappearance of A is given by

$$-r_A = -\frac{dC_A}{dt} = k\,C_A^2\,C_B \qquad \ldots (2.49\ b)$$

Let a and b be the initial concentrations of A and B and x be the amount of B transformed in time t. The amount of unreacted reactants at t will be (a – 2x) and (b – x).

Hence, differential rate equation based on component B is

$$-\frac{d\,(b-x)}{dt} = k\,(a-2x)^2\,(b-x) \qquad \ldots (2.50)$$

$$\frac{dx}{dt} = k\,(a-2x)^2\,(b-x)$$

$$\int_0^x \frac{dx}{(b-x)(a-2x)^2} = k\int_0^t dt$$

$$I_1 = k\,t \qquad \ldots (1)$$

$$I_1 = \int_0^x \frac{1}{(b-x)(a-2x)^2}\,dx$$

By partial fraction method,

$$\frac{1}{(b-x)(a-2x)^2} = \frac{A}{b-x}+\frac{B}{a-2x}+\frac{C}{(a-2x)^2} \qquad \ldots (2)$$

$$\therefore \quad 1 = A(a-2x)^2 + B(b-x)(a-2x) + C(b-x) \qquad \ldots (3)$$

Putting x = b in equation (3),

$$1 = A(a-2b)^2 + 0 + 0$$

$$A = \frac{1}{(a-2b)^2} = \frac{1}{(2\,b-a)^2}$$

Putting x = a/2 in equation (3).

$$\therefore \quad 1 = 0+0+C(b-a/2)$$

$$\therefore \quad C = 2/2b-a$$

Putting $x = 0,\ A = \dfrac{1}{(a-2b)^2}$ and $C = \dfrac{2}{2b-a}$ in equation (3),

$$(3) \Rightarrow 1 = \frac{1}{(a-2b)^2}[a-2\times 0]^2 + B(b-0)(a-2\times 0) + \frac{2}{2b-a}(b-0)$$

$$1 = \frac{a^2}{(a-2b)^2} + ab\,B + \frac{2\,b}{2b-a}$$

$$1 = \frac{a^2}{(2b-a)^2} + ab\,B + \frac{2\,b}{2b-a}$$

$$1 = \frac{a^2 + 2b\,(2b-a)}{(2b-a)^2} + ab\,B$$

$$1 = \frac{a^2+4b^2-2\,ab}{(2b-a)^2} + ab\,B$$

$$1 - \frac{a^2+4b^2-2\,ab}{(2b-a)^2} = ab\,B$$

$$\frac{(2b-a)^2-(a^2+4\,b^2-2ab)}{(2b-a)^2} = ab\,B$$

$$\frac{4b^2-4ab+a^2-a^2-4b^2+2ab}{(2b-a)^2} = ab\,B$$

$$\frac{-2ab}{ab\,(2b-a)^2} = B$$

$$\frac{-2}{(2b-a)^2} = B$$

Putting values of A, B, C in equation (2),

$$\frac{1}{(b-x)(a-2x)^2} = \frac{\frac{1}{(2b-a)^2}}{b-x} + \frac{\frac{-2}{(2b-a)^2}}{a-2x} + \frac{\frac{2}{2b-a}}{(a-2x)^2}$$

$$\int_0^x \frac{1}{(b-x)(a-2x)^2}\,dx = \frac{1}{(2b-a)^2}\int_0^x \frac{1}{b-x}\,dx - \frac{2}{(2b-a)^2}\int_0^x \frac{1}{a-2x}\,dx + \frac{2}{2b-a}\int_0^x \frac{1}{(a-2x)^2}\,dx$$

$$I_1 = \frac{1}{(2b-a)^2}\left[\frac{\ln(b-x)}{-1}\right]_0^x - \frac{2}{(2b-a)^2}\left[\frac{\ln(a-2x)}{-2}\right]_0^x + \frac{2}{2b-a}\int_0^x (a-2x)^{-2}\,dx$$

$$= \frac{-1}{(2b-a)^2}[\ln(b-x)]_0^x + \frac{1}{(2b-a)^2}[\ln(a-2x)]_0^x + \frac{2}{2b-a}\left[\frac{(a-2x)^{-2+1}}{-2(-2+1)}\right]_0^x$$

$$I_1 = -\frac{1}{(2b-a)^2}[\ln(b-x) - \ln(b-0)] + \frac{1}{(2b-a)^2}[\ln(a-2x)$$

$$-\ln(a-2\times 0)] + \frac{1}{2b-a}\left[\frac{(a-2x)^{-1}}{+1}\right]_0^x$$

$$I_1 = -\frac{1}{(2b-a)^2}[\ln(b-x) - \ln b] + \frac{1}{(2b-a)^2}[\ln(a-2x) - \ln a]$$

$$= -\frac{1}{(2b-a)^2}\ln\left(\frac{b-x}{b}\right) + \frac{1}{(2b-a)^2}\ln\left(\frac{a-2x}{a}\right) - \frac{1}{2b-a}\times\left[\frac{1}{a-2x} - \frac{1}{a-2\times 0}\right]$$

$$= -\frac{1}{(2b-a)^2}\left[\ln\left(\frac{a-2x}{a}\right) - \ln\left(\frac{b-x}{b}\right)\right] + \frac{1}{2b-a}\left[\frac{1}{a-2x} - \frac{1}{a}\right]$$

$$= -\frac{1}{(2b-a)^2}\ln\left[\frac{\frac{a-2x}{a}}{\frac{b-x}{b}}\right] + \frac{1}{2b-a}\left[\frac{a-(a-2x)}{a(a-2x)}\right]$$

$$= -\frac{1}{(2b-a)^2}\ln\left[\frac{a-2x}{a}\times\frac{b}{b-x}\right] + \frac{1}{2b-a}\left[\frac{2x}{a(a-2x)}\right]$$

$$= -\frac{1}{(2b-a)^2}\ln\left[\frac{b(a-2x)}{a(b-2x)}\right] + \frac{2x}{(2b-a)\,a\,(a-2x)}$$

$$= -\frac{1}{(2b-a)^2}\left\{\ln\left[\frac{b(a-2x)}{a(b-2x)}\right] + \frac{2(2b-a)x}{a(a-2x)}\right\}$$

Putting value of I_1 in equation (1)

$$(1) \Rightarrow \frac{1}{(2b-a)^2}\left\{\ln\left[\frac{b(a-2x)}{a(b-x)}\right] + \frac{2(2b-a)x}{a(a-2x)}\right\} = kt$$

$$\therefore \quad \frac{1}{(2b-a)^2}\left\{\frac{2x(2b-a)}{a(a-2x)} + \ln\frac{b(a-2x)}{a(b-x)}\right\} = kt \qquad \ldots (2.51)$$

Similarly for reaction

$$A + 2B \rightarrow \text{Products}$$

we can write

$$\frac{1}{(2a-b)^2}\left[\frac{2x\,(2a-b)}{b\,(b-2x)}+\ln\frac{a\,(b-2x)}{b\,(a-x)}\right] = kt \qquad \ldots (2.52)$$

a = initial concentration of A = C_{Ao}

b = initial concentration of B = C_{Bo}

$a - x$ = concentration of A at time t = C_A

$b - 2x$ = concentration of B at time t = C_B

$b - 2x = C_B$

$C_{Bo} - 2x = C_B$

$2x = C_{Bo} - C_B$

Replacing a, b, etc. by C_{Ao}, C_{Bo} , etc., in equation (2.51), we get

$$\frac{1}{(2\,C_{Ao}-C_{Bo})^2}\left[\frac{(2\,C_{Ao}-C_{Bo})\,(C_{Bo}-C_B)}{C_{Bo}\,C_B}+\ln\frac{C_{Ao}\,C_B}{C_A\,C_{Bo}}\right] = kt \qquad \ldots (2.53)$$

$$\frac{(2\,C_{Ao}-C_{Bo})\,(C_{Bo}-C_B)}{C_{Bo}\,C_B}+\ln\frac{C_{Ao}\,C_B}{C_A\,C_{Bo}} = (2\,C_{Ao}-C_{Bo})^2\,kt,\; M=\frac{C_{Bo}}{C_{Ao}}\neq 2$$

For $M = 2$, we get

$$1/C_A^2 - 1/C_{Ao}^2 = 8\,kt \qquad \ldots (2.54)$$

Examples of third order gaseous reaction are :

(i) $2\,NO + H_2 \rightarrow N_2O + H_2O$

(ii) $2\,NO + Cl_2 \rightarrow 2\,NOCl$

EMPIRICAL RATE EQUATION OF nth ORDER

For the reaction $A \rightarrow \text{Products}$ ... (2.55 a)

Rate is given by $-r_A = -\dfrac{dC_A}{dt} = k\,C_A^n$ ... (2.55 b)

Rearranging, we get,

$$-\frac{dC_A}{C_A^n} = k\,dt$$

Integrating above equation within the below given limits

$C_A = C_{Ao}$ at $t = 0$

$C_A = C_A$ at $t = t$

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

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

$$\frac{1}{(n-1)}\left[\frac{1}{C_A^{n-1}}-\frac{1}{C_{Ao}^{n-1}}\right] = kt$$

$$\left[\frac{1}{C_A^{n-1}}-\frac{1}{C_{Ao}^{n-1}}\right] = (n-1)\,kt,\; n\neq 1 \qquad \ldots (2.56)$$

The dimensions of rate constant (k) for nth order reaction are $(\text{time})^{-1}\,(\text{concentration})^{1-n}$.

Half-life Method : 10

✓ Now we will deal with method of determination of overall order of irreversible reaction from the half-life.

The half-life of a reaction, $t_{1/2}$, is defined as *the time required for the concentration of the reactant to fall to one-half of its initial value*. The reaction order and rate constant of a reaction can be determined from the data of half-life of a reaction as a function of the initial concentration obtained by performing experiments in laboratory.

For irreversible reaction,

$$aA + bB + \ldots \rightarrow \text{products} \qquad \ldots (2.57\text{ a})$$

we may write

$$-r_A = \frac{-dC_A}{dt} = k\,C_A^{\alpha}\,C_B^{\beta}\ldots\ldots \qquad \ldots (2.57\text{ b})$$

If the reactants are present in the stoichiometric ratios initially, they will remain at that ratio during the course of reaction.

∴ For reactants A and B at any time,

$$\frac{C_B}{C_A} = \frac{b}{a}$$

So

$$-r_A = \frac{-dC_A}{dt} = k\,C_A^{\alpha}\left(\frac{b}{a}C_A\right)^{\beta}$$

$$= k\,(b/a)^{\beta}\ldots\;C_A^{\alpha+\beta+\ldots}$$

$$-r_A = k'\,C_A^{n} \qquad \ldots (2.58)$$

Integrating with initial condition $C_A = C_{Ao}$ at $t = 0$, we get

$$C_A^{1-n} - C_{Ao}^{1-n} = k'(n-1)\,t, \quad \text{for } n \neq 1 \qquad \ldots (2.59)$$

The half-life is the time required for the concentration of reactants to fall to one-half of its initial value, i.e.,

$$t = t_{1/2} \quad \text{when} \quad C_A = \frac{1}{2}C_{Ao}$$

$$\therefore \quad \left(\frac{1}{2}C_{Ao}\right)^{1-n} - C_{Ao}^{1-n} = k'(n-1)\,t_{1/2}$$

$$\frac{C_{Ao}^{1-n}}{2^{1-n}} - C_{Ao}^{1-n} = k'(n-1)\,t_{1/2}$$

$$\therefore \quad C_{Ao}^{1-n}\left[\frac{1}{2^{1-n}} - 1\right] = k'(n-1)\,t_{1/2}$$

$$C_{Ao}^{1-n}\left[2^{n-1} - 1\right] = k'(n-1)\,t_{1/2}$$

$$\boxed{t_{1/2} = \frac{(2^{n-1}-1)}{k'(n-1)}\,C_{Ao}^{1-n}} \qquad \ldots (2.60)$$

Taking the natural log of both sides of equation (2.60), we get

$$\ln(t_{1/2}) = \ln\left[\frac{2^{n-1}-1}{k'(n-1)}\right] + (1-n)\ln C_{Ao} \qquad \ldots (2.61)$$

So the plot of ln $t_{1/2}$ v/s ln C_{Ao} yields a straight line with slope equal to 1 – n.

graph is m.m.imp

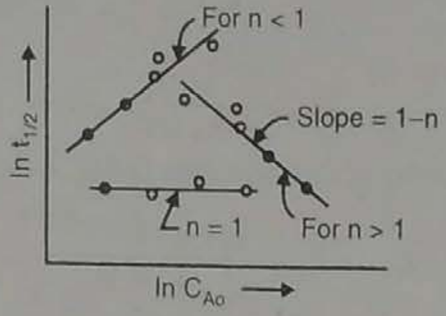


Fig. 2.8 : Overall order of reaction from a series of half-life experiments

So this method requires taking series of runs, each at different initial concentrations.

For reactions involving single reacting component,

$$A \rightarrow \text{products}$$

For determining order of reaction, we have to determine half-life of a reaction, each at different initial concentrations of A to determine n and k.

$$-r_A = \frac{-dC_A}{dt} = k\,C_A^{\alpha} = k\,C_A^{n}$$

Integration yields

$$C_A^{1-n} - C_{Ao}^{1-n} = k\,(n-1)\,t$$

$$t = t_{1/2} \quad \text{at} \quad C_A = C_{Ao}/2$$

$$\therefore \quad t_{1/2} = \frac{2^{n-1}-1}{k\,(n-1)} \cdot C_{Ao}^{1-n}$$

$$\ln t_{1/2} = \ln\left[\frac{2^{n-1}-1}{k\,(n-1)}\right] + (1-n)\ln C_{Ao} \qquad \ldots (2.62)$$

Here n is the order with respect to A.

Another reaction of this procedure is – if reaction involves two components then we have to use method of excess (isolation method) in conjunction with the half-life method. In such procedure, if A and B are reacting components and if we take B in large excess so that $C_B = C_{Bo}$ then

$$\frac{-dC_A}{dt} = k''\,C_A^{\alpha}$$

where $\quad k'' = k\,(C_{Bo}^{\beta})$

Irreversible Reactions in Parallel :

In case of parallel reactions, the reactant is consumed by two different reactions to form different products. Such reactions are also called as *competing reactions.*

Industrially important parallel reaction is the oxidation of ethylene to produce ethylene oxide along with formation of CO_2 and H_2O

$$CH_2 = CH_2 + \frac{1}{2}\,O_2 \rightarrow C_2H_4O$$

$$CH_2 = CH_2 + 3\,O_2 \rightarrow 2\,CO_2 + 2\,H_2O$$

Consider a decomposition of A by two elementary reactions in parallel.

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow{k_2} S$$

The rate of disappearance of A is given by

$$-r_A = \frac{-dC_A}{dt} = k_1 C_A + k_2 C_A \quad \text{... (2.63)}$$

On integration, we get

$$-\ln (C_A/C_{A_0}) = (k_1 + k_2)\,t \quad \text{... (2.64)}$$

The rates of formation of R and S are given by

$$r_R = \frac{dC_R}{dt} = k_1 C_A \quad \text{... (2.65)}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A \quad \text{... (2.66)}$$

$$\frac{r_R}{r_S} = \frac{dC_R/dt}{dC_S/dt} = \frac{k_1}{k_2}$$

$$\therefore \quad \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

which on integration gives

$$\frac{C_R - C_{R_0}}{C_S - C_{S_0}} = \frac{k_1}{k_2} \quad \text{... (2.67)}$$

In case of such system to know k_1 and k_2, we must follow the concentration of at least two components. The concentration of the third component is obtained by noting that $C_A + C_R + C_S$ is constant.

A plot of $-\ln (C_A/C_{A_0})$ v/s t yields a straight line with slope equal to $k_1 + k_2$.

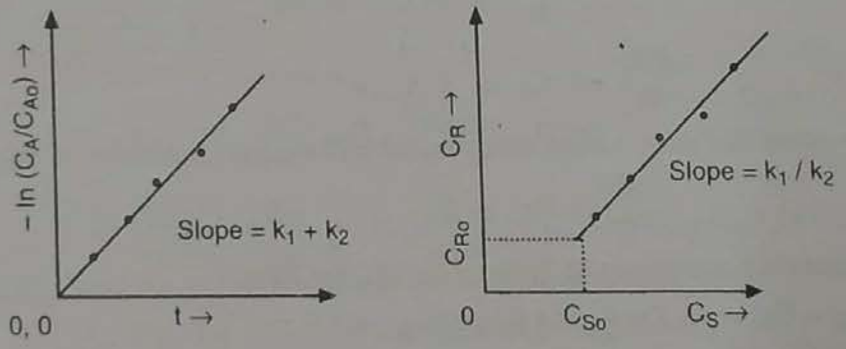


Fig. 2.9 : Evaluation of rate constants for first order parallel reactions

Knowing k_1/k_2 and $k_1 + k_2$ from plots, we get the value of individual rate constants.

The concentration-time curves for the three components in a batch reactor for $C_{R_0} = C_{S_0} = 0$ and $k_1 > k_2$ are shown in Fig. 2.10.

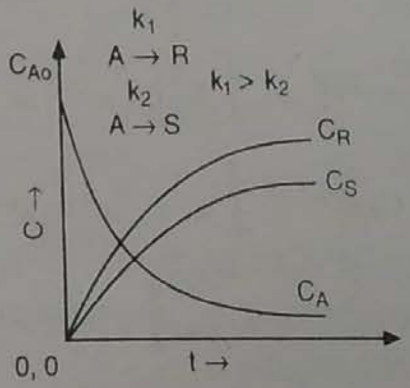


Fig. 2.10 : Typical concentration-time curves for parallel reactions

— [illegible]

IRREVERSIBLE REACTIONS IN SERIES

Consider unimolecular, first order series reaction of the type

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

Rate equations for A, R and S are

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A \qquad \text{... (2.68)}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_{\underset{A}{R}} - k_2 C_R \qquad \text{... (2.69)}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R \qquad \text{... (2.70)}$$

Assume initially no R or S present and let C_{A_0} be the initial concentration of A.

$$-\frac{dC_A}{dt} = k_1 C_A$$

Rearranging and integrating, we get

$$-\ln C_A/C_{A_0} = k_1 t$$

$$\therefore \quad C_A = C_{A_0} . e^{-k_1 t} \qquad \text{... (2.71)}$$

In order to find the variation in concentration of R, put the value of C_A from equation (2.71) into the differential equation governing the rate of change of R i. e. equation (2.69).

$$\frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A_0} e^{-k_1 t} \qquad \text{... (2.72)}$$

Equation (2.72) is a first order linear differential equation of the form

$$\frac{dy}{dx} + Py = Q \qquad \text{... (2.73)}$$

Comparing equations (2.72) and (2.73), we have

$y = C_R$, $x = t$, $P = k_2$ and $Q = k_1 C_{A_0} . e^{-k_1 t}$

By multiplying through with the integrating factor $e^{\int P\,dx}$ the solution is

$$y \cdot e^{\int P\,dx} = \int Q \cdot e^{\int P\,dx} \cdot dx + C$$

Putting values we get,

$$C_R \cdot e^{\int . k_2\,dt} = \int k_1 C_{A_0} e^{-k_1 t} . e^{\int k_2\,dt} \cdot dt + C$$

$$C_R e^{k_2 t} = \int k_1 C_{A_0} e^{-k_1 t} . e^{k_2 t} . dt + C$$

$$C_R e^{k_2 t} = k_1 C_{A_0} \int e^{(k_2 - k_1) t} dt + C$$

$$C_R \cdot e^{k_2 t} = k_1 C_{A_0} \frac{e^{(k_2 - k_1)t}}{(k_2 - k_1)} + C \qquad \text{... (2.74)}$$

The constant of integration is found from the initial condition, $C_{Ro} = 0$ at $t = 0$.

$$\therefore \quad 0 = \frac{k_1 C_{Ao}}{k_2 - k_1} + C$$

$$\therefore \quad C = -\frac{k_1 C_{Ao}}{k_2 - k_1} \qquad \dots (2.75)$$

Substituting the value of C in equation (2.74), we get

$$C_R \cdot e^{k_2 t} = \frac{k_1 C_{Ao} \, e^{(k_2 - k_1)t}}{k_2 - k_1} - \frac{k_1 C_{Ao}}{k_2 - k_1}$$

Dividing each term by $e^{k_2 t}$,

$$\therefore \quad C_R = k_1 C_{Ao} \left[\frac{e^{-k_1 t}}{k_2 - k_1} - \frac{e^{-k_2 t}}{k_2 - k_1} \right]$$

$$C_R = k_1 C_{Ao} \left[\frac{e^{-k_1 t}}{k_2 - k_1} - \frac{e^{-k_2 t}}{k_2 - k_1} \right] \qquad \dots (2.76)$$

$$= k_1 C_{Ao} \left[\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right] \qquad \dots (2.77$$

Note that there is no change in total number of moles, the stoichiometry relate th concentration of reacting component by

$$C_{Ao} = C_A + C_R + C_S$$

$$C_S = C_{Ao} - C_A - C_R$$

Putting the values of C_A from equation (2.71) and of C_R from equation (2.76) in abov equation we get,

$$C_S = C_{Ao} - C_{Ao} \cdot e^{-k_1 t} - k_1 C_{Ao} \left[\frac{e^{-k_1 t}}{k_2 - k_1} - \frac{e^{-k_2 t}}{k_2 - k_1} \right]$$

$$= C_{Ao} - C_{Ao} \cdot e^{-k_1 t} - \frac{k_1 C_{Ao} \, e^{-k_1 t}}{k_2 - k_1} + \frac{k_1 C_{Ao} e^{-k_2 t}}{k_2 - k_1}$$

$$= C_{Ao} \left[1 - e^{-k_1 t} \left(1 + \frac{k_1}{k_2 - k_1} \right) + \frac{k_1 \, e^{-k_2 t}}{k_2 - k_1} \right]$$

$$= C_{Ao} \left[1 - e^{-k_1 t} \left(\frac{k_2}{k_2 - k_1} \right) + \frac{k_1 \, e^{-k_2 t}}{k_2 - k_1} \right] \qquad \dots (2.78$$

Thus we have found how the concentrations of compounds A, R and S vary with time.

If k_2 is much larger than k_1, equation (2.78) reduces to

$$C_S = C_{Ao} \left[1 - e^{-k_1 t} \right] \qquad \dots (2.79)$$

In other words, the rate is determined by k_1 or the first step of the two-step reaction.

If k_1 is much larger than k_2, then

$$C_S = C_{Ao} \left[1 - e^{-k_2 t} \right] \qquad \dots (2.80)$$

The rate is determined by k_2, the slowest step in the two-step reaction. Hence for reactions in series it is the slowest step that has the greatest influence on the overall reaction rate.

The time at which maximum concentration of R occurs is obtained by differentiating equation (2.76) and setting $dC_R/dt = 0$.

$$C_R = C_{Ao}\, k_1 \left(\frac{e^{-k_1 t}}{k_2 - k_1} - \frac{e^{-k_2 t}}{k_2 - k_1} \right)$$

$$C_R = \frac{C_{Ao}\, k_1}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right)$$

$$\frac{dC_R}{dt} = \frac{C_{Ao}\, k_1}{k_2 - k_1} \left[-k_1 e^{-k_1 t} + k_2 e^{-k_2 t} \right]$$

$\dfrac{C_{Ao}\, k_1}{k_2 - k_1}$ can not be zero

$$\therefore \quad k_2 e^{-k_2 t} - k_1 e^{-k_1 t} = 0$$

Taking logarithm, we get

$$\ln k_2 - k_2 t - \ln k_1 + k_1 t = 0$$

$$\ln k_2/k_1 = k_2 t - k_1 t$$

$$t(k_2 - k_1) = \ln k_2/k_1$$

$$\therefore \quad t_{max} = \frac{1}{k\,(\log \text{mean})} = \frac{\ln k_2/k_1}{(k_2 - k_1)} \qquad \dots (2.81)$$

The maximum concentration of R is found by combining equations (2.76) and (2.81), to give

$$\frac{C_{R\,max}}{C_{Ao}} = \left(\frac{k_1}{k_2} \right)^{k_2/(k_2 - k_1)} \qquad \dots (2.82)$$

Fig. 2.11 shows the general characteristics of the concentration-time curves for the three components. We see from this plot that A decreases exponentially, R rises to maximum and then falls and S rises continuously. The greatest rate of increase of S occurs where R is maximum.

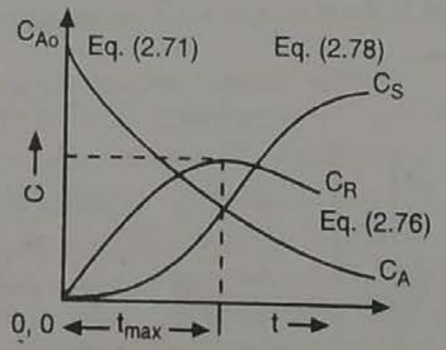


Fig. 2.11 : Typical concentration-time curves for first order series reactions

Autocatalytic Reactions :

A reaction in which one of the products of reaction acts as a catalyst is called as *autocatalytic reaction*.

Consider the following simple autocatalytic reaction

$$A + R \rightarrow R + R \qquad \dots (2.83\ a)$$

The rate of reaction is given by

$$-r_A = \frac{-dC_A}{dt} = k\, C_A\, C_R \qquad \dots (2.83\ b)$$

As the total number of moles of A and R remain unchanged, as A is consumed we can write

$$C_o = C_A + C_R = C_{Ao} + C_{Ro} = \text{constant, at any time t}$$

$$\therefore \quad -r_A = \frac{-dC_A}{dt} = k\,C_A(C_o - C_A)$$

Rearranging, we get,

$$\frac{-dC_A}{C_A(C_o - C_A)} = k\,dt$$

Braking into partial fractions, we get

$$\frac{-1}{C_o}\left[\frac{dC_A}{C_A} + \frac{dC_A}{C_o - C_A}\right] = k\,dt$$

$$-\int_{C_{Ao}}^{C_A}\frac{dC_A}{C_A} - \int_{C_{Ao}}^{C_A}\frac{dC_A}{C_o - C_A} = C_o kt$$

$$\ln\left(\frac{C_{Ao}}{C_A}\right) + \ln\left(\frac{C_o - C_A}{C_o - C_{Ao}}\right) = C_o kt$$

$$A + R \rightarrow R + R$$

total conⁿ C_{Ao} C_{R_1} C_{R_2} C_{R_3}

i.e. $C_o = C_{Ao} - x \quad C_{Ao} - x \quad C_{R_2} + x \quad C_{R_2}$

$$C_{Ao} - x + (C_{R_1} - x) + C_{R_2} + x + C_{R_3} + x$$

$$= C_{Ao} + \underbrace{C_{R_1} + C_{R_2} + C_{R_3}}$$

$$= C_{Ao} + C_{Ro}$$

$$\therefore \quad \ln\frac{C_{Ao}(C_o - C_A)}{C_A(C_o - C_{Ao})} = C_o kt \qquad \dots (2.84)$$

$$C_o = C_{Ro} + C_{Ao} = C_A + C_R$$

$$\therefore \quad C_A = C_o - C_R$$

$$C_{Ao} = C_o - C_{Ro}$$

$$\ln\frac{C_{Ao}(C_o - C_o + C_R)}{C_A(C_o - C_o + C_{Ro})} = C_o kt$$

$$\ln\left(\frac{C_{Ao}\cdot C_R}{C_A\cdot C_{Ro}}\right) = \ln\frac{C_R/C_{Ro}}{C_A/C_{Ao}} = C_o kt$$

$$\ln\frac{C_{Ao}(C_o - C_A)}{C_A(C_o - C_{Ao})} = \ln\frac{C_R/C_{Ro}}{C_A/C_{Ao}} = C_o kt = (C_{Ao} + C_{Ro})\,kt \qquad \dots (2.85)$$

If $M = C_{Ro}/C_{Ao}$ and X_A is the fractional conversion of A then

$$C_{Ao}(C_o - C_A) = C_{Ao}[C_{Ao} + C_{Ro} - C_{Ao}(1 - X_A)]$$

$$= C_{Ao}[C_{Ao} + C_{Ro} - C_{Ao} + C_{Ao}X_A]$$

$$= C_{Ao}\cdot C_{Ao}\left[\frac{C_{Ro}}{C_{Ao}} + X_A\right]$$

$$= C_{Ao}^2\,[M + X_A]$$

$$C_A(C_o - C_{Ao}) = C_{Ao}(1 - X_A)\,[C_{Ao} + C_{Ro} - C_{Ao}]$$

$$= C_{Ao}(1 - X_A)\,C_{Ro}$$

$$= C_{Ao}^2\,(1 - X_A)\,\frac{C_{Ro}}{C_{Ao}}$$

$$= C_{Ao}^2\,(1 - X_A)\cdot M = M(1 - X_A)\,C_{Ao}^2$$

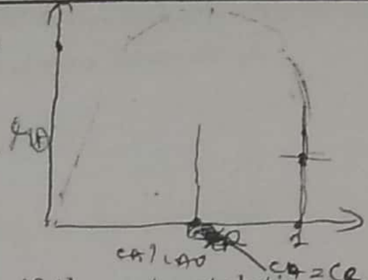
$$C_o kt = (C_{Ao} + C_{Ro})\,kt$$

$$= C_{Ao}[1 + C_{Ro}/C_{Ao}]\,kt$$

$$= C_{Ao}[1 + M]\,kt$$

$\therefore$ In terms of M and X_A, the equation (2.85) becomes

$$\ln\left[\frac{C_{Ao}^2 (M + X_A)}{C_{Ao}^2 (1 - X_A) M}\right] = C_{Ao} (M + 1) kt$$



$$\ln\left[\frac{M + X_A}{M (1 - X_A)}\right] = C_{Ao} (M + 1) kt \quad \ldots (2.86)$$

Note that some product R should be present initially if the autocatalytic reaction is to proceed at all.

Reversible Reactions :

A reaction that proceed simultaneously and independently in both the directions is called *reversible reaction*. Strictly speaking, no chemical reaction is completely irreversible, but then also we consider/treat many reactions to be essentially irreversible because of large values of equilibrium constants. For reversible reactions, complete conversion is not possible as the reaction proceeds in both the directions.

Reversible unimolecular type first order reactions :

Consider the reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$$

This reaction is composed of two elementary reactions :

$$A \xrightarrow{k_1} R$$

and

$$R \xrightarrow{k_2} A$$

where k_1 is rate constant for forward reaction and k_2 is the rate constant for reverse reaction.

The net rate of disappearance of A

$$-r_A = k_1 C_A - k_2 C_R$$

The net rate of formation of R

$$r_R = k_1 C_A - k_2 C_R$$

$$\therefore \quad \frac{dC_R}{dt} = \frac{-dC_A}{dt} = k_1 C_A - k_2 C_R$$

Let initial mole ratio of R to A to be M.

$$\therefore \quad M = C_{Ro}/C_{Ao}$$

Concentration of A at time t is

$$C_A = C_{Ao} (1 - X_A)$$

$$-dC_A = C_{Ao}\, dX_A$$

Concentration of R at time t is

$$C_R = C_{Ro} + C_{Ao} X_A$$

$$-\frac{dC_A}{dt} = C_{Ao} \frac{dX_A}{dt} = k_1 C_{Ao} (1 - X_A) - k_2 (C_{Ro} + C_{Ao} X_A)$$

$$-\frac{dC_A}{dt} = C_{Ao} \frac{dX_A}{dt} = C_{Ao} [k_1 (1 - X_A) - k_2 (M + X_A)] \quad \ldots (2.87)$$

At equilibrium, net rate is zero (rates of forward and reverse reaction are equal) $dC_A/dt = 0$ and $X_A = X_{Ae}$ (equilibrium conversion).

$$\therefore \quad 0 = C_{Ao} [k_1 (1 - X_{Ae}) - k_2 (M + X_{Ae})]$$

$$k_1 (1 - X_{Ae}) = k_2 (M + X_{Ae})$$

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{k_1}{k_2} = \frac{(M + X_{Ae})}{(1 - X_{Ae})} \quad \text{... (2.8}$$

$$\therefore \quad k_2 = \frac{k_1 (1 - X_{Ae})}{(M + X_{Ae})} \quad \text{... (2.8}$$

From equation (2.87), we have

$$\frac{dX_A}{dt} = k_1 (1 - X_A) - k_2 (M + X_A)$$

Substituting the value of k_2 from equation (2.89) in above equation

$$\frac{dX_A}{dt} = k_1 (1 - X_A) - \frac{k_1 (1 - X_{Ae})}{(M + X_{Ae})} (M + X_A)$$

$$\frac{dX_A}{dt} = k_1 \left[\frac{(1 - X_A)(M + X_{Ae}) - (1 - X_{Ae})(M + X_A)}{(M + X_{Ae})}\right]$$

$$\frac{dX_A}{dt} = k_1 \left[\frac{\cancel{M} + X_{Ae} - X_A M - \cancel{X_A X_{Ae}} - \cancel{M} - X_A + MX_{Ae} + \cancel{X_A} X}{(M + X_{Ae})}\right]$$

Collecting the terms, we get

$$\frac{dX_A}{dt} = \frac{k_1 [X_{Ae} (M + 1) - X_A (M + 1)]}{(M + X_{Ae})}$$

$$\frac{dX_A}{dt} = \frac{k_1 (M + 1)}{(M + X_{Ae})} (X_{Ae} - X_A)$$

$$\int_0^{X_A} \frac{dX_A}{X_{Ae} - X_A} = \frac{k_1 (M + 1)}{(M + X_{Ae})} \int_0^t dt$$

$$-\ln\left(\frac{X_{Ae} - X_A}{X_{Ae}}\right) = \frac{(M + 1)}{(M + X_{Ae})} k_1 t \quad \text{... (2.90}$$

$$-\ln\left(\frac{X_{Ae} - X_A}{X_{Ae}}\right) = -\ln\left(\frac{C_A - C_{Ae}}{C_{Ao} - C_{Ae}}\right) = \frac{(M + 1)}{(M + X_{Ae})} k_1 t \quad \text{... (2.91}$$

Equation (2.91) is the desired integrated rate equation for reversible first order reaction.

A plot of $-\ln\left(\frac{X_{Ae} - X_A}{X_{Ae}}\right)$ versus t gives a straight line with slope equal to $\frac{k_1 (M + 1)}{(M + X_{Ae})}$.

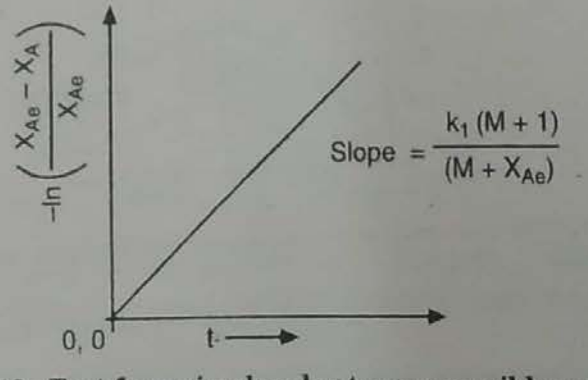


Fig. 2.12 : Test for unimolecular type reversible reactions

For first order irreversible reaction, we have

$$-\ln (1 - X_A) = -\ln (C_A/C_{Ao}) = kt$$

For reversible reaction with $C_{Ro} = 0$

$$-\ln\left[\frac{X_{Ae} - X_A}{X_{Ae}}\right] = -\ln\left[\frac{C_A - C_{Ae}}{C_{Ao} - C_{Ae}}\right] = \frac{1}{X_{Ae}} k_1 t$$

If $X_{Ae} = 1$ or $C_{Ae} = 0$ then above equation reduces to

$$-\ln (1 - X_A) = -\ln (C_A/C_{Ao}) = k_1 t$$

So the irreversible first order reaction is simply a special case of the reversible reaction in which $X_{Ae} = 1$ or $C_{Ae} = 0$ or $K_C = \infty$.

Second order reversible reactions :

For bimolecular type second order reactions in both the directions having the forms

(1) $$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$$

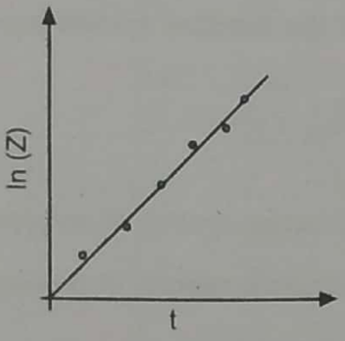
(2) $$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$$

(3) $$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R$$

(4) $$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R$$

With $C_{Ao} = C_{Bo}$ and $C_{Ro} = C_{So} = 0$, the integrated rate equation applicable to all forms is

$$\ln \left[\frac{X_{Ae} - (2X_{Ae} - 1) X_A}{X_{Ae} - X_A}\right] = 2k_1 \left[\frac{1}{X_{Ae}} - 1\right] C_{Ao} t \quad \ldots (2.92)$$



$$Z = \frac{X_{Ae} - (2X_{Ae} - 1) X_A}{(X_{Ae} - X_A)}$$

Fig. 2.13 : Test for the bimolecular reversible reaction

Integral method of analysis of data can be carried out (i) graphically and (ii) analytically. So far we have considered the graphical procedure.

In analytical procedure, certain rate equation is assumed, and the reaction rate constant is calculated from the available data using integrated rate expression. If we get the almost same values of the rate constants for the data provided then the assumed rate equation is correct. If there is large variation in values of rate constant then another equation should be tested.

Differential Method of Analysis of Data :

This method deals directly with the rate equation to be tested. All that we have to do is – assume the rate equation, evaluate all terms of rate equation including dC_i/dt, and test the fit of the data to the rate equation.

Procedure for analysis of the complete rate equation by differential method :

(i) Hypothesize a mechanism and obtain the rate equation from it. Assume a rate equation. The rate equation will be of the form

$$-r_A = -dC_A/dt = k\,f(C)$$

(ii) Plot a graph of concentration v/s time from the data collected by performing the experiment.

Ru Assum

(iii) Draw a smooth curve through these data.

(iv) Determine the slope of this curve by drawing tangents to the curve at suitably selected concentration values. These slopes, dC_A/dt are the rates of reaction at the selected concentrations.

(v) Evaluate f(C) for each of the selected concentrations.

(vi) Plot a graph of $-(dC_A/dt)$ i.e. $-r_A$ v/s f(C). If we get a straight line passing through the origin then the rate equation is consistent with the data (i.e. assumed rate equation is correct). If we do not get a straight line then another equation should be tested.

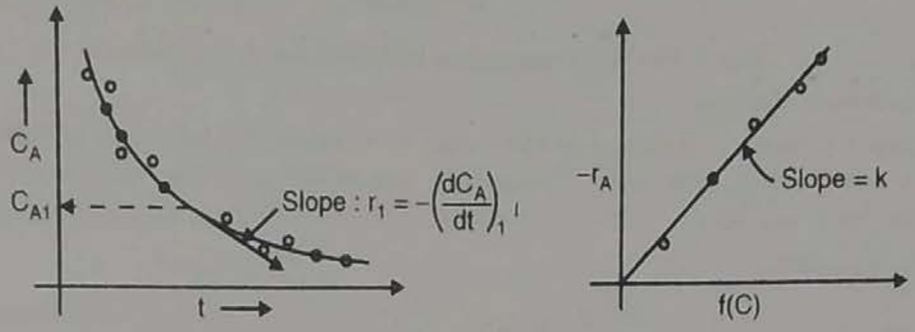


Fig. 2.14 : Procedure for testing a rate equation of the type $-r_A = f(C)$ by the differential method of analysis of data

Procedure for analysis of the data by differential method when the rate is function of concentration of only one reactant :

For a reaction of the type

$$A \rightarrow \text{products}$$

(i) Assume rate equation of the form

$$-r_A = \frac{-dC_A}{dt} = k\,C_A^n$$

(ii) Plot a graph of C_A v/s time from the data collected by performing experiment.

(iii) Draw a smooth curve through these data.

(iv) Determine the slope of this curve by drawing the tangents to the curve at suitably selected concentrations (C_A values). These slopes are the rates of reactions at these concentrations.

(v)

C_A	C_{A1}	C_{A2}	C_{A3}	....
$-r_A = -(dC_A/dt)$	$(-r_A)_1$	$(-r_A)_2$	$(-r_A)_3$	....

(vi) We have

$$(-r_A) = -(dC_A/dt) = k\,C_A^n$$

$$\therefore \quad \ln(-r_A) = \ln k + n \ln C_A$$

$\ln C_A$	–	–	–	–
$\ln(-r_A)$	–	–	–	–

Plot a graph of $\ln(-r_A)$ v/s $\ln C_A$. It yields a straight line with slope equal to n (i.e. order of reaction with respect to A) and intercept gives value of k.

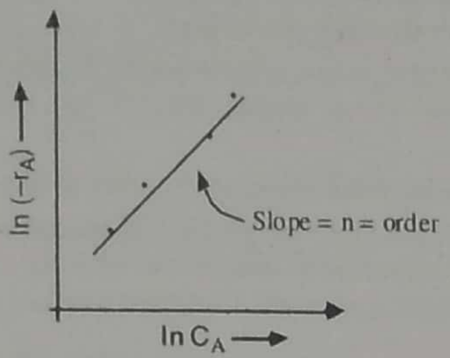


Fig. 2.15 : Determination of order for A → products

Ostwald's Isolation Method :

This method is used to determine the order of reaction by taking a number of reactants in large excess except one. The rate of reaction depends upon this isolated reactant which is present in the least amount.

The rate equation

$$\frac{-dC_A}{dt} = k\,C_A^{\alpha}\,C_B^{\beta}\,C_C^{\gamma}$$

If B and C are taken in large excess, then

$$\frac{-dC_A}{dt} = k'\,C_A^{\alpha}$$

The order with respect to A may be determined by any one of the methods discussed previously. The values of β and γ are determined in the same way using a large excess of the reactants A and C, and B and A in turn. The sum of orders with respect to A, B, and C is the overall order of the reaction.

Variable–Volume Batch Reactor :

So far we considered systems in which the reaction volume did not vary as the reaction progressed. Most liquid phase and some gas-phase systems fall into this category. Now we will deal with systems in which volume does vary. The gas-phase reactions with change in number of moles at a given pressure and temperature is a variable-volume system. In such cases, the pressure is held constant, so variable-volume batch reactor is also referred to as constant-pressure batch reactor.

Consider the decomposition reaction

$$N_2O \rightarrow N_2 + \frac{1}{2}O_2$$

carried out at constant pressure.

As 1 mol of N_2O gives 1.5 moles of products and as the pressure prevailing is constant at a given temperature, the volume will increase. So there is a variation in volume of the reaction system during the course of reaction.

For variable-volume reaction system, the rate of change of component i is given by

$$r_i = \frac{1}{V}\frac{dN_i}{dt}$$

$$N_i = C_i V$$

$$r_i = \frac{1}{V}\frac{d(C_iV)}{dt} = \frac{1}{V}\left[V\frac{dC_i}{dt} + C_i\frac{dV}{dt}\right]$$

$$r_i = \frac{dC_i}{dt} + \frac{C_i}{V}\frac{dV}{dt} \quad \text{or} \quad \frac{dC_i}{dt} + C_i\frac{d\ln V}{dt} \qquad \ldots (2.93)$$

In case of constant-volume system, the second term drops out and we have simple expression :

$$r_i = \frac{dC_i}{dt}$$

For variable-volume reaction system, the two terms of equation (2.93) must be evaluated from experiment for finding r_i.

For constant-volume reaction systems,

$$r_i = \frac{dC_i}{dt} \quad \text{... (2.94)}$$

For variable-volume reaction systems,

$$r_i = \frac{dC_i}{dt} + \frac{C_i}{V}\frac{dV}{dt} \quad \text{... (2.95)}$$

The equation (2.94) is applicable for constant-volume batch reactor and the equation (2.95) is applicable for variable-volume constant-pressure batch reactor.

By making use of fractional conversion instead of concentration as a primary variable, we can avoid the use of cumbersome two-term expression [equation (2.95)] for the variable-volume reactor and this is done by treating the relationship between the volume of reaction system and conversion to be linear. For the volume of reaction system varying linearly with conversion, we write

$$V = V_o(1 + \varepsilon_A X_A) \quad \text{... (2.96)}$$

where ε_A is the fractional change in volume of the reaction system between no conversion and complete conversion of reactant A.

$$\therefore \quad \varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \quad \text{... (2.97)}$$

$V_{X_A=1}$ = volume of reaction system at complete conversion

$V_{X_A=0}$ = volume of reaction system at no conversion

ε_A is also defined as,

$$\varepsilon_A = \frac{\text{change in total number of moles of reaction system when reaction is completed}}{\text{total number of moles fed to the reactor}}$$

Following examples will clear the procedure of calculation of ε_A.

Consider isothermal gas phase reaction

$$A \rightarrow 3R$$

By starting with pure reactant A, one volume of reactant on complete conversion yields three volumes of product.

$$\therefore \quad \varepsilon_A = \frac{3-1}{1} = 2$$

With 50 mole % inerts present at the start, two volumes of reaction mixture yield on complete conversion four volumes of product mixture.

$$\therefore \quad \varepsilon_A = \frac{4-2}{2} = 1.0$$

~~2A → 4R~~

for 50 mole % A + 50 mole % inerts.

2A → 4R   2A → 4R

A → [illegible]

For 100 moles of initial reaction mixture :

no conversion	on complete conversion
50 mol of A 50 mol of A	150 mol of R 50 mol of inerts
Total = 100 mol	200 mol

$$\therefore \quad \varepsilon_A = \frac{200-100}{100} = 1.0$$

For A → 4 R

with 60 mole % inerts and 40 mole % of A.

For 100 moles of initial reaction mixture :

no conversion	on complete conversion
60 mol of A 40 mol of inerts	240 mol of R 40 mol of inerts
Total = 100 mol	Total = 280 mol

$$\varepsilon_A = \frac{280-100}{100} = 1.8$$

Hence ε_A accounts for both the reaction stoichiometry and the presence of inerts.

Variable volume or density enters the picture when we express the concentration as a function of conversion.

Concentration of reactant A at time t is given by

$$C_A = \frac{N_A}{V}$$

We have
$$N_A = N_{A0}(1-X_A)$$
and
$$V = V_0(1+\varepsilon_A X_A)$$

$$\therefore \quad C_A = \frac{N_{A0}(1-X_A)}{V_0(1+\varepsilon_A X_A)}$$

$$C_A = \frac{C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)} \qquad \ldots (2.98)$$

$$\therefore \quad \frac{C_A}{C_{A0}} = \frac{1-X_A}{1+\varepsilon_A X_A}$$

$$(1+\varepsilon_A X_A)\,C_A = C_{A0}(1-X_A)$$

$$C_A + C_A\,\varepsilon_A X_A = C_{A0} - C_{A0} X_A$$

$$\frac{C_A}{C_{A0}} + \frac{C_A}{C_{A0}}\,\varepsilon_A X_A = 1 - X_A$$

or
$$X_A = \frac{1 - C_A/C_{A0}}{1+\varepsilon_A C_A/C_{A0}} \qquad \ldots (2.99)$$

Rate of disappearance of A is given by

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

$$-r_A = \frac{N_{A0}\,d(1-X_A)}{V_0(1+\varepsilon_A X_A)\,dt}$$

$$-r_A = \frac{C_{A0}\,dX_A}{(1+\varepsilon_A X_A)\,dt} \qquad \ldots (2.100)$$

Concentration of A for iso~~thermal constant~~ pressure batch system (process) is given by

$$C_A = \frac{C_{A0}(1-X_A)}{(1+\varepsilon_A X_A)}$$

Rv Assim

General equation relating V and V_o is

$$V = V_o(1+\varepsilon_A X_A)\frac{T}{T_o} \cdot \frac{P_o}{P}$$

For constant-pressure batch system,

$$V = V_o(1+\varepsilon_A X_A)\frac{T}{T_o}, \text{ as } P = P_o$$

$$\therefore \quad C_A = \frac{C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)}\left(\frac{T}{T_o}\right)$$

For isothermal constant-pressure batch system,

$$C_A = \frac{C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)}, \text{ as } T = T_o$$

Consider a reaction

$$A \rightarrow 2R$$

with 50 mole % A and 50 mole % inerts initially has a rate

$$-r_A = k C_A^2$$

For constant-volume system,

$$-r_A = k C_A^2 = k C_{Ao}^2 \, (1-X_A)^2$$

For variable-volume system,

$$\varepsilon_A = \frac{1.5-1}{1} = 0.5$$

$$\therefore \quad -r_A = k C_A^2 = \frac{C_{Ao}^2 (1-X_A)^2}{(1+0.5 X_A)^2}$$

So it is clear from expressions given above ε_A does make the difference and we should not neglect it.

We have
$$-r_A = \frac{C_{Ao}}{(1+\varepsilon_A X_A)} \frac{dX_A}{dt} \qquad \ldots (2.101)$$

which on integration yields

$$C_{Ao}\int_0^{X_A} \frac{dX_A}{(1+\varepsilon_A X_A)(-r_A)} = t \qquad \ldots (2.102)$$

Equation (2.102) is the general expression in which the volume is a linear function of conversion of a reactant A.

For first order reaction,

$$-r_A = k C_A = \frac{k C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$\frac{r_A}{dA}$

$\therefore$ Combining equations (2.101) and (2.102), we get,

$$C_{Ao}\int_0^{X_A} \frac{dX_A}{(1+\varepsilon_A X_A)\cdot \dfrac{k C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)}} = t$$

$$\therefore \quad \int_0^{X_A} \frac{dX_A}{1-X_A} = kt, \quad -\ln(1-X_A) = kt$$

$$V = V_o(1 + \varepsilon_A X_A)$$

$$V - V_o = \Delta V = V_o \varepsilon_A X_A$$

$$X_A = \frac{\Delta V}{V_o \varepsilon_A}$$

$$\therefore \quad -\ln(1 - X_A) = -\ln\left(1 - \frac{\Delta V}{\varepsilon_A V_o}\right) = kt \qquad \ldots (2.103)$$

The equation (2.103) is the integrated rate equation for first order reaction for variable-volume system.

This way we can make use of equation (2.102) and obtain the integrated rate expressions for reactions of different orders.

Zero-Order Reactions

For zero-order reaction, the rate of change of any reactant A is independent of the concentration of materials.

$$\therefore \quad -r_A = -\frac{1}{V}\frac{dN_A}{dt} = \frac{C_{Ao}}{1 + \varepsilon_A X_A}\frac{dX_A}{dt} = k$$ C_A^n (n=0)

$$\frac{C_{Ao}}{1 + \varepsilon_A X_A}\frac{dX_A}{dt} = k$$

Integrating above equation within the limits : at t = 0, $X_A = 0$, and at t = t, $X_A = X_A$

$$C_{Ao}\int_0^{X_A}\frac{dX_A}{1 + \varepsilon_A X_A} = k\int_0^t dt$$

$$1 + \varepsilon_A X_A = Y$$

$$\varepsilon_A\, dX_A = dY$$

$$dX_A = dY/\varepsilon_A$$

$$\therefore \quad \frac{C_{Ao}}{\varepsilon_A}\int_1^{1 + \varepsilon_A X_A}\frac{dY}{Y} = kt$$

$$\frac{C_{Ao}}{\varepsilon_A}\ln(1 + \varepsilon_A X_A) = kt \qquad \ldots (2.104)$$

We have, $V = V_0(1 + \varepsilon_A X_A) \;\therefore\; (1 + \varepsilon_A X_A) = V/V_0$

$$\frac{C_{Ao}}{\varepsilon_A}\ln(1 + \varepsilon_A X_A) = \frac{C_{Ao}}{\varepsilon_A}\ln\frac{V}{V_o} = kt \qquad \ldots (2.105)$$

The equation (2.105) is the integrated rate equation for zero order reaction for a variable-volume system.

A plot of logarithm of the fractional change in volume versus time yields a straight line with slope equal to $k\varepsilon_A/C_{Ao}$.

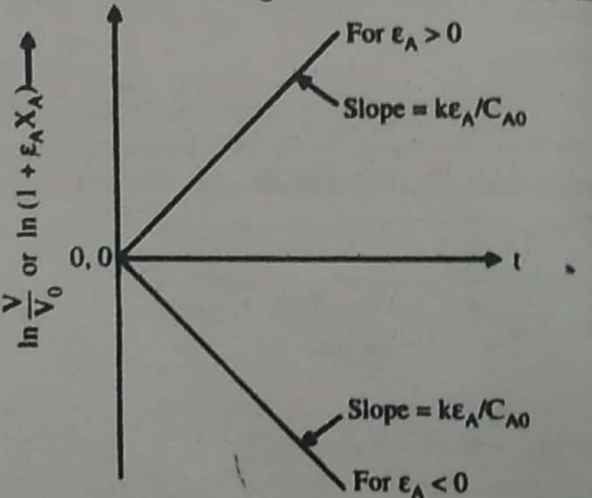


Fig. 2.16 : Test for zero-order reaction in constant-pressure variable-volume reactor

First-Order Reactions :

Consider unimolecular first-order reaction of the type

$$A \rightarrow \text{Products}$$

The rate of disappearance of A is given by

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

Putting the values of $-r_A$ and C_A in terms of X_A, we get

$$\frac{C_{A0}}{1+\varepsilon_A X_A}\cdot\frac{dX_A}{dt} = \frac{k\,C_{A0}\,(1-X_A)}{1+\varepsilon_A X_A}$$

$$\frac{dX_A}{dt} = k\,(1-X_A)$$

$$\int_0^{X_A}\frac{dX_A}{1-X_A} = k\int_0^t dt$$

$$\therefore \quad -\ln(1-X_A) = k\,t \qquad \dots (2.106)$$

We know, $V = V_0\,(1+\varepsilon_A X_A)$

$$V = V_0 + V_0\varepsilon_A X_A$$

$$\frac{V-V_0}{V_0\varepsilon_A X_A} = \frac{\Delta V}{\varepsilon_A V_0} = X_A$$

$$\therefore \quad \boxed{-\ln(1-X_A) = -\ln\left(1-\frac{\Delta V}{\varepsilon_A V_0}\right) = k\,t} \qquad \dots (2.107)$$

The equation (2.107) is the integrated rate expression for first-order reaction for variable-volume system.

A plot of $-\ln(1-\Delta V/\varepsilon_A V_0)$ versus t yields a straight line with slope equal to k.

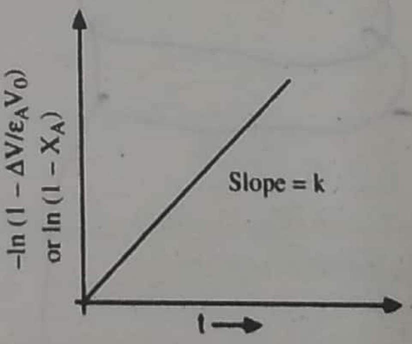


Fig. 2.17 : Test for a first-order reaction in a constant-pressure, variable-volume reactor

Second-Order Reactions :

For a bimolecular type second order reaction,

$$2A \rightarrow \text{Products}$$

or

$$A + B \rightarrow \text{Products},\ C_{A0} = C_{B0}$$

The rate of reaction of A is given by

$$-r_A = k\,C_A^2$$

Putting values of $-r_A$ and C_A, we get

$$\frac{C_{A0}}{1+\varepsilon_A X_A}\cdot\frac{dX_A}{dt} = k\,C_{A0}^2\left(\frac{1-X_A}{1+\varepsilon_A X_A}\right)^2$$

Rearranging, we get,

$$\int_0^{X_A} \frac{(1+\varepsilon_A X_A)}{(1-X_A)^2}\, dX_A = k\, C_{Ao} \int_0^{t} dt$$

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)^2} + \varepsilon_A \int_0^{X_A} \frac{X_A\, dX_A}{(1-X_A)^2} = k\, C_{Ao}\, t \qquad \ldots (2.108)$$

$$\text{Let } 1 - X_A = Y \qquad \therefore dX_A = -dY$$

$$X_A = 1 - Y$$

At $X_A = 0,\ Y = 1$

At $X_A = X_A,\ Y = 1 - X_A$

$$-\int_1^{1-X_A} \frac{dY}{Y^2} - \varepsilon_A \int_1^{1-X_A} \frac{(1-Y)}{Y^2}\, dY = k\, C_{Ao}\, t$$

$$-\left[-\frac{1}{Y}\right]_1^{1-X_A} - \varepsilon_A \left[-\frac{1}{Y}\right]_1^{1-X_A} + \varepsilon_A\, [\ln Y]_1^{1-X_A} = k\, C_{Ao}\, t$$

$$\left[\frac{1}{1-X_A} - 1\right] + \varepsilon_A \left[\frac{1}{1-X_A} - 1\right] + \varepsilon_A \ln(1-X_A) = k\, C_{Ao} t$$

$$\frac{X_A}{1-X_A} + \frac{\varepsilon_A X_A}{1-X_A} + \varepsilon_A \ln(1-X_A) = k\, C_{Ao} t$$

$$\frac{(1+\varepsilon_A)\, X_A}{1-X_A} + \varepsilon_A \ln(1-X_A) = k\, C_{Ao}\, t \qquad \ldots (2.109)$$

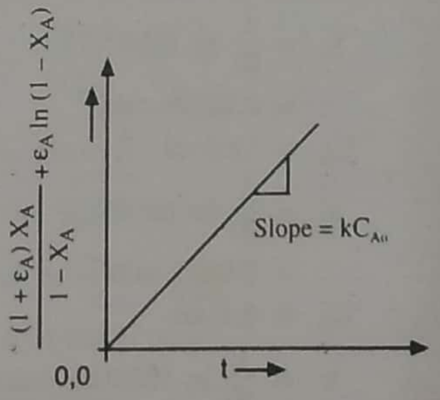


Fig. 2.18 : Test for the second order reaction in a constant pressure-variable volume batch reactor

SOLVED EXAMPLES

Ex. 2.1 : The rate constant of a zero order reaction is 0.2 mol/(l.h). What will be the initial concentration of the reactant if, after half an hour, its concentration is 0.05 mol/l ?

Solution : The concentration of the reactant (C_A) after time 't' for zero order reaction is given by :

$$C_A = C_{Ao} - kt$$

$$C_A = 0.05,\ k = 0.2\ \text{mol}/(l\cdot\text{h}),\quad t = 0.5\ \text{h}$$

Initial concentration, C_{Ao} is given as :

$$C_{Ao} = C_A + kt$$
$$= 0.05 + 0.2 \times 0.5$$
$$= 0.15\ \text{mol}/l \qquad \ldots \textbf{Ans.}$$

Ex. 2.2 : The half-life period of a reaction of the first order is 240 seconds. Calculate its rate constant in seconds and minutes.

Solution : For first order reaction :

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

$$\therefore \quad k = \frac{0.693}{t_{1/2}}$$

$$t_{1/2} = 240\ \text{s}$$

$$k = \frac{0.693}{240} = 2.89 \times 10^{-3}\ (\text{s})^{-1}$$

$$k = 2.89 \times 10^{-3} \times 60$$

$$= 0.1732\ (\text{min})^{-1} \qquad \text{... Ans.}$$

$C_A = 0.25\ C_{A0}$

Ex. 2.3 : The half life period for a certain first order reaction is 2.5×10^3 s. How long will it take for 1/4 of the reactant to be left behind ?

Solution : For the first order reaction :

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

Now

$$t_{1/2} = 2.5 \times 10^3\ \text{s}$$

$$k = \frac{0.693}{2.5 \times 10^3}$$

$$= 2.77 \times 10^{-4}\ \text{s}$$

Let the time required for the reactant to decrease in concentration to 1/4th of its original concentration to be t then

$$C_{A_0} = 1\ \text{mol}/l, \quad C_A = 1/4\ \text{mol}/l$$

$$t = \frac{1}{k} \ln [C_{A_0}/C_A]$$

$$= \frac{1}{2.77 \times 10^{-4}} \ln \left[\frac{1}{1/4}\right]$$

$$= 5005.5\ \text{s} \qquad \text{... Ans.}$$

Ex. 2.4 : Show that the decomposition of N_2O_5 at 67 °C is a first order reaction. Calculate the value of the rate constant.

Data :

Time, min	0	1	2	3	4
$C_{N_2O_5}$, mol/l	0.16	0.113	0.08	0.056	0.040

Solution : $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2} O_2$

$$N_2O_5 \rightarrow \text{Products}$$

$$A \rightarrow \text{Products}$$

For the first order reaction, we have :

$$-\ln\left(\frac{C_A}{C_{A_0}}\right) = k.\,t$$

(1) $C_A = 0.113$ mol/l at $C_{Ao} = 0.16$; t = 1 min.

$$\therefore \quad k = \frac{-\ln(C_A/C_{A0})}{t}$$

$$= \frac{-\ln(0.113/0.160)}{1} = 0.3478 \text{ min}^{-1}$$

(2) $C_A = 0.08$ mol/l at t = 2 min.

$$k = \frac{-\ln(0.08/0.160)}{2} = 0.3466 \text{ min}^{-1}$$

(3) $C_A = 0.056$ mol/l at t = 3 min

$$k = \frac{-\ln(0.056/0.160)}{3} = 0.3499 \text{ min}^{-1}$$

(4) $C_A = 0.040$ mol/l at t = 4 min.

$$k = \frac{-\ln(0.040/0.160)}{4} = 0.3466 \text{ min}^{-1}$$

As the values of rate constant (k) for all the observations are approximately same, the reaction is first order in N_2O_5.

N. B. : Graphically, if we plot ln (C_{Ao}/C_A) v/s 't' then we will get a straight line through origin indicating that the reaction is first order in N_2O_5.

$$\text{Average value of rate constant (k)} = \frac{0.3478 + 0.3466 + 0.3499 + 0.3466}{4}$$

$$= 0.3477 \text{ min}^{-1}$$

... **Ans.**

LB **Ex. 2.5 :** In a gaseous reaction, time for half change ($t_{1/2}$) for various initial partial pressures (p) of the reactant was given as follows :

p_{Ao} (torr)	200	300	400
$t_{1/2}$ (min)	150	99.8	75.3

Find the order of the reaction.

Solution : We have

$$t_{1/2} \propto C_{Ao}^{1-n}$$

$$t'_{1/2}/t''_{1/2} = \left(C'_{Ao}/C''_{Ao}\right)^{1-n}$$

$$\ln\left(t'_{1/2}/t''_{1/2}\right) = (1-n)\ln\left(C'_{Ao}/C''_{Ao}\right)$$

$$\ln\left(t'_{1/2}/t''_{1/2}\right) = (n-1)\ln\left(C''_{Ao}/C'_{Ao}\right)$$

$$n = 1 + \frac{\ln\left(t'_{1/2}/t''_{1/2}\right)}{\ln\left(C''_{Ao}/C'_{Ao}\right)}$$

We know $C_{Ao} \propto p_{Ao}$

$$\therefore \quad n = 1 + \ln\left(\frac{t'_{1/2}/t''_{1/2}}{p''_{Ao}/p'_{Ao}}\right)$$

For $t'_{1/2} = 150$, $p'_{Ao} = 200$, and for $t''_{1/2} = 99.8$, $p''_{Ao} =$ ~~99.8~~ 300

$$n = 1 + \log\left(\frac{150/99.8}{300/200}\right)$$

$$= 2.0$$

Similarly, $n = 1 + \log\left(\frac{99.8/75.3}{400/300}\right)$

$= 1.97 = 2$ ... **Ans.**

Thus, the order of the reaction is two.

Ex. 2.6 : From the following data, show that the decomposition of hydrogen peroxide in aqueous solution is a first order reaction. What is the value of rate constant ?

Time, min	0	10	20	30	40
no. of N C_{A_o}	25.0	20.0	15.7	12.5	9.6

where 'N' is the number of ml of $KMnO_4$ required to decompose a definite volume of H_2O_2 solution.

Solution : The initial volume of $KMnO_4$, V_o (i. e. when $t = 0$) corresponds to initial concentration of H_2O_2 (i. e. C_{A_o}) and the volume of $KMnO_4$ at any time 't' corresponds to the undecomposed H_2O_2 at that time (i. e. C_A).

As decomposition is a first order reaction, for first order reaction, we have :

$$k = \frac{1}{t} \ln\left(\frac{C_{Ao}}{C_A}\right)$$

$$C_{Ao} \equiv 25 \text{ ml}$$

For $t = 10$ min, $C_A \equiv 20$ ml

$$\therefore \quad k = \frac{1}{10} \ln(25/20)$$

$$= 0.0223 \text{ min}^{-1}$$

For $t = 20$ min, $C_A \equiv 15.7$ ml

$$\therefore \quad k = \frac{1}{20} \ln(25/15.7)$$

$$= 0.02326 \text{ min}^{-1}$$

For $t = 30$ min, $C_A \equiv 12.5$ ml

$$k = \frac{1}{30} \ln(25/12.5)$$

$$= 0.0231 \text{ min}^{-1}$$

For $t = 40$ min, $C_A \equiv 9.8$ ml

$$k = \frac{1}{40} \ln(25/9.8)$$

$$= 0.0239 \text{ min}^{-1}$$

Average value of k (Rate constant) $= \dfrac{(0.0223 + 0.02326 + 0.0231 + 0.0239)}{4}$

$= 0.02314 \text{ min}^{-1}$ ... **Ans.**

Ex. 2.7 : The half life of a first order reaction A → B is 10 min. What per cent of A remains after 60 min ?

Solution : $t_{1/2} = \dfrac{0.693}{k}$

$\therefore \quad k = 0.693/10 = 0.0693 \text{ min}^{-1}$

For first order reaction, $\ln C_{Ao}/C_A = k\,t$

$t = 60$ min, $k = 0.0693 \text{ min}^{-1}$

$$\ln C_{Ao}/C_A = 0.0693 \times 60$$

$$\ln C_{A_0}/C_A = 4.158 \quad \therefore\ C_{A_0}/C_A = 63.94$$

$$\frac{C_A}{C_{A0}} : \frac{1}{63.64}$$

$$\therefore \quad C_A = 0.01563\, C_{A_0}$$

$$\therefore \quad \%\text{ of A remaining} = \frac{C_A}{C_{A_0}} \times 100 = \frac{0.01563\, C_{A_0}}{C_{A_0}} \times 100 = 1.563\ \%$$ ... **Ans.**

Imp

Ex. 2.8 : Decomposition of a gas is of second order when initial concentration of gas is 5×10^{-4} mol/*l*, it is 40 % decomposed in 50 min. Calculate the value of rate constant.

Solution : For second order reaction, we have

$$k = \frac{1}{t}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$$

$$t = 50 \text{ min}$$

$$C_{A0} = 5 \times 10^{-4} \text{ mol}/l$$

Gas is 40 % decomposed $\therefore\ C_A = 0.6 \times 5 \times 10^{-4}$

$$= 3 \times 10^{-4} \text{ mol}/l$$

$$k = \frac{1}{50}\left[\frac{1}{3 \times 10^{-4}} - \frac{1}{5 \times 10^{-4}}\right]$$

$$= 26.67\ (l/\text{mol})\ (\text{min})^{-1}$$ ... **Ans.**

Ex. 2.9 : At 25°C the rate constant for the hydrolysis of ethyl acetate by NaOH is 6.5 $(l/\text{mol}) \cdot (\text{min})^{-1}$ starting with concentration of base and ester of 0.03 mol/*l* of each. What proportion of ester will be hydrolysed in 10 min ?

Solution : Rate constant = k = 6.5 $(l/\text{mol})\ (\text{min})^{-1}$

It is a rate constant of reaction of second order kinetics.

For same initial concentration (0.03 mol/*l*) of both ester and alkali, we have

$$k = \frac{1}{t}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$$

$$-r_A = kC_A^n$$

$$\frac{1}{C_A} = kt + \frac{1}{C_{A0}}$$

k = 6.5 *l*(mol·min), t = 10 min, $C_{A0} = 0.03$ mol/*l*

$$\therefore \quad \frac{1}{C_A} = 6.5 \times 10 + \frac{1}{0.03}$$

$$C_A = 0.01017 \text{ mol}/l$$

$$\frac{\text{Mol}}{41.5} \quad \frac{\text{mo}}{\text{lit}}$$

Proportion of ester hydrolysed

$$= \frac{0.03 - 0.01017}{0.03} \times 100$$

$$= 66.1\ \%.$$ ... **Ans.**

B

Ex. 2.10 : The half life for the conversion of ammonium cynate into urea at 303 K at initial concentrations of ammonium cynate of 0.1 mol/*l* and 0.2 mol/*l* are 1152 min and 568 min, respectively. What is the order of reaction ?

Solution : In terms of half life times at different concentrations, the order of reaction is given by

$$t_{1/2} \propto C_{A0}^{1-n}$$

$$t_{1/2} = m\, C_{A0}^{1-n}$$

RV ASSUM.

$$\frac{t'_{1/2}}{t''_{1/2}} = \left(\frac{C'_{Ao}}{C''_{Ao}}\right)^{1-n}$$

$$\ln\left(t'_{1/2}/t''_{1/2}\right) = (1-n)\ln\left(C'_{Ao}/C''_{Ao}\right)$$

$$\ln\left(t'_{1/2}/t''_{1/2}\right) = (n-1)\ln\left(C''_{Ao}/C'_{Ao}\right)$$

$$n = 1+\frac{\ln\left(t'_{1/2}/t''_{1/2}\right)}{\ln\left(C''_{Ao}/C'_{Ao}\right)}$$

where $C'_{Ao} = 0.1$ mol/l at $t_{1/2} = 1152$ min.

$C''_{Ao} = 0.2$ mol/l at $t''_{1/2} = 568$ min.

$$n = 1+\frac{\ln 1152/568}{\ln 0.2/0.1}$$

$$= 1+\frac{0.3071}{0.3010}$$

$$= 1+1.02$$

$$= 2.02$$

... **Ans.**

Hence, the order of reaction is 2.

Ex. 2.11 : The partial pressure of azomethane, $CH_3N_2CH_3$, was observed as a function of time at 600 K with results given below. Confirm that the decomposition

$CH_3N_2CH_3 \rightarrow CH_3CH_3 + N_2$

is first order in $CH_3N_2CH_3$, and find the rate constant at this temperature.

Time, (s)	0	1000	2000	3000	4000
Partial pressure, torr (mmHg)	820	572	399	278	194

Solution : $CH_3N_2CH_3 \rightarrow CH_3CH_3 + N_2$

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

$$C_A = p_A/RT$$

$$\frac{dC_A}{dt} = \frac{1}{RT}\frac{dp_A}{dt}$$

$$-r_A = -\frac{dC_A}{dt} = k\,C_A$$

$$-\frac{dp_A/dt}{RT} = \frac{k\,p_A}{RT}$$

$$\therefore \quad \ln(p_{Ao}/p_A) = kt$$

$$k = \frac{1}{t}\ln(p_{Ao}/p_A)$$

(i) $p_{Ao} = 820$ torr (mmHg), [1 torr = 1 mm Hg]

$p_A = 572$ torr, $t = 1000$ s

$$k = \frac{1}{t}\ln\left(\frac{p_{A_o}}{p_A}\right) = \frac{1}{1000}\ln(820/572)$$

$$= 3.6 \times 10^{-4}\ (s)^{-1}$$

(ii)
$$k = \frac{1}{t}\ln(p_{A_o}/p_A)$$

$$t = 2000\ s,\ p_A = 399\ \text{torr},\ p_{A_o} = 820\ \text{torr}$$

$$k = \frac{1}{2000}\ln(820/399) = 3.6 \times 10^{-4}\ (s)^{-1}$$

Calculate values of k for various values of t and p_A. If we get almost same value for k then we confirm the decomposition to be first order or if we plot ln (p_{A_o}/p_A) versus t and if plot yields a straight line through origin then we conclude the decomposition to be first order.

t, s	0	1000	2000	3000	4000
p_A, torr	820	572	399	278	194
k, $(s)^{-1}$	–	3.6×10^{-4}	3.6×10^{-4}	3.6×10^{-4}	3.6×10^{-4}

As we have obtained the same value of k for all readings, the decomposition of azomethane is first order.

Average value of rate constant = k = $3.6 \times 10^{-4}\ (s)^{-1}$. ... **Ans.**

Ex. 2.12 : The half-life periods for decomposition of PH_3 for different initial pressures are given below :

p, torr	707	79	37.5
$t_{1/2}$, min.	84	84	84

Confirm order of reaction.

Solution : A → Products.

$$p_{A_o} = P_o \text{ (pure A initially)}$$

$$C_{A_o} \propto p_{A_o}$$

$$C_{A_o} \propto P_o$$

In terms of half-life times at different concentrations (pressures), the order of reaction is

$$t_{1/2} \propto C_{A_o}^{1-n}$$

$$t_{1/2} \propto p_{A_o}^{1-n}$$

$$t_{1/2} \propto P_o^{1-n}$$

1° $C_A C_B$

$$\therefore \quad n = 1 + \frac{\ln[t'_{1/2}/t''_{1/2}]}{\ln[P''_o/P'_o]}$$

In this problem, $t'_{1/2} = t''_{1/2} = t'''_{1/2} = 84$ min

$$\therefore \quad n = 1 + 0$$

$$= 1$$

For first order reaction, half-life period is independent of initial concentration of reactant.

∴ Order of reaction = 1. ... **Ans.**

Ex. 2.13 : Determine the order of reaction from the following data

Conc. of A, mol/l	1.0	1.0	0.02	0.04
Conc. of B, mol/l	0.02	0.04	1.0	1.0
Rate of reaction, mol/(l·min)	4.6×10^{-4}	9.2×10^{-4}	9.2×10^{-6}	3.68×10^{-5}

Determine the true rate constant also.

$-r = k\ C_A\ C_B$

Solution : When the concentration of A is very large and constant, the rate depends upon the concentration of B only. Therefore order of reaction with respect to B is calculated as

$$n_B = \frac{\ln r_1/r_2}{\ln C_{B_1}/C_{B_2}}$$

$$\frac{r_1}{r_2} = \left(\frac{C_{B_1}}{C_{B_2}}\right)^n$$

$r_1 = 4.6 \times 10^{-4}$ mol/(l·min), $C_{B_1} = 0.02$ mol/l

$r_2 = 9.2 \times 10^{-4}$ mol/(l·min), $C_{B_2} = 0.04$ mol/l

$$\therefore \quad n_B = \frac{\ln (4.6 \times 10^{-4}/9.2 \times 10^{-4})}{\ln (0.02/0.04)}$$

$$= \frac{-0.301}{-0.301} = 1$$

When the concentration of B is very large and constant, the rate depends upon the concentration of A, hence

$$n_A = \frac{\ln r'_1/r'_2}{\ln C_{A_1}/C_{A_2}}$$

$r'_1 = 9.2 \times 10^{-6}$ mol/(l·min), $C_{A_1} = 0.02$ mol/l

$r'_2 = 3.68 \times 10^{-5}$ mol/(l·min), $C_{A_2} = 0.04$ mol/l

$$\therefore \quad n_A = \frac{\ln (9.2 \times 10^{-6}/3.68 \times 10^{-5})}{\ln (0.02/0.04)}$$

$$= \frac{-0.602}{-0.301} = 2$$

Therefore, the order of reaction

$$= n = n_A + n_B$$

$$= 2 + 1 = 3$$

The rate equation may be given as

$$\text{Rate} = k\, C_A^2 \cdot C_B$$

$$\text{True rate constant} = k = \frac{\text{Rate}}{C_A^2 \cdot C_B}$$

$$\text{(i)} \quad k = \frac{4.6 \times 10^{-4}}{(1)^2\,(0.02)} = 2.3 \times 10^{-2}\,(\text{mol}/l)^{-2}\,(\text{min})^{-1}$$

$$\text{(i)} \quad k = \frac{9.2 \times 10^{-4}}{(1.0)^2\,(0.04)} = 2.3 \times 10^{-2}\,(\text{mol}/l)^{-2}\,(\text{min})^{-1}$$

$$\text{(i)} \quad k = \frac{9.2 \times 10^{-6}}{(0.02)^2\,(1.0)} = 2.3 \times 10^{-2}\,(\text{mol}/l)^{-2}\,(\text{min})^{-1}$$

$$\text{(i)} \quad k = \frac{3.68 \times 10^{-5}}{(0.04)^2\,(1.0)} = 2.3 \times 10^{-2}\,(\text{mol}/l)^{-2}\,(\text{min})^{-1}$$

Hence, true rate constant = $2.3 \times 10^{-2}\,(\text{mol}/l)^{-2}\,(\text{min})^{-1}$.

Ex. 2.14 : The rates of reaction at concentrations 0.15 mol/l and 0.05 mol/l are 2.7 × and 0.3×10^{-3} mol/(l·min). What is the order of reaction with respect to the reactant ?

Solution : Order of reaction is given by the equation

$$(-r_1) \propto C_{A_1}^n$$

-1.38

$$(-r_2) \propto C_{A_2}^n$$

$$\therefore \quad \frac{(-r_1)}{(-r_2)} = (C_{A_1}/C_{A_2})^n$$

$$\ln(-r_1/-r_2) = n \ln C_{A_1}/C_{A_2}$$

$$n = \frac{\ln\left[\frac{-r_1}{-r_2}\right]}{\ln(C_{A_1}/C_{A_2})}$$

$$n = \frac{\ln(-r_1) - \ln(-r_2)}{\ln C_{A_1} - \ln C_{A_2}}$$

$$(-r_1) = 2.7 \times 10^{-3} \text{ mol/}(l.\text{min})$$

$$C_{A_1} = 0.15 \times 10^{-3} \text{ mol/}l$$

$$(-r_2) = 0.3 \times 10^{-3} \text{ mol/}(l\cdot\text{min})$$

$$C_{A_2} = 0.05 \text{ mol/}l$$

$$\therefore \quad n = \frac{\ln(2.7 \times 10^{-3}/0.3 \times 10^{-3})}{\ln(0.15/0.05)}$$

$$n = 2$$

∴ Order of reaction is 2.

(1) Reaction is of second order. ... **Ans.**

Ex. 2.15 : In case of first order reaction, show that time required for 75 % conversion is double the time required for 50 % conversion.

t_1

$x = 0.75$

Solution : Integrated first order rate equation in terms of conversion is

$$\ln\left(\frac{1}{1-X_A}\right) = kt$$

$$\therefore \quad t = \frac{1}{k}\ln\left(\frac{1}{1-X_A}\right)$$

t_2

$x = 0.50$

$t_1 = 2t_2$

Let us first find time t for 50 % conversion,

$$X_A = 0.5$$

$$t' = \frac{1}{k}\ln\left(\frac{1}{1-0.5}\right)$$

$$t' = \frac{0.693}{k}$$

For 75 % conversion,

$$X_A = 0.75$$

$$\therefore \quad t'' = \frac{1}{k}\ln\left(\frac{1}{1-0.75}\right)$$

$$t'' = \frac{1.386}{k}$$

$$\therefore \quad t'' = \frac{1.386}{k} = 2t'$$

∴ Time required for 75 % conversion is double that required for 50 % conversion.

By Assum.

Imp

Ex. 2.16 : In studying the kinetics of decomposition of a reaction, the concentrations of reactants were determined analytically at different times. The following results were obtained :

Time, min	0	10	20	40	100	125
Conc., mol/*l*	0.10	0.0714	0.0556	0.0385	0.02	0.0167

Determine the order and rate constant for the reaction.

Solution : Let us first try the first order reaction.

$$k = \frac{1}{t} \ln \left(\frac{C_{A0}}{C_A}\right)$$

Time	C, mol/*l*	k, min^{-1}
0	0.10	–
10	0.0714	0.0343
20	0.0556	0.0342
40	0.0385	0.0239
100	0.02	0.0161
125	0.0167	0.0062

It can be seen from above table that k is not constant at different times. Hence, the reaction is not of first order.

Let us try the second order rate equation.

$$k = \frac{1}{t}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$$

t, min	C_A, mol/*l*	k, (*l*/mol) (min)$^{-1}$
0	0.1	–
10	0.0714	0.40
20	0.0556	0.399
40	0.0385	0.399
100	0.02	0.400
125	0.0167	0.399

It can be seen from above table that the second order rate constant k is nearly constant at different data. Therefore, the given reaction is of second order with rate constant equal to 0.40 (*l*/mol) (min)$^{-1}$. ... **Ans.**

$\therefore$ Rate of decomposition = 0.40 (*l*/mol) (min)$^{-1}$ C_A^2 ... **Ans.**

Ex. 2.17 : The data for a chemical reaction A + B → P is given below :

Imp system 2 eqn

C_A	C_B	– dC_A/dt, initial rate
0.5	0.5	0.02
1.0	0.5	0.08
1.0	1.0	0.16

Determine the overall order of reaction.

Solution : Rate of disappearance of A is given by

$$\frac{-dC_A}{dt} = k\, C_A^{\alpha}\, C_B^{\beta}$$

where α and β are the orders with respect to A and B.

Using the above equation, we get from data :

$$0.08 = k\,(1.0)^{\alpha} \times (0.5)^{\beta} \quad \dots (1)$$

and

$$0.02 = k\,(0.5)^{\alpha} \times (0.5)^{\beta} \quad \dots (2)$$

Dividing (1) by (2), we get

$$\frac{0.08}{0.02} = \frac{k\,(1.0)^{\alpha} \times (0.5)^{\beta}}{k\,(0.5)^{\alpha} \times (0.5)^{\beta}}$$

$$\frac{4}{1} = 2^{\alpha}$$

$$\therefore \quad \alpha = 2$$

Thus order with respect to A is 2.

Similarly,

$$\frac{0.16}{0.08} = \frac{k\,(1.0)^{\alpha} \times (1.0)^{\beta}}{k\,(1.0)^{\alpha} \times (0.5)^{\beta}}$$

$$2 = 2^{\beta} \quad \therefore \ \beta = 1$$

Thus order with respect to B is 1.

Overall order of reaction = $\alpha + \beta = 2 + 1 = 3$. ... **Ans.**

Ex. 2.18 : For the reaction A → Products the following data were obtained at 25° C, in which the concentration of A is given at different intervals of time :

t, min	0	10	20	30	40
C_A, mol/*l*	0.860	0.740	0.635	0.546	0.405

Find the order of reaction, and calculate the rate constant and the half life period.

Solution : A → Products

Let us try first order reaction.

$$k = \frac{1}{t} \ln \left(\frac{C_{Ao}}{C_A} \right)$$

t, min.	C_A, mol/*l*	k, min^{-1}
0	0.860	–
10	0.740	0.01503
20	0.635	0.01516
30	0.546	0.01514
50	0.405	0.01506

It can be seen from column 3 of above table the first order k is nearly constant at different times. Therefore, the given reaction is first order.

Average value of k = 0.01509 (min)$^{-1}$

$$\text{Rate} = k\,C_A$$

$$\text{Rate} = 0.01509\ (\text{min})^{-1}.\ C_A \quad \dots \textbf{Ans.}$$

$$\text{Half-life period} = t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.01509}$$

$$= 45.92 \text{ min.} \quad \dots \textbf{Ans.}$$

Imp

Ex. 2.19 : At certain temperature, the half-life periods and initial concentrations for a reaction are

$t_{1/2} = 420$ s, $C_{Ao} = 0.405$ mol/*l*

$t_{1/2} = 275$ s, $C_{Ao} = 0.64$ mol/*l*

Find the rate constant of a reaction.

25
50
70

Solution :

$$n = 1 + \frac{\ln t'_{1/2}/t''_{1/2}}{\ln C''_{A_0}/C'_{A_0}}$$

where $t'_{1/2} = 420$ s, $t''_{1/2} = 275$ s.

$C'_{A_0} = 0.405$ mol/l, $C''_{A_0} = 0.64$ mol/l

$$\therefore \quad n = 1 + \frac{\ln 420/275}{\ln 0.64/0.405}$$

$$= 1 + 0.925$$

$$= 1.925$$

$$\approx 2$$

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)\,k\,C_{A_0}^{n-1}}$$

$$k = \frac{2^{n-1} - 1}{t_{1/2}\,C_{A_0}^{n-1}}$$

Putting n = 2, we get

$$k = \frac{2-1}{t_{1/2}\,C_{A_0}}$$

$$= \frac{1}{t_{1/2}\,C_{A_0}} = \frac{1}{420 \times 0.405}$$

$$= 5.88 \times 10^{-3} \ (l/\text{mol})\ (\text{min})^{-1}$$

... **Ans.**

B

Ex. 2.20 : The reaction 2 B (g) → B_2 (g) was carried out at a temperature of 325°C and constant volume. Measurement of the total pressure as the reaction proceed gave the following data :

t, min.	0	10	20	30	40	50	60	70	80
P, kPa	84.25	78.91	74.25	71.12	68.52	66.25	64.52	63.05	61.72

A rate expression of the following form is assumed

$$-\frac{dp}{dt} = k\,p^n$$

where p is the partial pressure of B. Determine the values of k and n.

Solution : $2\,B\,(g) \rightarrow B_2\,(g)$

$$\Delta n = 1 - 2 = -1$$

$$a = 2.$$

Partial pressure of B at any time t is given by

$$p_B = p = p_{B_0} - \frac{a}{\Delta n}(P - P_0)$$

At $t = 0$, $p_{B_0} = P_0$

$$\therefore \quad p = P_0 - \frac{2}{(-1)}(P - P_0)$$

$$p = P_0 + 2\,(P - P_0)$$

$$p = 2P - P_0$$

(Partial pressure in terms of total pressure)

$$\therefore \quad dp = 2\,dP$$

We have given

$$-\frac{dp}{dt} = k\,p^n$$

Expressing this equation in terms of total pressure, we get

$$-2\frac{dP}{dt} = k\,(2\,P - P_0)^n$$

$$-2\frac{dP}{(2\,P - P_0)^n} = k\,dt$$

This equation is in terms of total pressure as a function of time.

$$-2\int_{P_0}^{P} \frac{dP}{(2P - P_0)^n} = k\int_0^t dt = kt$$

Let $2P - P_0 = y$

$2\,dP = dy \;\therefore\; dP = dy/2$

At $P = P_0$, $y = P_0$

At $P = P$, $y = 2P - P_0$

$$-\frac{2}{2}\int_{P_0}^{2P-P_0} \frac{dy}{y^n} = kt$$

$$-\left[\frac{y^{1-n}}{1-n}\right]_{P_0}^{2P-P_0} = kt$$

$$\frac{1}{(n-1)}\left[\frac{1}{(2P - P_0)^{n-1}} - \frac{1}{(P_0)^{n-1}}\right] = kt$$

$$\therefore \quad k = \frac{1}{t\,(n-1)}\left[\frac{1}{(2P - P_0)^{n-1}} - \frac{1}{(P_0)^{n-1}}\right]$$

Referring above equation, $n = 1$ is not possible

$\therefore$ Assume $n = 2$ i. e. second order reaction

If we get constant values of k then the assumed order will be correct.

For $n = 2$, above equation becomes

$$k = \frac{1}{t}\left[\frac{1}{2P - P_0} - \frac{1}{P_0}\right]$$

$P_0 = 84.25$ kPa

Evaluate k at different times

(i) $t = 10$, $P = 78.91$ kPa

$$\therefore \quad k = \frac{1}{10}\left[\frac{1}{2 \times 78.91 - 84.25} - \frac{1}{84.25}\right]$$

$$= 1.723 \times 10^{-4}\ (\text{kPa})^{-1}\ (\text{min})^{-1}$$

(ii) $t = 20$, $P = 74.25$ kPa

$$\therefore \quad k = \frac{1}{20}\left[\frac{1}{2 \times 74.25 - 84.25} - \frac{1}{84.25}\right]$$

$$= 1.799 \times 10^{-4}\ (\text{kPa})^{-1}\ (\text{min})^{-1}$$

(iii) $t = 30$, $P = 71.25$ kPa

$$\therefore \quad k = \frac{1}{30}\left[\frac{1}{2 \times 71.25 - 84.25} - \frac{1}{84.25}\right]$$

$$= 1.766 \times 10^{-4}\ (\text{kPa})^{-1}\ (\text{min})^{-1}$$

(iv) $t = 40$, $P = 68.52$ kPa

$$\therefore \quad k = \frac{1}{40}\left[\frac{1}{2 \times 68.52 - 84.25} - \frac{1}{84.25}\right]$$

$$= 1.768 \times 10^{-4}\ (\text{kPa})^{-1}\ (\text{min})^{-1}$$

We are getting almost same values of k. Therefore assumed order of reaction is correct.

t, min	P, (kPa)	k, (kPa. min)$^{-1}$
0	84.25 (P_0)	–
10	78.91	1.723×10^{-4}
20	74.25	1.799×10^{-4}
30	71.52	1.766×10^{-4}
40	68.52	1.768×10^{-4}
50	66.25	1.77×10^{-4}
60	64.52	1.743×10^{-4}
70	63.05	1.718×10^{-4}
80	61.72	1.706×10^{-4}
		1.749×10^{-4} (avg.)

Order of reaction is 2, and Average value of $k = 1.749 \times 10^{-4}\ (\text{kPa.min})^{-1}$. .... **Ans.**

Ex. 2.21 : A gas A, decomposes irreversibly to form gas C, according to the reaction n = 1

$$A \rightarrow 2C$$

The reaction is known to be first order with respect to A. The decomposition reaction is carried out in an isothermal, constant volume batch reactor. Derive an expression relating the pressure of the system with time. Assume that the reacting gases behave ideally.

Solution : Consider a reaction

$$A \rightarrow 2C$$

At $t = 0$, no. of moles $= N_0 = N_{Ao}$ and $P = P_0$

Let x be the moles of A decomposed.

$\therefore$ At $t = t$, no. of moles of reaction mixture $= N = N_{Ao} - x + 2x = N_{Ao} + x$

$$= N_0 + x$$

The temperature and volume of system remain constant and as the reacting gases behave ideally, we have

$$\frac{P}{P_0} = \frac{N}{N_0} = \frac{N_0 + x}{N_0}$$

$$\frac{P}{P_0} = 1 + \frac{x}{N_0}$$

$$\therefore \quad x = \left(\frac{N_0}{P_0}\right)(P - P_0)$$

At time $t = t$, moles of A present is

$$N_A = N_0 - x$$

$$= N_0 - \frac{N_0}{P_0}(P - P_0)$$

$$N_A = \frac{N_0}{P_0}(2P_0 - P)$$

At time $t = t$, concentration of A is

$$C_A = \frac{N_A}{V} = \left(\frac{N_0}{P_0 V}\right)(2P_0 - P)$$

$$dC_A = -\frac{N_0}{P_0 V}(dP)$$

Rate of decomposition is given by

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

$$\frac{N_0}{P_0 V}\frac{dP}{dt} = k\left(\frac{N_0}{P_0 V}\right)(2P_0 - P)$$

$$\frac{dP}{dt} = k(2P_0 - P) \qquad \ldots(A)$$

where P_0 is the initial pressure.

Equation (A) is the desired relation between the total pressure of a system and time.

Ex. 2.22 : A gas A, decomposes irreversibly to form a gas C as per the below given reaction

$$A \rightarrow 2C$$

The decomposition of A is a first order reaction which is carried out in an isothermal constant pressure batch reactor. Derive an expression for the volume of the system as a function of time. Assume that the reacting gases behave ideally.

Solution : Consider a reaction

$$A \rightarrow 2C$$

Rate of reaction is given by

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

Let N_{A0} be the moles of A present at time $t = 0$

Let x be the moles of A reacted.

$\therefore$ moles of C produced $= 2x$

At time $t = t$, total moles $= N = N_{A0} - x + 2x = N_{A0} + x = N_0 + x$

At time $t = 0$, moles of system $= N_0 = N_{A0}$

As reacting gases behave ideally, and the temperature and pressure of the system remain constant,

$$\frac{V_0}{V} = \frac{N_0}{N} = \frac{N_0}{N_0 + x}$$

$$\frac{N_0 + x}{N_0} = \frac{V}{V_0}$$

$$x = N_0\left(\frac{V}{V_0} - 1\right)$$

$$x = \frac{N_0}{V_0}(V - V_0)$$

At time $t = t$, moles of A present

$$N_A = N_0 - x = N_0 - \frac{N_0}{V_0}(V - V_0)$$

$$N_A = N_0 - \frac{N_0 V}{V_0} + N_0$$

$$= \frac{N_0}{V_0}(2V_0 - V)$$

$$N_A = \frac{N_0}{V_0}(2V_0 - V) \quad \text{... (1)}$$

$$\frac{dN_A}{dt} = -\frac{N_0}{V_0}dV$$

$$-\frac{dN_A}{dt} = \frac{N_0}{V_0}\frac{dV}{dt}$$

$$C_A = \frac{N_A}{V} = \frac{N_0}{V_0 V}(2V_0 - V) \quad \text{... (2)}$$

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = kC_A \quad \text{... (3)}$$

Putting the values of N_A and C_A from (1) and (2) in (3), we get

$$\frac{N_0}{V_0 V}\frac{dV}{dt} = \frac{kN_0}{V_0 V}(2V_0 - V)$$

$$\frac{dV}{dt} = k(2V_0 - V) \quad \text{...(B)}$$

Equation (B) is the desired relation between the volume of system and time, where V_0 is the initial volume of the system.

Ex. 2.23 : The decomposition of NH_3 on tungsten wire at 856 °C gave the following results :

Total pressure, (torr)	228	250	273	318
Time, s	200	400	600	1000

Determine the order of reaction and calculate its rate constant.

Solution :

$$2NH_3 \longrightarrow N_2 + 3H_2$$

$$2A \longrightarrow R + 3S$$

For total pressure data :

The relationship between partial pressure and total pressure is :

$$p_A = p_{A0} - \frac{a}{\Delta n}(P - P_0)$$

At $t = 0$, $p_{A0} = P_0$ (only A is present)

$a = 2$, $\Delta n = 4 - 2 = 2$

$$p_A = P_0 - \frac{2}{2}(P - P_0)$$

$$p_A = 2P_0 - P$$

$$p_A = C_A RT = 2P_0 - P$$

$$C_A = (2P_0 - P)/RT$$

Assume that the reaction is zero order

$$\therefore \quad -r_A = -\frac{dC_A}{dt} = kC_A^0$$

$$\therefore \quad \frac{1}{RT}\frac{dP}{dt} = k\left[\frac{2P_0 - P}{RT}\right]^0$$

$$\therefore \quad dP = k'\,dt, \quad k' = kRT$$

Integrating we get

$$(P - P_0) = k' t$$
$$228 - P_0 = 200 k'$$
$$250 - P_0 = 400 k'$$

Solving for P_0, we get

$$P_0 = 206 \text{ torr}$$

k' = rate constant $= (P - P_0)/t$

For $P = 228$, $\quad k' = \dfrac{228-206}{200} = 0.11 \text{ (torr)}.(\text{s})^{-1}$

For $P = 250$, $\quad k' = \dfrac{250-206}{400} = 0.11 \text{ (torr)}.(\text{s})^{-1}$

For $P = 273$, $\quad k' = \dfrac{273-206}{600} = 0.111 \text{ (torr)}.(\text{s})^{-1}$

For $P = 318$, $\quad k' = \dfrac{318-206}{1000} = 0.112 \text{ (torr)}.(\text{s})^{-1}$

As we are getting almost same value of k' for all the total pressure data, value of order of reaction assumed is correct.

∴ The reaction is zero order and value of rate constant

$$= 0.11 \text{ (torr)}.(\text{s})^{-1}$$ **... Ans.**

$$k = k'/RT = (0.11/760)/(0.08206 \times 1129)$$
$$= 1.56 \times 10^{-6} \text{ (mol/}l\text{) (s)}^{-1}$$ **... Ans.**

Ex. 2.24 : A polymerisation reaction occurs at constant temperature in a homogeneous phase. For initial monomer concentrations of 0.3, 0.5 and 0.9 mol/l, 30 % of the monomer reacts in 40 minutes. Find the reaction rate.

Solution : Consider the polymerisation reaction to be first order w.r.t. monomer (A).

76 = Cn

t =

$$\therefore \quad -r_A = k C_A$$
$$k = \frac{1}{t} \ln (C_{A_0}/C_A)$$

In $t = 40$ min, 30 % of monomer is reacted.

(1) $C_{A_0} = 0.3$, A reacted $= 0.3 \times 0.3 = 0.09$

∴ $C_A = 0.3 - 0.09 = 0.21$ mol/l

$$k = \frac{1}{40} \ln (0.3/0.21) = 0.00892 \text{ (min)}^{-1}$$

(2) $C_{A_0} = 0.5$ mol/l, A reacted $= 0.3 \times 0.5 = 0.15$

$C_A = 0.5 - 0.15 = 0.35$ mol/l

$$k = \frac{1}{40} \ln (0.5/0.35) = 0.00892 \text{ (min)}^{-1}$$

(3) $C_{A_0} = 0.9$ mol/l, A reacted $= 0.3 \times 0.9 = 0.27$

$C_A = 0.9 - 0.27 = 0.63$ mol/l

$$k = \frac{1}{40} \ln (0.9/0.63) = 0.00892 \text{ (min)}^{-1}$$

As values of k are same, the reaction is first order.

∴ Rate of reaction $= -r_A = 0.00892 \text{ (min)}^{-1} C_A$ **... Ans.**

Ex. 2.25 : From the data given below show that the conversion of N-chloroacetanilide to para-chloroacetanilide is a reaction of first order.

Time, h	0	1	2	3
N	49.3	35.6	25.75	18.5

where N is the number of ml of $Na_2S_2O_3$ solution required for a definite volume of reaction mixture.

Solution : For first order reaction, we have,

$$k = \frac{1}{t} \ln (C_{Ao}/C_A)$$

where C_{Ao} = initial concentration and C_A the concentration at any time t.

In this problem, C_{Ao} in terms of ml of thiosulphate is equal to 49.3 and C_A in terms of ml of thiosulphate at different times 35.6, 25.75 and 18.5. Substituting these values in above equation,

(i) $$k = \frac{1}{1} \ln \left(\frac{49.3}{35.6}\right) = 0.32214\ (h)^{-1}$$

(ii) $$k = \frac{1}{2} \ln \left(\frac{49.3}{25.75}\right) = 0.32357\ (h)^{-1}$$

(iii) $$k = \frac{1}{3} \ln \left(\frac{49.3}{18.5}\right) = 0.32610\ (h)^{-1}$$

Since the values of k are fairly constant, it is a first order reaction.

Ex. 2.26 : From the following data for the decomposition of N_2O_5 in carbon tetrachloride solution at 48 °C, show that the decomposition is first order.

Time, min	10	15	20	25	∞
Vol. of oxygen evolved, ml	6.30	8.95	11.40	13.50	34.75

Solution : N_2O_5 in CCl_4 decomposes as

$$N_2O_5 \rightarrow N_2O_4 + 1/2\ O_2$$

$$N_2O \rightleftharpoons 2\ NO_2$$

If V_t is the volume of oxygen evolved at any time t and hence, it is a measure of N_2O_5 decomposed (x).

If V_∞ is the total volume of oxygen evolved at the completion of reaction i.e. $t = \infty$ then V_∞ is proportional to the initial concentration C_{Ao} of N_2O_5 and $V_\infty - V_t$ is proportional to C_A, the amount of undecomposed N_2O_5.

For first order reaction, we have

$$k = \frac{1}{t} \ln (C_{Ao}/C_A)$$

Above equation is modified as :

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

In this case, $V_\infty = 34.75$

Time	10	15	20	25	∞
V_t	6.30	8.95	11.40	13.50	34.75
$V_\infty - V_t$	28.45	25.80	23.35	21.25	–

Put the values of t, V_∞, $V_\infty - V_t$ in above equation for all observations.

(i) $$k = \frac{1}{10} \ln\left(\frac{34.75}{28.45}\right) = 0.00868\ (\text{min})^{-1}$$

(ii) $$k = \frac{1}{15} \ln\left(\frac{34.75}{25.80}\right) = 0.00862\ (\text{min})^{-1}$$

(iii) $$k = \frac{1}{20} \ln\left(\frac{34.75}{23.75}\right) = 0.00863\ (\text{min})^{-1}$$

(iv) $$k = \frac{1}{25} \ln\left(\frac{34.75}{21.25}\right) = 0.00854\ (\text{min})^{-1}$$

Since the value of k is constant, it is a first order reaction .

Ex. 2.27 : Following results are obtained for the decomposition of nitrous oxide in contact with gold surface at 900 °C:

Time (min)	15	30	45	65	80
% N_2O decomposed	17	32	44.5	57	65

Show that order of reaction is unity.

Solution : For first order reaction, we have

$$-\ln(1 - X_A) = kt$$

$$k = \frac{1}{t} \ln\left(\frac{1}{1-X_A}\right)$$

(i) At t = 15 min

% A decomposed = % A converted = 17

$\therefore$ $X_A = 0.17$

$$k = \frac{1}{15} \ln\left(\frac{1}{1-0.17}\right)$$

$$k = 0.01243\ \text{min}^{-1}$$

(ii) At t = 30 min, % A decomposed = 32

$\therefore$ $X_A = 0.32$

$$k = \frac{1}{30} \ln\left(\frac{1}{1-0.32}\right)$$

$$= 0.01266\ \text{min}^{-1}$$

(iii) At t = 45 min, % A decomposed = 44.5

$X_A = 0.445$

$$k = \frac{1}{45} \ln\left(\frac{1}{1-0.445}\right)$$

$$= 0.01289\ \text{min}^{-1}$$

(iv) At t = 65 min, % A decomposed = 57

$\therefore$ $X_A = 0.57$

$$k = \frac{1}{65} \ln\left(\frac{1}{1-0.57}\right)$$

$$= 0.01289\ \text{min}^{-1}$$

(v) At t = 80 min, % A decomposed = 65

$$\therefore \quad X_A = 0.65$$

$$k = \frac{1}{80} \ln\left(\frac{1}{1-0.65}\right)$$

$$= 0.01289 \text{ min}^{-1}$$

Since the values of k are fairly constant, the order of reaction is unity i.e. decomposition is a first order.

Ex. 2.28 : The concentrations of a compound undergoing chemical change were 5.72, 3.23 and 1.96 at the times 0, 20 and 50 min from the commencement of reaction. Ascertain the order of reaction.

Solution : Assume the reaction to be first order then,

$$k = \frac{1}{t} \ln (C_{Ao}/C_A)$$

At $t = 20$ min, $C_A = 3.23$ mol/l

$C_{Ao} = 5.72$ mol/l (concentration of A at t = 0)

$$\therefore \quad k = \frac{1}{20} \ln (5.72/3.23) = 0.01241 \text{ min}^{-1}$$

At $t = 50$ min, $C_A = 1.96$ mol/l

$$k = \frac{1}{50} \ln (5.72/1.96) = 0.0693 \text{ min}^{-1}$$

Since there is a large variation in k values, the reaction is not unimolecular i.e. it is not first order reaction.

Assume the reaction to be second order then,

$$\left[\frac{1}{C_A} - \frac{1}{C_{Ao}}\right] = kt$$

$$k = \frac{1}{t}\left[\frac{1}{C_A} - \frac{1}{C_{Ao}}\right]$$

At $t = 20$ min, $C_A = 3.23$ mol/l

$$k = \frac{1}{20}\left[\frac{1}{3.23} - \frac{1}{5.72}\right] = 0.00674 \text{ (l/mol) (min)}^{-1}$$

At $t = 50$ min, $C_A = 1.96$ mol/l

$$k = \frac{1}{50}\left[\frac{1}{1.96} - \frac{1}{5.72}\right] = 0.00671 \text{ (l/mol) (min)}^{-1}$$

Since the k values are fairly same, it is a second order reaction. ... **Ans.**

1D

Ex. 2.29 : In case of gaseous reaction, the period of half change $t_{1/2}$ for different initial concentrations C_{Ao} is given below. Determine the order of reaction.

C_{Ao} (mol/l)	5	10	15	20
$t_{1/2}$, h	40	20.1	13.3	10

Juni system

Solution : For first order reaction $t_{1/2}$ is independent of initial concentration. In the data provided $t_{1/2}$ is different for different values of C_{Ao}. So reaction is not first order.

For second order reaction,

$$t_{1/2} \times C_{Ao} = \text{constant} = m \quad \text{as } t_{1/2} \propto \frac{1}{C_{Ao}^{n-1}}$$

If we get fairly constant values of m for all the data then reaction is second order.

(i) $m = t_{1/2} \times C_{Ao} = 40 \times 5 = 200$

(ii) $m = t_{1/2} \times C_{Ao} = 10 \times 20.1 = 201$

(iii) $m = t_{1/2} \times C_{Ao} = 15 \times 13.3 = 199.5$

(iv) $m = t_{1/2} \times C_{Ao} = 20 \times 10 = 200$

Since the values of m are fairly same, the reaction is second order.

Alternatively,

$$n = 1 + \frac{\ln t'_{1/2}/t''_{1/2}}{\ln (C''_o/C'_o)}$$

For $t'_{1/2} = 40\text{ h}$, $t''_{1/2} = 20.1\text{ h}$, $C''_o = 10\text{ mol}/l$, $C'_o = 5\text{ mol}/l$

$$n = 1 + \frac{\ln (40/20.1)}{\ln (10/5)} = 1.993 \approx 2$$

For $t'_{1/2} = 20.1\text{ h}$, $t''_{1/2} = 13.3\text{ h}$, $C''_o = 15\text{ mol}/l$, $C'_o = 10\text{ mol}/l$

$$n = 1 + \frac{\ln (20.1/13.3)}{\ln (15/10)} = 2.098$$

$t'_{1/2} = 13.3\text{ h}$, $t''_{1/2} = 10\text{ h}$, $C'_o = 15\text{ mol}/l$, $C''_o = 20\text{ mol}/l$

$$n = 1 + \frac{\ln (13.3/10)}{\ln (20/15)} = 1.991 \approx 2$$

Thus the order of reaction is 2. ... **Ans.**

Ex. 2.30 : The time for half change ($t_{1/2}$) of a gaseous substance undergoing the thermal decomposition was determined for various initial pressure (P) with the following results :

P mmHg	250	300	350	400	450
$t_{1/2}$, min	136	112.5	97	85	75.5

Find the order of reaction.

Juni system

Solution : As the pressure of a gas is proportional to its concentration, we can use P instead of C_{Ao}, the initial concentration.

As $t_{1/2}$ is not constant in the above data, the reaction is clearly not of first order.

For second order reaction, we have,

$$t_{1/2} \propto \frac{1}{C_{Ao}}$$

$$C_{Ao} \propto p_{Ao}$$

$$p_{Ao} = P_o \text{ (pure A initially)}$$

$$t_{1/2} \propto 1/P_o$$

$$t_{1/2} \cdot P_o = \text{constant}$$

P	250	300	350	400	450
$t_{1/2}$	136	112.5	97	85	75.5
$P \times t_{1/2}$	34000	33750	33950	34000	33975

Since the product $P \times t_{1/2}$ is fairly constant, decomposition is a second order reaction.

Order of reaction = 2. ... **Ans.**

LB **Ex. 2.31 :** Nitrous oxide decomposes according to the second order rate equation :

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

The reaction rate constant is $\overset{k}{977}$ cm³/(mol.s) at 895 °C. Calculate the fraction decomposed at 1 s, 10 s and at 10 min in a constant volume batch reactor. The initial pressure [all N_2O] is 1 atm.

$x = ?$

$P_{Ao} = 1$ atm

Solution :

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

$$2\,A \rightarrow 2\,B + C$$

$$k_2 = 977 \text{ cm}^3/(\text{mol.s}) = 0.977\ l/(\text{mol.s})$$

Let N_{Ao} moles of N_2O initially present in reactor and X_A be the fraction of N_2O decomposed in time t.

Initial pressure $= P_0 = 1$ atm

Initial moles $= N_0 = N_{Ao}$ (all N_2O initially)

Moles of A decomposed $= X_A \cdot N_{Ao}$

Moles of A undecomposed $= N_A = N_{Ao}\,(1 - X_A)$

Moles of B produced $= X_A \cdot N_{Ao}$

Moles of C produced $= X_A\,N_{Ao}/2$

Total moles of reaction mixture at t $= N_{Ao}\,(1 - X_A) + X_A N_A + X_A N_{Ao}/2$

$= N_{Ao}\,(1 + 0.5\,X_A) = N_o(1 + 0.5\,X_A)$

Let pressure at t be P.

$$\therefore \quad \frac{P_0}{P} = \frac{N_0}{N_o\,(1 + 0.5\,X_A)} = \frac{1}{(1 + 0.5\,X_A)}$$

$$\therefore \quad P = (1 + 0.5\,X_A)\,P_0$$

$$C_A = \frac{N_A}{V} = \frac{N_o\,(1 - X_A)}{N_o\,(1 + 0.5\,X_A)\,RT/P}$$

$$= \frac{(1 - X_A)\,(1 + 0.5\,X_A)\,P_0}{(1 + 0.5\,X_A)\,RT}$$

$$= \frac{(1 - X_A)\,P_0}{RT}$$

$$dC_A = -\frac{P_0}{RT}\,dX_A$$

For second order kinetics,

$$-\frac{dC_A}{dt} = k\,C_A^2$$

$$\left(\frac{P_0}{RT}\right)\frac{dX_A}{dt} = k\left[\frac{(1 - X_A)\,P_0}{RT}\right]^2$$

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)^2} = \frac{kP_0}{RT}\int dt$$

$$\therefore \quad \left[\frac{1}{1 - X_A} - 1\right] = \frac{kP_0}{RT}\,(t)$$

$$\left[\frac{X_A}{1 - X_A}\right] = \frac{kP_0}{RT}\,(t)$$

$R = 0.08206\ l.\text{atm}/(\text{mol.K})$, $T = 1168$ K, $P_0 = 1$ atm

At t = 1 s

$$\frac{X_A}{1-X_A} = \frac{0.977 \times 1 \times 1}{0.08206 \times 1168} = 0.0102$$

$\therefore$ $X_A = 0.01$ i. e. 1% decomposed ... **Ans.**

At t = 10 s

$X_A = 0.0925$ i.e. 9.25 % decomposed ... **Ans.**

At t = 10 min = 600 s.

$$\frac{X_A}{1-X_A} = \frac{0.977 \times 600}{0.08206 \times 1168} = 6.116$$

$\therefore$ $X_A = 0.86$ i.e. 86% decomposed ... **Ans.**

Ex. 2.32 : The decomposition of phosphine is irreversible and first order at 650°C.

$$4\,PH_{3(g)} \rightarrow P_{4\,(g)} + 6\,H_{2\,(g)}$$

The rate constant in $(s)^{-1}$ is reported as

$$\log k = -\frac{18963}{T} + 2 \log T + 12.130$$

where T is in degrees Kelvin. In a closed vessel (constant volume) initially containing phosphine at 1 atm pressure, what will be the pressure after 50, 100 and 500 seconds ? The temperature is maintained at 650°C.

Solution :

$$4\,PH_{3\,(g)} \rightarrow P_{4\,(g)} + 6\,H_{2\,(g)}$$

$$4\,A \rightarrow R + 6\,S$$

$P_0 = 1$ atm, T = 650°C = 923 K

$$\log k = -\frac{18963}{T} + 2 \log T + 12.130$$

$$= -\frac{18963}{923} + 2 \log (923) + 12.130$$

$\therefore$ $k = 3.28 \times 10^{-3}\ (s)^{-1}$

At t = 0

Let the moles of A = N_{Ao}

Total moles at t = 0, = $N_0 = N_{Ao}$

Let X_A be the fraction of phosphine (A) decomposed at time t = t

$\therefore$ Moles of A = $N_{Ao} - X_A$

Moles of B = $0.25\,X_A$

Moles of C = $1.5\,X_A$

Total moles at time t = $N_{Ao} + 0.75\,X_A$

Let P be the total pressure at time t.

Total moles at t = $N_{Ao} + 0.75\,X_A = N_0 + 0.75\,X_A$

At T = constant for closed vessel

$$\frac{P_0}{P} = \frac{N_0}{N_0 + 0.75\,X_A}$$

$$X_A = \frac{N_0}{0.75\,P_0}\,(P - P_0)$$

$$C_A = \frac{N_A}{V}$$

$$N_A = N_{Ao} - X_A = N_0 - X_A$$

$$C_A = \frac{N_o - X_A}{V}$$

$$\therefore \quad C_A = \frac{N_0}{V} - \frac{N_0\,(P - P_0)}{0.75\ VP_0}$$

$$C_A = \frac{P_0}{RT} - \frac{1.33\,(P - P_0)}{RT}$$

$$C_A = (2.33\ P_0 - 1.33\ P)/RT$$

OR

$$4A \rightarrow R + 6S$$

Partial pressure of A is related to total pressure by

$$p_A = p_{Ao} - \frac{a}{\Delta n}\,(P - P_o)$$

$$a = 4, \quad \Delta n = 1 + 6 - 4 = 3$$

$$p_{Ao} = P_o \text{ (only phosphine initially)}$$

$$\therefore \quad p_A = P_o - \frac{4}{3}\,(P - P_o)$$

$$p_A = 2.33\ P_o - 1.33\ P$$

$$p_A = C_A RT = 2.33\ P_o - 1.33\ P$$

$$C_A = (2.33\ P_o - 1.33\ P)/RT$$

$$\therefore \quad dC_A = -\ 1.33\ dP/RT$$

Reaction is first order

$$\therefore \quad -\ dC_A/dt = kC_A$$

$$\frac{1.33}{RT}\,\frac{dP}{dt} = \frac{k}{RT}\,(2.33\ P_0 - 1.33\ P)$$

$$1.33 \int_{P_0}^{P} \frac{dP}{(2.33\ P_0 - 1.33\ P)} = kt$$

$$\ln\ P_0 - \ln\,(2.33\ P_0 - 1.33\ P) = kt$$

$$\ln\ [P_0/(2.33\ P_0 - 1.33\ P)] = kt$$

$$[P_0/(2.33\ P_0 - 1.33\ P)] = e^{kt}$$

$P_0 = 1$ atm, $k = 3.28 \times 10^{-3}$ s

For $t = 50$ s

$$\frac{1}{(2.33 \times 1 - 1.33\ P)} = e^{3.28 \times 10^{-3} \times 50}$$

$\therefore$ $P = 1.114$ atm ... An

For $t = 100$ s, $P = 1.21$ atm ... Ans.

For $t = 500$ s, $P = 1.61$ atm ... An

Ex. 2.33 : An aqueous solution of ethyl acetate is to be saponified with sodium hydroxide. The initial concentration of ethyl acetate is 5 g/*l* and that of caustic is 0.1 normal. The values of second order rate constant at 0 °C and 20 °C are k = 0.235 and 0.924 (*l*/mol) (min)$^{-}$ respectively. The reaction is irreversible. Calculate the time required to saponify 95% of ester at 40 °C.

Solution : $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

$$\begin{aligned}
A + B &\rightarrow R + S \\
C_{Ao} &= 5\ g/l = 5/88\ mol/l = 0.0568\ mol/l \\
C_{Bo} &= 0.10\ \text{normal} = 0.10\ \text{molar}
\end{aligned}$$

(as for NaOH, normality = molarity)

$$\begin{aligned}
&= 0.10\ mol/l \\
k_1 &= 0.235\ (l/mol)\ (min)^{-1}\ \text{at}\ T_1 = 0\ ^\circ C = 273\ K \\
k_2 &= 0.924\ (l/mol)\ (min)^{-1}\ \text{at}\ T_2 = 20\ ^\circ C = 293\ K \\
\ln (k_2/k_1) &= E/R \left[\frac{1}{T_1} - \frac{1}{T_2}\right] \\
\ln\left(\frac{0.924}{0.235}\right) &= \frac{E}{1.987}\left[\frac{1}{273} - \frac{1}{293}\right] \\
E &= 10887\ cal/mol \\
T_3 &= 40\ ^\circ C = 313\ K \\
\ln (k_3/k_2) &= \frac{10887}{1.987}\left[\frac{1}{293} - \frac{1}{313}\right] \\
k_3/k_2 &= 3.30 \\
\therefore \quad k_3 &= 3.30\ k_2 \\
&= 3.30 \times 0.924 = 3.05\ (l/mol)\ (min)^{-1}
\end{aligned}$$

At 40 °C, $k = 3.05\ (l/mol)\ (min)^{-1}$

For second order irreversible reaction,

$$\begin{aligned}
\ln\left[\frac{M - X_A}{M\,(1 - X_A)}\right] &= C_{Ao}\ (M - 1)\ kt \\
M &= C_{Bo}/C_{Ao} = 0.10/0.0568 = 1.76
\end{aligned}$$

For $X_A = 0.95$

$$\begin{aligned}
\ln\left[\frac{1.76 - 0.95}{1.76\ (1 - 0.95)}\right] &= 0.0568 \times (1.76 - 1) \times 3.05 \times t \\
\therefore \quad t &= 17\ min.
\end{aligned}$$

BC The time required to saponify 95% of ester = 17 min ... **Ans.**

Ex. 2.34 : Aqueous solutions of diazobenzene decompose irreversibly according to the reaction

$$C_6H_5N_2Cl\ (aq) \rightarrow C_6H_5Cl\ (aq) + N_2\ (g)$$

The reaction follows first order kinetics. In one experimental run at 50 °C the initial concentration of $C_6H_5N_2Cl$ was 10 g/l and the following amounts of N_2 were collected.

Time, min	6	9	12	14	18	20	24	26
N_2 liberated, cm^3 at 50 °C, 1 atm	19.3	26	32.6	36	41.3	43.3	46.5	48.4

Complete decomposition of the diazo salt liberated 58.3 cm^3 of N_2. Determine the value of the rate constant.

Solution : $C_6H_5N_2Cl\ (aq) \rightarrow C_6H_5Cl\ (aq) + N_2\ (g)$

$$A \rightarrow R + S\ (g)$$

The reaction follows first order kinetics.

$$\begin{aligned}
\therefore \quad \ln\ [C_{Ao}/C_A] &= kt \\
C_{Ao} &\propto \text{initial moles} \\
C_A &\propto \text{moles at any time t}
\end{aligned}$$

Total volume of N_2 liberated at the completion of reaction i.e. at complete decomposition of the diazo salt is 58.3 cm³.

$$V = 58.3 \text{ cm}^3$$

This V is proportional to the initial moles of diazobenzene and so C_{A_0} as it is liberated out of its decomposition.

V_t is the volume of N_2 liberated at any time t. It is a measure of $C_6H_5N_2Cl$ decomposed.

Then , $V - V_t$ is proportional to the C_A, the amount of undecomposed $C_6H_5N_2Cl$.

$$C_{A_0} \propto V$$

$$C_A \propto V - V_t$$

$$\frac{C_{A_0}}{C_A} = \frac{m\,V}{m\,(V - V_t)} = \frac{V}{V - V_t}$$

$$\ln\left[\frac{V}{V - V_t}\right] = kt$$

$$k = \frac{1}{t}\ln\left[\frac{V}{V - V_t}\right]$$

$t = 6$ min, $V_t = 19.3$ cm³, $V = 58.3$ cm³

$$k = \frac{1}{6}\ln\left[\frac{58.3}{58.3 - 19.3}\right]$$

$$= 0.067 \text{ (min)}^{-1}$$

$t = 9$ min, $V_t = 26$ cm³

$$k = \frac{1}{9}\ln\left[\frac{58.3}{58.3 - 26}\right]$$

$$= 0.066 \text{ (min)}^{-1}$$

$t = 12$ min, $V_t = 32.6$ cm³

$$k = \frac{1}{12}\ln\left[\frac{58.3}{58.3 - 32.6}\right]$$

$$= 0.068 \text{ (min)}^{-1}$$

$t = 14$ min, $V_t = 36$ cm³

$$k = \frac{1}{14}\ln\left[\frac{58.3}{58.3 - 36}\right]$$

$$= 0.069 \text{ (min)}^{-1}$$

$t = 18$ min, $V_t = 41.3$ cm³

$$k = \frac{1}{18}\ln\left[\frac{58.3}{58.3 - 41.3}\right]$$

$$= 0.0685 \text{ (min)}^{-1}$$

$t = 20$ min, $V_t = 43.3$ cm³

$$k = \frac{1}{20}\ln\left[\frac{58.3}{58.3 - 43.3}\right]$$

$$= 0.0679 \text{ (min)}^{-1}$$

$t = 24$ min, $V_t = 46.5$ cm³

$$k = \frac{1}{24}\ln\left[\frac{58.3}{58.3 - 46.5}\right]$$

$$= 0.0666 \text{ (min)}^{-1}$$

$t = 26$ min, $V_t = 48.4$ cm^3

$$k = \frac{1}{26}\ln\left[\frac{58.3}{58.3-48.4}\right]$$

$$= 0.0682\ (\text{min})^{-1}$$

As the values of k are approximately same at all data points, the reaction follows first order kinetics.

$$\text{Average value of k} = \frac{(0.067+0.066+0.068+0.069+0.0685+0.0679+0.0666+0.0682)}{8}$$

$$= 0.06765\ (\text{min})^{-1}$$

$$= 0.0676\ (\text{min})^{-1}$$ ... **Ans.**

Volume of N_2 is liberated at 50 °C and 1 atm.

Moles of N_2 produced after complete decomposition $= \frac{PV}{RT}$.

where, $R = 0.08206\ l.\text{atm}/(\text{mol}\cdot\text{K})$, $P = 1$ atm

$T = 50\ ^\circ C = 323$ K, $V = 58.3$ cm$^3 = 58.3\times10^{-3}\ l$

Moles of N_2 produced by complete decomposition $= \frac{1\times58.3\times10^{-3}}{0.08206\times323} = 2.2\times10^{-3}$ mol

From reaction :

1 mol $C_6H_5N_2Cl \equiv 1$ mol N_2

$\therefore$ $C_6H_5N_2Cl$ reacted to produce $N_2 = \frac{1}{1}\times2.2\times10^{-3} = 2.2\times10^{-3}$ mol

At complete decomposition :

diazobenzene charged/fed = diazobenzene reacted

$\therefore$ $C_6H_5N_2Cl$ charged $= 2.2\times10^{-3}$ mol

(i) At $t = 6$ min, $V_t = 19.3$ cm^3

$$\therefore \text{Moles of } N_2 \text{ liberated/produced} = \frac{1\times19.3\times10^{-3}}{0.08206\times323}$$

$$= 7.28\times10^{-4}\ \text{mol}$$

$$\therefore \text{At } t = 6 \text{ min, moles of } C_6H_5N_2Cl \text{ reacted} = \frac{1}{1}\times7.28\times10^{-4}$$

$$= 7.28\times10^{-4}\ \text{mol}$$

$$\%\ \text{conversion of } C_6H_5N_2Cl = \frac{7.28\times10^{-4}}{2.2\times10^{-3}}\times100$$

$$= 33.10$$

$$\therefore X_A = 0.331,\quad (A = C_6H_5N_2Cl)$$

For first order reaction, we have,

$$-\ln(1-X_A) = kt$$

$$\therefore k = \frac{1}{t}[-\ln(1-X_A)]$$

$$= \frac{1}{6}[-\ln(1-0.331)]$$

$$= 0.067\ (\text{min})^{-1}$$

(ii) At $t = 9$ min, $V_t = 26$ cm^3

$$\therefore \text{Moles of } N_2 \text{ produced} = \frac{1\times26\times10^{-3}}{0.08206\times323}$$

$$= 9.81\times10^{-4}\ \text{mol}$$

Moles of $C_6H_5N_2Cl$ reacted for N_2 $= \frac{1}{1} \times 9.81 \times 10^{-4} = 9.81 \times 10^{-4}$ mol

$$\% \text{ conversion of } C_6H_5N_2Cl = \frac{9.81 \times 10^{-4}}{2.2 \times 10^{-3}} \times 100$$

$$= 44.59$$

$$\therefore \quad X_A = 0.4459$$

$$k = \frac{1}{t}\,[-\ln(1 - X_A)]$$

$$= \frac{1}{9}\,[-\ln(1 - 0.4459)]$$

$$= 0.066\ (\text{min})^{-1}$$

Similarly, calculate moles of N_2, moles of $C_6H_5N_2Cl$ reacted, % conversion of $C_6H_5N_2C$ and k at other data.

t	6	9	12	14	18	20	24	26
X_A	0.331	0.4459	0.56	0.62	0.71	0.74	0.80	0.83
k	0.067	0.066	0.068	0.069	0.069	0.067	0.067	0.068
V	19.3	26	32.6	36	41.3	43.3	46.5	48.4

... **Ans.**

Average value of rate constant $= 0.0675\ (\text{min})^{-1}$

B

Ex. 2.35 : The thermal decomposition of dimethyl ether in gas phase was studied by measuring the increase in pressure in a constant volume reactor. At 504 °C and initia pressure of 312 mmHg, the following results were obtained.

t, s	390	777	1195	3155	∞
P, mmHg	408	488	562	779	731

Find the rate equation to represent this decomposition assuming only ether was present initially and decomposition reaction is

$$(CH_3)_2O \rightarrow CH_4 + H_2 + CO$$

Solution : $(CH_3)_2O \rightarrow CH_4 + H_2 + CO$, gas phase reaction

$$A \rightarrow R + S + T$$

$$\text{Initial pressure} = P_o = 312 \text{ mmHg}$$

$p_{Ao} = P_o = 312$ mmHg (as pure ether initially)

p_A is the partial pressure of A at any time t and is given by

$$p_A = p_{Ao} - \frac{a}{\Delta n}(P - P_o)$$

where $a = 1$, $\Delta n = 3 - 1 = 2$

$$P = \text{total pressure at any time t}$$

$$\therefore \quad p_A = P_o - \frac{1}{2}(P - P_o)$$

$$p_A = (1.5\,P_o - 0.5\,P)$$

Assume the decomposition to be first order, then

$$(-r_A) = k\,C_A$$

$$\ln(C_{Ao}/C_A) = kt$$

$$C_A = p_A/RT$$

$$-dC_A/dt = \frac{-dp_A}{RT\,dt}$$

$$\frac{-dp_A}{RT\,dt} = k\,C_A = k \cdot \frac{p_A}{RT}$$

$$\therefore \qquad \ln(p_{Ao}/p_A) = kt$$

$$k = \frac{1}{t}\ln(p_{Ao}/p_A)$$

$$= \frac{1}{t}\ln\left(\frac{P_o}{1.5\,P_o - 0.5\,P}\right) \quad \text{as } p_{Ao} = P_o \text{ and } p_A = 1.5\,P_o - 0.5\,P$$

(i) At $t = 390$ s, $P_o = 312$ mmHg, $P = 408$ mmHg

$$k = \frac{1}{390}\ln\left[\frac{312}{1.5 \times 312 - 0.5 \times 408}\right]$$

$$= 4.28 \times 10^{-4}\,(s)^{-1}$$

(ii) At $t = 777$ s, $P = 488$ mmHg

$$k = \frac{1}{777}\ln\left[\frac{312}{1.5 \times 312 - 0.5 \times 488}\right]$$

$$= 4.26 \times 10^{-4}\,(s)^{-1}$$

(iii) At $t = 1195$ s, $P = 562$ mmHg

$$k = 4.28 \times 10^{-4}\,(s)^{-1}$$

(iv) At $t = 3155$ s, $P = 779$ mmHg

$$k = 4.37 \times 10^{-4}\,(s)^{-1}$$

As we are getting approximately same values of k for all given data it can be concluded that decomposition follows first order kinetics.

$$\text{Average value of } k = 4.2975 \times 10^{-4}\,(s)^{-1}$$

The rate equation for decomposition of dimethyl ether is

$$(-r_A) = 4.2975 \times 10^{-4}\,(s)^{-1} \cdot C_A$$

... **Ans.**

Ex. 2.36 : If $(-r_A) = -dC_A/dt = 0.20$ mol/(l·s) when $C_A = 1$ mol/l, what is the rate of reaction when $C_A = 10$ mol/l ? Note that the order of reaction is not known.

Solution : $-r_A = -dC_A/dt = 0.20$ mol/(l·s), $C_A = 1$ mol/l, $r_A = ?$, $C_A = 10$ mol/l.

Order of reaction is not known. We are not provided with enough information to find the rate. Assume the reaction to be of first order with respect to A.

$$-r_A = k\,C_A$$

$$0.2 = k \times 1 \qquad \therefore\ k = 0.2\ s^{-1}$$

$$-r_A = k\,C_A$$

$$= 0.2 \times 10 = 2\ \text{mol/}(l\cdot s)$$

... **Ans.**

Ex. 2.37 : Liquid A decomposes by first order kinetics, and in a batch reactor 50% of A is converted in a 5 minutes. How long it will take to reach 75% conversion ?

Solution : A → products.

First order reaction.

$$\therefore \qquad -r_A = k\,C_A$$

In terms of conversion, integrated rate expression is

$$\ln\left(\frac{1}{1 - X_A}\right) = kt$$

Case I : $X_A = 0.5$ when $t = 5$ min

$$\ln\left[\frac{1}{1 - 0.5}\right] = k \times 5 \qquad \therefore\ k = 0.1386\ (\text{min})^{-1}$$

Case II : $X_A = 0.75,\ t = ?$

$$\ln\left[\frac{1}{1-0.75}\right] = 0.1386 \times t$$

$$t = 10 \text{ min}$$ ... **Ans.**

Ex. 2.38 : Repeat Ex. 2.37 for second order kinetics i.e. Assuming that decomposition of A is a second order reaction.

Solution : A → products

$$-r_A = k\,C_A^2$$

Integrated rate expression for second order reaction in terms of conversion is

$$\frac{X_A}{1-X_A} = k\,C_{A0}\,t$$

Case I : $X_A = 0.5$ when $t = 5$ min

$$\frac{0.5}{1-0.5} = k\,C_{A0} \times 5 = k' \times 5, \quad \text{when } k' = k\,C_{A0}$$

$$\therefore \quad k' = 0.2$$

Case II : $X_A = 0.75,\ t = ?$

$$\frac{0.75}{1-0.75} = 0.2\,t$$

$$t = 15 \text{ min}$$ ... **Ans.**

i.e. Additional time of 10 minutes is required to increase conversion level from 50% to 75%.

Ex. 2.39 : A 10 minutes experimental run shows that 75% of liquid reactant 'A' is converted to product by a 1/2 order rate. What would be the amount of A converted in 30 minutes run ?

Solution : A → products.

$$-r_A = k\,C_A^{0.5} = k\,C_A^{1/2}$$

$$C_{A0}\frac{dX_A}{dt} = k\,C_{A0}^{1/2}\,(1-X_A)^{1/2}$$

$$\int_0^{X_A} \frac{dX_A}{(1-X_A)^{1/2}} = k\,C_{A0}^{1/2}\,dt$$

Integration yields

$$\left[\frac{(1-X_A)^{1/2}}{-1/2}\right]_0^{X_A} = k't, \quad k' = k\,C_{A0}^{1/2}$$

$$2\,[-(1-X_A)^{1/2} + 1] = k't$$

Case I : $X_A = 0.75$ when $t = 10$ min

$$\therefore \quad 2\,[-(1-0.75)^{1/2} + 1] = k' \times 10$$

$$k' = 0.10$$

Case II : $X_A = ?$ when $t = 30$ min

$$2\,[-(1-X_A)^{1/2} + 1] = 0.1 \times 30$$

Solving we get,

$$X_A = 0.75$$

∴ 75% of the original amount of A would be converted in 30 minutes run. ... **Ans.**

Ex. 2.40 : In a homogeneous isothermal liquid polymerisation, 20% of the monomer gets disappeared in 34 minutes for initial monomer concentration of 0.04 and also for 0.8 mol/l. What is the rate expression for the disappearance of the monomer ?

Solution : $X_A = 0.20 \quad t = 34 \text{ min} \quad C_{A0} = 0.04 \text{ mol}/l$

$X_A = 0.20 \quad t = 34 \text{ min} \quad C_{A0} = 0.8 \text{ mol}/l$

Trial : Consider the polymerisation follows first order kinetics.

$$-r_A = k\,C_A$$

Integrated rate expression in terms of concentration is :

$$\ln\left(\frac{C_{Ao}}{C_A}\right) = kt$$

Case I : $X_A = 0.20$, $t = 34$ min, $C_{Ao} = 0.04$ mol/l

$$C_A = C_{Ao}(1 - X_A)$$

$$C_A = 0.04\,(1 - 0.2) = 0.032 \text{ mol/l}$$

$$\ln\left(\frac{0.04}{0.032}\right) = k \times 34$$

$$k = 6.56 \times 10^{-3} \ (\text{min})^{-1}$$

Case II : $X_A = 0.2$, $t = 34$ min, $C_{Ao} = 0.80$ mol/l

$$C_A = C_{Ao}(1 - X_A)$$

$$= 0.8\,(1 - 0.2) = 0.64 \text{ mol/l}$$

$$\therefore \quad \ln\left(\frac{0.8}{0.64}\right) = k \times 34$$

$$k = 6.56 \times 10^{-3} \ (\text{min})^{-1}$$

As the value of k is same for both the cases, the reaction is first order.

∴ Rate equation is

$$-r_A = -dC_A/dt = 6.56 \times 10^{-3} \ (\text{min})^{-1} \cdot C_A \qquad \text{... Ans.}$$

Ex. 2.41 : After 8 minutes in a batch reactor, reactant is 80% converted and after 18 minutes the conversion is 90%. Find the rate expression to represent this reaction if $C_{Ao} = 1$ mol/l.

Solution :

$$A \rightarrow \text{products}$$

$$C_{Ao} = 1 \text{ mol/l}$$

$$X_A = 0.80 \quad \text{when } t = 8 \text{ min}$$

$$X_A = 0.90 \quad \text{when } t = 18 \text{ min}$$

Trial and error procedure is to be adopted for finding the rate expression.

First assume that the reaction follows first order kinetics.

$$-r_A = k\,C_A$$

$$\therefore \quad \ln\left[\frac{1}{1 - X_A}\right] = kt$$

Case I : $$\ln\left[\frac{1}{1 - 0.80}\right] = k \times 8, \qquad \therefore k = 0.201 \ (\text{min})^{-1}$$

Case II : $$\ln\left[\frac{1}{1 - 0.90}\right] = k \times 18, \qquad \therefore k = 0.128 \ (\text{min})^{-1}$$

As the values of k are different (variation in k values), the reaction is not first order with respect to A.

Assume that the reaction is second order :

For second order kinetics,

$$-r_A = k\,C_A^2$$

Integrated rate expression in terms of conversion is :

$$\frac{X_A}{1 - X_A} = k\,C_{Ao}\,t$$

$$X_A = 0.80, \qquad t = 8 \text{ min}, \quad C_{Ao} = 1 \text{ mol/l}$$

$$\frac{0.80}{1 - 0.80} = k \times 1 \times 8 \qquad \therefore k = 0.5 \ (\text{mol/l})^{-1} (\text{min})^{-1}$$

$$X_A = 0.90, \qquad t = 18 \text{ min}, \quad C_{Ao} = 1 \text{ mol/l}$$

$$\frac{0.90}{1-0.90} = k\times1\times18 \quad \therefore \quad k = 0.5\ (\text{mol}/l)^{-1}(\text{min})^{-1}$$

As we are getting same value of k for both the cases, the reaction obeys second order kinetics.

∴ Rate expression representing the said reaction is

$$-r_A = -dC_A/dt = 0.50\,C_A^2$$

$$-r_A = \frac{-dC_A}{dt} = 0.50\ (\text{mol}\cdot\text{min}/l)^{-1}\,C_A^2$$

OR

$$-r_A = 0.50\ (l/\text{mol})\ (\text{min})^{-1}\,C_A^2 \qquad \text{... Ans.}$$

Ex. 2.42 : Snake-Eyes Magoo is a man of habit. For instance/example, his Friday evenings are all alike – into the joint with his week's salary of Rs. 180, steady gambling at '2-up' for two hours, then home to his family leaving Rs. 45 behind. Snake-Eyes' betting pattern is predictable. He always bets in amounts proportional to his cash in hand, and his losses are also predictable – at a rate proportional to his cash at hand. This week Snake-Eyes received a raise, so he played for three hours, but as usual went home with Rs. 135. How much was his raise ?

Solution : Salary i.e. initial cash in hand is Rs. 180 and is just like C_{Ao}.

$$\therefore \quad C_{Ao} = 180$$

After 2 hours, cash in hand is Rs. 180 – 45 = Rs. 135 (leaving behind Rs. 45 means he goes home with Rs. 135 which is stated in last sentence of the problem).

Cash in hand at any time 't' is just like C_A.

$$\therefore \quad C_A = 180-45 = 135 \text{ when } t = 2\,\text{h}$$

Rate of loss is directly proportional to cash in hand. Rate of loss is just like rate of disappearance of A.

$$\therefore \quad \text{Rate of loss} \propto \text{Cash in hand}$$

$$-\frac{dC_A}{dt} \propto C_A$$

$$-\frac{dC_A}{dt} = k\,C_A$$

Hence, it is a first order kinetics. Integrating we get

$$\ln\left[\frac{C_{Ao}}{C_A}\right] = kt$$

$C_A = 135,\ C_{Ao} = 180,\ t = 2\,\text{h}.$

$$\ln\left[\frac{180}{135}\right] = k\,(2)$$

$$\therefore \quad k = 0.144\ \text{h}^{-1}$$

$C_{Ao} = ?,\ C_A = 135,\ t = 3\,\text{h}$

$$\ln\left[\frac{C_{Ao}}{135}\right] = 0.144\times3$$

$$\therefore \quad C_{Ao} = 207.94 \simeq 208$$

$$\therefore \quad \text{His raise was} = 208-180 = \text{Rs. } 28 \qquad \text{... Ans.}$$

Ex. 2.43 : Find the overall order of the irreversible reaction 10

$$2\,H_2 + 2\,NO \longrightarrow N_2 + 2\,H_2O$$

from the following constant volume data obtained by using equimolar amounts/quantities of hydrogen and nitric oxide. Take T = 296 K.

Half life (seconds)	265	186	115	104	67
Total pressure (mmHg)	200	240	280	320	360

Solution : Consider irreversible reaction of the type

$$\alpha A + \beta B + \ldots \rightarrow \text{products}$$

$$-r_A = -\frac{dC_A}{dt} = k\,C_A^a \cdot C_B^b \ldots\ldots$$

$$-r_A = -\frac{dC_A}{dt} = k\,C_A^a\,(\beta/\alpha)^b\,C_A^b \ldots\ldots$$

$$-\frac{dC_A}{dt} = k\,(\beta/\alpha)^b \ldots C_A^{a+b+\ldots}$$

$$-\frac{dC_A}{dt} = k'\,C_A^n$$

Integrating for $n \neq 1$ gives

$$\left[C_A^{1-n} - C_{Ao}^{1-n}\right] = k'\,(n-1)\,t$$

At $t = t_{1/2}$, $C_A = \frac{C_{Ao}}{2}$

$$(1/2\,C_{Ao})^{1-n} - C_{Ao}^{1-n} = k'\,(n-1)\,t_{1/2}$$

$$C_{Ao}^{1-n} - 2^{(1-n)} \cdot C_{Ao}^{1-n} = 2^{(1-n)} \cdot (n-1)\,k'\,t_{1/2}$$

$$-(2^{(1-n)} - 1)\,C_{Ao}^{(1-n)} = 2^{(1-n)} \cdot (n-1) \cdot k' \cdot t_{1/2}$$

$$t_{1/2} = \frac{-(2^{1-n} - 1)}{(n-1)\,k' \cdot 2^{1-n}} \cdot C_{Ao}^{1-n}$$

$$t_{1/2} = \frac{2^{-(1-n)}\,[-(2^{(1-n)} - 1)]}{(n-1)\,k'} \cdot C_{Ao}^{1-n}$$

$$= \frac{2^{n-1}\,[-(2^{1-n} - 1)]}{(n-1)\,k'} \cdot C_{Ao}^{1-n}$$

$$= \frac{-[2^{1-n+n-1} - 2^{n-1}]}{(n-1)\,k'} \cdot C_{Ao}^{1-n}$$

$\therefore$

$$t_{1/2} = \frac{(2^{n-1} - 1)}{(n-1)\,k'} \cdot C_{Ao}^{1-n}$$

$$\overset{Y}{\boxed{\ln t_{1/2}}} = \overset{\text{slope}}{(1-n)}\,\overset{X}{\boxed{\ln C_{Ao}}} + \ln\left[\frac{2^{n-1} - 1}{(n-1)\,k'}\right]$$

$$y = mx + c$$

For ideal gases :

$$C_A = p_A/RT, \quad C_{Ao} = p_{Ao}/RT$$

For equimolar amounts $p_{Ao} = P_o/2$, P_o = initial total pressure

$\therefore$

$$p_{Ao} = \frac{P_o}{2}$$

$$C_{Ao} = \frac{p_{Ao}}{RT}$$

$$C_{Ao} = p_{Ao}/RT = \frac{P_o}{2\,RT}$$

P_o in atm, $R = 0.08206\,(l\cdot\text{atm})/(\text{mol}\cdot\text{K})$, T in K

P_o(mmHg) : 200, 240, 280, 320 and 360

(i)

$$P_o = 200 \text{ mmHg (initial total pressure)}$$

$$P_o = 200/760 = 0.263 \text{ atm}$$

(ii)

$$C_{Ao} = 0.263/(2 \times 0.08206 \times 296)$$

$$= 5.414 \times 10^{-3}$$

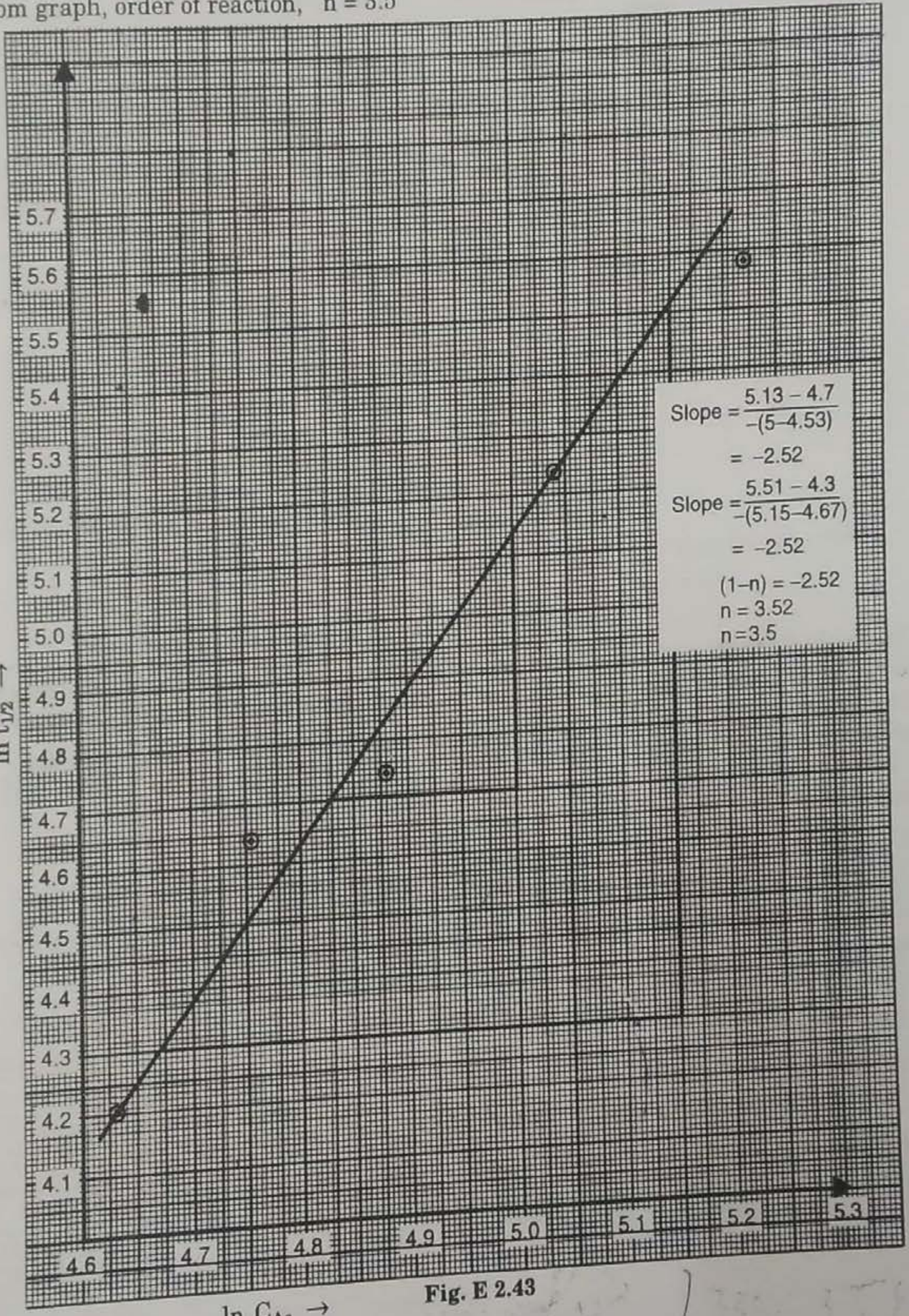
$$\ln C_{Ao} = -5.22$$

Convert data in : $\ln t_{1/2}$ and $\ln C_{Ao}$ and plot $\ln t_{1/2}$ v/s $\ln C_{Ao}$.

P (mmHg)	200	240	280	320	360
P (atm)	0.263	0.316	0.368	0.421	0.474
C_{Ao}	5.414×10^{-3}	6.5×10^{-3}	7.57×10^{-3}	8.67×10^{-3}	9.76×10^{-3}
$\ln C_{Ao}$	−5.22	−5.04	−4.88	−4.75	−4.63
$t_{1/2}$	265	186	115	104	67
$\ln t_{1/2}$	5.58	5.23	4.74	4.64	4.20

... **Ans.**

From graph, order of reaction, n = 3.5



$\text{Slope} = \frac{5.13 - 4.7}{-(5-4.53)}$

$= -2.52$

$\text{Slope} = \frac{5.51 - 4.3}{-(5.15-4.67)}$

$= -2.52$

$(1-n) = -2.52$

$n = 3.52$

$n = 3.5$

Fig. E 2.43

Ex. 2.44 : The first order reversible liquid phase reaction

$$A \rightleftharpoons R$$

takes place in a batch reactor. After 8 minutes, conversion of A is 33.3% while equilibrium conversion is 66.7%. Find the rate equation for this reaction taking $C_{A_o} = 0.50$ mol/l and $C_{R_o} = 0$.

Solution : First order kinetics

$$A \rightleftharpoons R$$

$C_{A_o} = 0.50$ mol/l, $C_{R_o} = 0.0$

$t = 8$ min, $X_A = 0.333$, $X_{Ae} = 0.667$, Rate equation ?

$$M = C_{R_o}/C_{A_o} = 0/0.5 = 0$$

Integrated rate equation for first order reaction is

$$-\ln[1 - X_A/X_{Ae}] = \frac{M+1}{M+X_{Ae}} k_1 t$$

$$-\ln\left[1 - \frac{0.333}{0.667}\right] = \frac{1}{0.667} k_1 \times 8$$

$$k_1 = 0.0577 \text{ (min)}^{-1}$$

$$K_c = \frac{C_{Re}}{C_{Ae}} = \frac{M+X_{Ae}}{1-X_{Ae}} = \frac{k_1}{k_2}$$

$$\therefore \quad \frac{k_1}{k_2} = \frac{0+0.667}{1-0.667}$$

$$\therefore \quad k_2 = k_1(1-0.667)/0.667$$

$$= 0.0288 \text{ (min)}^{-1}$$

∴ Rate equation is

$$-r_A = -dC_A/dt = k_1 C_A - k_2 C_R$$

$$= 0.0577\, C_A - 0.0288\, C_R, \quad \text{mol/}(l.\text{min})$$

... **Ans.**

Ex. 2.45 : In units of moles, litres, and seconds, find the rate equation for the decomposition of ethane at 620 °C from the following information obtained at atmospheric pressure.

The decomposition rate of pure ethane is 7.7% per second and with 85.26 mole % inerts present the decomposition rate is 2.9% per second (i.e. with inerts present the rate reduces from 7.7% to 2.9% per second).

Solution : Ethane → products

i.e. A → products

$P = 1$ atm, $T = 620 + 273 = 893$ K

$R = 0.08206$ l·atm/(mol·K)

Initial concentration of A when pure (pure ethane) is $(C_{A_o})_1$.

$$\therefore \quad (C_{A_o})_1 = P/RT = 1/(0.08206 \times 893)$$

$$= 0.0136 \text{ mol}/l$$

Rate of decomposition of pure A (i.e. pure ethane) is 7.7% per second.

$\therefore \quad X_{A_1} = 0.077$, as $dX_{A_1}/dt = 7.7\%$ per second.

Concentration of pure A after decomposition (unreacted A)

$$(C_A)_1 = (C_{A_o})_1 (1 - X_{A_1})$$

$$= 0.0136(1 - 0.077) = 0.0125 \text{ mol}/l$$

Initial concentration of A with inerts present is $(C_{A_o})_2$.

$$\begin{aligned}
\text{Inerts with A} &= 85.26 \text{ mole } \% \\
\text{Molefraction of inerts} &= 0.8526 \\
\text{Molefraction of A} &= (1-0.8526) \\
\therefore \quad (C_{A_o})_2 &= (P \times \text{molefraction of A})/RT \\
&= 1 \times (1-0.8526)/(0.08206 \times 893) \\
&= 2.011 \times 10^{-3} \text{ mol}/l
\end{aligned}$$

Rate of disappearance of A :

$$\begin{aligned}
\text{of pure A} &= (-r_A)_1 \\
\text{of A with inerts} &= (-r_A)_2 \\
-r_A &= -dC_A/dt \\
C_A &= C_{A_o}(1-X_A) \\
dC_A/dt &= -C_{A_o}\, dX_A/dt \\
\therefore \quad (-r_A) &= C_{A_o} \cdot dX_A/dt \\
(dX_A/dt)_1 &= 0.077 \\
(-r_A)_1 &= (C_{A_o})_1 \ (dX_A/dt)_1 \\
(-r_A)_1 &= 0.0136 \times 0.077 = 1.047 \times 10^{-3} \quad \text{mol}/(l \cdot \text{s}) \\
(dX_A/dt)_2 &= 2.9\% \text{ per second (in percent)} \\
\therefore \quad (-r_A)_2 &= (C_{A_o})_2 \cdot (dX_A/dt)_2 \\
&= 2.011 \times 10^{-3} \times 0.029 \\
&= 5.83 \times 10^{-5} \text{ mol}/(l \times \text{s}) \\
-r_A &= k\, C_A^n \\
\therefore \quad (-r_A)_1 &= k\, (C_A)_1^n \\
(-r_A)_2 &= k\, (C_A)_2^n
\end{aligned}$$

With inerts present, $(X_A)_2$ is 0.029

$$\begin{aligned}
(C_A)_2 &= (C_{A_o})_2\, [1-(X_A)_2] \\
&= 2.011 \times 10^{-3}\, [1-0.0299] \\
&= 1.95 \times 10^{-3} \text{ mol}/l \\
\frac{(-r_A)_1}{(-r_A)_2} &= \frac{(C_A)_1^n}{(C_A)_2^n} \\
\frac{1.0472 \times 10^{-3}}{5.83 \times 10^{-5}} &= (C_A)_1^n / (C_A)_2^n \\
\left[\frac{(C_A)_1}{(C_A)_2}\right]^n &= 17.96 \\
n \ln\, [(C_A)_1/(C_A)_2] &= \ln 17.96 \\
n &= \frac{\ln (17.96)}{\ln\left[\dfrac{0.0125}{1.95 \times 10^{-3}}\right]} \\
&= \frac{2.89}{1.86} = 1.55 \\
(-r_A)_1 &= k\, [(C_A)_1]^n
\end{aligned}$$

$$1.0472 \times 10^{-3} = k\,[0.0125]^{1.55}$$

$$\therefore \quad k = 0.933$$

∴ Rate equation for decomposition of ethane is :

$$(-r_A) = -\frac{dC_A}{dt} = 0.933\ C_A^{1.55}$$

$$-r_A = 0.933\ (\text{mol}/l)^{-0.55}\,(\text{s})^{-1} \cdot C_A^{1.55}\ , \quad \text{mol}/(l\cdot\text{s})$$

... **Ans.**

Dw

Ex. 2.46 : The liquid phase reaction $A \rightarrow R + S$ proceeds as follows : Dout

Time, min	0	36	65	100	160	∞
C_A, mol/l	0.1823	0.1453	0.1216	0.1025	0.0795	0.0494

With $C_{Ao} = 0.1823$ mol/l, $C_{Ro} = 0$ and $C_{So} \equiv 55$ mol/l, find the rate expression for this reaction.

Solution : $A \rightarrow R + S$, $C_{Ao} = 0.1823$ mol/l, $C_{Ro} = 0$, $C_{So} \equiv 55$ mol/l

As C_{So} is very large compared to C_{Ao}, C_{Ro} we can assume that it remains constant throughout the reaction $C_S = C_{So}$.

$$\therefore \quad A \rightarrow R$$

At $t = \infty$, the conversion is not 100%, thus it will be treated as reversible reaction.

$$\therefore \quad A \rightleftharpoons R$$

For first order reversible reaction, we have

$$-\ln\left[\frac{C_A - C_{Ae}}{C_{Ao} - C_{Ae}}\right] = \left(\frac{M+1}{M+X_{Ae}}\right) k_1 t = -\ln\left[1 - \frac{X_A}{X_{Ae}}\right]$$

C_{Ae} – concentration of A at $t = \infty$ $\quad \therefore \ C_{Ae} = 0.0494$

$$M = C_{Ro}/C_{Ao} = 0/0.1823 = 0$$

$$X_{Ae} = \frac{C_{Ao} - C_{Ae}}{C_{Ao}} = \frac{0.1823 - 0.0494}{0.1823} = 0.729$$

$t = 36$ min, $C_A = 0.1453$ mol/l

$$-\ln\left[\frac{0.1453 - 0.0494}{0.1823 - 0.0494}\right] = \left[\frac{0+1}{0+0.729}\right] k_1 \times 36$$

$$\therefore \quad k_1 = 6.61 \times 10^{-3}\ \text{min}^{-1}$$

$t = 65$ min, $C_A = 0.1216$ mol/l

$$-\ln\left[\frac{0.1216 - 0.0494}{0.1823 - 0.0494}\right] = \left(\frac{1}{0.729}\right) k_1 \times 65$$

$$k_1 = 6.84 \times 10^{-3}\ \text{min}^{-1}$$

$t = 100$ min, $C_A = 0.1025$ mol/l

$$-\ln\left[\frac{0.1025 - 0.0494}{0.1823 - 0.0494}\right] = \left[\frac{1}{0.729}\right] k_1 \times 100$$

$$k_1 = 6.69 \times 10^{-3}\ \text{min}^{-1}$$

$t = 160$ min, $C_A = 0.0795$ mol/l

$$-\ln\left[\frac{0.0795 - 0.0494}{0.1823 - 0.0494}\right] = \frac{1}{0.729} \times k_1 \times 160$$

$$k_1 = 6.77 \times 10^{-3}\ \text{min}^{-1}$$

$$\text{Average value of } k_1 = 6.73 \times 10^{-3}\ \text{min}^{-1}$$

Values of k_1 are nearly same, so reaction obeys first order kinetics.

$$\frac{k_1}{k_2} = \frac{M + X_{Ae}}{1 - X_{Ae}}$$

$$\frac{k_1}{k_2} = \frac{0 + 0.729}{1 - 0.729} = 2.69$$

$$k_2 = 0.372\, k_1 = 0.372 \times (6.73 \times 10^{-3}) = 2.50 \times 10^{-3}\ \text{min}^{-1}$$

∴ Rate equation is

$$-r_A \doteq (6.73 \times 10^{-3}\ \text{min}^{-1})\, C_A - (2.50 \times 10^{-3}\ \text{min}^{-1})\, C_R \qquad \text{... Ans.}$$

Ex. 2.47 : It is stated that the half-life method for finding reaction order can be extended to any fractional-life data. Do this, defining $t_{1/m}$ as the time required for the reactant concentration to drop to 1/mth of its original value.

Solution : For nth order reaction we can write rate as :

$$-r_A = -\frac{dC_A}{dt} = k\, C_A^n$$

$$-\frac{dC_A}{C_A^n} = k\, dt$$

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

$$C_A^{1-n} - C_{Ao}^{1-n} = (n-1)\, kt$$

Now at $t = t_{1/m}$, $C_A = \frac{1}{m} \cdot C_{Ao}$

$$\left[\frac{1}{m} \cdot C_{Ao}\right]^{1-n} - [C_{Ao}]^{1-n} = (n-1)\, k\, t_{1/m}$$

$$\left[\left(\frac{1}{m}\right)^{1-n} - 1\right] C_{Ao}^{1-n} = (n-1)\, k\, t_{1/m}$$

$$\left[\frac{1 - m^{1-n}}{m^{1-n}}\right] C_{Ao}^{1-n} = (n-1)\, k\, t_{1/m}$$

$$\therefore \quad t_{1/m} = \frac{m^{n-1}\,[1 - m^{1-n}]}{m^{n-1}\,(m^{1-n})} \; \frac{C_{Ao}^{1-n}}{(n-1)\, k}$$

$$= \left[\frac{m^{n-1} - m^{n-1+1-n}}{m^{n-1+1-n}}\right] \frac{C_{Ao}^{1-n}}{(n-1)\, k}$$

$$t_{1/m} = (m^{n-1} - 1) \cdot \frac{C_{Ao}^{1-n}}{(n-1)\, k} \qquad \text{... Ans.}$$

Ex. 2.48 : The kinetic data on the reaction of sulphuric acid with diethyl sulphate in aqueous solution at 22.9 °C is

Time, min	0	41	48	55	75	96	127
$C_2H_5SO_4H$, mol/l	0	1.18	1.38	1.63	2.24	2.75	3.31

Time, min	146	162	180	194	212	267	318	368	379	410	∞
$C_2H_5SO_4H$, mol/l	3.76	3.81	4.11	4.31	4.45	4.86	5.15	5.32	5.35	5.42	5.80

The reaction taking place is

$$H_2SO_4 + (C_2H_5)_2\,SO_4 = 2\, C_2H_5SO_4H$$

Find the rate equation for this reaction if initial concentrations of H_2SO_4 and are each 5.5 mol/l.

Solution : $H_2SO_4 + (C_2H_5)_2SO_4 \rightleftharpoons 2\,C_2H_5SO_4H$

$$A + B \rightleftharpoons 2R$$

$$C_{Ao} = C_{Bo} = 5.5 \text{ mol}/l$$

$$\boxed{-r_A = -\frac{dC_A}{dt} = k_1 C_A C_B - k_2 C_R^2}$$

Integrated rate equation is

$$\boxed{\ln\left[\frac{X_{Ae} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A}\right] = 2k_1\left(\frac{1}{X_{Ae}} - 1\right)C_{Ao}t}$$

$$\text{Change in concentration of A} = \frac{\text{Change in concentration of R}}{2}$$

$$C_A = C_{Ao} - \text{change in concentration of A}$$

At $t = 41$ min, $C_R = 1.18$

$$\text{Change in } H_2SO_4 = 1.18/2 = 0.59$$

$\therefore$
$$C_A = 5.5 - 0.59 = 4.91 \text{ mol}/l$$

$$X_A = (C_{Ao} - C_A)/C_{Ao}$$

$$= (5.5 - 4.91)/5.5 = 0.107$$

time (t), min	C_A	X_A	$\ln\left[\frac{X_{Ae} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A}\right]$
0	0	0	0
41	4.91	0.107	0.216
48	4.81	0.125	0.258
55	4.685	0.148	0.314
75	4.38	0.204	0.468
96	4.125	0.25	0.617
127	3.845	0.30	0.811
146	3.62	0.342	1.011
162	3.595	0.346	1.033
180	3.445	0.374	1.198
194	3.345	0.392	1.321
212	3.275	0.404	1.412
267	3.07	0.442	1.778
318	2.925	0.468	2.14
368	2.84	0.483	2.43
379	2.825	0.486	2.50
410	2.79	0.492	2.66
∞	2.6	0.527	∞

$$X_{Ae} = X_A \text{ at } t = \infty = 0.527$$

$$\text{For } t = 41 \text{ min}, X_A = 0.107$$

$$\text{Let } z = \frac{X_{Ae} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A}$$

$$\ln z = \ln\left[\frac{X_{Ae} - (2\,X_{Ae} - 1)\,X_A}{X_{Ae} - X_A}\right]$$

$$= \ln\left[\frac{0.527 - (2 \times 0.527 - 1) \times 0.107}{0.527 - 0.107}\right] = 0.216$$

Plot ln z v/s t, which should be straight line through the origin.

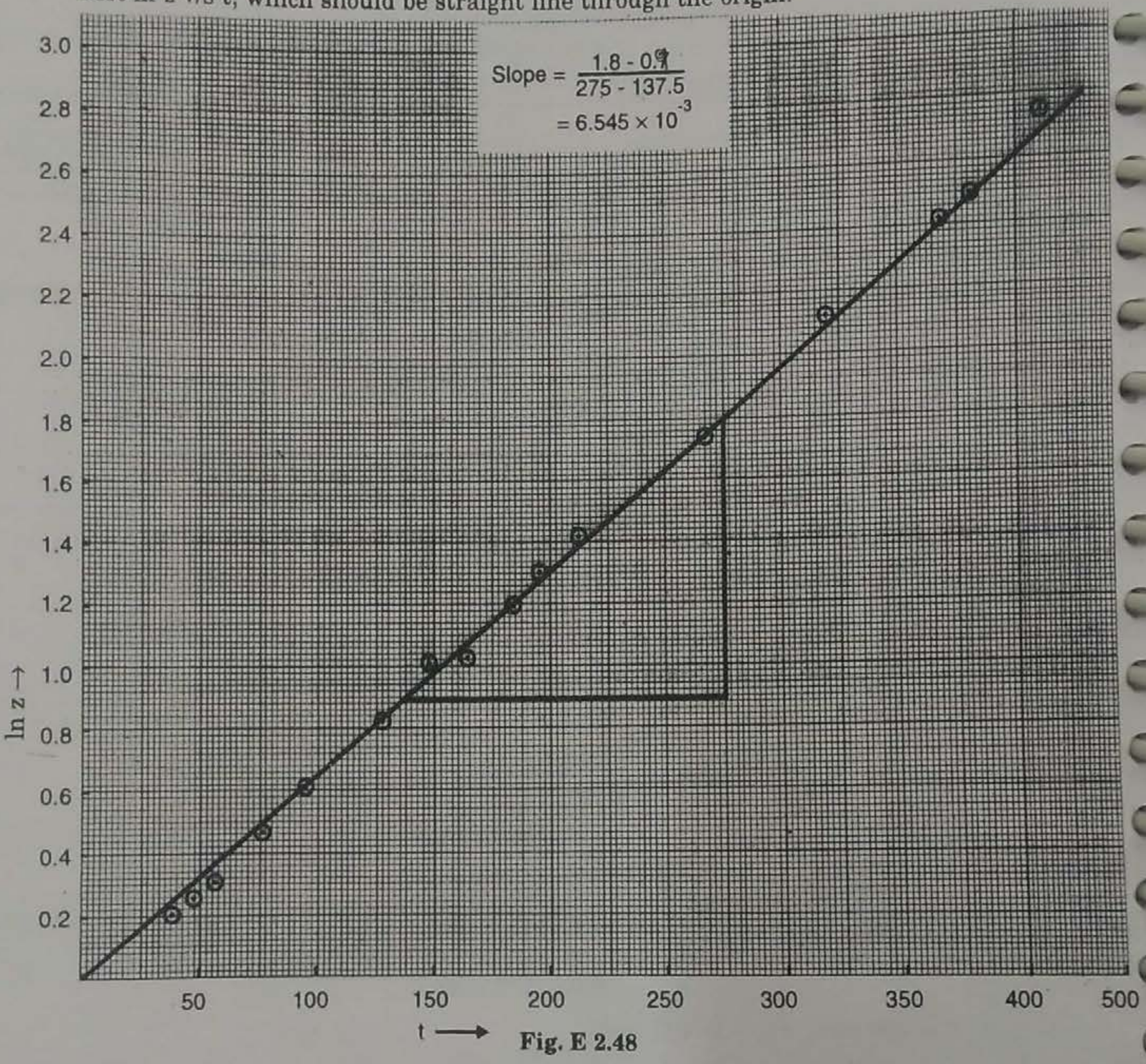


Fig. E 2.48

$$\text{Slope} = 6.545 \times 10^{-3}$$

$$6.545 \times 10^{-3} = 2\,k_1\left(\frac{1}{X_{Ae}} - 1\right)C_{Ao}$$

$$6.545 \times 10^{-3} = 2\,k_1\left[\frac{1}{0.527} - 1\right] \times 5.5$$

$$\therefore \quad k_1 = 6.63 \times 10^{-4}\ (\text{mol}/l)^{-1}\ (\text{min})^{-1}$$

At t = ∞, $C_R = 5.8$ mol/l (see data given)

$\therefore$ $C_{Re} = 5.8$ mol/l (as concentration at infinite time is equilibrium concentration)

At $t = \infty$, C_A calculated $= 2.6$ mol/l

$$\therefore \quad C_{Ae} = 2.6 \text{ mol}/l$$

We have, $C_{Be} = C_{Ae}$

Values at $t = \infty$ represent the equilibrium values.

$$K_C = \frac{k_1}{k_2} = \frac{C_{Re}^2}{C_{Ae} \cdot C_{Be}}$$

$$\frac{k_1}{k_2} = \frac{C_{Re}^2}{(C_{Ae})^2} = \frac{(5.8)^2}{(2.6)^2} = 4.976$$

$$\therefore \quad k_2 = 6.63 \times 10^{-4}/4.976 = 1.33 \times 10^{-4}$$

$\therefore$ Rate equation is :

$$-r_A = (6.63 \times 10^{-4})\, C_A\, C_B - (1.33 \times 10^{-4})\, C_R \qquad \text{... Ans.}$$

Ex. 2.49 : A small reaction bomb equipped with a sensitive pressure measuring device is flushed out and then filled with pure reactant A at one atmosphere pressure. The operation is carried out at 25 °C, at which the reaction does not proceed to an appreciable extent. The temperature is then rapidly increased to 100 °C by plunging the bomb into boiling water and the following data is obtained.

t, min	1	2	3	4	5	6	7	8	9	10	15	20
P, atm	1.14	1.04	0.982	0.940	0.905	0.870	0.850	0.832	0.815	0.800	0.754	0.728

The stoichiometry of reaction is 2A → R, and after leaving the bomb in bath over the week's period the contents are analysed for A and none can be found.

Find the rate expression in units of moles, litres, and minutes which can satisfactorily fit the data.

Solution : $2A \rightarrow R$

A reaction bomb is a constant-volume reactor.

Initially A is at 25 °C (298 K) and 1 atm pressure.

Before reaction A is at 100 °C (373 K) at pressure P_2 (not known) which can be calculated as :

$P_1 = 1$ atm, $T_1 = 298$ K, $V = V_1$

$P_2 = ?$, $T_2 = 373$ K, $V = V_2$

As constant volume reactor, we have

$$V_1 = V_2$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\therefore \quad P_2 = \left(\frac{T_2}{T_1}\right) P_1$$

$$= \left(\frac{373}{298}\right) \times 1 = 1.25 \text{ atm}$$

$P_2 = 1.25$ atm is the total pressure of the system before the commencement of reaction, so it is the initial pressure.

$$\therefore \quad P_o = P_2 = 1.25 \text{ atm}$$

As initially only pure A is there in the bomb,

$$p_{Ao} = P_o = 1.25 \text{ atm}$$

$$\therefore \quad p_{Ao} = 1.25 \text{ atm}$$

For constant volume reactor, we have :

$$p_A = p_{Ao} - \frac{a}{\Delta n}(P - P_o)$$

$$\Delta n = 1 - 2 = -1$$

$$a = 2$$

At t = 0 i.e. before the commencement of a reaction

$$C_{Ao} = p_{Ao}/RT = P_o/RT$$
$$= 1.25/(0.08206 \times 373)$$
$$= 0.041 \text{ mol}/l$$

C_{Ao} is the initial concentration of A.

p_A is the partial pressure of A at any time t.

$$p_A = p_{Ao} - \frac{2}{(-1)}(P - P_o) = P_o + 2(P - P_o) = 2P - P_o, \quad \text{as } p_{Ao} = P_o$$

Calculate p_A and C_A for the data given.

At t = 1 min, P = 1.14 atm,

$$p_A = 2 \times 1.14 - 1.25 = 1.03 \text{ atm}$$

$$\therefore \quad C_A = \frac{p_A}{RT} = \frac{1.03}{0.08206 \times 373} = 0.034 \text{ mol}/l$$

Similarly, calculate p_A and C_A at different values of time with the help of given data and tabulate the data of C_A as a function of t.

t	0	1	2	3	4	5	6	7	8	9	10	15	20
C_A	0.041	0.034	0.027	0.023	0.021	0.018	0.016	0.015	0.0136	0.012	0.0114	0.0089	0.0067

Assume that reaction follows first order kinetics. Then

$$\ln C_{Ao}/C_A = kt$$

t = 1 min, $C_{Ao} = 0.041$ mol/l, $C_A = 0.034$ mol/l

$$\therefore \quad k = \frac{\ln(0.041/0.034)}{1} = 0.1872 \text{ min}^{-1}$$

t = 2 min, $C_{Ao} = 0.041$ mol/l, $C_A = 0.027$ mol/l

$$\therefore \quad k = \frac{\ln(0.041/0.027)}{2} = 0.209 \text{ min}^{-1}$$

t = 8 min, $C_A = 0.0136$ mol/l

$$k = \frac{\ln(0.041/0.0136)}{8} = 0.138 \text{ min}^{-1}$$

t = 15 min, $C_A = 0.0089$ mol/l

$$k = \frac{\ln(0.041/0.0089)}{15} = 0.102 \text{ min}^{-1}$$

t = 20 min, $C_A = 0.0067$ mol/l

$$k = \frac{\ln(0.041/0.0067)}{20} = 0.090 \text{ min}^{-1}$$

As there is large variation in k values, the reaction does not obeys first order kinetics.

Assume that the reaction follows second order kinetics. Then,

$$\left[\frac{1}{C_A} - \frac{1}{C_{Ao}}\right] = kt$$

$$\therefore \quad k = [1/C_A - 1/C_{Ao}]/t$$

$t = 1$ min, $C_A = 0.034$ mol/l

$$k = [(1/0.034) - (1/0.041)]/1 = 5.02$$

$t = 2$ min, $C_A = 0.027$ mol/l

$$k = [(1/0.027) - (1/0.041)]/2 = 6.32$$

$t = 3$ min, $C_A = 0.023$ mol/l

$$k = [(1/0.023) - (1/0.041)]/3 = 6.36$$

$t = 4$ min, $C_A = 0.021$ mol/l

$$k = [(1/0.021) - (1/0.041)]/4 = 5.81$$

$t = 5$ min, $C_A = 0.018$ mol/l

$$k = [(1/0.018) - (1/0.041)]/5 = 6.23$$

$t = 6$ min, $C_A = 0.016$ mol/l

$$k = [(1/0.016) - (1/0.041)]/6 = 6.35$$

$t = 7$ min, $C_A = 0.015$ mol/l

$$k = [(1/0.015) - (1/0.041)]/7 = 6.04$$

$t = 8$ min, $C_A = 0.0136$ mol/l

$$k = [(1/0.0136) - (1/0.041)]/8 = 6.14$$

$t = 9$ min, $C_A = 0.012$ mol/l

$$k = [(1/0.012) - (1/0.041)]/9 = 6.55$$

$t = 10$ min, $C_A = 0.0114$ mol/l

$$k = [(1/0.0114) - (1/0.041)]/10 = 6.33$$

$t = 15$ min, $C_A = 0.0089$ mol/l

$$k = [(1/0.0089) - (1/0.041)]/15 = 5.86$$

$t = 20$ min, $C_A = 0.0067$ mol/l

$$k = [(1/0.0067) - (1/0.041)]/20 = 6.24$$

As there is not much variation in values of k, the reaction follows second order kinetics.

$$\text{Average value of k} = 6.10\ (\text{mol}/l)^{-1}\ (\text{min})^{-1}$$

$$= 6.10\ (l/\text{mol})\ (\text{min})^{-1}$$

∴ Rate equation is

$$-r_A = [6.10\ (l/\text{mol}) \cdot (\text{min})^{-1}]\ C_A^2 \qquad \textbf{... Ans.}$$

Order of reaction may not be always 0, 1 or 2 (for which integrated rate equations are known) therefore it is always advisable to find order of reaction graphically. We will now obtain the order of reaction graphically.

Assume the rate equation be

$$(-r_A) = -dC_A/dt = k\,C_A^n$$

$$\ln\ (-r_A) = \ln k + n \ln C_A$$

Plot of $\ln(-r_A)$ v/s $\ln C_A$ gives the values of n and k.

OR

$$\ln\ (-r_{A_1}) = \ln k + n \ln C_{A_1}$$

$$\ln\ (-r_{A_2}) = \ln k + n \ln C_{A_2}$$

$$\therefore \quad n = \frac{\ln\ (-r_{A_2}/r_{A_1})}{\ln\ (C_{A_2}/C_{A_1})}$$

For this procedure first plot graph of C_A v/s t, draw smooth curve then draw tangents to the curve at various values of concentration (C_A) and find the slopes of the tangents drawn. The slopes of the tangents are the rates of reaction at various values of C_A.

$$\text{Slope of tangent} = -\frac{dC_A}{dt} = -r_A.$$

So obtain $(-r_A) - C_A$ data from the plot of C_A v/s t.

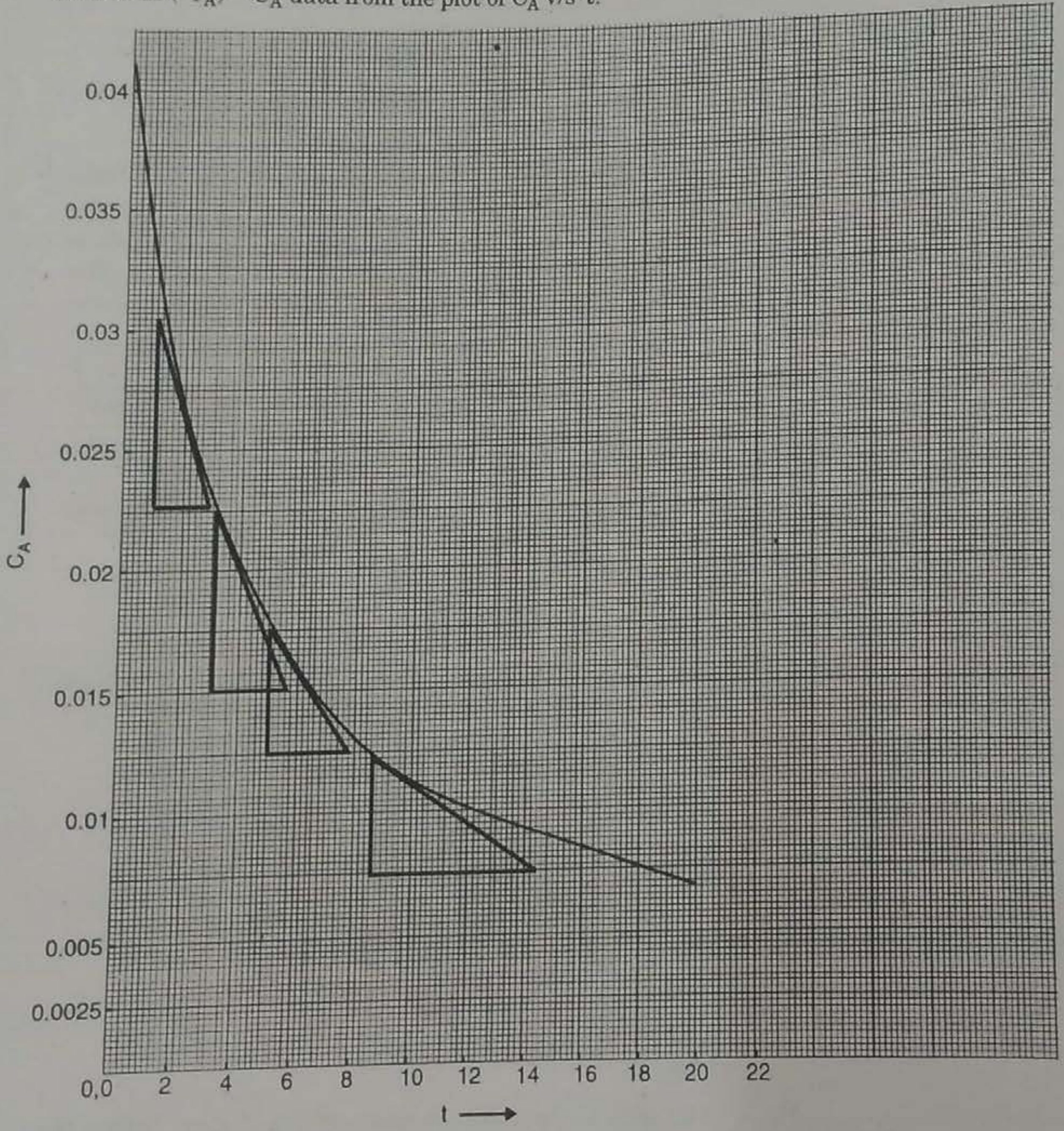


Fig. E 2.49 (1)

From graph of C_A v/s t :

(i) $C_A = 0.0125$ mol/l, slope $= 8.62 \times 10^{-4}$

$$\text{slope} = \frac{0.0125 - 0.0075}{5.8} = 8.62 \times 10^{-4}$$

$$(-r_A) = 8.62 \times 10^{-4} \ \text{mol}/(l \cdot \text{min})$$

C_A	$(-r_A)$ = slope at C_A
0.0125	8.62×10^{-4}
0.0175	1.75×10^{-3}
0.0225	2.9×10^{-3}
0.0275	4.4×10^{-3}

$$n = \frac{\ln(-r_{A2}/-r_{A1})}{\ln(C_{A2}/C_{A1})}$$

For

$$-r_{A2} = 1.75 \times 10^{-3}, \quad -r_{A1} = 8.62 \times 10^{-4}$$

$$C_{A2} = 0.0175, \quad C_{A1} = 0.0125$$

$$n = \frac{\ln(1.75 \times 10^{-3}/8.62 \times 10^{-4})}{\ln(0.0175/0.0125)} = 2.10$$

For

$$-r_{A2} = 4.4 \times 10^{-3}, \quad -r_{A1} = 2.9 \times 10^{-3}$$

$$C_{A2} = 0.0275, \quad C_{A1} = 0.0225$$

$$n = \frac{\ln(4.4 \times 10^{-3}/2.9 \times 10^{-3})}{\ln(0.0275/0.0225)} = 2.07$$

For

$$-r_{A2} = 2.9 \times 10^{-3}, \quad -r_{A1} = 1.75 \times 10^{-3}$$

$$C_{A2} = 0.0225, \quad C_{A1} = 0.0175$$

$$n = \frac{\ln(2.9 \times 10^{-3}/1.75 \times 10^{-3})}{\ln(0.0225/0.0175)} = 2.0$$

For

$$-r_{A2} = 4.4 \times 10^{-3}, \quad -r_{A1} = 8.62 \times 10^{-4}$$

$$C_{A2} = 0.0275, \quad C_{A1} = 0.0125$$

$$n = \frac{\ln(4.4 \times 10^{-3}/8.62 \times 10^{-4})}{\ln(0.0275/0.0125)} = 2.06$$

For

$$-r_{A2} = 4.4 \times 10^{-3}, \quad -r_{A1} = 1.75 \times 10^{-3}$$

$$C_{A2} = 0.0275, \quad C_{A1} = 0.0175$$

$$n = \frac{\ln(4.4 \times 10^{-3}/1.75 \times 10^{-3})}{\ln(0.0275/0.0175)} = 2.04$$

So for any combination of $-r_A$ and C_A, the order is closely equal to 2. Hence order of reaction is 2.

$$(-r_A) = k C_A^2$$

$$\therefore \quad k = (-r_A)/C_A^2$$

C_A	$(-r_A)$	k
0.0125	8.62×10^{-4}	5.5
0.0175	1.75×10^{-3}	5.71
0.0225	2.9×10^{-3}	5.73
0.0275	4.4×10^{-3}	5.82

Average k = 5.69 (*l*/mol) (min)$^{-1}$

We have

$$(-r_A) = k C_A^n$$

$$\therefore \quad \ln(-r_A) = \ln k + n \ln C_A$$

C_A	$(-r_A)$	$\ln C_A$	$\ln(-r_A)$
0.0125	8.62×10^{-4}	−4.4	−7.0
0.0175	1.75×10^{-3}	−4.0	−6.3
0.0225	2.9×10^{-3}	−3.8	−5.8
0.0275	4.4×10^{-3}	−3.6	−5.4

Plot a graph of $\ln(-r_A)$ v/s $\ln C_A$.

From plot, we have, slope = 2.03

$\therefore$ Order of reaction is 2.03 = 2

$$\text{Intercept} = 1.75$$
$$\ln k = 1.75$$
$$k = 5.75\ (l/\text{mol})\ (\text{min})^{-1}$$

So values calculated and obtained graphically are almost equal.

$$\therefore \quad -r_A = 5.75\ (l/\text{mol})\ (\text{min})^{-1}\ C_A^2 \qquad \text{... Ans.}$$

Note : It is usual practice to obtain the values of n and k graphically as order may not be always 1 or 2.

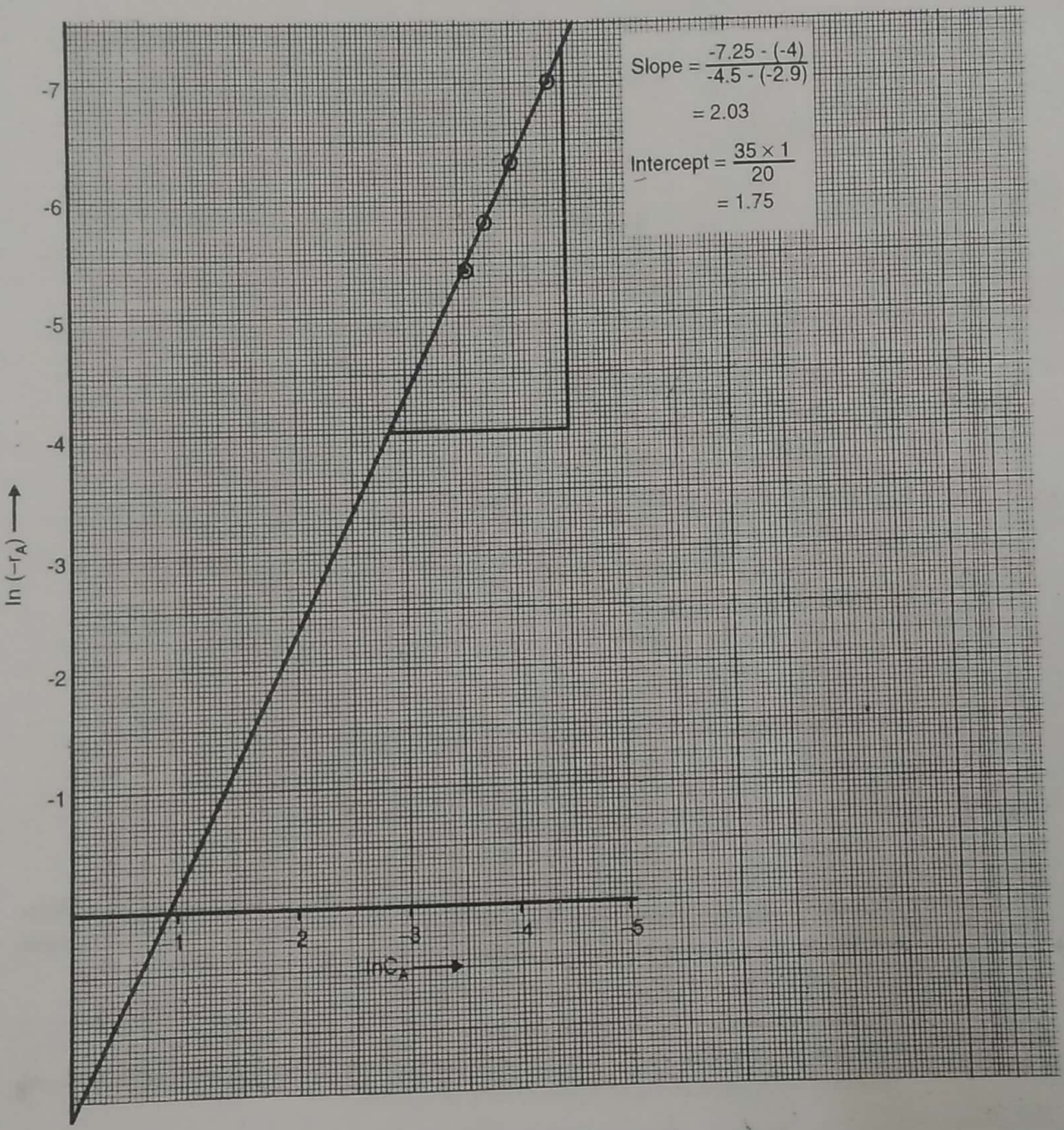


Fig. E 2.49 (2)

M. J. P

Ex. 2.50 : Raju likes to play the gambling tables for relaxation. He does not expect to win and he doesn't, so he picks games in which losses are given small fraction of the money bet. He plays steadily without a break, and the size of his bets are proportional to the money he has. If at gambling table 1 it takes him four hours to lose half of his money and at gambling table 2 it takes two hours to lose half of his money, how long can he play both the games simultaneously if he starts with Rs. 1000 and quits with Rs. 10 ?

Solution : He picks up the games in which losses are given as small fraction of the money bet and his size of bets are proportional to the money he has. Therefore,

$$-\frac{dC_A}{dt} \propto C_A$$

$$-\frac{dC_A}{dt} = kC_A \quad \ldots \quad \text{first order kinetics.}$$

Game 1 : $t = 4\,h,\ C_A = \frac{1}{2} C_{A_0}$

C_{A_0} – initial money he has

C_A – money he has at time t

$$\ln C_{A_0}/C_A = k_1 t$$

$$\therefore \quad \ln\left(\frac{C_{A_0}}{\frac{1}{2}C_{A_0}}\right) = k_1 \times 4$$

$$\therefore \quad k_1 = 0.1733\ (h)^{-1}$$

Game 2 : $t = 2\,h,\ C_A = 1/2\, C_{A_0}$

$$\ln (C_{A_0}/C_A) = k_2 t$$

$$\ln\left(C_{A_0}/\frac{1}{2}C_{A_0}\right) = k_2 \times 2$$

$$\therefore \quad k_2 = 0.3466\ (h)^{-1}$$

For both the games simultaneously,

C_{A_0} = Rs. 1000 and C_A = Rs. 10

$$-\frac{dC_A}{dt} = (k_1 + k_2)\, C_A$$

$$\therefore \quad \ln (C_{A_0}/C_A) = (k_1 + k_2)\, t$$

$$t = \frac{\ln (C_{A_0}/C_A)}{(k_1 + k_2)}$$

$$= \frac{\ln (1000/10)}{(0.1733 + 0.3466)}$$

$$= 8.86\ h$$

He can play both the games simultaneously for 8.86 h ... **Ans.**

... **Ans.**

Ex. 2.51 : Nitrogen pentaoxide decomposes as follows :

$N_2O_5 \rightarrow 1/2\, O_2 + N_2O_4,\ -r_{N_2O_5} = (2.2 \times 10^{-3}\ \text{min}^{-1})\ C_{N_2O_5}$

$N_2O_4 \rightleftharpoons 2NO_2$, instantaneous, $K_p = 45$ mmHg.

Calculate the partial pressure of each of the components present in constant volume bomb after 6.5 hours if we start with pure N_2O_5 at atmospheric pressure.

Solution :

$$N_2O_5 = \frac{1}{2} O_2 + N_2O_4$$

$$N_2O_4 \rightleftharpoons 2\,NO_2$$

Initial component : N_2O_5

Final components : N_2O_5, O_2, N_2O_4 and NO_2

$$-r_{N_2O_5} = 2.2 \times 10^{-3}\,(\text{min})^{-1}\,C_{N_2O_5}$$

$$-r_A = 2.2 \times 10^{-3}\,C_A$$

Initially, pressure is 1 atm and pure N_2O_5, so

P_o = 1 atm and $p_{Ao} = P_o$ = 1 atm = 760 mmHg, t = 6.5 h = 390 min.

For first order reaction,

$$\ln\frac{C_{Ao}}{C_A} = kt \Rightarrow \ln\left(\frac{p_{Ao}}{p_A}\right) = kt$$

$$\ln(1/p_A) = 2.2 \times 10^{-3} \times 390$$

$$p_A = 0.424 \text{ atm}$$

$\therefore$ Fraction conversion of N_2O_5 $= \dfrac{1-0.424}{1} = 0.576$

As concentration is directly proportional to partial pressure,

$$X_A = (C_{Ao} - C_A)/C_{Ao}$$

$$= (p_{Ao} - p_A)/p_{Ao}$$

Partial pressure of N_2O_5 = 0.424 atm

If we start with 1 mol of N_2O_5 in 1 litre bomb then

N_2O_5 reacted = 1 × 0.576 = 0.576 mol

N_2O_5 unreacted = 1 − 0.576 = 0.424 mol

O_2 produced $= \frac{1}{2}(0.576) = 0.288$ mol

N_2O_4 produced $= \frac{1}{1}(0.576) = 0.576$ mol

$$N_2O_4 \rightleftharpoons 2\,NO_2$$

Let x be the moles of N_2O_4 converted to NO_2. Moles of N_2O_4 unreacted = (0.576 − x) mol

Moles of NO_2 produced = 2x mol

Final total moles = (1 − 0.576) + (0.576 − x) + 2x + 0.288

= (1.288 + x) mol

At constant V and T, we have

$$P \propto n$$

$$\frac{P_1}{P_2} = \frac{n_1}{n_2}$$

$$P_2 = \frac{n_2}{n_1}P_1$$

$$= \frac{(1.288+x)}{1} \times 1 = (1.288 + x) \text{ atm}$$

P_2 is the final pressure and P_1 is the initial pressure.

$$N_2O_4 \rightleftharpoons 2\,NO_2$$

$$K_p = 45 \text{ mmHg} = 45/760 = 0.06 \text{ atm}$$

$$K_p = p^2_{NO_2}/p_{N_2O_4}$$

$$p_{NO_2} = \left(\frac{2x}{1.288+x}\right)P_2$$

$$p_{N_2O_4} = \left(\frac{0.576 - x}{1.288 + x}\right) P_2$$

$$0.06 = \frac{\left(\dfrac{2x}{1.288 + x}\right)^2 \cdot P_2^2}{\left(\dfrac{0.576 - x}{1.288 + x}\right) P_2}$$

$$0.06 = \frac{4x^2}{(1.288 + x)^2} \times \frac{(1.288 + x)^2}{\dfrac{(0.576 - x)}{(1.288 + x)} \times (1.288 + x)}$$

$$0.06 = \frac{4x^2}{(0.576 - x)}$$

$$4x^2 + 0.06\,x - 0.03456 = 0$$

$$\therefore \quad x = 0.086$$

$$\begin{aligned}
\text{Total final pressure} &= 1.288 + 0.086 = 1.374 \text{ atm} \\
&= 1044.24 \text{ mmHg} \\
\text{Moles of } N_2O_4 &= 0.576 - 0.086 = 0.49 \text{ mol} \\
\text{Moles of } N_2O_5 &= 0.424 \text{ mol} \\
\text{Moles of } O_2 &= 0.288 \text{ mol} \\
\text{Moles of } NO_2 &= 2 \times 0.086 = 0.172 \text{ mol} \\
\text{Total moles} &= 1.288 + 0.086 = 1.374 \text{ mol}
\end{aligned}$$

$$\text{Partial pressure of } N_2O_5 = \frac{0.424}{1.374} \times 1044.24$$

$$= 322.24 \text{ mmHg}$$ ... **Ans.**

$$\text{Partial pressure of oxygen} = \frac{0.288}{1.374} \times 1044.24$$

$$= 218.88 \approx 219 \text{ mmHg}$$ ... **Ans.**

$$\text{Partial pressure of } NO_2 = \frac{0.172}{1.374} \times 1044.24$$

$$= 130.72 \text{ mmHg}$$ ... **Ans.**

$$\text{Partial pressure of } N_2O_4 = \frac{0.49}{1.374} \times 1044.24$$

$$= 372.4 \text{ mmHg}$$ ... **Ans.**

Ex. 2.52 : Sucrose is hydrolysed at room temperature by the catalytic action of the enzyme sucrase as follows :

$$\text{Sucrose} \xrightarrow{\text{sucrase}} \text{products}$$

Following kinetic data are obtained in a batch reactor by starting run with a sucrose concentration C_{A_0} = 1.0 millimol/*l* and an enzyme concentration C_{E_0} = 0.01 millimol/*l*.

C_A, millimol/*l*	0.84	0.68	0.53	0.38	0.27	0.16	0.09	0.04	0.018	0.006	0.0025
time, h	1	2	3	4	5	6	7	8	9	10	11

Show by calculation whether these data can reasonably fit a kinetic equation of the type

$$-r_A = k\,C_A\,C_{E_0}/(C_A + M)$$

where M is constant.

If so evaluate the constants k and M.

Solution : Sucrose $\xrightarrow{\text{sucrase}}$ products

$$A + E \rightarrow P$$

$C_{A_0} = 1.0$ mmol/*l*, $C_{E_0} = 0.01$ mmol/*l*

$$-r_A = \frac{k\,C_A\,C_{E_0}}{(C_A + M)}$$

$$\frac{1}{-r_A} = \frac{C_A + M}{k\,C_A\,C_{E_0}}$$

$$\frac{1}{-r_A} = \frac{1}{k\,C_{E_0}} + \frac{M}{k\,C_A\,C_{E_0}}$$

$$\frac{1}{-r_A} = \left(\frac{M}{k\,C_{E_0}}\right)\frac{1}{C_A} + \frac{1}{k\,C_{E_0}}, \quad \text{M is constant.}$$

If the data is to fit a kinetic equation, then the plot of $1/(-r_A)$ v/s $1/C_A$ should yield a straight line with intercept equal to $1/kC_{E_0}$ on y-axis.

Plot a graph of C_A v/s t from the data given. By drawing tangents to the curve drawn at various values of C_A, find the values of $-dC_A/dt = -r_A$. The slope of the tangent at C_A is equal to $-dC_A/dt = -r_A$. Finally plot a graph of $1/(-r_A)$ v/s $1/C_A$.

C_A	0.38	0.225	0.10	0.078
$-dC_A/dt = -r_A$	0.139	0.097	0.052	0.042
$1/C_A$	2.63	4.44	10	12.82
$1/(-r_A)$	7.2	10.3	19.23	23.80

As the plot of $1/(-r_A)$ v/s $1/C_A$ yields a straight line, the kinetic data fit a given kinetic equation.

For graph :

$$\text{Slope} = \frac{(20-8)}{(10.5-3.1)} = 1.62$$

$$\text{Intercept} = \frac{4}{20} \times 15 = 3$$

$$\text{Intercept} = \frac{1}{kC_{E_0}} = 3, \quad C_{E_0} = 0.01 \text{ mmol}/l$$

$$k = 1/3\ C_{E_0} = 1/(3 \times 0.01)$$

$$k = 33.33$$

$$\text{Slope} = 1.62 = M/k\,C_{E_0}$$

$$\therefore \quad M = 1.62 \times 33.33 \times 0.01$$

$$M = 0.54$$

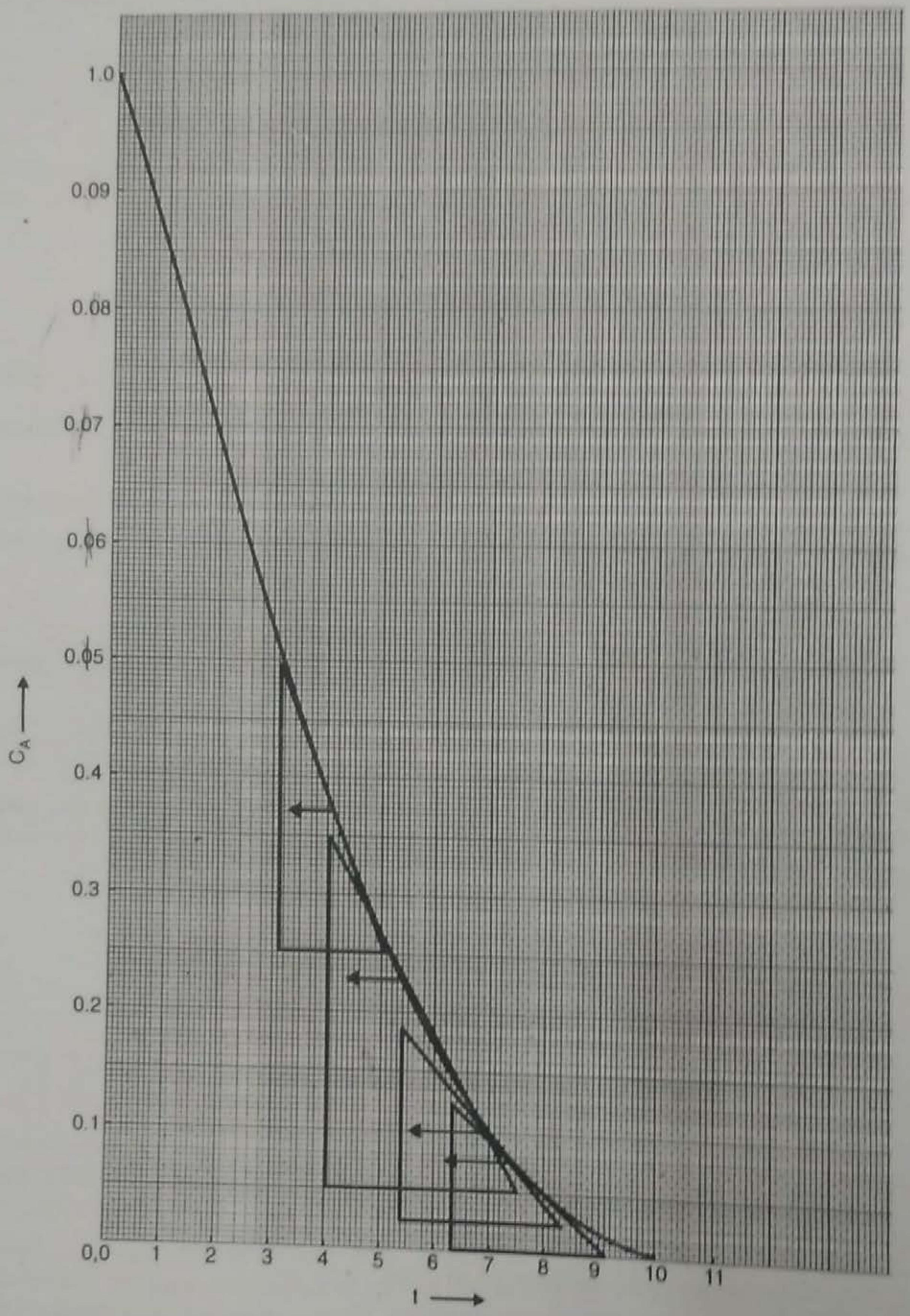


Fig. E 2.52 (1)

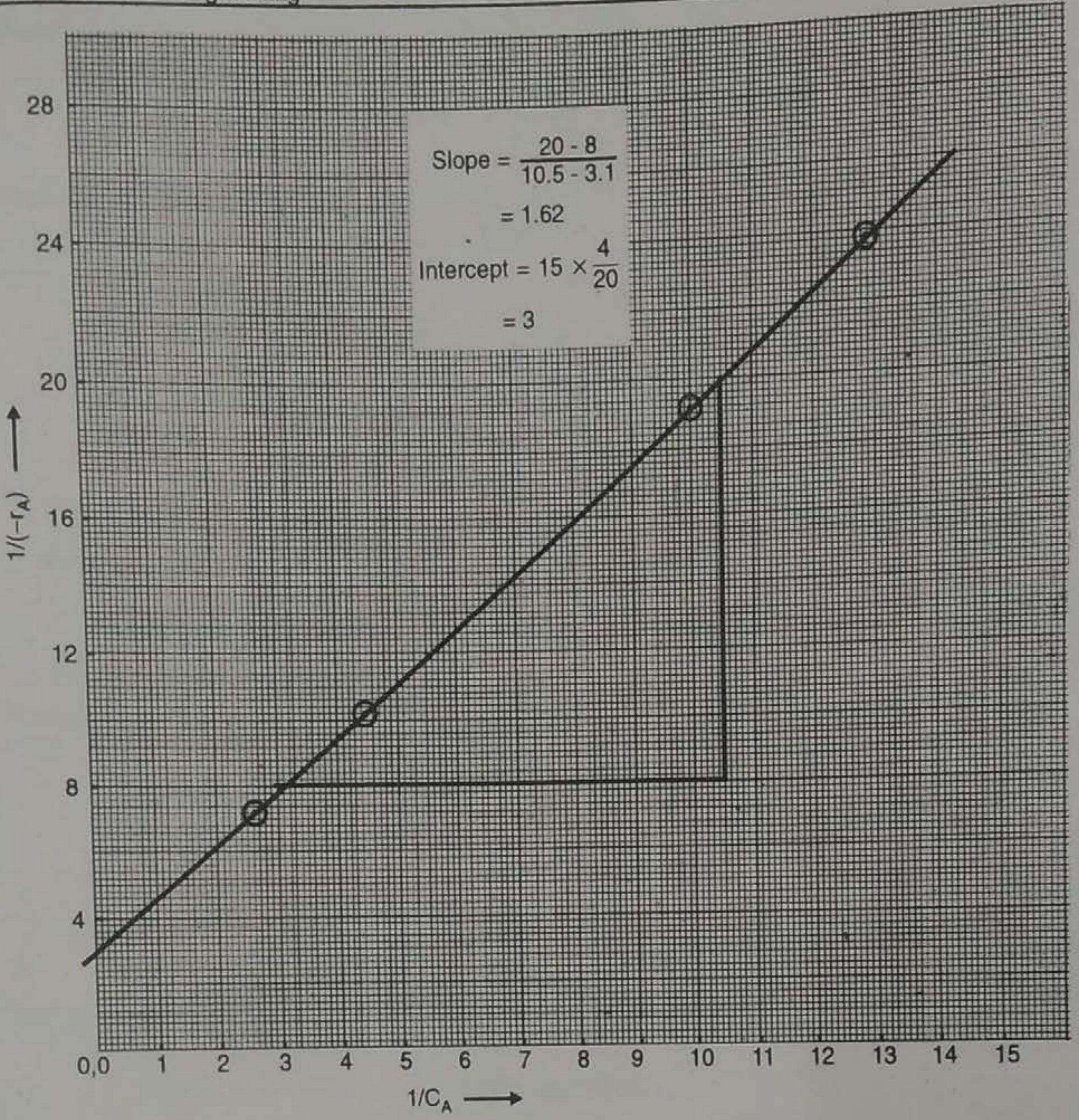


Fig. E 2.52 (2)

Ex. 2.53 : For the series reaction of the type

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S, \quad k_1 = k_2$$

Find the maximum concentration of R and the time at which it is reached.

Solution : $A \xrightarrow{k_1} R \xrightarrow{k_2} S, \quad k_1 = k_2$

The rate equations for components A and R are

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

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R \qquad \text{... (2)}$$

Integration of equation (1) yields

$$-\ln(C_A/C_{Ao}) = k_1 t$$

$$C_A = C_{Ao} \cdot e^{-k_1 t}$$

From equation (2),

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_A$$

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{Ao} \cdot e^{-k_1 t} \qquad \text{... (3)}$$

This is a first order linear differential equation of the form

$$\frac{dy}{dx} + Py = Q \qquad \text{... (4)}$$

Comparing equations (3) and (4), we have

$y = C_R$, $x = t$, $P = k_2$, and $Q = k_1 C_{Ao} \cdot e^{-k_1 t}$.

By multiplying through with the integrating factor $e^{\int P\,dx}$, the solution of equation (4) is

$$y \cdot e^{\int P\,dx} = \int Q\, e^{\int P\,dx} \cdot dx + c$$

$$C_R e^{\int k_2 dt} = \int (k_1 C_{Ao} \cdot e^{-k_1 t} \cdot e^{\int k_2\, dt})\, dt + c \qquad \text{... (5)}$$

We have : $e^{\int k_2 dt} = e^{k_2 t}$

and $k_2 = k_1$

Equation (5) becomes

$$C_R e^{k_1 t} = \int (k_1 C_{Ao} \cdot e^{-k_1 t} \cdot e^{k_1 t})\, dt + c$$

$$C_R e^{k_1 t} = \int (k_1 C_{Ao})\, dt + c$$

$$C_R \cdot e^{k_1 t} = k_1 C_{Ao} t + c \qquad \text{... (6)}$$

Evaluate c with the help of the condition :

At $t = 0$, $C_R = 0$

$$\therefore \quad c = 0$$

Equation (6) becomes

$$C_R e^{k_1 t} = k_1 C_{Ao} t \qquad \text{... (7)}$$

For C_R to be maximum, $dC_R/dt = 0$

Rearranging equation (7), we get,

$$C_R = k_1 C_{Ao} t \cdot e^{-k_1 t} \qquad \text{... (8)}$$

differentiate C_R w.r.t. t and set $dC_R/dt = 0$

$$\frac{dC_R}{dt} = k_1 C_{Ao} [t \cdot e^{-k_1 t} (-k_1) + e^{-k_1 t} \times 1] = 0$$

$$k_1 C_{Ao} \neq 0$$

$$\therefore \quad t\, e^{-k_1 t} \cdot (-k_1) + e^{-k_1 t} = 0$$

$$e^{-k_1 t} [-k_1 t + 1] = 0$$

$$k_1 t = 1$$

$$t = 1/k_1 \quad \therefore \boxed{t_{max} = 1/k_1} \qquad \text{... Ans.}$$

Put the value of t in equation (8).

$$\therefore \quad C_{R_{max}} = k_1 C_{Ao} (1/k_1) \cdot e^{-k_1 (1/k_1)}$$

$$\boxed{C_{R_{max}} = C_{Ao}/e} \qquad \text{... Ans.}$$

1 M3

Ex. 2.54 : A small reaction bomb equipped with a sensitive pressure measuring device is flushed out and charged with a mixture containing 76.94 mole % reactant A and 23.06 mole % inerts at one atm pressure and 287 K (14 °C), a temperature low enough that the reaction does not proceed to any appreciable extent. The temperature is rapidly increased to 383 K (100 °C) and the data of total pressure v/s time is collected. The stoichiometry of the reaction is A → 2 R and the reaction proceeds to completion after sufficient time. Find the rate expression which will fit the data reasonably in units of moles, litres, and minutes. Data :

t, min	P, atm	t, min	P, atm
0.5	1.5	3.5	1.99
1	1.65	4	2.025
1.5	1.76	5	2.08
2	1.84	6	2.12
2.5	1.90	7	2.15
3	1.95	8	2.175

Solution : $A \rightarrow 2R$

Charge – 76.94 mole % A and 23.06 mole % inerts.

$$P = 1 \text{ atm} \quad \text{at} \quad T = 287 \text{ K} (14 ^{\circ}\text{C})$$

$$P = ? \quad \text{at} \quad T = 373 \text{ K} (100 ^{\circ}\text{C})$$

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$$

But $V_1 = V_2$ (as volume is constant i.e. it is a constant volume variable pressure system).

$$\frac{P_1}{T_1} = \frac{P_2}{T_2}$$

$$\frac{1}{287} = \frac{P_2}{373}$$

$$\therefore \quad P_2 = 1.3 \text{ atm}$$

initial total pressure (i.e. pressure at the start of reaction) = total pressure at 100 °C

$$P_o = 1.3 \text{ atm}$$

At $t = 0$, $P_o = 1.3$ atm and there are two components – 76.94 mole % A and 23.06 mole % inerts.

$$p_{Ao} = \text{initial partial pressure of A i.e. partial pressure of A at } t = 0$$

$$p_{Ao} = \text{molefraction of A} \times \text{total pressure}$$

$$= \left(\frac{76.94}{100}\right) \times 1.3$$

$$= 0.7694 \times 1.3 = 1 \text{ atm}$$

Partial pressure of A at any time t is related to the total pressure P at any time t by the relation

$$p_A = p_{Ao} - \frac{a}{\Delta n}(P - P_o)$$

$$p_A = 1.0 - \left(\frac{1}{2-1}\right)(P - 1.3)$$

$$p_A = 2.3 - P$$

$$C_A = p_A/RT$$

$$C_A = \left(\frac{2.3 - P}{RT}\right)$$

At $t = 0.5$ min, $P = 1.5$ atm, $R = 0.08206$ (l.atm)/(mol.K), $T = 373$ K.

$$C_A = \frac{(2.3 - 1.5)}{0.08206 \times 373} = 0.026 \text{ mol}/l$$

t, min	P, atm	C_A, mol/l
0.5	1.5	0.026
1	1.65	0.021
1.5	1.76	0.018
2	1.84	0.015
2.5	1.90	0.0131
3	1.95	0.0114
3.5	1.99	0.01
4	2.025	0.009
5	2.08	0.0072
6	2.12	0.0059
7	2.15	0.005
8	2.175	0.0041

$$C_{Ao} = \frac{2.33 - P_o}{RT}$$

$$C_{Ao} = \frac{(2.3 - 1.3)}{0.08206 \times 373} = 0.0327 \text{ mol}/l \quad \text{at } t = 0$$

Plot a graph of C_A v/s t. Obtain $-dC_A/dt = -r_A$ at various values of C_A by drawing tangents to C_A v/s t curve at various values of C_A.

$$-r_A = k\,C_A^n$$

$$\ln(-r_A) = \ln k + n \ln C_A$$

Plot graph of $\ln(-r_A)$ v/s $\ln C_A$ and obtain values of k and n.

C_A	Slope = $-r_A$	$\ln C_A$	$\ln(-r_A)$
0.016	5.5×10^{-3}	− 4.13	− 5.20
0.0114	3×10^{-3}	− 4.47	− 5.81
0.008	1.765×10^{-3}	− 4.83	− 6.34
0.0058	1.16×10^{-3}	− 5.15	− 6.76

From graph of $\ln(-r_A)$ v/s $\ln C_A$,

$$\text{slope} = 1.5$$

$$n = \text{slope} = 1.5$$

$$\text{Intercept} = \ln k = 0.975$$

$$k = 2.65$$

Rate expression is

$$-r_A = k\,C_A^n$$

$$-r_A = 2.65\ (\text{mol}/l)^{-0.5}\ (\text{min})^{-1}\ C_A^{1.50}$$

... **Ans.**

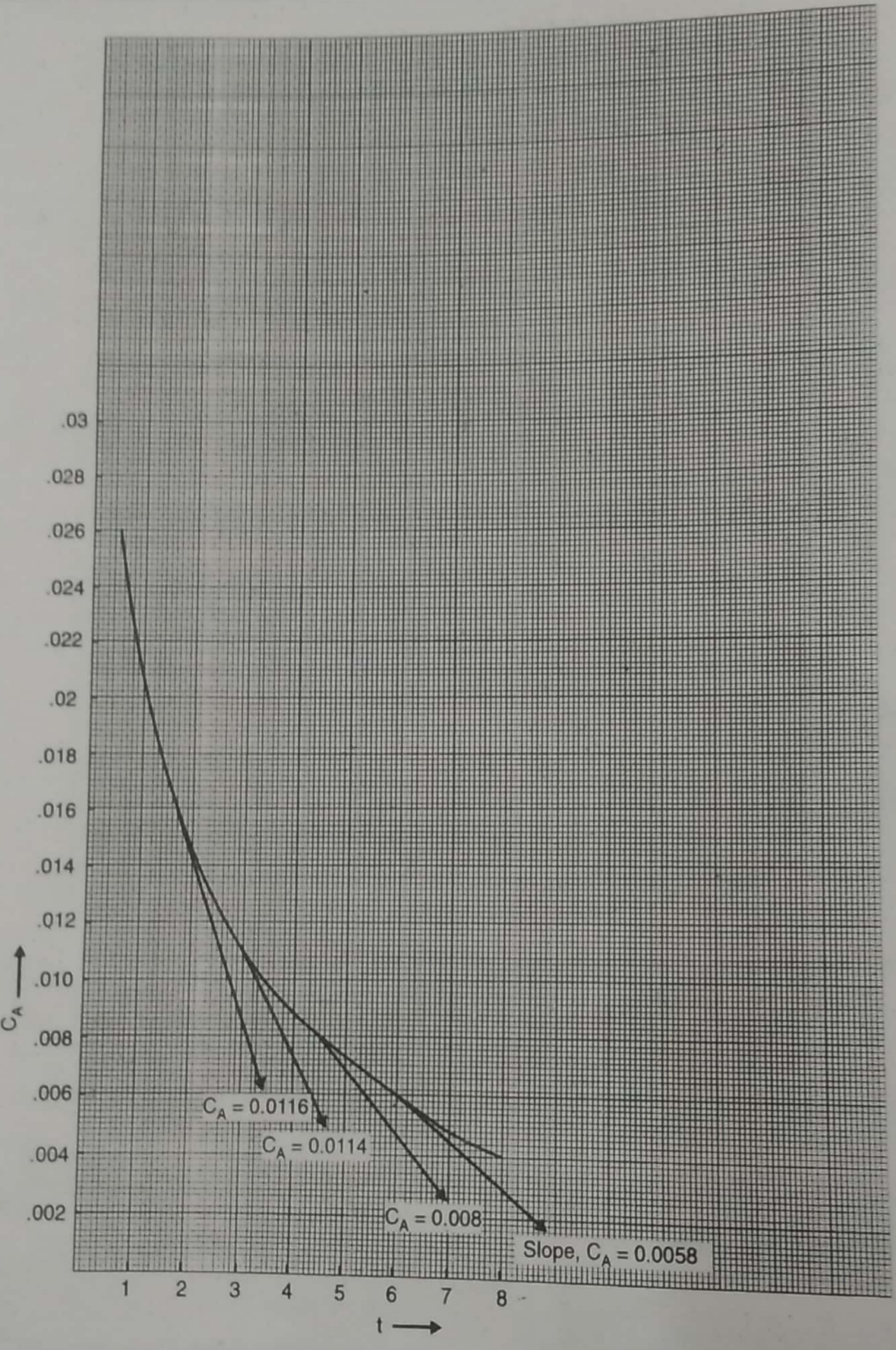
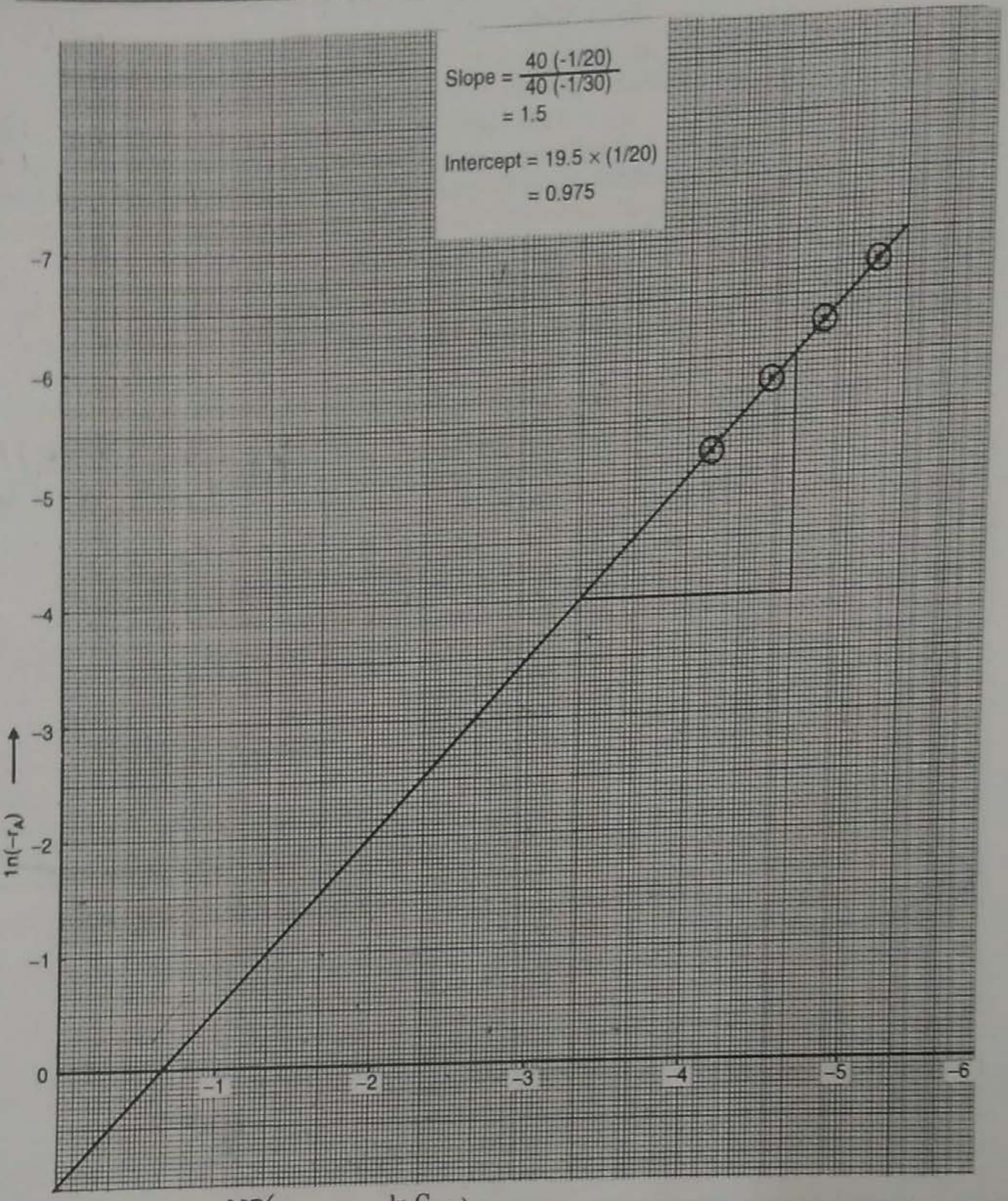

.03
.028
.026
.024
.022
.02
.018
.016
.014
.012
.010
.008
.006
.004
.002
C_A
1
2
3
4
5
6
7
8
t
$C_A = 0.0116$
$C_A = 0.0114$
$C_A = 0.008$
Slope, $C_A = 0.0058$

Fig. E 2.54 (1)



$$\text{Slope} = \frac{40\,(-1/20)}{40\,(-1/30)} = 1.5$$

$$\text{Intercept} = 19.5 \times (1/20) = 0.975$$

Fig. E 2.54 (2)

Ex. 2.55 : The following kinetic data are obtained in a constant volume batch reactor at 273 K (0 °C) using pure gaseous A.

Time, min	0	2	4	6	8	10	12	14	∞
Partial pressure of A (in mmHg)	760	600	475	390	320	275	240	215	150

The stoichiometry of decomposition is A → 2.5 R. Find a rate equation which will satisfactorily fit the data.

$kt = \ln\left(\frac{P_{A0}}{P_A}\right)$

Solution : $A \rightarrow 2.5\,R$

We have, $C_A = p_A/RT$

where
$R = 0.08206\ l\cdot\text{atm}/(\text{mol}\cdot\text{K})$
$T = 273\ \text{K}$
C_A = concentration of A in mol/l
p_A = the partial pressure of A in atm

At $t = 2$ min, $p_A = 600$ mmHg

$$\therefore \quad C_A = p_A/RT = \frac{(600/760)}{0.08206 \times 273} = 0.035\ \text{mol}/l$$

time, min	C_A, mol/l
0	0.045
2	0.035
4	0.028
6	0.023
8	0.019
10	0.016
12	0.014
14	0.0126
∞	0.0088

Assume decomposition to be first order then

$$\ln(C_{A_0}/C_A) = k_1 t$$

$$k_1 = \frac{\ln(C_{A_0}/C_A)}{t}$$

(i) $C_{A_0} = 0.045$ mol/l, $C_A = 0.035$ mol/l, $t = 2$ min

$$k_1 = \frac{\ln(0.045/0.035)}{2} = 0.1256\ \text{min}^{-1}$$

(ii) $C_{A_0} = 0.045$ mol/l, $C_A = 0.028$ mol/l, $t = 4$ min

$$k_1 = \frac{\ln(0.045/0.028)}{4} = 0.119\ \text{min}^{-1}$$

(iii) $C_{A_0} = 0.045$ mol/l, $C_A = 0.023$ mol/l, $t = 6$ min

$$k_1 = \frac{\ln(0.045/0.023)}{6} = 0.112\ \text{min}^{-1}$$

(iv) $C_{A_0} = 0.045$ mol/l, $C_A = 0.019$ mol/l, $t = 8$ min

$$k_1 = \frac{\ln(0.045/0.019)}{8} = 0.11\ \text{min}^{-1}$$

(v) $C_{A_0} = 0.045$ mol/l, $C_A = 0.016$ mol/l, $t = 10$ min

$$k_1 = \frac{\ln(0.045/0.016)}{10} = 0.103\ \text{min}^{-1}$$

(vi) $C_{A_0} = 0.045$ mol/l, $C_A = 0.014$ mol/l, $t = 12$ min

$$k_1 = \frac{\ln(0.045/0.014)}{12} = 0.097\ \text{min}^{-1}$$

(vii) $C_{A_0} = 0.045$ mol/l, $C_A = 0.0126$ mol/l, $t = 14$ min

$$k_1 = \frac{\ln(0.045/0.0126)}{14} = 0.091\ \text{min}^{-1}$$

As there is no large variation in values of k from the data, the reaction follows first order kinetics.

Average value of k = 0.1082 min^{-1}

The rate equation is :

$$-r_A = k\,C_A^n$$

$$k = 0.1082\ (min)^{-1},\quad n = 1$$

$$-r_A = 0.1082\ (min)^{-1}\,C_A \qquad \text{... Ans.}$$

OR

Plot graph of C_A v/s t. Obtain the values of $(-r_A)$, the rates equal to slope of tangents to the curve at various values of C_A. Plot a graph of ln $(-r_A)$ v/s ln C_A and get the values of k and n from graph.

$$(-r_A) = k\,C_A^n$$

$$\ln(-r_A) = \ln k + n \ln C_A$$

slope = n, intercept = ln k from the plot of ln $(-r_A)$ v/s ln C_A.

2014

Ex. 2.56 : Determine the value of first order reaction rate constant (k) for the disappearance of A in the gas reaction 2A → P if, on holding the pressure constant, the volume of the reaction mixture, starting with 80 mole % A and 20 mole % inerts, decreases by 20% in 3 minutes.

Solution : $2A \rightarrow P$

$$\varepsilon_A = \frac{(1/2 \times 0.8 + 0.2) - 1.0}{1.0} = -0.40$$

For no conversion	For complete conversion
A = 80 mol I = 20 mol	P = 40 mol I = 20 mol
Total = 100 mol	Total = 60 mol

V_0^2

$$\varepsilon_A = \frac{60 - 100}{100} = -0.40$$

2 mol A → 1 mol P

80 mol A → ?

$\frac{80}{20} \times 1$

40 mol

For first order reaction,

$$-\ln(1 - X_A) = kt$$

$$-\ln\left[1 - \left(\frac{V - V_o}{V_o}\right)\frac{1}{\varepsilon_A}\right] = kt$$

$V = 0.8\,V_o$, $\varepsilon_A = -0.40$, $t = 3$ min

$$-\ln\left[1 - (-0.2) \times \frac{1}{(-0.40)}\right] = k \times 3$$

$$k = 0.231\ (min)^{-1}$$

OR

$$V = V_o(1 + \varepsilon_A X_A)$$

$$\frac{V}{V_o} = 1 + \varepsilon_A X_A$$

V is the final volume, V_o is the initial volume.

In 3 min, volume decreases by 20 %.

$$\therefore \quad V = (1 - 0.20)\,V_o = 0.8\,V_o$$

$$\frac{0.8\,V_o}{V_o} = 1 + (-0.40)\,X_A$$

$$\therefore \quad X_A = 0.50$$

$$-\ln(1-X_A) = kt$$

$$-\ln(1-0.50) = k \times 3$$

$$k = 0.231\ (\text{min})^{-1} \qquad \textbf{... Ans.}$$

Ex. 2.57 : Calculate the first order rate constant for the disappearance of A as per the gas phase reaction A → 1.6 R if the volume of the reaction mixture, starting with pure A increases by 50 % in 4 minutes. The total pressure of the system remains constant at 1.2 atm and the temperature is 25 °C.

Solution :

$$A \rightarrow 1.6\,R$$

$$\varepsilon_A = \frac{1.6-1}{1} = 0.60$$

For first order reaction,

$$-\ln(1-X_A) = kt$$

$$V = V_o(1+\varepsilon_A X_A)$$

$$X_A = \left(\frac{V-V_o}{V_o}\right)\frac{1}{\varepsilon_A}$$

$kt = \left[1 - \left(\frac{V-V_0}{V_0}\right)\frac{1}{\varepsilon_A}\right]$

V is the final volume and volume increases by 50 % therefore,

$$V = 1.5\,V_o$$

$$X_A = \left(\frac{1.5\,V_o - V_o}{V_o}\right)\left(\frac{1}{0.60}\right)$$

$$X_A = 0.833$$

$$-\ln(1-0.833) = k \times 4$$

$$\therefore \quad k = 0.4474$$

$$= 0.45\ (\text{min})^{-1} \qquad \textbf{... Ans.}$$

Ex. 2.58 : A zero order homogeneous gas phase reaction with stoichiometry A → rR proceeds in a constant volume bomb, with 20 mole % inerts pressure rises from 1 to 1.3 atm in 2 min. If the same reaction is carried in a constant pressure batch reaction, what is the fractional volume change in 4 minutes if the feed is at 3 atm and contains 40 mole % inerts ?

Solution : A → rR

For constant volume reactor, pressure rises from 1 atm to 1.3 atm in 2 min.

P_o = 1 atm, P = 1.3 atm

A – 80 mole %, Inerts – 20 mole %.

For 1 mol A, Moles of feed = $\frac{1}{0.8}$ = 1.25 mol

Moles of R = r mol, moles of inerts = 0.25 mol.

$$\Delta n = (r + 0.25) - 1.25 = (r-1)$$

$$a = 1$$

Partial pressure of A at any time t is related to total pressure by

$$p_A = p_{Ao} - \frac{a}{\Delta n}(P - P_o)$$

$$p_A = p_{Ao} - \frac{1}{(r-1)}(1.3-1)$$

$$p_A = p_{Ao} - \frac{0.3}{(r-1)}$$

$$p_A - p_{Ao} = -0.3/(r-1)$$

$$p_{Ao} - p_A = 0.3/(r-1)$$

For zero order reaction :

$$C_{Ao} - C_A = kt$$

We have : $C_{Ao} = p_{Ao}/RT$ and $C_A = p_A/RT$

$$\therefore \quad p_{Ao} - p_A = kt\,(RT)$$

$$\therefore \quad k = \frac{p_{Ao} - p_A}{t \cdot RT} = \frac{0.3}{2\,(r-1)\,RT}$$

For variable volume reactor :

$$A \to rR$$

Feed : 60 mole % A, 40 mole % inerts.

For no conversion	For complete conversion
A = 60 I = 40	R = 60 r I = 40
Total = 100	Total = 60 r + 40

$$\varepsilon_A = \frac{(60\,r + 40) - 100}{100}$$

$$\varepsilon_A = \frac{60\,r - 60}{100} = 0.6\,(r-1)$$

For zero order reaction for variable volume :

$$\frac{C_{Ao}}{\varepsilon_A} \ln (V/V_o) = kt$$

$$C_{Ao} = p_{Ao}/RT, \quad t = 4 \text{ min}, \quad \varepsilon_A = 0.6\,(r-1)$$

$$k = 0.3/2\,(r-1)\,RT$$

$$\frac{p_{Ao}}{RT \times 0.6\,(r-1)} \ln (V/V_o) = \frac{0.3}{2\,(r-1)\,RT} \times 4$$

$$\frac{p_{Ao}}{0.60} \ln (V/V_o) = 0.60$$

Feed is at 3 atm and contains 60 mole % A.

$$\therefore \quad p_{Ao} = 0.60 \times 3 = 1.8 \text{ atm}$$

(as $p_{Ao} = y_A \cdot P$)

$$\frac{1.8}{0.60} \ln (V/V_o) = 0.6$$

$$\ln (V/V_o) = 0.20$$

$$\therefore \quad \frac{V}{V_o} = 1.221$$

$$V = 1.221\,V_o$$

$$\text{Fractional volume change} = \frac{1.221\,V_o - V_o}{V_o} = 0.221$$

$$\% \text{ volume change} = 0.221 \times 100$$

$$\% \text{ change in volume} = 22.1$$

... **Ans.**

Ex. 2.59 : A zero order homogeneous gaseous reaction A → rR takes place in a constant volume bomb, P = 1 atm when t = 0 and P = 1.5 atm when t = 1 min. If the same reaction, same feed composition, and initial pressure proceeds in a constant pressure apparatus, find V at t = 1 min if V = 1 l at t = 0.

yes

Solution : $A \to rR$

Constant volume reactor :

At t = 0 min, P_o = 1 atm; At t = 1 min, P = 1.5 atm

Partial pressure of A at any time t is given by

$$p_A = p_{A0} - \frac{a}{\Delta n}(P - P_o), \qquad a = 1, \quad \Delta n = r - 1$$

$$p_A = p_{A0} - \frac{1}{(r-1)}(1.5 - 1)$$

$$p_A = p_{A0} - 0.5/(r-1)$$

$$\therefore \quad p_{A0} - p_A = 0.5/(r-1)$$

For zero order reaction :

$$C_{A0} - C_A = kt$$

$$\therefore \quad p_{A0} - p_A = k\,(RT)\,t$$

$$\therefore \quad k = \frac{p_{A0} - p_A}{RT\,t}$$

$$= \frac{0.5}{(r-1)\,RT \times 1} = \frac{0.5}{(r-1)\,RT}$$

For variable volume reactor :

$$\varepsilon_A = \frac{r-1}{1} = (r-1)$$

Integrated rate expression for zero order reaction for variable volume reactor :

$$\frac{C_{A0}}{\varepsilon_A}\ln(V/V_o) = kt$$

$$C_{A0} = \frac{p_{A0}}{RT} = \frac{1}{RT} \quad (\text{as } p_{A0} = P_o = 1 \text{ atm, given})$$

$t = 1$ min, $\varepsilon_A = (r-1)$, $k = 0.5/(r-1)\,RT$

$$\therefore \quad \left(\frac{1}{RT}\right) \times \frac{1}{(r-1)}\ln(V/V_o) = \frac{0.5}{(r-1)\,RT} \times 1$$

$$\ln(V/V_o) = 0.5$$

$$\frac{V}{V_o} = e^{0.5}$$

$$V = 1.648\,V_o$$

but $V_o = 1\,l$

$V = 1.648 \times l = 1.648\,l$ ... **Ans.**

v. mgmr

Ex. 2.60: The first order homogeneous gaseous reaction $A \rightarrow 2.5\,R$ is carried out in an isothermal batch reactor at 2 atm pressure with 20 mole % inerts present, and the volume increases by 60% in 20 minutes. In case of constant volume reactor, determine the time required for the pressure to reach 8 atm if the initial pressure is 5 atm, 2 atm of which consists of inerts.

Solution : $A \rightarrow 2.5\,R$

Variable volume reactor :

For first order reaction in variable volume reactor, we have

$$-\ln(1 - X_A) = kt$$

$$-\ln\left[1 - \frac{\Delta V}{V_o \cdot \varepsilon_A}\right] = kt$$

For no conversion	For complete conversion
A = 80 mol I = 20 mol	R = 200 mol I = 20 mol
Total = 100 mol	Total = 220 mol

$$\varepsilon_A = \frac{220 - 100}{100} = 1.20$$

In 20 minutes, volume increases by 60 %

$$
\begin{aligned}
\therefore \quad V &= 1.6\ V_o \\
\Delta V &= V - V_o = 1.6\ V_o - V_o = 0.6\ V_o \\
t &= 20 \text{ min} \\
-\ln\left[1 - \frac{0.6\ V_o}{1.2\ V_o}\right] &= k \times 20 \\
\therefore \quad k &= 0.0346\ (\text{min})^{-1}
\end{aligned}
$$

OR

$$
\begin{aligned}
V &= V_o(1 + \varepsilon_A X_A) \\
\frac{V}{V_o} &= 1 + \varepsilon_A X_A \\
\frac{1.6\ V_o}{V_o} &= 1 + 1.2\ X_A \\
X_A &= 0.50 \quad \text{Conversion is 50 \%} \\
-\ln(1 - X_A) &= kt \\
-\ln(1 - 0.5) &= k \times 20 \\
k &= 0.0346\ (\text{min})^{-1}
\end{aligned}
$$

For constant volume reactor :

$$
\begin{aligned}
P &= 8 \text{ atm at } t = ? \quad A \\
P_o &= 5 \text{ atm} \quad \text{at } t = 0 \quad A + \text{inc,} \\
p_{io} &= 2 \text{ atm} \\
p_{Ao} + p_{io} &= P_o \\
p_{Ao} &= 5 - 2 = 3 \text{ atm}
\end{aligned}
$$

a A → 2.5 V

Partial pressure is related to total pressure by

$$
\begin{aligned}
p_A &= p_{Ao} - \frac{a}{\Delta n}(P - P_o), \quad a = 1, \quad \Delta n = 2.5 - 1 = 1.5 \\
p_A &= 3 - \frac{1}{1.5}(8 - 5) = 1 \text{ atm}
\end{aligned}
$$

For first order reactor, we have

$$
\begin{aligned}
\ln(C_{Ao}/C_A) &= kt \\
\therefore \quad \ln(p_{Ao}/p_A) &= kt \quad (\text{as } C \propto p) \\
\ln(3/1) &= 0.0346 \times t \\
t &= 31.75 \text{ min}
\end{aligned}
$$

... **Ans.**

OR

For constant volume reactor :

Initial pressure = 5 atm

Final pressure = 8 atm

$A \rightarrow 2.5\ R$

Pressure exerted by inerts = 2 atm (at t = 0)

p_{Ao} = partial pressure of A at t = 0 is 5 − 2 = 3 atm

mole % A at t = 0 = 3/5 × 100 = 60

Inerts = 40 mole %

Initial feed : A = 60 mole %

I = 40 mole %

For 1 mol feed : A = 0.6 mol, I = 0.4 mol

Let x be the A reacted in time t.

$$\text{Final moles} = 2.5\,x + (0.6 - x) + 0.4$$

$$= 1 + 1.5\,x$$

$$P = \text{Final pressure} = 8 \text{ atm}$$

$$P_o = \text{Initial pressure} = 5 \text{ atm}$$

For constant V and T, we have

$$\frac{P}{P_o} = \frac{n}{n_o}$$

$$\frac{8}{5} = \frac{1 + 1.5\,x}{1}$$

$$\therefore \quad x = 0.4 \text{ mol} \quad \text{(A reacted)}$$

$$\therefore \quad X_A = \text{fractional conversion of A} = 0.4/0.6 = 0.667$$

For constant volume first order kinetics, we have :

$$-\ln(1 - X_A) = kt$$

$$-\ln(1 - 0.667) = 0.0346 \times t$$

$$t = 31.78 \text{ min} \qquad \textbf{... Ans.}$$

Ex. 2.61 : The gaseous reaction 2A → R + 2S is second order with respect to A. If pure A is introduced at 1 atm into a constant volume batch reactor, the pressure rises by 40% in 3 minutes. In case of a constant pressure batch reactor, find (i) the time required for the same conversion, and (ii) the fractional increase in volume at that time.

Solution : $2A \rightarrow R + 2S$

For constant volume-variable pressure reactor :

$$p_{Ao} = 1 \text{ atm (as pure A)}$$

$$P_o = \text{Initial pressure} = 1 \text{ atm (given)}$$

Pressure rises by 40% in 3 min.

$$\therefore \quad \text{At } t = 3 \text{ min}$$

$$P = 1.40\,P_o = 1.4 \times 1 = 1.4 \text{ atm}$$

p_A is the partial pressure of A at t = 3 min

$$p_A = p_{Ao} - \frac{a}{\Delta n}(P - P_o)$$

$a = 2, \quad \Delta n = 3 - 2 = 1$

$$p_A = 1 - \frac{2}{1}(1.40 - 1) = 0.2 \text{ atm}$$

For second order kinetics :

$$\left[\frac{1}{C_A} - \frac{1}{C_{Ao}}\right] = kt$$

$$[1/(p_A/RT) - 1/(p_{Ao}/RT)] = kt$$

$$RT\,[1/p_A - 1/p_{Ao}] = kt$$

$$\therefore \quad k = \frac{RT\,[(1/0.2) - (1/1)]}{3}$$

$$k = 1.333\,RT$$

$$C_A = C_{Ao}(1 - X_A)$$

$$\frac{p_A}{RT} = \frac{p_{Ao}}{RT}(1 - X_A)$$

$$p_A = p_{A_o}(1 - X_A)$$

$$0.2 = 1 \times (1 - X_A)$$

$$\therefore \quad X_A = 0.8$$

$$\%\ \text{conversion of A} = 80$$

For variable volume-constant pressure batch reactor :

For second order kinetics, we have

$$\boxed{\frac{(1+\varepsilon_A)\,X_A}{1-X_A} + \varepsilon_A \ln(1-X_A) = k\,C_{A_o}\,t}$$

$$2A \rightarrow R + 2S$$

$$\therefore \quad \varepsilon_A = \frac{3-2}{2} = 0.5$$

Conversion is same $\therefore$ $X_A = 0.8$

$$C_{A_o} = p_{A_o}/RT = 1/RT$$ (same initial pressure and pure A)

$$\therefore \quad \frac{(1+0.5)}{(1-0.8)} \times 0.8 + 0.5 \ln(1-0.80) = 1.333\ RT \times \frac{1}{RT} \times t$$

... **Ans. (i)**

$$t = 3.906 \text{ min}$$

$$V = V_o(1 + \varepsilon_A X_A)$$

$$V = V_o[1 + (0.5) \times 0.8]$$

$$V = 1.4\ V_o$$

$$\text{Final volume, } V = 1.40\ V_o$$

$$\text{Fractional increase in volume} = \frac{V - V_o}{V_o}$$

$$= \frac{1.4\ V_o - V_o}{V_o}$$

$$= 0.40$$

... **Ans. (ii)**

% increase in volume at 3.906 min = 40

i.e. volume increases by 40 %.

Ex. 2.62 : Gaseous A in pure form is prepared under refrigeration and is introduced into a thin-walled capillary acting as a reaction vessel as shown in Fig. E 2.62. No reaction takes place during handling.

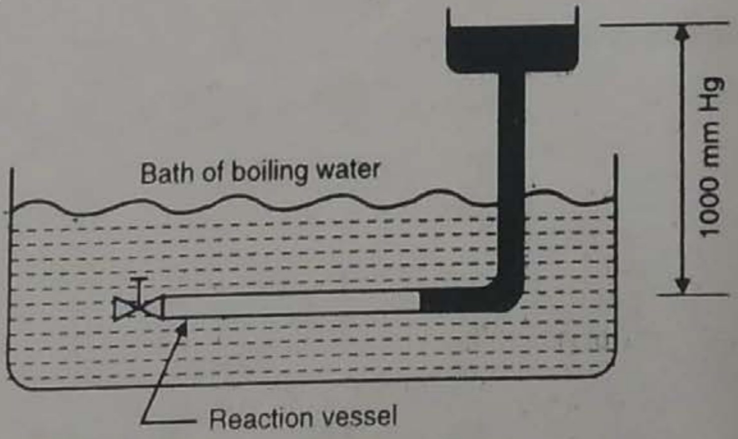


Fig. E 2.62

The reaction vessel is rapidly plunged into a bath of boiling water, reactant A decomposes to completion, and the following data are obtained.

Time, min	0.5	1	1.5	2	3	4	6	10	∞
Length of capillary occupied by reaction mixture, cm	6.1	6.8	7.2	7.5	7.85	8.1	8.4	8.7	9.4

The stoichiometry of decomposition is $A \rightarrow R + S$. Find the rate equation in units of moles, litres, and minutes which satisfactorily represents this decomposition.

Solution : $A \rightarrow R + S$, gas phase reaction

$$\varepsilon_A = \frac{2-1}{1} = 1$$

It is given that decomposition goes to completion.

Decomposition is complete at $t = \infty$.

Let d be the inside diameter of tube.

Volume of capillary occupied by reaction mixture at any time $t = \pi/4\ d^2 L$, where L is length in cm, d is in cm, the volume will be in cm³.

$$\begin{aligned} V &= \pi/4\ d^2 L \text{ cm}^3 \\ &= \pi/4\ d^2 L \times 10^{-3}\ l \\ &= (\pi/4 \times 10^{-3}\ d^2) \cdot L \\ &= mL\ l,\ \text{where } m = \pi/4 \times 10^{-3}\ d^2 \end{aligned}$$

At $t = \infty$, decomposition is complete, so $X_A = 1.0$

$$\begin{aligned} V_{X_A = 1} = V \text{ at } X_{A=1} &= mL, \quad \text{where } L = 9.4 \\ &= 9.4\ ml \end{aligned}$$

At $t = 0$, i.e. at initial condition, $X_A = 0$.

$V_{X_A = 0} = V$ at $X_{A=0}$ = volume of reaction mixture at $X_{A=0}$ i.e. at no conversion.

$V_{X_A = 1}$ = volume of reaction mixture at $X_{A=1}$ i.e. at complete conversion

We have

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=1}}$$

$$1.0 = \frac{9.4\ m - mL_o}{mL_o}$$

$$1.0 = \frac{9.4 - L_o}{L_o}$$

$$L_o = 4.7 \text{ cm}$$

$\therefore$ V at $X_A = 0$ i.e. initial volume $= V_o = 4.7\ m$

We have

$$V = V_o(1 + \varepsilon_A X_A)$$

$$\varepsilon_A = 1$$

$$V = V_o(1 + X_A)$$

$$\therefore \quad X_A = \frac{V - V_o}{V_o}$$

At $t = 0.5$ min, $L = 6.1$ cm

$$\therefore \quad V = 6.1\ m,\ l$$

$$\therefore \quad X_A = \frac{6.1\ m - 4.7\ m}{4.7\ m} = 0.30$$

At t = 1 min, L = 6.8 cm

$$\therefore \quad V = 6.8 \text{ m}, l$$

$$\therefore \quad X_A = \frac{6.8 \text{ m} - 4.7 \text{ m}}{4.7 \text{ m}} = 0.45$$

t	0.5	1	1.5	2	3	4	6	10	∞
L	6.1	6.8	7.2	7.5	7.85	8.1	8.4	8.7	9.4
X_A	0.30	0.45	0.53	0.60	0.67	0.72	0.79	0.85	1.0

$$P = P_o = 1000 \text{ mmHg} = 1.316 \text{ atm}$$

$$T = 100\ ^{o}\text{C (boiling water and thin-walled capillary)}$$

$$T = 373 \text{ K}$$

$$p_{Ao} = P_o = 1.316 \text{ atm (pure gas A initially)}$$

$$\therefore \quad C_{Ao} = p_{Ao}/RT, \quad R = 0.08206\ l.\text{atm/(mol.K)}$$

$$= \frac{1.316}{0.08206 \times 373}$$

$$= 0.043 \text{ mol}/l$$

Consider the decomposition to be second order.

For second order kinetics :

For variable volume system for second order, we have :

$$\frac{(1+\varepsilon_A)X_A}{(1-X_A)} + \varepsilon_A \ln(1-X_A) = k\, C_{Ao}\, t$$

$$\therefore \quad \frac{(1+1)X_A}{1-X_A} + 1 \times \ln(1-X_A) = k\, C_{Ao}\, t$$

$$k = \frac{2X_A/(1-X_A) + \ln(1-X_A)}{C_{Ao}\, t}$$

At t = 0.5 min, C_{Ao} = 0.043 mol/l, X_A = 0.30

$$k = \frac{2 \times 0.3/(1-0.3) + \ln(1-0.30)}{0.043 \times 0.5}$$

$$= 23.25\ (l/\text{mol})\ (\text{min})^{-1}$$

At t = 1 min, X_A = 0.45

$$k = \frac{2 \times 0.45/(1-0.45) + \ln(1-0.45)}{0.043 \times 1}$$

$$= 24.1\ (l/\text{mol})\ (\text{min})^{-1}$$

At t = 1.5 min, X_A = 0.53

$$k = \frac{2 \times 0.53/(1-0.53) + \ln(1-0.53)}{0.043 \times 1.5}$$

$$= 23.3\ (l/\text{mol})\ (\text{min})^{-1}$$

At t = 2 min, X_A = 0.60

$$k = \frac{2 \times 0.6/(1-0.6) + \ln(1-0.60)}{0.043 \times 2}$$

$$= 24.23\ (l/\text{mol})\ (\text{min})^{-1}$$

At t = 3 min, $X_A = 0.67$ $\therefore$ $k = 22.9\ (l/\text{mol})\ (\text{min})^{-1}$

At t = 4 min, $X_A = 0.72$ $\therefore$ $k = 22.5\ (l/\text{mol})\ (\text{min})^{-1}$

At t = 6 min, $X_A = 0.79$ $\therefore$ $k = 23.11\ (l/\text{mol})\ (\text{min})^{-1}$

At t = 10 min, $X_A = 0.85$ $\therefore$ $k = 21.94\ (l/\text{mol})\ (\text{min})^{-1}$

As there is no large variation in values of k calculated at different times, we say that the decomposition of A is a second order reaction.

Average value of k = 23.17 (l/mol) (min)$^{-1}$

Rate equation is

$$-r_A = 23.17\ (l/\text{mol})\ (\text{min})^{-1}\ C_A^2 \quad \text{... Ans.}$$

Ex. 2.63 : Nitrous oxide N_2O decomposes into nitrogen and oxygen. Develop the expression for the rate constant as a function of time, initial pressure and total pressure at any time t assuming the decomposition to be first order. Decomposition is carried in constant volume reactor.

Solution : $N_2O \rightarrow N_2 + \frac{1}{2} O_2$

$$A \rightarrow R + \frac{1}{2} S$$

$$a = 1, \quad \Delta n = 1.5 - 1 = 0.5$$

It is a total pressure analysis.

$\therefore$ Partial pressure of A at any time t is given by

$$p_A = p_{A_0} - \frac{a}{\Delta n}\ (P - P_o)$$

where P is the total pressure at any time t and P_o is the initial total pressure i.e. total pressure at t = 0.

Initially assume there is pure and only N_2O was present.

$\therefore$

$$p_{A_0} = P_o$$

$$p_A = P_o - \frac{1}{0.5}\ [P - P_o]$$

$$p_A = 3\,P_o - 2\,P$$

Now,

$$C_A = \frac{p_A}{RT}$$

$$C_A = \frac{p_A}{RT} = \frac{3\,P_o - 2P}{RT}$$

$$\frac{dC_A}{dt} = \frac{-2\,dP}{RT\,dt}$$

Decomposition is first order.

$$(-r_A) = \frac{-dC_A}{dt} = k\,C_A$$

$$\frac{2\,dP}{RT\,dt} = \frac{k\,(3\,P_o - 2\,P)}{RT}$$

$$2\int_{P_o}^{P} \frac{dP}{(3\,P_o - 2\,P)} = k\int_0^t dt$$

$$y = 3\,P_o - 2\,P$$

$$dy = -2\,dP \qquad \therefore\ dP = -dy/2$$

Limits :

$$P = P_o \qquad y = P_o$$

$$P = P \qquad y = 3\,P_o - 2\,P$$

$$\therefore \quad 2\int_{P_0}^{3P_0-2P} \frac{-dy}{2\cdot y} = kt$$

$$[-\ln y]_{P_0}^{3P_0-2P} = kt$$

$$\ln\left[\frac{P_0}{3P_0-2P}\right] = kt$$

$$\therefore \quad k = \frac{1}{t}\ln\left[\frac{P_0}{3P_0-2P}\right] \qquad \text{... Ans.}$$

Ex. 2.64 : Find the rate equation that satisfactorily represent decomposition of A with stoichiometry A → R + 2S from following total pressure data. Assume that initially pure A was present in a isothermal constant volume reactor.

Time, min	Total pressure, mmHg
0	7.5
2.5	10.5
5	12.5
10	15.8
15	17.9
20	19.4

$P_0 = P_{A0}$

Solution : $A \rightarrow R + 2S$

$$a = 1, \quad \Delta n = 3 - 1 = 2$$

p_A – partial pressure of A at any time t.

p_A is given by

$$p_A = p_{A0} - \frac{a}{\Delta n}(P - P_0)$$

Initially pure A was present $\therefore p_{A0} = P_0$

P_0 is the initial total pressure (i.e. at t = 0)

$$p_A = P_0 - \frac{1}{2}(P - P_0)$$

$$p_A = \frac{3P_0 - P}{2}$$

$$C_A = \frac{p_A}{RT}$$

$$C_A = \frac{3P_0 - P}{2\,RT}$$

$$\frac{dC_A}{dt} = \frac{-1}{2\,RT}\left(\frac{dP}{dt}\right)$$

$$C_{A0} = p_{A0}/RT$$

$$= P_0/RT$$

Assume decomposition to be first order.

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

$$\frac{1}{2\,RT}\left(\frac{dP}{dt}\right) = \frac{k\,(3\,P_o - P)}{2\,RT}$$

$$\frac{dP}{dt} = k\,(3\,P_o - P)$$

$$\int_{P_o}^{P} \frac{dP}{3\,P_o - P} = k\int_0^t dt$$

$$\ln\,[2\,P_o/(3\,P_o - P)] = kt$$

$$k = \frac{1}{t}\ln\left[\frac{2\,P_o}{3\,P_o - P}\right]$$

At $t = 2.5$ min, $P = 10.5$ mmHg, $P_o = 7.5$ mmHg

$$k = \frac{1}{2.5}\ln\left[\frac{2\times 7.5}{3\times 7.5 - 10.5}\right]$$

$$= 0.089\ (\text{min})^{-1}$$

At $t = 5$ min, $P = 12.5$ mmHg, $P_o = 7.5$ mmHg

$$k = \frac{1}{5}\ln\left[\frac{2\times 7.5}{3\times 7.5 - 12.5}\right]$$

$$= 0.081\ (\text{min})^{-1}$$

At $t = 10$ min, $P = 15.8$ mmHg

$$k = \frac{1}{10}\ln\left[\frac{2\times 7.5}{3\times 7.5 - 15.8}\right]$$

$$= 0.0806\ (\text{min})^{-1}$$

At $t = 15$ min, $P = 17.9$ mmHg

$$k = \frac{1}{15}\ln\left[\frac{2\times 7.5}{3\times 7.5 - 17.9}\right]$$

$$= 0.0788\ (\text{min})^{-1}$$

At $t = 20$ min, $P = 19.4$ mmHg

$$k = \frac{1}{20}\ln\left[\frac{2\times 7.5}{3\times 7.5 - 19.4}\right]$$

$$= 0.0788\ (\text{min})^{-1}$$

As there is no large variation in values of k for different data, we can say that the reaction follows first order kinetics.

$$\text{Average value of k} = \frac{0.089 + 0.081 + 0.0806 + 0.0788 + 0.0788}{5}$$

$$= 0.08164\ (\text{min})^{-1}$$

∴ The rate equation is

$$-r_A = 0.08164\ (\text{min})^{-1}\ C_A$$ ... **Ans.**

OR

$$-r_A = \frac{-dC_A}{dt} = k\,C_A^n$$

$$\frac{1}{2\,RT}\,\frac{dP}{dt} = \frac{k\,(3\,P_o - P)^n}{(2\,RT)^n}$$

$$\frac{dP}{dt} = k\,(2\,RT)^{1-n}\,(3\,P_o - P)^n$$

$$\frac{dP}{dt} = k'\,(3\,P_o - P)^n$$

$$\ln\left(\frac{dP}{dt}\right) = \ln k' + n \ln (3\,P_o - P)$$

Plot a graph of P v/s t and obtain dP/dt at various values of P.

P	dP/dt	$(3\,P_o - P)$	ln (dP/dt)	$\ln(3\,P_o - P)$
–	–	–	–	–
–	–	–	–	–

Plot a graph of ln (dP/dt) v/s $\ln (3\,P_o - P)$.

The slope of graph is equal to *n* and intercept equal to ln k', if we get, say, n = 1

$$(-r_A) = k\,C_A$$

$$(-r_A) = \frac{1}{2\,RT}\,\frac{dP}{dt} = \frac{k\,(3\,P_o - P)}{2\,RT}$$

$$\frac{dP}{dt} = k\,(3\,P_o - P)$$

$$k = \frac{dP/dt}{3\,P_o - P}$$

Obtain dP/dt from a graph at any value of $(3\,P_o - P)$ and put in above equation to get k.

Ex. 2.65 : For first order irreversible reaction A → R + S, the pressure variation of the reaction mixture is as follows :

Time, min	0	2	4	8
P, mmHg	200	208	215	226

If the initial reaction mixture contains 40 mole % A and 60 % inerts, find the rate expression for this reaction.

Solution : We are supplied with total pressure data.

$$A \rightarrow R + S$$

Initial reaction mixture contains 40 mole % A and 60 mole % inerts.

$$\text{Initial total pressure} = P_o = 200\ \text{mmHg}$$

$$\therefore \quad p_{Ao} = \left(\frac{\text{mole \% A}}{100}\right) P_o$$

PA0

$$= \frac{40}{100} \times 200$$

$$= 80\ \text{mmHg}$$

p_A is the partial pressure of A at any time t. p_A is related to total pressure at any time t, P by the equation

$$p_A = p_{Ao} - \frac{a}{\Delta n}\,(P - P_o)$$

From reaction, $a = 1, \quad \Delta n = 2 - 1 = 1$

$$p_A = p_{Ao} - \frac{1}{1}\,(P - P_o)$$

$$p_A = p_{Ao} - P + P_o$$

we have $P_o = 200 \text{ mmHg}, \quad p_{A_0} = 80 \text{ mmHg}$

$$\therefore \quad p_A = 200 - P + 80 = 280 - P$$

At $t = 0, \quad P = 200 \text{ mmHg} \; \therefore \; p_A = 80 \text{ mmHg}$

At $t = 2 \text{ min}, \quad P = 208 \text{ mmHg}$

$$\therefore \quad p_A = 280 - 208 = 72 \text{ mmHg}$$

t, min	0	2	4	8
p_A	80	72	65	54

Assume the reaction to be first order.

$$(-r_A) = k\,C_A$$

$$\ln (C_{A_0}/C_A) = kt$$

$$C_A = p_A/RT \quad \text{and} \quad C_{A_0} = p_{A_0}/RT$$

$$\therefore \quad \ln (p_{A_0}/p_A) = kt$$

$$k = \frac{\ln (p_{A_0}/p_A)}{t}$$

(i) At $t = 2 \text{ min}, \quad p_A = 72 \text{ mmHg}, \quad p_{A_0} = 80 \text{ mmHg}$

$$k = \frac{\ln (80/72)}{2}$$

$$= 0.0527 \ (\text{min})^{-1}$$

(ii) At $t = 4 \text{ min}, \quad p_A = 65 \text{ mmHg}$

$$k = \frac{\ln (80/65)}{4}$$

$$= 0.052 \ (\text{min})^{-1}$$

At $t = 8 \text{ min}, \quad p_A = 54 \text{ mmHg}$

$$k = \frac{\ln (80/54)}{8}$$

$$= 0.0491 \ (\text{min})^{-1}$$

As we have obtained approximately constant values of k at different data, the reaction follows first order kinetics.

$$\text{Average value of k} = \frac{0.0527 + 0.052 + 0.0491}{3}$$

$$= 0.05127 \ (\text{min})^{-1}$$

The rate equation is

$$-r_A = k\,C_A^n$$

$$k = 0.05127 \ (\text{min})^{-1}, \quad n = 1$$

$$\therefore \quad -r_A = 0.05127 \ (\text{min})^{-1} \, C_A$$ ... **Ans.**

Ex. 2.66 ✓**:** Thermal decomposition of dimethyl ether is carried out in a constant volume batch reactor. The reactor is initially filled with pure ether and the reactor pressure is 312 mmHg. From the following data find the rate equation that satisfactorily represents this decomposition.

Time, s	390	777	1195	3355
Rise in pressure, mmHg	96	176	250	476

Solution : $CH_3OCH_3 \rightarrow CH_4 + CO + H_2$, gas phase decomposition

$$A \rightarrow R + S + T$$

$$\text{Initial pressure of reactor} = P_o = 312 \text{ mmHg (at } t = 0)$$

For pure A initially i.e. at $t = 0$

$$p_{Ao} = P_o = 312 \text{ mmHg}$$

p_{Ao} is the partial pressure of A at $t = 0$

p_A is the partial pressure of A at any time t.

Let P is the total pressure at any time t. Then

$$P = P_o + \text{rise in pressure}$$

At $t = 390$ s, rise in pressure = 96 mmHg

$$\therefore \quad P = 312 + 96 = 408 \text{ mmHg}$$

t, s	390	777	1195	3355
P, mmHg	408	488	562	788

p_A at any time, in constant volume reactor, is given by equation

$$p_A = p_{Ao} - \frac{a}{\Delta n}(P - P_o)$$

$$a = 1, \quad \Delta n = 3 - 1 = 2$$

$$p_A = p_{Ao} - \frac{1}{2}(P - P_o)$$

but $\quad p_{Ao} = P_o$

$$\therefore \quad p_A = P_o - 0.5(P - P_o)$$

$$p_A = 1.5\,P_o - 0.5\,P$$

At $t = 390$ s, $P = 408$ mmHg and $P_o = 312$ mmHg

$$\therefore \quad p_A = 1.5(312) - 0.5(408)$$

$$= 264 \text{ mmHg}$$

t, s	390	777	1195	3355
p_A, mmHg	264	224	187	74

Assume decomposition to be of first order.

For first order reaction :

$$\ln(C_{Ao}/C_A) = kt$$

$$C_A = p_A/RT \quad \text{and} \quad C_{Ao} = p_{Ao}/RT$$

$$\therefore \quad \ln(p_{Ao}/p_A) = kt$$

$$k = \frac{1}{t}\ln(p_{Ao}/p_A)$$

(i) At $t = 390$ s, $p_A = 264$ mmHg, $p_{Ao} = 312$ mmHg

$$k = \frac{1}{390}\ln(312/264)$$

$$= 4.28 \times 10^{-4}\,(s)^{-1}$$

(ii) At $t = 777$ s, $p_A = 224$ mmHg

$$k = \frac{1}{777}\ln(312/224)$$

$$= 4.26 \times 10^{-4}\,(s)^{-1}$$

(iii) At $t = 1195$ s, $p_A = 187$ mmHg

$$k = \frac{1}{1195}\ln(312/187)$$

$$= 4.28 \times 10^{-4}\,(s)^{-1}$$

(iv) At t = 3355 s, p_A = 74 mmHg

$$\therefore \quad k = \frac{1}{3355} \ln (312/74)$$

$$= 4.29 \times 10^{-4} \text{ (s)}^{-1}$$

As we have obtained almost same values of k at different instants of time, the decomposition reaction is first order in A.

$$\text{Average value of k} = 4.2775 \times 10^{-4} \text{ (s)}^{-1}$$

The rate equation is

$$(-r_A) = k\, C_A^n, \qquad k = 4.2775 \times 10^{-4}, \ n = 1$$

$$(-r_A) = 4.2775 \times 10^{-4} \text{ (s)}^{-1}\, C_A \qquad \text{... Ans.}$$

Ex. 2.67 : A parallel liquid phase reaction

$$A \xrightarrow{k_1} R, \quad A \xrightarrow{k_2} S$$

has the rate constants $k_1 = 5 \text{ (h)}^{-1}$ and $k_2 = 0.8 \text{ (h)}^{-1}$

Find the moles of R produced in 15 min.

Take $C_{Ao} = 8.5$ mol/*l*, $C_{Ro} = C_{So} = 0$

Solution :

$$A \xrightarrow{k_1} R \quad , \quad k_1 = 5 \text{ (h)}^{-1}$$

$$A \xrightarrow{k_2} S \quad , \quad k_2 = 0.8 \text{ (h)}^{-1}$$

$$(-r_A) = k_1 C_A + k_2 C_A$$

$$(-r_A) = -dC_A/dt = (k_1 + k_2)\, C_A$$

$$\ln (C_{Ao}/C_A) = (k_1 + k_2) \times t$$

$$t = 15 \text{ min}$$

$$\ln (C_{Ao}/C_A) = (5 + 0.8) \times \frac{15}{60}$$

$$C_{Ao}/C_A = 4.263$$

$$\therefore \quad C_A = \frac{C_{Ao}}{4.263}$$

$$C_{Ao} = 8.5 \text{ mol}/l$$

$$C_A = \frac{8.5}{4.263} = 1.994 \approx 2 \text{ mol}/l$$

$$\text{Moles of A reacted} = 8.5 - 2 = 6.5 \text{ mol}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A$$

$$\frac{dC_R}{dC_S} = \frac{k_1 C_A}{k_2 C_A} = \frac{k_1}{k_2}$$

$$\therefore \quad \frac{C_R - C_{Ro}}{C_S - C_{So}} = \frac{k_1}{k_2}$$

$$C_{Ro} = C_{So} = 0$$

$$\therefore \quad \frac{C_R}{C_S} = \frac{k_1}{k_2}$$

$$= \frac{5}{0.8}$$

$$= 6.25$$

$$C_R = 6.25\, C_S$$

Let moles of R produced be x mol and that of S be y mol.

$$\therefore \quad \frac{x}{y} = 6.25$$

$$x = 6.25\,y$$

$$x + y = 6.5$$

$$6.25\,y + y = 6.5$$

$$\therefore \quad y = 0.896 \approx 0.90 \text{ mol}$$

$$x = 6.25\,y$$

$$= 6.25 \times 0.90$$

$$= 5.625 \text{ mol}$$

$\therefore$ Moles of R produced in 15 min = 5.625 mol ... **Ans.**

Ex. 2.68 : For irreversible first order series reaction $A \xrightarrow{k_1} R \xrightarrow{k_2} S$, the values of rate constants k_1 and k_2 are 0.17 $(\text{min})^{-1}$ and 0.11 $(\text{min})^{-1}$ respectively. Calculate (i) the time at which the concentration of R is maximum and (ii) maximum concentration of R.

Take $C_{Ao} = 1.25$ mol/l

Solution : $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

$$k_1 = 0.17\ (\text{min})^{-1}, \quad k_1 = 0.11\ (\text{min})^{-1}$$

$$C_{Ao} = 1.25 \text{ mol}/l$$

For series reaction the time at which the concentration of R is maximum is given by

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

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

$$= \frac{\ln (0.17/0.11)}{(0.17 - 0.11)}$$

$$= 7.255 \text{ min} = 435 \text{ s}$$ ... **Ans. (i)**

The maximum concentration of R [i.e. $C_{R\,max}$] is given by the equation

$$\frac{C_{R\,max}}{C_{Ao}} = \left[\frac{k_1}{k_2}\right]^{k_2/(k_2 - k_1)}$$

$$C_{R\,max} = \left(\frac{0.17}{0.11}\right)^{0.11/(0.11 - 0.17)} \times 1.25$$

$$= 0.563 \text{ mol}/l$$ ... **Ans. (ii)**

Ex. 2.69 : A liquid phase second order reversible reaction $A + B \rightleftharpoons R + S$ is carried out with equimolal concentrations of A and B in the reaction mixture ($C_{Ao} = C_{Bo} = 0.052$ mol/l). The equilibrium constant of the reaction is (K = 1.45). From the following data, find the rate equation for this reaction.

Time, h	0.187	0.45	0.60
Fraction of A converted	0.18	0.34	0.40

Solution : $A + B \rightleftharpoons R + S$, liquid phase reaction.

$C_{Ao} = C_{Bo} = 0.052$ mol/l, equimolal concentrations of A and B

$$K = 1.45$$

$$(-r_A) = k_1 C_A C_B - k_2 C_R C_S$$

$$(-r_A) = k_1 C_A^2 - k_2 C_R C_S \quad [C_{Ao} = C_{Bo}]$$

$$K = \frac{k_1}{k_2} = \frac{C_{Re} \cdot C_{Se}}{C_{Ae}^2}$$

$$1.45 = \frac{C_{Re}^2}{C_{Ae}^2}$$

$$C_{Re} = C_{Ro} + C_{Ao} X_{Ae}$$

$$= C_{Ao} X_{Ae} \quad \text{as} \quad C_{Ro} = 0$$

$$C_{Re} = \frac{C_{Ao}\,[C_{Ao} - C_{Ae}]}{C_{Ao}}$$

$$C_{Re} = C_{Ao} - C_{Ae}$$

$$1.45 = \frac{[C_{Ao} - C_{Ae}]^2}{C_{Ae}^2}$$

$$1.45\,C_{Ae}^2 = C_{Ao}^2 - 2\,C_{Ao}\,C_{Ae} + C_{Ae}^2$$

$$2.45\,C_{Ae}^2 + 2\,C_{Ao}\,C_{Ae} - C_{Ao}^2 = 0$$

$$C_{Ao} = 0.052 \text{ mol}/l$$

$$2.45\,C_{Ae}^2 + 2 \times 0.052\,C_{Ae} - (0.052)^2 = 0$$

$$2.45\,C_{Ae}^2 + 0.104\,C_{Ae} - 2.704 \times 10^{-4} = 0$$

$$C_{Ae} = \frac{-0.104 \pm [(0.104)^2 - 4 \times 2.45 \times (-2.704 \times 10^{-4})]^{1/2}}{2 \times 2.45}$$

$$= 2.46 \times 10^{-3} \text{ mol}/l$$

$$X_{Ae} = \frac{C_{Ao} - C_{Ae}}{C_{Ao}}$$

$$= \frac{0.052 - 2.46 \times 10^{-3}}{0.052} = 0.953$$

Integrated rate expression for second order reversible reaction is

$$\ln\left[\frac{X_{Ae} - (2\,X_{Ae} - 1)\,X_A}{X_{Ae} - X_A}\right] = 2\,k_1\left[\frac{1}{X_{Ae}} - 1\right] C_{Ao}\,t$$

(i) $t = 0.187$ h, $X_A = 0.18$, $X_{Ae} = 0.953$

$$\ln\left[\frac{0.953 - (2 \times 0.953 - 1) \times 0.18}{0.953 - 0.18}\right] = 2 \times 0.052 \times 0.187 \times \left[\frac{1}{0.953} - 1\right] k_1$$

∴ $$k_1 = 22.57\ (l/\text{mol})\ (\text{h})^{-1}$$

(ii) $t = 0.45$ h, $X_A = 0.34$

$$\ln\left[\frac{0.953 - (2 \times 0.953 - 1) \times 0.34}{0.953 - 0.34}\right] = 2 \times 0.052 \times 0.45\left[\frac{1}{0.953} - 1\right] k_1$$

$$k_1 = 22\ (l/\text{mol})\ (\text{h})^{-1}$$

(iii) $t = 0.60$ h, $X_A = 0.40$

$$\ln\left[\frac{0.953 - (2 \times 0.953 - 1) \times 0.40}{0.953 - 0.40}\right] = 2 \times 0.052 \times 0.60\left[\frac{1}{0.953} - 1\right] k_1$$

$$k_1 = 21.36\ (l/\text{mol})\ (\text{h})^{-1}$$

$$\text{Average value of } k_1 = \frac{22.57 + 22 + 21.36}{3}$$

$$= 21.98\ (l/\text{mol})\ (\text{h})^{-1}$$

$$K = \frac{k_1}{k_2} = 1.45$$

$$k_2 = 21.98/1.45 = 15.16\ (l/\text{mol})\ (\text{h})^{-1}$$

∴ The rate equation is

$$(-r_A) = 21.98\ (l/\text{mol})\ (\text{h})^{-1}\ C_A\,C_B - 15.16\ (l/\text{mol})\ (\text{h})^{-1}\ C_R\,C_S$$ ... **Ans.**

❑❑❑

Chapter ... ❸

DESIGN OF SINGLE IDEAL REACTORS

At present we are familiar with the procedures of determining the rate equation by analysing the kinetic data. In this chapter, we will derive the performance equations/design equations for ideal reactors, involving the term – the rate of reaction, which is used to determine the size (volume) of a given reactor for a given duty. So in order to determine the size of given reactor by making use of performance equation, the kinetics of reaction must be known. By the term-design of reactor, we mean determination of size and type of a reactor required for a given duty and for given operating conditions for carrying out a particular reaction with known kinetics in most economical way.

In the design of a reactor, we have to consider the parameters such as operating conditions, production rate, mode of operation, heat and mass transfer effects, materials of construction and cost.

Chemical Reactors :

The economics of the overall process is largely decided by the chemical step. To carry out a chemical step, best possible reactor is used so chemical reactor may be thought as a heart of the chemical process. Chemical reactors vary widely in size and shape and in method of operation/mode of operation. Based upon the shape of reactor, we have tank reactors and tubular reactors. As per the mode of operation (mode of operation refers to how reactants are fed to and how the products are discharged from reactor), we have batch reactors, semibatch reactors and continuous flow reactors. Batch reactors are used when relatively small amounts of material are to be treated while continuous flow reactors are used when large quantities of material are to be treated. The semibatch reactor is used when good control of reaction is required as the reaction proceeds only when reactant(s) are added.

Batch Reactor :

In case of batch reactor, the reactants are charged at the beginning into a container, left to react for certain time period in the reactor under agitation during which no material is fed or removed from it, and the resultant product mixture is withdrawn at a subsequent time.

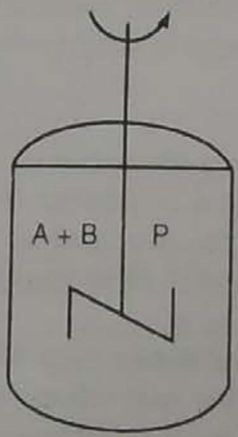


Fig. 3.1 : Batch reactor

The batch reactor is characterised by the variation of extent of reaction (conversion) and properties of the reaction mixture with time. It operates under unsteady state conditions as in it composition changes with time; however, at any instant of time the composition throughout the reactor is same.

Batch reactor consists of a vertical cylindrical vessel equipped with an agitator/stirrer for stirring the contents. It is provided with either external jacket or cooling coil or both for heating or cooling the reactor contents.

Advantages of batch reactor :

1. It is simple in construction.
2. It is simple to operate.
3. It has flexibility of operation (may be shut down quickly and easily).
4. Its cost is relatively low.
5. It requires small instrumentation and less supporting equipment.
6. It can give high conversion that can be obtained by leaving the reactant in the reactor for long periods of time.

Disadvantages of batch reactor :

1. High labour costs per unit volume of production.
2. Requires considerable time to empty, clean out and refill.
3. Poorer quality control of product. It is difficult to maintain the same quality in different batches.
4. Large scale production is difficult.

Applications of batch reactor :

Batch reactors are often used for liquid phase reactions when the required production rates are low i.e. a batch reactor is used for small scale production, to produce many different products from the same piece of equipments, to carry out reactions having long reaction times, for testing new processes that have not been fully developed, for kinetic study, and for manufacture of expensive products such as pharmaceuticals, dyes, dye intermediates, etc.

Semibatch Reactor : (unsteady state)

In semibatch reactor, one of the reactants (say A) is charged initially and the other reactant (say B) is added continuously to the reactor over a certain time period under agitation. After addition is over, holding of reactor mass is done for certain time period and finally the product mixture is withdrawn from the reactor.

This reactor offers good control of reaction speed because the reaction proceeds as the reactant is added. So when the heat of reaction is large, the evolution of heat energy can be controlled by regulating the rate of addition of the reactant (say B). The construction features of semibatch reactor are same as the batch reactor.

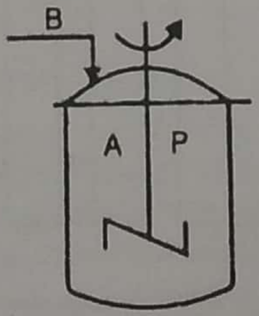


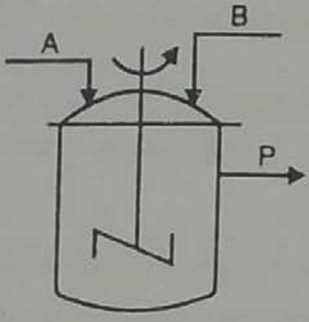
Fig. 3.2 : Semibatch reactor

Semibatch reactor has advantages of good temperature control and the capability of minimizing unwanted side reactions by maintaining a low conversion of one of the reactants. The disadvantages of this reactor are essentially same as that of batch reactor.

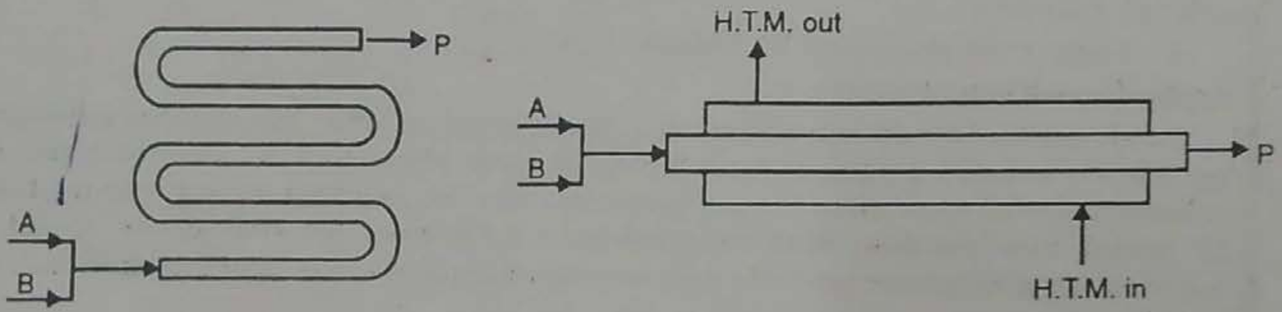
Semibatch reactor is used for liquid phase reactions and also for two-phase reactions in which the gas is continuously bubbled through the pool of liquid in the reactor.

Continuous Reactors :

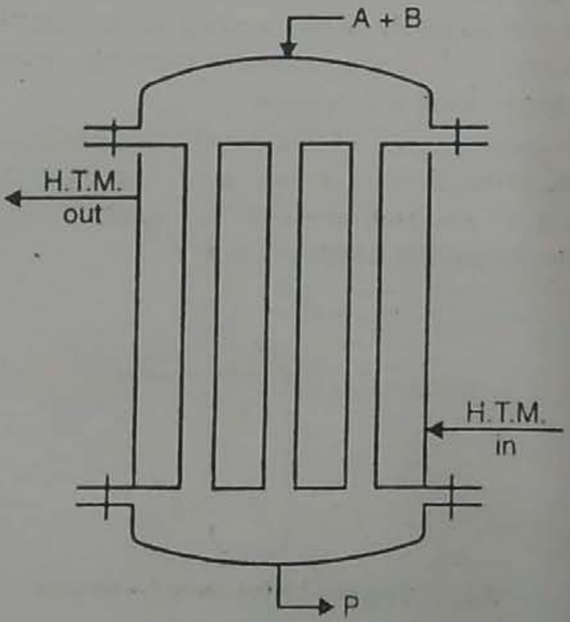
In these reactors, admission of reactants, chemical reaction and removal of product mixture occur simultaneously i.e. in these reactors, reactants are introduced and product mixture is withdrawn simultaneously in a continuous manner.



(a) Continuous tank type reactor



(b) Coiled tube reactor (c) Jacketed single tube reactor



(d) Multitubular reactor

Fig. 3.3 : Continuous flow reactors

Continuous reactors have a tank or tubular structure. Tank type reactor is essentially a tank whose contents are agitated by mechanical stirrer. A tubular reactor consists of one or more tubes in parallel in which the reaction progresses as the reactants move through tube(s). The tubes may be packed with catalyst pellets or inert solids. The single tube may be provided with jacket for heat transfer and multitubular construction is more or less same as shell and tube heat exchanger.

The continuous reactors are used for higher production rate (large scale plants), comparatively short reaction times, for reducing the operating cost and facilitating control of quality of product. These reactors require little supervision and well suited for automatic control. Initial cost of continuous reactors is quite high and the operating cost is low. These reactors offer greater constancy in operating conditions and hence offer greater constancy in the quality of the products.

Tank Reactor :

This is probably the most common type of reactor used in chemical industry. It is a vertical cylindrical vessel equipped with mechanical stirrer and provision for heat transfer (either jacket, coil or both). This type can comprises either batch operation (batch reactor) or continuous operation (constant flow stirred tank reactor).

Constant flow-stirred tank reactor [Continuous stirred tank reactor (CSTR)] MFR

It is also referred to as backmix or **mixed flow reactor**. It is very commonly used in industrial processing. It has provisions for continuous inflow of reactants and outflow of the product mixture. A certain pool of reaction mixture is always maintained in it. It normally runs at steady state and is usually operated so as to be quite well-mixed. So there is no variation of concentration, temperature or reaction rate throughout the reactor volume.

It is relatively easy to maintain good temperature control with CSTR. It is possible to operate CSTR under isothermal condition even when heat of reaction is high. CSTR required large volumes so they provide long residence time. The isothermal nature together with long residence time permits the use of CSTR at the optimum temperature for long reaction time. CSTR may be used in single or in series.

With these reactors, the conversion of reactant per unit volume of reactor is smallest of the flow reactors and consequently very large reactors are required to obtain high conversion. For high pressure reactions CSTR are not recommended because of cost consideration – CSTR operated at high pressures requires a large wall thickness and complex sealing arrangements required for agitator increases both initial and maintenance cost. They are also not suited for reactions with very high heat of reaction due to low area heat transfer is available per unit volume (as compared to tubular reactor) and low heat transfer coefficients.

CSTRs are normally employed on a commercial scale, mainly for liquid phase reactions at low or medium pressures. These can be used when the heat of reaction is high only if the temperature level obtained in their isothermal operation is satisfactory from other stand points.

Tubular Reactor : PFR

Tubular reactor (i.e. plug flow reactor) consists essentially of a single continuous long tube or several tubes arranged in parallel (tube bank). The reactants enter at one end and product mixture leaves from the other end with continuous variation of composition of reaction mixture in between (along length). Heat transfer can be accomplished either by use of jacket o shell and tube type design.

Tubular reactors are relatively easy to maintain as there are no moving parts and i gives the highest conversion per unit volume of reactor of any of the flow reactors.

It is difficult to control the temperature with the reactor and hot spots can occur in case of exothermic reaction system.

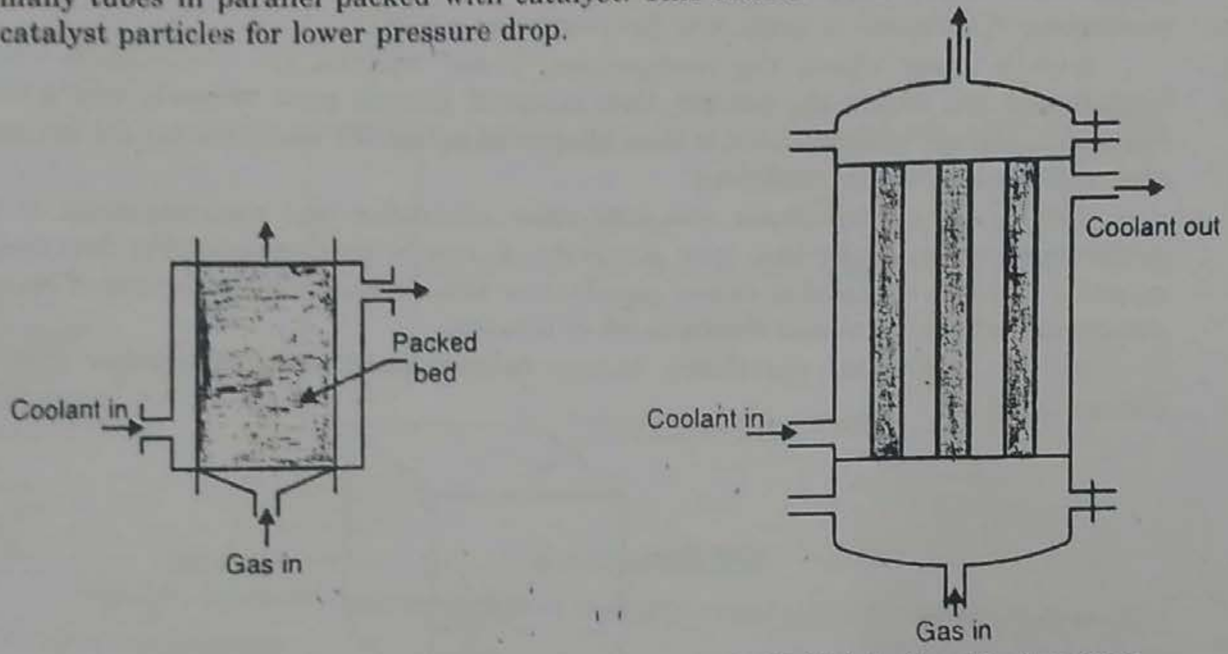
Tubular flow reactors are well suited for high pressure reactions because of cost considerations – as it uses small diameter tubes and for reactions with high heat of reaction as the rate of heat transfer per unit volume of reaction mixture is high (high ratio of heat transfer surface per unit volume of reactor and higher heat transfer coefficients).

A large number of commercially important reactions are of the fluid-solid class and are carried out in tubular reactors. e.g. catalytic cracking of petroleum, oxidation of SO_2, ammonia synthesis, etc.

Most homogeneous liquid phase reactors are CSTRs and most homogeneous gas phase flow reactors are tubular reactors.

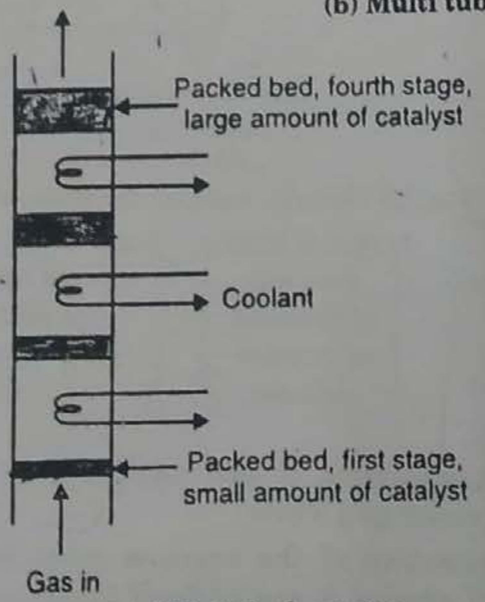
Fixed-bed Reactor :

A fixed-bed (packed-bed) reactor is essentially a tubular reactor which is packed with solid catalyst particles. In this reactor, reaction mixture is passed through the mass of small catalyst particles. It consists of a cylinder of large diameter with multiple catalyst beds or many tubes in parallel packed with catalyst. This reactor makes use of relatively large size catalyst particles for lower pressure drop.



(a)

(b) Multi tube fixed bed reactor



(c) Multi bed reactor

Fig. 3.4 : Fixed-bed reactors

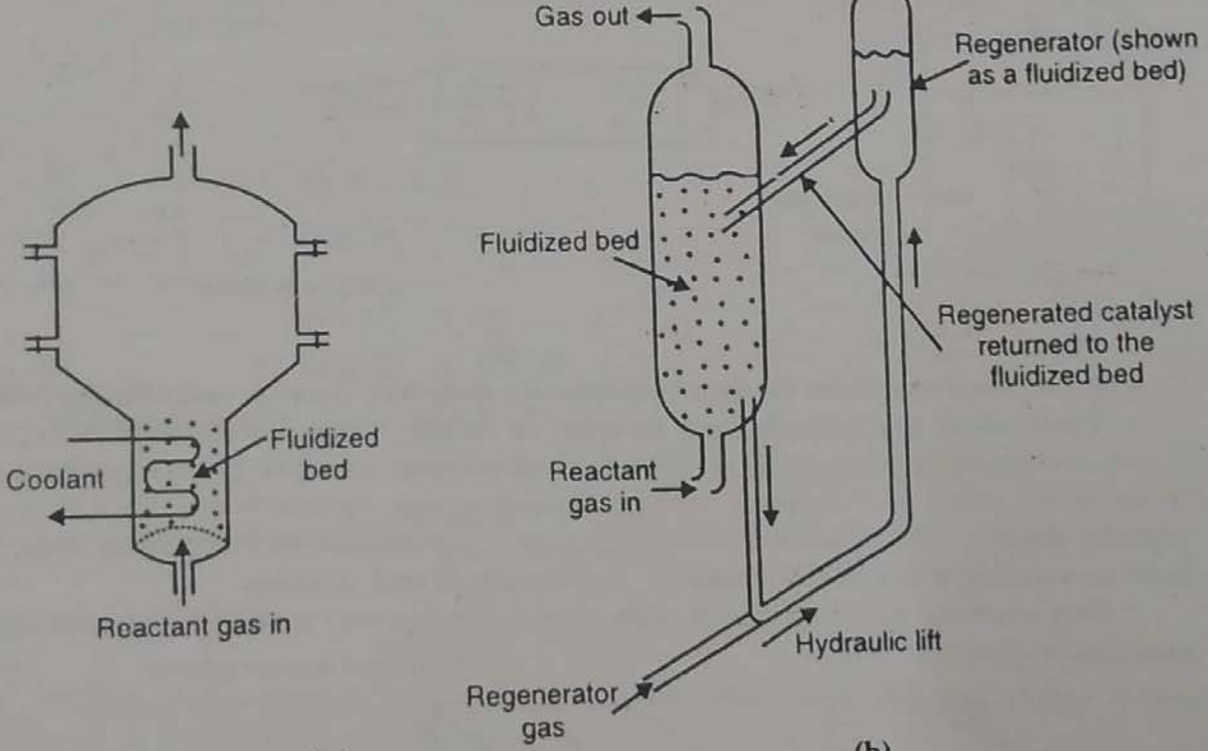
Such type of heterogeneous reaction system is used commercially to catalyse gas phase reactions. It is difficult to control temperature and formation of hot spots is there in the reactor when the reaction is exothermic. In case of this reactor, replacement of the catalyst is troublesome i.e. regeneration on continuous basis is not possible. There are also chances of channeling of gas flow to occur that result in ineffective use of parts of the reactor bed.

The advantage of the fixed bed reactor is that it gives the highest conversion per unit weight of catalyst of any catalytic reactors for most reactions.

Fluidised-Bed Reactor :

It is another catalytic reactor in common use and is analogous to the CSTR in that its contents, though heterogeneous, are well-mixed that result in even temperature distribution throughout the bed.

It consists of vertical cylindrical vessel containing fine solid catalyst particles. The fluid stream (usually gas) is introduced through the bottom of the reactor at a rate such that solids are suspended in the fluid stream without being carried out. Under these conditions the entire bed of catalyst particles behaves like a boiling liquid which tends to make the composition of reaction mixture and temperature throughout the bed uniform. As temperature is uniform throughout there are no hot spots in this reactor. With this reactor, it is possible to regenerate the catalyst continuously without shutting down the reactor. This reactor is particularly suitable when the heat effect is very large or when frequent catalyst regeneration is required.



(a) (b)

Fig. 3.5 : Fluidised-bed reactors

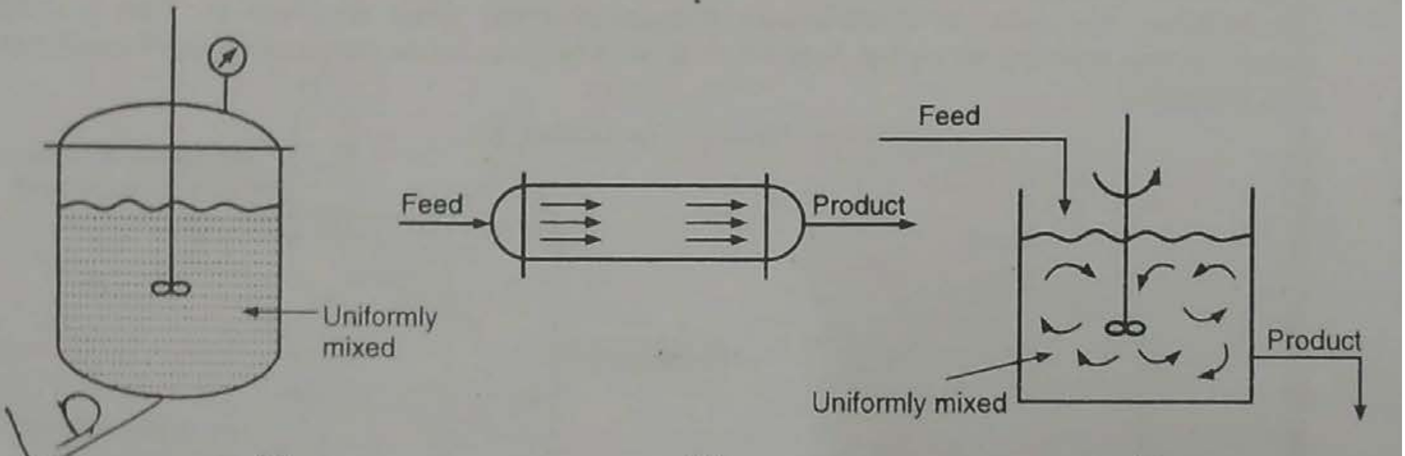
This reactor can handle large amounts of feed and catalyst and has good temperature control and therefore, it is used in a large number of applications. The advantages of ease in replacement of catalyst or regeneration of catalyst on continuous basis without shutting down reactor are sometimes offset by high cost of reactor and catalyst regeneration equipment.

Now we will derive the performance equation (also called as design equation) for a single fluid reacting in three ideal reactors, namely, batch reactor, mixed flow reactor and plug flow reactor (latter two are ideal steady-state flow reactors).

In batch reactor [Fig. 3.6 (a)] the reactants are charged at the beginning, left to react for certain time period under agitation, and the resultant product mixture is taken out at subsequent time. It is characterised by the variation of the extent of reaction and properties such as temperature and composition with time. In this reactor, at any instant of time, the composition is uniform throughout the reactor zone.

Mixed flow reactor is a ideal steady state flow reactor. It is also called as back mix reactor, mixed reactor, continuous stirred tank reactor (CSTR), or constant flow stirred tank reactor. In this reactor, the contents are well stirred so that the properties of reaction mass such as temperature and composition are uniform throughout. Hence, the exist stream from this reactor has the same composition as the fluid within the reactor. This type of flow is referred to as mixed flow and hence the reactor is named as mixed flow reactor. [Refer Fig. 3.6 (c)].

Plug flow reactor is another ideal steady-state flow reactor (also called as ideal tubular reactor). In this reactor, there is no mixing in the direction of flow and there is complete mixing in radial direction. Hence the reaction mass consists of elements of fluid in the axial direction that are independent of each other, each one having different composition and temperature. Such type of flow pattern is called as plug flow. Therefore, the extent of reaction, temperature and composition may vary with the position in the reactor. [Refer Fig. 3.6 (b)].



(a) (b) (c)

Fig. 3.6 : Ideal reactors : (a) batch reactor, (b) plug flow reactor, and (c) mixed flow reactor

These ideal reactors are easy to treat as simple forms of mass and energy conservation equations are applicable to them. These ideal reactors represent extremes in mixing states – (i) no mixing and (ii) complete mixing. Real reactors approach either of these types to the varying degree. These models when suitably corrected for the deviation from ideal may be used as starting point in the analysis and design of real reactors.

The starting point in the design of reactors is the material balance written for any reactant or product.

M.B. of batch

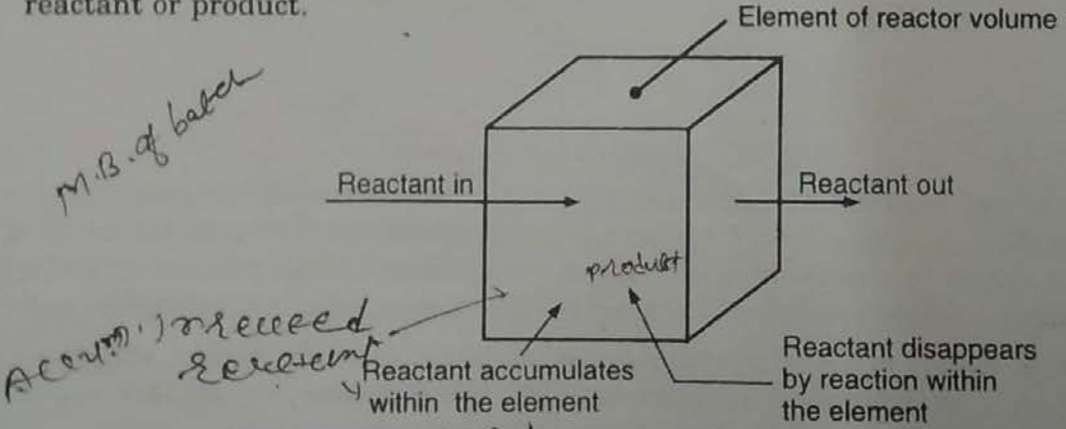


Fig. 3.7 : Material balance over an element of volume of the reactor

Material balance on mole basis for any reactant A at any instant of time, 't, is :

$$\begin{pmatrix}\text{rate of flow}\\ \text{of A into}\\ \text{element of}\\ \text{reactor volume}\\ \text{(moles/time)}\end{pmatrix} = \begin{pmatrix}\text{rate of flow}\\ \text{of A out}\\ \text{of element}\\ \text{of reactor}\\ \text{volume}\\ \text{(moles/time)}\end{pmatrix} + \begin{pmatrix}\text{rate of loss}\\ \text{of A due}\\ \text{to chemical}\\ \text{reaction}\\ \text{within the}\\ \text{element}\\ \text{of reactor}\\ \text{volume}\\ \text{(moles/time)}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of A in}\\ \text{element of}\\ \text{reactor volume}\end{pmatrix} \quad \ldots (3.1)$$

Input = output + disappearance + accumulation

(i) In cases where the composition within the reactor is uniform i.e. where composition is independent of position within the reactor then the material balance may be made over th reactor as a whole. So in case of batch reactor and mixed flow reactor, material balance (i.e. accounting of material) is made over the reactor as a whole.

(ii) In cases where the composition is not uniform i.e. composition varies with location/position within the reactor, then material balance must be made over a differential element of reactor volume which is then integrated across the whole reactor for the appropriat flow and concentration conditions.

The resultant expression obtained after integration and rearrangement is the bas performance equation for that type of reactor. In case of batch reactor, the first two terms of equation (3.1) are zero and in case of steady-state flow reactors the fourth term of equation (3. disappears where the accumulation is nil or constant.

In non-isothermal operations, energy balance must be used together with materi balance.

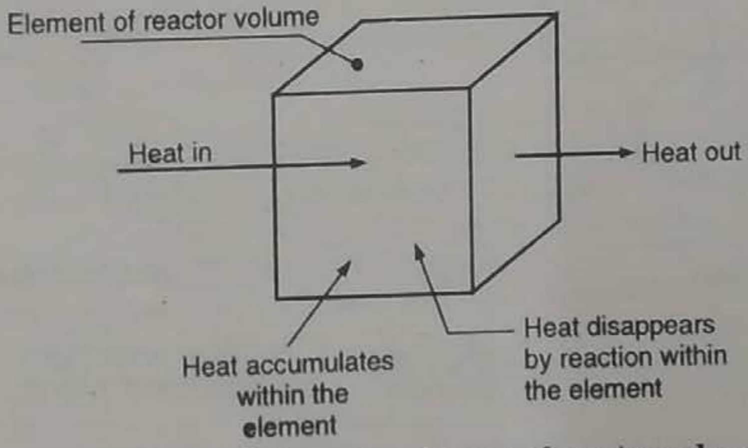


Fig. 3.8 : Energy balance for element of reactor volume

$$\begin{pmatrix}\text{rate of heat}\\ \text{flow into element}\\ \text{of reactor}\\ \text{volume}\end{pmatrix} = \begin{pmatrix}\text{rate of heat}\\ \text{flow out}\\ \text{of element}\\ \text{of reactor}\\ \text{volume}\end{pmatrix} + \begin{pmatrix}\text{rate of disappearance}\\ \text{of heat by}\\ \text{reaction within}\\ \text{element of reactor}\\ \text{volume}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of heat within}\\ \text{element of}\\ \text{reactor volume}\end{pmatrix} \quad \ldots (3.2)$$

Here also the accounting of heat may be made either about a differential element reactor or over the reactor as a whole.

When the properties of the reaction mass such as temperature and compositio i.e. concentration of species A are uniform throughout the element of volume, the rate disappearance of any reactant A is just the product of reaction volume V and the rate of loss of A due to chemical reaction $(-r_A)$. So the third term in equation (3.1) is equal to $(-r_A)$ V. This is valid in case of batch reactor and mixed flow reactor.

When the properties of reaction mass such as concentration, temperature vary with location in the reactor then the third term of equation (3.1) is equal to $\int^{V} (-r_A)\, dV$ indicating that the rate is indirect function of position. This is the case with plug flow reactor.

Relationship between C_A and X_A :

Now we will develop relationship between two related measures of extent of reaction, namely, the concentration C_A and the conversion X_A for batch as well as flow reactor.

Consider a reaction $aA + bB \rightarrow rR$ with inerts i is taking place in batch and flow reactors.

For batch reactor :

At constant volume :

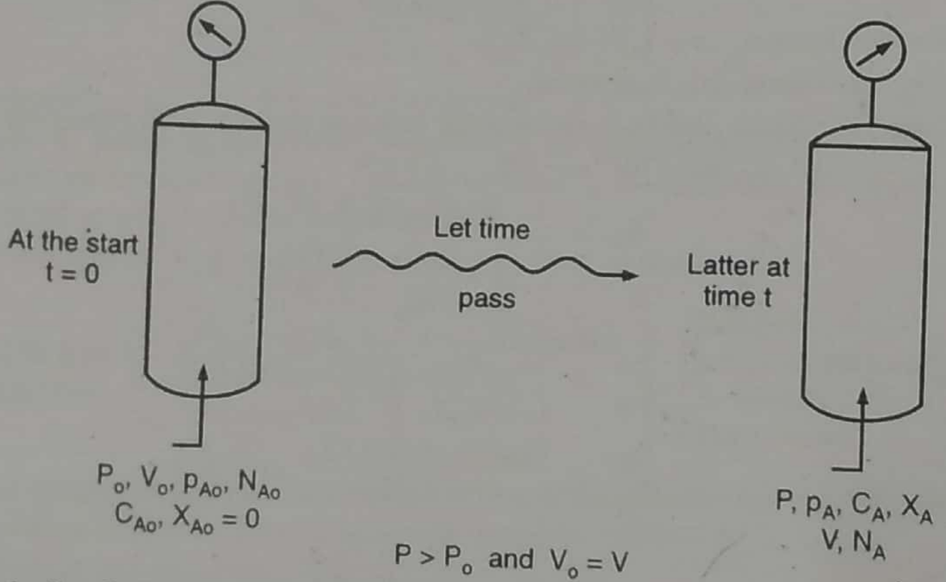


Fig. 3.9 : Symbolic representation of constant volume batch reactor system

At constant pressure :

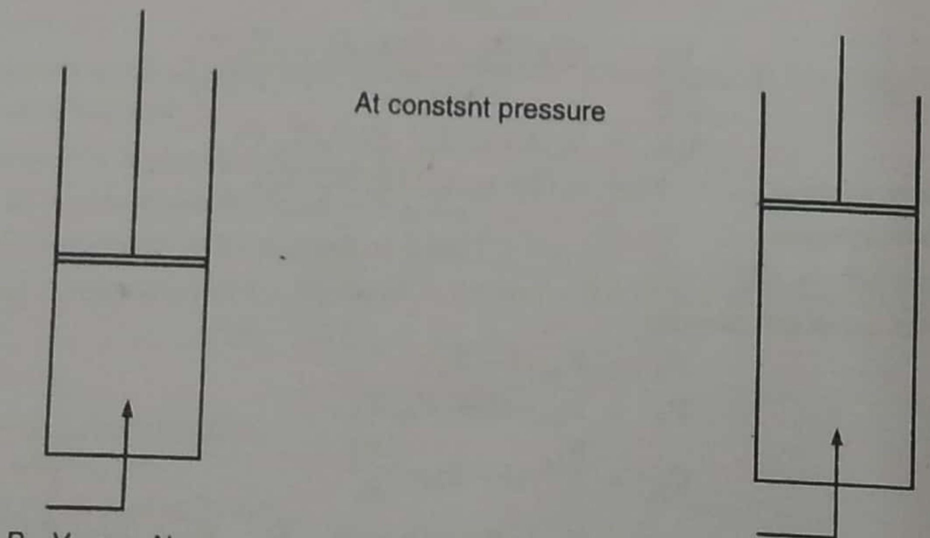


Fig. 3.10 : Symbolic representation of constant pressure batch reactor system

For flow reactor :

F_{A_0} – moles of A fed per h, C_{A_0} – concentration of A in feed stream

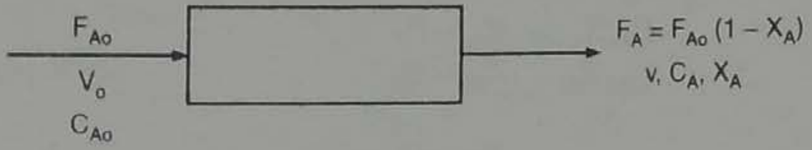


Fig. 3.11 : Symbolic representation of flow reactor

Now we will consider three special cases.

Case I : Constant density batch and flow systems.

This case includes most liquid phase reactions and the gas phase reaction carried at constant temperature and density. For this case, C_A and X_A are related as :

$$X_A = 1 - \frac{C_A}{C_{A_0}} \quad \text{and} \quad dX_A = \frac{-dC_A}{C_{A_0}}$$

$$\frac{C_A}{C_{A_0}} = 1 + X_A \quad \text{and} \quad dC_A = -C_{A_0}\,dX_A \qquad \dots (3.3)$$

$$\therefore \quad C_A = C_{A_0}(1 - X_A) \quad \text{and} \quad N_A = N_{A_0}(1 - X_A)$$

These relations are valid for

$$\varepsilon_A = \frac{V_{X_A = 1} - V_{X_A = 0}}{V_{X_A = 0}} = 0$$

To relate changes in B and R,

$$\frac{C_{A_0} X_A}{a} = \frac{C_{B_0} X_B}{b}$$

$$aA + bB \rightarrow rR$$

$$A + (b/a)\,B \rightarrow (r/a)\,R$$

Moles of A reacted at any time t = $N_{A_0} X_A$

From reaction, for every mole of A reacted, (b/a) moles of B must react.

$$\text{Moles B reacted} = \frac{\text{moles B reacted}}{\text{moles A reacted}} \times \text{moles A reacted}$$

$$= \frac{b}{a}(N_{A_0} X_A)$$

If X_B is the conversion of B and N_{B_0} are the initial moles of B then moles of B reacted at any time t in terms of N_{B_0} and X_B are

$$\text{Moles B reacted} = N_{B_0} X_B$$

$$\therefore \quad N_{B_0} X_B = \frac{b}{a}(N_{A_0} X_A)$$

$$\frac{N_{B_0} X_B}{V_0} = \frac{b}{a}\,\frac{(N_{A_0} X_A)}{V_0}$$

$$\therefore \quad \frac{C_{A_0} X_A}{a} = \frac{C_{B_0} X_B}{b}$$

Also we have in terms of concentration,

$$\frac{C_{Ao} - C_A}{a} = \frac{C_{Bo} - C_B}{b} = \frac{C_R - C_{Ro}}{r} \quad \ldots (3.4)$$

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao}}$$

$$C_{Ao} X_A = C_{Ao} - C_A$$

$$\therefore \quad \frac{C_{Ao} X_A}{a} = \frac{C_{Ao} - C_A}{a}$$

$$X_B = \frac{C_{Bo} - C_B}{C_{Bo}}$$

$$C_{Bo} X_B = C_{Bo} - C_B$$

$$\therefore \quad \frac{C_{Bo} X_B}{b} = \frac{C_{Bo} - C_B}{b}$$

Concentration of R at any time t is given by

$$C_R = C_{Ro} + (r/a)\, C_{Ao} X_A$$

$$= C_{Ro} + (r/a) \frac{(C_{Ao} - C_A)}{C_{Ao}} \cdot C_{Ao}, \text{ as } X_A = \frac{C_{Ao} - C_{Ao}}{C_{Ao}}$$

$$C_R - C_{Ro} = \frac{r}{a} (C_{Ao} - C_A)$$

$$\therefore \quad \frac{(C_{Ao} - C_A)}{a} = \frac{C_R - C_{Ro}}{r}$$

$$\therefore \quad \frac{C_{Ao} - C_A}{a} = \frac{C_{Bo} - C_B}{b} = \frac{C_R - C_{Ro}}{r}$$

Case II : Changing density of batch and flow systems with T and P constant.

Here density changes due to change in number of moles during gaseous reaction are taken into account.

Volume of a fluid element changes linearly with conversion, therefore, at any time t,

$$V = V_o (1 + \varepsilon_A X_A)$$

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao} + \varepsilon_A C_A} = \frac{1 - C_A/C_{Ao}}{1 + \varepsilon_A C_A/C_{Ao}}$$

and

$$dX_A = \frac{-C_{Ao}(1 + \varepsilon_A)}{(C_{Ao} + \varepsilon_A C_A)^2}\, dC_A$$

$$\frac{C_A}{C_{Ao}} = \frac{1 - X_A}{(1 + \varepsilon_A X_A)} \text{ and } \frac{dC_A}{C_{Ao}} = -\frac{(1 + \varepsilon_A)}{(1 + \varepsilon_A X_A)^2}\, dX_A \quad \ldots (3.5)$$

$$\text{for } \varepsilon_A \neq 0$$

For following the changes in other components :

Between reactants :

$$\varepsilon_A X_A = \varepsilon_B X_B$$

$$\frac{a\, \varepsilon_A}{C_{Ao}} = \frac{b\, \varepsilon_B}{C_{Bo}}$$

For products and inerts :

$$\frac{C_R}{C_{Ao}} = \frac{(r/a) X_A + C_{Ro}/C_{Ao}}{(1 + \varepsilon_A X_A)} \quad \ldots (3.6)$$

$$\frac{C_i}{C_{io}} = \frac{1}{(1 + \varepsilon_A X_A)}$$

We have concentration of R at any time t is ... (3.7)

$$C_R = \frac{N_{Ro} + (r/a)\, N_{Ao}\, X_A}{V}$$

$$C_R = \frac{N_{Ro} + (r/a)\, N_{Ao}\, X_A}{V_o\,(1 + \varepsilon_A X_A)}$$

$$C_R = \frac{1}{(1 + \varepsilon_A X_A)}\left[\frac{N_{Ro}}{V_o} + \frac{(r/a)\, N_{Ao}}{V_o}\cdot X_A\right]$$

$$C_R = \frac{C_{Ro} + (r/a)\, C_{Ao}\, X_A}{(1 + \varepsilon_A X_A)}$$

Dividing both sides of above equation by C_{Ao}, we get,

$$\frac{C_R}{C_{Ao}} = \frac{C_{Ro}/C_{Ao} + (r/a)\, X_A}{(1 + \varepsilon_A X_A)}$$

For flow system, $v = v_o\,(1 + \varepsilon_A X_A)$

v, v_o are volumetric feed rates.

Case III : Batch and flow systems for gases in general with changing ρ, T and P for

$$aA + bB \rightarrow rR, \quad a + b \neq r$$

$$X_A = \frac{1 - C_A/C_{Ao}\,(T\,P_o/T_o\,P)}{1 + \dfrac{\varepsilon_A C_A}{C_{Ao}}\left(\dfrac{T\,P_o}{T_o\,P}\right)}$$

or

$$\frac{C_A}{C_{Ao}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}\cdot\left(\frac{T_o\,P}{T\,P_o}\right) \quad \text{... (3.}$$

$$\frac{C_R}{C_{Ao}} = \frac{C_{Ro}/C_{Ao} + (r/a)\, X_A}{(1 + \varepsilon_A X_A)} \times \left(\frac{T_o\,P}{T\,P_o}\right)$$

$$X_B = \frac{\dfrac{C_{Bo}}{C_{Ao}} - \dfrac{C_B}{C_{Ao}}\left(\dfrac{T\,P_o}{T_o\,P}\right)}{\dfrac{b}{a} + \varepsilon_A \dfrac{C_B}{C_{Ao}}\left(\dfrac{T\,P_o}{T_o\,P}\right)}$$

or

$$\frac{C_B}{C_{Ao}} = \left(\frac{C_{Bo}/C_{Ao} - (b/a)\, X_A}{1 + \varepsilon_A X_A}\right)\cdot\left(\frac{T_o\,P}{T\,P_o}\right)$$

$$V = V_o(1 + \varepsilon_A X_A)\;\;(T\,P_o/T_o\,P) \quad \text{... (3.9)}$$

For flow system, $v = v_o(1 + \varepsilon_A X_A)\,(P_o\,T/P\,T_o)$ ... (3.10)

For flow system :

for $aA + bB \rightarrow rR$

(i) For constant density :

$$F_A = F_{Ao}(1 - X_A)$$

$$F_B = F_{Bo} - (b/a)\, F_{Ao}\, X_A$$

$$C_A = \frac{F_{Ao}}{v}\,(1 - X_A)$$

$$C_B = \frac{F_B}{v} = \frac{F_{Bo} - (b/a)\, F_{Ao}\, X_A}{v} = \frac{F_{Bo} - (b/a)\, F_{Ao}\, X_A}{v_o}$$

$$C_R = \frac{F_{Ro} + (r/a)\, F_{Ao}\, X_A}{v_o}$$

(ii) For constant pressure-isothermal-changing density system :

$$C_A = \frac{F_{Ao}(1 - X_A)}{v_o\ (1 + \varepsilon_A X_A)}$$

$$C_R = \frac{F_{Ro} + (r/a)\, F_{Ao} X_A}{v_o\ (1 + \varepsilon_A X_A)}$$

$$C_B = \frac{F_{Bo} - (b/a)\, F_{Ao} X_A}{v_o\ (1 + \varepsilon_A X_A)}$$

F is the molar feed rate.

(iii) For gas phase system with changing ρ, T and P :

$$C_A = \frac{F_{Ao}(1 - X_A)}{v_o (1 + \varepsilon_A X_A)}\left(\frac{P\,T_o}{P_o\,T}\right)$$

$$C_B = \frac{F_{Bo} - (b/a)\, F_{Ao} X_A}{v_o (1 + \varepsilon_A X_A)}\left(\frac{P\,T_o}{P_o\,T}\right)$$

Ideal Batch Reactor : D Performance eqn

As in case of batch reactor the composition is uniform throughout the reaction zone (it is independent of location) at any instant of time t, we can take the material balance of limiting component say A over reactor as a whole.

Material balance of A on mole basis at any instant of time, t :

$$\begin{pmatrix}\text{Rate of A flow}\\ \text{into reactor}\end{pmatrix} = \begin{pmatrix}\text{Rate of A}\\ \text{flow out}\\ \text{of reactor}\end{pmatrix} + \begin{pmatrix}\text{Rate of}\\ \text{disappearance}\\ \text{of A by}\\ \text{chemical}\\ \text{reaction}\end{pmatrix} + \begin{pmatrix}\text{Rate of}\\ \text{accumulation of}\\ \text{A within}\\ \text{the reactor}\end{pmatrix} \quad \ldots (3.11)$$

In case of batch reactor no fluid enters or leave the reactor during the course of reaction, inflow of A = outflow of A = 0. Therefore, above equation reduces to

$$\begin{pmatrix}\text{Rate of disappearance}\\ \text{of A by chemical}\\ \text{reaction within}\\ \text{the reactor}\\ \text{(moles/time)}\end{pmatrix} = -\begin{pmatrix}\text{Rate of accumulation}\\ \text{of A within the}\\ \text{reactor}\\ \text{(moles/time)}\end{pmatrix} \quad \ldots (3.12)$$

Rate of disappearance of A by chemical reaction in moles/time in reaction volume V = $(-r_A)\,V$

Moles of A fed = N_{Ao}

Conversion of A at any time t = X_A

Moles of A consumed/reacted = $N_{Ao} X_A$

Moles of A remained in reactor at time t = N_A

Moles of A remained at t = Moles of A fed at t = 0 – Moles of A reacted upto t

$$\begin{aligned} N_A &= N_{Ao} - N_{Ao} X_A \\ &= N_{Ao}(1 - X_A) \end{aligned}$$

$$\therefore \begin{matrix}\text{Rate of accumulation}\\ \text{of A within the}\\ \text{reactor in moles/time}\end{matrix} = \frac{dN_A}{dt}$$

$$= \frac{d\,[N_{Ao}(1 - X_A)]}{dt}$$

$$= -N_{Ao}\frac{dX_A}{dt}$$

Putting values of the terms, equation (3.12) becomes

$$(-r_A)\,V = -\left(-N_{Ao}\frac{dX_A}{dt}\right)$$

$$(-r_A)\,V = N_{Ao}\frac{dX_A}{dt} \qquad \ldots (3.13)$$

Rearranging we get,

$$dt = N_{Ao}\frac{dX_A}{(-r_A)\,V}$$

Integrating within limits

$$\text{At } t=0,\ X_A = 0$$

$$\text{At } t=t,\ X_A = X_A$$

$$\int_0^t dt = N_{Ao}\int_0^{X_A}\frac{dX_A}{(-r_A)\,V}$$

$$\therefore \qquad t = N_{Ao}\int_0^{X_A}\frac{dX_A}{(-r_A)\,V} \qquad \ldots (3.14)$$

$y = mx + c$

$1 \quad r_A$

Equation (3.14) is the general equation showing the time needed to achieve conversion X_A for either isothermal or non-isothermal operation. The volume and rate remain under the integral sign as they both may change as the reaction proceeds.

For constant density (or constant volume) system, $\varepsilon_A = 0$ and $V = V_o$, so the above equation reduces to

$$t = \frac{N_{Ao}}{V_o}\int_0^{X_A}\frac{dX_A}{(-r_A)}$$

$x_A = \frac{C_{Ao} - C_A}{C_{Ao}}$

$$\boxed{t = C_{Ao}\int_0^{X_A}\frac{dX_A}{(-r_A)} = -\int_{C_{Ao}}^{C_A}\frac{dC_A}{-r_A}} \qquad \ldots (3.15)$$

$dx_A = -\frac{dC_A}{C_{Ao}}$

Equation (3.14) is the performance/design equation for batch reactor for general case. Equation (3.15) is the performance equation for batch reactor for constant density reaction system.

For reactions in which the volume of reaction mixture changes proportionately with conversion with significant density changes such as gas phase reactions with changing number of moles due to reaction, the equation (3.14) becomes

$$t = N_{Ao}\int_0^{X_A}\frac{dX_A}{(-r_A)\,V_o\,(1+\varepsilon_A X_A)}, \quad \text{as } V = V_o(1+\varepsilon_A X_A)$$

$$t = C_{Ao}\int_0^{X_A}\frac{dX_A}{(-r_A)\,(1+\varepsilon_A X_A)} \qquad \ldots (3.16)$$

Equation (3.16) is performance equation for batch reactor for variable density/volume reaction system. The above equations are applicable to both isothermal and non-isothermal operations. For non-isothermal operation, we should know variation of rate with temperature, and variation of temperature with conversion before solution is possible.

Graphical representation of the performance equations (3.14) and (3.15) is shown in Fig. 3.12.

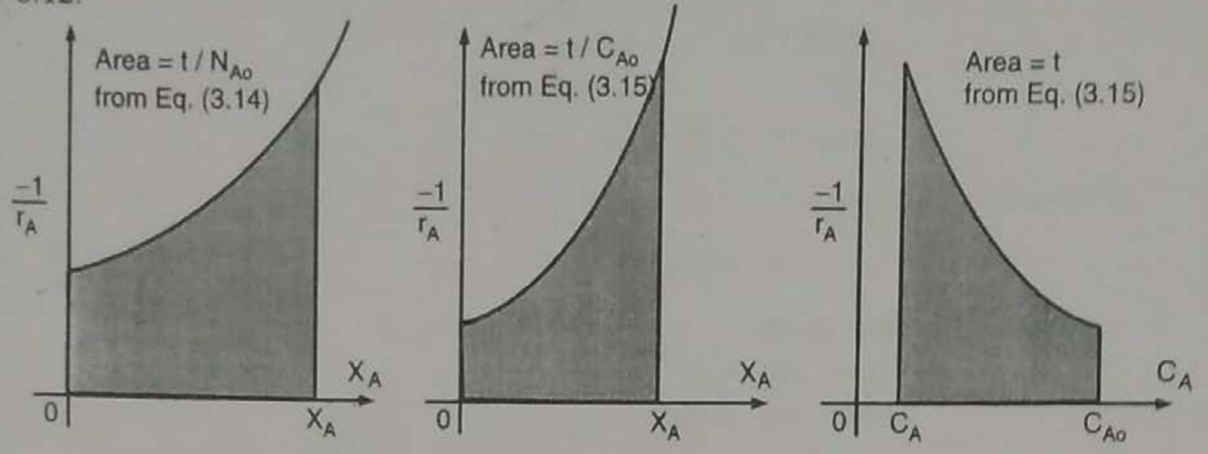


Fig. 3.12 : Graphical representation of performance equations for batch reactors, isothermal or non-isothermal operation

The performance measures of flow reactors are the space time and the space velocity just as the reaction time t which is the natural measure of the performance for a batch reactor.

Space time : It is the time required to process one reactor volume of feed at specified conditions. It is denoted by symbol 'τ' and has units of time.

Space velocity : It is the number of reactor volumes of feed at specified conditions which can be treated in unit time. It is denoted by symbol 's' which is reciprocal of 'τ'.

Thus, a space velocity of 4 h^{-1} means that four reactor volumes of feed at a specified conditions are being fed into the reactors per hour. A space time of 2 minutes means that in every two minutes one reactor volume of feed at specified conditions is being treated by the reactor.

Based upon the conditions of a stream entering the reactor, the relation between τ, s and the other pertinent variable is,

$$\tau = \frac{1}{s} = \frac{C_{A0} \cdot V}{F_{A0}} = \frac{\left(\frac{\text{moles A entering}}{\text{volume of feed}}\right)(\text{volume of reactor})}{\left(\frac{\text{moles A entering}}{\text{time}}\right)}$$

$$= \frac{V}{v_o} = \frac{\text{reactor volume}}{\text{volumetric feed rate}} \qquad \ldots (3.17)$$

In some cases it is more convenient to measure the volumetric flow rate at some standard state. If the material is in gaseous state when fed to the reactor though it is in liquid state at standard state then care must be taken to specify the state that is chosen.

Space velocity and space time denoted by s and τ at actual feed conditions.

Space velocity and space time denoted by s' and τ' at standard conditions,

then they are related by

$$\tau' = \frac{1}{s'} = \frac{C'_{A0} V}{F_{A0}} = \tau \frac{C'_{A0}}{C_{A0}} = \frac{1}{s} \frac{C'_{A0}}{C_{A0}} \qquad \ldots (3.18)$$

Steady-State Mixed Flow Reactor/CSTR :

In the mixed flow reactor as the composition is uniform throughout the performance equation can be obtained by taking the material balance of reactant A over the reactor as a whole.

Derive performance eq for MFR for 1st & zero order

Material balance of A on mole basis over reactor is :

$$\begin{pmatrix}\text{Input of A}\\ \text{to the reactor}\\ \text{(moles/time)}\end{pmatrix} = \begin{pmatrix}\text{output of A}\\ \text{from the reactor}\\ \text{(moles/time)}\end{pmatrix} + \begin{pmatrix}\text{disappearance}\\ \text{of A by}\\ \text{reaction within}\\ \text{the reactor}\\ \text{(moles/time)}\end{pmatrix} + \begin{pmatrix}\text{accumulation of}\\ \text{A within the}\\ \text{reactor}\\ \text{(moles/time)}\end{pmatrix}$$

... (3.19)

For mixed flow reactor operating at steady state, the fourth term of equation (3.19) is zero. (For accumulation, nil or constant).

$$\therefore \begin{matrix}\text{Input of A}\\ \text{to the reactor}\\ \text{(moles/time)}\end{matrix} = \begin{matrix}\text{output of A}\\ \text{from the reactor}\\ \text{(moles/time)}\end{matrix} + \begin{matrix}\text{disappearance}\\ \text{of A by reaction}\\ \text{within the reactor}\\ \text{(moles/time)}\end{matrix} \qquad \text{... (3.20)}$$

Let,

F_{Ao} = molar feed rate of component A to the reactor in moles/time

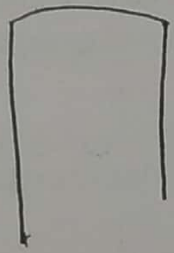
V = volume of reactor

C_{Ao} = molar concentration of A in stream entering the reactor in moles/volume

v_o = volumetric feed rate of feed stream entering the reactor in volume/time

We have, $F_{Ao} = C_{Ao} \cdot v_o$ ... (3.21)

X_A = conversion of component A



Molar flow rate of A to the reactor $= F_{Ao}$.

The molar rate at which A is reacting in system $= F_{Ao} X_A$.

$$F_{Ao} X_A = \frac{\text{moles A fed}}{\text{time}} \times \frac{\text{moles A reacted}}{\text{moles A fed}}$$

$$\frac{\text{Moles A reacted}}{\text{time}} = F_{Ao} X_A$$

Molar flow rate of A leaving the reactor $= F_A$.

$$\begin{pmatrix}\text{Molar flow rate}\\ \text{at which A}\\ \text{is fed to}\\ \text{the reactor}\end{pmatrix} - \begin{pmatrix}\text{molar rate at which}\\ \text{A is consumed}\\ \text{in reactor}\end{pmatrix} = \begin{pmatrix}\text{molar rate at which}\\ \text{A leaves the}\\ \text{reactor}\end{pmatrix}$$

$$F_{Ao} - F_{Ao} X_A = F_A$$

$F_{Ao}(1-(X_A))$

Output of A from reactor in moles/time $= F_A = F_{Ao}(1 - X_A)$

Rate of disappearance of A by reaction within the reactor in moles/time $\overset{F_r}{=} (-r_A)\,V$

Substituting the values of terms in equation (3.20), we get,

$$F_{Ao} = F_{Ao}(1 - X_A) + (-r_A)\,V$$

$$F_{Ao} X_A = (-r_A)\,V$$

Rearranging, we get,

$$\frac{V}{F_{Ao}} = \frac{X_A}{(-r_A)}$$

$$\frac{V}{F_{Ao}} = \frac{\tau}{C_{Ao}} = \frac{X_A}{(-r_A)}$$

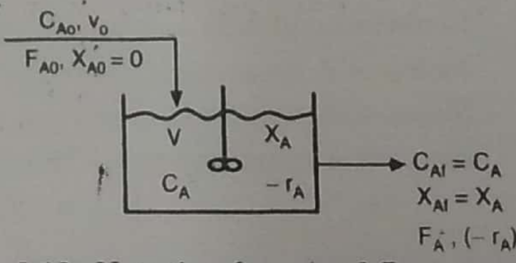


Fig. 3.13 : Notation for mixed flow reactor

or $$\tau = \frac{1}{s} = \frac{V}{v_o} = \frac{V C_{Ao}}{F_{Ao}} = \frac{C_{Ao} X_A}{(-r_A)} \qquad \text{... (3.22)}$$

where X_A and $(-r_A)$ are evaluated at exit stream conditions which are same as the conditions within the reactor.

The equation (3.22) is the desired performance equation for mixed flow reactor applicable for any value of ε_A.

If the feed on which the conversion is based, subscript o, enters the reactor partially converted, subscript i and leaves at conditions given by subscript f then

$$\frac{V}{F_{Ao}} = \frac{X_{Af} - X_{Ai}}{(-r_A)_f}$$

or

$$\tau = \frac{V\,C_{Ao}}{F_{Ao}} = \frac{C_{Ao}\,(X_{Af} - X_{Ai})}{(-r_A)_f} \qquad \ldots (3.23)$$

For special case of constant-density reaction system ($\varepsilon_A = 0$), the performance equation (3.22) can be written in terms of concentration.

$$X_A = 1 - C_A/C_{Ao} \quad \text{for } \varepsilon_A = 0$$

$$X_A = (C_{Ao} - C_A)/C_{Ao},$$

$$\frac{V}{F_{Ao}} = \frac{X_A}{(-r_A)} = \frac{C_{Ao} - C_A}{C_{Ao}\,(-r_A)}$$

or

$$\tau = \frac{V}{v} = \frac{C_{Ao}\,X_A}{(-r_A)} = \frac{C_{Ao} - C_A}{(-r_A)} \qquad \ldots (3.24)$$

These performance equations are used to determine the size of reactor required to achieve a given conversion or to find the extent of reaction in a reactor of given size.

Graphical representation of the performance equations (3.22) and (3.24) is shown in Fig. 3.14.

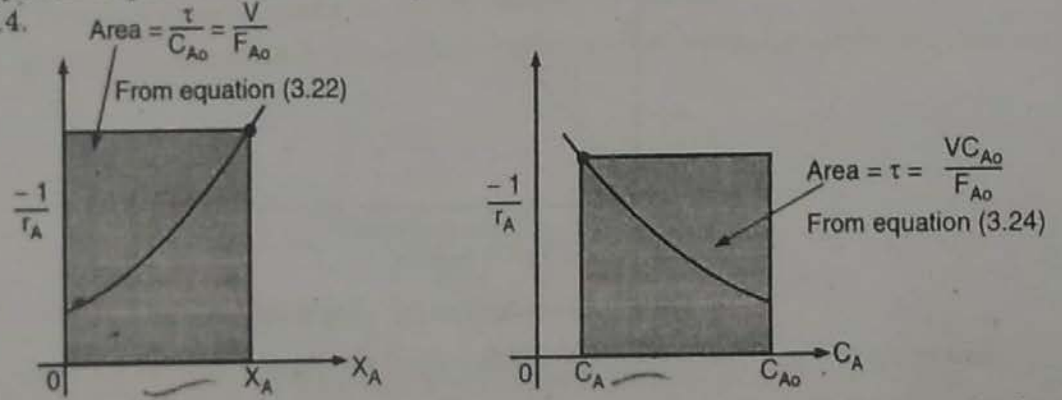


Fig. 3.14 : Graphical representation of the design/performance equations for mixed reactor

Note that, it is the rectangular area for the mixed flow reactor.

For CSTR the performance equation can be written directly for any kinetic form.

For example :

(1) The performance equation in case of constant-density system ($\varepsilon_A = 0$) for first order reaction :

$$\tau = \frac{C_{Ao} - C_A}{(-r_A)}$$

$$\tau = \frac{C_{Ao} - C_A}{k\,C_A}$$

$$\therefore \quad \tau\,k = \frac{C_{Ao} - C_A}{C_A}$$

$$\tau = \frac{C_{Ao}\,X_A}{(-r_A)}$$

$$(-r_A) = k\,C_A = k\,C_{Ao}\,(1 - X_A)$$

$$= \frac{C_{Ao}\,X_A}{k\,C_{Ao}\,(1 - X_A)}$$

$$\therefore \quad \tau k = \frac{X_A}{(1-X_A)}$$

$$\tau k = \frac{X_A}{(1-X_A)} = \frac{C_{Ao}-C_A}{C_A} \quad \text{for } \varepsilon_A = 0 \qquad \text{... (3.25)}$$

(2) For changing density reaction system and first order kinetics :

$$V = v_o(1+\varepsilon_A X_A)$$

and

$$C_A/C_{Ao} = \frac{1-X_A}{(1+\varepsilon_A X_A)}$$

$$C_A = \frac{C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$$\tau = \frac{C_{Ao}X_A}{(-r_A)}$$

$$\tau = \frac{C_{Ao}X_A}{k\,C_A}$$

$$\tau k = \frac{C_{Ao}X_A}{\frac{C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)}}$$

$$\therefore \quad \tau k = \frac{X_A(1+\varepsilon_A X_A)}{(1-X_A)} \quad \text{for any } \varepsilon_A \qquad \text{... (3.26)}$$

(3) For second order reaction A → products with $-r_A = k\,C_A^2$ and $\varepsilon_A = 0$, the performance equation (3.24) becomes

$$\tau k = \frac{C_{Ao}-C_A}{C_A^2} \qquad \text{... (3.27)}$$

Fractional conversion in terms of Damkohler number :

(1) First order reaction in mixed flow reactor/CSTR with $\varepsilon_A = 0$:

The performance equation for CSTR for constant-density reaction system is

$$\tau = \frac{V}{v_o} = \frac{C_{Ao}-C_A}{-r_A} \qquad \text{... (3.28)}$$

For first order reaction, the rate equation is

$$-r_A = k\,C_A \qquad \text{... (3.28 a)}$$

Combining equations (3.28) and (3.28 a), we get,

$$\tau = \frac{C_{Ao}-C_A}{k\,C_A}$$

For the case with no change in volume during the course of reaction, the conversion is given by

$$X_A = \frac{C_{Ao}-C_A}{C_{Ao}}$$

$$\therefore \quad C_A = C_{Ao}(1-X_A)$$

$$\therefore \quad \tau = \frac{C_{Ao}-C_{Ao}(1-X_A)}{k\,C_{Ao}(1-X_A)}$$

$$\tau k = \frac{X_A}{(1-X_A)}$$

$$\tau k - \tau k X_A = X_A$$

$$\therefore \quad X_A(1+\tau k) = \tau k$$

$$X_A = \frac{\tau k}{1+\tau k} \qquad \text{... (3.29)}$$

The product τk is referred as the reaction Damkohler number (D_a).

$$\therefore \quad X_A = \frac{D_a}{1 + D_a} \qquad \dots (3.30)$$

The Damkohler number (D_a) is the dimensionless number that helps us to make quick estimates of conversion that can be achieved in flow reactors. High value of D_a indicates high value of conversion and low value of D_a indicates low value of conversion.

For $D_a \le 0.1$, X_A is less than 10%

For $D_a \ge 10$, X_A is greater than 90%

(2) Second order reaction in mixed flow reactor [CSTR] with $\varepsilon_A = 0$:

$$(-r_A) = k\,C_A^2$$

$$(-r_A) = k\,C_{Ao}^2\,(1 - X_A)^2 \text{ (for constant density)}$$

The performance equation for CSTR is

$$\tau = \frac{C_{Ao} - C_A}{(-r_A)}$$

$$\tau = \frac{C_{Ao} - C_A}{k\,C_A^2}$$

$$\tau = \frac{C_{Ao} - C_A}{k\,C_{Ao}^2\,(1 - X_A)^2}$$

We have,

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao}}$$

$$\therefore \quad \tau = \frac{C_{Ao} - C_A}{C_{Ao} \cdot k\,C_{Ao}\,(1 - X_A)^2}$$

$$\tau = \frac{X_A}{k\,C_{Ao}\,(1 - X_A)^2}$$

$$\tau\,k\,C_{Ao}\,(1 - X_A)^2 = X_A$$

$$\tau k C_{Ao} = D_a \text{ for second order reaction}$$

$$D_a\,(1 + X_A^2 - 2\,X_A) = X_A$$

$$D_a\,X_A^2 - 2\,D_a\,X_A + D_a = X_A$$

$$D_a\,X_A^2 - (1 + 2\,D_a)\,X_A + D_a = 0$$

$$\therefore \quad X_A = \frac{(1 + 2\,D_a) - \sqrt{(1 + 2\,D_a)^2 - 4\,(D_a)\,(D_a)}}{2\,D_a}$$

$$X_A = \frac{(1 + 2\,D_a) - \sqrt{1 + 4\,D_a^2 + 4\,D_a - 4\,D_a^2}}{2\,D_a}$$

$$X_A = \frac{(1 + 2\,D_a) - \sqrt{1 + 4\,D_a}}{2\,D_a} \qquad \dots (3.31)$$

The equation (3.31) expresses the conversion as a function of Damkohler number for second order liquid phase reactions.

Steady-State Plug Flow Reactor :

In case of a plug flow reactor, the composition of fluid varies from point to point along the flow path (composition is a function of location), the material balance for any reacting component A must be done over a differential element of volume dV of reactor.

For any component A material balance on mole basis on differential element of volume dV is

$$\begin{pmatrix}\text{Input of A}\\ \text{in moles/time}\\ \text{to dV}\end{pmatrix} = \begin{pmatrix}\text{output of A}\\ \text{in moles/time}\\ \text{from dV}\end{pmatrix} + \begin{pmatrix}\text{rate of disappearance}\\ \text{of A by reaction}\\ \text{within dV}\\ \text{in moles/time}\end{pmatrix} + \begin{pmatrix}\text{rate of}\\ \text{accumulation}\\ \text{of A within}\\ \text{dV in moles/time}\end{pmatrix}$$

For steady-state, the fourth term of above equation is zero. Therefore,

$$\begin{pmatrix}\text{Input of A}\\ \text{in moles/time}\\ \text{to dV}\end{pmatrix} = \begin{pmatrix}\text{output of A}\\ \text{in moles/time}\\ \text{from dV}\end{pmatrix} + \begin{pmatrix}\text{rate of disappearance}\\ \text{of A by reaction}\\ \text{within dV}\\ \text{in moles/time}\end{pmatrix} \quad \dots (3.32)$$

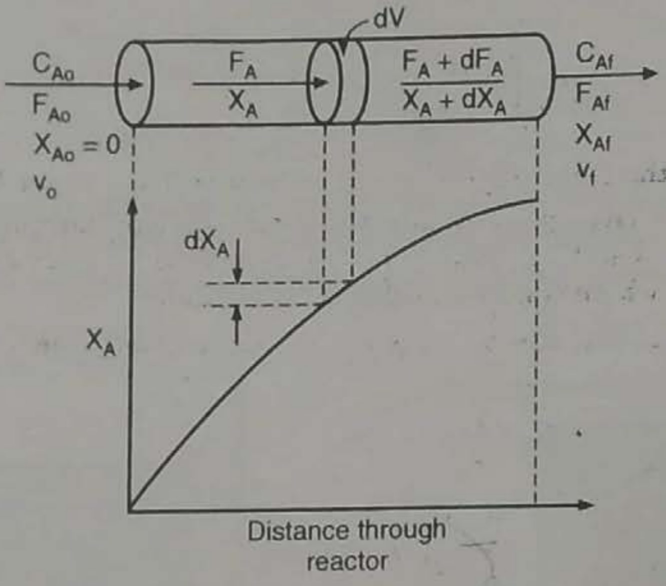


Fig. 3.15 : Notation for plug flow reactor

Referring to Fig. 3.15, we see for a differential element of volume dV that

input of A, moles/time = F_A

output of A, moles/time = $F_A + dF_A$

Rate of disappearance of A by reaction, moles/time = $(-r_A)\,dV = \dfrac{\text{moles A reacting}}{\text{(time) (volume of fluid)}}$ × (volume of element)

Putting the values of these three terms in equation (3.32), we get,

$$F_A = (F_A + dF_A) + (-r_A)\,dV$$

We know $\quad F_A = F_{Ao}(1 - X_A)$

$$\therefore \quad dF_A = d[F_{Ao}(1 - X_A)] = -F_{Ao}.dX_A$$

$$F_A = F_A + dF_A + (-r_A)\,dV$$

$$F_A = F_A - F_{Ao}\,dX_A + (-r_A)\,dV$$

$$\therefore \quad F_{Ao}\,dX_A = (-r_A)\,dV \quad \dots (3.33)$$

Equation (3.33) is accounting for A in the differential section of reactor volume dV. For a reactor as a whole, this equation must be integrated. F_{Ao} in equation (3.33) is constant, but $(-r_A)$ certainly depends upon the concentration or conversion.

So rearranging the terms accordingly, we get,

$$\int_0^V \frac{dV}{F_{Ao}} = \int_0^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$\therefore \quad \frac{V}{F_{Ao}} = \int_0^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$\frac{V}{F_{Ao}} = \frac{\tau}{C_{Ao}} = \int_0^{X_{Af}} \frac{dX_A}{(-r_A)}$$

or
$$\tau = \frac{V}{v_0} = \frac{V\,C_{Ao}}{F_{Ao}} = C_{Ao}\int_0^{X_{Af}} \frac{dX_A}{(-r_A)}, \text{ for any } \varepsilon_A \qquad \ldots (3.34)$$

The equation (3.34) is the performance equation for plug flow reactor for any ε_A.

With the help of above cited performance equation, one can determine reactor size for a given feed rate and conversion. Comparing equations (3.22) and (3.34) we see the difference – that in plug flow r_A varies whereas in mixed flow r_A is constant.

If feed on which conversion is based enters the reactor, partially converted then we have,

$$\frac{V}{F_{Ao}} = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)}$$

or
$$\boxed{\tau = \frac{V}{v_0} = C_{Ao}\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{-r_A}} \qquad \ldots (3.35)$$

where X_{Ai} is conversion of A at inlet and X_{Af} is conversion of A at outlet of reactor.

For constant-density systems, the performance equation can be expressed in terms of concentration.

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao}} \qquad \because\ dX_A = \frac{1}{C_{Ao}}\,dC_A$$

From equation (3.34), we get,

$$\frac{V}{F_{Ao}} = \frac{\tau}{C_{Ao}} = \int_0^{X_{Af}} \frac{dX_A}{-r_A} = -\frac{1}{C_{Ao}}\int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{(-r_A)}$$

or
$$\tau = \frac{V}{v_0} = C_{Ao}\int_0^{X_{Af}} \frac{dX_A}{-r_A}$$

$$= -\int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{-r_A} \quad \text{for } \varepsilon_A = 0 \qquad \ldots (3.36)$$

(i) Performance equation in case of constant-density systems for first order reaction :

$$\tau = C_{Ao}\int_0^{X_{Af}} \frac{dX_A}{-r_A}, \quad -r_A = kC_A = k\,C_{Ao}\,(1-X_A)$$

$$\tau = C_{Ao}\int_0^{X_A} \frac{dX_A}{k\,C_{Ao}\,(1-X_A)}$$

$$k\tau = -\ln(1-X_A) \qquad \dots (3.37)$$

Equation (3.37) is a performance equation for plug flow for first order reactions (for constant-density).

(ii) Performance equation for first order reaction with any ε_A :

For cases in which the volume of reaction mixture changes proportionately with conversion, we have,

$$V = V_0\,(1+\varepsilon_A X_A)$$

$$\frac{C_A}{C_{Ao}} = \frac{1-X_A}{1+\varepsilon_A X_A}$$

For first order reactions, we know,

$$-r_A = k\,C_A$$

$$\therefore \quad -r_A = k\,C_{Ao}\frac{(1-X_A)}{(1+\varepsilon_A X_A)}$$

We have,

$$\tau = C_{Ao}\int_0^{X_A} \frac{dX_A}{-r_A}$$

$$\tau = C_{Ao}\int_0^{X_A} \frac{dX_A}{\dfrac{k\,C_{Ao}\,(1-X_A)}{(1+\varepsilon_A X_A)}}$$

$$\therefore \quad k\tau = \int_0^{X_A} \frac{(1+\varepsilon_A X_A)\,dX_A}{1-X_A}$$

$$= \int_0^{X_A} \frac{dX_A}{1-X_A} + \varepsilon_A\int_0^{X_A} \frac{X_A\,dX_A}{1-X_A}$$

$$k\tau = -\ln(1-X_A) + \varepsilon_A I_1 \qquad \dots (3.38)$$

$$I_1 = \int_0^{X_A} \frac{X_A\,dX_A}{1-X_A}$$

Put $1-X_A = y$

$\therefore$ $dX_A = -dy$

At $X_A = 0,\ y = 1$

At $X_A = X_A,\ y = 1-X_A$

$X_A = 1-y_A$

$$\therefore \quad I_1 = \int_0^{X_A} \frac{X_A\, dX_A}{1-X_A} = -\int_1^{1-X_A} \frac{1-y}{y}\, dy$$

$$= -\int_1^{1-X_A} \frac{1}{y}\, dy + \int_1^{1-X_A} dy$$

$$= -\ln(1-X_A) + (1-X_A-1)$$

$$= -\ln(1-X_A) - X_A$$

Putting value of I_1 in equation (3.38), we get,

$$k\tau = -\ln(1-X_A) - \varepsilon_A \ln(1-X_A) - \varepsilon_A X_A$$

$$k\tau = -(1+\varepsilon_A)\ln(1-X_A) - \varepsilon_A X_A \qquad \dots (3.39)$$

Equation (3.39) is a performance equation for first order reaction in case of changing density systems.

(iii) For first order reversible reaction,

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$$

with (i) $\frac{C_{Ro}}{C_{Ao}} = M$

(ii) $-r_A = k_1 C_A - k_2 C_R$

and (iii) X_{Ae} = equilibrium conversion

Performance equation is,

$$k_1\tau = \frac{M + r X_{Ae}}{M + r}\left[-(1+\varepsilon_A X_{Ae}) \ln\left(\frac{X_{Ae}-X_A}{X_{Ae}}\right) - \varepsilon_A X_A\right] \qquad \dots (3.40)$$

(iv) For second order reversible reaction of the type

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

with equimolar feed or 2A → products, for any constant ε_A

Performance equation is,

$$C_{Ao} k\tau = 2\varepsilon_A(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + (\varepsilon_A+1)^2 \frac{X_A}{1-X_A} \qquad \dots (3.41)$$

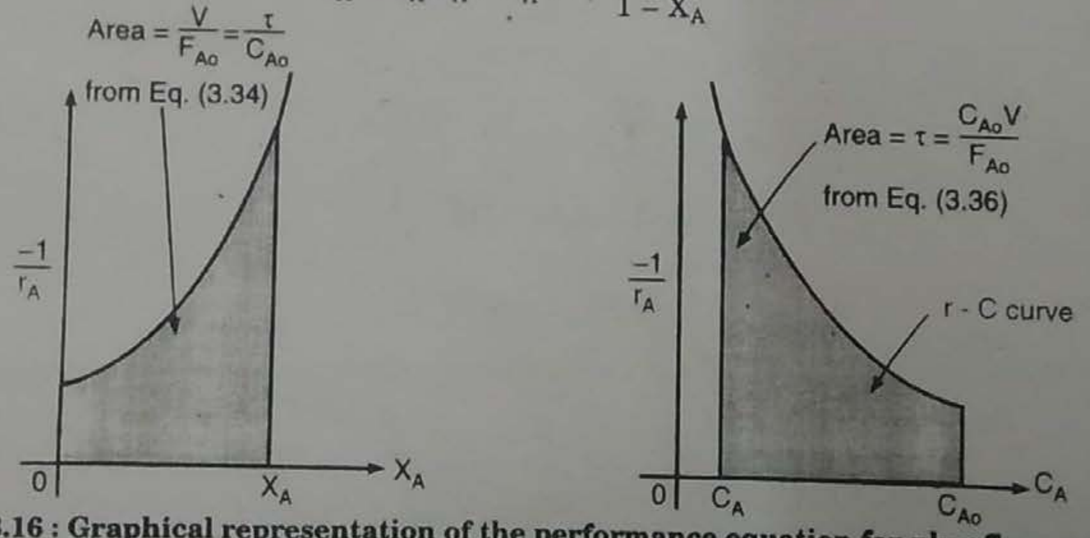


Fig. 3.16 : Graphical representation of the performance equation for plug flow reactor

In case of systems of constant-density (constant-volume batch and constant-density plug flow), the performance equations are identical, τ for plug flow is equivalent to t for batch reactor, and the equations can be used interchangeably whereas in case of systems of changing-density there is no direct correspondence between the batch and plug flow equations and hence one has to use correct equation for each particular situation.

Holding time and Space time for Flow reactors :

One must be aware of the distinction between two measures of time – the holding or mean residence time $(\bar{t})$ and the space time (τ).

$$\tau = \begin{pmatrix}\text{time required to process}\\ \text{one reactor volume}\\ \text{of feed}\end{pmatrix} = \frac{V}{v_o} = \frac{C_{Ao}V}{F_{Ao}}, \text{ (h)}$$

$$\text{holding (time) } \bar{t} = \begin{pmatrix}\text{mean residence time}\\ \text{of flowing material}\\ \text{in the reactor}\end{pmatrix} = C_{Ao}\int_0^{X_A} \frac{dX_A}{(-r_A)(1+\varepsilon_A X_A)}, \text{ (h)}$$

(i) For all constant-density systems (all liquid phase reaction systems and gas phase reaction systems with $\varepsilon_A = 0$),

$$\tau = \bar{t} = V/v$$

(ii) For changing-density systems (variable volume systems),

$$\tau \neq \bar{t} \quad \text{for} \quad \varepsilon_A \neq 0$$

Suppose 1 l/s of gaseous reactant A is introduced into a mixed flow reactor. The stoichiometry is A → 3R, the conversion is 50%, and under these conditions the leaving flow rate is 2 l/s then

$$\text{space time, } \tau_m = \frac{V}{v_o} = \frac{1}{1} = 1\,\text{s}$$

As each element of fluid expands to twice its original volume immediately on entering reactor, the holding time or mean residence time in mixed flow reactor is

$$\bar{t}_m = \frac{V}{v_o(1+\varepsilon_A X_A)} = \frac{V}{v_f}$$

$$\bar{t}_m = \frac{1}{2} = 0.5\,\text{s}$$

$$\bar{t}_m = \frac{V}{v_o(1+\varepsilon_A X_A)}$$

$$\varepsilon_A = \frac{3-1}{1} = 2$$

$$\bar{t}_m = \frac{1}{1\times(1+2\times 0.5)}$$

$$= \frac{1}{2} = 0.5\,\text{s}$$

Suppose the previous conditions are applicable to a plug flow reactor, then

$$\tau_p = \frac{V}{v_o} = \frac{1}{1} = 1\,\text{s}$$

In case of the plug flow reactor as the gas reacts progressively as it passes through the reactor, it expands correspondingly and not immediately on entering and also not all at one time as it leaves the reactor. So in this case

$$\bar{t}_{plug} = 0.5 - 1\,\text{s}$$

For obtaining the precise value of $\bar{t}_{plug}$, the kinetics of reaction must be known.

SOLVED EXAMPLES

Ex. 3.1 : Consider a feed with $C_{Ao} = 100$, $C_{Bo} = 200$ and $C_{io} = 100$ enters a steady flow reactor in which isothermal gas phase reaction $A + 3B \rightarrow 6R$ takes place. Determine C_B, X_B, X_A at the exit of the reactor if C_A at exit is 40.

Solution : $A + 3B \rightarrow 6R$

Isothermal gas phase reaction, so $\varepsilon_A \neq 0$ (changing density system)

Volume of system at $X_A = 0$ is $100\,A + 200\,B + 100\,i = 400$

Volumetric of system of $X_A = 1$ is $0\,A - 100\,B + 600\,R + 100\,i = 600$

$$\varepsilon_A = \frac{600 - 400}{400} = \frac{1}{2} = 0.5$$

Moles of system at $X_A = 0$	Moles of system at $X_A = 1$
$100\,A + 200\,A + 100\,i$	$0\,A + 600\,A + 100\,i - 100\,B$
Total = 400	Total = 600

We are supplied with $C_{Bo} = 200$

For 100 moles of A reacted, 300 moles of B must react. So moles of B at $X_A = 1 = 200 - 300 = -100$.

We have,

$$\frac{a\,\varepsilon_A}{C_{Ao}} = \frac{b\,\varepsilon_B}{C_{Bo}}$$

$$\varepsilon_B = \frac{a\,\varepsilon_A\,C_{Bo}}{b\,C_{Ao}} = \frac{1 \times 0.5 \times 200}{3 \times 100} = \frac{1}{3} = 0.333$$

$$X_A = \frac{1 - C_A/C_{Ao}}{1 + \varepsilon_A\,C_A/C_{Ao}} = \frac{1 - (40/200)}{1 + 0.5\,(40/100)}$$

$$= 0.50 \qquad \text{... Ans.}$$

$$X_B = b\,C_{Ao}\,X_A/a$$

$$= 3 \times 100 \times 0.5/1 = 0.75 \qquad \text{... Ans.}$$

$$C_B = C_{Bo}\left(\frac{1 - X_B}{1 + \varepsilon_B X_B}\right) = \frac{200\,(1 - 0.75)}{1 + \frac{1}{3}(0.75)} = 40 \qquad \text{... Ans.}$$

Ex. 3.2 : Consider a gaseous feed $C_A = 100$, $C_{Bo} = 200$ enters a isothermal flow reactor. For $X_A = 0.8$, find C_A, C_B and X_B.

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

Solution : $A + B \rightarrow R + S$, gas phase reaction

$$V \text{ at } X_A = 0 = 100\,A + 200\,B = 300$$

$$V \text{ at } X_A = 1 = 0\,A + 100\,B + 100\,R + 100\,S = 300$$

$$\varepsilon_A = \frac{300 - 300}{300} = 0$$

$$X_A = 0.80$$

$$\frac{C_A}{C_{Ao}} = \left(\frac{1 - X_A}{1 + \varepsilon_A X_A}\right)$$

$$\therefore \quad C_A = C_{Ao}(1 - X_A) = 100\,(1 - 0.8) = 20 \qquad \text{... Ans.}$$

$$\frac{C_{Ao}\,X_A}{a} = \frac{C_{Bo}\,X_B}{b}$$

$$\therefore \quad X_B = \frac{100 \times 0.8}{200} \times \frac{1}{1} = 0.40 \qquad \text{... Ans.}$$

$$C_B = C_{B_0}\left(\frac{1-X_B}{1+\varepsilon_B X_B}\right)$$

$$\varepsilon_B = 0 \text{ as } \varepsilon_A = 0$$

$$\therefore \quad C_B = C_{B_0}(1-X_B)$$

$$C_B = 200\,(1-0.4) = 120$$ ... **Ans.**

Ex. 3.3 : Consider a gaseous feed at $T_o = 1000$ K, $P_o = 5$ atm, $C_{A_0} = 100$, $C_{B_0} = 200$ enters a flow reactor in which $A + B \rightarrow 5R$ occurs. The product stream leaves the reactor at $T = 400$ K, $P = 4$ atm. With $C_A = 20$, find X_A, C_B, X_B.

Solution : $A + B \rightarrow 5R$, gas phase reaction

V at $X_A = 0 : 100\,A + 200\,B = 300$

V at $X_A = 1 : 0\,A + 100\,B + 500\,R = 600$

$$\varepsilon_A = \frac{600-300}{300} = 2$$

(i) Moles of A and B at $X_A = 0 = 100 + 200 = 300$

Moles of A at $X_A = 1 = 0$

Moles of B at $X_A = 1 = 200 - \frac{1}{1} \times 100 = 100$

Moles of R at $X_A = 1 = \frac{5}{1} \times 100 = 500$

(ii) Total moles at $X_A = 1 = 100 + 500 = 600$

$$X_A = \frac{1-(C_A/C_{A_0})\,(T\,P_o/T_o\,P)}{1+\varepsilon_A \dfrac{C_A}{C_{A_0}}\left(\dfrac{T\,P_o}{T_o\,P}\right)}$$

$$= \frac{1-(20/100)\,(400\times 5/1000\times 4)}{1+2\times\dfrac{20}{100}\left(\dfrac{400\times 5}{1000\times 4}\right)}$$

$$= 0.75$$ ... **Ans.**

$$\frac{C_B}{C_{A_0}} = \frac{(C_{B_0}/C_{A_0}) - b/a\,X_A}{(1+\varepsilon_A X_A)}\left[\frac{T_o\,P}{P_o\,T}\right]$$

$$= \frac{[(200/100)-(1/1)\times 0.75]}{(1+2\times 0.75)}\left[\frac{1000\times 4}{5\times 400}\right]$$

$$C_B = 1\times C_{A_0} = 1\times 100 = 100$$ ... **Ans.**

$$X_B = \frac{\dfrac{C_{B_0}}{C_{A_0}} - \dfrac{C_B}{C_{A_0}}\left(\dfrac{T\,P_o}{T_o\,P}\right)}{\dfrac{b}{a} + \varepsilon_A \dfrac{C_B}{C_{A_0}}\left(\dfrac{T\,P_o}{T_o\,P}\right)}$$

$$= \frac{\left(\dfrac{200}{100}\right) - \left(\dfrac{100}{100}\right)\left(\dfrac{400\times 5}{1000\times 4}\right)}{\dfrac{1}{1} + 2\times\dfrac{100}{100}\left(\dfrac{400\times 5}{1000\times 4}\right)}$$

$$= 0.75$$ ... **Ans.**

Ex. 3.4 : Consider a gas phase reaction $2A = R + 2S$ with unknown kinetics. If for 90% conversion of A in a plug flow reactor the space velocity of 1/min is needed, find the corresponding space time and mean residence time or holding time of a fluid in the reactor.

Solution :

$$2A = R + 2S$$

$$X_A = 0.90$$

$$s = \text{space velocity} = 1\ (\text{min})^{-1}$$

$$s = \frac{V}{v_o} = 1\ \text{min}^{-1}$$

$$\tau = \text{space time} = 1/s = 1/[1\ (\text{min})^{-1}] = 1\ \text{min} \qquad \text{... Ans.}$$

$$\varepsilon_A = \frac{3-2}{2} = 0.5$$

$$X_A = 0.90$$

$$v_f = v_o\,(1 + \varepsilon_A X_A)$$

$$v_f = v_o(1 + 0.5 \times 0.9) = 1.45\ v_o$$

Mean residence time or holding time for immediate expansion of fluid element is given by

$$\bar{t} = \frac{V}{v_f} = \frac{V}{1.45\ v_o} = \frac{1}{1.45} = 0.69\ \text{min}$$

In the plug flow reactor the gas reacts progressively as it passes through reactor, it expands correspondly and therefore

Holding time (Mean residence time) for plug flow is

$$\bar{t}_p = 0.69 \sim 1\ \text{min} \qquad \text{... Ans.}$$

We can determine the precise value of holding time if we know the kinetics of a reaction.

The time required for an element of reaction mixture to flow through an element of volume dV is

$$d\bar{t}_p = \frac{dV}{v_f}$$

For plug flow reactor, we have

$$V = F_{Ao} \int \frac{dX_A}{(-r_A)}$$

$$dV = F_{Ao} \cdot \frac{dX_A}{(-r_A)}$$

$$d\bar{t} = F_{Ao} \cdot \frac{dX_A}{(-r_A)} \times \frac{1}{v_f}, \quad \text{integrating we get}$$

$$\bar{t}_p = F_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)\ v_f}$$

Multiplying and dividing RHS by v_o,

$$\bar{t}_p = F_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)\, v_f} \times \frac{v_o}{v_o}$$

we have $\quad F_{Ao} = C_{Ao} \cdot v_o \qquad \therefore\ C_{Ao} = F_{Ao}/v_o$

$$\bar{t}_p = \frac{F_{Ao}}{v_o} \int_0^{X_A} v_o \cdot \frac{dX_A}{(-r_A)\, v_f}$$

$$\bar{t}_p = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)\, v_f/v_o}$$

We have, $\quad v_f = v_o(1+\varepsilon_A X_A)$

$\therefore \quad v_f/v_o = (1+\varepsilon_A X_A) = (1+0.5\, X_A)$

$X_A = 0.90$

$$\boxed{\therefore \quad \bar{t}_p = C_{Ao} \int_0^{0.90} \frac{dX_A}{(-r_A)\,(1+0.5\, X_A)}}$$

With this equation knowing kinetics we can calculate precise value of holding time o mean residence time of fluid in the plug flow reactor.

If it is a back mix/mixed flow reactor then :

For back mix reactor,

$$\bar{t}_m = \frac{V}{v_f} = \frac{V}{v_o\,(1+\varepsilon_A X_A)}$$

$$\bar{t}_m = \frac{1}{(1+0.5\times 0.90)}, \quad \text{as} \quad \tau_m = \frac{V}{v_o} = 1 \text{ min}$$

$$= 0.69 \text{ min}$$

... **Ans.**

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Ex. 3.5 : In an isothermal batch reactor 70% of a reactant A is converted in 13 minutes. Find the space time and space velocity needed to effect this conversion in a plug flow reactor and in a mixed flow reactor.

Solution : First order kinetics is considered.

For batch reactor :

$$-\ln(1-X_A) = kt$$

$$X_A = 0.70, \quad t = 13 \text{ min}$$

$$\therefore \quad -\ln(1-0.70) = k \times 13$$

$$k = 0.0926\ (\text{min})^{-1}$$

For mixed flow reactor :

$$\tau = \frac{C_{Ao} X_A}{(-r_A)}$$

$$\tau = \frac{C_{Ao}\cdot X_A}{kC_A} = \frac{C_{Ao}\cdot X_A}{k\, C_{Ao}(1-X_A)}$$

$$= \frac{X_A}{k\,(1-X_A)}$$

$$= \frac{0.70}{0.0926\,(1-0.7)} = 25.2 \text{ min}$$

... **Ans.**

For plug flow reactor for constant density :

$$\tau_p = \text{t for batch reactor} = 13 \text{ min}$$

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\tau = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)} = C_{Ao} \int_0^{X_A} \frac{dX_A}{k\, C_{Ao}\,(1 - X_A)} = \int_0^{X_A} \frac{dX_A}{k\,(1 - X_A)}$$

$$\tau = \frac{1}{k}\,[-\ln (1 - X_A)]_0^{0.7} = \frac{1}{0.0926}\,[-\ln (1 - 0.7)]$$

$$= 13 \text{ min}$$

... **Ans.**

Ex. 3.6 : We are planning to operate a batch reactor for converting A into R. This is a liquid phase reaction with stoichiometry A → R. How long must we react each batch for concentration to drop from $C_{Ao} = 1.3$ mol/*l* to $C_{Af} = 0.30$ mol/*l* ? The data of rate of reaction v/s concentration of A is given below :

C_A, mol/*l*	$-r_A$, mol/(*l*.min)
0.1	0.1
0.2	0.3
0.3	0.5
0.4	0.6
0.5	0.5
0.6	0.25
0.7	0.10
0.8	0.06
1.0	0.05
1.3	0.045
2.0	0.042

Solution : For batch reactor, we have

$$t = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$= -\int_{C_{Ao}}^{C_A} \frac{dC_A}{(-r_A)} = \int_{C_A}^{C_{Ao}} \frac{dC_A}{(-r_A)}$$

So we have to plot $\frac{1}{(-r_A)}$ versus C_A. The time 't' required will be obtained from this plot as it is the area bounded by the curve and x-axis between $C_A = 1.3$ and $C_A = 0.3$ mol/*l*.

C_A	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0	1.3	2.0
$-r_A$	0.1	0.3	0.5	0.6	0.5	0.25	0.1	0.06	0.05	0.045	0.042
$\frac{1}{(-r_A)}$	10	3.33	2	1.66	2	4	10	16.67	20	22.22	23.80

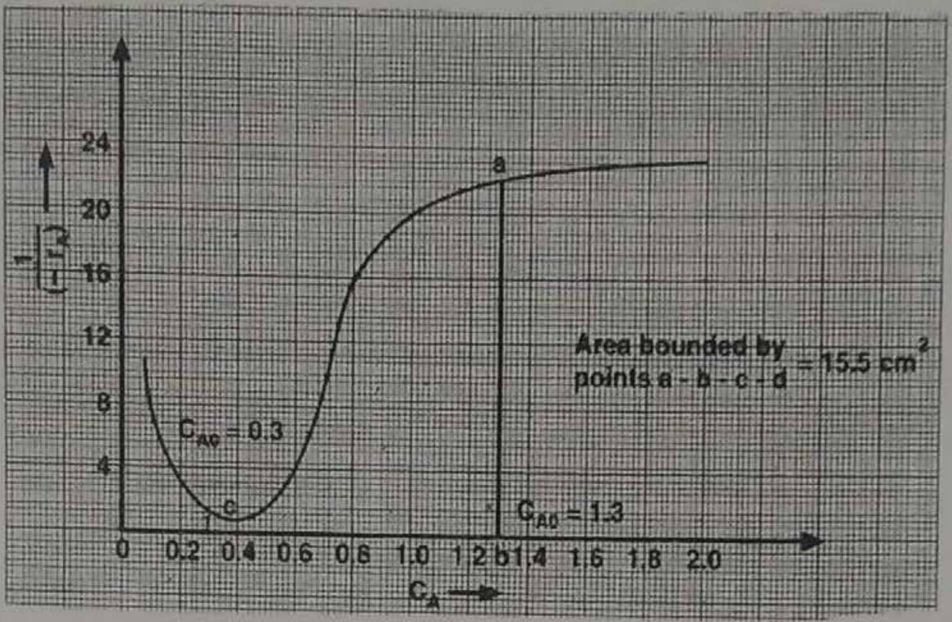

Fig. E 3.6

For batch reactor :

t = time required to drop concentration from 1.3 to 0.03 mol/l in batch reactor

$$t = \left(\begin{array}{l}\text{Area bounded by} \\ \text{points a - b - c - d}\end{array}\right) \times (\text{Scale x-axis}) \times (\text{Scale y-axis})$$

$$= 15.5 \times \frac{0.2}{1} \times \frac{4}{1}$$

$$= 12.4 \text{ min}$$

... **Ans.**

Ex. 3.7 : For the reaction of Ex. 3.6, determine the size of plug flow reactor that would be needed for 80% conversion of a feed stream of 1000 mol A/h at $C_{Ao} = 1.5$ mol/l.

Solution : For plug flow reactor :

$$\frac{V}{F_{Ao}} = \frac{-1}{C_{Ao}} \int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{(-r_A)}$$

Initial concentration of A and conversion level is :

$$C_{Ao} = 1.5 \text{ mol}/l \ , \ X_A = 0.80$$

Final concentration of A is obtained as

$$C_{Af} = C_{Ao}(1 - X_A)$$

$$= 1.5(1 - 0.8) = 0.30 \text{ mol}/l$$

$$F_{Ao} = 1000 \text{ mol A/h}$$

$= 16.67$ mol/min as the rate of reaction is given in mol/(l·min)

$$V = \frac{F_{Ao}}{C_{Ao}} \int_{C_{Af}}^{C_{Ao}} \frac{dC_A}{(-r_A)}$$

$$V = \frac{16.67}{1.5} \int_{C_{Af}}^{C_{Ao}} \frac{dC_A}{(-r_A)}$$

Plot a graph of $1/(-r_A)$ v/s C_A and find the value of integral on RHS as area under the curve between $C_{Ao} = 1.5$ and $C_{Af} = 0.3$ mol/*l*.

C_A	0.1	0.2	0.4	0.5	0.6	0.7	0.8	1.0	1.3	2.0
$-r_A$	0.1	0.3	0.6	0.5	0.25	0.1	0.06	0.05	0.045	0.042
$1/(-r_A)$	10	3.33	1.67	2	4	10	16.67	20	22.22	23.80

For plug flow reactor :

$$\tau = \frac{V\,C_{Ao}}{F_{Ao}} = -\int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{(-r_A)}$$

Plot $1/(-r_A)$ v/s C_A. This plot gives value of integral on R.H.S. which is equal to τ. The value of τ is equal to the area under the curve bounded by curve and x-axis within $C_{Af} = 0.3$ and $C_{Ao} = 1.5$ mol/*l*.

$$\tau = \frac{V\,C_{Ao}}{F_{Ao}} = \text{Area} \times \text{Scale y-axis} \times \text{Scale x-axis}$$

$$\frac{V\,C_{Ao}}{F_{Ao}} = 43.15 \times \frac{2}{1} \times \frac{0.2}{1}$$

$$\frac{V\,C_{Ao}}{F_{Ao}} = 17.26 \text{ min}$$

$$V = 17.26 \times \frac{F_{Ao}}{C_{Ao}} = 17.26 \times \frac{16.67}{1.5}$$

$$= 191.8\, l$$

... Ans.

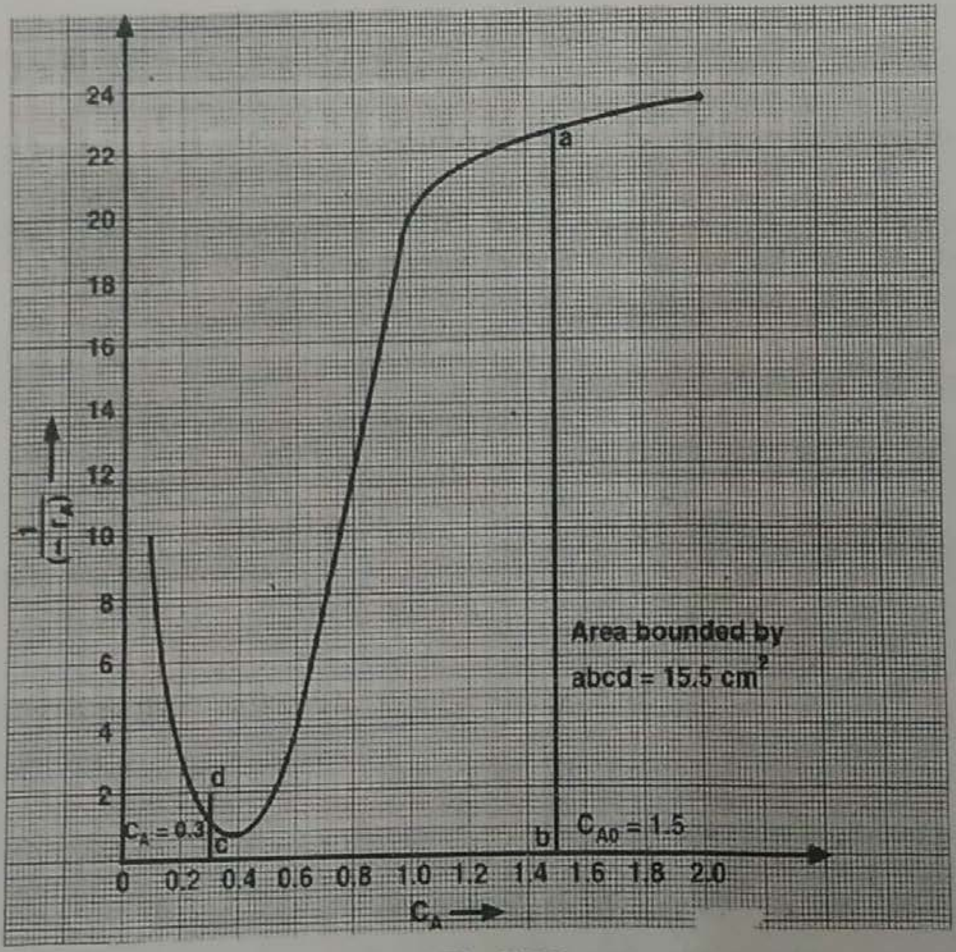

Fig. E 3.7

Ex. 3.6 : (a) We are planning to operate a mixed reactor to convert A into R. This is a liquid reaction, with the stoichiometry A → R. The rate of reaction is given in table below. What size of mixed flow reactor is needed for 75% conversion of a feed stream of 1000 molA/h at $C_{A0} = 1.2$ mol/l ?

(b) Repeat part (a) with the modification that the feed rate is doubled, hence 2000 mol A/h at $C_{A0} = 1.20$ mol/l are treated.

(c) Repeat part (a) with the modification that $C_{A0} = 2.4$ mol/l; however, 1000 mol A/h are still to be treated down to $C_{Af} = 0.30$ mol/l.

Data :

C_A, mol/l	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0	1.3	2.0
$-r_A$, mol/(l·min)	0.1	0.3	0.5	0.6	0.5	0.25	0.1	0.06	0.05	0.045	0.042

Solution : For mixed flow reactor, we have,

$$\tau = \frac{V}{v_o} = \frac{V\,C_{A0}}{F_{A0}} = \frac{C_{A0} - C_A}{-r_A}$$

Initial concentration of A = C_{A0} = 1.2 mol/l

Given, $X_A = 0.75$

$$\therefore \quad C_A = C_{A0}\,(1 - X_A)$$
$$= 1.2\,(1 - 0.75) = 0.3 \text{ mol}/l$$

So we have to plot a graph of $\frac{1}{(-r_A)}$ versus C_A in order to get the value of τ and V.

C_A	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	1.0	1.3	2.0
$-r_A$	0.1	0.3	0.5	0.6	0.5	0.25	0.1	0.06	0.05	0.045	0.042
$\frac{1}{(-r_A)}$	10	3.33	2	1.66	2	4	10	16.67	20	22.22	23.80

(a) $C_{A0} = 1.2$ mol/l , $C_A = 0.3$ mol/l

$$\tau = \frac{V \cdot C_{A0}}{F_{A0}} = (C_{A0} - C_A) \times \left(\frac{1}{-r_A}\right)$$

From $C_A = 0.3$ mol/l draw the vertical, which will cut a curve at A then draw a horizontal line through A upto $C_{A0} = 1.2$ mol/l.

$C_A = 0.30$ mol/l is the concentration of A within the reactor as well as at exit from reactor.

From graph,

$$\text{Area} = 4.5 \text{ cm}^2$$
$$\tau = \text{Area} \times (\text{Scale y-axis}) \times (\text{Scale x-axis})$$
$$= 4.5 \times \frac{2}{1} \times \frac{0.2}{1}$$
$$= 1.8 \text{ min}$$
$$F_{A0} = 1000 \text{ mol A/h} = 16.67 \text{ mol A/min}$$
$$\frac{V\,C_{A0}}{F_{A0}} = 1.8 \text{ min}$$
$$V = 1.8\,F_{A0}/C_{A0}$$
$$= 1.8 \times 16.67/1.2$$
$$= 25\,l$$

Volume of mixed flow reactor required = 25 l ... **Ans. (a)**

Refer Fig. E 3.8 (1) for part (a) and (b)

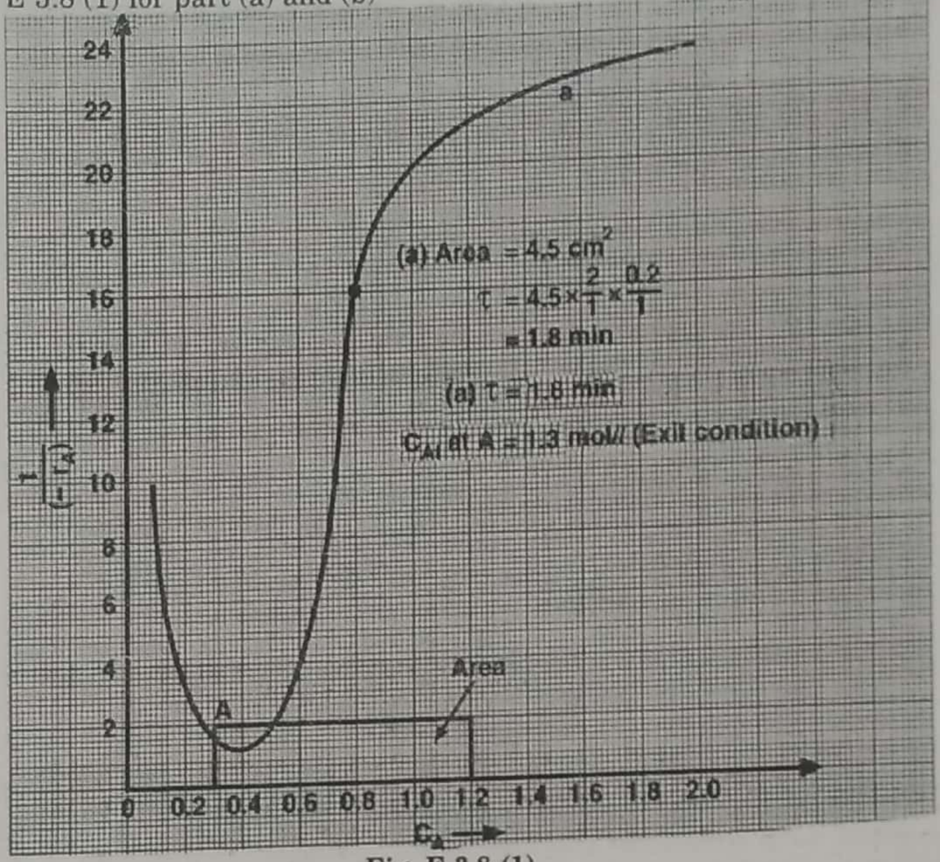

Fig. E 3.8 (1)

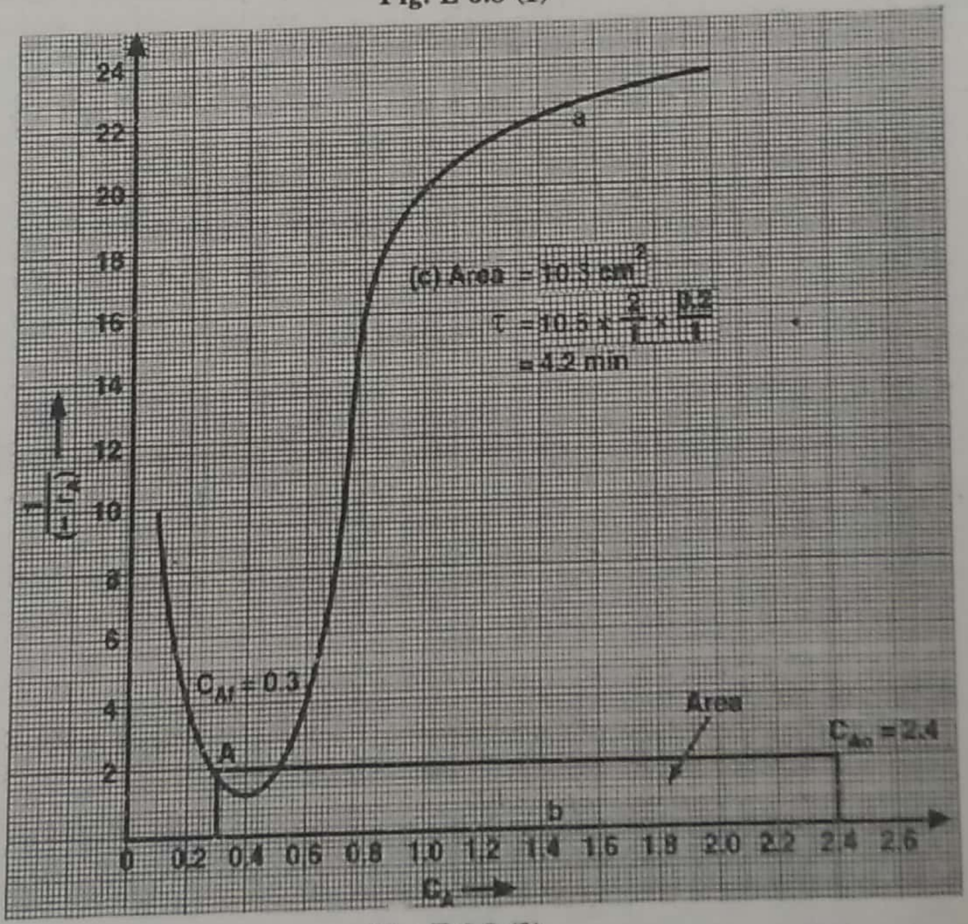

Fig. E 3.8 (2)

(b)

$$F_{Ao} = 2000 \text{ mol A/h} = 33.33 \text{ mol/min}$$

$$C_{Ao} = 1.2 \text{ mol}/l$$

$$\text{Conversion} = 75\% \quad \therefore \quad C_{Af} = 0.30 \text{ mol}/l$$

$$\therefore \quad \tau = 1.8 \text{ min} \quad [\text{same as in part (a)}]$$

$$\frac{V\,C_{Ao}}{F_{Ao}} = 1.8$$

$$V = 1.8 \times 33.33/1.2$$

$$= 50\,l$$

... **Ans. (b)**

(c)

$$C_{Ao} = 2.4 \text{ mol}/l, \quad C_{Af} = 0.3 \text{ mol}/l$$

So τ is equal to the area of rectangle from $C_{Af} = 0.3$ mol/l to $C_{Ao} = 2.4$ mol/l

Height of rectangle is the height of vertical drawn from $C_{Af} = 0.3$ mol/l from x-axis.

$$\tau = \text{Area} \times (\text{Scale y-axis}) \times (\text{Scale x-axis})$$

$$= 10.5 \times \frac{2}{1} \times \frac{0.2}{1}$$

$$= 4.2 \text{ min}$$

$$F_{Ao} = 1000 \text{ mol A/h} = 16.67 \text{ mol/min}$$

$$V = \frac{4.2\,F_{Ao}}{C_{Ao}}$$

$$= \frac{4.2 \times 16.67}{2.4}$$

$$= 29.2\,l$$

Volume of mixed flow reactor required = 29.2 l ... **Ans. (c)**

Ex. 3.9 : One gaseous feed stream containing A with $C'_{Ao} = 0.01$ mol/l at a rate of 1 l/min and second gaseous stream containing B with $C'_{Bo} = 0.02$ mol/l at a rate of 3 l/min enter a mixed flow reactor of volume 1 litre and react to form number of products R, S, T .... Analysis of the outgoing stream of 6 l/min shows that $C_{Af} = 0.0005$ mol/l and $C_{Rf} = 0.001$ mol/l . All measurements of flow rate and concentrations are done at the uniform temperature and pressure of the reactor. Estimate the rate of reaction of A and rate of formation of R in the reactor.

Solution : $A + B \rightarrow R + S + T + \ldots$

$$C'_{Ao} = 0.01 \text{ mol}/l, \quad C'_{Bo} = 0.02 \text{ mol}/l$$

$$V = 1 \text{ litre}$$

$$v_f = 6\ l/\text{min}$$

$$C_{Af} = 0.0005 \text{ mol}/l$$

$$C_{Rf} = 0.001 \text{ mol}/l$$

$$(v_o)_A = 1\ l/\text{min}$$

$$(v_o)_B = 3\ l/\text{min}$$

$$v_o = 1 + 3 = 4\ l/\text{min}$$

For mixed flow reactor :

$$\tau = \frac{C_{Ao}\,X_A}{(-r_A)}$$

$$v_f = v_o(1 + \varepsilon_A X_A)$$

$$6 = 4(1 + \varepsilon_A X_A)$$

$$\therefore \quad \varepsilon_A X_A = 0.50$$

Concentration of A in stream entering the reactor is

$$C_{Ao} = C'_{Ao} \times \frac{1}{4}$$

$$= 0.01/4$$

$$= 0.0025 \text{ mol}/l$$

$$C_A = \frac{C_{Ao}(1 - X_A)}{(1 + \varepsilon_A X_A)}$$

$$0.0005 = \frac{0.0025(1 - X_A)}{(1 + 0.5)}$$

$$X_A = 0.70$$

$\tau = V/v_o = 1/4 = 0.25$ min

$$\tau = \frac{C_{Ao} X_A}{(-r_A)}$$

$$(-r_A) = \frac{C_{Ao} X_A}{\tau} = \frac{0.0025 \times 0.7}{0.25}$$

$$= 0.007 \text{ mol}/(l.\text{min})$$ ... Ans

$$r_R = \frac{C_R - C_{Ro}}{\tau}$$

$$C_R = C_{Rf} = 0.001 \text{ mol}/l, \quad C_{Ro} = 0$$

$$r_R = \frac{0.001}{0.25} = 0.004 \text{ mol}/(l.\text{min})$$ ... Ans

B **Ex. 3.10 :** A homogeneous liquid phase reaction

$$A \rightarrow S, \quad -r_A = k C_A^2$$

takes place with 50% conversion in a mixed flow reactor.

3 (i) What will be the conversion if this reactor is replaced by another mixed flow reactor having volume 6 times that of original reactor – all else remain unchanged ?

(ii) What will be the conversion if the original reactor is replaced by a plug flow reactor of same size – all else remain unchanged ?

Solution : $A \rightarrow S$

$$-r_A = k C_A^2, \quad \text{second order kinetics}$$

For mixed flow reactor :

$$\tau = \frac{V}{v_o} = \frac{C_{Ao} X_A}{(-r_A)}$$

$$\tau = \frac{C_{Ao} \cdot X_A}{k C_A^2}$$

$$\tau = \frac{C_{Ao} X_A}{k [C_{Ao}(1 - X_A)]^2}$$

$$\tau = \frac{X_A}{k C_{Ao} (1 - X_A)^2}$$

$$X_A = 0.50$$

$$\tau = \frac{V}{v_o} = \frac{0.50}{k C_{Ao} (1 - 0.50)^2}$$

$$k = 2 v_o / C_{Ao} V$$

(i)

$$V' = \text{volume of new mixed flow reactor}$$

$$V' = 6\,V, \quad V = \text{volume of original reactor.}$$

$$\tau = \frac{V'}{v_o} = \frac{C_{Ao}\,X_A}{-r_A}$$

$$\frac{V'}{v_o} = \frac{C_{Ao}\,X_A}{k\,C_{Ao}^2\,(1-X_A)^2}$$

$$\frac{V'}{v_o} = \frac{X_A}{k\,C_{Ao}\,(1-X_A)^2}$$

$$\frac{k\,C_{Ao}\,V'}{v_o} = \frac{X_A}{(1-X_A)^2}$$

But $V' = 6\,V$

$\therefore$ $$\frac{k\,C_{Ao}\,(6\,V)}{v_o} = \frac{X_A}{(1-X_A)^2}$$

We have, $k = 2\,v_o/C_{Ao}V$

$$\frac{2\,v_o}{C_{Ao}\,V} \times \frac{C_{Ao}\,(6\,V)}{v_o} = \frac{X_A}{(1-X_A)^2}$$

$$12 = \frac{X_A}{(1-X_A)^2}$$

$$12\,X_A^2 - 25\,X_A + 12 = 0$$

$$X_A = \frac{25 \pm [(25)^2 - 4 \times 12 \times 12]^{1/2}}{2 \times 12}$$

$$= \frac{25 \pm 7}{24}$$

$\therefore$ $X_A = 0.75$

Conversion in new mixed flow reactor = 75% ... **Ans. (i)**

(ii) For plug flow reactor, we have

$$\frac{V}{v_o} = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\frac{V}{v_o} = C_{Ao} \int_0^{X_A} \frac{dX_A}{k\,C_{Ao}^2\,(1-X_A)^2} \quad \text{as } -r_A = k\,C_A^2$$

$$\frac{V}{v_o} = \frac{1}{k\,C_{Ao}} \left[\frac{X_A}{1-X_A}\right]$$

$$kC_{Ao}\frac{V}{v_o} = \frac{X_A}{1-X_A}$$

$$\frac{2\,v_o}{C_{Ao}\,V} \times C_{Ao} \times \frac{V}{v_o} = \frac{X_A}{1-X_A}$$

$$\frac{X_A}{1-X_A} = 2$$

$\therefore$ $X_A = 0.67$

OR

For mixed flow reactor, we have

$$k = 2 v_o / C_{Ao} V$$

$$\therefore \quad \tau k C_{Ao} = 2, \qquad \tau_p = \tau_m = \tau$$

For plug flow reactor,

$$\tau = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\tau = C_{Ao} \int_0^{X_A} \frac{dX_A}{k\, C_{Ao}^2 (1 - X_A)^2}$$

$$k \tau C_{Ao} = \int_0^{X_A} \frac{dX_A}{(1 - X_A)^2}$$

But

$$\tau k C_{Ao} = 2$$

$$\therefore \quad 2 = \int_0^{X_A} \frac{dX_A}{(1 - X_A)^2} = \frac{X_A}{1 - X_A}$$

$$\therefore \quad X_A = 0.67$$

$\therefore$ Conversion in plug flow of same size = 67%. ... **Ans. (ii)**

Ex. 3.11 : Assuming a stoichiometry A → R for a first order gas phase reaction, the size (volume) of a plug flow reactor for 99% conversion of pure A is calculated to be 32 litres. In fact, however, the reaction stoichiometry is A → 3R. With this corrected stoichiometry, what is the required volume of a reactor ?

Solution : $A \rightarrow R, \quad -r_A = k C_A$

$$\varepsilon_A = \frac{1-1}{1} = 0$$

For plug flow reactor :

$$\frac{V}{v_o} = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$-r_A = k C_A = k C_{Ao} (1 - X_A)$$

$$\frac{V}{v_o} = C_{Ao} \int_0^{X_A} \frac{dX_A}{k C_{Ao} (1 - X_A)}$$

$$\frac{V}{v_o} = \frac{1}{k} \ln \left(\frac{1}{1 - X_A} \right)$$

$$X_A = 0.99 \quad \text{and} \quad V = 32\, l$$

$$\frac{32}{v_o} = \frac{1}{k} \ln \left(\frac{1}{1 - 0.99} \right)$$

$$\therefore \quad k/v_o = 0.144$$

For corrected stoichiometry

$$A \rightarrow 3R$$

we have,

$$k/v_o = 0.144, \qquad X_A = 0.99$$

$$\varepsilon_A = \frac{3-1}{1} = 2$$

For variable volume,

$$\frac{C_A}{C_{A_0}} = \frac{1-X_A}{1+\varepsilon_A X_A}$$

$$\therefore \quad C_A = \frac{C_{A_0}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$$\therefore \quad \frac{V}{v_0} = C_{A_0}\int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\frac{V}{v_0} = C_{A_0}\int_0^{X_A} \frac{dX_A}{k\,C_{A_0}(1-X_A)/(1+\varepsilon_A X_A)}$$

$$V\,(k/v_0) = \int_0^{X_A} \frac{dX_A}{(1-X_A)} + \varepsilon_A \int_0^{X_A} \frac{X_A \cdot dX_A}{(1-X_A)}$$

$$V\,(k/v_0) = \ln\left[\frac{1}{1-X_A}\right] + \varepsilon_A\left[\ln\left(\frac{1}{1-X_A}\right) - X_A\right]$$

$$X_A = 0.99, \quad k/v_0 = 0.144$$

$$V \times 0.144 = \ln\left[\frac{1}{1-0.99}\right] + 2\left[\ln\left(\frac{1}{1-0.99}\right) - 0.99\right]$$

$$V = 82.2\,l$$

Reactor volume with corrected reaction stoichiometry = 82.2 *l* ... **Ans.**

Ex. 3.12. A high molecular weight hydrocarbon stream A is continuously fed to a heated high temperature mixed flow reactor where it thermally cracks into lower molecular materials, collectively called R, as per the reaction A → 5R. It is a homogeneous gas phase reaction. The different extents of cracking obtained by varying the feed rate to the reactor are as follows :

F_{A_0}, millimol/h	300	1000	3000	5000
$C_{A,\text{out}}$, millimol/*l*	16	30	50	60

The reactor volume is V = 0.1 litre, and feed concentration at the temperature of reactor is C_{A_0} = 100 millimol/*l*. Find a rate equation which satisfactorily represents the cracking reaction.

Solution : A → 5 R, (gas phase reaction)

$$\therefore \quad \varepsilon_A = \frac{5-1}{1} = 4$$

$$C_{A_0} = 100 \text{ millimol}/l, \quad V = 0.1\,l$$

For variable volume system :

$$C_A = \frac{C_{A_0}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$$\therefore \quad X_A = \frac{1 - C_A/C_{A_0}}{1 + \varepsilon_A C_A/C_{A_0}}$$

$$X_A = \frac{1 - C_A/C_{A_0}}{1 + 4\, C_A/C_{A_0}}$$

For mixed flow reactor :

$$\tau = \frac{C_{A_0} X_A}{(-r_A)}$$

$$\frac{V}{F_{A_0}} = \frac{X_A}{(-r_A)}$$

$$(-r_A) = \frac{F_{A_0} X_A}{V}, \quad \text{millimol}/(l\cdot h)$$

Calculate $-r_A$ for the data given using above equation and tabulate.

For $C_A = 16$ millimol/l, $C_{A_0} = 100$ millimol/l

$$\therefore \quad X_A = \frac{1-(16/100)}{1+4\,(16/100)} = 0.512$$

$$(-r_A) = \frac{300 \times 0.512}{0.1}$$

$$= 1536 \ \text{millimol}/(l\cdot h)$$

F_{A_0}	$C_{A,\text{out}}$	X_A	$(-r_A)$
300	16	0.512	1536
1000	30	0.318	3180
3000	50	0.167	5010
5000	60	0.117	5850

Assume rate equation :

$$(-r_A) = k\, C_A^n$$

$$\ln\,(-r_A) = \ln k + n \ln C_A$$

Plot of $\ln(-r_A)$ v/s $\ln C_A$ yields a straight line with slope equal to n and intercept equal to ln k.

C_A	$\ln C_A$	$(-r_A)$	$\ln\,(-r_A)$
16	2.8	1536	7.34
30	3.40	3180	8.10
50	3.91	5010	8.52
60	4.10	5850	8.70

From graph : n = 1.08 and k = 73.7.

∴ Rate equation is

$$(-r_A) = 73.7\ C_A^{1.08}$$ ... **Ans.**

Note that slight error in drawing straight line through points leads to large variation in value of slope (n) and intercept.

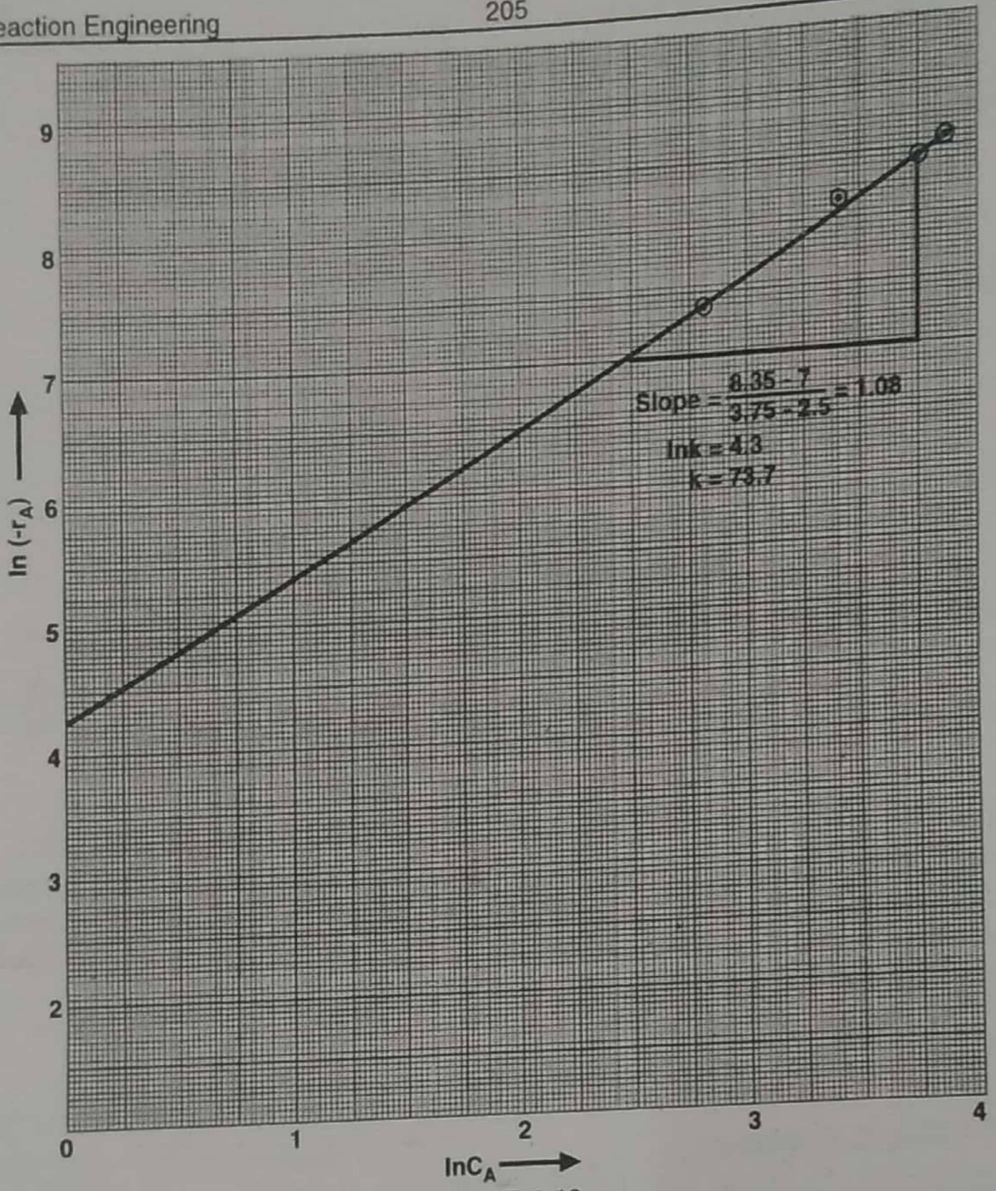

Fig. E 3.12

Ex. 3.13 : In Ex. 3.12 if we ignore the density change i.e. if we assume ε_A = 0 then what wil be the reaction order and rate equation ?

Solution :

$$A \rightarrow 5R$$

$$\varepsilon_A = 0$$

For constant density, $C_A = C_{A0}(1-X_A)$

$$\therefore \quad X_A = \frac{C_{A0}-C_A}{C_{A0}}$$

Calculate $-r_A$ and tabulate.

$$C_{A0} = 100 \text{ millimol}/l, \quad C_A = 16 \text{ millimol}/l$$

$$X_A = \frac{100-16}{100} = 0.84$$

$$(-r_A) = \frac{F_{A0}\cdot X_A}{V}$$

$$(-r_A) = \frac{300\times 0.84}{0.10} = 2520 \text{ millimol}/(l\cdot h)$$

C_A	$\ln C_A$	$(-r_A)$	$\ln(-r_A)$	F_{A_0}	X_A
16	2.80	2520	7.83	300	0.84
30	3.40	7000	8.85	1000	0.70
50	3.91	15000	9.61	3000	0.50
60	4.10	20000	9.9	5000	0.40

Plot a graph of $\ln(-r_A)$ v/s $\ln C_A$.

From graph, n = 1.6 and k = 29.22

Order of reaction = n = 1.6 ... **Ans.**

∴ Rate equation is $(-r_A) = 29.22\ C_A^{1.6}$ ... **Ans.**

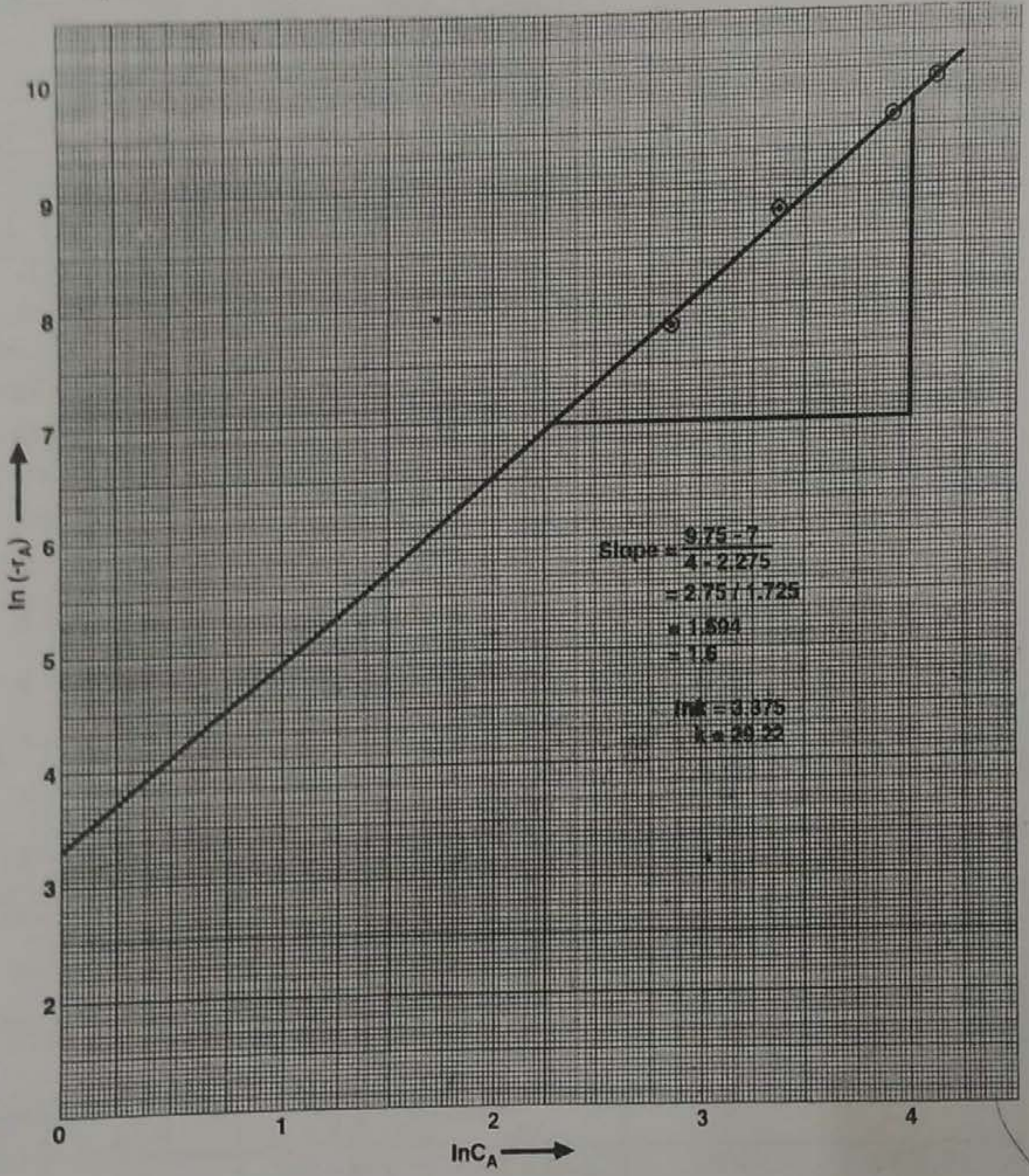

Fig. E 3.13

Ex. 3.14. The liquid phase decomposition of A is studied in an experimental mixed reactor. The results of steady state runs are tabulated below, In order to obtain 75% conversion of reactant in a feed, C_{A_0} = 0.8 mol/*l*, what holding time is required (i) in a plug flow reactor, (ii) in a mixed flow reactor ?

Concentration of A, mol/*l*		Holding time seconds
In feed	**In exit stream**	
2.00	0.65	300
2.00	0.92	240
2.00	1.00	250
1.00	0.56	110
1.00	0.37	360
0.48	0.42	24
0.48	0.28	200
0.48	0.20	560

Solution : A → Products, liquid phase reaction

$$C_{A_0} = 0.8 \text{ mol}/l$$

For mixed flow reactor :

$$\frac{\tau}{C_{A_0}} = \frac{X_A}{(-r_A)}$$

$$\tau = \frac{C_{A_0} - C_A}{(-r_A)}$$

$$\therefore \quad \frac{1}{(-r_A)} = \frac{\tau}{C_{A_0} - C_A}$$

$$X_A = 0.75$$

$$C_{Af} = C_A = C_{A_0}(1 - X_A) = 0.8\,(1 - 0.75) = 0.2 \text{ mol}/l$$

We have,

$$\frac{1}{(-r_A)} = \tau/(C_{A_0} - C_A)$$

$$C_A = 0.65,\ C_{A_0} = 2.0 \text{ mol}/l,\ \tau = 300 \text{ s}$$

$$1/(-r_A) = 300/(0.8 - 0.65) = 222.22$$

$$C_A = 0.92,\ C_{A_0} = 2.0 \text{ mol}/l,\ \tau = 240 \text{ s}$$

$$\frac{1}{(-r_A)} = \frac{240}{2 - 0.92} = 222.22$$

C_A	$1/(-r_A)$
0.65	222.22
0.92	222.22
1.0	250
0.56	250
0.37	571
0.42	400
0.28	1000
0.20	2000

$$C_{Af} = 0.20 \text{ mol}/l \quad \text{and} \quad C_{A_0} = 0.8 \text{ mol}/l$$

From graph of $1/(-r_A)$ v/s C_A :

For mixed flow reactor : $\tau = \bar{t} =$ Area × (Scale y-axis) × (Scale x-axis)

$$= 120 \times \frac{100}{1} \times \frac{0.10}{1} = 1200 \text{ s} \qquad \text{... Ans.}$$

For plug flow reactor : $\tau = \bar{t} =$ Area × (Scale y-axis) × (Scale x-axis)

$$= 29 \times \frac{100}{1} \times \frac{0.10}{1} = 290 \text{ s} \qquad \text{... Ans.}$$

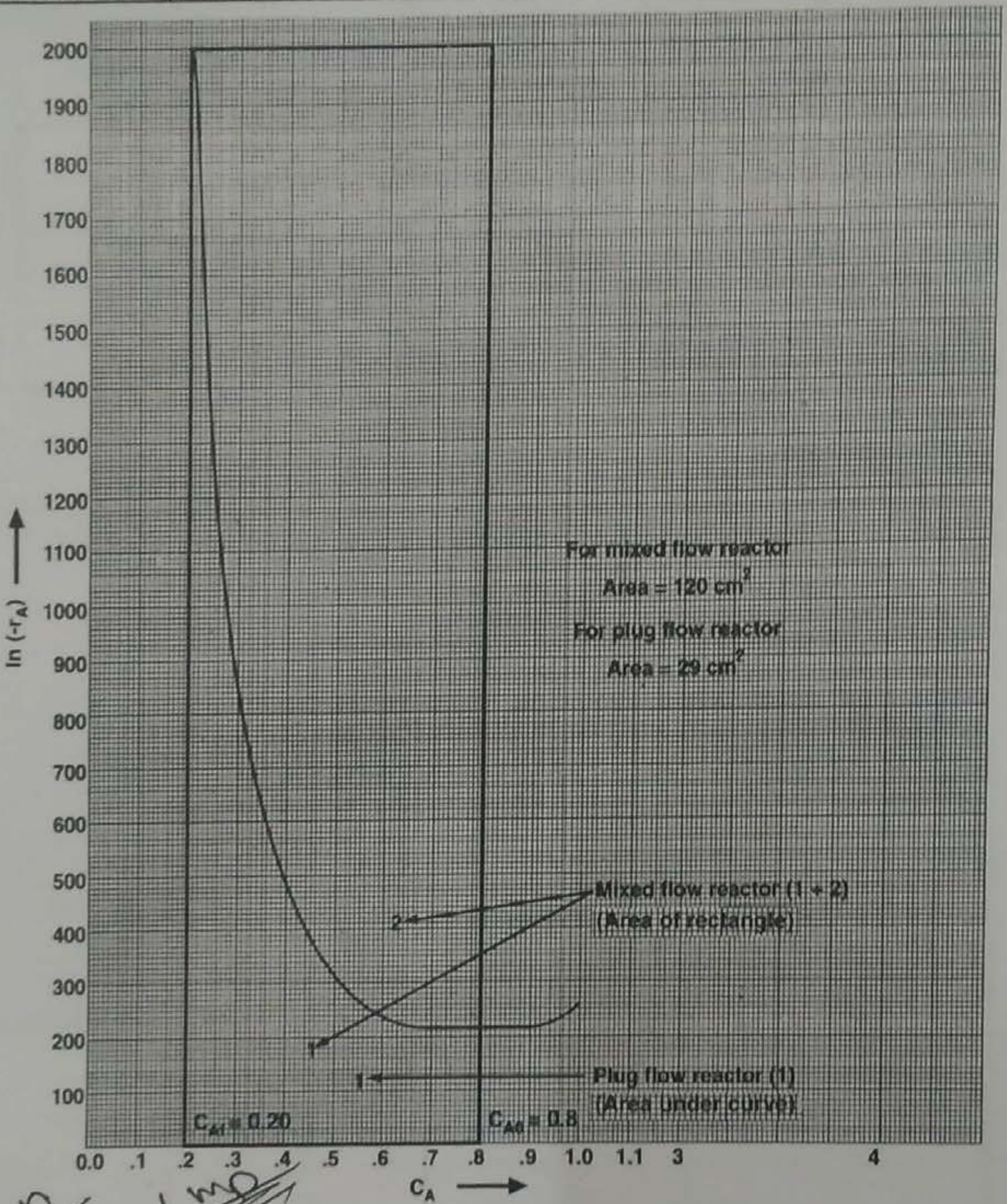

Fig. E 3.14

Ex. 3.15 : Find a rate equation for the gas phase decomposition A → R + S occurring isothermally in a mixed flow reactor from the following data :

Run number	1	2	3	4	5
τ based on inlet feed condition in seconds	0.423	5.10	13.5	44	192
X_A	0.22	0.63	0.75	0.88	0.96

X_A values given for $C_{A0} = 0.002$ mol/l

Solution : $A \rightarrow R + S$, gas phase reaction

$$\varepsilon_A = \frac{2-1}{1} = 1$$

$$C_A = \frac{C_{A0}(1 - X_A)}{1 + \varepsilon_A X_A} = \frac{C_{A0}(1 - X_A)}{(1 + X_A)}$$

For mixed flow reactor :

$$\tau = \frac{C_{A0} X_A}{(-r_A)}$$

$$(-r_A) = \frac{C_{A0} X_A}{\tau}$$

Evaluate C_A and $-r_A$ for the data provided.

$$C_{A0} = 0.002 \text{ mol}/l, \quad C_A = ?, \quad X_A = 0.22$$

$$C_A = \frac{C_{A0}(1 - X_A)}{(1 + X_A)}$$

$$= \frac{0.002\,(1 - 0.22)}{(1 + 0.22)} = 1.28 \times 10^{-3} \text{ mol}/l$$

$$(-r_A) = C_{A0}\, X_A/\tau = 0.002 \times 0.22/0.423$$

$$= 1.04 \times 10^{-3} \text{ mol}/(l \cdot s)$$

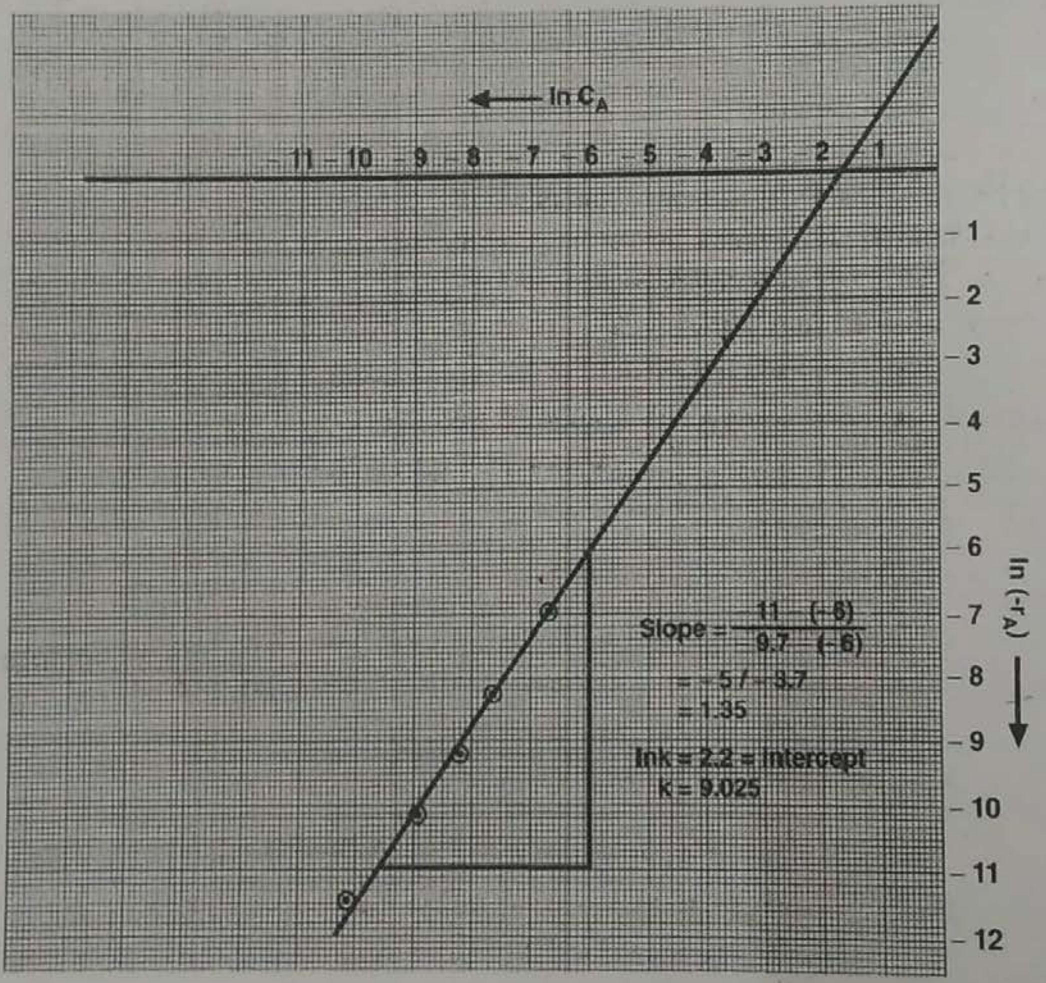

Fig. E 3.15

τ	X_A	C_A	$(-r_A)$	ln C_A	ln $(-r_A)$
0.423	0.22	1.28×10^{-3}	1.04×10^{-3}	– 6.7	– 6.87
5.10	0.63	4.54×10^{-4}	2.47×10^{-4}	– 7.7	– 8.31
13.5	0.75	2.86×10^{-4}	1.11×10^{-4}	– 8.16	– 9.1
44	0.88	1.28×10^{-4}	4×10^{-5}	– 8.96	– 10.13
192	0.96	4.98×10^{-5}	1×10^{-5}	– 10.11	– 11.51

Rate equation is

$$(-r_A) = k\,C_A^n$$

$$\ln(-r_A) = n \ln C_A + \ln k$$

Plot a graph of $\ln(-r_A)$ v/s $\ln C_A$. The slope is equal to order of reaction (n) and intercept equal to ln k.

From graph :

$$n = \text{slope} = 1.35$$

$$\ln k = 2.2$$

$$k = 9.025 \quad (l/\text{mol})^{-0.35}\,(\text{s})^{-1}$$

$\frac{3-1}{1} = (2) \times 0.6$

$= 1.2$

The required rate equation is

$$-r_A = 9.025\ [(l/\text{mol})^{-0.35}\,(\text{s})^{-1}]\ C_A^{1.35}\ ,\quad \text{mol}/(l\cdot\text{s})$$ **... Ans.**

Ex. 3.16 : A homogeneous gas phase reaction A → 3R satisfactorily follows second order kinetics. For a feed rate of 4 m³/h of pure A at 350 °C and 5 atm, an experimental reactor (25 mm ID pipe × 2 m length) gives 60% conversion of feed. A commercial plant is to handle 320 m³/h of feed containing 50 mole % A and 50 mole % inerts at 350 °C and 25 atm for obtaining 80% conversion of A.

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(i) How many 2 m lengths of 25 mm ID pipe are required ?

(ii) Should they be installed in parallel or in series ?

(Assume plug flow in pipe and ideal gas behaviour).

Solution : $A \rightarrow 3R$, gas phase reaction.

$v_o = 4\ \text{m}^3/\text{h}$, $P = 5$ atm, $T = 350\ ^\circ\text{C} = 623$ K

$-r_A = k\,C_A^2$, second order kinetics.

For plug flow reactor and second order kinetics, we have :

$$C_{A_0} k \tau = 2\varepsilon_A(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + (\varepsilon_A+1)^2\,[X_A/(1-X_A)]$$

For experimental reactor :

$$\varepsilon_A = \frac{3-1}{1} = 2$$

$$X_A = 0.60$$

$$C_{A_0} k \tau = 2\times 2(1+2)\ln(1-0.60) + (2)^2(0.60) + (2+1)^2 \times \frac{0.60}{(1-0.60)}$$

$$C_{A_0} k \tau = 4.90$$

$$C_{A_0} = p_{A_0}/RT$$

For pure A : $p_{A_0} = P_o = 5$ atm, $T = 623$ K

$$C_{A_0} = \frac{5}{0.08206\times 623} = 0.0978\ \text{kmol/m}^3$$

$$R = 0.08206\ \text{m}^3\cdot\text{atm}/(\text{kmol.K})$$

$$V = \pi/4 \cdot D^2 \cdot L$$

$$D = 25\ \text{mm} = 0.025\ \text{m},\quad L = 2\ \text{m}$$

$$V = \pi/4\ (0.025)^2 \times 2 = 9.82\times 10^{-4}\ \text{m}^3$$

$$v_o = 4\ \text{m}^3/\text{h}$$

$$\tau = \frac{V}{v_o} = \frac{9.82\times 10^{-4}}{4} = 2.455\times 10^{-4}\ (\text{h})^{-1}$$

$$
\begin{aligned}
C_{A_0} k\tau &= 4.90 \\
k &= \frac{4.90}{C_{A_0}\,\tau} \\
&= \frac{4.90}{2.455 \times 10^{-4} \times 0.0978} \\
&= 204082
\end{aligned}
$$

For commercial reactor :

$$
\begin{aligned}
\text{Feed} &= 50 \text{ mole \% A and 50 mole \% inerts} \\
A &\rightarrow 3R
\end{aligned}
$$

100 mol A + 100 mol inerts → 300 mol R + 100 mol inerts.

∴ 2 volumes of reactant mixture yield on complete conversion 4 volumes of product mixture.

∴

$$
\begin{aligned}
\varepsilon_A &= \frac{4-2}{2} = 1.0 \\
X_A &= 0.80
\end{aligned}
$$

For plug flow and second order kinetics, we have :

$$
\begin{aligned}
C_{A_0} k\,\tau &= 2\,\varepsilon_A\,(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + (1+\varepsilon_A)^2\,\frac{X_A}{1-X_A} \\
C_{A_0} k\,\tau &= 2 \times 1 \times (1+1)\ln(1-0.80) + (1)^2\,(0.80) + \frac{(1+1)^2\,(0.80)}{(1-0.80)} \\
&= 10.36
\end{aligned}
$$

For 50 mole % A and 50 mole % inerts,

$$
\begin{aligned}
P_o &= 25 \text{ atm}, \quad T = 623 \text{ K} \\
p_{A_0} &= 0.50 \times 25 = 12.5 \text{ atm} \\
C_{A_0} &= \frac{p_{A_0}}{RT} \\
&= \frac{12.5}{0.08206 \times 623} \\
&= 0.244 \text{ kmol/m}^3 \\
C_{A_0} k\,\tau &= 2.362 \\
\tau &= \frac{2.362}{C_{A_0} \cdot k} \\
&= \frac{10.36}{0.244 \times 204082} = 2.08 \times 10^{-4}\,(h)^{-1} \\
v_o &= 320 \text{ m}^3/\text{h} \\
\tau &= \frac{V}{v_o}
\end{aligned}
$$

∴

$$
\begin{aligned}
V &= \tau \cdot v_o \\
V &= 2.08 \times 10^{-4} \times 320 \\
&= 0.066 \text{ m}^3
\end{aligned}
$$

no. of lengths of pipe × volume of each pipe = total volume of reactor.

$$
\begin{aligned}
\text{No. of lengths of } 25 \text{ mm} \times 2 \text{ m size} &= \frac{0.066}{9.82 \times 10^{-4}} \\
&= 67 \approx 67
\end{aligned}
$$

... Ans.

OR

Graphical procedure :

$$\frac{\tau}{C_{A_0}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

$$-r_A = k\,C_A^2$$

$$= k\left[\frac{C_{A_0}(1-X_A)}{1+\varepsilon_A X_A}\right]^2$$

We have, $\varepsilon_A = 2$, for experimental reactor

$\therefore$

$$-r_A = \frac{k\,C_{A_0}^2(1-X_A)^2}{(1+2\,X_A)^2}$$

$$\frac{\tau}{C_{A_0}} = \int_0^{X_A} \frac{dX_A}{\dfrac{k\,C_{A_0}^2\,(1-X_A)^2}{(1+2\,X_A)^2}}$$

$$\tau\,k\,C_{A_0} = \int_0^{X_A} \frac{(1+2\,X_A)^2}{(1-X_A)^2}\,dX_A$$

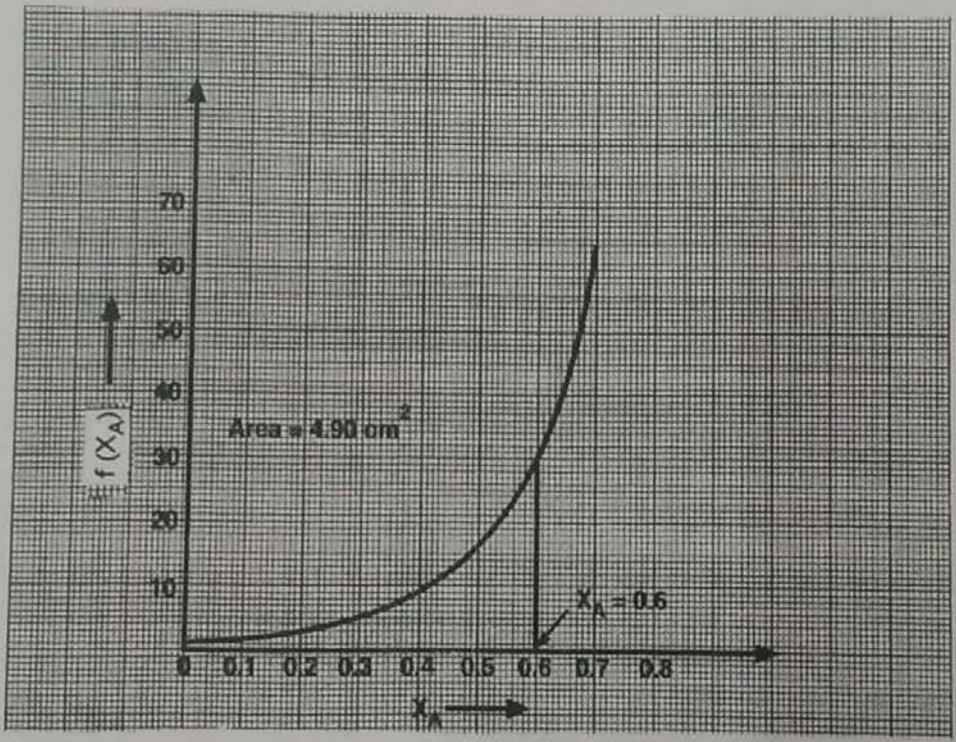


Fig. E 3.16 (a)

We will adopt the graphical procedure to solve this integral. The value of this integral is the area under the curve $f(X_A)$ v/s X_A between $X_A = 0$ and X_A (in our case $X_A = 0.60$).

Take $X_A = 0,\ 0.2,\ 0.4,\ 0.6,\ 0.7$ and find corresponding value of $f(X_A)$.

X_A	$f(X_A) = (1 + 2X_A)^2/(1 - X_A)^2$
0	1
0.2	3.06
0.4	9
0.6	30.25
0.7	64

$$\text{Area under curve} = 4.90\ \text{cm}^2$$

$$\therefore \quad \tau k C_{Ao} = 4.90 \times (\text{Scale y-axis}) \times (\text{Scale x-axis})$$

$$\tau k C_{Ao} = 4.90 \times \frac{10}{1} \times \frac{0.1}{1}$$

$$\tau k C_{Ao} = 4.9$$

$$\tau = 2.455 \times 10^{-4}\ \text{h}$$

$$C_{Ao} = 0.0978\ \text{mol}/l$$

$$k = \frac{4.9}{\tau C_{Ao}} = \frac{4.9}{2.455 \times 10^{-4} \times 0.0978} = 204082$$

For commercial reactor :

$A \rightarrow 3R$

50 A	150 R
50 I	50 I
100	200

$$\varepsilon_A = \frac{200 - 100}{100} = 1.0$$

$$C_A = \frac{C_{Ao}(1 - X_A)}{(1 + \varepsilon_A X_A)} = \frac{C_{Ao}(1 - X_A)}{(1 + X_A)}$$

$$\frac{\tau}{C_{Ao}} = \int_0^{X_A} \frac{dX_A}{\dfrac{k C_{Ao}^2 (1 - X_A)^2}{(1 + X_A)^2}}$$

$$\therefore \quad \tau k C_{Ao} = \int_0^{X_A} \frac{(1 + X_A)^2}{(1 - X_A)^2}\, dX_A$$

We will evaluate the integral graphically between $X_A = 0$ and $X_A = 0.80$ (given) in a same manner as done previously.

X_A	$f(X_A) = (1 + X_A)^2/(1 - X_A)^2$
0	1
0.2	2.25
0.4	5.44
0.6	16
0.7	32.11
0.75	49
0.8	81

From graph,

$$\text{Area} = 20.2 \text{ cm}^2$$

$$\tau C_{A_0} k = 20.2 \times (\text{Scale y-axis}) \times (\text{Scale x-axis})$$

$$\tau C_{A_0} k = 20.2 \times \frac{10}{2} \times \frac{0.1}{1}$$

$$= 10.1$$

For 50 mole % A and 50 mole % inerts,

$$P_o = 25 \text{ atm}, \quad T = 623 \text{ K}$$

$$p_{A_0} = \left(\frac{\text{mole \% A}}{100}\right) \times P_o$$

$$= \left(\frac{50}{100}\right) \times 25$$

$$= 12.5 \text{ atm}$$

$$C_{A_0} = \frac{p_{A_0}}{R\,T}$$

$$= \frac{12}{0.08206 \times 623}$$

$$= 0.244 \text{ mol}/l$$

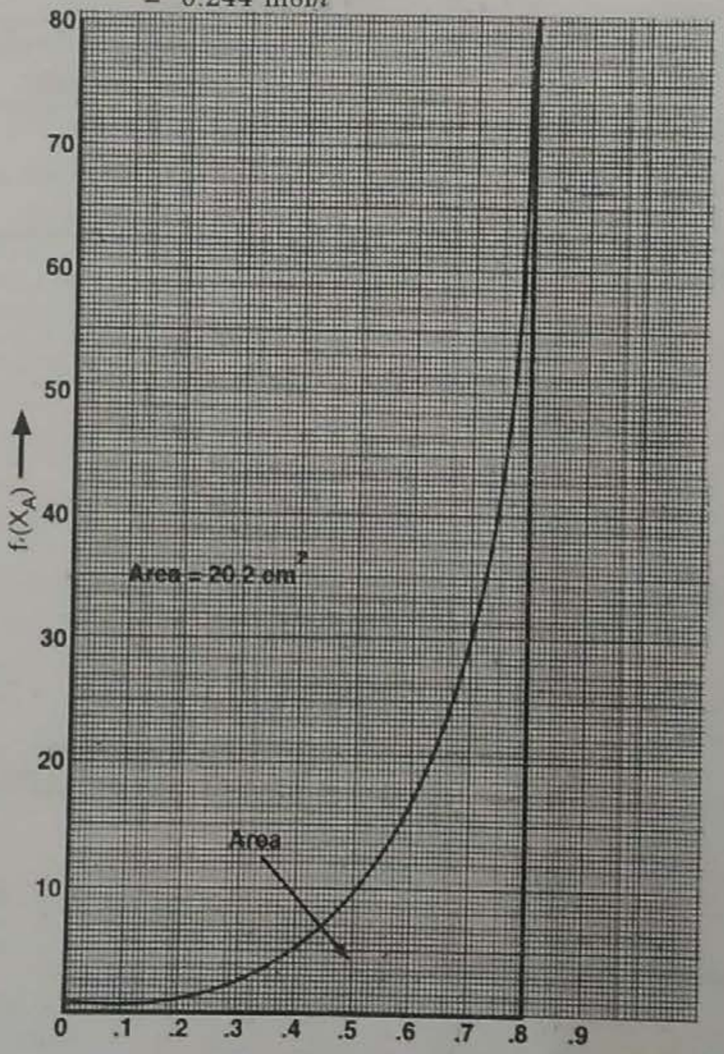


Fig. E 3.16 (b) X_A →

$$\tau C_{A0} k = 10.1$$

$$\tau = \frac{10.1}{C_{A0} k}$$

$$= \frac{10.1}{0.244 \times 204082} = 2.028 \times 10^{-4} \text{ h}$$

$$v_o = 320 \text{ m}^3/\text{h}$$

$$\tau = \frac{V}{v_o}$$

$$\therefore \quad V = \tau \cdot v_o$$

$$= 2.028 \times 10^{-4} \times 320$$

$$= 0.0649 \text{ m}^3$$

Volume of one pipe of 2 m length = 9.82×10^{-4} m^3

Number of lengths of 25 mm ID × 2 m pipe required $= \dfrac{0.0649}{9.82 \times 10^{-4}} = 66$ ... **Ans.**

Answer by both methods is almost same.

Ex. 3.17 : The data on decomposition of gaseous reactant A in constant volume batch reactor at 100 °C is given below. The stoichiometry of decomposition is 2A → R + S. Determine size of plug flow reactor operating at 100 °C and 1 atm that can process 100 mol A/h in a feed containing 20 mole % inerts to obtain 95% conversion of A.

Data :

t, s	0	20	40	60	80	100	140	200	260	330	420
p_A, atm	1.0	0.80	0.68	0.56	0.45	0.37	0.25	0.14	0.08	0.04	0.02

Solution : $2A \rightarrow R + S$, gas phase reaction

$$P_o = 1 \text{ atm}, \quad T = 100\,^{\circ}\text{C}$$

20 mole % inerts and 80 mole % A.

5 volumes of feed yield 5 volumes of product mixture on complete conversion.

4 volumes of A + 1 volume inerts ⇒ 4 volumes of (R + S) + 1 volume of inerts

[**OR :** 0.8 mol A + 0.2 mol inerts give 0.4 mol R + 0.4 mol S + 0.2 mol inerts

i.e. 1 volume of feed yields 1 volume of product on complete conversion]

$$\therefore \quad \varepsilon_A = \frac{5-5}{5} = 0$$

$$\frac{\tau}{C_{A0}} = \frac{V}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$P_o = 1 \text{ atm}$$

$$p_{A0} = 0.8 \times 1 = 0.8 \text{ atm}$$

$$p_A = p_{A0}(1 - X_A)$$

$$X_A = 0.95$$

$$\therefore \quad p_A = 0.8\,(1 - 0.95) = 0.04 \text{ atm}$$

We have, concentration is proportional to partial pressure.

So in batch reactor, time required for change in partial pressure of A from p_{A0} = 0.8 atm to p_A = 0.04 atm (to have 95 % conversion of A) is obtained from the data.

At $t = 330$ s, $p_A = 0.04$ atm

At $t = 20$ s, $p_A = 0.8$ atm $= p_{Ao}$ with inerts

$$\therefore \quad t_{batch} = 330 - 20 = 310 \text{ s}$$

As $\varepsilon_A = 0$, we have constant density system and for constant density system

$$t_{batch} = \tau_{plug}$$

$\therefore$ τ for plug flow reactor $= 310$ s

For plug flow reactor,

$$\frac{V}{F_{Ao}} = \frac{\tau}{C_{Ao}}$$

$$C_{Ao} = \frac{p_{Ao}}{RT}$$

$p_{Ao} = 0.8$ atm, $T = 373$ K, $R = 0.08206\ l.\text{atm/(mol.K)}$

$$C_{Ao} = \frac{0.80}{0.08206 \times 373}$$

$$= 0.0261 \text{ mol}/l$$

$$F_{Ao} = 100 \text{ mol/h}$$

$$= 0.0278 \text{ mol/s}$$

$$V = \frac{\tau F_{Ao}}{C_{Ao}}$$

$$= \frac{310 \times 0.0278}{0.0261}$$

$$= 330\ l$$

Volume of a plug flow reactor for 95% conversion $= 330\ l$ ... **Ans.**

Ex. 3.18 : A tank of volume 208 litres is to be used as a mixed flow reactor to effect the decomposition reaction of the Ex. 3.17. What conversion of A may be expected from this reactor for identical feed and identical operating conditions ?

Solution : $2A \rightarrow R + S$

80 mole % A and 20 mole % inerts.

Volume of mixed flow reactor $= V = 208\ l$

For this stoichiometry, we have $\varepsilon_A = 0$

For mixed flow reactor,

$$\tau = \frac{V C_{Ao}}{F_{Ao}}$$

$$C_{Ao} = 0.0261 \text{ mol}/l, \; F_{Ao} = 100 \text{ mol/h}$$

$$\tau = \frac{208 \times 0.0261}{(100/3600)}$$

$$= 195.44 \text{ s}$$

For $\varepsilon_A = 0$ i.e. for constant density, space time and holding time are identical.

From the data given in Ex. 3.17 by interpolation :

$$t = 140 \text{ s}, \quad p_A = 0.25 \text{ atm}$$

$$t = 200 \text{ s}, \quad p_A = 0.14 \text{ atm}$$

$$\therefore \quad \Delta t = 60 \text{ s}, \quad \Delta p_A = 0.11 \text{ atm}$$

At t = 195.44 s

$$p_A \text{ at } 195.44\text{ s} = p_A \text{ at } 140\text{ s} - \frac{0.11}{60} \times (195.44 - 140)$$

$$= 0.25 - 0.102$$

$$= 0.148 \text{ atm}$$

We have, for $\varepsilon_A = 0$,

$$C_A = C_{Ao}(1 - X_A)$$

$$\therefore \quad \frac{p_A}{RT} = \frac{p_{Ao}}{RT}(1 - X_A)$$

$$p_A = p_{Ao}(1 - X_A)$$

$$0.148 = 0.8\,(1 - X_A)$$

$$\therefore \quad X_A = 0.815$$

... **Ans.**

Conversion of A in mixed flow reactor = 81.5 %

Ex. 3.19 : A laboratory-size steady state flow system is used to study aqueous reaction having stoichiometry A → 2R. The reactor is a flask whose contents (5 litres of fluid) are well stirred and uniform in composition. The reactant A is introduced at the concentration of 1 mol/*l*. The results of experimental investigation are tabulated below. Find a rate equation for this reaction.

Run	Feed rate (cm³/s)	Temperature of run in (°C)	Concentration of R in effluent (mol/*l*)
1	2	13	1.8
2	15	13	1.5
3	15	84	1.8

Solution : For mixed flow reactor,

$$\tau = \frac{C_{Ao} X_A}{(-r_A)}$$

$$A \rightarrow 2R \ , \quad C_{Ao} = 1 \text{ mol}/l$$

At any time t :

$$C_R = C_{Ro} + 2\,C_{Ao} X_A$$

$$C_{Ro} = 0$$

$$\therefore \quad C_R = 2\,C_{Ao} X_A$$

(i) For

$$C_R = 1.8 \text{ mol}/l$$

$$X_A = C_R / 2\,C_{Ao}$$

$$= \frac{1.8}{2 \times 1}$$

$$= 0.90 \quad \text{(for run no. 1)}$$

(ii) For

$$C_R = 1.5 \text{ mol}/l$$

$$X_A = \frac{1.5}{2 \times 1}$$

$$= 0.75 \quad \text{(for run no. 2)}$$

For mixed flow reactor,

$$\frac{V}{v_o} = \frac{C_{Ao} X_A}{(-r_A)}$$

$$\therefore \quad (-r_A) = \frac{C_{A_0} X_A \cdot v_0}{V}$$

$$V = 5\,l, \quad C_{A_0} = 1 \text{ mol}/l$$

(1) For Run no. 1 :

$$v_0 = 2 \text{ cm}^3/\text{s} = 2 \times 10^{-3}\ l/\text{s} \quad \text{and } X_A = 0.90$$

$$(-r_A)_1 = \frac{1 \times 0.9 \times 2 \times 10^{-3}}{5}$$

$$= 3.6 \times 10^{-4}, \quad \text{mol}/(l \cdot \text{s})$$

$$\ln(-r_A)_1 = -7.93$$

(2) For

$$v_0 = 15 \text{ cm}^3/\text{s} = 15 \times 10^{-3}\ l/\text{s} \quad \text{and } X_A = 0.75$$

$$(-r_A)_2 = \frac{1 \times 0.75 \times 15 \times 10^{-3}}{5}$$

$$= 2.25 \times 10^{-3} \text{ mol}/(l \cdot \text{s})$$

$$\ln(-r_A)_2 = -6.097 \approx -6.10$$

$$-r_A = k\, C_A^n$$

$$-r_A = k\, [C_{A_0}(1 - X_A)]^n$$

$$\ln(-r_A) = \ln k + n \ln [C_{A_0}(1 - X_A)]$$

For $X_A = 0.90$: $\quad -7.93 = \ln k + n(-2.3)$ ... (1)

For $X_A = 0.75$: $\quad -6.1 = \ln k + n(-1.39)$ ... (2)

Subtracting equation (1) from (2),

$$0.91\, n = 1.83$$

$$n = 2.01 \approx 2$$

So the reaction is second order.

$$\therefore \quad (-r_A) = k\, C_A^2 = k\, C_{A_0}^2\, (1 - X_A)^2$$

$$-r_A = 3.6 \times 10^{-4} \quad \text{and} \quad X_A = 0.90 \text{ at } 13\,^\circ\text{C}$$

$$k = \frac{3.6 \times 10^{-4}}{(1)^2 \times (1 - 0.90)^2}$$

$$= 0.036\ l/(\text{mol} \cdot \text{s})$$

At $\quad T = 84\,^\circ\text{C}$

$$v_0 = 15 \times 10^{-3}\ l/\text{s}, \quad C_R = 1.8 \text{ mol}/l$$

As $\quad C_R = 1.8 \text{ mol}/l, \quad X_R = 0.90$

$$(-r_A) = \frac{C_{A_0} X_A \cdot v_0}{V}, \quad V = 5\,l$$

$$= \frac{1 \times 0.9 \times 15 \times 10^{-3}}{5}$$

$$= 2.7 \times 10^{-3} \text{ mol}/(l \cdot \text{s})$$

$$k \text{ at } 84\,^\circ\text{C} = \frac{2.7 \times 10^{-3}}{(1)^2 (1 - 0.90)^2}$$

$$= 0.27\ l/(\text{mol} \cdot \text{s})$$

At $T_1 = 13\,^\circ\text{C} = 286$ K, $\quad k_1 = 0.036$

At $T_2 = 84\,^\circ\text{C} = 357$ K, $\quad k_2 = 0.27$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$R = 1.987 \text{ cal}/(\text{mol} \cdot \text{K})$$

$$\ln(0.27/0.036) = \frac{-E}{1.987}\left[\frac{1}{357}-\frac{1}{286}\right]$$

$$E = 5762 \text{ cal/mol}$$

$$k = k_o \cdot e^{-E/RT}$$

$$\ln k = \ln k_o - \frac{E}{RT}$$

$$\ln(0.036) = \ln k_o - \frac{5762}{1.987\times 286}$$

$$k_o = 9.16\times 10^2$$

Complete rate expression is :

$$-r_A = k\,C_A^n$$

$$-r_A = k_o\,e^{-E/RT}\cdot C_A^n$$

$$-r_A = [9.16\times 10^2\cdot e^{-5762/RT}]\cdot C_A^2$$ ... **Ans.**

Ex. 3.20 : A homogeneous gas phase reaction A → 2B is carried out at 100 °C at a constant pressure of 1 atm in an experimental batch reactor. Starting with pure A, the below given data were obtained. Determine the size of plug flow reactor to be operated at 100 °C and 10 atm that would result in 90% conversion of A for a total feed rate of 10 mol/s, the feed contains 40 mole % inerts.

Data :

Time, min	V/V_o	Time, min	V/V_o
0	1.0	8	1.82
1	1.2	9	1.86
2	1.35	10	1.88
3	1.48	11	1.91
4	1.58	12	1.92
5	1.66	13	1.94
6	1.72	14	1.95
7	1.78		

Solution : $A \rightarrow 2B$, gas phase reaction

For plug flow reactor,

$$\frac{V}{F_{Ao}} = \frac{\tau}{C_{Ao}}$$

$$V = \frac{\tau F_{Ao}}{C_{Ao}}$$

Feed : 60 mole % A + 40 mole % inerts

P = 10 atm, T = 100 °C = 373 K.

$$C_{Ao} = \frac{p_{Ao}}{RT}, \quad R = 0.08206\ l\text{·atm/(mol·K)}$$

$$p_{Ao} = x_A\cdot P_o = 0.6\times 10 = 6 \text{ atm}$$

$$C_{Ao} = \frac{6}{0.08206\times 373}$$

$$= 0.196 \text{ mol}/l$$

$$A \rightarrow 2B$$

60 mole A 40 mole I	120 mole B 40 mole I
100 mole feed	160 mole product

$$\therefore \quad \varepsilon_A = \frac{160-100}{100} = 0.60$$

For variable volume constant pressure, we have

$$V = V_o(1+\varepsilon_A X_A)$$

$$\frac{V}{V_o} = 1+\varepsilon_A X_A$$

$$\varepsilon_A = 0.6, \quad X_A = 0.90 \text{ (given)}$$

$$\frac{V}{V_o} = 1+0.6\times 0.9$$

$$= 1.54$$

At $t = 3$ min, $V/V_o = 1.48$

At $t = 4$ min, $V/V_o = 1.58$

$$\therefore \quad t = \tau \text{ for } V/V_o = 1.54 = 3+\frac{1}{0.10}(1.54-1.48) = 3.6 \text{ min.}$$

$$\tau = 3.6 \text{ min} = 216 \text{ s}$$

$$\text{Total feed rate} = 10 \text{ mol/s}$$

$$F_{Ao} = 0.60\times 10 = 6 \text{ mol/s}$$

$$V = \frac{216\times 6}{0.196}$$

$$= 6612\, l$$

$$= 6.612 \text{ m}^3$$

... **Ans.**

Ex. 3.21 : Find the rate equation for the decomposition of liquid A from the results of kinetic runs taken in a mixed reactor at steady state.

Concentration of A liquid in feed, (mol/l)	Concentration of A in reactor, (mol/l)	Mean residence time of fluid in reactor, (s)	Temperature, °C
1.0	0.40	220	44
1.0	0.40	100	57
1.0	0.40	30	77
1.0	0.10	400	52
1.0	0.10	120	72
1.0	0.10	60	84

Solution : For mixed flow reactor :

$$\tau = \frac{C_{Ao}-C_A}{(-r_A)}$$

$$\therefore \quad (-r_A) = \frac{C_{Ao}-C_A}{\tau}$$

For constant density system, $\tau = \bar{t}$.

From the data given, plot a graph of τ v/s T for (i) $C_{Ao} = 1$ to $C_A = 0.4$ mol/l and (ii) $C_{Ao} = 1$ mol/l to 0.10 mol/l.

From graph at T = 60 °C, drop the vertical from T = 60 °C which will cut both the curves and get the values of τ for $C_A = 0.4$ and $C_A = 0.10$ mol/*l*.

At T = 60 °C from graph :

For $C_A = 0.4$ mol/*l* $\tau = 80$ s

For $C_A = 0.1$ mol/*l* $\tau = 250$ s

For $C_A = 0.4$ mol/*l* and $\tau = 80$ s :

$$(-r_A)_1 = \frac{C_{A0} - C_A}{\tau}$$

$$= \frac{(1 - 0.4)}{80} = 7.5 \times 10^{-3}, \quad \text{mol/}(l\cdot\text{s})$$

$$\ln\,(-r_A)_1 = -4.89$$

For $C_A = 0.1$ mol/*l* and $\tau = 250$ s :

$$(-r_A)_2 = \frac{C_{A0} - C_A}{\tau}$$

$$= \frac{(1 - 0.1)}{255} = 3.53 \times 10^{-3}, \quad \text{mol/}(l\cdot\text{s})$$

$$\ln\,(-r_A)_2 = -5.65$$

Assume rate equation of the type

$$-r_A = k\,C_A^n$$

$$\ln\,(-r_A) = \ln k + n \ln C_A$$

For $C_A = 0.1$ mol/*l* : $-5.65 = \ln k + n\,(-2.3)$ ... (1)

For $C_A = 0.4$ mol/*l* : $-4.89 = \ln k + n\,(-0.92)$ ... (2)

Subtracting (1) from (2), we get

$$-4.89 + 5.65 = -0.92\,n + 2.3\,n$$

$$\therefore \quad n = 0.55$$

$$-r_A = k\,C_A^n$$

$$\therefore \quad k = \frac{(-r_A)}{(C_A)^{0.55}}$$

For $C_A = 0.4$ mol/*l*, $(-r_A) = 7.5 \times 10^{-3}$

$$k = \frac{7.5 \times 10^{-3}}{(0.4)^{0.55}} = 0.0124$$

For $C_A = 0.1$ mol/*l*, $(-r_A) = 3.53 \times 10^{-3}$

$$k = \frac{3.53 \times 10^{-3}}{(0.1)^{0.55}} = 0.0125$$

From graph :

At T = 70 °C

For $C_A = 0.4$ mol/*l* , $\tau = 45$ s

For $C_A = 0.1$ mol/*l* , $\tau = 140$ s

$$(-r_A)_1 = \frac{C_{A0} - C_A}{\tau}$$

For $C_A = 0.4$ mol/*l*

$$(-r_A)_1 = \frac{(1 - 0.4)}{45} = 0.013$$

$$\ln\,(-r_A)_1 = -4.32, \quad \ln C_{A1} = -0.92$$

For $C_A = 0.10 \text{ mol}/l$

$$(-r_A)_2 = \frac{1-0.1}{145} = 6.21 \times 10^{-3}$$

$$\ln(-r_A)_2 = -5.08, \quad \ln C_{A2} = -2.30$$

$$\ln(-r_A) = \ln k + n \ln C_A$$

$$-5.08 = \ln k + n(-2.3) \qquad \ldots (1)$$

$$-4.32 = \ln k + n(-0.92) \qquad \ldots (2)$$

$$\therefore \quad 0.76 = 1.38\,n \qquad \ldots \text{ subtracting (1) from (2)}$$

$$\therefore \quad n = 0.55$$

So order of reaction at T = 60 °C and at T = 70 °C is same (0.55). Hence statement "order is independent of temperature" is valid for this case.

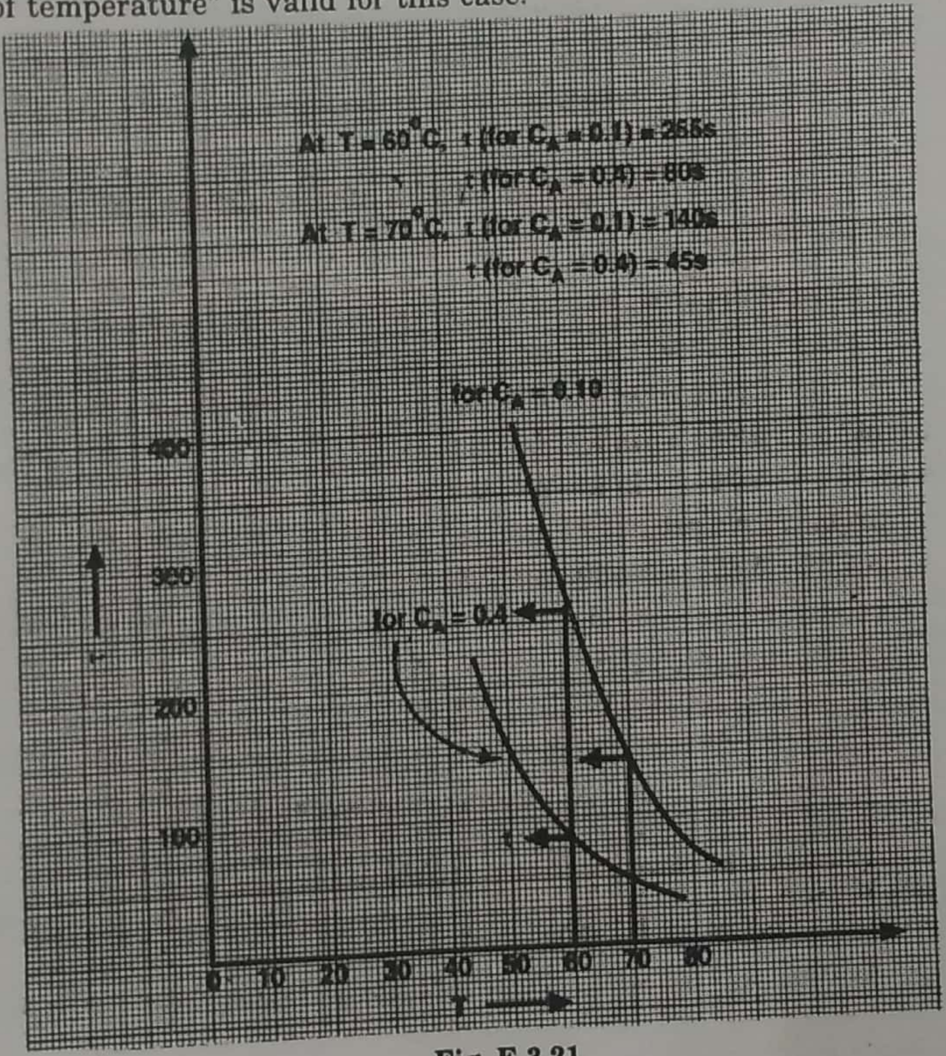


Fig. E 3.21

At $T = 70\,^{\circ}C$

$$(-r_A) = k\,C_A^{0.55}$$

For $C_A = 0.1 \text{ mol}/l$

$$k = -r_A / C_A^{0.55}$$

$$= \frac{6.21 \times 10^{-3}}{(0.1)^{0.55}} = 0.022$$

At $T_1 = 60\,^{\circ}C = 333\,K,\; k_1 = 0.0125$

At $T_2 = 70\,^{\circ}C = 343\,K,\; k_2 = 0.022$

$$k = k_o \cdot e^{-E/RT}$$

$$\therefore \quad \ln(k_2/k_1) = \frac{-E}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right], \quad R = 1.987 \text{ cal/(mol.K)}$$

$$\ln(0.022/0.0125) = \frac{-E}{1.987}\left[\frac{1}{343} - \frac{1}{333}\right]$$

$$\therefore \quad E = 12848 \text{ cal/mol}$$

$$k = k_o\, e^{-E/RT}$$

$k = k_1 = 0.0125$, $E = 12848$ cal/mol, $R = 1.987$ cal/(mol.K) and $T = 333$ K

$$\ln k = \ln k_o - \frac{E}{RT}$$

$$\ln(0.0125) = \ln k_o - \frac{12848}{1.987 \times 333}$$

$$\ln k_o = 15.04$$

$$k_o = 3.40 \times 10^6$$

$$\therefore \quad -r_A = k\,C_A^n = k_o\, e^{-E/RT}\, C_A^n$$

Complete rate equation is :

$$-r_A = [3.40 \times 10^6\, e^{-12848/RT}] \cdot C_A^{0.55}$$ ... **Ans.**

Ex. 3.22 : A gas phase reaction

$$C_2H_4 + Br_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_2H_4Br_2$$

has rate constants at 600 K

$$k_1 = 500\ l/(\text{mol}\cdot\text{h})$$

$$k_2 = 0.032\ (\text{h})^{-1}$$

If a plug flow reactor is to be fed at a rate of 600 m³/h of a gas containing 60% Br_2, 30% C_2H_4 and 10% inerts by volume at 600 K and 1.5 atm, calculate : (i) the maximum possible fractional conversion of C_2H_4 into $C_2H_4Br_2$, and (ii) the volume of reaction vessel required to get 60% of this maximum conversion.

Solution : $$C_2H_4 + Br_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C_2H_4Br_2$$

$$k_1 = 500\ l/(\text{mol}\cdot\text{h}), \quad k_2 = 0.032\ (\text{h})^{-1}$$

$$A + B \rightleftharpoons R$$

(i) For plug flow reactor, v = 600 m³/h, 60 mole % Br_2, 30 mole % C_2H_4 and 10 mole % inerts at T = 600 K and P = 1.5 atm.

$$-r_A = k_1 C_A C_B - k_2 C_R, \quad \text{rate of disappearance of A}$$

$$-r_A = 500\, C_A C_B - 0.032\, C_R$$

$$C_{Ao} = \frac{p_{Ao}}{RT}$$

$$p_{Ao} = y_A P_o$$

$$p_{Ao} = \left(\frac{30}{100}\right)\times 1.5 = 0.45 \text{ atm}$$

$$C_{Ao} = \frac{0.45}{0.08206\times 600} = 0.00914 \text{ mol}/l$$

$$p_{Bo} = 0.6\times 1.5 = 0.90 \text{ atm}$$

$$C_{Bo} = \frac{0.90}{0.08206\times 600}$$

$$= 0.01828 \text{ mol}/l$$

$$\varepsilon_A = \frac{1-2}{2} = -0.50$$

$$C_R = C_{Ro} + C_{Ao}X_A$$

$$C_R = 0 + 0.00914\,X_A$$

$$= 0.00914\,X_A$$

We have,

$$C_{Ao} - C_A = C_{Bo} - C_B$$

$$C_{Ao}X_A = C_{Bo}X_B$$

$$\therefore \quad X_B = \frac{C_{Ao}}{C_{Bo}}\,X_A$$

$$X_B = \frac{0.00914}{0.01828}\,X_A$$

$$= 0.5\,X_A$$

$$C_A = \frac{C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$$\varepsilon_A = -0.50$$

$$C_A = \frac{C_{Ao}(1-X_A)}{(1-0.5\,X_A)}$$

$$= \frac{0.00914\,(1-X_A)}{(1-0.5\,X_A)}$$

$$C_B = \frac{C_{Bo}(1-X_B)}{(1+\varepsilon_A X_B)}$$

$$X_B = 0.5\,X_A, \quad \text{and} \quad \varepsilon_A = -0.50$$

$$C_B = \frac{C_{Bo}(1-0.5\,X_A)}{(1-0.25\,X_A)}$$

$$-r_A = k_1\,C_A\,C_B - k_2\,C_R$$

$$-r_A = \left(\frac{C_{Ao}}{1+\varepsilon_A X_A}\right)\frac{dX_A}{dt} \quad \text{and} \quad \varepsilon_A = -0.50$$

$$\therefore \quad \frac{C_{Ao}}{(1-0.5\,X_A)}\,\frac{dX_A}{dt} = \frac{k_1 C_{Ao}(1-X_A)}{(1-0.5\,X_A)}\cdot\frac{C_{Bo}(1-0.5\,X_A)}{(1-0.25\,X_A)} - k_2\,C_{Ao}X_A$$

$$\frac{dX_A}{dt} = \frac{k_1(1-X_A)\,C_{Bo}\,(1-0.5\,X_A)}{(1-0.25\,X_A)} - k_2\,X_A\,(1-0.5\,X_A)$$

For X_A to be maximum, $dX_A/dt = 0$.

$$\frac{k_1(1-X_A)\,C_{Bo}\,(1-0.5\,X_A)}{(1-0.25\,X_A)} - k_2\,X_A\,(1-0.5\,X_A) = 0$$

$$\frac{k_1(1-X_A)\,C_{Bo}\,(1-0.5\,X_A) - k_2 X_A\,(1-0.5\,X_A)\,(1-0.25\,X_A)}{(1-0.25\,X_A)} = 0$$

$$k_1 (1 - X_A) C_{Bo} - k_2 X_A (1 - 0.25 X_A) = 0$$

$$\frac{k_1 C_{Bo}}{k_2} (1 - X_A) - X_A (1 - 0.25 X_A) = 0$$

$$\frac{500 \times 0.01828}{0.032} (1 - X_A) - X_A + 0.25 X_A^2 = 0$$

$$285.625 (1 - X_A) - X_A + 0.25 X_A^2 = 0$$

$$0.25 X_A^2 - 286.625 X_A + 285.625 = 0$$

$$X_A^2 - 1146.5 X_A + 1142.5 = 0$$

$$\therefore \quad X_A = 0.9974$$

Maximum possible conversion of A = 99.74 ... **Ans. (i)**

(ii) For plug flow reactor :

$$X_A = 60 \text{ \% of maximum conversion}$$

$$= 0.60 \times 0.9974$$

$$= 0.5984 \approx 0.60$$

$$\tau = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\frac{\tau}{C_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$(-r_A) = k_1 C_A C_B - k_2 C_R$$

$$= \frac{k_1 C_{Ao} (1 - X_A)}{(1 - 0.5 X_A)} \frac{(1 - 0.5 X_A) C_{Bo}}{(1 - 0.25 X_A)} - k_2 X_A C_{Ao}$$

$$= \frac{k_1 C_{Ao} C_{Bo} (1 - X_A)}{(1 - 0.25 X_A)} - k_2 C_{Ao} X_A$$

$$= \frac{500 \times 0.00914 \times 0.01828 (1 - X_A)}{(1 - 0.25 X_A)} - 0.032 \times 0.00914 X_A$$

$$= \frac{0.08354 (1 - X_A)}{(1 - 0.25 X_A)} - 2.925 \times 10^{-4} X_A$$

$$= \frac{0.08354 (1 - X_A) - 2.925 \times 10^{-4} X_A (1 - 0.25 X_A)}{(1 - 0.25 X_A)}$$

$$\therefore \quad \frac{\tau}{C_{Ao}} = \int_0^{X_A} \frac{(1 - 0.25 X_A)\, dX_A}{0.08354 (1 - X_A) - 2.925 \times 10^{-5} X_A (1 - 0.25 X_A)}$$

$$= \int_0^{X_A} f(X_A)\, dX_A$$

Take various values of X_A and evaluate $f(X_A)$.

X_A	$f(X_A)$
0	12 (11.97)
0.2	14.21
0.4	18 (17.96)
0.6	25.44
0.7	32.94

Plot a graph of $f(X_A)$ v/s X_A and get area under curve upto $X_A = 0.60$ which is equal to LHS and get V.

From graph, area under curve between $X_A = 0$ and $X_A = 0.60$ is :

$$\text{Area} = 25\ \text{cm}^2$$

$$\therefore \quad \frac{\tau}{C_{A0}} = 25 \times (\text{Scale of x-axis}) \times (\text{Scale of y-axis})$$

$$= 25 \times \frac{0.1}{1} \times \frac{4}{1}$$

$$= 10$$

$$\tau = 10\, C_{A0}$$

$$= 10 \times 0.00914 = 0.0914\ (\text{h})$$

In rate equation, k_1 is in $l/(\text{mol.h})$ and k_2 is in $(\text{h})^{-1}$, so τ will be in (h).

$$\frac{V}{v_0} = \tau = 0.0914$$

$$V = 0.0914\, v_0, \quad v_0 = 600\ \text{m}^3/\text{h}$$

$$\therefore \quad V = 0.0914 \times 600 = 54.84\ \text{m}^3 = 55\ \text{m}^3$$

Volume of plug flow reactor $= 55\ \text{m}^3$ ... **Ans. (ii)**

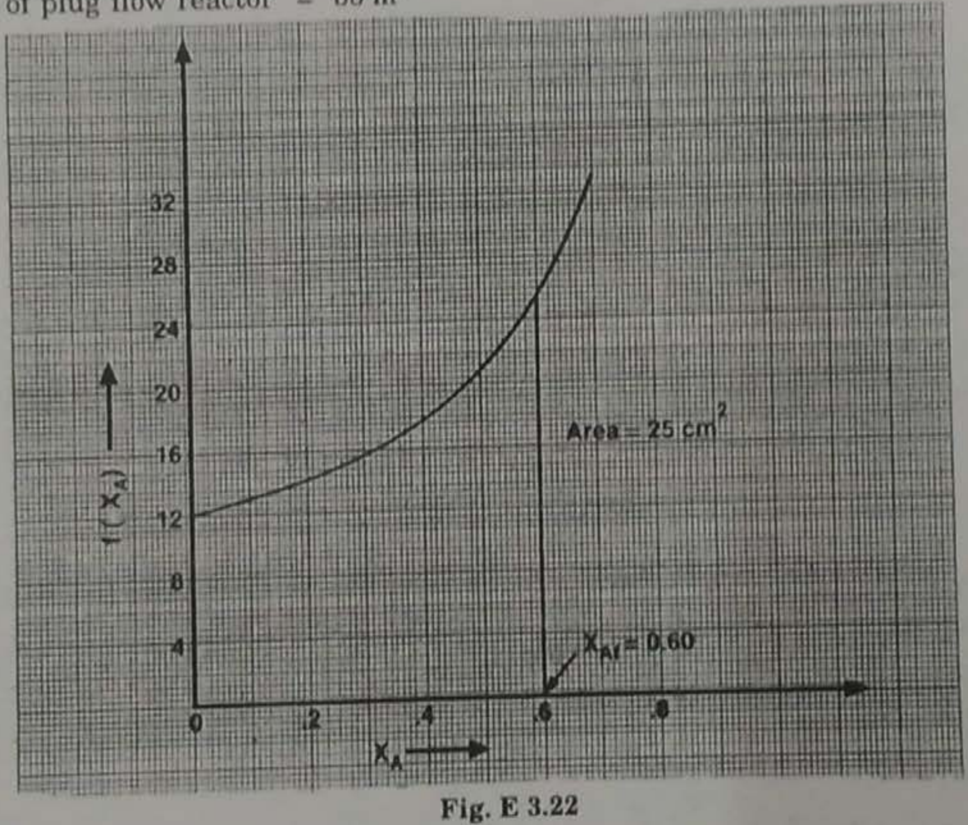


Fig. E 3.22

Ex. 3.23 : The saponification reaction

$$\text{NaOH (aq)} + CH_3COOC_2H_5 \rightarrow CH_3COONa + C_2H_5OH$$

is a second order irreversible reaction. A laboratory well-stirred tank reactor is charged with an aqueous solution containing NaOH and ethyl acetate, both of initial concentration of 0.1 molar. After 15 minutes, the conversion of ethyl acetate is 18%.

For the initial charge containing NaOH and ethyl acetate in equal concentration of 0.2 molar, what time is required to obtain a conversion of 30% in a commercial batch reactor ?

Solution : $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$

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

For same initial concentrations, we have

$$(-r_A) = -dC_A/dt = k\,C_A^2$$

For laboratory reactor,

$$t = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$t = C_{Ao} \int_0^{X_A} \frac{dX_A}{kC_{Ao}^2\,(1-X_A)^2}\ , \quad \text{as } C_A = C_{Ao}(1-X_A)$$

$$t = \frac{1}{kC_{Ao}}\left[\frac{X_A}{1-X_A}\right]$$

At $t = 18$ min, $X_A = 0.18$

$$k = \frac{1}{15 \times 0.10}\left[\frac{0.18}{1-0.18}\right]$$

$$\therefore \quad k = 0.146\ (l/\text{mol})\ (\text{min})^{-1}$$

For commercial batch reactor,

$$C_{Ao} = 0.20\ \text{mol}/l\ ,\ X_A = 0.30,\ t = ?$$

$$t = \frac{1}{0.146 \times 0.20}\left[\frac{0.30}{1-0.30}\right]$$

$$= 14.68 \text{ min}$$

... **Ans.**

Ex. 3.24 : A first order homogeneous gas phase reaction, A → 3R, is first studied in a constant pressure batch reactor. At a pressure of 2 atm and starting with pure A, the volume increases by 75% in 15 min. If the same reaction is carried out in constant volume reactor and the initial pressure is 2 atm, how long is required for the pressure to reach 3 atm ?

Solution :

$$A \rightarrow 3\,R$$

$$\varepsilon_A = (3-1)/1 = 2$$

For first order reaction for constant pressure variable volume reactor, we have :

$$-\ln\left[1 - \frac{\Delta V}{\varepsilon_A V_0}\right] = k\,t$$

$$\Delta V = V - V_0$$

$$V = 1.75\,V_0 \text{ at } t = 15 \text{ min}$$

$$\therefore \quad \Delta V = 0.75\,V_0$$

$$-\ln\left[1 - \frac{0.75\,V_0}{2\,V_0}\right] = k\,t$$

$$t = 15 \text{ min}$$

$$\therefore \quad k = 0.0313 \text{ min}^{-1}$$

For constant volume reactor with variable pressure, we have,

$$-\frac{dC_A}{dt} = k\,C_A$$

$$A \rightarrow 3\,R$$

Initial moles of A = N_{Ao}

Initial total moles = $N_0 = N_{Ao}$

Let X_A be the conversion of A in time t.

At time t :

$$\text{Moles of A} = N_A = N_{Ao} - X_A = N_0 - X_A$$

$$\text{Moles of R} = 3X_A$$

$$\text{Final total moles} = N_0 + 2X_A = N_0 + 2X_A$$

Let P be the pressure at time t.

Let P_0 be the pressure at time t = 0.

$$\therefore \quad \frac{P_0}{P} = \frac{N_0}{N_0 + 2X_A}$$

$$\therefore \quad X_A = \frac{N_0(P - P_0)}{2P_0}$$

$$C_A = \frac{N_A}{V} = \frac{N_0 - X_A}{V} = \frac{N_0}{V} - \frac{N_0(P - P_0)}{2P_0 V}$$

$$C_A = \frac{P_0}{RT} - \frac{P_0}{RT}\left(\frac{P - P_0}{2P_0}\right) = \frac{P_0}{RT}\left[\frac{3P_0 - P + P_0}{2P_0}\right]$$

$$C_A = \left(\frac{3P_0 - P}{RT}\right)$$

$$\frac{dC_A}{dt} = \frac{1}{RT}\left(-\frac{dP}{dt}\right)$$

$$\frac{1}{RT}\frac{dP}{dt} = \frac{k(3P_0 - P)}{RT}$$

$$\int_{P_0}^{P} \frac{dP}{(3P_0 - P)} = k\int_0^t dt = kt$$

$$\ln\left(\frac{2P_0}{3P_0 - P}\right) = kt$$

$k = 0.0313\ \text{min}^{-1}$, $t = ?$, $P_0 = 2$ atm, $P = 3$ atm

$$\ln\left[\frac{2 \times 2}{3 \times 2 - 3}\right] = 0.0313 \times t$$

Time required to reach pressure of 3 atm = t

$$\therefore \quad t = 9.2 \text{ min}$$ **... Ans.**

2012 ✓

Ex. 3.25 : ✓ A homogeneous gas reaction A → 3R has a reported rate at 200°C.

$$-r_A = 10^{-1}\,C_A, \quad [\text{mol}/(l.\text{s})]$$

Find the space time required for 80% conversion of a 50% A and 50% inerts feed to a plug flow reactor operating at 200°C and 5 atm. pressure. Initial concentration of A is 0.0625 mol/l.

Solution : A → 3R

For above stoichiometry and with 50% inerts and 50% A, two volumes of feed would give four volumes of completely converted product gas.

2 moles of feed contain 1 mole A and 1 mole inerts. 1 mole of A on complete conversion gives 3 moles of R and therefore product moles are (3 + 1) = 4 moles.

$$\therefore \quad \varepsilon_A = \frac{4-2}{2} = 1$$

For first order reaction in plug flow reactor, we have

$$k\tau = -(1+\varepsilon_A)\ln(1-X_A) - \varepsilon_A X_A$$

$$\tau = C_{Ao}\int_0^{X_A}\frac{dX_A}{-r_A} = C_{Ao}\int_0^{X_A}\frac{dX_A}{kC_{Ao}\left[\frac{1-X_A}{1+\varepsilon_A X_A}\right]}$$

$$k\tau = -(1+\varepsilon_A)\ln(1-X_A) - \varepsilon_A X_A$$

$$\tau = \frac{-(1+\varepsilon_A)\ln(1-X_A) - \varepsilon_A X_A}{k}$$

$$k = 10^{-1}\,\text{s.},\ \varepsilon_A = 1,\ X_A = 0.80$$

$$\tau = -\frac{(1+1)\ln(1-0.80) - 1\times 0.80}{10^{-1}}$$

$$= 24.19\ \text{s}$$

... Ans.

Ex. 3.26 : The liquid - phase reaction :

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P + Q$$

$$k_1 = 7\ l/(\text{mol.min})$$

$$k_2 = 3\ l/(\text{mol.min})$$

is to take place in a 120 litres steady state mixed reactor. The two feed streams, one containing 1.4 mol A/l and the other containing 0.8 mol B/l, are to be introduced in equal volumes into the reactor, and 75% conversion of the limiting component is desired. What should be the flow rate of each stream assuming constant density throughout ?

Solution : $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} P + Q$

$k_1 = 7\ l/(\text{mol.min})$, $k_2 = 3\ l/(\text{mol.min})$

The concentrations of the components in the mixed feed stream are :

$$C_{Ao} = 1.4/2 = 0.7\ \text{mol}/l$$

$$C_{Bo} = 0.8/2 = 0.4\ \text{mol}/l$$

$$C_{Po} = C_{Qo} = 0$$

As the concentration of A is more than that required by stoichiometry, A is excess component and B is the limiting component.

Amount of B reacted = $0.4 \times 0.75 = 0.3\ \text{mol}/l$

For 75% conversion of B and $\varepsilon = 0$, the composition within the reactor and in the exit stream is

$$C_A = 0.7 - 0.3 = 0.4\ \text{mol}/l$$

$$C_B = 0.4 - 0.3 = 0.1\ \text{mol}/l$$

$$C_P = C_Q = 0.3\ \text{mol}/l$$

The rate of reaction at the conditions within the reactor is

$$-r_A = -r_B = k_1 C_A C_B - k_2 C_P C_Q$$

$$= 7\times 0.4\times 0.1 - 3\times 0.3\times 0.3$$

$$= 0.01\ \text{mol}/(l.\text{min})$$

For constant density and for mixed flow reactor,

$$\tau = V/v = \frac{C_{Ao} - C_A}{-r_A}$$

$$\therefore \quad v = \frac{V(-r_A)}{C_{Ao} - C_A} = \frac{120 \times 0.01}{(0.7 - 0.4)} = 4\ l/\text{min}$$

Volumetric flow rate of mixed stream = 4*l*/min

For introduction of two streams in equal volume, the flow of each stream = 4/2 = 2 *l*/min.

... Ans.

Ex. 3.27 : The liquid phase reaction

$$A + B \rightleftharpoons R + S$$

$k_1 = 7\ l/(\text{mol.min})$, $k_2 = 3\ l/(\text{mol.min})$

is to take place in a 120 litres steady state mixed reactor. Two feed streams, one containing 2.8 mol A per litre and the other containing 1.6 mol B per litre, are to be introduced in a volume ratio of 1 : 1.5 (one volume of stream containing A to 1.5 volumes of stream containing B) into the reactor. 75% conversion of the limiting reactant is desired. What should be the volumetric flow rate of each stream assuming constant density throughout ?

Solution : $A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$

$k_1 = 7\ l/(\text{mol.min})$, $k_2 = 3\ l/(\text{mol.min})$

The concentrations of components in the mixed feed stream to the reactor are :

For 1 volume of feed stream containing A and 1.5 volume of feed stream containing B, the mixed stream to reactor is 2.5 volumes.

$$\therefore \quad C_{Ao} = 2.8/2.5 = 1.12\ \text{mol}/l$$

$$C_{Bo} = 1.6/2.5 = 0.64\ \text{mol}/l$$

$$C_{Ro} = C_{So} = 0$$

From above initial concentrations of A and B, it is clear that B is the limiting component.

B reacted = $0.75 \times 0.64 = 0.48$ mol/*l*

For 75% conversion of B and $\varepsilon = 0$, the composition within the reactor and in the exit stream is

$$C_A = 1.12 - 0.48 = 0.64\ \text{mol}/l$$

$$C_B = 0.64 - 0.48 = 0.16\ \text{mol}/l$$

$$C_R = C_S = 0.48\ \text{mol}/l$$

The rate of reaction at the conditions within the reactor is

$$-r_A = k_1 C_A C_B - k_2 C_R C_S$$

$$= 7 \times 0.64 \times 0.16 - 3 \times 0.48 \times 0.48$$

$$= 0.0256\ \text{mol}/(l.\text{min})$$

For mixed flow reactor,

$$\tau = \frac{V}{v} = \frac{C_{Ao} - C_A}{-r_A}$$

$$v = \frac{V(-r_A)}{C_{Ao} - C_A} = \frac{120 \times 0.0256}{(1.12 - 0.64)} = 6.4\ l/\text{min}$$

Volumetric flow rate of mixed stream to the reactor = 6.4 *l*/min

Volumetric flow rate of stream containing A = $\frac{1}{2.5} \times 6.4 = 2.56\ l/\text{min}$

Volumetric flow rate of stream containing B = $\frac{1.5}{2.5} \times 6.4 = 3.84\ l/\text{min}$. **... Ans.**

Ex. 3.28 : A kinetic study of the decomposition of acetaldehyde at 518°C and 1 atm pressure is made in a flow reactor. The decomposition proceeds as :

$$CH_3CHO \rightarrow CH_4 + CO$$

Acetaldehyde is boiled in a flask and passed through a reaction tube maintained by a surrounding furnace at 518°C. The reaction tube has a inside diameter of 33 mm and length 800 mm. The flow rate through the tube is varied by changing the boiling rate. Analysis of the products from the end of the tube are given below. Find the satisfactory rate equation to fit the data.

Data :

Rate of flow, g/h	130	50	21	10.8
Fraction of acetaldehyde decomposed	0.06	0.13	0.24	0.35

Solution :

$$CH_3CHO \rightarrow CH_4 + CO$$

$$A \rightarrow B + C, \quad \text{gas phase reaction}$$

$$\varepsilon_A = \frac{2-1}{1} = 1.0$$

$$C_A = \frac{C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)} = \frac{C_{Ao}(1-X_A)}{(1+X_A)}$$

Assume the decomposition to be second order.

$$\therefore \quad (-r_A) = k\,C_A^2 = \frac{k\,C_{Ao}^2(1-X_A)^2}{(1+X_A)^2}$$

For plug flow reactor,

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{\frac{k\,C_{Ao}^2(1-X_A)^2}{(1+X_A)^2}}$$

$$\frac{V\,k\,C_{Ao}^2}{F_{Ao}} = \int_0^{X_A} \frac{(1+X_A)^2\,dX_A}{(1-X_A)^2}$$

$$\frac{V\,k\,C_{Ao}^2}{F_{Ao}} = \frac{4}{1-X_A} + 4\ln(1-X_A) + X_A - 4$$

$$C_{Ao} = \frac{p_{Ao}}{RT} = \frac{P_o}{RT} \quad \text{as pure acetaldehyde}$$

$$\frac{V\,k\,P_o^2}{(RT)^2\,F_{Ao}} = \frac{4}{1-X_A} + 4\ln(1-X_A) + X_A - 4 \qquad \ldots (1)$$

$$V = \pi/4\,D^2\,L, \quad D = 3.3\text{ cm}, \; L = 800\text{ mm} = 80\text{ cm}$$

$$= \pi/4 \times (3.3)^2 \times 80 = 684\text{ cm}^3 = 0.684\,l$$

Molecular weight of acetaldehyde = 44

$$\text{Molal flow rate of acetaldehyde} = F_{Ao} = \frac{\text{mass flow rate}}{\text{molecular weight}}$$

$$\therefore \quad F_{Ao} = \frac{130}{44}$$

$$= 2.9545 \text{ mol/h}$$

$$= \frac{2.9545}{3600} = 0.000821 \text{ mol/s}$$

Feed rate, g/h	130	50	21	10.8
F_{Ao}, mol/s	0.000821	0.000316	0.000132	0.0000682
X_A	0.06	0.13	0.24	0.35

P_o = 1 atm, R = 0.08206 l.atm/(mol.K), T = 518 °C = 791 K

Putting the values of various terms in equation (1),

$$\frac{0.684 \times (1)^2 k}{(0.08206)^2 (791)^2 F_{Ao}} = \frac{4}{1-X_A} + 4 \ln(1-X_A) + X_A - 4$$

$$\frac{1.62 \times 10^{-4} k}{F_{Ao}} = \frac{4}{1-X_A} + 4 \ln(1-X_A) + X_A - 4$$

$$k = \frac{F_{Ao}}{1.62 \times 10^{-4}} \left[\frac{4}{1-X_A} + 4 \ln(1-X_A) + X_A - 4\right]$$

(i) $F_{Ao} = 0.000821$ mol/s, $X_A = 0.06$

$$k = \frac{0.000821}{1.62 \times 10^{-4}} \left[\frac{4}{1-0.06} + 4 \ln(1-0.06) + 0.06 - 4\right]$$

$$= 0.3436 \ (l/\text{mol})\ (\text{s})^{-1}$$

(ii) $F_{Ao} = 0.000316$ mol/s, $X_A = 0.13$

$$k = \frac{0.000316}{1.62 \times 10^{-4}} \left[\frac{4}{1-0.13} + 4 \ln(1-0.13) + 0.13 - 4\right]$$

$$k = 0.3328 \ (l/\text{mol})\ (\text{s})^{-1}$$

(iii) $F_{Ao} = 0.000132$ mol/s, $X_A = 0.24$

$$k = 0.3303 \ (l/\text{mol})\ (\text{s})^{-1}$$

(iv) $F_{Ao} = 0.0000682$ mol/s, $X_A = 0.35$

$$k = 0.3286 \ (l/\text{mol})\ (\text{s})^{-1}$$

Values of k are approximately same for all data points, so decomposition follows second order kinetics.

$$\text{Average } k = 0.3338 \ (l/\text{mol})\ (\text{s})^{-1}$$

∴ The rate equation is

$$(-r_A) = 0.3338 \ [(l/\text{mol})\ (\text{s})^{-1}] \ C_A^2$$

... **Ans.**

Ex. 3.29 : The laboratory measurements of rate v/s conversion for reactant A are given below. Compare the volumes of a CSTR and plug flow reactor required to achieve 60% conversion. The feed conditions are same in both cases and molar flow rate of A entering a reactor is 10 mol/s.

X_A	0	0.20	0.40	0.60	0.80
$-r_A$, mol/(l.s)	0.182	0.143	0.10	0.0667	0.0357

Solution : $A \rightarrow \text{products}$

$X_A = 0.60$

We have to find out volumes of a CSTR and a plug flow reactor for 60% conversion of A.

X_A	0	0.2	0.4	0.6	0.80
$-r_A$	0.182	0.143	0.10	0.0667	0.0357
$1/(-r_A)$	5.5	7.0	10	15	28

For CSTR,

$$\frac{V}{F_{Ao}} = \frac{X_A}{(-r_A)}$$

For plug flow reactor,

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)} = \int_0^{X_A} \left(\frac{1}{-r_A}\right) dX_A$$

Plot a graph of $1/(-r_A)$ v/s X_A.

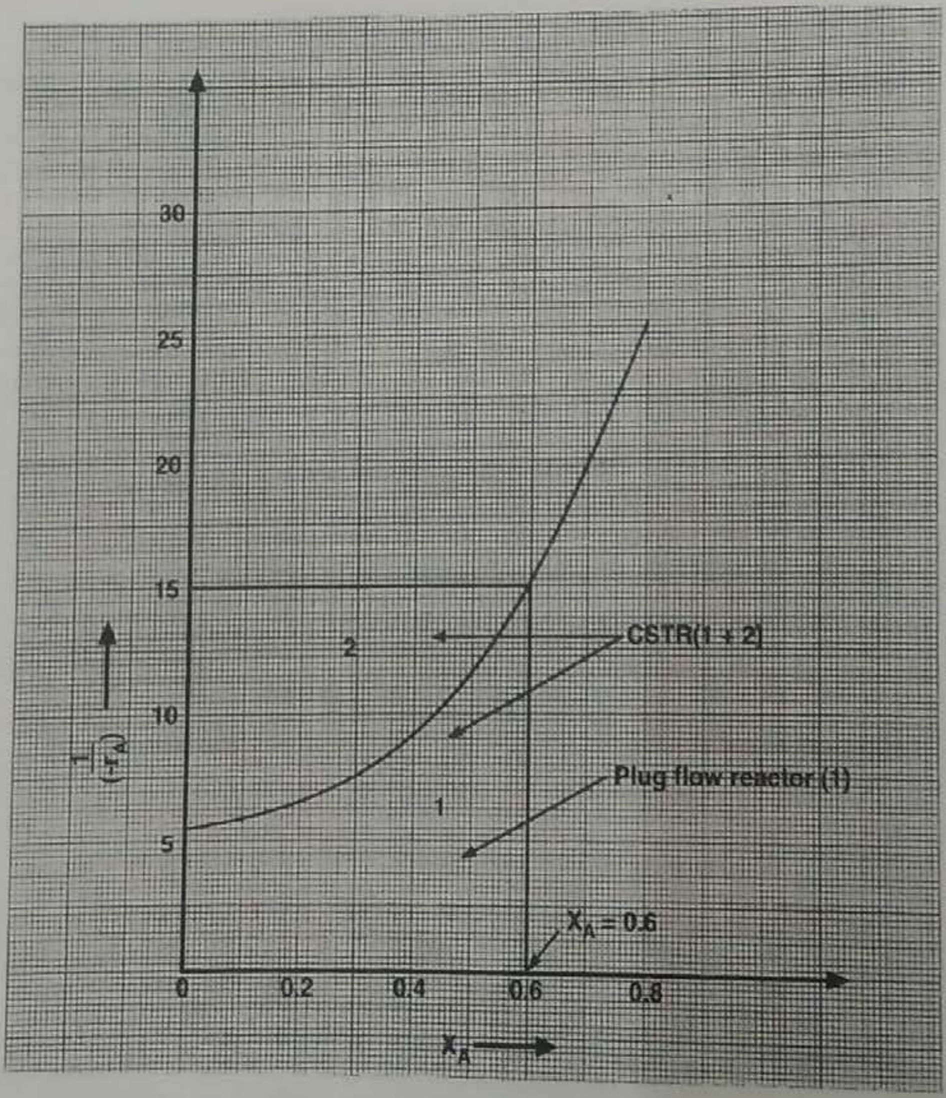


Fig. E 3.29

For CSTR,

V/F_{A_0} is the rectangular area

$$= \text{Area for CSTR} = 36\ \text{cm}^2$$

$$\frac{V}{F_{A_0}} = \text{Area} \times (\text{Scale y-axis}) \times (\text{Scale x-axis})$$

$$= 36\ \text{cm}^2 \times \frac{5}{2\ \text{cm}} \times \frac{0.1}{1\ \text{cm}}$$

$$= 9\ (l.s)/\text{mol}$$

Or directly from x and y axis, A = xy

$$\therefore \quad \frac{V}{F_{A_0}} = 15 \times 0.6 = 9\ (l.s)/\text{mol}$$

$$F_{A_0} = 10\ \text{mol/s}$$

$$V = 9\,F_{A_0}$$

$$= 9 \times 10 = 90\,l$$

$$\text{Volume of CSTR} = 90\,l$$ ... **Ans.**

For plug flow reactor,

V/F_{A_0} is the area under curve.

$$\text{Area under curve} = 21.5\ \text{cm}^2$$

$$\frac{V}{F_{A_0}} = \text{Area} \times (\text{Scale y-axis}) \times (\text{Scale x-axis})$$

$$\frac{V}{F_{A_0}} = 21.5 \times 5/2 \times 0.1/1 = 5.375\ (l.s)/\text{mol}$$

$$V = 5.375 \times F_{A_0} = 5.375 \times 10 = 53.75\,l$$

$$\text{Volume of plug flow reactor} = 53.75\,l$$ ... **Ans.**

So volume of plug flow reactor is less than that of CSTR for same conversion.

For CSTR, V/F_{A_0} is the rectangular area.

For plug flow reactor, V/F_{A_0} is the area under the curve.

Ex. 3.30 : A gas phase decomposition of A is carried out in a mixed reactor. The stoichiometry of decomposition is A → R + S. Initial concentration of A is 0.003 mol/l. The following data is obtained at various runs.

Run No.	1	2	3	4	5
τ, s	0.4	5.0	14	45	195
X_A	0.20	0.60	0.76	0.90	0.97

Find the rate equation for this decomposition.

Solution : $A \rightarrow R + S$, gas phase reaction

$$\varepsilon_A = \frac{2-1}{1} = 1.0$$

$$C_{A_0} = 0.003\ \text{mol}/l$$

$$C_A = \frac{C_{A_0}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$$C_A = \frac{C_{A_0}(1-X_A)}{(1+X_A)}$$

Put X_A values in above equation and get corresponding values of C_A.

For mixed reactor,

$$\tau = \frac{C_{A_0} X_A}{(-r_A)}$$

$$\therefore \quad (-r_A) = \frac{C_{A_0} X_A}{\tau}$$

Get values of $(-r_A)$ at different values of τ and X_A.

We have :

$$(-r_A) = k\,C_A^n$$

$$\ln(-r_A) = n \ln C_A + \ln k$$

Plot of $\ln(-r_A)$ v/s $\ln C_A$ gives values of n and k.

X_A	$C_A = \frac{C_{A_0}(1-X_A)}{(1+X_A)}$	$\ln C_A$
0.20	2×10^{-3}	– 6.21
0.60	7×10^{-4}	– 7.20
0.76	4.1×10^{-4}	– 7.80
0.90	1.58×10^{-4}	– 8.75
0.97	4.57×10^{-5}	– 10.00

X_A	τ	$-r_A = \frac{C_{A_0} X_A}{\tau}$	$\ln(-r_A)$
0.20	0.40	1.5×10^{-3}	– 6.50
0.60	5.0	3.6×10^{-4}	– 7.93
0.76	14	1.63×10^{-4}	– 8.72
0.90	45	6×10^{-5}	– 9.72
0.97	195	1.5×10^{-5}	– 11.11

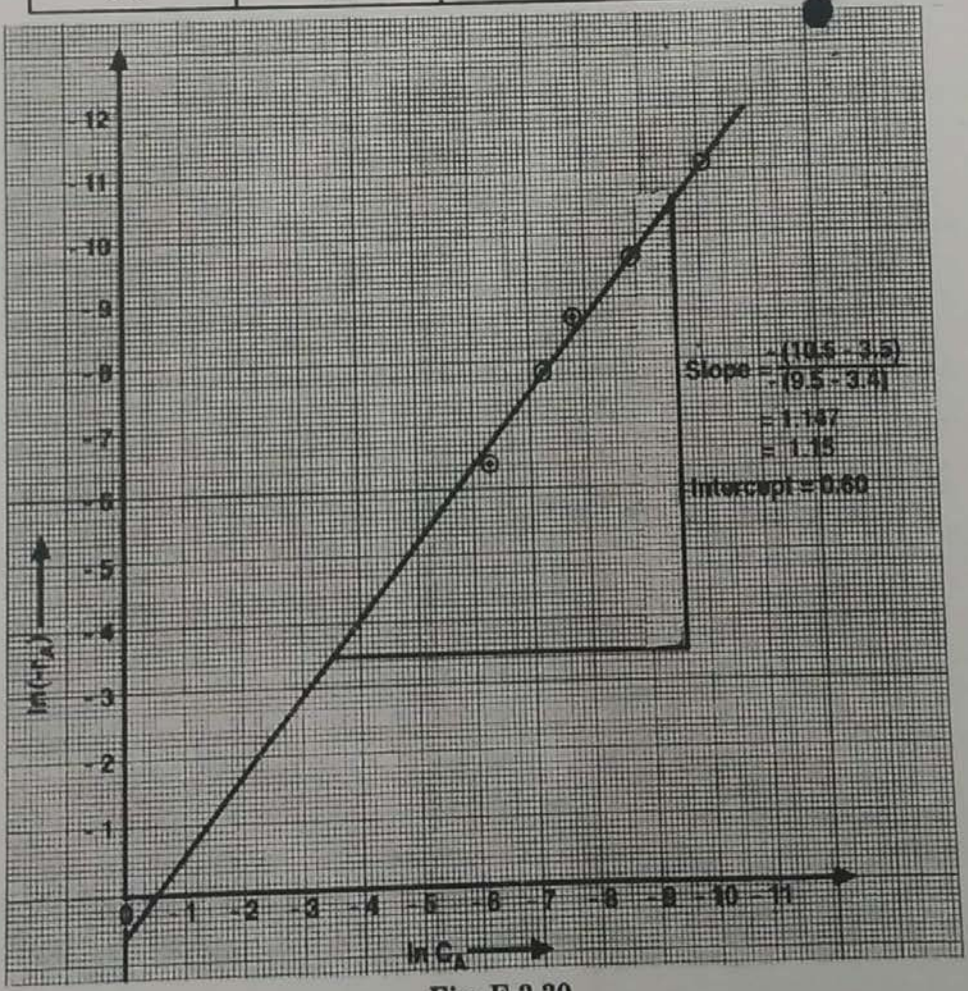


Fig. E 3.30

From graph :

$$\begin{aligned} \text{Slope} &= 1.15 \\ \text{Intercept} &= 0.60 \\ n = \text{Slope} &= 1.15 \\ \text{Intercept} &= \ln k = 0.60 \\ \therefore \quad k &= 1.82 \end{aligned}$$

$\therefore$ The rate equation is

$$-r_A = k\,C_A^n$$

$$-r_A = 1.82\ (\text{mol}/l)^{-0.15}\ (\text{s})^{-1}\ C_A^{1.15}\ ,\ \text{mol}/(l.\text{s}) \qquad \text{... Ans.}$$

✓**Ex. 3.31 :** Acetaldehyde vapour is decomposed in an ideal tubular flow reactor (plug flow reactor) into methane and carbon monoxide.

$$CH_3CHO \rightarrow CH_4 + CO$$

The decomposition is a irreversible reaction and follows second order kinetics with rate constant k equal to 0.33 $(l/\text{mol})^{-1}\ (\text{s})^{-1}$ at 518 °C. The reactor is 33 mm 1 D × 0.8 m pipe maintained at a constant temperature of 518 °C. The pressure is essentially atmospheric. At the space velocity (reported at 273 °C and 1 atm pressure) of 8 $(\text{h})^{-1}$, 35% of acetaldehyde get decomposed. Calculate the mean residence time and compare it with space time.

Solution : The time required for element of reaction mixture to flow through an element of reactor volume V is,

$$d\bar{t}_p = \frac{dV}{v_f}$$

For plug flow reactor,

$$V = F_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$dV = F_{Ao} \cdot \frac{dX_A}{(-r_A)}$$

$$d\bar{t}_p = \frac{F_{Ao} \cdot dX_A}{(-r_A)} \times \frac{1}{v_f}$$

We have

$$\begin{aligned} CH_3CHO &\rightarrow CH_4 + CO \\ A &\rightarrow B + C \\ \varepsilon_A &= \frac{2-1}{1} = 1 \\ C_A &= \frac{C_{Ao}(1-X_A)}{(1+\varepsilon_A X_A)} \\ C_A &= \frac{C_{Ao}(1-X_A)}{(1+X_A)} \\ C_{Ao} &= \frac{p_{Ao}}{RT} \\ \therefore \quad C_A &= \frac{p_{Ao}}{RT}\left(\frac{1-X_A}{1+X_A}\right) \end{aligned}$$

$$-r_A = kC_A^2 = k\left(\frac{p_{Ao}}{RT}\right)^2 \frac{(1-X_A)^2}{(1+X_A)^2}$$

$$v_f = v_o(1+\varepsilon_A X_A)$$

$$= v_o(1+X_A)$$

$$\therefore \quad v_f/v_o = (1+X_A)$$

$$d\bar{t}_p = \frac{F_{Ao}\, dX_A}{(-r_A)\, v_f}$$

$$\bar{t}_p = F_{Ao} \int \frac{dX_A}{(-r_A)\, v_f}$$

$$\bar{t}_p = F_{Ao} \int \frac{dX_A}{(-r_A)\, v_f} \times \frac{v_o}{v_o}$$

$$\bar{t}_p = \frac{F_{Ao}}{v_o} \int_0^{X_A} \frac{dX_A}{(-r_A) \times v_f/v_o}$$

$$\bar{t}_p = \frac{F_{Ao}}{v_o} \int_0^{X_A} \frac{dX_A}{k\,(p_{Ao}/RT)^2 \dfrac{(1-X_A)^2}{(1+X_A)^2} \times (1+X_A)}$$

$$\bar{t}_p = \frac{F_{Ao}}{v_o} \left[\frac{1}{k\,(p_{Ao}/RT)^2}\right] \int_0^{X_A} \frac{(1+X_A)}{(1-X_A)^2}\, dX_A$$

$$F_{Ao} = C_{Ao} \cdot v_o$$

$$\therefore \quad C_{Ao} = \frac{F_{Ao}}{v_o} = \frac{p_{Ao}}{RT}$$

Putting value of F_{Ao}/v_o and integrating, we get,

$$\bar{t}_p = \frac{p_{Ao}/RT}{k\,(p_{Ao}/RT)^2} \left[\frac{2}{1-X_A} + \ln(1-X_A)\right]_0^{X_A}$$

$$\bar{t}_p = \frac{RT}{k\, p_{Ao}} \left[\frac{2}{1-X_A} + \ln(1-X_A)\right]_0^{0.35}$$

$$R = 0.08206\ l.\text{atm}/(\text{mol.K})$$

$$T = 518\,^\circ C = 791\ K$$

$$P_o = 1\ \text{atm}$$

Initially, pure acetaldehyde is present.

$$\therefore \quad p_{Ao} = P_o = 1\ \text{atm}$$

$$k = 0.33\ (l/\text{mol})^{-1}\,(s)^{-1}$$

$$\bar{t}_p = \frac{0.08206 \times 791}{0.33 \times 1} \left[\frac{2}{1-0.35} + \ln(1-0.35) - 2\right]$$

$$\bar{t}_p = 127.06 = 127.1\ s$$

Space time, τ = 1/space velocity

Space velocity at 273 K and 1 atm = $8\ (h)^{-1}$

Reactor is at 791 K and 1 atm pressure.

$\therefore$ Space velocity at the reactor temperature = $8 \times \dfrac{791}{273} = 23.2\ (h)^{-1}$

∴ Space time at the reactor temperature

$$= 1/\text{space velocity} = 1/23.2$$

$$= 0.0431 \text{ h}$$

$$= 0.0431 \times 3600$$

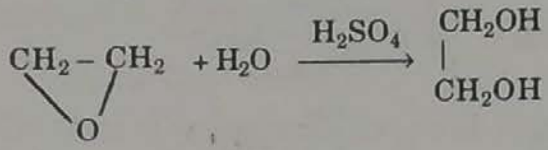
$$= 155.2 \text{ s}$$

Residence time is 127.1 s and space time is 155.2 s. The difference in these values is due to the increase in the number of moles occurring as a result of reaction.

Residence time/holding time = 127.1 s ... **Ans.**

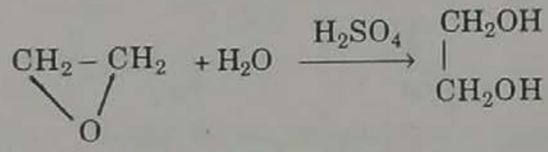
Space time = 155.2 s ... **Ans.**

Ex. 3.32 : It is desired to produce 170 kg/min of ethylene glycol using mixed flow reactor operated isothermally. A 16 kmol/m^3 solution of ethylene oxide in water is fed to the reactor together with an equal volumetric solution of water containing 0.98% by weight H_2SO_4. Determine the size (volume) of the reactor required to achieve 80% conversion.



It may be assumed that the concentration of water remains constant during the course of reaction. The reaction is first order in ethylene oxide with k = 0.311 (min)$^{-1}$.

Solution :



$$A + B \xrightarrow{\text{Cat.}} C$$

Concentration of B remains constant during the course of reaction, so the rate is independent of C_B.

The reaction is first order in A.

$$-r_A = k\,C_A$$

For mixed flow reactor,

$$\frac{V}{v_o} = \frac{C_{Ao}\,X_A}{(-r_A)}$$

$$V = \frac{v_o\,C_{Ao}\,X_A}{k\,C_A}$$

For liquid phase reaction, $v = v_o$

∴

$$C_A = C_{Ao}(1 - X_A)$$

$$V = \frac{v_o\,C_{Ao}\,X_A}{k\,C_{Ao}\,(1 - X_A)}$$

$$V = \frac{v_o\,X_A}{k\,(1 - X_A)}$$

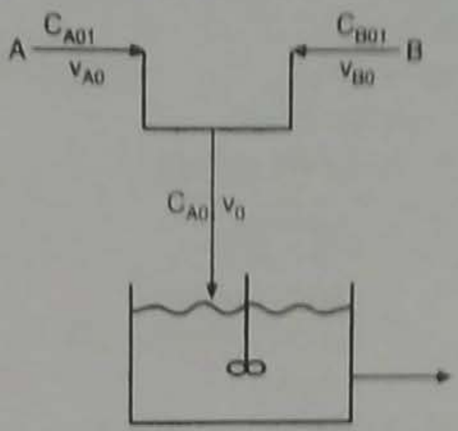


Fig. E 3.32 : CSTR set-up

v_{Ao} = volumetric flow rate of stream A entering reactor before mixing of streams.

v_{Bo} = volumetric flow rate of stream B entering reactor before mixing.

v_o = total volumetric feed rate to the reactor.

Form the statement of problem-equal volumetric flow rate of both streams.

$$v_{Bo} = v_{Ao}$$

$$v_o = v_{Ao} + v_{Bo} = 2\,v_{Ao}$$

Production rate of C = 170 kg/min

Molecular weight of C = 62

$$\text{Production rate of C (molal)} = \frac{170}{62} = 2.742 \text{ kmol/min}$$

From reaction stoichiometry

1 kmol A ≡ 1 kmol C

$$\text{Moles of A reacted to C per min} = \frac{1}{1} \times 2.742 = 2.742 \text{ kmol}$$

Conversion of A = 80% (given)

$$\text{\% conversion of A} = \frac{\text{kmol A reacted}}{\text{kmol A charged}} \times 100$$

∴ Molal flow rate of A to the reactor is

$$F_{Ao} = \frac{2.742}{0.80} = 3.4275 \text{ kmol/h}$$

C_{Ao1} = concentration of A in stream entering before mixing of streams

= 16 kmol/m^3

C_{Ao} = concentration of A in mixed stream to the reactor i.e. total feed stream (mixed stream) to the reactor

$$\text{Volumetric flow rate of stream A entering (before mixing)} = v_{Ao} = \frac{F_{Ao}}{C_{Ao1}}$$

$$= \frac{3.4275}{16} = 0.2142 \text{ m}^3\text{/min}$$

$X_A = 0.80, \quad k = 0.311\ (\text{min})^{-1}$

$$\begin{aligned} v_o &= 2\, v_{Ao} \qquad \text{(equal volumetric flow rate of streams)} \\ &= 2 \times 0.2142 \\ &= 0.4284\ \text{m}^3/\text{min} \\ V &= \frac{v_o X_A}{k\,(1 - X_A)} \\ &= \frac{0.4284 \times 0.80}{0.311\,(1 - 0.80)} \\ &= 5.51\ \text{m}^3 \end{aligned}$$

$$\text{Volume of CSTR required} = 5510\ l \qquad \text{... Ans.}$$

Ex. 3.33 : The conversion data obtained in a tubular flow reactor (plug flow behaviour) for gas phase pyrolysis of acetone at 520 °C and 1 atmosphere is given below. The reaction is

$$CH_3COCH_3 \rightarrow CH_2 = C = O + CH_4$$

The reactor dimensions were : inside diameter = 33 mm and length = 80 cm.

What rate equation is suggested by the data ?

Flow rate, g/h	130	50	21	10.8
Conversion of acetone	0.05	0.13	0.24	0.35

Solution : $CH_3COCH_3 \rightarrow CH_2 = C = O + CH_4$, gas phase reaction

$$A \rightarrow R + S$$

$$\varepsilon_A = \frac{2-1}{1} = 1.0$$

$$\text{Molecular weight of acetone} = 58$$

$$\text{Molal flow rate of acetone} = \frac{\text{mass flow rate}}{\text{molecular weight}}$$

e.g. For mass flow rate = 130 g/h

$$F_{Ao} = \frac{130}{58} = 2.241\ \text{mol/h} = 6.225 \times 10^{-4}\ \text{mol/s}$$

Convert mass flow rate into molar flow rate and tabulate.

F_{Ao}, mol/s	6.225×10^{-4}	2.395×10^{-4}	1.006×10^{-4}	5.172×10^{-5}
X_A	0.05	0.13	0.24	0.35

$$\begin{aligned} V &= \frac{\pi}{4} \times (3.3)^2 \times 80 \\ &= 684\ \text{cm}^3 \\ &= 0.684\ l \\ C_{Ao} &= \frac{p_{Ao}}{RT} \\ p_{Ao} &= P_o = 1\ \text{atm (as pure acetone)} \\ T &= 520\ ^\circ\text{C} = 793\ \text{K}, \quad R = 0.08206\ l\cdot\text{atm/(mol}\cdot\text{K)} \\ C_{Ao} &= \frac{1}{0.08206 \times 793} \\ &= 0.01537\ \text{mol}/l \approx 0.0154\ \text{mol}/l \end{aligned}$$

For plug flow reactor,

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

Now, $\varepsilon_A = 1.0$

$$\therefore \quad C_A = \frac{C_{Ao}(1 - X_A)}{(1 + \varepsilon_A X_A)}$$

$$= \frac{C_{Ao}(1 - X_A)}{(1 + X_A)}$$

Assume decomposition to be first order.

$$\therefore \quad -r_A = k\, C_A$$

$$= \frac{k\, C_{Ao}(1 - X_A)}{(1 + X_A)}$$

$$\therefore \quad \frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{\dfrac{k\, C_{Ao}(1 - X_A)}{(1 + X_A)}}$$

$$\frac{V}{F_{Ao}} = \frac{1}{k\, C_{Ao}} \int_0^{X_A} \frac{(1 + X_A)}{(1 - X_A)}\, dX_A$$

$$\frac{V}{F_{Ao}} = \frac{1}{k\, C_{Ao}} \left[2 \ln\left(\frac{1}{1 - X_A}\right) - X_A\right]$$

$$k = \frac{F_{Ao}}{C_{Ao} \cdot V}\left[2 \ln\left(\frac{1}{1 - X_A}\right) - X_A\right]$$

$$C_{Ao} = 0.0154 \text{ mol}/l, \quad V = 0.684\, l$$

(i) $F_{Ao} = 6.225 \times 10^{-4}, \quad X_A = 0.0$[illegible]$5$

$$k = \frac{6.225 \times 10^{-4}}{0.0154 \times 0.684}\left[2 \ln\left(\frac{1}{1 - 0.05}\right) - 0.05\right]$$

$$= 3.11 \times 10^{-3} \, (s)^{-1}$$

(ii) $F_{Ao} = 2.395 \times 10^{-4}, \quad X_A = 0.13$

$$k = \frac{2.395 \times 10^{-4}}{0.0154 \times 0.684}\left[2 \ln\left(\frac{1}{1 - 0.13}\right) - 0.13\right]$$

$$= 3.38 \times 10^{-3} \, (s)^{-1}$$

(iii) $F_{Ao} = 1.006 \times 10^{-4}, \quad X_A = 0.24$

$$k = \frac{1.006 \times 10^{-4}}{0.0154 \times 0.684}\left[2 \ln\left(\frac{1}{1 - 0.24}\right) - 0.24\right]$$

$$= 2.95 \times 10^{-3} \, (s)^{-1}$$

(iv) $F_{Ao} = 5.172 \times 10^{-5}, \quad X_A = 0.35$

$$k = \frac{5.172 \times 10^{-5}}{0.0154 \times 0.684}\left[2 \ln\left(\frac{1}{1 - 0.35}\right) - 0.35\right]$$

$$= 2.51 \times 10^{-3} \, (s)^{-1}$$

As there is no large variation in k values at different data points, the reaction follows first order kinetics.

$$\text{Average value of k} = \frac{(3.11 + 3.38 + 2.95 + 2.51) \times 10^{-3}}{4}$$

$$= 2.9875 \times 10^{-3}\,(\text{s})^{-1}$$

$$= 2.99 \times 10^{-3}\,(\text{s})^{-1}$$

The rate equation suggesting decomposition is

$$-r_A = k\,C_A$$

$$-r_A = 2.99 \times 10^{-3}\,(\text{s})^{-1} \cdot C_A \qquad \text{... Ans.}$$

OR

Differential method may be used.

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$d(V/F_{Ao}) = \frac{dX_A}{(-r_A)}$$

$$dX_A = (-r_A)\,d(V/F_{Ao})$$

Plot X_A v/s V/F_{Ao}. The slope of tangents to this curve at any value of X_A, $-dX_A/d(V/F_{Ao})$ gives the rate of reaction $(-r_A)$.

From graph of X_A v/s V/F_{Ao} :

X_A	$-r_A$
X_{A1}	$-r_{A1}$
X_{A2}	$-r_{A2}$
:	:

$$C_A = C_{Ao}(1 - X_A)/(1 + X_A)$$

Get values of C_A at various values of X_A mentioned in above table.

X_A	C_A	$(-r_A)$
X_{A1}	C_{A1}	$(-r_A)_1$
:	:	:
:	:	:

$$(-r_A) = k\,C_A^n$$

$$\ln(-r_A) = n \ln C_A + \ln k$$

Plot $\ln(-r_A)$ v/s $\ln C_A$ and get values of n and k.

Ex. 3.34 : The gas phase decomposition of A is carried out in a experimental tubular reactor (plug flow reactor) packed with 2.5 litres of catalyst. At a flow rate of 2.65 m^3/h of pure A at 22 atm and 320 °C, 70% of A decomposes to product. The decomposition follows second order kinetics and the stoichiometry of decomposition is $A \rightarrow R$.

The data obtained in an experimental reactor is used to design a large scale tubular reactor (plug flow behaviour) to treat 165 m^3/h of gases feed containing 60 mole % A and balance inerts at a pressure of 36 atm and temperature of 320 °C. Calculate the volume of catalyst required to achieve 90% conversion in large scale reactor.

Assume ideal gas behaviour.

Solution : $A \rightarrow R$, gas phase reaction.

Experimental reactor :

$P = 22$ atm, $T = 320\,^{\circ}C = 593$ K

Pure gaseous A,

$$\varepsilon_A = \frac{1-1}{1} = 0$$

For plug flow reactor :

$$\frac{V}{v_o} = C_{Ao}\int_0^{X_A}\frac{dX_A}{(-r_A)}$$

$$= C_{Ao}\int_0^{X_A}\frac{dX_A}{k\,C_{Ao}^2\,(1-X_A)^2}$$

$[\text{as } -r_A = k\,C_A^2 \text{ (given)} = k\,C_{Ao}^2\,(1-X_A)^2]$

$$\frac{V}{v_o} = \frac{1}{k\,C_{Ao}}\int_0^{X_A}\frac{dX_A}{(1-X_A)^2}$$

$$\frac{V}{v_o} = \frac{1}{k\,C_{Ao}}\left[\frac{X_A}{1-X_A}\right]$$

V is the volume of reactor which is the volume of catalyst in present case.

$V = 2.5\,l$, $v_o = 2.65$ m³/h $= 2.65 \times 10^3$ l/h, $P_o = 22$ atm, $T = 320\,^{\circ}C = 593$ K

$$C_{Ao} = \frac{p_{Ao}}{RT} \quad (p_{Ao} = P_o,\ \text{pure A})$$

$$= \frac{22}{0.08206 \times 593}$$

$$= 0.452 \text{ mol}/l$$

$$X_A = 0.70$$

$$\therefore \quad k = \frac{1}{C_{Ao}}\left[\frac{X_A}{1-X_A}\right]\frac{v_o}{V}$$

$$= \frac{1}{0.452}\left[\frac{0.70}{1-0.70}\right] \times \frac{2.65 \times 10^3}{2.5}$$

$$= 5472\ (l/\text{mol})\ (\text{h})^{-1}$$

Commercial reactor :

The value of k calculated is to be used for calculating the volume of catalyst i.e. volume of a commercial reactor.

$v_o = 165$ m³/h $= 165 \times 10^3$ l/h

Feed = 60 mole % A and 40 mole % inerts

$P = 36$ atm, $T = 320\,^{\circ}C = 593$ K

$$p_{Ao} = 0.60 \times 36 = 21.6 \text{ atm}$$

$$C_{Ao} = \frac{p_{Ao}}{RT}$$

$$C_{Ao} = \frac{21.6}{0.08206 \times 593}$$

$$= 0.444 \text{ mol}/l$$

$$v_o = 165 \times 10^3 \ l/h$$

$$F_{Ao} = C_{Ao} \cdot v_o$$

$$= 0.444 \times 165 \times 10^3$$

$$= 73260 \text{ mol/h}$$

For plug flow reactor,

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$(-r_A) = k\,C_A^2$$

$$A \rightarrow R$$

feed	product
0.60 A	0.6 R
0.40 I	0.4 I
1.0	1.0

$$\varepsilon_A = \frac{1-1}{1} = 0$$

$$\therefore \quad (-r_A) = k\,C_{Ao}^2\,(1-X_A)^2$$

$$V = F_{Ao} \int_0^{X_A} \frac{dX_A}{k\,C_{Ao}^2\,(1-X_A)^2}$$

$$V = \frac{F_{Ao}}{k\,C_{Ao}^2}\left[\frac{X_A}{1-X_A}\right], \quad X_A = 0.90 \text{ and } k = 5472$$

$$V = \frac{73260}{5472 \times (0.444)^2}\left[\frac{0.90}{1-0.90}\right]$$

$$= 611\ l$$

The volume of catalyst required for 90% conversion = 611 l ... **Ans.**

Ex. 3.35 : Stream of aqueous monomer A (1 mol/l, 4 l/min) enters a mixed flow reactor of volume 2 litres. It is radiated therein, and polymerises as follows :

$$A \xrightarrow{+A} R \xrightarrow{+A} S \xrightarrow{+A} T \ldots\ldots$$

In the exit stream $C_A = 0.01$ mol/l, and for a particular reaction product W, $C_W = 0.0002$ mol/l. Find the rate of reaction of A and the rate of formation of W.

Solution : $A \xrightarrow{+A} R \xrightarrow{+A} S \xrightarrow{+A} T \ldots\ldots$

Liquid phase reaction, so $\varepsilon_A = 0$.

Volume of mixed flow reactor = $V = 2\ l$

$$v_o = 4\ l/\text{min}$$

$$C_{Ao} = 1 \text{ mol}/l, \quad C_A = 0.01 \text{ mol}/l$$

$$\tau = \frac{V}{v_o} = \frac{C_{Ao} - C_A}{(-r_A)} = \frac{C_{Ao}\,X_A}{(-r_A)}$$

$$\therefore \quad V = \frac{540}{54 \times 660} [-[1+(-0.667)] \ln(1-0.75) - (-0.667) \times 0.75]$$

$$= 0.0146\ l$$

... **Ans.**

Ex. 3.48 : One litre per second of a 20% ozone – 80% air mixture at 1.5 atm pressure and temperature of 93 °C passes through a plug flow reactor. Under these conditions, the ozone decomposes as per the reaction :

$$2\,O_3 \rightarrow 3\,O_2$$

with $-r_{O_3} = k\,C^2_{ozone}$

where $k = 0.05\ l/(mol.s)$

Find the size of reactor required for 50% decomposition of ozone.

Solution : $2\,O_3 \rightarrow 3\,O_2$, gas phase reaction

Feed : 20% ozone – 80% inerts

20 mol O_3 80 mol inerts	30 mol O_2 80 mol inerts
100 mol feed	110 mol product

$$\varepsilon_A = \frac{110-100}{100} = 1.1$$

$$2A \rightarrow 3R$$

$$-r_A = k\,C_A^2, \quad k = 0.05\ l/(mol.s)$$

20 mol % A and 80 mol % air (inert)

$$\text{Mole fraction of A} = \frac{20}{100} = 0.20$$

$$p_{Ao} = \text{mole fraction of A} \times P$$

$P = 1.5$ atm, $T = 93\ ^\circ C = 366$ K

$$C_{Ao} = \frac{p_{Ao}}{RT} = \frac{0.20 \times 1.5}{0.08206 \times 366} = 9.99 \times 10^{-3}\ mol/l$$

$$= 0.01\ mol/l$$

$$v_o = 1\ l/s$$

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)} = \int_0^{X_A} \frac{dX_A}{k\,C_A^2} = \int_0^{X_A} \frac{dX_A}{\left[\frac{C^2_{Ao}(1-X_A)^2}{(1+\varepsilon_A X_A)^2}\right]}$$

Integrated performance equation for second order reaction for $\varepsilon_A \neq 0$:

$$C_{Ao}\,k\,\tau = 2\varepsilon_A(1+\varepsilon_A)\ln(1-X_A) + \varepsilon_A^2 X_A + (\varepsilon_A+1)^2 \cdot \frac{X_A}{1-X_A}$$

with $\varepsilon_A = 1.1$ and $X_A = 0.5$

$$C_{Ao}\,k\,\tau = 2 \times 1.1\,(1+1.1)\ln(1-0.50) + (1.1)^2 \times 0.50 + (1.1+1)^2 \frac{(0.5)}{(1-0.5)}$$

$$C_{Ao}\,k\,\tau = 1.8127, \quad \tau = V/v_o$$

$$V = \frac{1.8127 \times v_o}{C_{Ao}\ \ k} = \frac{1.8127 \times 1}{0.01 \times 0.05} = 3625.4\ l$$

Volume of plug flow reactor = 3625.4 l ... **Ans.**

Ex. 3.49 : Pure gaseous A at about 3 atm and 30 °C is fed to a mixed reactor of 1 litre volume at various flow rates. In reactor, it decomposes and the exit concentration of A is measured at each flow rate.

A decomposes as per $A \rightarrow 3R$ with $C_{A_0} = 120$ mmol/l. Find a rate equation to represent the kinetics of decomposition of A from the following data.

v_o, l/min	0.06	0.48	1.5	8.1
C_A, mmol/l	30	60	80	105

Solution : $A \rightarrow 3R$, gas phase reaction, $\varepsilon_A \neq 0$

$$\varepsilon_A = \frac{3-1}{1} = 2$$

For changing-density system, C_A is given by

$$C_A = \frac{C_{A_0}(1-X_A)}{(1+\varepsilon_A X_A)}$$

$$\therefore \quad X_A = \frac{1-C_A/C_{A_0}}{1+\varepsilon_A C_A/C_{A_0}}$$

$$X_A = \frac{1-C_A/C_{A_0}}{1+2C_A/C_{A_0}}$$

$$C_{A_0} = 120 \text{ mmol}/l, \quad C_A = 30 \text{ mmol}/l$$

$$X_A = \frac{1-30/120}{1+2(30/120)}$$

$$= 0.50$$

For CSTR :

$$\frac{V}{v_o} = \frac{C_{A_0} X_A}{(-r_A)}$$

$$-r_A = \frac{C_{A_0} \cdot X_A \cdot v_o}{V}$$

$$C_{A_0} = 120 \text{ mmol}/l, \quad V = 1\,l$$

For data given, find X_A and $-r_A$ and tabulate.

Run	v_o	C_A	X_A	$(-r_A)_{out}$, mmol/(l.min)	ln C_A	ln $(-r_A)$
1	0.06	30	0.50	3.6	3.40	1.28 ≈ 1.3
2	0.48	60	0.25	14.4	4.10	2.67
3	1.5	80	0.143	25.74	4.40 (4.38)	3.25
4	8.1	105	0.0454	44.13	4.65	3.80

The rate of decomposition is given by

$$(-r_A) = k\,C_A^n$$

$$\ln(-r_A) = \ln k + n \ln C_A$$

Plot of ln $(-r_A)$ v/s ln C_A yields a straight line with slope equal to n and intercept equal to ln k.

From graph, n = 1.5 and k = 0.0302

∴ The rate equation for decomposition of A is

$$-r_A = 0.0302\,C_A^{1.5}$$

... **Ans.**

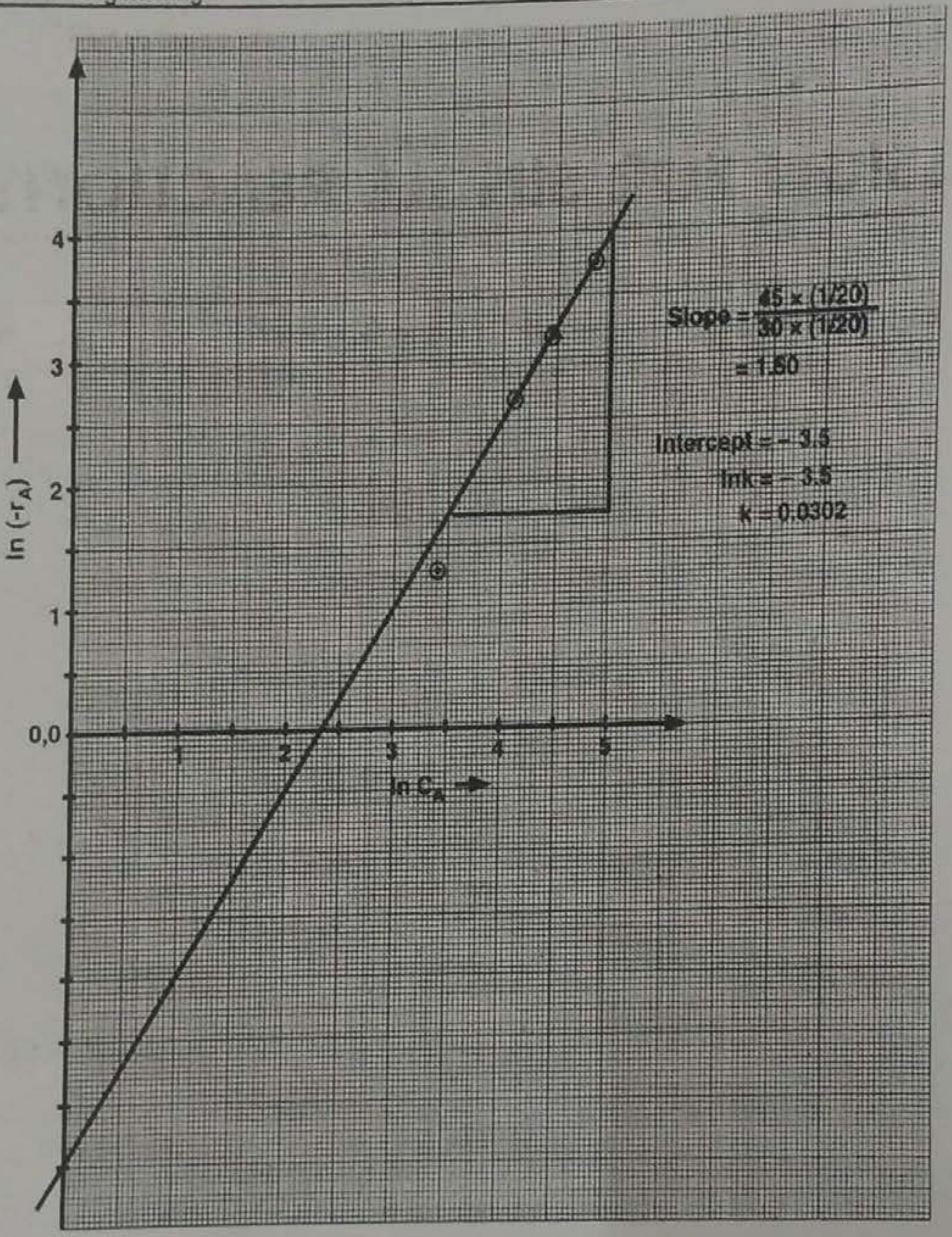

4
3
2
1
0,0
ln (-r_A) ⟶
1
2
3
4
5
ln C_A ⟶
Slope = 45 × (1/20) / 30 × (1/20)
= 1.50
Intercept = – 3.5
lnk = – 3.5
k = 0.0302

Fig. E 3.49

❏❏❏

Chapter ... 4

DESIGN FOR SINGLE REACTIONS

We can carry chemical reactions either in liquid or in vapour phase. We can carry out chemical reactions by making use of a single batch or flow reactor, chain of reactors, recycle reactor, and so on. While selecting a reactor system to carry out a particular reaction, we have to take into account the following factors :

(i) type of reaction, (ii) scale of production, (iii) cost of equipment and operation, (iv) stability and flexibility of operation, (v) equipment life, (vi) time period over which product is to be manufactured, (vii) ease of convertibility of equipment to modified operating conditions or to new unit processes and (viii) safety.

As the factors to be considered are so many, for selecting reasonable good reactor system/set-up, we require experience, engineering judgement and sound knowledge of the characteristics of various reactor systems. Ultimately, the choice of reactor system rests on the economics of the overall process. The reactor system selected will influence the economics of the overall process through reactor size needed and product distribution.

In this chapter, we will deal with single reactions. These are reactions of which the progress can be described and followed by making use of only one rate expression together with necessary stoichiometric and equilibrium expressions. In case of single reactions, the distribution is fixed and therefore the important factor in comparing various designs is the reactor size. i.e. primary consideration in case of single reactions is the reactor size. So in this chapter we will consider the size comparison of various single and multiple ideal reactor systems along with recycle reactor.

Size Comparison of Single Reactors :

Let us mention the batch reactor briefly before we do the comparison of flow reactors.

Batch Reactor :

The advantages of batch reactor include : (i) high conversion which can be achieved by leaving the reactant in the reactor for long periods of time, (ii) simple to operate, (iii) small instrumentation cost, and (iv) flexibility of operation (easy and quick shut down of reactor is possible). It has disadvantages of (i) high labour cost per unit of production, (ii) poorer quality control of the product, and (iii) considerable shut down time to empty, cleanout, and refill. Therefore, we may say that the batch reactor is well suited to produce small amounts of material i.e. for small-scale operation, to produce varied materials from single piece of equipment, for long reaction times, and for testing new processes which are not fully developed. On the other hand, for large scale production of materials, the continuous process is nearly always seems to be more economical. While making discussion regarding sizes here, we compare the performance equations of the reactors. A comparison of performance equation for the batch reactor [equation (3.15)] and that for the plug flow reactor [equation (3.34)] for given duty i.e. for a specified level of conversion and for constant density system ($\varepsilon = 0$) shows that an element of fluid reacts for the same length of time in the batch and in the plug flow reactors. Hence, the same volume of these reactors is required for doing a given job. Of course, we must correct the size requirement estimate to take into account the shut down between batches in case of long-term production. Therefore, it is easy to relate the performance capabilities of the batch reactor with the plug flow reactor.

Comparison of Mixed Flow Reactor/CSTR and Plug Flow Reactor for first order and second order reaction :

For a given duty, the ratio of size (volume) of mixed flow reactor to the size (volume) of the plug flow reactor depends upon the extent of reaction (level of conversion), the stoichiometry, and the form of the rate equation/expression. For the general case, a comparison of the performance equations of CSTR and PFR will give this size ratio.

We will now do the comparison of CSTR and PFR for simple n^th^ order reaction.

The rate equation for n^th^ order reaction is

$$-r_A = -\frac{1}{V}\frac{dN_A}{dt} = k\,C_A^n$$

where n varies from zero to three.

For mixed flow/CSTR, the performance equation is

$$\tau_m = \left(\frac{C_{Ao}\,V}{F_{Ao}}\right)_m = \frac{C_{Ao}\,X_A}{-r_A}$$

$$\tau_m = \frac{C_{Ao}\,X_A}{k\,C_A^n}$$

$$C_A = \frac{C_{Ao}\,(1-X_A)}{(1+\varepsilon_A X_A)}$$

$$\therefore \quad \tau_m = \frac{C_{Ao}\,X_A\,(1+\varepsilon_A X_A)^n}{k\,C_{Ao}^n\,(1-X_A)^n}$$

$$\tau_m \cdot C_{Ao}^{n-1} = \left(\frac{C_{Ao}^n\,V}{F_{Ao}}\right)_m = \frac{X_A\,(1+\varepsilon_A X_A)^n}{k\,(1-X_A)^n} \qquad \dots (4.1)$$

For plug flow reactor, the performance equation is

$$\tau_p = \left(\frac{C_{Ao}\,V}{F_{Ao}}\right)_p = C_{Ao}\int_0^{X_A}\frac{dX_A}{(-r_A)}$$

$$\tau_p = C_{Ao}\int_0^{X_A}\frac{(1+\varepsilon_A X_A)^n}{k\,C_{Ao}^n\,(1-X_A)^n}\,dX_A$$

$$\therefore \quad \tau_p\,C_{Ao}^{n-1} = \left(\frac{C_{Ao}^n\,V}{F_{Ao}}\right)_p = \frac{1}{k}\int_0^{X_A}\frac{(1+\varepsilon_A X_A)^n}{(1-X_A)^n}\,dX_A \qquad \dots (4.2)$$

Dividing equation (4.1) by (4.2), we get,

$$\frac{(\tau\,C_{Ao}^{n-1})_m}{(\tau\,C_{Ao}^{n-1})_p} = \frac{(C_{Ao}^n\,V/F_{Ao})_m}{(C_{Ao}^n\,V/F_{Ao})_p} = \frac{X_A\,(1+\varepsilon_A X_A)^n/(1-X_A)^n}{\left[\displaystyle\int_0^{X_A}\frac{(1+\varepsilon_A X_A)^n}{(1-X_A)^n}\,dX_A\right]} \qquad \dots (4.3)$$

For constant density system ($\varepsilon = 0$), the above equation integrates to

$$\frac{(\tau\,C_{Ao}^{n-1})_m}{(\tau\,C_{Ao}^{n-1})_p} = \frac{[X_A/(1-X_A)^n]_m}{\left[\dfrac{(1-X_A)^{n-1}-1}{n-1}\right]_p}, \quad n \neq 1 \qquad \dots (4.4)$$

For first order reaction with $\varepsilon_A = 0$, $n = 1$, equation (4.3) becomes

$$\frac{(\tau C_{Ao}^{n-1})_m}{(\tau C_{Ao}^{n-1})_p} = \frac{\tau_m}{\tau_p} = \frac{[X_A/(1-X_A)]_m}{[-\ln(1-X_A)]_p} \qquad \dots (4.5)$$

For second order reaction, n = 2, therefore equation (4.5) becomes

$$\frac{(\tau C_{Ao}^{n-1})_m}{(\tau C_{Ao}^{n-1})_p} = \frac{[X_A/(1-X_A)^2]_m}{[X_A/(1-X_A)]_p} \qquad \dots (4.6$$

Above equations are displayed in graphical form in Fig. 4.1 for quick comparison of the performance of mixed flow and plug flow reactors. For identical feed rate F_{Ao} and feed composition C_{Ao}, the ordinate of Fig. 4.1 gives directly the volume/size ratio of these two single reactors required for any specified conversion.

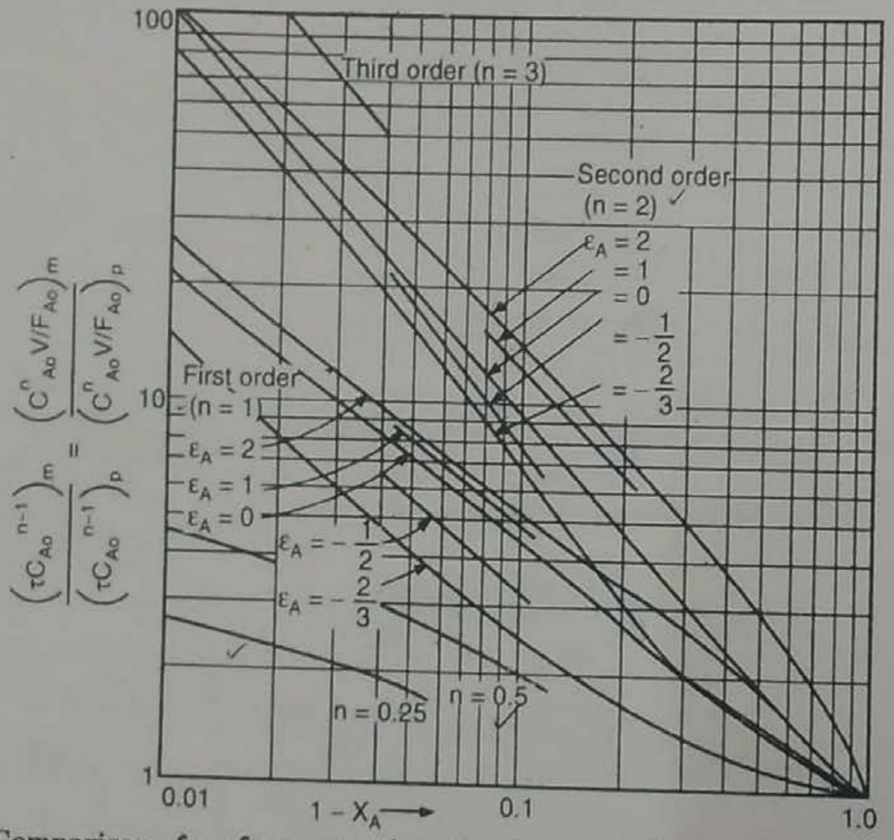


Fig. 4.1 : Comparison of performance of single mixed and plug flow reactors for the n^{th} order reactions

It is clear from the Fig. 4.1 that :

(a) For any given duty (any given conversion level), and for all positive reaction rders, the size of CSTR is always larger than the PFR. The ratio of volumes V_m/V_p increases vith the reaction order. The size of reactor is independent of type of flow (completely mixed nd one without mixing) for zero order reactions.

(b) For low values of conversion, the reactor size is only slightly affected by the type of low. As the conversion approaches zero, the volume/size ratio of two reactors approaches nity. The size ratio increases very rapidly at high values of conversion.

(c) The design of reactor gets affected by density variation during the reaction. xpansion (or density decrease) during reaction increases the size ratio. In other words ensity decrease further decreases the effectiveness of CSTR with respect to PFR. The density crease during reaction decreases the size ratio V_m/V_p. In order words, if the density creases during reaction, the effectiveness of CSTR is better as compared to PFR.

Comparison of CSTR (mixed flow reactor) with plug flow reactor for first order reaction :

Size comparison of CSTR with plug flow is done by comparing the performance equations of these reactors with reference to first order reaction.

Performance equation for CSTR is

$$\tau_m = \frac{V_m}{v_0} = \frac{C_{A0}\, X_A}{-r_A},\quad V_m = \text{volume of CSTR}$$

For constant volume first-order reaction, above equation becomes

$$\frac{V_m}{v_0} = \frac{C_{A0}\, X_A}{k\, C_{A0}(1 - X_A)} \qquad \ldots (4.7)$$

$$k\frac{V_m}{v_0} = \frac{X_A}{1 - X_A}$$

$$k\frac{V_m}{v_0} - k\frac{V_m}{v_0} X_A = X_A$$

$$\therefore \quad X_A = \frac{k\,(V_m/v_0)}{1 + (k\, V_m/v_0)} \qquad \ldots (4.8)$$

Performance equation for the plug flow reactor is

$$\tau_p = \frac{V_p}{v_0} = C_{A0}\int_0^{X_A} \frac{dX_A}{-r_A}$$

For constant volume first order reaction,

$$\frac{V_p}{v_0} = C_{A0}\int_0^{X_A} \frac{dX_A}{k\, C_{A0}\,(1 - X_A)} \qquad \ldots (4.9)$$

$$\frac{V_p}{v_0} = -\frac{1}{k}\ln(1 - X_A)$$

$$-k\,(V_p/v_0) = \ln(1 - X_A)$$

$$e^{-k\,(V_p/v_0)} = 1 - X_A$$

$$\therefore \quad X_A = 1 - e^{-k\,(V_p/v_0)} \qquad \ldots (4.10)$$

Equations (4.8) and (4.10) are plotted in Fig. 4.2 as conversion versus k (V/v_0). For equal flow rate, k (V_p/v_0) is proportional to volume.

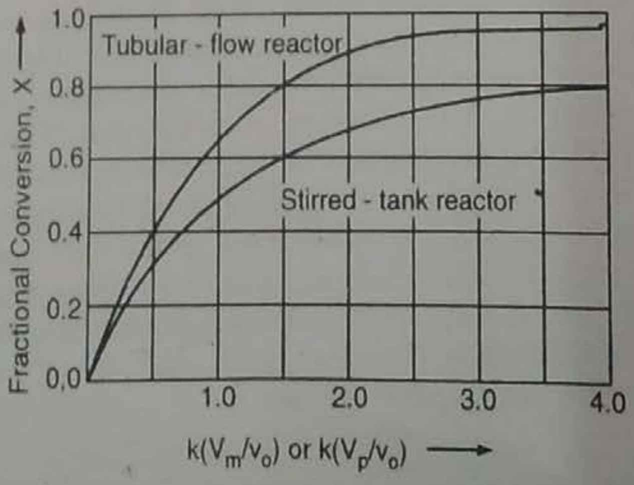


Fig. 4.2 : Conversion in stirred - tank and plug-flow reactors

It is clear from Fig. 4.2 that, for any conversion the volume required is largest for C.S.T.R. and that the difference increases with residence time. From Fig. 4.2, it can also be concluded that for given τ (space time) conversion in plug flow reactor is higher than in mixed flow reactor.

We can obtain a direct measure of the ratio of volume V_m of the stirred tank reactor to volume V_p of the tubular / plug flow reactor at same conversion by equating equations (4.8) and (4.10).

$$\frac{k\,(V_m/v_0)}{1 + k\,(V_m/v_0)} = 1 - e^{-k\,(V_p/v_o)}$$

If α is the ratio of volumes, $\alpha = V_m/V_p$ then previous equation can be written in terms of V_p and α.

$$\frac{\alpha k\,(V_p/v_0)}{1 + \alpha k\,(V_p/v_0)} = 1 - e^{-k\,(V_p/v_o)} \qquad \dots (4.11)$$

If we now replace $k\,(V_p/v_0)$ in equation (4.11) with the function of X_A from equation (4.10) and solve for α, we have the ratio of volumes as a function of X_A.

$$X_A = 1 - e^{-k\,(V_p/v_o)}$$

$$\therefore \quad k\,(V_p/v_0) = -\ln(1 - X_A)$$

$$\frac{-\alpha \ln(1 - X_A)}{1 - \alpha \ln(1 - X_A)} = X_A$$

$$-\alpha \ln(1 - X_A) = X_A - X_A\,\alpha \ln(1 - X_A)$$

$$\alpha \ln(1 - X_A)\,(X_A - 1) = X_A$$

$$\therefore \quad \alpha = \frac{X_A}{(X_A - 1)\ln(1 - X_A)}$$

$$\alpha = \frac{V_m}{V_p} = \frac{X_A}{(X_A - 1)\ln(1 - X_A)} \qquad \dots (4.12)$$

Equation (4.12) gives the ratio of volumes as a function of conversion X_A.

This result is plotted in Fig. 4.3 and shows that at low conversions there is little to be gained in using a tubular flow / plug flow reactor, but at conversions of 70 % or larger more than twice as much volume is required for a stirred tank reactors. i.e. volume of CSTR is more than twice the volume of plug flow reactor for a given conversion.

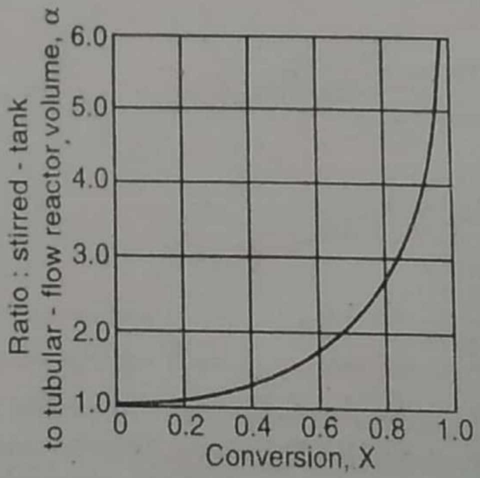


Fig. 4.3 : Ratio of volumes required for stirred-tank and tubular-flow (plug-flow) reactors

General Graphical Comparison :

Graphical comparison of the performance capabilities of CSTR and PFR for reactions with arbitrary but known rate is illustrated in Fig. 4.4.

The ratio of shaded areas gives the ratio of space times required in these two reactors.

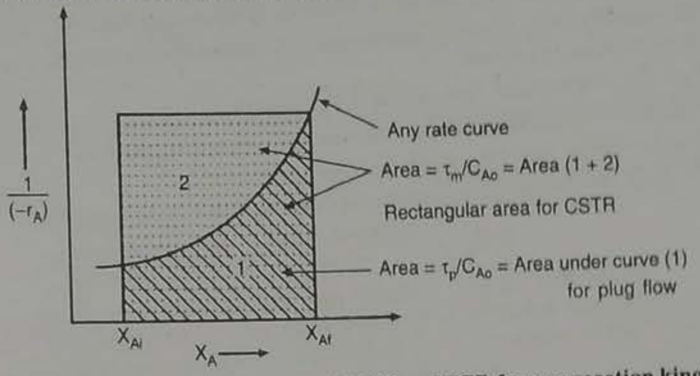


Fig. 4.4 : Comparison of performance of CSTR and PFR for any reaction kinetics

The rate curve drawn in Fig. 4.4 is valid for all nth order reactions ($n > 0$). It can be seen from Fig. 4.4 that for such reactions the volume of CSTR is always larger than PFR for any given duty.

Multiple-Reactor Systems :

Reactors in Series :

Many times the reactors are connected in series so that the exit stream of one reactor serves as the feed stream to the another reactor. We can have either same type of reactors in series or different type of reactors in series and that too with equal or unequal sizes.

CSTRs in series / Mixed flow reactors in series : LP

It is always advantageous to use CSTR in series as the total volume required to achieve specific conversion is less than the volume of a single CSTR. Using larger number of CSTRs in series, it is possible to approach the plug flow behaviour.

Unequal-size CSTRs / Different-size CSTRs in series : For n-no. also.

Here we will see the procedure of finding a conversion from a given reactor system and of finding the best reactor setup to achieve a given conversion.

Consider three CSTRs of volumes V_1, V_2, and V_3 are arranged in series as shown in Fig. 4.5.

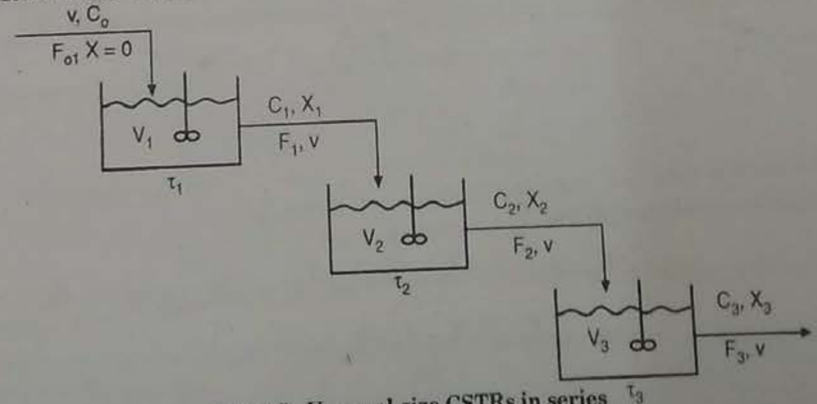


Fig. 4.5 : Unequal-size CSTRs in series

Note that $V_1 \neq V_2 \neq V_3$

The system of three CSTRs in series is to be used for reaction with negligible density change so that the volumetric flow rate is constant throughout the system.

The rate of disappearance of A in CSTR-1 is $(-r)_1 = (-r_A)_1$, that in CSTR-2 is $(-r)_2$ and that in CSTR-3 is $(-r)_3$. Let X_1, X_2, and X_3 be the conversions of A achieved upto points 1, 2, and 3 respectively. The rate $(-r)_1$ is evaluated at X_1, $(-r)_2$ at conversion X_2 and so on.

The relationship between conversion and molal flow rates for the system of CSTRs is given by following equations :

F_o or F_{Ao} is the molar flow rate of A entering reactor-1

F_oX_1 is the molar flow rate at which A is consumed in reactor-1

F_1 is the molar flow rate at which A leaves reactor-1

and X_1 is the fractional conversion of A in reactor-1 (upto point 1).

$$F_oX_1 = \frac{\text{moles of A fed}}{\text{time}} \times \frac{\text{moles of A reacted}}{\text{moles of A fed}}$$

$$\begin{pmatrix}\text{Molar flow rate}\\ \text{at which A is}\\ \text{fed to reactor}\end{pmatrix} = \begin{pmatrix}\text{Molar rate at}\\ \text{which A is}\\ \text{consumed}\end{pmatrix} + \begin{pmatrix}\text{Molar flow rate}\\ \text{at which A}\\ \text{leaves the reactor}\end{pmatrix}$$

$$F_o = F_oX_1 + F_1$$

$$\therefore \quad F_1 = F_o - F_oX_1 = F_o(1 - X_1)$$

$$F_2 = F_o - F_oX_2 = F_o(1 - X_2)$$

$$F_3 = F_o - F_oX_3 = F_o(1 - X_3)$$

OR

$$F_{A_1} = F_{Ao}(1 - X_{A_1}), \quad \text{if } F_{Ao} \text{ is used}$$

$$F_{A_2} = F_{Ao}(1 - X_{A_2})$$

$$F_{A_3} = F_{Ao}(1 - X_{A_3})$$

One can use any notations, we are using F_0, F_1, C_0, C_1, X_1, X_2, $-r_1$, $-r_2$ etc.

where $$X_2 = \frac{\text{total moles of A reacted upto point-2}}{\text{moles of A fed to the first reactor}}$$

Point-2 is the exit stream from reactor-2.

i.e. X_2 is the total conversion achieved upto reactor-2.

Note that similar definitions exist for X_1 and X_3.

Suppose that we are using three CSTRs in series and we obtain 40% conversion in reactor-1, intermediate conversion of 60% and the overall conversion of 80%. Then

$$X_1 = 0.40, \quad X_2 = 0.60, \quad \text{and} \quad X_3 = 0.80$$

A mole balance of species A for reactor-2 gives

$$\text{in} = \text{out} + \text{disappearance}$$

$$F_1 = F_2 + (-r)_2 \, V_2$$

$$\therefore \quad V_2 = \frac{F_1 - F_2}{(-r)_2} \quad \dots (4.13)$$

The reaction rate $(-r)_2$ is evaluated at the conversion X_2.

Substituting values of F_1 and F_2 in equation (4.13),

$$V_2 = \frac{F_o(1 - X_1) - F_o(1 - X_2)}{(-r)_2}$$

$$\therefore \quad V_2 = \frac{F_o - F_oX_1 - F_o + F_oX_2}{(-r)_2}$$

$$\therefore \quad \frac{V_2}{F_o} = \frac{X_2 - X_1}{(-r)_2} \qquad \text{... (4.1}$$

We have,

$$\tau = \frac{VC_o}{F_o}$$

$$\therefore \quad \frac{\tau_2}{C_o} = \frac{V_2}{F_o} = \frac{X_2 - X_1}{(-r)_2} \qquad \text{... (4.15}$$

Similarly, for the first reactor,

$$\frac{\tau_1}{C_o} = \frac{X_1 - X_o}{(-r)_1}$$

$$\frac{\tau_1}{C_o} = \frac{X_1}{(-r)_1} \quad \text{as } X_o = 0 \qquad \text{... (4.16)}$$

For third reactor,

$$\frac{\tau_3}{C_o} = \frac{X_3 - X_2}{(-r)_3} \qquad \text{... (4.17}$$

The reaction rate $(-r)_3$ is evaluated at conversion X_3.

As v is constant throughout the system of CSTRs in series,

$$v = \frac{F_o}{C_o} = \frac{F_1}{C_1}$$

$$\therefore \quad F_1 = F_o \frac{C_1}{C_o}$$

Similarly,

$$F_2 = F_o \frac{C_2}{C_o}$$

and

$$F_3 = F_o \frac{C_3}{C_o}$$

Now we will develop the required equations in terms of concentration.

A mole balance of species A over CSTR-2 in terms of concentration is

$$vC_1 = vC_2 + (-r)_2 V_2$$

$$\frac{V_2}{v} = \frac{C_1 - C_2}{(-r)_2}$$

$$\tau_2 = \frac{C_1 - C_2}{(-r)_2} \qquad \text{... (4.18)}$$

Similarly, for CSTR-1,

$$\tau_1 = \frac{C_o - C_1}{(-r)_1} \qquad \text{... (4.19)}$$

For CSTR-3,

$$\tau_3 = \frac{C_2 - C_3}{(-r)_3} \qquad \text{... (4.20)}$$

For CSTR-2, we have,

$$\tau_2 = \frac{C_1 - C_2}{(-r)_2}$$

$$C_1 = C_o(1 - X_1)$$

$$C_2 = C_o(1 - X_2)$$

$$\therefore \quad \tau_2 = \frac{C_o(1-X_1) - C_o(1-X_2)}{(-r)_2}$$

$$\therefore \quad \frac{\tau_2}{C_o} = \frac{X_2 - X_1}{(-r)_2}$$

So we can very easily convert the equation in terms of concentration into conversion and vice-versa and use them.

For i^{th} reactor, we can write,

$$\tau_i = \frac{C_{i-1} - C_i}{(-r)_i}$$

and

$$\frac{\tau_i}{C_o} = \frac{X_i - X_{i-1}}{(-r)_i} \quad \ldots (4.21)$$

Now we will discuss the graphical procedure of finding the concentration of material A from series of mixed flow reactors (CSTRs).

Finding the conversion in a given system :

Now we will deal with a graphical procedure of finding outlet composition/concentration from a series of mixed reactors of various sizes of system with negligible change in density. For this, plot a graph of $(-r_A)$ v/s C_A that indicates the reaction rate at various concentrations.

Consider the case of three CSTRs in series. System of CSTRs in series is shown in Fig. 4.5.

For component A in the first reactor,

$$\tau_1 = \frac{C_o - C_1}{(-r)_1}$$

$$\therefore \quad -\frac{1}{\tau_1} = \frac{(-r)_1}{C_1 - C_o} \quad \ldots (4.22)$$

Similarly for i^{th} reactor we can write,

$$-\frac{1}{\tau_i} = \frac{(-r)_i}{C_i - C_{i-1}} \quad \ldots (4.23)$$

Plot a graph of (–r) v/s C for component A as shown in Fig. 4.6.

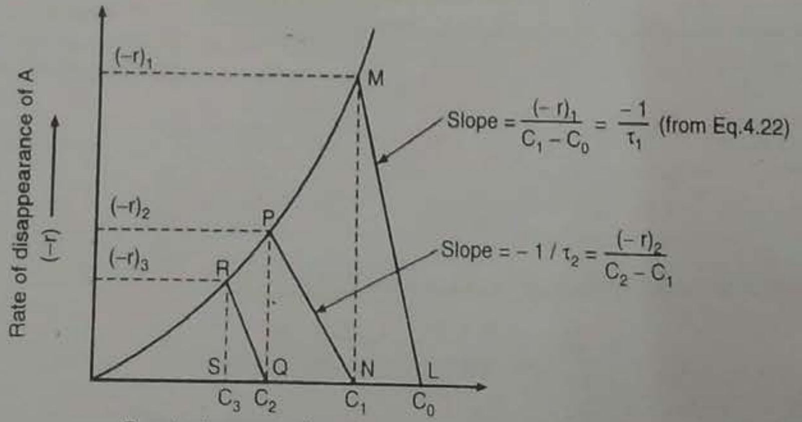


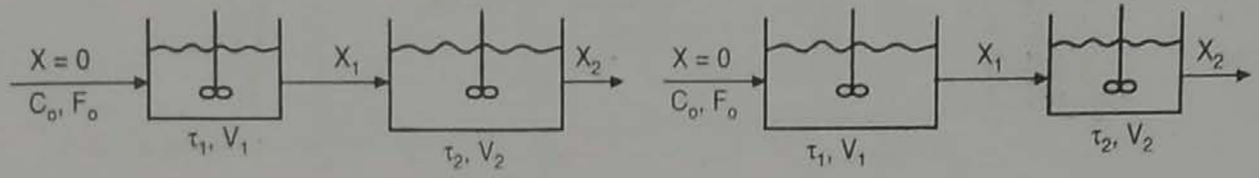
Fig. 4.6 : Graphical procedure for finding the concentration in a series of CSTRs

For CSTR, the rate $(-r)_1$ and C_1 will represent the point on this rate curve. The location of this point and, hence the concentration C_1 leaving the first reactor is found out by the following procedure. First locate the inlet concentration C_o at the proper point on the abscissa (X-axis), point L in Fig. 4.6. Then draw a straight line with a slope equal to $(-r)_1/C_1 - C_o = -(1/\tau_1)$ through C_o until it cuts the rate curve. The intersection of this line with rate curve gives C_1 (point M). To find the concentration of reaction mixture leaving the reactor-2, locate C_1 on abscissa (point N) and draw a straight line of slope equal to $-(1/\tau_2)$ through N until it cuts the rate curve. The intersection of this line with the rate curve gives C_2 (point P). Similar construction is shown for the reactor-3 in Fig. 4.6 and leads to the desired concentration C_3 (point S) leaving the third reactor.

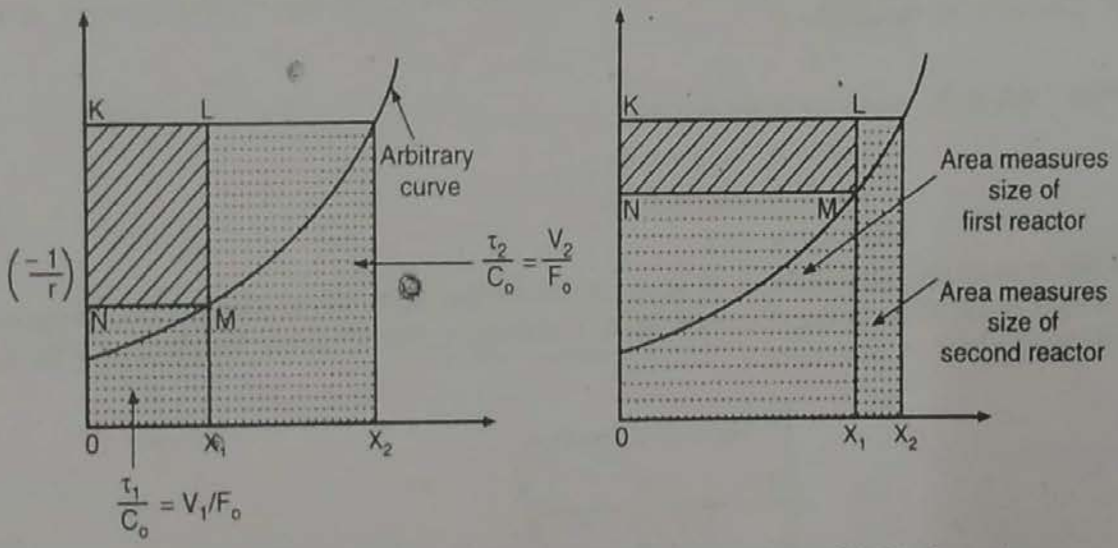
Determining the best system for a given conversion :

The best system of different-size CSTRs in series is the one having minimum size of CSTRs in series for a specified conversion.

In case of two CSTRs in series of different sizes, we can have two possible arrangements as – smaller size CSTR is followed by the larger one and vice versa as shown in Fig. 4.7.



(a) $V_1 < V_2$ **(b)** $V_1 > V_2$



(c) Graphical representation of the variables of two CSTRs in series

Fig. 4.7

We have for the first CSTR,

$$\frac{\tau_1}{C_o} = \frac{X_1}{(-r)_1}$$

and for the second CSTR,

$$\frac{\tau_2}{C_o} = \frac{X_2 - X_1}{(-r)_2}$$

These relationships are shown in Fig. 4.7 (c) for two different arrangements for same final conversion X_2.

As the intermediate conversion changes, the size ratio of two reactors as well as the total volume of two CSTRs changes.

Referring to Fig. 4.7 (c), it is clear that total volume of reactor system is as small as possible (represented by total shaded area) when the rectangle KLMN is as large as possible. So as to maximize the area of rectangle KLMN, we have to select proper X_1 (or point M on the curve).

Now we will see how to maximise the area of rectangle.

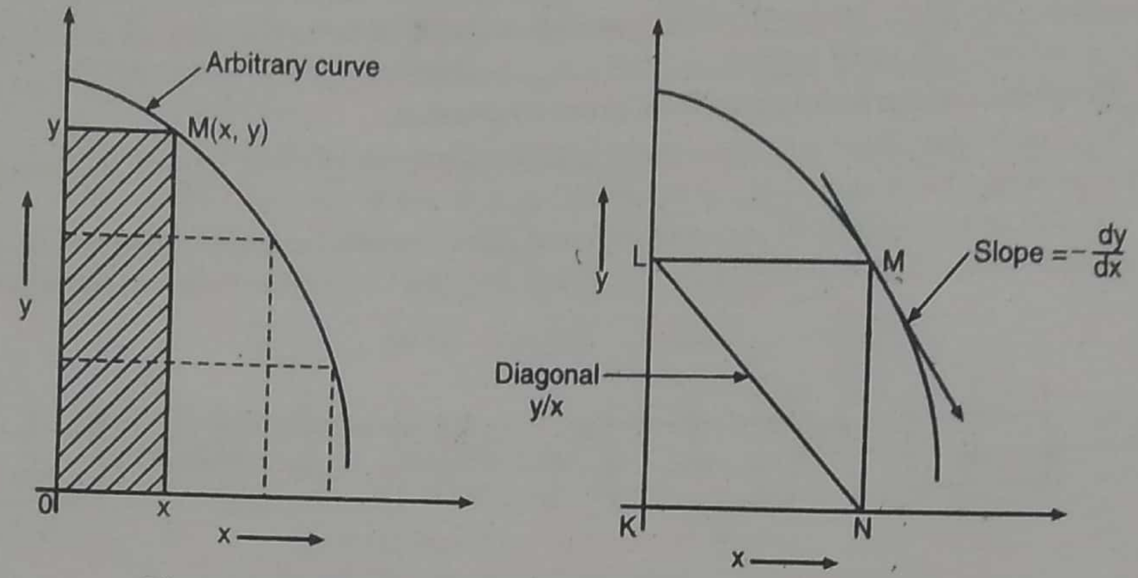


Fig. 4.8 : Graphical procedure for maximising area of rectangle

Construct a rectangle between the x-y axes and touching the arbitrary curve at point M (x, y). The area of rectangle is

$$A = xy$$

when $dA = 0$, the area is maximised

$$dA = x\,dy + y\,dx$$

$$0 = x\,dy + y\,dx$$

$$\therefore \quad -dy/dx = y/x$$

So the area is maximised when M is at a point on the curve where slope of (the tangent to) the curve equals the slope of the diagonal NL of a rectangle. For nth order kinetics (n > 0), there is only one such point on the curve.

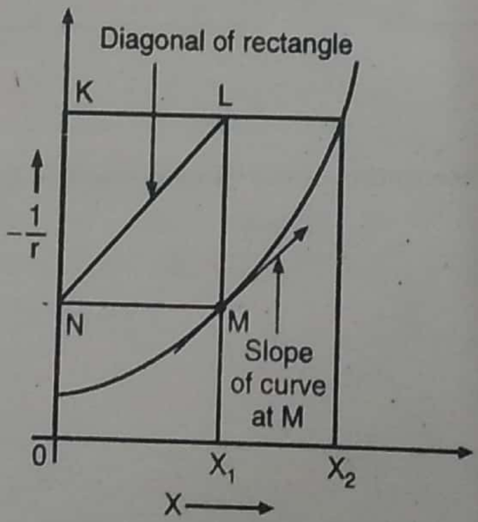


Fig. 4.9 : Maximisation of rectangle for determining optimum X_1 and optimum size of two CSTRs in series

The point M on the rate curve (Fig. 4.9) is the one at which the slope of the rate curve is equal to the diagonal NL i.e. it is the point at which area of rectangle KLMN is maximum and the total volume of CSTRs in series required is small. So the (intermediate) conversion corresponding to point M as well as sizes of two CSTRs in series corresponding to point M a optimum one. So we have to find the best point M on the rate curve which gives values of X_1 as well as sizes of CSTRs.

In general, the optimum size ratio of two CSTRs in series is found to be dependent on the reaction kinetics and on level of conversion. For the reactions following first order kineti equal-size CSTRs are the best, for the reactions with order greater than one, the smaller size CSTR should be followed by the larger size; and for the reactions with order less than one, th larger size CSTR should be followed by one with the smaller size.

Whenever we have to use CSTRs in series, the overall economic consideration wou always recommend the use of equal-size CSTRs in series rather than the use of different-size CSTRs in series as the advantage of the minimum size CSTR-system over the equal-siz CSTR-system is found to be quite small.

Equal-size CSTRs in series :

Consider the case in which two equal size CSTRs are arranged in series (Fig. 4.10). This system is to be used to carry a first order reaction with negligible (volume) densit change ($v = v_o$).

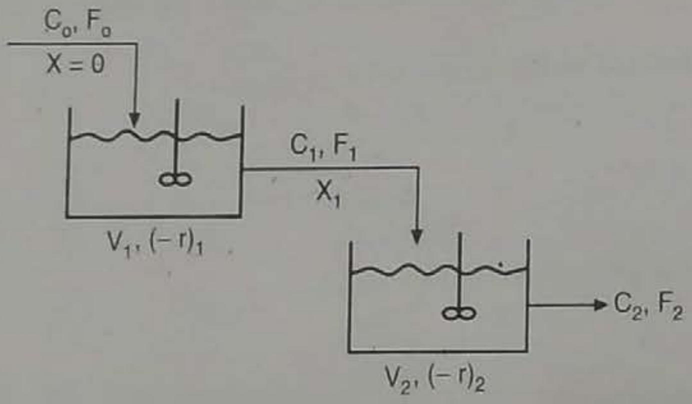


Fig. 4.10 : Two CSTRs in series

A material balance of reactant A on CSTR-1 yields

$$V_1 = \frac{F_o - F_1}{(-r)_1} = \frac{v_o C_o - v_o C_1}{(-r)_1}$$

$$\frac{V_1}{v_o} = \tau_1 = \frac{C_o - C_1}{(-r)_1}$$

$$\tau_1 = \frac{C_o - C_1}{(-r)_1} \quad \text{... (4.2}$$

From a material balance of reactant A on CSTR-2,

$$V_2 = \frac{F_1 - F_2}{(-r)_2} = \frac{v_o (C_1 - C_2)}{(-r)_2}$$

$$\therefore \quad \tau_2 = \frac{C_1 - C_2}{(-r)_2} \quad \text{... (4.2}$$

For first order reaction, the rate equation is

$$-r = k C_A = k C$$

Here we assume that the reactors are operating at same temperature.

So $\quad k_1 = k_2 = k$ (rate constant is same)

$$\therefore \quad (-r)_1 = k C_1 \quad \text{... (4.2}$$

Combining equations (4.24) and (4.26), we get

$$\tau_1 = \frac{C_o - C_1}{k\,C_1}$$

$$\tau_1 k\,C_1 = C_o - C_1$$

$$C_1(1 + \tau_1 k) = C_o$$

$$\therefore \quad C_1 = \frac{C_o}{(1 + \tau_1 k)} \qquad \text{... (4.27)}$$

Above equation gives the concentration of A leaving CSTR-1.

$$(-r)_2 = k\,C_2 \qquad \text{... (4.28)}$$

Combining equations (4.25) and (4.28), we get

$$C_2 = \frac{C_1}{(1 + \tau_2 k)} \qquad \text{... (4.29)}$$

Putting value of C_1 from equation (4.27) into equation (4.29),

$$C_2 = \frac{C_o}{(1 + \tau_1 k)\,(1 + \tau_2 k)} \qquad \text{... (4.30)}$$

Above equation gives the value of concentration of A leaving CSTR-2.

$$\frac{C_2}{C_o} = \frac{C_2}{C_1} \cdot \frac{C_1}{C_o}$$

$$\therefore \quad \frac{C_2}{C_o} = \frac{1}{(1 + \tau_2 k)} \cdot \frac{1}{(1 + \tau_1 k)}$$

$$C_2 = \frac{C_o}{(1 + \tau_1 k)\,(1 + \tau_2 k)}$$

For equal-size CSTRs,

$$\tau_1 = \tau_2 = \tau$$

∴ Equation (4.30) becomes

$$C_2 = \frac{C_o}{(1 + \tau k)^2} \qquad \text{... (4.31)}$$

For N equal-size CSTRs connected in series ($\tau_1 = \tau_2 = \ldots = \tau_n = \tau$) operating at same emperature ($k_1 = k_2 = \ldots = k_n = k$), the concentration of A leaving the last reactor (in same way as for two CSTRs) is given by,

$$C_N = \frac{C_o}{(1 + \tau k)^N}$$

$$\frac{C_N}{C_o} = \frac{C_N}{C_{N-1}} \cdot \frac{C_{N-1}}{C_{N-2}} \cdots\cdots\cdots \cdot \frac{C_2}{C_1} \cdot \frac{C_1}{C_o}$$

$$\frac{C_N}{C_o} = \frac{1}{(1 + \tau k)} \cdot \frac{1}{(1 + \tau k)} \cdots \cdot \frac{1}{(1 + \tau k)} \cdot \frac{1}{(1 + \tau k)} \quad \text{for N times}$$

$$\frac{C_N}{C_o} = \frac{1}{(1 + \tau k)^N} \qquad \text{... (4.32)}$$

$$C_N = \frac{C_o}{(1 + \tau k)^N} \qquad \text{... (4.33)}$$

The conversion of A for N equal-size CSTRs in series is obtained as follows :

$$C_N = C_o(1 - X_N) \qquad \text{... (4.34)}$$

$$\frac{C_N}{C_o} = (1 - X_N) \qquad \text{... (4.35)}$$

Combining equations (4.32) and (4.34), we get

$$(1 - X_N) = \frac{1}{(1 + \tau k)^N}$$

$$\therefore \quad X_N = 1 - \frac{1}{(1 + \tau k)^N} \qquad \dots (4.36)$$

Equation (4.36) expresses conversion as a function of the number of CSTRs in series.

The product τk is referred to as reaction Damkohler number (D_a). The Damkohler is a dimensionless number which gives us a quick estimates of conversion that can be achieved in continuous flow reactions.

Equation (4.32) in terms of Damkohler number is

$$\frac{C_N}{C_o} = \frac{1}{(1 + D_a)^N} \qquad \dots (4.37)$$

We have,

$$\frac{C_N}{C_o} = \frac{1}{(1 + \tau k)^N}$$

$$\therefore \quad \frac{C_o}{C_N} = (1 + \tau k)^N \qquad \dots (4.38)$$

We have,

$$C_N = C_o (1 - X_N)$$

$$\therefore \quad \frac{C_o}{C_N} = \frac{1}{(1 - X_N)} \qquad \dots (4.39)$$

Combining equations (4.38) and (4.39), we get

$$\frac{C_o}{C_N} = \frac{1}{1 - X_N} = (1 + \tau k)^N \qquad \dots (4.40)$$

This is only the alternate form of equation (4.32).

$$\frac{C_o}{C_N} = (1 + \tau k)^N$$

$$\therefore \quad (1 + \tau k) = \left(\frac{C_o}{C_N}\right)^{1/N}$$

$$\tau k = \left[\left(\frac{C_o}{C_N}\right)^{1/N} - 1\right]$$

$$\tau = \frac{1}{k}\left[\left(\frac{C_o}{C_N}\right)^{1/N} - 1\right] \qquad \dots (4.41)$$

For system of N equal-size CSTRs in series as a whole,

$$\tau_{N \text{ reactors}} = N \cdot \tau \qquad \dots (4.42)$$

Combining equations (4.41) and (4.42), we get

$$\tau_N = N \cdot \tau = \frac{N}{k}\left[\left(\frac{C_o}{C_N}\right)^{1/N} - 1\right] \qquad \dots (4.43)$$

τ_N is the total space time for N reactors.

In limit, N → ∞, the above equation reduces to the plug flow equation :

$$\tau_p = \frac{1}{k} \ln \frac{C_o}{C} \qquad \dots (4.44)$$

A plot of the conversion, X, v/s the number of equal-size CSTRs in series for the first order reaction with no volume change for various values of Damkohler number τk is shown in Fig. 4.11.

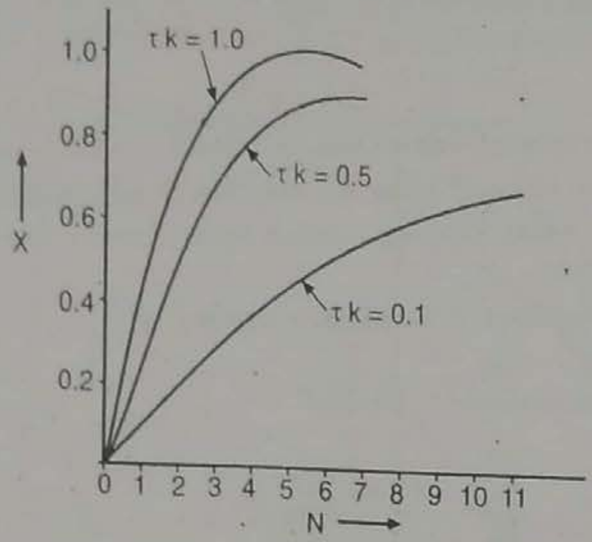


Fig. 4.11 : Conversion as a function of number of equal-size CSTRs in series for a first order reaction

It is clear from the Fig. 4.11 that when τk is relatively large, say, $D_a \geq 1$, approximately 90% conversion is obtained in two or three reactors, and hence the cost of adding subsequent reactors might not be justified. When τk is small, $D_a \leq 0.10$, the conversion increases significantly with addition of each reactor.

The rate of disappearance of A in the nth reactor is

$$-r_N = k\,C_N = k\,\frac{C_0}{(1+\tau k)^N} \quad \ldots (4.45)$$

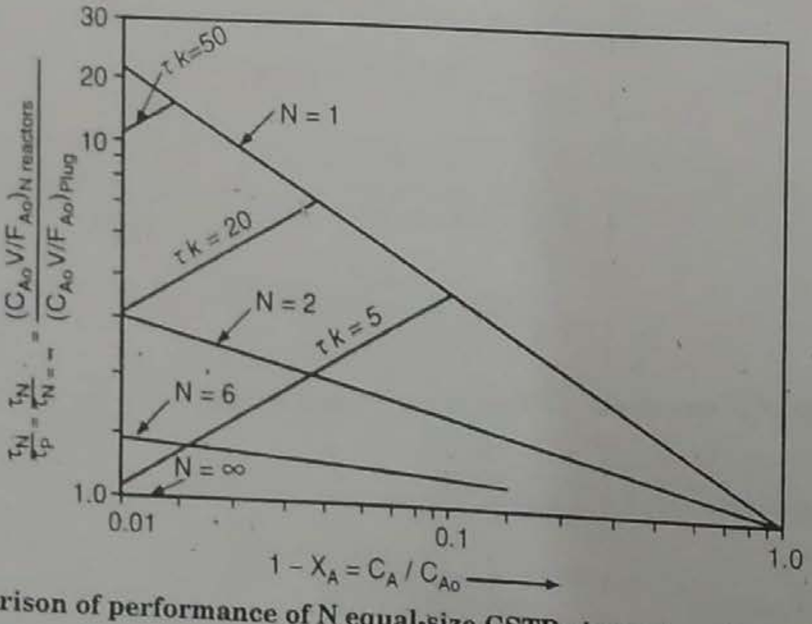


Fig. 4.12 : Comparison of performance of N equal-size CSTRs in series with plug flow reactor for a first order reaction

For the same molar flow rate of A, the coordinate measures the volume ratio V_N/V_P directly.

CSTRs in parallel :

Consider the case in which equal-size CSTRs are placed in parallel as shown in Fig. 4.13.

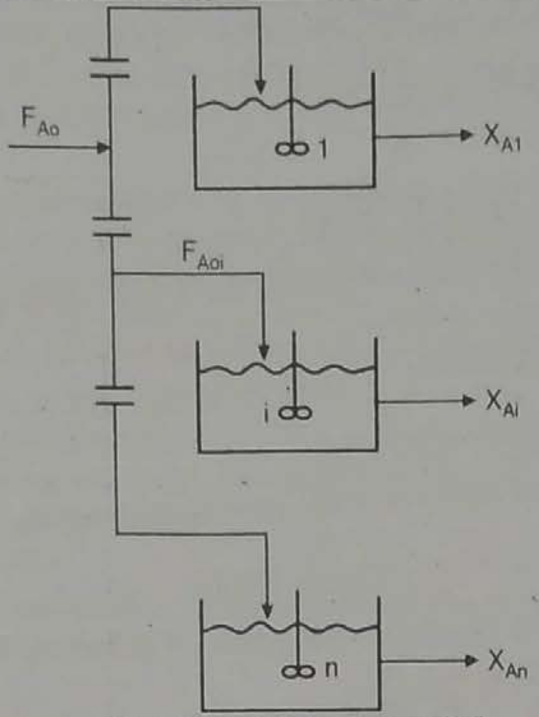


Fig. 4.13 : CSTRs in parallel

The feed is distributed equally among each of the reactors.

A mole balance on any reactor i gives the volume of individual reactor.

$$V_i = \frac{F_{Aoi}\,(X_{Ai})}{(-r_{Ai})} \qquad \dots (4.46)$$

As the reactors are of equal size, operate at same temperature, and have identical flow rates,

$$X_{A_1} = X_{A_2} = \dots\dots = X_{A_n} = X_A = X$$

and
$$-r_{A_1} = -r_{A_2} = \dots = -r_{A_n}. = -r_A = -r$$

If there are N reactors in parallel and V is the total volume of all the N reactors, then the volume of each individual reactor, V_i is

$$V_i = \frac{V}{N} \qquad \dots (4.47)$$

If F_{Ao} is the total molar flow rate of A to the entire system of CSTRs in parallel, then

$$F_{Aoi} = \frac{F_{Ao}}{N} \qquad \dots (4.48)$$

$$F_{Ao1} = \frac{F_{Ao}}{N}$$

$$V = V_1 + V_2 + \dots + V_n = NV_i \quad [V_1 = V_2 = V_i = \dots]$$

$$F_{Ao} = F_{Ao1} + F_{Ao2} + \dots + F_{AoN} = N\,F_{Aoi} \qquad \dots (4.49)$$

Substituting the value of V_i from equation (4.47) and that of F_{Aoi} from equation (4.48) into equation (4.46), we get

$$\frac{V}{N} = \frac{F_{Ao}}{N}\left[\frac{X_{Ai}}{-r_{Ai}}\right]$$

$$V = F_{Ao} \cdot \frac{X_A}{(-r_A)} \qquad \dots (4.50)$$

This result shows that in case of CSTRs in parallel, the conversion achieved in any one of the reactors is same as that would be achieved if the reactants were fed in one stream to one large reactor of volume V.

Plug flow reactors in series :

Consider the case of two plug flow reactors in series as shown in Fig. 4.14 (to be used for reaction with negligible density change).

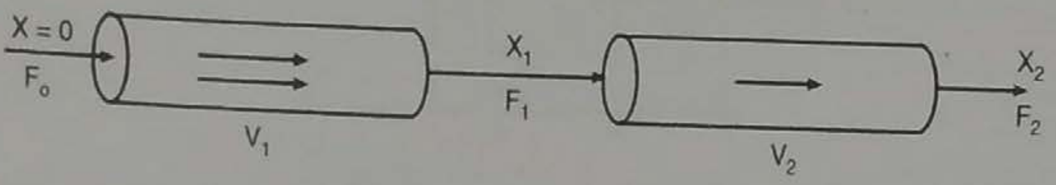


Fig. 4.14 : PFRs in series

Let X_1 and X_2 be the fractional conversions of component A leaving reactors 1 and 2.

X_1 is the conversion of A from first reactor and

X_2 is the overall conversion of A from reactor system.

The performance equation for PFR-1 is

$$\frac{V_1}{F_o} = \int_{X=0}^{X_1} \frac{dX}{(-r)} = \int_{0}^{X_1} \frac{dX}{(-r)}$$

Similarly, for PFR-2,

$$\frac{V_2}{F_o} = \int_{X_1}^{X_2} \frac{dX}{(-r)}$$

For two reactors in series,

$$\frac{V}{F_o} = \frac{V_1}{F_o} + \frac{V_2}{F_o} = \int_{0}^{X_1} \frac{dX}{(-r)} + \int_{X_1}^{X_2} \frac{dX}{-r}$$

$$\frac{V}{F_o} = \int_{0}^{X_2} \frac{dX}{(-r)} = \int_{0}^{X_1} \frac{dX}{(-r)} + \int_{X_1}^{X_2} \frac{dX}{(-r)} \qquad \text{... (4.51)}$$

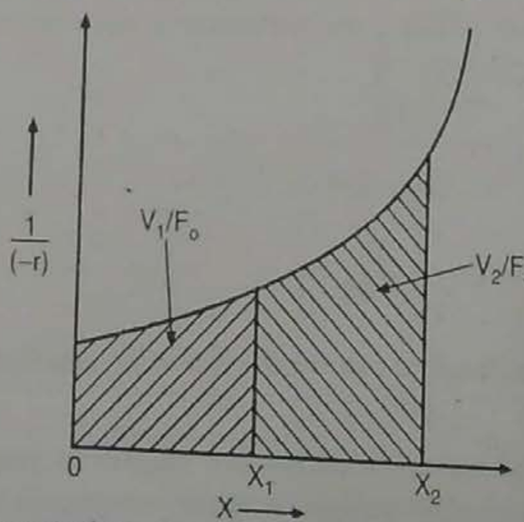


Fig. 4.15 : Graphical presentation of performance equation for two plug flow reactors in series

From equation (4.51) and Fig. 4.15, it is clear that it is immaterial whether you place two plug flow reactors in series or have only one large plug flow reactor, the total volume required, to achieve the specified degree of conversion, is same in both the cases. i.e. for conversion X_2, the total volume of two plug flow reactors in series is $V = V_1 + V_2$. We can achieve the same conversion X_2 using single larger plug flow reactor of volume V.

For N plug flow reactors in series,

$$\frac{V}{F_o} = \sum_{i=1}^{N} \frac{V_i}{F_o} = \frac{V_1 + V_2 + \ldots + V_N}{F_o}$$

$$= \int_0^{X_1} \frac{dX}{-r} + \int_{X_1}^{X_2} \frac{dX}{-r} + \ldots + \int_{X_{N-1}}^{X_N} \frac{dX}{-r} = \int_0^{X_N} \frac{dX}{-r_A} \quad \ldots (4.52)$$

Therefore, the system of N plug flow reactors in series having total volume V gives the same conversion as a single plug flow reactor of volume V.

If, say for example, to obtain 80% conversion of A in two plug flow reactors each with volume 100 litres then the same conversion can be achieved using single plug flow reactor of volume 200 litres.

Plug flow reactors in parallel :

For plug flow reactors placed in parallel or any parallel-series combination V/F or τ must be same for each parallel line to have conversion to be same in each branch. In case of parallel-series combination, the reactors in series are to be treated as a single reactor having volume equal to sum of volumes of reactors in series.

Consider a system consisting of three PFRs in two branches as shown in Fig. 4.16. Branch-1 is having a reactor of volume V_1 followed by volume V_2. Branch-2 has a reactor of volume V_3.

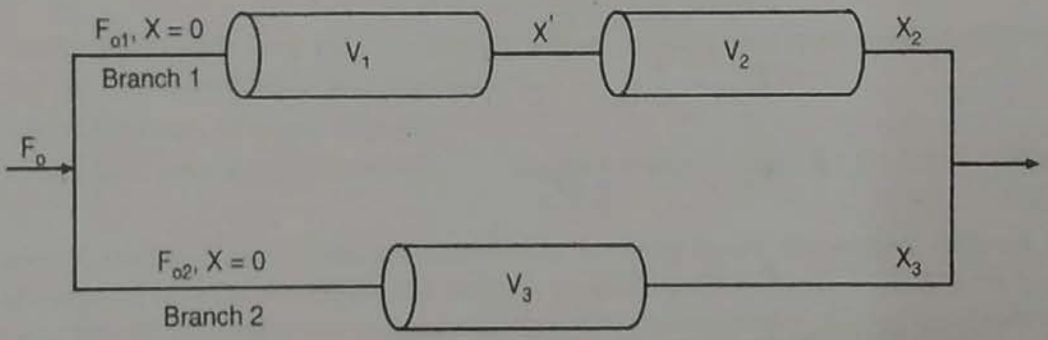


Fig. 4.16 : PFRs in series-parallel combination

Branch-1 consists of two PFRs in series, hence a system of two PFRs in series may be considered as a single reactor of volume V.

$$V = V_1 + V_2$$

For branch-1,

$$\frac{V}{F_{o1}} = \int_0^{X_2} \frac{dX}{(-r)}$$

For branch-2,

$$\frac{V_3}{F_{o2}} = \int_0^{X_3} \frac{dX}{(-r)}$$

For PFRs in parallel V/F must be identical if the conversion is to be same in each branch.

Therefore, for $X_2 = X_3 = X$

$$\frac{V}{F_{o1}} = \frac{V_3}{F_{o2}}$$

and $$F_o = F_{o1} + F_{o2}$$

In Fig. 4.16, if $V_1 = 40\ l$, $V_2 = 20\ l$ and $V_3 = 30\ l$ then what fraction of feed should go to branch-1 for conversion to be same in each branch.

For branch-1,

$$V = \text{total volume of two reactors}$$

$$= 40 + 20 = 60\ l$$

$$F_{o1} = \text{Feed rate}$$

For reactors in parallel, V/F must be identical if the conversion is to be same in each branch.

$$\therefore \quad \left(\frac{V}{F}\right)_1 = \left(\frac{V}{F}\right)_2$$

$$\frac{60}{F_{o1}} = \frac{30}{F_{o2}}$$

$$\therefore \quad F_{o1} = 2\,F_{o2}$$

We have

$$F_o = F_{o1} + F_{o2}$$

$$F_o = 2\,F_{o2} + F_{o2}$$

$$F_{o2} = \frac{1}{3}\,F_o$$

and $$F_{o1} = \left(1 - \frac{1}{3}\right) F_o$$

$$F_{o1} = \frac{2}{3}\,F_o$$

$\therefore$ Two-thirds of the feed must be fed to branch-1.

Reactors of different types in series :

Consider a system of reactors in series as shown in Fig. 4.17 in which CSTR is followed by PFR (plug flow reactor) which is followed by another CSTR.

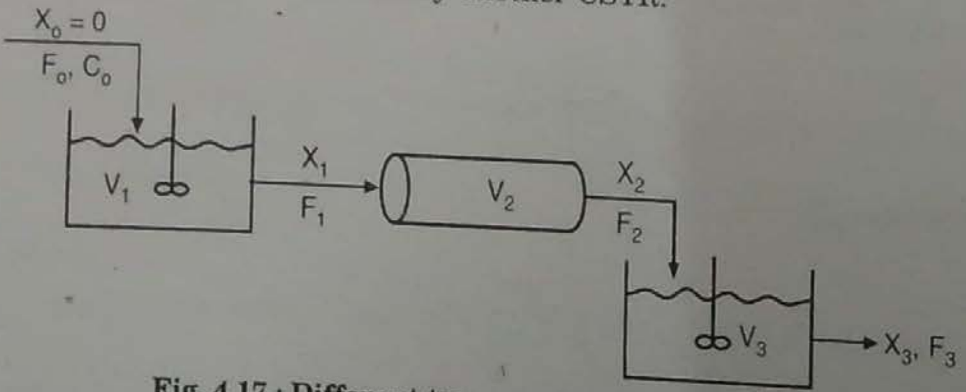


Fig. 4.17 : Different type reactors in series

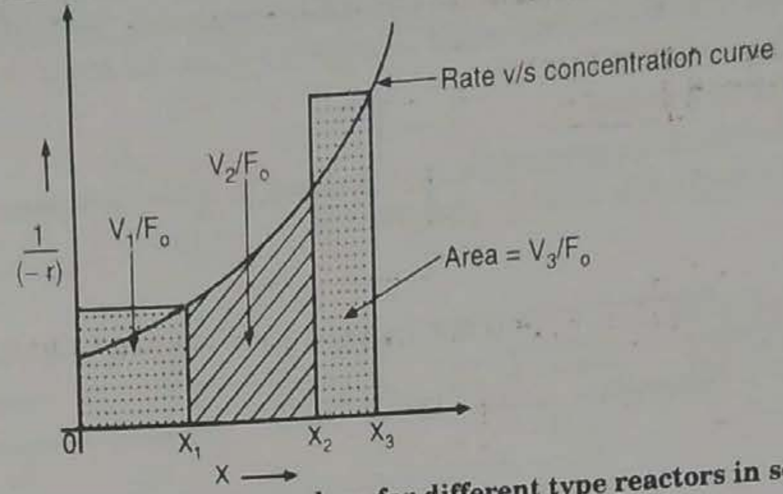


Fig. 4.18 : Graphical design procedure for different type reactors in series

The relationship between conversion and molar flow rates for the reactor sequence shown in Fig. 4.18 is given by following equations :

$$F_1 = F_o - F_o X_1 = F_o(1 - X_1)$$

$$F_2 = F_o(1 - X_2)$$

$$F_3 = F_o(1 - X_3)$$

where $$X_2 = \frac{\text{total moles of A reacted upto point 2}}{\text{moles of A fed to first reactor}}$$

A mole balance of species A for the CSTR at the end of reactor system gives

$$\text{in} = \text{out + disappearance}$$

$$F_2 = F_3 + (-r)_3 V_3$$

$$V_3 = \frac{F_2 - F_3}{(-r)_3}$$

$$= \frac{F_o(1 - X_2) - F_o(1 - X_3)}{(-r)_3}$$

$$\therefore \quad \frac{V_3}{F_o} = \frac{X_3 - X_2}{(-r)_3} \quad \text{... (4.53)}$$

The corresponding rate of reaction $(-r)_3$ is evaluated at the conversion X_3.

Similarly, for first reactor (CSTR), the performance equation is

$$\frac{V_1}{F_o} = \frac{X_1 - X}{(-r)_1} \quad \text{... (4.54)}$$

For intermediate, PFR is

$$\frac{V_2}{F_o} = \int_{X_1}^{X_2} \frac{dX}{(-r)} \quad \text{.. (4.55)}$$

X_1 is the conversion from the first reactor, X_2 is the intermediate conversion and X_3 is the overall conversion of A.

The performance equations/relationships are shown in graphical form in Fig. 4.18 which will be helpful to us to predict the intermediate conversions or overall conversion from the entire system of reactors.

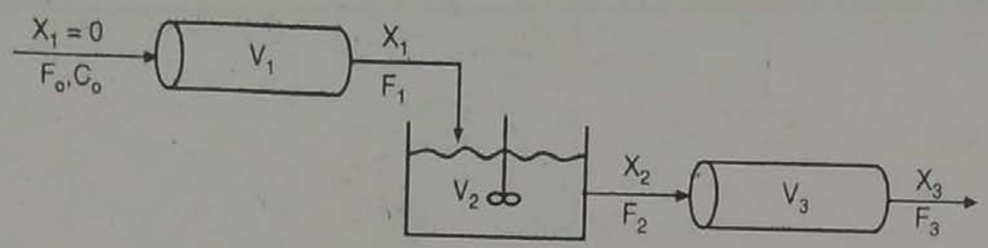


Fig. 4.19 : PFR followed by CSTR followed by PFR

$$\frac{V_1}{F_o} = \int_{X_o}^{X_1} \frac{dX}{(-r)}$$

$$\frac{V_2}{F_o} = \frac{X_2 - X_1}{(-r)_2}$$

$$\frac{V_3}{F_o} = \int_{X_2}^{X_3} \frac{dX}{(-r)}$$

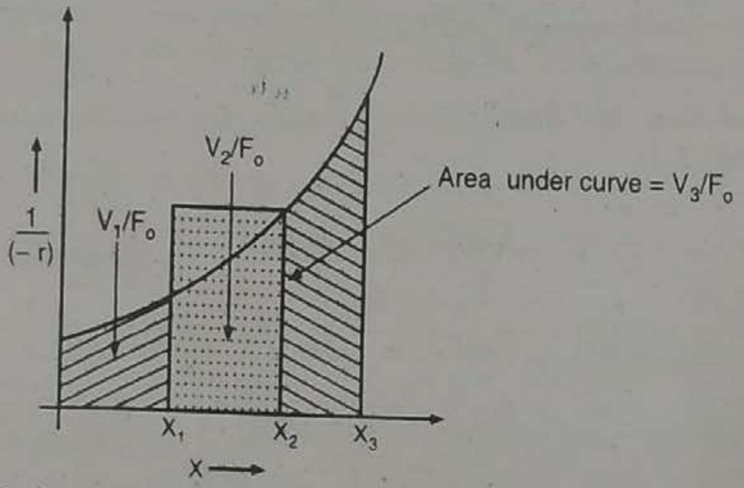
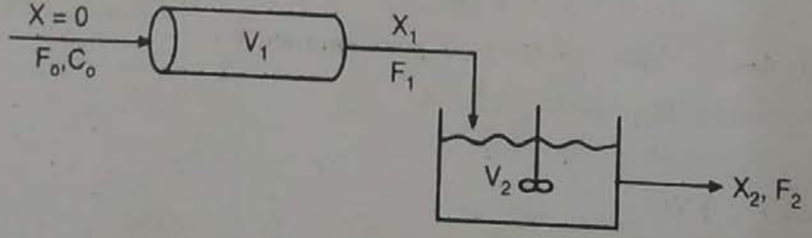
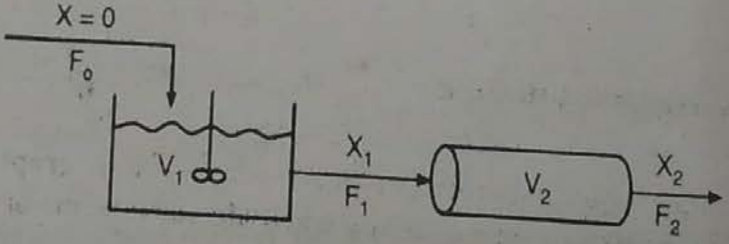


Fig. 4.20 : Graphical design procedure for different type reactors in series

Consider a case of two different reactors in series, say for example CSTR and PFR. There are two ways in which the reactors can be put in series as shown in Fig. 4.21.



(a) Scheme-I



(b) Scheme-II

Fig. 4.21 : Different type reactors in series

If the size of each reactor is fixed then different final conversion, X_2, will be obtained depending on whether the CSTR is first or PFR is placed first. If the intermediate and overall conversions are fixed then the reactor volumes as well as their sum can be different for different arrangements.

Recycle Reactor :

In some cases, it seems to be beneficial to return a part of effluent stream/product stream leaving a plug flow reactor to the entrance of the reactor.

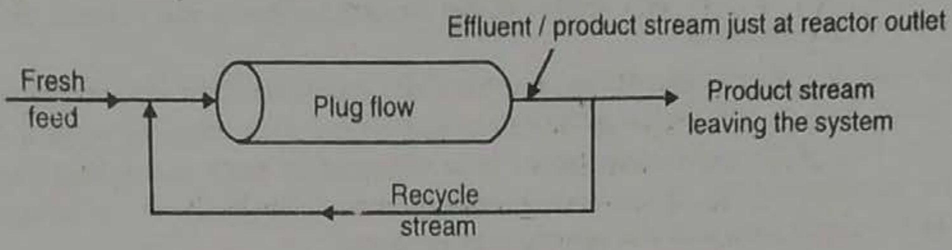


Fig. 4.22 : Recycle reactor

In this case the product stream/effluent stream leaving the reactor is divided in two parts – (i) some part of it is recycled to the reactor inlet where it combines with the fresh feed to form what we call as mixed feed that enters the reactor and (ii) remaining part of it is removed from the system.

$\therefore$ Product/Effluent stream leaving the reactor

= Product stream recycled + Product stream leaving the system (actually taken out)

Let us define the recycle ratio (R) as follows :

$$R = \frac{\text{Volume of fluid returned to the reactor inlet}}{\text{Volume of fluid leaving the system}}$$

If v_f is the volumetric flow rate of product stream leaving the system/exiting the system and R is the recycle ratio then by above definition of R,

Volumetric flow rate of recycle stream $= R \cdot v_f$

Volumetric flow rate of product stream leaving the reactor/exiting the reactor $= R\,v_f + v_f$

$= (R + 1)\,v_f$

The recycle ratio can vary from zero to infinity. As we increase the recycle ratio i.e. as the fraction of recycled stream increases, the behaviour shifts from plug flow (at $R = 0$) to mixed flow ($R = \infty$). For $R = 0$, there is no mixing axially – the characteristic of ideal plug flow and at $R = \infty$, there is complete mixing. So we can obtain various degrees of backmixing with a plug flow reactor with the help of recycling technique i.e. varying the recycle ratio.

We will now develop the performance equation for the recycle reactor.

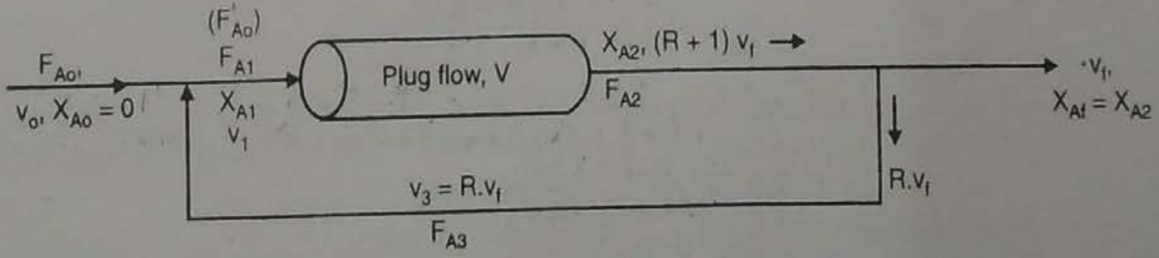


Fig. 4.23 : Notations for the recycle reactor

For plug flow reactor, the performance equation for partially converted feed based upon the molar flow rate of A with no conversion (molar flow rate of unconverted A) is

$$\frac{V}{F'_{Ao}} = \int_{X_{A1}}^{X_{A2}} \frac{dX_A}{(-r_A)} \qquad \ldots (4.56)$$

where F'_{Ao} is the hypothetical feed rate of A in mixed feed to reactor with no conversion i.e. the molar flow rate of A to the reactor if the stream entering the reactor (fresh feed and recycle feed) were unconverted.

In case of the recycle reactor, the partially converted feed enters the reactor. The partially converted feed is the feed consisting of fresh feed with zero conversion (no conversion) and recycled feed with some conversion. It is assumed in such cases that there is no conversion results in recycle path. If the recycle stream is completely unconverted then the concentration of A in the fresh feed and the recycle feed is same.

To use equation (4.56) we must get F'_{Ao} and X_{A1} in terms of known quantities .

$$\therefore \quad F'_{Ao} = \begin{pmatrix}\text{A entering}\\ \text{in fresh feed}\end{pmatrix} + \begin{pmatrix}\text{A which would enter}\\ \text{in an unconverted}\\ \text{recycle stream}\end{pmatrix}$$

$$= F_{Ao} + R\,F_{Ao}$$

$$= (R+1)\,F_{Ao} \qquad \ldots (4.57)$$

$$\begin{pmatrix}\text{A which would enter}\\ \text{in an unconverted}\\ \text{recycle stream}\end{pmatrix} = v_3\,C_{Ao} = R\,v_f C_{Ao} = R\,v_o C_{Ao} = R\,F_{Ao}$$

To get X_{A1} in terms of known quantities, we may write

$$X_{A1} = \frac{1 - C_{A1}/C_{Ao}}{1 + \varepsilon_A C_{A1}/C_{Ao}} \qquad \ldots (4.58)$$

For constant pressure throughout, we have,

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{Ao} + F_{A3}}{v_o + R\,v_f} = \frac{F_{Ao} + R\,F_{Ao}\,(1 - X_{Af})}{v_o + R\,v_o\,(1 + \varepsilon_A X_{Af})}$$

$$= C_{Ao}\left[\frac{1 + R\,(1 - X_{Af})}{1 + R\,(1 + \varepsilon_A X_{Af})}\right] = C_{Ao}\left[\frac{1 + R - R\,X_{Af}}{1 + R + R\,\varepsilon_A X_{Af}}\right] \qquad \ldots (4.59)$$

$$\frac{C_{A1}}{C_{Ao}} = \left[\frac{1 + R - R\,X_{Af}}{1 + R + R\,\varepsilon_A X_{Af}}\right]$$

Putting this value of C_{A1}/C_{Ao} in equation (4.58)

$$X_{A1} = \frac{1 - \left[\dfrac{(1 + R - R\,X_{Af})}{1 + R + R\,\varepsilon_A X_{Af}}\right]}{1 + \varepsilon_A\left[\dfrac{1 + R - R\,X_{Af}}{1 + R + R\,\varepsilon_A X_{Af}}\right]}$$

$$= \frac{1 + R + R\,\varepsilon_A X_{Af} - 1 - R + R\,X_{Af}}{1 + R + R\,\varepsilon_A X_{Af} + \varepsilon_A + R\,\varepsilon_A - R\,\varepsilon_A X_{Af}} = \frac{R\,(1 + \varepsilon_A)\,X_{Af}}{(1 + \varepsilon_A) + R\,(1 + \varepsilon_A)}$$

$$X_{A1} = \frac{R\,(1 + \varepsilon_A)\,X_{Af}}{(1 + \varepsilon_A)\,(R + 1)}$$

$$X_{A1} = \left(\frac{R}{R+1}\right) X_{Af} \qquad \ldots (4.60)$$

Putting the value of F'_{Ao} from the equation (4.57) and of X_{A1} from the equation (4.60) in equation (4.56), we get,

$$\frac{V}{F_{Ao}(R+1)} = \int_{\left(\frac{R}{R+1}\right)X_{Af}}^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$\frac{V}{F_{Ao}} = (R+1)\int_{\left(\frac{R}{R+1}\right)X_{Af}}^{X_{Af}} \frac{dX_A}{(-r_A)} \quad \text{, for any } \varepsilon_A \qquad \dots (4.61)$$

Equation (4.61) is the desired performance equation for recycle reactor applicable for any kinetics, any value of ε_A and for $X_{Ao} = 0$ (fresh feed with no conversion).

For special case of constant density reaction system (i.e. $\varepsilon_A = 0$), the above equation can be written in terms of concentrations.

The performance equation for plug flow reactor in terms of concentration for $\varepsilon_A = 0$ and no recycle is

$$\tau = \frac{C_{Ao}V}{F_{Ao}} = -\int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{(-r_A)}$$

On the same line, the performance equation for recycle reactor for feed containing partially converted A is

$$\tau = \frac{C_{Ao}V}{F'_{Ao}} = -\int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{(-r_A)} \quad \dots \text{ for } \varepsilon_A = 0 \qquad \dots (4.62)$$

$$C_{A1} = \frac{F_{A1}}{v_1} = \frac{F_{Ao} + F_{A3}}{v_o + v_3} = \frac{F_{Ao} + R\,F_{Ao}(1 - X_{Af})}{v_o + R\,v_f}$$

$$= \frac{F_{Ao} + R\,F_{Ao}(1 - X_{Af})}{v_o + R\,v_o} \quad , \; v_o = v_f \text{ for } \varepsilon_A = 0$$

$$= \frac{F_{Ao}}{v_o}\left[\frac{1 + R(1 - X_{Af})}{R+1}\right]$$

$$= \frac{C_{Ao}\,[1 + R(1 - X_{Af})]}{(R+1)} = \frac{C_{Ao} + R\,C_{Ao}(1 - X_{Af})}{(R+1)}$$

but $$C_{Af} = C_{Ao}(1 - X_{Af})$$

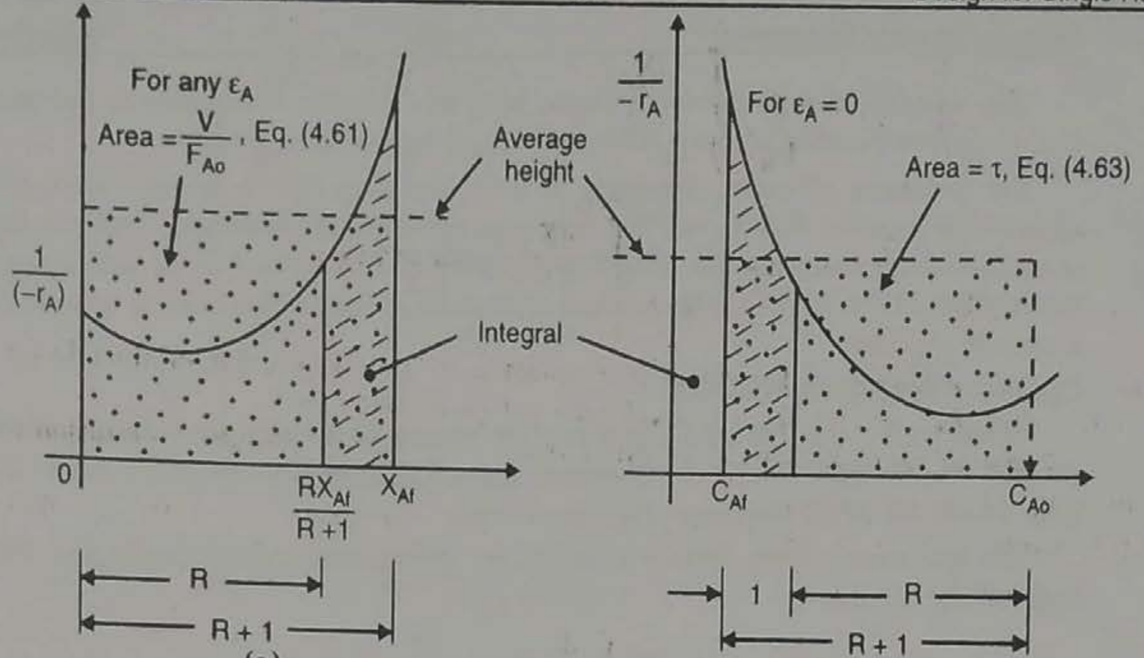
∴ $$C_{A1} = \frac{C_{Ao} + R\,C_{Af}}{R+1}$$

∴ $$\tau = \frac{C_{Ao}V}{F_{Ao}(R+1)} = -\int_{\frac{C_{Ao} + R\,C_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{(-r_A)}$$

$$\tau = \frac{C_{Ao}V}{F_{Ao}} = -(R+1)\int_{\frac{C_{Ao} + R\,C_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{(-r_A)} \quad \text{, for } \varepsilon_A = 0 \qquad \dots (4.63)$$

This is the desired performance equation for recycle reactor in terms of concentration for $\varepsilon_A = 0$. This equation is applicable for reaction systems with negligible density changes such as most liquid phase reactions and gaseous reactions involving no change in number of moles.

Fig. 4.24 shows the graphical representations of equations (4.61) and (4.63).



(a) (b)

Fig. 4.24 : Graphical representation of the performance equation for recycle reactor

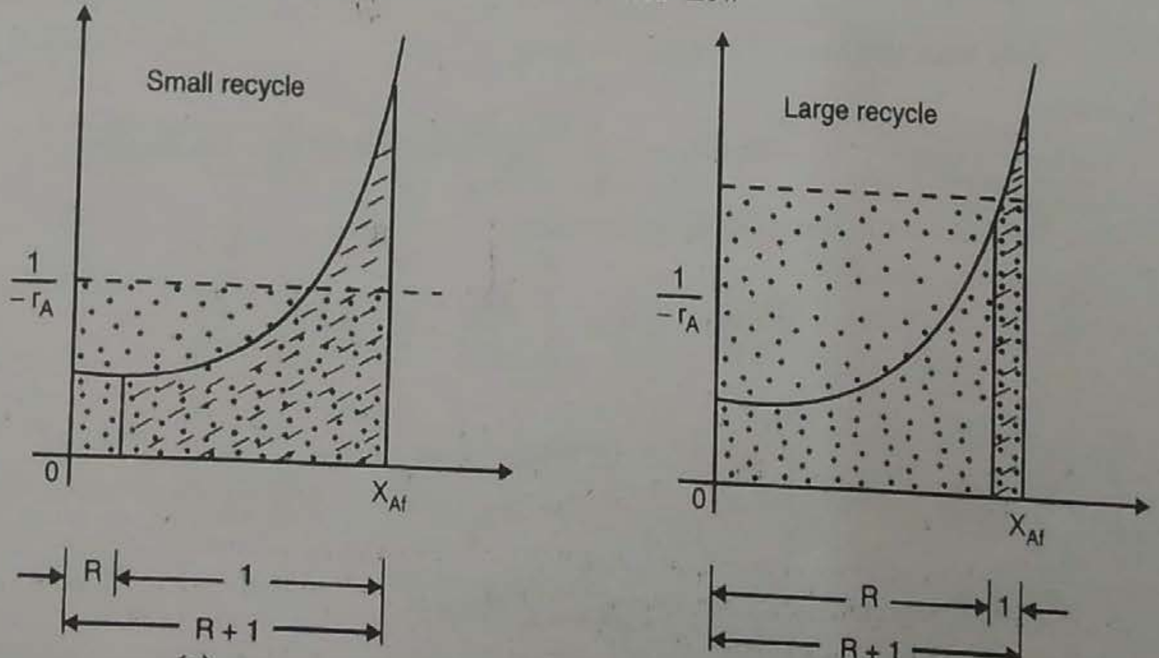
For extreme conditions of recycle i.e. $R = 0$ and $R = \infty$, the reaction system approaches plug flow or mixed flow.

$$\frac{V}{F_{A0}} = (R+1)\int_{\left(\frac{R}{R+1}\right)X_{Af}}^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$R = 0 \qquad\qquad R = \infty$$

$$\frac{V}{F_{A0}} = \int_0^{X_{Af}} \frac{dX_A}{(-r_A)} \qquad \frac{V}{F_{A0}} = \frac{X_{Af}}{(-r_A)_f}$$

plug flow mixed flow



(a) (b)

Fig. 4.25 : The recycle extremes approach plug flow (R → 0) and mixed flow (R → ∞)

The approach to these extreme conditions of recycle is shown in Fig. 4.25.

(1) For first order reaction and constant density ($\varepsilon_A = 0$), the integrated form of performance equation for recycle reactor is

$$\frac{k\tau}{R+1} = \ln\left[\frac{C_{A0} + R\,C_{Af}}{(R+1)\,C_{Af}}\right] \qquad \dots (4.64)$$

$$\tau = -(R+1)\int_{\frac{C_{A0}+R\,C_{Af}}{(R+1)}}^{C_{Af}} \frac{dC_A}{(-r_A)} \qquad -r_A = kC_A$$

$$= -(R+1)\int_{\frac{C_{A0}+R\,C_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{kC_A}$$

$$= \frac{-(R+1)}{k}\,[\ln C_A]_{\frac{C_{A0}+R\,C_{Af}}{R+1}}^{C_{Af}} = \frac{(R+1)}{k}\ln\left[\frac{C_{A0}+R\,C_{Af}}{(R+1)\,C_{Af}}\right]$$

$$\therefore \quad \frac{k\tau}{R+1} = \ln\left[\frac{C_{A0}+R\,C_{Af}}{(R+1)\,C_{Af}}\right]$$

(2) For second order reaction, 2A → products for $\varepsilon_A = 0$, the integrated form of performance equation for recycle reactor is

$$\frac{k\,C_{A0}\,\tau}{(R+1)} = \frac{C_{A0}\,(C_{A0} - C_{Af})}{C_{Af}\,(C_{A0} + R\,C_{Af})} \qquad \dots (4.65)$$

$$\tau = -(R+1)\int_{\frac{C_{A0}+R\,C_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{(-r_A)}$$

$$-r_A = k\,C_A^2$$

$$\tau = -(R+1)\int_{\frac{C_{A0}+R\,C_{Af}}{R+1}}^{C_{Af}} \frac{dC_A}{k\,C_A^2}$$

$$= \frac{-(R+1)}{k}\left[-\frac{1}{C_A}\right]_{\frac{C_{A0}+R\,C_{Af}}{R+1}}^{C_{Af}}$$

$$= \frac{(R+1)}{k}\left[\frac{1}{C_{Af}} - \frac{R+1}{C_{A0}+R\,C_{Af}}\right]$$

$$= \frac{(R+1)}{k}\left[\frac{C_{A0}+R\,C_{Af}-R\,C_{Af}-C_{Af}}{(C_{A0}+R\,C_{Af})\,C_{Af}}\right]$$

$$= \left(\frac{R+1}{k}\right)\left[\frac{C_{A0}-C_{Af}}{C_{Af}\,(C_{A0}+R\,C_{Af})}\right]$$

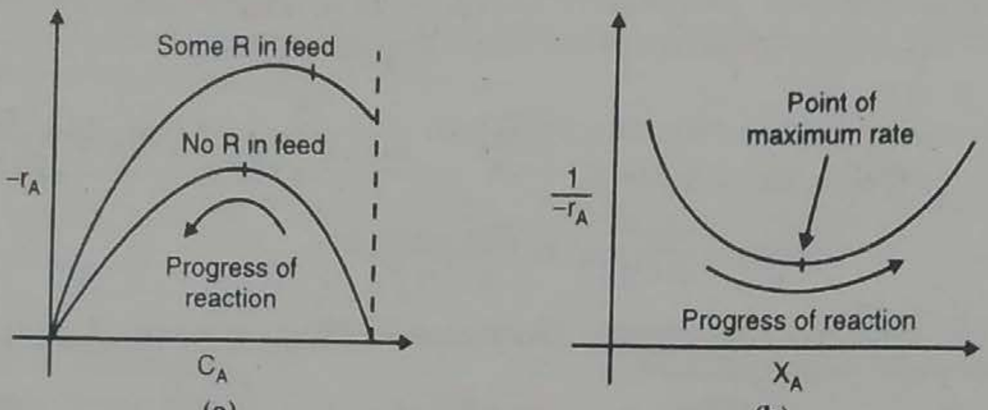
$$\therefore \quad \frac{\tau k}{R+1} = \frac{(C_{A0}-C_{Af})}{C_{Af}\,(C_{A0}+R\,C_{Af})}$$

By multiplying both sides by C_{Ao}, we get,

$$\frac{\tau k\, C_{Ao}}{R+1} = \frac{C_{Ao}(C_{Ao}-C_{Af})}{C_{Af}(C_{Ao}+R\,C_{Af})}$$

Autocatalytic Reactions :

When reactant A reacts by any n^{th} order rate ($n > 0$) in a batch reactor, its rate of disappearance is fast at the start due to its higher initial concentration. As the reactant get consumed, this rate decreases progressively. In autocatalytic reactions, however, the rate of reaction at start is low because the little product is present initially. This rate increases to the maximum as product is formed and then decreases progressively as the reactant is consumed by reaction. The rate-concentration curve for ordinary n^{th} order reaction and autocatalytic reaction is shown in Fig. 4.26.



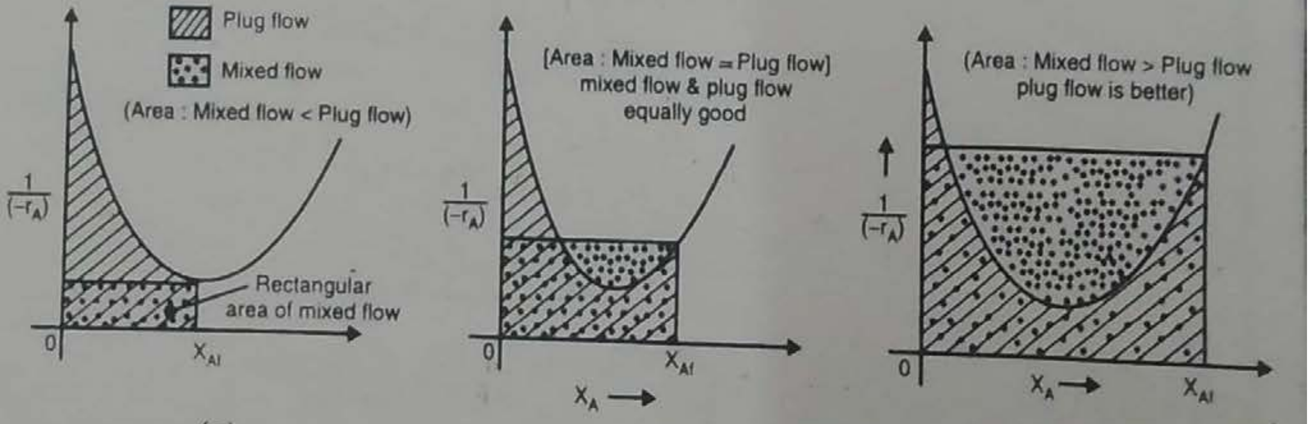
(a) (b)

Fig. 4.26 : Typical rate-concentration curve for autocatalytic reaction

$$A + R \rightarrow R + R, \quad -r_A = k\, C_A^{\alpha} \cdot C_B^{\gamma}$$

Plug flow versus mixed flow, no recycle for autocatalytic reactions :

For such reactions in order to determine the type of reactor which requires a smaller volume for a given level of conversion, we have to plot rate-concentration curve as : $1/(-r_A)$ v/s X_A and do the comparison of areas. Smaller the area, smaller will be the size of reactor (means superior is the reactor) and vice-versa.



(a) (b) (c)

Fig. 4.27 : Comparison of mixed flow and plug flow reactors for autocatalytic reactions

Findings referring to Fig. 4.27 are :

(1) At low conversions the mixed flow reactor is superior to the plug flow reactor (i.e. mixed flow is more efficient at low conversions).

(2) At high enough conversions the plug flow reactor is superior to the mixed flow reacto (i.e. plug flow reactor is more efficient at high conversion levels).

For ordinary nth order reactions (n > 0), the plug flow is always more efficient than th mixed flow reactor. This is not the case with autocatalytic reactions (refer to findings). In case of autocatalytic reactions, the plug flow reactor will not operate at all with a pure reactant feed, the feed should be primed with product and hence in such cases there is an opportunity for usin a recycle reactor.

Optimum Recycle Operations :

When we process materials in a recycle reactor to achieve some fixed conversion there is a certain recycle ratio which is optimum. By optimum recycle ratio we mean the recycle rati with which we need minimum reactor volume.

The optimum recycle ratio is obtained by differentiating equation (4.61) with respect to R and setting to zero,

$$\frac{V}{F_{Ao}} = (R+1) \int_{\left(\frac{R}{R+1}\right) X_{Af}}^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$\frac{\tau}{C_{Ao}} = \int_{X_{Ai} = \frac{R\, X_{Af}}{R+1}}^{X_{Af}} \frac{(R+1)}{(-r_A)}\, dX_A \qquad \ldots (4.66)$$

Differentiate τ/C_{Ao} w.r.t. R and set

$$\frac{d\,(\tau/C_{Ao})}{dR} = 0$$

This operation requires differentiating under integral sign.

If
$$F(R) = \int_{a(R)}^{b(R)} f(x, R)\; dx \qquad \ldots (4.67)$$

then from theorems of calculus we have,

$$dF/dR = \int_{a(R)}^{b(R)} \frac{\partial f(x, R)}{\partial R}\, dx + f(b, R)\frac{db}{dR} - f(a, R)\frac{da}{dR} \qquad \ldots (4.68)$$

For our case in line with above equation,

$$\frac{d(\tau/C_{Ao})}{dR} = 0 = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)} + 0 - \left.\frac{R+1}{(-r_A)}\right|_{X_{Ai}} \frac{dX_i}{dR}$$

$$\therefore \quad \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)} = \left.\frac{(R+1)}{(-r_A)}\right|_{X_{Ai}} \frac{dX_{Ai}}{dR}$$

We have,
$$X_{Ai} = \left(\frac{R}{R+1}\right) X_{Af}$$

$$\frac{dX_{Ai}}{dR} = X_{Af}\left[\frac{(R+1)\times 1 - R\times 1}{(R+1)^2}\right]$$

$$\frac{dX_{Ai}}{dR} = \frac{X_{Af}}{(R+1)^2}$$

$$\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)} = \left.\frac{(R+1)}{(-r_A)}\right|_{X_{Ai}} \left[\frac{X_{Af}}{(R+1)^2}\right]$$

$$\therefore \qquad \left.\frac{1}{(-r_A)}\right|_{X_{Ai}} \cdot \frac{X_{Af}}{(R+1)} = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$X_{Ai} = \left(\frac{R}{R+1}\right)X_{Af}$$

$$\therefore \qquad X_{Af} - X_{Ai} = X_{Af} - \left(\frac{R}{R+1}\right)X_{Af}$$

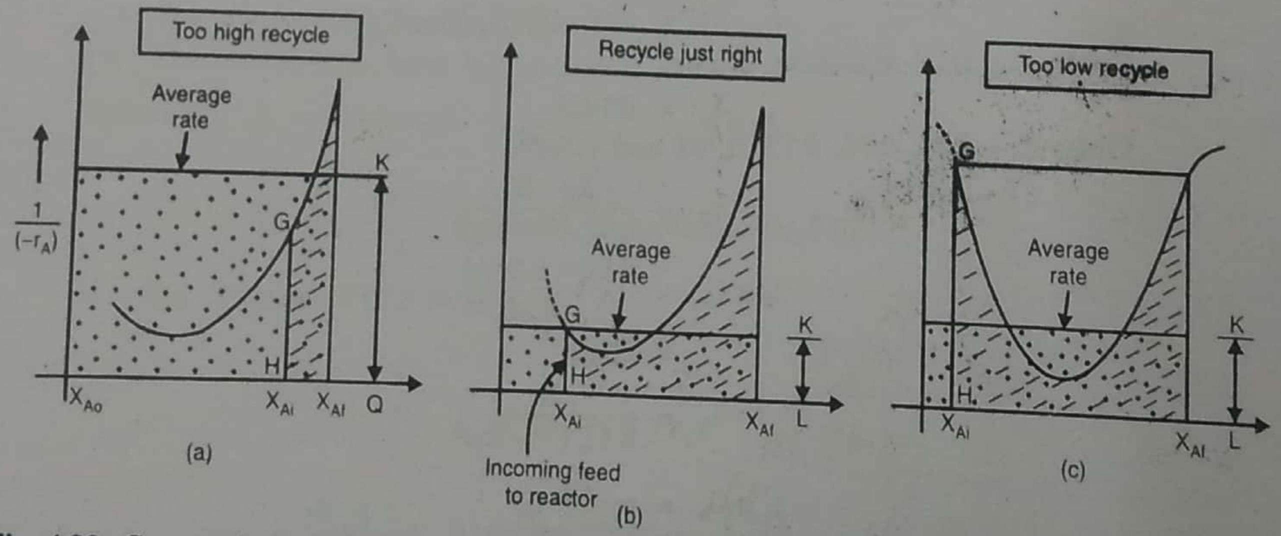
$$(X_{Af} - X_{Ai}) = X_{Af}\left[1 - \frac{R}{R+1}\right] = \frac{X_{Af}}{(R+1)}$$

$$\therefore \qquad \left.\frac{1}{(-r_A)}\right|_{X_{Ai}} \times (X_{Af} - X_{Ai}) = \int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)}$$

∴ For optimum, we have,

$$\therefore \qquad \left.\frac{1}{(-r_A)}\right|_{X_{Ai}} = \frac{\displaystyle\int_{X_{Ai}}^{X_{Af}} \frac{dX_A}{(-r_A)}}{(X_{Af} - X_{Ai})} \qquad \ldots (4.69)$$

i.e. the optimum recycle ratio introduces a feed to the reactor whose $1/(-r_A)$ value (GH Fig. 4.28) equals the average $1/(-r_A)$ value in the reactor as a whole (KL Fig. 4.28). Comparison of this optimum recycle ratio with conditions where recycle ratio is too high and too low is shown in Fig. 4.28.



(a) (b) (c)

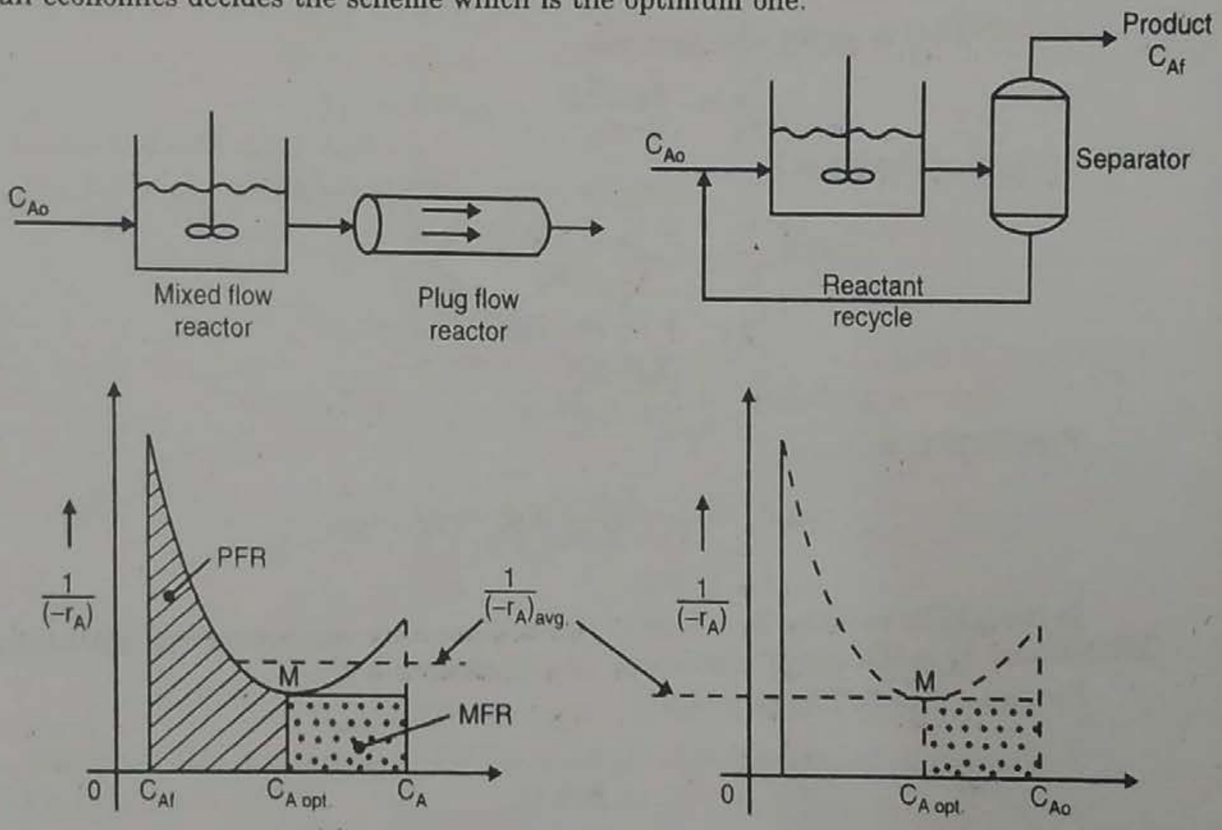
Fig. 4.28 : Comparison of correct recycle ratio with recycle ratios that are too high and too low for autocatalytic reaction

Examples of Autocatalytic Reactions :

(i) Fermentation reactions which involve action of microorganism on an organic feed, (ii) Combustion of fuel gas occurring in an adiabatic manner with feed of cool reactants to the system. Such combustion reactions are referred as autothermal because here heat is considered as a product which sustains the reaction and will die with plug flow and will be self-sustaining with backmix/mixed flow as the heat generated by the reaction can heat the fresh reactants to a temperature at which they will react.

Reactor Combinations for Autocatalytic reactions :

For carrying out autocatalytic reactions where product recycle or product separation with recycle is permitable, we have to consider all sorts of reactor arrangements. In general, when rate-concentration curve is of the type (shape) as shown in Fig. 4.29 one has to try to reach point M (point of maximum rate) in one step (using a mixed flow in a single unit) and then follow with plug flow. Fig. 4.29 (a) shows clearly that the shaded area (representing size) required for combination-mixed flow followed by plug flow is always small than that would be required for reverse order of reactors. Whenever separation and reuse of unconverted reactant is possible, operate at point M using mixed flow reactor for minimum possible volume. In such cases we have to consider the cost of separation and recycle in addition to the cost of unit and hence, overall economics decides the scheme which is the optimum one.



(a) (b)

Fig. 4.29 : (a) The best multiple reactor scheme

(b) The best scheme for separation and reuse (by recycle) of unconverted reactant

SOLVED EXAMPLES

Ex. 4.1 : At present 90% of reactant A is converted into product by a second order reaction in a single mixed flow reactor. We plan to place a second reactor similar to the one being used in series with it.

(i) For same treatment rate as that used at present, how will this addition affect the conversion of reactant ?

(ii) For the same 90% conversion, by how much can the treatment rate be increased ?

Solution : Consider the case of single CSTR.

For CSTR, we have

$$\frac{\tau}{C_{Ao}} = \frac{X_A}{(-r_A)}$$

For second order reaction,

$$(-r_A) = k\,C_A^2 = k\,C_{Ao}^2\,(1-X_A)^2 \quad \text{for } \varepsilon_A = 0$$

$$\frac{\tau}{C_{Ao}} = \frac{X_A}{k\,C_{Ao}^2\,(1-X_A)^2}$$

$$\tau\,k\,C_{Ao} = \frac{X_A}{(1-X_A)^2}$$

We have, $X_A = 0.90$

$$\tau\,k\,C_{Ao} = \frac{0.90}{(1-0.90)^2}$$

$\therefore$ $\tau\,k\,C_{Ao} = 90$

(i) Now we will find conversion that can be achieved using two equal-size CSTRs in series.

For CSTR-2 in series with first one,

$$\frac{\tau_2}{C_o} = \frac{X_2 - X_1}{(-r)_2}$$

$(-r)_2$ is evaluated at X_2

$$(-r)_2 = k\,C_o^2\,(1-X_2)^2 = k\,C_2^2$$

$$\therefore \quad \frac{\tau_2}{C_o} = \frac{X_2 - X_1}{k\,C_o^2\,(1-X_2)^2}$$

$$\tau_2\,k\,C_o = \frac{X_2 - X_1}{(1-X_2)^2}$$

For CSTR-1, we have,

$$\tau_1\,k\,C_o = \frac{X_1}{(1-X_1)^2} = 90, \quad X_1 = 0.90$$

$$\tau_1 = 90/k\,C_o$$

In two CSTRs in series $X_1 = 0.90$ is the intermediate conversion (i.e. conversion leaving CSTR-1) and X_2 is the overall conversion from system as a whole.

For equal-size CSTRs in series,

$$\tau_1 = \tau_2 = \tau$$

$$\therefore \quad \tau_2 = \tau_1 = 90/k\,C_o$$

$$\tau_2\,k\,C_o = \frac{X_2 - X_1}{(1-X_2)^2}$$

$$\left(\frac{90}{k\,C_o}\right) k\,C_o = \frac{X_2 - X_1}{(1-X_2)^2}$$

$$90 = \frac{X_2 - 0.90}{(1-X_2)^2}$$

$$90\,(1-X_2)^2 = X_2 - 0.90$$

$$90\,X_2^2 - 181\,X_2 + 90.90 = 0$$

$$\therefore \quad X_2 = 0.972$$

So using two equal-size CSTRs in series, 97.2% conversion of A is achieved.

$$\% \text{ increase in conversion} = \left(\frac{0.972 - 0.90}{0.90}\right) \times 100 = 8$$

So addition of second CSTR of equal size in series with first one results in 8% increase in conversion. ... **Ans.** (i

(ii) Now we will consider a case of two equal-size CSTRs in series for obtaining 90% overall conversion.

$$\therefore \quad X_2 = 0.90$$

For CSTR-1 :

$$\frac{\tau_1}{C_o} = \frac{X_1}{(-r)_1}$$

$$(-r)_1 = k\,C_o (1 - X_1)^2$$

$$\therefore \quad \tau_1 = \frac{X_1}{k\,C_o\,(1 - X_1)^2}$$

Similarly, for CSTR-2 :

$$\frac{\tau_2}{C_o} = \frac{X_2 - X_1}{(-r)_2}$$

$$(-r)_2 = k\,C_o (1 - X_2)^2$$

$$\therefore \quad \tau_2 = \frac{X_2 - X_1}{k\,C_o\,(1 - X_2)^2}$$

For equal-size CSTRs in series,

$$\tau_1 = \tau_2 \quad (= \tau)$$

$$\therefore \quad \frac{X_1}{k\,C_o\,(1 - X_1)^2} = \frac{X_2 - X_1}{k\,C_o\,(1 - X_2)^2}$$

$$\frac{X_1}{(1 - X_1)^2} = \frac{X_2 - X_1}{(1 - X_2)^2}$$

$$X_2 = 0.90$$

$$\frac{X_1}{(1 - X_1)^2} = \frac{0.90 - X_1}{(1 - 0.90)^2}$$

$$X_1 = (90 - 100\,X_1)\,(1 - X_1)^2$$

Solving by trial-and-error, we get,

$$X_1 = 0.7635$$

(Take $X_1 = 0.75$, 0.76, 0.77, 0.763 and 0.7635)

$$\therefore \quad \tau_2 = \frac{X_2 - X_1}{k\,C_o\,(1 - X_2)^2}$$

$$\tau_2\,k\,C_o = \frac{0.90 - 0.7635}{(1 - 0.90)^2}$$

$$= 13.65$$

$$\tau_1 = \frac{X_1}{k\,C_o\,(1 - X_1)^2}$$

$$\tau_1\,k\,C_o = \frac{X_1}{(1 - X_1)^2}$$

$$= \frac{0.7635}{(1 - 0.7635)^2}$$

$$= 13.65$$

$$\tau_2 = \tau_1 = 13.65/k\,C_o$$

$$\tau_1 = \tau_2 = \tau \text{ for}$$

$$\tau_{N \text{ reactors}} = N\,\tau_i$$

$$(\tau)_{N=2} = 2 \times 13.65/k\,C_o = 27.3/k\,C_o$$

We have for single CSTR for 90% conversion,

$$\tau\,k\,C_{Ao} = 90$$

$$\therefore \quad \tau\,k\,C_o = 90$$

$$(\tau)_{N=1} \quad 90/k\,C_o$$

$$\therefore \quad \frac{(\tau)_{N=2}}{(\tau)_{N=1}} = \frac{(V/v)_{N=2}}{(V/v)_{N=1}}$$

We have,

$$V_{N=2} = 2\,V_{N=1}$$

$$\frac{(\tau)_{N=2}}{(\tau)_{N=1}} = \frac{(V)_{N=2}}{(V)_{N=1}} \times \frac{(v)_{N=1}}{(v)_{N=2}}$$

$$\therefore \quad (v)_{N=2} = \frac{2\,(V)_{N=1}}{(V)_{N=1}} \times \frac{(\tau)_{N=1}}{(\tau)_{N=2}} \times (v)_{N=1}$$

$$(v)_{N=2} = \frac{2 \times 90}{k\,C_o} \times \frac{1}{\left(\frac{27.3}{k\,C_o}\right)} \times (v)_{N=1}$$

$$(v)_{N=2} = \frac{2 \times 90}{27.3} \times (v)_{N=1}$$

$$= 6.59\,(v)_{N=1}$$

$$\approx 6.6\,(v)_{N=1}$$

Hence, the treatment rate can be raised to 6.6 times the original. ... **Ans. (ii)**

If we use the second reactor in parallel with the original one then the treatment rate would only be doubled (as for two CSTRs in parallel $F_{Ao} = F_{Ao1} + F_{Ao1} = 2\,F_{Ao1}$). Hence there is a definite advantage in operating the two CSTRs in series. This advantage becomes much more pronounced at high degrees of conversion.

Ex. 4.2 : Substance A reacts according to second-order kinetics and conversion is 95% from a single flow reactor. We buy a second unit identical to the first. For the same degree of conversion, by how much is the capacity increased if we operate these two units in parallel or in series ?

(i) The reactors are both plug flow.

(ii) The reactors are both mixed flow.

Solution : A → products, $-r_A = k\,C_A^2$, $X_A = 0.95$

$$\frac{V}{F_{Ao}} = C_{Ao} \int_0^{X_A} \frac{dX}{(-r_A)} \text{ . performance equation for PFR.}$$

(i) For identical PFRs in series,

$$\frac{V_1}{F_o} = C_o \int_0^{X_1} \frac{dX}{(-r)}, \quad \frac{V_2}{F_o} = C_o \int_{X_1}^{X_2} \frac{dX}{-r}$$

$$\frac{V_1 + V_2}{F_o} = C_o \int_0^{X_1} \frac{dX}{(-r)} + C_o \int_{X_1}^{X_2} \frac{dX}{-r} = C_o \int_0^{X_2} \frac{dX}{(-r)}$$

$$V_1 = V_2 = V$$

$$\therefore \quad \frac{2V}{F_o} = C_o \int_0^{X_2} \frac{dX}{(-r)} = C_o \int_0^{0.95} \frac{dX}{(-r)}$$

For single PFR, $\frac{V}{F_{Ao}} = C_o \int_0^{0.95} \frac{dX}{(-r_A)}$

RHS of above equation remains same (unchanged for single PFR and two identical PFRs in series).

$$F_o = 2 F_{Ao}$$

$\therefore$ Feed rate can be doubled. ... **Ans.**

For plug flow reactors in parallel, τ should be same for each parallel line for conversion to be same.

$$\tau_1 = \tau_2 \text{ and we have identical PFRs}$$

$$\therefore \quad V_1 = V_2$$

We have, $F_o = (F_o)_1 + (F_o)_2$

$$V/(F_o)_1 = V/(F_{o2})$$

$$\therefore \quad (F_o)_1 = (F_o)_2$$

$$\therefore \quad F_o = 2(F_o)_1$$

So the feed rate can be doubled. ... **Ans.**

(ii) For single CSTR/mixed flow reactor we have :

$$\tau = \frac{C_{Ao} V}{F_{Ao}} = \frac{C_{Ao} X_A}{(-r_A)} \text{ for single CSTR}$$

$$r_A = k C_{Ao}^2 (1 - X_A)^2$$

$$\tau = \frac{C_{Ao} V}{F_{Ao}} = \frac{C_{Ao} X_A}{k C_{Ao}^2 (1 - X_A)^2}$$

$$\tau = \frac{X_A}{k C_{Ao} (1 - X_A)^2}$$

$$\tau k C_{Ao} = X_A/(1 - X_A)^2$$

$$X_A = 0.95$$

$$\therefore \quad \tau k C_{Ao} = \frac{0.95}{(1 - 0.95)^2}$$

$$\tau k C_{Ao} = 380 \text{ for single CSTR.}$$

(a) Equal-size (i.e. identical) CSTRs in series with 95% overall conversion :

For CSTR-2 in series :

$$\frac{\tau_2}{C_o} = \frac{X_2 - X_1}{(-r)_2}$$

$$\tau_2 = \frac{X_2 - X_1}{k C_o (1 - X_2)^2}$$

For CSTR-1 in series :

$$\frac{\tau_1}{C_o} = \frac{X_1}{(-r)_1}$$

$$(-r)_1 = k C_o^2 (1 - X_1)^2$$

$$\therefore \quad \tau_1 = \frac{X_1}{k\,C_o\,(1-X_1)^2}$$

$$\tau_1 = \tau_2 \quad \text{for equal size CSTRs in series}$$

$$\therefore \quad \frac{X_1}{k\,C_o\,(1-X_1)^2} = \frac{X_2 - X_1}{k\,C_o\,(1-X_2)^2}$$

$$\frac{X_1}{(1-X_1)^2} = \frac{0.95 - X_1}{(1-0.95)^2} \quad \text{as } X_2 = 0.95$$

$$X_1 = (380 - 400\,X_1)\,(1-X_1)^2$$

Solving for X_1, we get,

$$X_1 = 0.8525 \text{ (approximately)}$$

$$\therefore \quad \tau_1 = \frac{X_1}{k\,C_o\,(1-X_1)^2}$$

$$\tau_1\,k\,C_o = \frac{X_1}{(1-X_1)^2}$$

$$= \frac{0.8525}{(1-0.8525)^2}$$

$$= 39.2$$

$$\tau_1 = 39.2/k\,C_o$$

$$\tau_2 = \tau_1 = \tau_i = 39.2/k\,C_o$$

$$\tau_{N=2} = N \cdot \tau_i$$

$$= 2 \times 39.2/k\,C_o$$

$$= 78.4/k\,C_o$$

For single CSTR, we have,

$$\tau\,k\,C_{Ao} = 380$$

$$\therefore \quad \tau_{N=1} = 380/k\,C_o \quad (\text{as } C_o = C_{Ao})$$

$$\frac{\tau_{N=2}}{\tau_{N=1}} = \frac{(V/v)_{N=2}}{(V/v)_{N=1}}$$

$$(v)_{N=2} = \frac{(V)_{N=2}}{(V)_{N=1}} \times \frac{\tau_{N=1}}{\tau_{N=2}} \times (v)_{N=1}$$

We have, $(V)_{N=2} = 2\,(V)_{N=1}$

$$\therefore \quad (v)_{N=2} = \frac{2\,(V)_{N=1}}{(V)_{N=1}} \times \frac{380/k\,C_o}{78.4/k\,C_o} \times (v)_{N=1}$$

$$\therefore \quad (v)_{N=2} = 9.694\,(v)_{N=1}$$

$$= 9.7\,(v)_{N=1}$$

i.e. $(F_{Ao})_{N=2} = 9.7\,(F_{Ao})_{N=1}$

So for two identical CSTRs in series for overall conversion of 95%, the feed rate is 9.7 times the feed rate for single CSTR. **... Ans.**

(b) For identical CSTRs in parallel :

$$(F_{Ao})_{N=2} = F_{o1} + F_{o2} \quad \text{and} \quad F_{o1} = F_{o2}$$

$$\therefore \quad (F_{Ao})_{N=2} = 2\,F_{o1} = 2\,[F_{Ao} \text{ for single CSTR}]$$

∴ For equal-size CSTRs in parallel, the feed rate would be doubled. **... Ans.**

Ex. 4.3 : (a) Derive the expression for the concentration of reactant in the effluent from a series of mixed reactors of different sizes. Let the reaction follows first order kinetics and let the holding time in the i^{th} reactor is τ_i.

(b) Show that this expression reduces to the appropriate equation in this chapter when the reactors are all of the same size.

Solution :

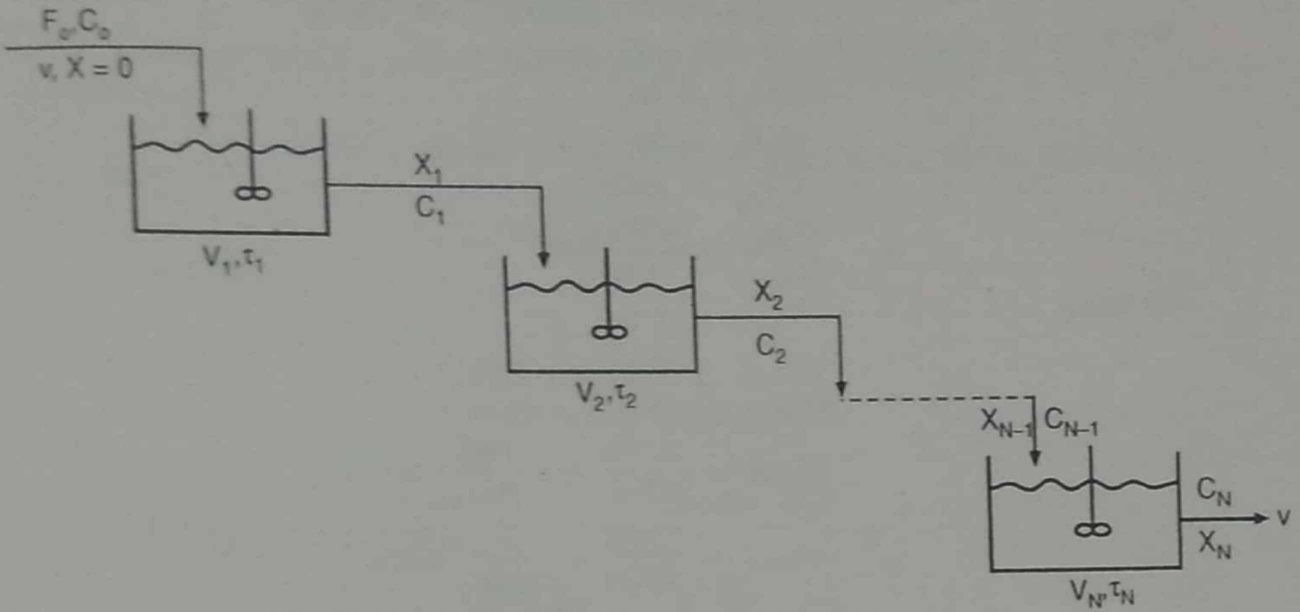


Fig. E 4.3 : Notation for N different size CSTRs in series

(a) Consider that a first order reaction with no volume change ($v = v_o$) is carried out in N different size CSTRs in series (Fig. E 4.3).

The performance equation of CSTR is

$$\tau = \frac{V}{v_o} = \frac{C_{Ao} - C_A}{(-r_A)}$$

For CSTR-1 in series, we can write,

$$\tau_1 = \frac{C_o - C_1}{(-r)_1}$$

This is a performance equation in terms of concentration.

For a first order reaction, the rate law is

$$-r_A = k\, C_A$$

$$\therefore \quad (-r)_1 = k\, C_1$$

Combining the rate law with performance equation, we get,

$$\tau_1 = \frac{C_o - C_1}{k\, C_1}$$

Solving for concentration of A from reactor-1, C_1,

$$C_1 = \frac{C_o}{(1 + \tau_1 k)}$$

For CSTR-2 in series, we can write

$$\tau_2 = \frac{C_1 - C_2}{(-r)_2}$$

$$(-r)_2 = k\, C_2$$

$$\therefore \quad \tau_2 = \frac{C_1 - C_2}{k\, C_2}$$

Solving for C_2, the concentration of A leaving the second order,

$$C_2 = \frac{C_1}{(1 + \tau_2 k)}$$

but $$C_1 = \frac{C_o}{(1+\tau_1 k)}$$

∴ $$C_2 = \frac{C_o}{(1+\tau_1 k)(1+\tau_2 k)}$$

Similarly, for CSTR-3 in series :

$$C_3 = \frac{C_2}{(1+\tau_3 k)}$$

∴ $$C_3 = \frac{C_o}{(1+\tau_1 k)(1+\tau_2 k)(1+\tau_3 k)}$$

For N CSTRs in series, therefore,

$$C_N = \frac{C_o}{(1+\tau_1 k)(1+\tau_2 k)\ldots(1+\tau_N k)}$$

We have, $C_1 = C_o/(1+\tau_1 k)$

∴ $C_o/C_1 = (1+\tau_1 k)$

We can write,

$$\frac{C_o}{C_N} = \frac{C_o}{C_1}\cdot\frac{C_1}{C_2}\cdot\frac{C_2}{C_3}\cdots\frac{C_{N-1}}{C_N}$$

$$\frac{C_o}{C_N} = (1+\tau_1 k)\cdot(1+\tau_2 k)\cdot(1+\tau_3 k)\ldots(1+\tau_N k)$$

∴ $$C_N = \frac{C_o}{(1+\tau_1 k)(1+\tau_2 k)(1+\tau_3 k)\ldots(1+\tau_N k)}$$ ... **Ans.**

(b) N equal-size CSTRs in series :

For N equal-size CSTRs placed in series, we have,

$$\tau_1 = \tau_2 = \tau_N = \tau$$

∴ For first CSTR

$$C_1 = \frac{C_o}{(1+\tau_1 k)} = \frac{C_o}{(1+\tau k)}$$

For CSTR-2 in series, we have,

$$C_2 = \frac{C_o}{(1+\tau_1 k)(1+\tau_2 k)}$$

For equal-size CSTRs,

$$C_2 = \frac{C_o}{(1+\tau k)(1+\tau k)}$$

$$C_2 = \frac{C_o}{(1+\tau k)^2}$$

Similarly, for CSTR-3,

$$C_3 = \frac{C_o}{(1+\tau k)^3}$$

∴ The concentration of A leaving the last reactor would be

$$C_N = \frac{C_o}{(1+\tau k)^N}$$ ... **Ans.**

$$\frac{C_N}{C_o} = \frac{1}{(1+\tau k)^N}$$

or $$\frac{C_o}{C_N} = (1+\tau k)^N$$ ... **Ans.**

Ex. 4.4 : Your company has two mixed reactors of unequal size for producing a specified product that forms by homogeneous first-order reaction. How should these reactors be connected to achieve a maximum production rate ?

Solution :

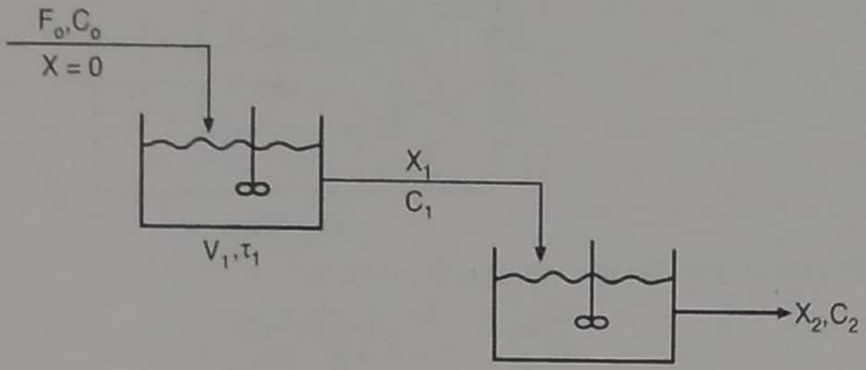


Fig. E 4.4

For first-order reaction,

$$-r_A = k\,C_A$$

For CSTR-1,

$$\tau_1 = \frac{C_o - C_1}{(-r)_1}$$

$$(-r)_1 = k\,C_1$$

$$\tau_1 = \frac{C_o - C_1}{k\,C_1}$$

Concentration of A leaving the first reactor is

$$C_1 = \frac{C_o}{(1 + \tau_1 k)}$$

For CSTR-2,

$$\tau_2 = \frac{C_1 - C_2}{(-r)_2}$$

$$(-r)_2 = k\,C_2$$

$$\tau_2 = \frac{C_1 - C_2}{k\,C_2}$$

Concentration of A leaving the second reactor is

$$C_2 = \frac{C_1}{(1 + \tau_2 k)}$$

$$\therefore \quad C_2 = \frac{C_o}{(1 + \tau_2 k)(1 + \tau_1 k)}$$

$$\frac{C_2}{C_o} = \frac{1}{(1 + \tau_1 k)(1 + \tau_2 k)}$$

So referring to above equation it is clear that even if τ_1 and τ_2 are interchanged, the ratio C_2/C_o remains unchanged. Hence for first order reaction, it makes no difference which reactor put first, conversion is unaffected. ... **Ans.**

Ex. 4.5 : A first-order liquid phase reaction, 92% conversion, is occurring in a mixed reactor. It has been suggested that a fraction of the product stream, with no additional treatment, be recycled. If the feed rate remains unchanged, in what way would this affect conversion ?

Solution : For first-order reaction liquid phase, $X = 0.92$.

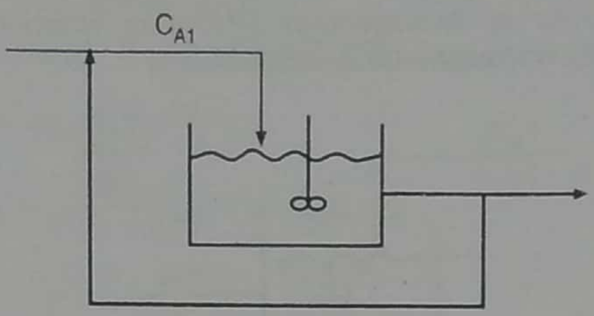


Fig. E 4.5

In case of recycle reactor, C_{A1} is given by

$$\frac{C_{A1}}{C_{Ao}} = \frac{1 + R - R\,X_{Af}}{1 + R + R\,\varepsilon_A\,X_{Af}}$$

For liquid phase reaction, $\varepsilon_A = 0$

$$\therefore \quad \frac{C_{A1}}{C_{Ao}} = \frac{1 + R - R\,X_{Af}}{1 + R}$$

$$\frac{C_{A1}}{C_{Ao}} = \frac{1/R + 1 - X_{Af}}{1/R + 1}$$

For mixed flow reactor, $R = \infty$.

$$\therefore \quad \frac{C_{A1}}{C_{Ao}} = \lim_{R \to \infty} \frac{1/R + 1 - X_{Af}}{1/R + 1}$$

$$\frac{C_{A1}}{C_{Ao}} = 1 - X_{Af} \quad \text{as } 1/R = 0$$

$$X_{Af} = 1 - C_{A1}/C_{Ao} = (C_{Ao} - C_{A1})/C_{Ao}$$

So conversion will be unaffected. ... **Ans.**

Ex. 4.6 : 100 *l*/h of radioactive fluid having a half life of 20 h is to be treated by passing it through two ideal stirred tanks in series. The volume of each stirred tank in series is 40000 litres. In passing through this system, how much has the activity decayed ? The reaction follows first order kinetics.

Solution : Volume of each stirred tank in series = 40000 *l*

v_o = volumetric flow rate = 100 *l*/h

Half-life for reaction = $t_{1/2}$ = 20 h

For first-order reaction, half-life is given by

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

$$\therefore \quad k = \frac{0.693}{t_{1/2}}$$

$$= 0.693/20$$

$$= 0.03465\ (h)^{-1}$$

Space time (τ) for stirred tank-1 is

$$\tau_1 = \frac{V}{v_o} = \frac{40000}{100} = 400\,h$$

For two equal size CSTRs in series,

$$\tau_1 = \tau_2 = \tau$$

$$\therefore \quad \tau_2 = 400\,h$$

For two equal-size CSTRs/stirred tanks in series for first order reaction, we have,

$$\frac{C_2}{C_o} = \frac{1}{(1 + k\,\tau)^2}$$

Concentration of radioactive fluid leaving second reactor is :

$$C_2 = \frac{C_o}{(1+\tau k)^2}$$

For CSTR-1, we have,

$$\tau_1 = \frac{C_o - C_1}{k\,C_1}, \quad \text{as } (-r)_1 = k\,C_1$$

$$\therefore \quad C_1 = \frac{C_o}{(1+\tau_1 k)}$$

For CSTR-2, we have,

$$\tau_2 = \frac{C_1 - C_2}{k\,C_2}, \quad \text{as } (-r)_2 = k\,C_2$$

$$\therefore \quad C_2 = \frac{C_1}{(1+\tau_2 k)}$$

$$\therefore \quad C_2 = \frac{C_o}{(1+\tau_1 k)(1+\tau_2 k)}$$

For equal size CSTRs in series,

$$\tau_1 = \tau_2 = \tau$$

$$\therefore \quad C_2 = \frac{C_o}{(1+\tau k)^2}$$

$$C_2 = \frac{C_o}{(1+400\times 0.03465)^2}$$

$$C_2 = 4.53\times 10^{-3}\,C_o$$

We have, $C_2 = C_o(1-X)$

$$\therefore \quad X = \frac{C_o - C_2}{C_o}$$

$$= \frac{C_o - 4.53\times 10^{-3}\,C_o}{C_o}$$

$$= 0.99547$$

As the conversion is 99.547%, the activity/concentration of radioactive fluid decreases by 99.547%.

... **Ans.**

Alternatively, for CSTR-1,

$$\frac{\tau_1}{C_o} = \frac{X_1}{(-r)_1}$$

$$\frac{\tau_1}{C_o} = \frac{X_1}{k\,C_o(1-X_1)} \quad \text{as } (-r)_1 = k\,C_1 = k\,C_o(1-X_1)$$

$$\tau_1 k = \frac{X_1}{1-X_1}$$

$$\frac{X_1}{1-X_1} = 400\times 0.03465 = 13.86$$

$$\therefore \quad X_1 = 0.9327$$

So, in first reactor, the activity of radioactive fluid decreases by 93.27%.

$$\frac{\text{Reacted}}{\text{Fed}} = 0.9327$$

$$\text{Reacted} = 0.9327 \text{ fed}$$

$$\text{Unreacted} = \text{fed} - \text{reacted}$$

$$= (1-0.9327)\text{ fed} = 0.0673 \text{ fed}$$

$$\therefore \quad \text{Decrease in activity or concentration of radioactive fluid from CSTR-1} = \frac{\text{fed} - \text{unreacted}}{\text{fed}} \times 100$$

$$= \left(\frac{\text{fed} - 0.0673\ \text{fed}}{\text{fed}}\right) \times 100$$

$$= 93.27\%$$

For CSTR-2,

$$\frac{\tau_2}{C_o} = \frac{X_2 - X_1}{k\, C_o\, (1 - X_2)}$$

$$\frac{X_2 - X_1}{(1 - X_2)} = \tau_2\, k$$

$$\frac{X_2 - 0.9327}{(1 - X_2)} = 400 \times 0.03465 = 13.86$$

Solving for X_2, we get

$$X_2 = 0.99547$$

So overall decrease in activity of radioactive fluid for two CSTRs in series is 99.547%. ... **Ans.**

$$\frac{\text{Overall reacted}}{\text{fed}} = 0.99547$$

$$\text{Overall reacted} = 0.99547\ \text{fed}$$

$$\text{Unreacted} = (1 - 0.99547)\ \text{fed}$$

$$= 4.53 \times 10^{-3}\ \text{fed}$$

$$\therefore \quad \text{Decrease in activity of radioactive fluid from two CSTRs in series} = \frac{\text{fed} - \text{unreacted}}{\text{fed}} \times 100$$

$$= \left(\frac{\text{fed} - 4.53 \times 10^{-3}\ \text{fed}}{\text{fed}}\right) \times 100$$

$$= 99.547\ \%$$

... **Ans.**

Ex. 4.7 : A liquid phase elementary reaction A + B → R + S is carried out in a plug flow reactor. For equimolar amounts of A and B ($C_{Ao} = C_{Bo} = 0.9$ mol/*l*), 94% conversion is achieved. If a CSTR, 10 times as large as the plug flow reactor, is arranged in series with the existing unit, which unit needs to be arranged first (in series) to enhance the production rate ?

Solution : First we will consider only plug flow reactor.

For plug flow reactor,

$$\tau = \frac{V}{v_o} = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

For elementary reaction with equimolar amounts,

$$-r_A = k\, C_A\, C_B = k\, C_A^2 = k\, C_{Ao}^2\ (1 - X_A)^2$$

$$\therefore \quad \tau = \frac{C_{Ao}}{k\, C_{Ao}^2} \int_0^{X_A} \frac{dX_A}{(1 - X_A)^2}$$

$$\tau = \frac{1}{k\,C_{Ao}}\left[\frac{1}{1-X_A}\right]_0^{X_A}$$

$$\tau = \frac{1}{k\,C_{Ao}}\left[\frac{1}{1-X_A}-1\right]$$

$$C_{Ao} = 0.9\ \text{mol}/l, \quad X_A = 0.94$$

$$\therefore \quad \tau = \frac{1}{k \times 0.90}\left[\frac{1}{1-0.94}-1\right]$$

$$= \frac{17.41}{k}$$

$$\tau = \frac{V}{v_o} = \frac{17.41}{k}$$

$$\therefore \quad V = \frac{17.41\,v_o}{k} \quad \text{(volume of plug flow reactor)}$$

Volume of CSTR, 10 times as large as PFR is

$$V_m = 10\,V_p$$

$$= \frac{10 \times 17.41\,v_o}{k} = \frac{174.1\,v_o}{k}$$

Now we will consider CSTR and PFR in series.

(i) PFR is followed by CSTR :

Conversion in PFR is $X_1 = 0.94$

Performance equation for CSTR in series,

$$\tau = \frac{V}{v_o} = \frac{C_o(X_2 - X_1)}{(-r)_2}$$

$(-r)_2$ is evaluated at X_2. In series of PFR followed by CSTR, X_1 is the intermediate conversion and X_2 is the overall conversion.

$$\frac{174.1\,v_o}{v_o\,k} = \frac{C_o(X_2 - X_1)}{k\,C_o^2(1-X_2)^2}$$

$$174.1 \cdot C_o(1-X_2)^2 = X_2 - X_1$$

$$174.1 \times 0.90\,(1-X_2)^2 = X_2 - 0.94$$

$$156.69\,X_2^2 - 314.38\,X_2 + 157.63 = 0$$

$$X_2 = 0.9833$$

So by arranging reactors in series (PFR followed by CSTR), the conversion increases from 94% to 98.33%.

$$\%\ \text{increase in conversion} = \left(\frac{98.33-94}{94}\right) \times 100$$

$$= 4.61$$

(ii) CSTR followed by PFR (in series arrangement) :

For CSTR, we have,

$$\tau = \frac{V}{v_o} = \frac{C_o(X_1)}{(-r)_1}$$

$$\frac{V}{v_o} = \frac{C_o X_1}{k\,C_o^2(1-X_1)^2}$$

$$\frac{174.1\ v_o}{k\ v_o} = \frac{X_1}{k\ C_o\ (1 - X_1)^2}$$

$$174.1 \times C_o\ (1 - X_1)^2 = X_1$$

$$174.1 \times 0.90\ (1 - X_1)^2 = X_1$$

$$156.69\ X_1^2 - 314.38\ X_1 + 156.69 = 0$$

$$\therefore \quad X_1 = 0.923$$

For PFR in series,

$$\tau = \frac{V}{v_o} = C_o \int_{X_1}^{X_2} \frac{dX}{(-r)}$$

$$\frac{17.41\ v_o}{k\ v_o} = C_o \int_{X_1}^{X_2} \frac{dX}{k\ C_o^2\ (1 - X)^2}$$

$$17.41\ C_o = \int_{X_1}^{X_2} \frac{dX}{(1 - X)^2}$$

$$17.41\ C_o = \left[\frac{1}{1 - X}\right]_{X_1}^{X_2}$$

$$17.41 \times 0.90 = \left[\frac{1}{1 - X_2}\right] - \left[\frac{1}{1 - X_1}\right]$$

$$X_1 = 0.923$$

$$15.669 = \left[\frac{1}{1 - X_2}\right] - \left[\frac{1}{1 - 0.923}\right]$$

$$\therefore \quad X_2 = 0.965$$

So with arrangement, CSTR followed by PFR, overall conversion is 96.5%.

$$\%\ \text{increase in conversion} = \left(\frac{96.5 - 94}{94}\right) \times 100 = 2.66$$

(i) For PFR-CSTR series arrangement, $X = 0.9833$

(ii) For CSTR-PFR series arrangement, $X = 0.965$

So it is clear that to enhance the production rate, PFR (is put first) should be followed by CSTR.

... **Ans.**

Ex. 4.8 : The elementary reaction $A + B \rightarrow R + S$ is effected in a setup consisting of a mixed reactor into which two reactant solutions are introduced followed by a plug flow reactor. The component B is used in a large excess so that the reaction is first order with respect to A. Various ways to increase the production are suggested, one of which is to reverse the order of units. How would this change affect conversion ?

Solution : $A + B \rightarrow R + S$, elementary reaction.

As B is in large excess, its concentration remains almost constant during the reaction and so the rate is independent of its concentration.

$$\therefore \quad (-r_A) = k\ C_A, \quad \text{first order in A}$$

So above reaction is a first order reaction.

Case I : CSTR followed by PFR :

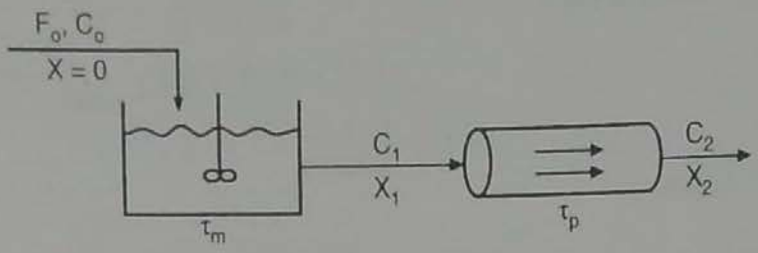


Fig. E 4.8 (1)

For CSTR we have,

$$\tau_m = \frac{C_o - C_1}{(-r)_1}$$

$$(-r)_1 = k\,C_1$$

$$\tau_m = \frac{C_o - C_1}{k\,C_1}$$

Rearranging, we get,

$$C_1 = \frac{C_o}{(1 + \tau_m k)} \quad \text{... (A)}$$

C_1 is the concentration of A existing unit 1 in series (i.e. CSTR).

For PFR, we have,

$$\tau_p = -\int_{C_{A0}}^{C_{Af}} \frac{dC_A}{(-r_A)} = C_{A0} \int_0^{X_{Af}} \frac{dX_A}{(-r_A)}$$

$$\therefore \quad \tau_p = -\int_{C_1}^{C_2} \frac{dC}{(-r)}$$

$$(-r) = kC$$

$$\tau_p = -\int_{C_1}^{C_2} \frac{dC}{kC}$$

$$k\,\tau_p = -\ln\left(\frac{C_2}{C_1}\right) = \ln\frac{C_1}{C_2}$$

$$\therefore \quad \frac{C_2}{C_1} = e^{-k\,\tau_p}$$

$$C_2 = C_1 \cdot e^{-k\,\tau_p} \quad \text{... (F}$$

Combining equations (A) and (B), we get, the concentration of A existing the second unit in series :

$$C_2 = \frac{C_o}{(1 + \tau_m k)} \cdot e^{-k\,\tau_p} \quad \text{... (}$$

Case II : PFR followed by CSTR :

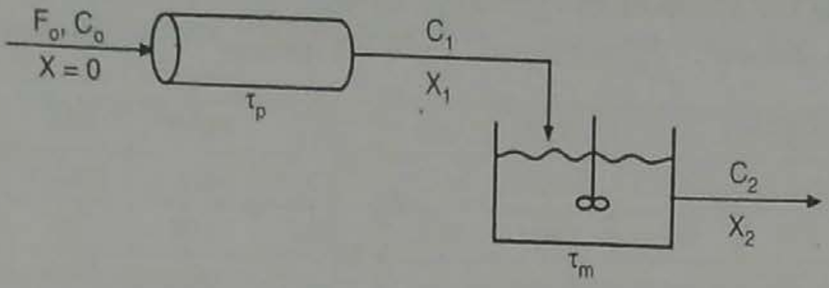


Fig. E 4.8 (2)

For PFR, we have,

$$\tau_p = -\int_{C_o}^{C_1} \frac{dC}{kC}$$

$$k\tau_p = -\ln (C_1/C_o)$$

Concentration of A existing the unit-1 is

$$C_1 = C_o \cdot e^{-k\tau_p} \qquad \text{... (C)}$$

For CSTR,

$$\tau_m = \frac{C_1 - C_2}{(-r)_2} = \frac{C_1 - C_2}{k\,C_2}$$

Rearranging we get,

$$C_2 = \frac{C_1}{(1 + \tau_m k)} \qquad \text{... (D)}$$

Combining equations (C) and (D), concentration of A leaving the unit-2 in series is

$$C_2 = \frac{C_o \cdot e^{-k\tau_p}}{(1 + \tau_m k)} \qquad \text{... (2)}$$

From equations (1) and (2) (for different arrangements), it is clear that concentration of A (C_2) leaving the system remains unchanged (same) for two different arrangements. Hence the order of hooking up the reactors has no effect on conversion (does not affect conversion).

... **Ans.**

Ex. 4.9 : The kinetics of the aqueous phase decomposition of A is investigated in two mixed flow reactors in series the second unit having twice the volume of the first one. At steady state with a feed composition of 1 mol A/litre and mean residence time of 96 seconds in the first reactor, the concentration in the first reactor is 0.5 mol A/litre and in the second is 0.25 mol A/litre. Find the kinetic equation that represents this decomposition.

Solution : A → products

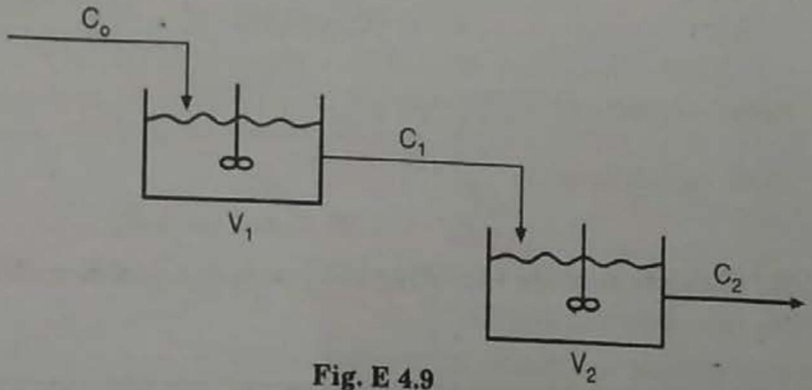


Fig. E 4.9

$$C_o = C_{Ao} = 1 \text{ mol}/l$$
$$C_1 = 0.5 \text{ mol}/l$$
$$C_2 = 0.25 \text{ mol}/l$$

For CSTR-1 in series,

$$\tau_1 = \frac{C_o - C_1}{(-r)_1}$$

Let the rate be given by, $-r_A = k\,C_A^n$

$$\therefore \quad (-r)_1 = k\,C_1^n$$

$$\tau_1 = \frac{C_o - C_1}{k\,C_1^n} \quad \text{... (A)}$$

Similarly, for CSTR-2 in series,

$$\tau_2 = \frac{C_1 - C_2}{k\,C_2^n} \quad \text{... (B)}$$

For CSTR-1, mean residence time is 96 s.

For liquid phase in CSTR,

$$\text{Space time} = \text{Mean residence time}$$
$$\tau_1 = \tau_m = 96 \text{ s}$$

Volume of CSTR-1 = V_1

Volume of CSTR-2 = $2V_1$

$$\therefore \quad \frac{\tau_1}{\tau_2} = \frac{(V/v)_1}{(V/v)_2}$$

$$\tau_2 = \frac{(V/v)_2}{(V/v)_1} \times \tau_1$$

$$= \frac{2V_1}{V_1} \times \tau_1 \qquad \text{as } (v)_1 = (v)_2 = v_o$$

$$\tau_2 = 2 \times 96$$
$$= 192 \text{ s}$$

Dividing equation (A) by (B), we get,

$$\frac{\tau_1}{\tau_2} = \frac{(C_o - C_1)}{k\,C_1^n} \times \frac{k\,C_2^n}{(C_1 - C_2)}$$

$$= \frac{(C_o - C_1)}{C_1 - C_2}\left(\frac{C_2}{C_1}\right)^n$$

$$\left(\frac{96}{192}\right) = \frac{(1-0.5)}{(0.5-0.25)}\left[\frac{0.25}{0.5}\right]^n$$

$$0.5 = \frac{0.5}{0.25}\,[0.5]^n$$

$$0.25 = [0.5]^n$$

$$\ln(0.25) = n \ln(0.5)$$

$$-1.386 = n(-0.69315)$$

$$n = 2$$

So the decomposition of A is second order.

Now we will calculate k.

$$\tau_1 = \frac{C_o - C_1}{k\,C_1^n} \qquad \therefore \quad \tau_1 = \frac{C_o - C_1}{k\,C_1^2}$$

$$k = \frac{(C_o - C_1)}{\tau_1\,C_1^2}$$

$$= \frac{(1 - 0.5)}{96 \times (0.5)^2}$$

$$= 0.0208\ l.(\text{mol.s})^{-1}$$

∴ The kinetic equation for decomposition of A is

$$-r_A = 0.0208\ l.(\text{mol.s})^{-1} \cdot C_A^2 \qquad \text{... Ans.}$$

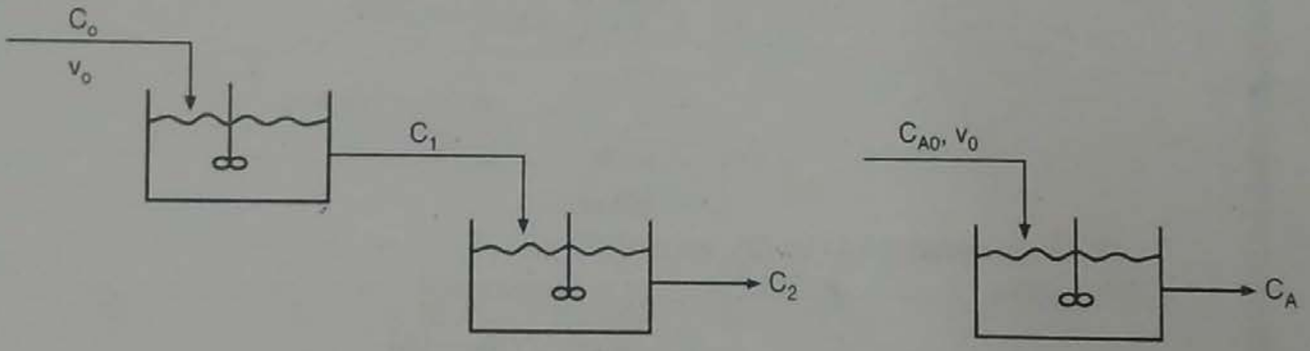
Ex. 4.10 : Using colour indicator which shows when concentration of A falls below 0.1 mol/*l*, the following scheme is devised to explore the kinetics of decomposition of A. The feed containing 0.6 molA/*l* is introduced into the first of the two CSTRs in series, each having a volume of 400 cm³. The colour change occurs in the first reactor (single reactor) for a steady state feed rate of 10 cm³/min, and in second reactor in series (two reactors set up) for a steady state feed rate of 50 cm³/min. Find the rate expression that represents the decomposition of A from the information provided.

Solution : A → products, decomposition reaction.

The rate of decomposition of A is given by,

$$-r_A = k\,C_A^n$$

We have to make use of information provided to find k and n (order of reaction).



(a) (b)

Fig. E 4.10

Case I : Consider only single CSTR.

$$C_{Ao} = 0.6\ \text{mol}/l, \quad C_A = 0.10\ \text{mol}/l$$

$$V = 400\ \text{cm}^3, \quad v_o = 10\ \text{cm}^3/\text{min}$$

For CSTR we have,

$$\tau = \frac{V}{v_o} = \frac{C_{Ao} - C_A}{(-r_A)}$$

$$(-r_A) = k\,C_A^n$$

$$\frac{V}{v_o} = \frac{C_{Ao} - C_A}{k\,C_A^n}$$

$$\frac{400}{10} = \frac{0.6 - 0.1}{k\,(0.1)^n}$$

$$k\,(0.1)^n = 0.0125$$

Case II : Consider two CSTRs in series.

$V_1 = 400\ cm^3, \quad V_2 = 400\ cm^3, \quad v_o = 50\ cm^3/min$

For CSTR-1 :

$$\tau_1 = \frac{V_1}{v_o} = \frac{C_o - C_1}{k\,C_1^n}, \quad \text{as } (-r)_1 = k\,C_1^n$$

$$\tau_1 = \frac{C_o - C_1}{k\,C_1^n}$$

$$\tau_1 = \frac{0.60 - C_1}{k\,C_1^n}$$

For CSTR-2 :

$$C_2 = 0.10\ mol/l, \quad C_o = 0.60\ mol/l$$

$$\tau_2 = \frac{V_2}{v_o} = \frac{C_1 - C_2}{k\,C_2^n}, \quad \text{as } (-r)_2 = k\,C_2^n$$

$$\frac{400}{50} = \frac{C_1 - 0.10}{k\,(0.1)^n}$$

$$8 \cdot k\,(0.1)^n = C_1 - 1.10$$

We have,

$$k\,(0.1)^n = 0.0125$$

$\therefore$

$$8 \times 0.0125 = C_1 - 0.10$$

$$C_1 = 0.20\ mol/l$$

For equal-size CSTRs in series,

$$\tau_1 = \tau_2$$

$\therefore$

$$\frac{C_o - C_1}{k\,C_1^n} = \frac{C_1 - C_2}{k\,C_2^n}$$

$$\frac{0.60 - 0.20}{(0.2)^n} = \frac{0.20 - 0.10}{(0.10)^n}$$

$$0.4\,(0.10)^n = 0.10\,(0.2)^n$$

$$4 = (0.2)^n/(0.1)^n = \left(\frac{0.2}{0.1}\right)^n = 2^n$$

$$\ln 4 = n \ln 2$$

$$1.3863 = n\,(0.69315)$$

$\therefore$

$$n = 2$$

$\therefore$

$$\tau_1 = \frac{C_o - C_1}{k\,(C_1)^n}$$

$\therefore$

$$k = (C_o - C_1)/\tau_1 \cdot C_1^n = \frac{(0.60 - 0.20)}{8 \times (0.2)^2}$$

$$(\text{as } \tau_1 = 400/50 = 8)$$

$$k = 1.25\ (l/mol)\ (min)^{-1}$$

$\therefore$ Rate equation is

$$-r_A = 1.25\ l/(mol.min)\ C_A^2$$

... An

Ex. 4.11 : A gas mixture consisting of 50 mole % A and 50 mole % inerts enters the reactor with the flow rate of 6 l/s at 144 °C.

The rate data is as follows :

X_A	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.85
$-r_A$	0.0053	0.0052	0.005	0.0045	0.004	0.0033	0.0025	0.0018	0.00125	0.001

If the reaction is carried out in two reactors in series with 40% conversion in the first reactor and 85% overall conversion, estimate the total volume of reactors when (i) reactors are both mixed flow and (ii) reactors are both plug flow.

Solution : The rate data is :

X_A	0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.85
$-r_A$	0.0053	0.0052	0.005	0.0045	0.004	0.0033	0.0025	0.0018	0.00125	0.001
$1/(-r_A)$	189	192	200	222	250	303	400	555	800	1000

(i) First we will consider a system of two mixed flow reactors/CSTRs in series.

Initial concentration of A $= C_{Ao} = \dfrac{p_{Ao}}{RT}$

$$p_{Ao} = y_{Ao} \cdot P$$

$$y_{Ao} = \text{mole \% A}/100 = 50/100 = 0.50$$

$$\therefore \quad C_{Ao} = \frac{y_{Ao} \cdot P}{RT}$$

$$P = 10 \text{ atm}, \quad R = 0.08206 \ l.\text{atm}/(\text{mol.K})$$

$$T = 144\,^{\circ}\text{C} = 144 + 273 = 417 \text{ K}$$

$$C_{Ao} = \frac{0.5 \times 10}{0.08206 \times 417} = 0.146 \text{ mol}/l$$

Molal flow rate of A to system $= F_{Ao} = C_{Ao} \cdot v_o$

$$F_{Ao} = 0.146 \times 6$$

$$= 0.876 \text{ mol/s} \qquad (\text{as } v_o = 6 \ l/\text{s})$$

$$F_o = F_{Ao} = 0.876 \text{ mol/s}$$

For CSTR-1 :

$$\frac{V_1}{F_o} = \frac{X_1}{(-r)_1} = \frac{1}{(-r)_1} \cdot X_1$$

$X_1 = 0.40$ and corresponding $1/(-r)_1 = 250$ (from data)

$$\therefore \quad V_1 = 250 \times 0.4 \times 0.876$$

$$= 87.6 \ l$$

Overall conversion (at exit of CSTR-2) is $X_2 = 0.85$, corresponding rate $(-r)_2 = 0.001$ (from data)

$$\therefore \quad 1/(-r)_2 = 1000$$

For CSTR-2 :

$$\frac{V_2}{F_o} = \frac{X_2 - X_1}{(-r)_2}$$

$$V_2 = 0.876 \times 1000 \times (0.85 - 0.40)$$

$$= 394 \ l$$

Total volume of two CSTRs in series = 87.6 + 394 = 481.6 l ≈ 482 l ... **Ans.**

If the same reaction is carried out in a single CSTR to achieve overall conversion of 85% then volume of single CSTR is

$$\frac{V}{F_{Ao}} = \frac{X_A}{(-r_A)}$$

$$V = F_{Ao} \cdot X_A \cdot \left(\frac{1}{-r_A}\right)$$

$$= 0.876 \times 0.85 \times 1000$$

$$= 744.6 \ l$$

So for same overall conversion, battery of CSTRs in series is always beneficial as volume of single CSTR is 744.6 *l* while that of two CSTRs in series is 482 *l*.

Thus by using two CSTRs in series, volume will be reduced by 35%.

(ii) Now we will consider two PFRs in series.

$$\frac{V_1}{F_o} = \int_0^{X_1} \frac{dX}{(-r)} \quad \text{for PFR-1}$$

$$\frac{V_2}{F_o} = \int_{X_1}^{X_2} \frac{dX}{(-r)} \quad \text{for PFR-2}$$

$$\frac{V}{F_o} = \frac{V_1 + V_2}{F_o} = \int_0^{X_1} \frac{dX}{(-r)} + \int_{X_1}^{X_2} \frac{dX}{(-r)} = \int_0^{X_2} \frac{dX}{(-r)}$$

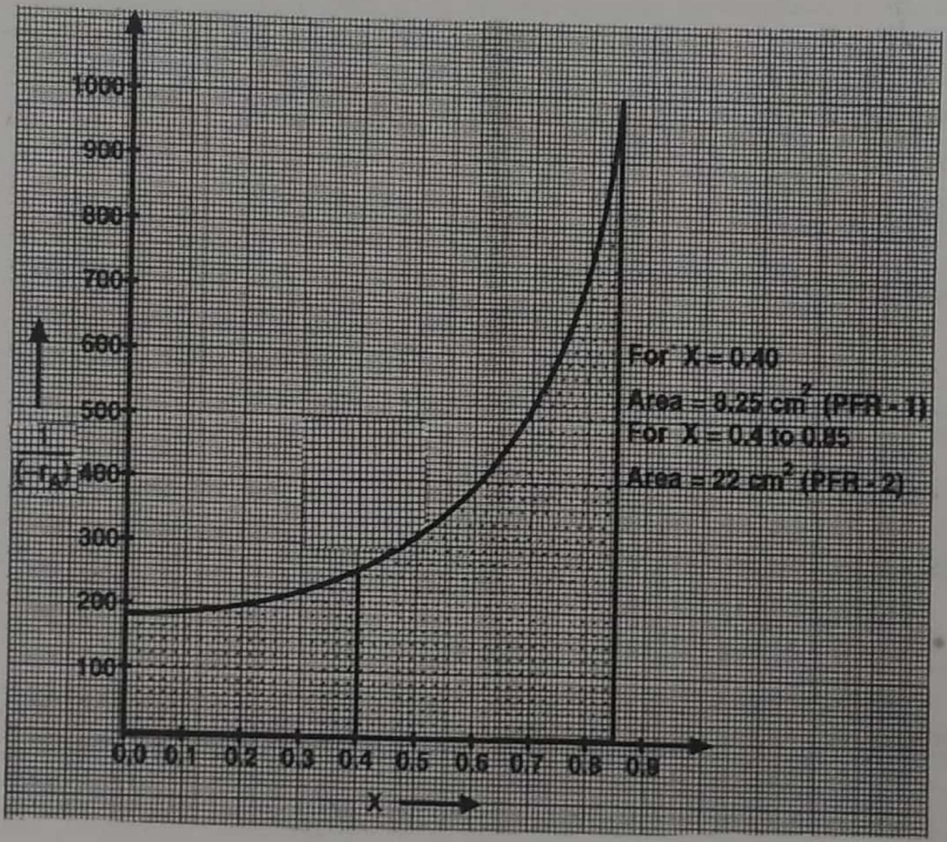


Fig. E 4.11

From graph, (i) area under the curve upto X = 0.4 is 8.25 cm^2

$$\frac{V_1}{F_o} = 8.25 \times \text{scale x-axis} \times \text{scale y-axis}$$

$$= 8.25 \times \frac{0.1}{1} \times \frac{100}{1}$$

$$= 82.5$$

$$V_1 = 82.5 \times 0.876 \qquad (\text{as } F_o = 0.876 \text{ mol/s})$$

$$= 72.3\ l$$

From graph, (ii) area under the curve between X = 0.4 and X = 0.85 is 22 cm^2

$$\therefore \quad \frac{V_2}{F_o} = 22 \times \frac{0.1}{1} \times \frac{100}{1}$$

$$= 220$$

$$V_2 = 220 \times 0.876$$

$$= 192.7\ l$$

Total volume of two PFRs in series = 72.3 + 192.7 = 265 l ... **Ans.**

Volume of single CSTR = 744.6 l

Volume of two CSTRs in series = 482 l

Volume of two PFRs in series = 265 l

So the arrangement of PFRs in series is recommended for given situation.

Ex. 4.12 : A second order reaction carried out in a single CSTR results in 80% conversion of reactant A. It is proposed to put another similar CSTR in series with the first one. For all other parameters remain identical (i) how will this addition affect the conversion of reactant and (ii) if same 80% conversion is maintained by how much can the treatment rate would be increased ?

Solution : First consider the case of a single reactor.

The performance equation for CSTR is

$$\frac{\tau}{C_{Ao}} = \frac{X_A}{(-r_A)}$$

For second order reaction with $\varepsilon_A = 0$,

$$-r_A = k\,C_A^2 = k\,C_{Ao}^2\,(1-X_A)^2$$

$$\therefore \quad \frac{\tau}{C_{Ao}} = \frac{X_A}{k\,C_{Ao}^2\,(1-X_A)^2}$$

$$\tau\,k\,C_{Ao} = \frac{X_A}{(1-X_A)^2}$$

We have, $X_A = 0.80$

$$\therefore \quad \tau\,k\,C_{Ao} = \frac{0.80}{(1-0.80)^2}$$

$$= 20$$

For N = 1, $\tau\,k\,C_o = 20$

$$(\tau)_{N=1} = 20/k\,C_o$$

(i) Now we will consider the case wherein identical additional reactor is put in series with the original one and find the overall conversion (X_2).

For CSTR-2 in series :

$$\tau_2 = \frac{X_2 - X_1}{k\,C_o\,(1-X_2)^2} \quad \text{as } (-r)_2 = k\,C_o\,(1-X_2)^2$$

For equal-size CSTRs in series :

$$\tau_1 = \tau_2 = \tau$$

$$\tau_1 = (\tau)_{N=1} = 20/k\,C_o = \tau_2$$

$$\therefore \quad \frac{20}{k\,C_o} = \frac{X_2 - X_1}{k\,C_o\,(1-X_2)^2}$$

In case of two CSTRs in series, $X_1 = 0.80$ is the intermediate conversion and X_2 is the overall conversion.

$$20(1-X_2)^2 = X_2 - 0.80$$

$$20X_2^2 - 41X_2 + 20.80 = 0$$

$$\therefore \quad X_2 = \frac{+41 \pm \sqrt{(41)^2 - 4 \times 20 \times 20.80}}{2 \times 20}$$

$$= 0.92$$

% conversion of A leaving two CSTRs in series is 92

$$X = 92\% \text{ for } N = 2$$

$$X = 80\% \text{ for } N = 1$$

$$\% \text{ increase in conversion} = \left(\frac{92-80}{80}\right) \times 100$$

$$= 15$$

So addition of second identical reactor in series with the original one results in 15% increase in conversion of A. ... **Ans. (i)**

(ii) Now we will consider the case of two equal-size CSTRs in series with overall conversion (X_2) = 0.80 and find the treatment rate.

For CSTR-1, we have,

$$\tau_1 = \frac{X_1}{k\,C_o\,(1-X_1)^2}$$

and for CSTR-2, we have,

$$\tau_2 = \frac{X_2 - X_1}{k\,C_o\,(1-X_2)^2}$$

For equal-size CSTRs in series,

$$\tau_1 = \tau_2$$

$$\frac{X_1}{k\,C_o\,(1-X_1)^2} = \frac{X_2 - X_1}{k\,C_o\,(1-X_2)^2}$$

$$\frac{X_1}{(1-X_1)^2} = \frac{0.80 - X_1}{(1-0.80)^2}$$

Solving for X_1 by trial-and-error,

$$X_1 = 0.623$$

(Put X_1 = 0.60, 0.62, 0.63 and 0.623 and see RHS = LHS).

So the fractional conversion of A leaving CSTR-1 for final conversion of 80% is 0.623.

For CSTR-1 in series,

$$\tau_1\,k\,C_o = \frac{X_1}{(1-X_1)^2}$$

$$X_1 = 0.623$$

$$\therefore \quad \tau_1\,k\,C_o = \frac{0.623}{(1-0.623)^2}$$

$$= 4.38$$

$$\tau_1 = 4.38/k\,C_o$$

$$\tau_N = N \cdot \tau_i$$

$$\text{For } N = 2, \quad (\tau)_{N=2} = 2 \times 4.38/k\,C_o$$

$$= 8.76/k\,C_o$$

$$(\tau)_{N=2} = (V/v)_{N=2}$$

$$(\tau)_{N=1} = (V/v)_{N=1}$$

$$\therefore \quad \frac{(\tau)_{N=2}}{(\tau)_{N=1}} = \frac{(V/v)_{N=2}}{(V/v)_{N=1}}$$

$$\therefore \quad (v)_{N=2} = \frac{(\tau)_{N=1}}{(\tau)_{N=2}} \times \frac{(V)_{N=2}}{(V)_{N=1}} \times (v)_{N=1}$$

Since,

$$(V)_{N=2} = 2\,(V)_{N=1}$$

$$(v)_{N=2} = \frac{(\tau)_{N=1}}{(\tau)_{N=2}} \times \frac{2\,(V)_{N=1}}{(V)_{N=1}} \times (v)_{N=1}$$

$$= \frac{20/k\,C_o}{8.76/k\,C_o} \times 2 \times (v)_{N=1}$$

$$= 4.57\,(v)_{N=1}$$

So the treatment rate is 4.57 times the original one. ... **Ans. (ii)**

Ex. 4.13 : A liquid reactant stream (1 mol/*l*) passes through two mixed flow reactors in series. The concentration of A in the exit of the first reactor is 0.5 mol/*l*. Find the concentration of A in the exit stream of a second reactor. The reaction follows second order kinetics with respect to A and $V_2/V_1 = 2$.

Solution : A → products, liquid phase reaction, $\varepsilon_A = 0$

$$-r_A = k\,C_A^2$$

For two CSTRs in series,

$$V_2 = 2\,V_1$$

For CSTR-1 :

$$\tau_1 = \frac{C_o - C_1}{k\,C_1^2}$$

$$\tau_1 k = \frac{1 - 0.5}{(0.5)^2} = 2 \quad \therefore\ k = 2/\tau_1$$

$$\tau_1 = \frac{V_1}{v_o} \quad \text{and} \quad \tau_2 = \frac{V_2}{v_o} = \frac{2V_1}{v_o}$$

For CSTR-2 :

$$\tau_2 = \frac{C_1 - C_2}{k\,C_2^2}$$

$$k\,\tau_2 = \frac{C_1 - C_2}{C_2^2}$$

$$\frac{2}{\tau_1}\,\tau_2 = \frac{C_1 - C_2}{C_2^2}$$

$$\frac{2}{(V_1/v_o)} \times \frac{2\,V_1}{(v_o)} = \frac{C_1 - C_2}{C_2^2}$$

$$4\,C_2^2 + C_2 - C_1 = 0$$

$$4\,C_2^2 + C_2 - 0.5 = 0$$

$$\therefore \quad C_2 = \frac{-1 \pm \sqrt{(1)^2 - 4 \times 4 \times (-0.5)}}{2 \times 4}$$

$$= 0.25\ \text{mol}/l$$

∴ Concentration of A in the exit stream of the second reactor is 0.25 mol/*l*. ... **Ans.**

Ex. 4.14 : An aqueous reactant stream (4 molA/l) passes through a mixed flow reactor followed by a plug flow reactor. Find the concentration at the exit of the plug flow reactor if in the mixed flow reactor, $C_A = 1$ mol/l. The reaction is second order with respect to A. The volume of the plug flow reactor is three times that of the mixed flow reactor/CSTR.

Solution : A → products, liquid phase, so $\varepsilon_A = 0$.

$$-r_A = k\,C_A^2$$

$$C_o = C_{Ao} = 4 \text{ mol}/l, \quad C_1 = C_A = 1 \text{ mol}/l$$

Set-up : CSTR followed by plug flow reactor.

For CSTR,

$$\tau_1 = \frac{V_1}{v_o} = \frac{C_o - C_1}{k\,C_1^2}$$

$$\tau_1 k = \frac{C_o - C_1}{C_1^2} = \frac{4-1}{(1)^2}$$

$$\tau_1 k = 3$$

$$k = 3/\tau_1$$

For plug flow reactor,

$$\tau_2 = \frac{V_2}{v_o} = -\int_{C_1}^{C_2} \frac{dC}{-r}, \quad \text{as } (-r) = k\,C^2$$

$$= -\int_{C_1}^{C_2} \frac{dC}{k\,C^2}$$

$$= -\frac{1}{k}\left[-\frac{1}{C}\right]_{C_1}^{C_2}$$

$$= \frac{1}{k}\left[\frac{1}{C}\right]_{C_1}^{C_2}$$

$$\tau_2 k = \frac{1}{C_2} - \frac{1}{C_1}$$

$$\frac{1}{C_2} - \frac{1}{C_1} = \tau_2 k = \tau_2 \cdot \frac{3}{\tau_1}$$

$$\frac{1}{C_2} - \frac{1}{C_1} = 3\frac{\tau_2}{\tau_1} = \frac{3\,(V_2/v_o)}{(V_1/v_o)}$$

We have, $V_2 = 3\,V_1$ (given)

$$\therefore \quad \frac{1}{C_2} - \frac{1}{C_1} = 3\left(\frac{3\,V_1}{V_1}\right)$$

$$\frac{1}{C_2} - \frac{1}{1} = 9 \qquad \therefore\ C_2 = 0.10 \text{ mol}/l$$

∴ Concentration of A at the exit of the plug flow reactor is 0.10 mol/l. ... **Ans.**

Ex. 4.15 : Reactant A (A → R) with $C_{Ao} = 26$ mol/m^3 passes in steady flow through four equal-size mixed reactors in series ($\tau_{total} = 2$ min). When the steady state is achieved the concentration of A is found to be 11, 5, 2 and 1 mol/m^3 in the four units. For this reaction, what must be τ_{plug} so as to reduce C_A from $C_{Ao} = 26$ to $C_{Af} = 1$ mol/m^3 ?

Solution : A → R, liquid phase, $\varepsilon_A = 0$.

$$C_{Ao} = 26 \text{ mol/m}^3$$

There are four equal-size CSTRs in series.

$$\tau_{total} = 2 \text{ min}$$

$$\tau_N = N\,\tau_i$$

$$2 = 4 \cdot \tau_i \quad \therefore \; \tau_i = 0.5 \text{ min}$$

For equal-size CSTRs in series,

$$\tau_1 = \tau_2 = \tau_3 = \tau_4 = \tau = 0.5 \text{ min}$$

For CSTR-1,

$$\tau_1 = \frac{C_o - C_1}{(-r)_1}$$

$$(-r)_1 = \frac{C_o - C_1}{\tau_1} = \frac{26-11}{0.5} = 30 \text{ mol/(m}^3\cdot\text{min)}$$

For CSTR-2,

$$\tau_2 = \frac{C_1 - C_2}{(-r)_2}$$

$$(-r)_2 = \frac{C_1 - C_2}{\tau_2} = \frac{11-5}{0.5} = 12 \text{ mol/(m}^3\text{.min)}$$

Similarly, $$(-r)_3 = \frac{C_2 - C_3}{\tau_3} = \frac{5-2}{0.50} = 6 \text{ mol/(m}^3\text{.min)}$$

$$(-r)_4 = \frac{2-1}{0.5} = 2 \text{ mol/(m}^3\text{.min)}$$

$-r_A$	30	12	6	2
C_A	11	5	2	1

$-r_A$	30	12	6	2
$\ln(-r_A)$	3.4	2.50	1.8	0.69
C_A	11	5	2	1
$\ln C_A$	2.4	1.61	0.69	0

$$(-r_A) = k\,C_A^n$$

$$\ln(-r_A) = \ln k + n \ln C_A$$

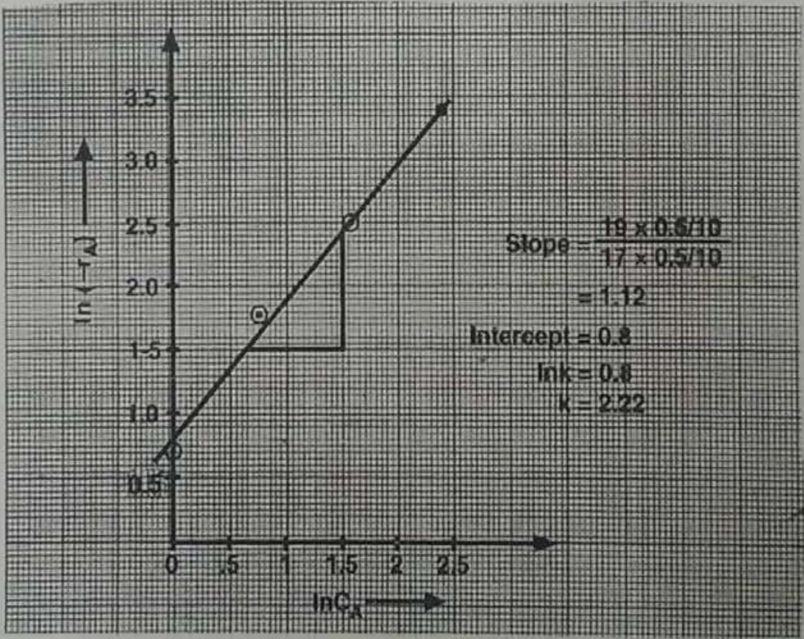


Fig. E 4.15

Plot graph of $\ln(-r_A)$ v/s $\ln C_A$.

Slope = n and intercept on y-axis = ln k

$\therefore$ k = 2.22 and n = 1.12

$$-r_A = 2.22\, C_A^{1.12}$$

For plug flow reactor, $C_{Ao} = 26$ mol/m^3 and $C_{Af} = 1$ mol/m^3

$$\tau_p = -\int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{(-r_A)}$$

$$= -\int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{k\, C_A^{1.12}}$$

$$= -\frac{1}{k}\left[\frac{C_A^{-1.12+1}}{-1.12+1}\right]_{C_{Ao}}^{C_{Af}}$$

$$= +\frac{1}{k\,(0.12)}\left[C_A^{-0.12}\right]_{C_{Ao}}^{C_{Af}}$$

$$= \frac{1}{2.22 \times 0.12}\left[(1)^{-0.12} - (26)^{-0.12}\right]$$

$$= \frac{1}{2.22 \times 0.12}\left[1 - 0.6764\right]$$

$$= 1.215 \text{ min}$$

... **Ans.**

Ex. 4.16 : The elementary irreversible aqueous phase reaction A + B → R + S is carried out isothermally as given below :

Equal volumetric flow rates of two liquid streams are fed into a 4 litres mixing tank. One stream contains A with $C_{Ao} = 0.020$ mol/*l* and the other contains B with $C_{Bo} = 1400$ mol/*l*. The mixed stream is then passed through a 16 litre plug flow reactor. It is found that some R is formed in a mixing tank, its concentration being 0.002 mol/*l*. Assume that the mixing tank acts as a mixed reactor. Find the concentration of R at the exit of the plug flow reactor and the fraction of initial A that has been converted in the system.

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

It is elementary bimolecular reaction with $\varepsilon_A = 0$ (liquid phase).

$$\therefore \quad -r_A = k\, C_A C_B$$

In stream of A, we have 0.020 mol A/*l*; in stream of B, we have 1400 mol B/*l*.

As C_{Bo} is in large excess,

$$C_{Bo} = C_B$$

$\therefore$ So it is pseudo first order reaction.

$$-r_A = k\, C_A$$

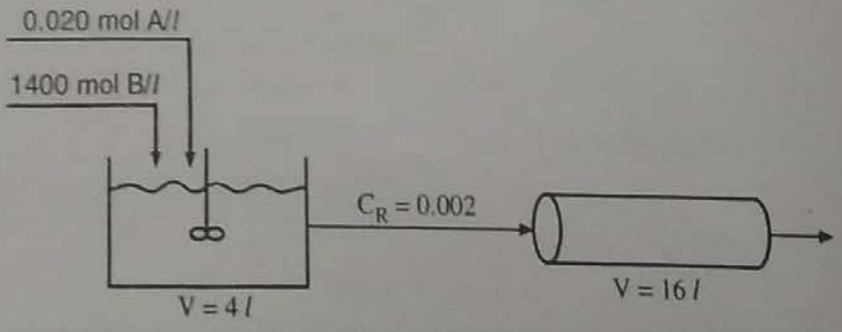


Fig. E 4.16

For mixed flow reactor :

$$\tau_m = \frac{C_o - C_1}{k\,C_1} \qquad \text{as } (-r)_1 = k\,C_1$$

$$k\,\tau_m = \frac{C_o - C_1}{C_1}$$

$$C_{R_1} = 0.002 \text{ mol}/l \text{ (given)}, \quad C_{R_o} = 0.0$$

Volumetric flow rates of streams entering mixed flow reactor are equal, so

$$C_{Ao} = 0.02/2 = 0.01 \text{ mol}/l$$

From reaction, 1 mol A ≡ 1 mol R

∴ A reacted in mixed flow reactor $= \frac{1}{1} \times C_{R1} = C_{R1}$

$$\therefore \quad C_1 = C_o - C_{R1} = 0.01 - 0.008 \;\; = 0.008 \text{ mol}/l$$

$$k\,\tau_m = \frac{C_o - C_1}{C_1}$$

$$k\,\tau_m = \frac{0.01 - 0.008}{0.008} = 0.25$$

For PFR :

$$\tau_p = -\int_{C_1}^{C_2} \frac{dC}{kC}$$

$$k\,\tau_p = \ln\frac{C_1}{C_2}$$

$$\tau_m = \frac{V_1}{v_o}, \qquad \tau_p = \frac{V_2}{v_o}$$

$$V_1 = 4\,l, \qquad V_2 = 16\,l$$

$$\therefore \quad v_o = \frac{4}{\tau_m},$$

$$v_o = \frac{16}{\tau_p}$$

$$\therefore \quad \frac{4}{\tau_m} = \frac{16}{\tau_p}$$

$$\therefore \quad \tau_p = 4\,\tau_m$$

We have, $k\,\tau_m = 0.25$

$$\therefore \quad \tau_m = 0.25/k$$

$$\tau_p = 4 \times 0.25/k$$

$$k\,\tau_p = 4 \times 0.25$$

$$\therefore \quad 4 \times 0.25 = \ln\frac{C_1}{C_2}$$

$$1.0 = \ln\frac{C_1}{C_2}$$

$$\frac{C_1}{C_2} = e^1 = 2.7183$$

$$C_2 = \frac{C_1}{2.7183} = \frac{0.008}{2.7183}$$

$$= 0.00294 \text{ mol}/l$$

We have,

$$\begin{aligned}
C_2 &= C_o(1 - X_2) \\
0.00294 &= 0.01\,(1 - X_2) \\
X_2 &= 0.706 \\
C_{R2} &= C_{Ao} \cdot X_2 \\
&= 0.01 \times 0.706 \\
&= 7.06 \times 10^{-3}\ \text{mol}/l
\end{aligned}$$

... **Ans.**

Fraction of initial A that has been converted = 0.706 ... **Ans.**

Ex. 4.17 : At present conversion is 66.67% for elementary second order reaction $2A \rightarrow 2R$ when operating in an isothermal plug flow reactor with a recycle ratio of unity. Determine the conversion if the recycle stream is shut off.

Solution : $2A \rightarrow 2R$, elementary liquid phase reaction

$$-r_A = k\,C_A^2 \quad \text{and} \quad \varepsilon_A = 0$$

For recycle reactor :

$$\tau = \frac{C_{Ao} \cdot V}{F_{Ao}} = (R+1) \int_{\left(\frac{R}{R+1}\right) X_{Af}}^{X_{Af}} \frac{dX_A}{-r_A}$$

$$-r_A = k\,C_A^2 = k\,C_{Ao}^2\,(1 - X_A)^2$$

$$\tau = (R+1) \int_{\left(\frac{R}{R+1}\right) X_{Af}}^{X_{Af}} \frac{dX_A}{k\,C_{Ao}^2\,(1 - X_A)^2}$$

$R = 1$, $X_{Af} = 0.6667$

$$\left(\frac{R}{R+1}\right) X_{Af} = \frac{1}{2} \times 0.6667 = 0.3333$$

$$\tau\,k\,C_{Ao} = 2 \int_{0.3333}^{0.6667} \frac{dX_A}{(1 - X_A)^2}$$

$$= 2\left[\frac{1}{1 - X_A}\right]_{0.3333}^{0.6667}$$

$$\tau\,k\,C_{Ao} = 3$$

For $R = 0$,

$$\frac{\tau}{C_{Ao}} = \int_0^{X_A} \frac{dX_A}{(-r_A)} = \int_0^{X_A} \frac{dX_A}{k\,C_{Ao}^2\,(1 - X_A)^2}$$

$$\tau\,k\,C_{Ao} = \left[\frac{1}{1 - X_A}\right]_0^{X_A}$$

$$3 = \left[\frac{1}{1 - X_A} - 1\right]$$

$$3 = \frac{X_A}{1 - X_A}$$

$$3 = 4\,X_A$$

$$\therefore \quad X_A = 0.75$$

Conversion, if the recycle stream is shut off = 75% ... **Ans.**

Ex. 4.18 : A first order reaction is to be carried out in series of two mixed reactors. Show that the total volume of two reactors is minimum when the reactors are of equal size.

Solution :

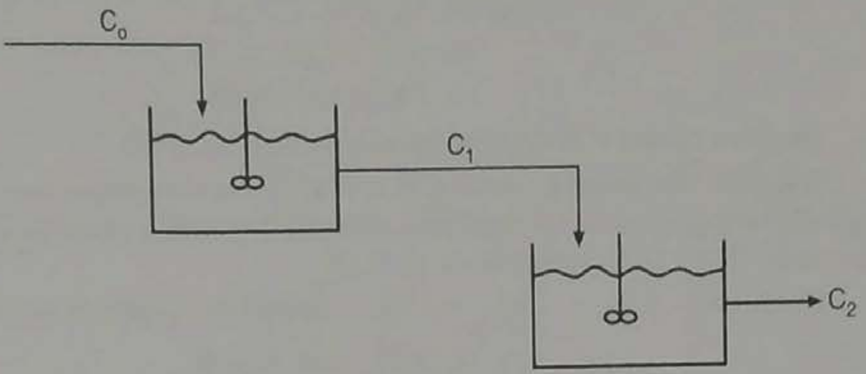


Fig. E 4.18

Consider constant density system.

So $\varepsilon_A = 0$

For CSTR-1 :

$$\tau_1 = \frac{C_o - C_1}{(-r)_1} = \frac{C_o - C_1}{k\,C_1} \quad \text{as } -r_A = kC_A$$

$$\tau_1 k = \frac{C_o}{C_1} - 1$$

For CSTR-2 :

$$\tau_2 = \frac{C_1 - C_2}{(-r)_2} = \frac{C_1 - C_2}{k\,C_2}$$

$$\tau_2 k = \frac{C_1}{C_2} - 1$$

$$\therefore \quad (\tau_1 + \tau_2)\,k = \frac{C_o}{C_1} + \frac{C_1}{C_2} - 2$$

We have $\tau = \frac{V}{v_o}$

So for $V_1 + V_2$ to be minimum, $(\tau_1 + \tau_2)$ is to be minimum.

To minimise $V_1 + V_2$ is to minimise $(\tau_1 + \tau_2)$.

By differentiating above equation w.r.t. C_1 and setting to zero, we obtain the condition for minimum volume.

$$\therefore \quad \frac{k\,d(\tau_1 + \tau_2)}{dC_1} = 0 = \frac{-C_o}{C_1^2} + \frac{1}{C_2}$$

$$\therefore \quad C_1^2 = C_o C_2$$

$$C_1 = (C_o C_2)^{1/2}$$

So for minimum total volume, we have,

$$k\,\tau_1 = \frac{C_o}{C_1} - 1$$

$$k\,\tau_1 = \frac{C_o}{(C_o C_2)^{1/2}} - 1$$

$$k\,\tau_1 = \left(\frac{C_o}{C_2}\right)^{1/2} - 1 \quad \text{... (A}$$

We have,

$$k\,\tau_2 = \frac{C_1}{C_2} - 1$$

$$k\,\tau_2 = \frac{(C_o\,C_2)^{1/2}}{C_2} - 1$$

$$k\,\tau_2 = \left(\frac{C_o}{C_2}\right)^{1/2} - 1 \qquad \dots (B)$$

From equations (A) and (B), we have,

$$k\,\tau_1 = k\,\tau_2$$

$$\therefore \quad \tau_1 = \tau_2$$

and $$\frac{C_o\,V_1}{v_o} = \frac{C_o\,V_2}{v_o}$$

$$\therefore \quad V_1 = V_2$$

So total volume of two CSTRs in series is minimum when reactors are of equal-size.

Ex. 4.19 : At present the elementary liquid phase reaction A + B → R + S takes place in a plug flow reactor using equimolar quantities of A & B. Conversion is 96%. $C_{Ao} = C_{Bo} = 1$ mol/*l*.

If a mixed reactor ten times as large as plug flow reactor were hooked up series with the existing unit, which unit should come first and by what fraction could the production be increased for that set-up ?

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

With equimolar quantities of A and B

$$-r_A = k\,C_A^2 = k\,C_{Ao}(1-X_A)^2, \quad \text{for liquid phase, } \varepsilon_A = 0$$

$$C_{Ao} = 1 \text{ mol}/l \quad \text{and} \quad X_A = 0.96$$, C_{Bo} = 1 mol/lit

For PFR :

$$\tau = \frac{V}{v_o} = C_{Ao}\int_0^{X_A} \frac{dX_A}{-r_A}$$

$$= C_{Ao}\int_0^{X_A} \frac{dX_A}{k\,C_{Ao}^2\,(1-X_A)^2}$$

$$\therefore \quad \tau = \frac{V}{v_o} = \frac{1}{C_{Ao}\,k}\left[\frac{1}{1-X_A}\right]_0^{X_A}$$

$$\frac{V}{v_o} = \frac{1}{C_{Ao}\,k}\left[\frac{1}{1-X_A} - 1\right]$$

$$C_{Ao} = 1 \text{ mol}/l \quad \text{and} \quad X_A = 0.96$$

$$\frac{V}{v_o} = \frac{1}{1 \times k}\left[\frac{1}{1-0.96} - 1\right]$$

$$V = \frac{24\,v_o}{k}, \quad \text{volume of plug flow reactor}$$

Volume of CSTR = 10 times the volume of plug flow reactor

$$\therefore \quad V_m = 10 \times \frac{24\,v_o}{k} = \frac{240\,v_o}{k}$$

New arrangement : Different type reactors in series :

(i) Plug flow followed by CSTR :

In plug flow the conversion achieved is 96%.

$$\therefore \quad X_1 = 0.96$$

For CSTR, the performance equation is

$$\frac{V_m}{v_o} = \frac{C_o(X_2 - X_1)}{(-r)_2} = \frac{C_o(X_2 - X_1)}{k\,C_o^2(1 - X_2)^2}$$

$$\frac{240\,v_o}{k \times v_o} = \frac{C_o(X_2 - X_1)}{k\,C_o^2(1 - X_2)^2}$$

$$C_o \times 240 = \frac{(X_2 - X_1)}{1 \times (1 - X_2)^2}$$

$$240(1 - X_2)^2 = X_2 - X_1 \quad , \quad X_1 = 0.96 \qquad (\because C_o = 1)$$

$$240 + 240X_2^2 - 480X_2 = X_2 - 0.96$$

$$240X_2^2 - 481X_2 + 240.96 = 0$$

$$\therefore \quad X_2 = 0.989 \text{ (overall conversion from PFR followed by CSTR)}$$

Hence, by arranging CSTR of volume 10 times as large as PFR in series, the conversion increases from 0.96 to 0.989.

$$\text{Percent increase in conversion} = \left(\frac{98.9 - 96}{96}\right) \times 100 = 3.021$$

Second arrangement :

(ii) CSTR followed by PFR in series :

For CSTR :

$$\frac{V_m}{v_o} = \frac{C_o \cdot X_1}{k\,C_o^2(1 - X_1)^2}$$

$$\frac{240\,v_o}{k \cdot v_o} = \frac{X_1}{k\,C_o(1 - X_1)^2}$$

$$240\,C_o = \frac{X_1}{(1 - X_1)^2}$$

$$240 \times 1 = \frac{X_1}{(1 - X_1)^2}$$

$$240(1 - X_1)^2 = X_1$$

$$240X_1^2 - 481X_1 + 240 = 0$$

$$\therefore \quad X_1 = 0.9375$$

For PFR :

$$\frac{V}{v_o} = C_o \int_{X_1}^{X_2} \frac{dX}{(-r)}$$

$$= C_o \int_{X_1}^{X_2} \frac{dX}{C_o^2(1 - X)^2}$$

$$\frac{V}{v_o} = \frac{1}{k\,C_o}\left[\frac{1}{1-X}\right]_{0.9375}^{X_2}$$

$$\frac{24\,v_o}{k\,v_o} = \frac{1}{k\,C_o}\left[\frac{1}{1-X_2} - 16\right]$$

$$24\,C_o = \left[\frac{1}{1-X_2} - 16\right]$$

$$24 \times 1 = \frac{1}{1-X_2} - 16$$

$$\therefore \qquad X_2 = 0.975 \text{ (overall conversion)}$$

By CSTR followed by PFR, the conversion increases from 96 to 97.5%.

$$\therefore \qquad \text{\% increase in conversion} = \frac{97.5-96}{96} \times 100$$

$$= 1.56$$

So it is clear that the first arrangement of PFR followed by CSTR is more beneficial to enhance the production rate as conversion increases by 3.021% by this arrangement as against 1.56% by CSTR followed by PFR.

By PFR followed by CSTR in series, the production rate increases by 3.021 %. ... **Ans.**

Ex. 4.20 : A 400 litre CSTR and a 100 litre PFR are available to process 1.0 litre of feed per second. The feed contains 41% A, 41% B and 18% inerts by volume. The irreversible gas phase reaction

$$A + B \rightarrow C$$

is to be carried out at 10 atm and 227 °C. The rate of reaction in mol/(l·min) is given below as a function of conversion.

$-r_A$	0.2	0.0167	0.00488	0.00286	0.00204
X_A	0.0	0.1	0.40	0.7	0.90

What is the maximum conversion that can be achieved with these two reactors connected in series ?

Solution : For sizing the reactors, we need only $(-r_A) = f(X_A)$ and F_{Ao}.

$A + B \rightarrow C$

Feed contains 41 mole % A, 41 mole % B and 18 mole % inerts.

Mole fraction of A in feed = 41/100 = 0.41

$P_o = 10$ atm, $T = 227\,°C = 500\,K$

$$\therefore \qquad p_{Ao} = 0.41 \times 10 = 4.1 \text{ atm}$$

$$C_{Ao} = \frac{p_{Ao}}{R\,T} = \frac{4.1}{0.08206 \times 500} = 0.0999 \text{ mol}/l = 0.10 \text{ mol}/l$$

Volumetric feed rate to reactor system = 1.0 l/s = 60 l/min.

$$\therefore \qquad F_{Ao} = C_{Ao} \cdot v_o = 0.10 \times 60 = 6 \text{ mol/min}$$

Multiple reactor system :

(a) CSTR followed by PFR :

$V_m = 400\,l, \quad V_p = 100\,l$

For CSTR :

$$\frac{V_m}{F_{Ao}} = \frac{X_1}{(-r)_1}$$

$$\frac{400}{6} = \frac{X_1}{(-r)_1} = \frac{1}{(-r)_1} \cdot X_1$$

$$\frac{X_1}{(-r)_1} = 66.67$$

X_A	0	0.1	0.40	0.70	0.90
$-r_A$	0.2	0.0167	0.00488	0.00286	0.00204
$1/(-r_A)$	5	59.9	204.9	349.65	490.2

Plot a graph of $1/(-r_A)$ v/s X_A.

We have.

$$V/F_{Ao} = \frac{X_1}{(-r)_1} = 66.67$$

From plot of $1/(-r_A)$ v/s X_A :

$$V/F_{Ao} = \frac{X_1}{(-r)_1} = \text{Area} \times \text{Scale y-axis} \times \text{Scale x-axis}$$

$$\text{Area} = \frac{66.67}{\frac{50}{1} \times \frac{0.1}{1}}$$

$$= 13.32 \text{ cm}^2 = 1332 \text{ mm}^2$$

From graph, if we choose $X_1 = 0.36$ then

$$\text{Area} = x \cdot y$$

$$= 36 \text{ mm} \times 37 \text{ mm}$$

$$= 1332 \text{ mm}^2$$

[For $X = 0.36$, $x = 36$ mm and from graph corresponding $y = 37$ mm]

For CSTR, it is the area of rectangle.

∴ Conversion in CSTR is 36%.

For plug flow reactor,

$$\frac{V}{F_{Ao}} = \int_{X_1}^{X_2} \frac{dX}{(-r)}$$

$$\frac{100}{6} = \int_{X_1}^{X_2} \frac{dX}{(-r)}$$

$$\int_{X_1}^{X_2} \frac{dX}{(-r)} = 16.67$$

$$16.67 = \text{Area} \times \text{Scale y-axis} \times \text{Scale x-axis}$$

$$\text{Area under the curve} = \frac{16.67}{\frac{50}{1} \times \frac{0.1}{1}} = 3.334 \text{ cm}^2 = 333.4 \text{ mm}^2$$

We have, $X_1 = 0.36$

From X_1 count area under the curve till area = 333.4 mm² and get value of X_2.

Area = 333.4 mm² from $X_1 = 0.36$ for $X_2 = 0.445$

∴ Total conversion in system of CSTR followed by PFR is 44.5 %. **... Ans.**

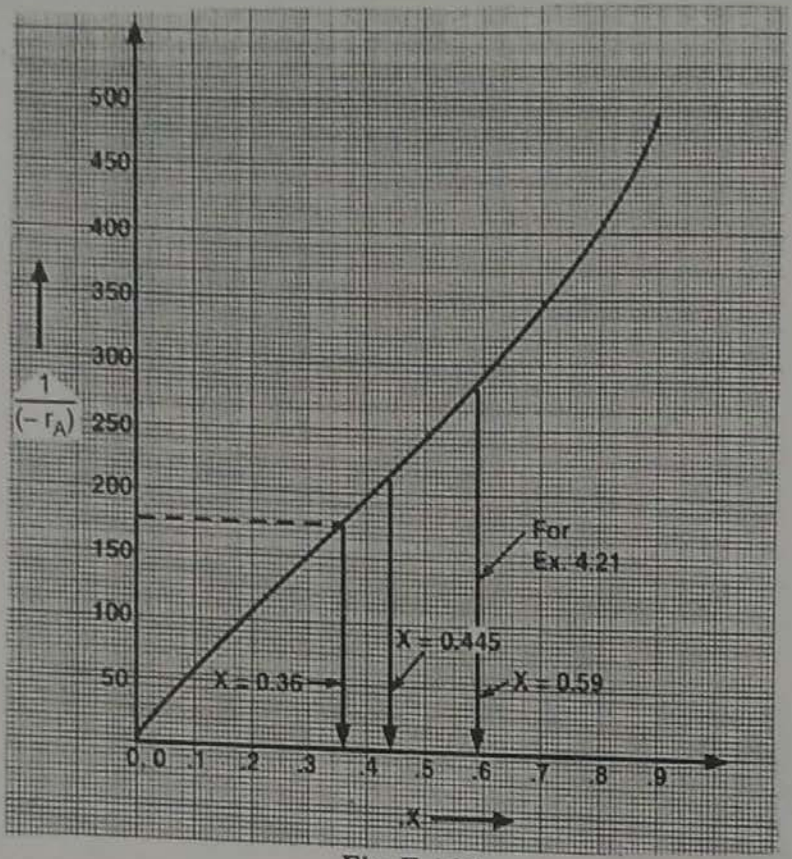


Fig. E 4.20

Second arrangement :

PFR followed by CSTR :

For PFR it is the area under the curve.

$$\frac{V}{F_{Ao}} = \int_0^{X_1} \frac{dX}{(-r)}$$

$$\int_0^{X_1} \frac{dX}{(-r)} = \frac{100}{6} = 16.67$$

$$\text{Area} = \frac{16.67}{(50/1) \times (0.1/1)} = 3.334 \text{ cm}^2 = 333.4 \text{ mm}^2$$

Count area under the curve till area = 333.4 mm² and get X_1.

From graph, $X_1 = 0.24$ for area = 333.4 mm²

For CSTR :

$$\frac{V}{F_{Ao}} = \frac{X_2 - X_1}{(-r)_2}$$

$$\frac{X_2 - X_1}{(-r)_2} = \frac{400}{6} = 66.67$$

For CSTR it is the area of rectangle.

$$\text{Area} = \frac{66.67}{\frac{50}{1} \times \frac{0.1}{1}} = 13.32 \text{ cm}^2 = 1332 \text{ mm}^2$$

Count the area of rectangle (x · y) from $X_1 = 0.24$ to X_2 till area equals 1332 mm^2.

For $X_2 = 0.5$, Area = 1300 mm^2

$X_2 = 0.51$, Area = 1377 mm^2

∴ Area under the curve is nearly equal to 1332 mm^2 when $X_2 = 0.505$.

∴ Overall conversion from CSTR followed by PFR = 44.5 %

Overall conversion from PFR followed by CSTR = 50.5 %

So the arrangement–PFR followed by CSTR would be preferred for obtaining higher conversion and also to enhance production rate. ... **Ans.**

Ex. 4.21 : In previous problem/exercise 4.20, (a) what would be the overall conversion if two 400 litre CSTRs were connected in series for the same feed and the operating conditions ?

(b) What is the volume of a single plug flow reactor necessary to achieve 60% conversion if the molar feed rate is 2 mol/min ?

Solution : (a) For CSTR-1 :

$$\frac{V}{F_o} = \frac{X_1}{(-r)_1}$$

$$\frac{400}{6} = \frac{X_1}{(-r)_1}$$

$$\frac{X_1}{(-r)_1} = 66.67 = \text{Area} \times \text{Scale y-axis} \times \text{Scale x-axis}$$

$$\text{Area} = 66.67/(50/1) \times (0.1/1) = 13.32\ cm^2 = 1332\ mm^2$$

From plot for area to be 1332 mm^2, $X_1 = 0.36$.

For CSTR-2,

$$\frac{V}{F_{Ao}} = \frac{400}{6} = \frac{X_2 - X_1}{(-r)_2}$$

$$\frac{X_2 - X_1}{(-r)_2} = 66.67$$

Area of rectangle between $X_1 = 0.36$ and X_2 is 13.32 cm^2 = 1332 mm^2.

Count the area of rectangle from $X_1 = 0.36$ to X_2.

For $X_2 = 0.59$ the area of rectangle is 1334 mm^2.

$$\text{Area} = (59 - 36)\ mm \times 58\ mm$$

$$= 23\ mm \times 58\ mm = 1334\ mm^2$$

Overall conversion from two 400 *l* CSTRs in series = 59%. ... **Ans. (a)**

There may be chances of slight variation in this value.

(b) F_{Ao} = 2 mol/min

For plug flow reactor,

$$V/F_{Ao} = \int_0^{X_1} \frac{dX}{(-r)}$$

For $X_1 = 0.60$ from plot (Refer Fig. E 4.20) area under the curve is 18 cm^2.

$$V/F_{Ao} = 18 \times \frac{50}{1} \times \frac{0.1}{1} = 90$$

$$V = 90 \times 2 = 180\ l$$ ... **Ans.**

see e

Ex. 4.22 : Laboratory measurements of rate as a function of conversion for isothermal gaseous decomposition $A \rightleftharpoons 3B$ are given below. The data was collected at 149 °C and total pressure of 10 atm with the initial charge an equimolar mixture of A and inerts.

X_A	$(-r_A)$, mol/(*l*.s)
0	0.0053
0.10	0.0052
0.20	0.0050
0.30	0.0045
0.40	0.0040
0.50	0.0033
0.60	0.0025
0.70	0.0018
0.80	0.00125
0.85	0.00100

(a) Find out the total volume of two CSTRs in series necessary to achieve 80% overall conversion of A entering the reactor system if the conversion of A in first CSTR is 50%.

(b) Find out the total volume of two plug flow reactors in series necessary to achieve 80% overall conversion of A entering the reactor system if the conversion of A in first plug flow reactor is 50%.

The volumetric flow rate to each sequence will be 6 *l*/s.

Solution : For sizing reactors, we need only $-r_A = f(X_A)$ and F_{Ao}.

Feed : 50 mole % A and 50 mole % inerts.

$\therefore$ Mole fraction of A in feed = 50/100 = 0.50

$P_o = 10$ atm $\therefore$ $p_{Ao} = 0.5 \times 10 = 5$ atm, $T = 422$ K

$$C_{Ao} = \frac{p_{Ao}}{RT} = \frac{5}{0.08206 \times 422}$$

$$= 0.1444 \text{ mol}/l$$

$X_1 = 0.40$ and $X_2 = 0.80$

Volumetric flow rate $= v_o = 6$ *l*/s

$$\therefore \quad F_{Ao} = C_{Ao} \cdot v_o$$

$$= 0.1444 \times 6$$

$$= 0.8664 \text{ mol}/l$$

(a) Two CSTRs in series :

For CSTR-1 :

$$\frac{V_1}{F_{Ao}} = \frac{X_1}{(-r)_1}$$

$$X_1 = 0.40$$

From data, $(-r)_1$ at $X_A = 0.40$ is 0.004 mol/(*l*.s)

$$V_1 = \frac{F_{Ao} \cdot X_1}{(-r)_1}$$

$$= \frac{0.8664 \times 0.40}{0.004} = 86.64\, l$$

For CSTR-2 :

$$\frac{V_2}{F_{Ao}} = \frac{X_2 - X_1}{(-r)_2}$$

$X_1 = 0.40,\ X_2 = 0.80$

From data, $(-r)_2$ at $X_2 = 0.80$ is 0.00125 mol/(*l*.s)

$$V_2 = \frac{0.8664\ (0.8 - 0.4)}{0.00125}$$

$$= 277.25\ l$$

The total volume is

$$V = V_1 + V_2$$

$$= 86.64 + 277.25 = 363.89 \approx 363.9\ l$$ ... **Ans.**

Note that for CSTRs in series, $(-r)_1$ is evaluated at X_1 and $(-r)_2$ is evaluated at X_2.

(b) For two plug flow reactors in series :

$$\int_0^{X_2} \frac{dX}{(-r)} = \int_0^{X_1} \frac{dX}{-r} + \int_{X_1}^{X_2} \frac{dX}{-r}$$

For plug flow it is immaterial whether you place two plug flow reactors in series or have one larger plug flow reactor, the total volume required to achieve specified conversion is identical.

Plot a graph of $-1/r_A$ v/s X_A.

X_A	0	0.10	0.20	0.30	0.40	0.50	0.60	0.70	0.80	0.85
$-r_A$	0.0053	0.0052	0.005	0.0045	0.004	0.0033	0.0025	0.0018	0.00125	0.001
$1/-r_A$	189	192	200	222	250	303	400	556	800	1000

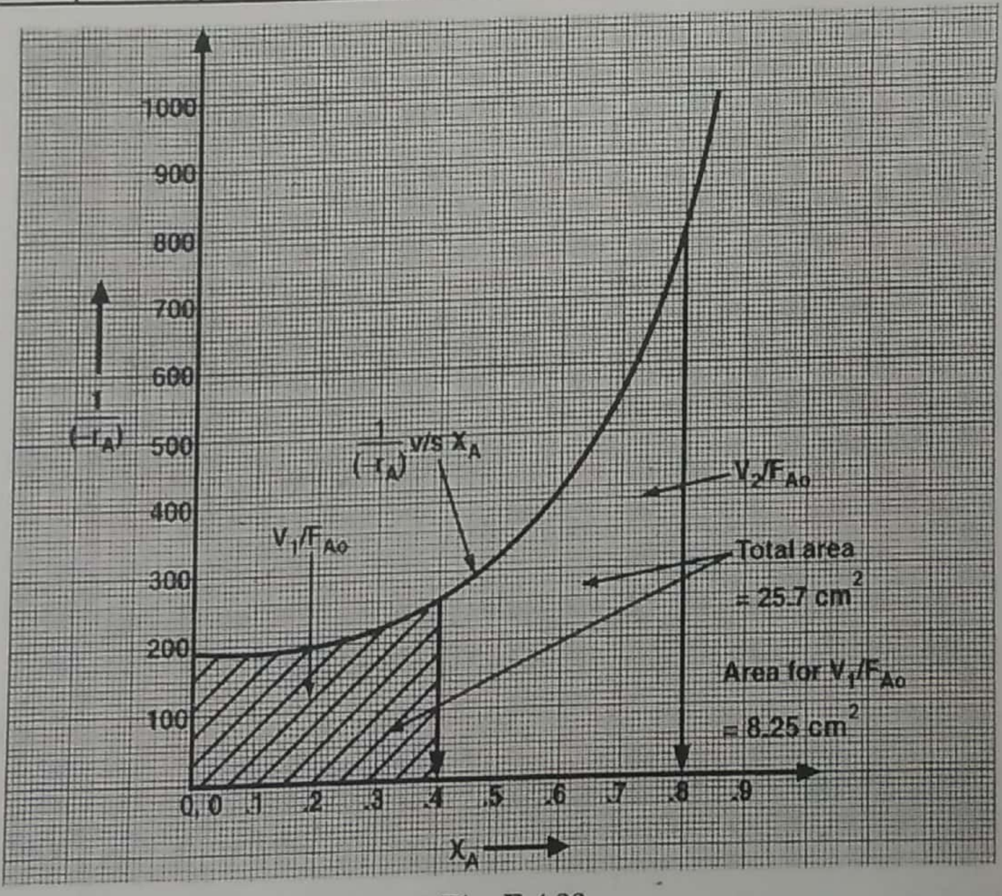


Fig. E 4.22

From graph, total area under the curve upto $X_A = 0.80 = 25.7\ \text{cm}^2$

$$\frac{V}{F_{Ao}} = \int_0^{X_2} \frac{dX}{(-r)} = \text{Area} \times \text{Scale y-axis} \times \text{Scale x-axis}$$

Total volume :

$$V = 25.7 \times \left(\frac{100}{1}\right) \times \left(\frac{0.1}{1}\right) \times 0.8664$$

$$= 222.7\ l \qquad \text{... Ans.}$$

From graph, area under the curve upto $X_A = 0.4$ is $8.25\ \text{cm}^2$.

$$\frac{V_1}{F_{Ao}} = 8.25 \times \frac{100}{1} \times \frac{0.1}{1}$$

$$\therefore \quad V_1 = 71.5\ l$$

$$V_2 = 151.2\ l \qquad \text{... Ans.}$$

Ex. 4.23 For the reaction data given in the following table, consider the series arrangement of a mixed flow reactor and plug flow reactor. If the intermediate conversion is 0.7 and final fractional conversion 0.8, which reactor should be placed first to obtain the smaller reactor volume ? $F_{Ao} = 0.083$ mol/s.

Data :

X_A	$-r_A$, mol/(l.s)
0	0.0053
0.1	0.0052
0.2	0.0050
0.3	0.0045
0.4	0.0040
0.5	0.0033
0.6	0.0025
0.7	0.0018
0.8	0.00125
0.85	0.001

Solution : Two possible schemes are :

1. Plug flow reactor followed by mixed flow reactor.

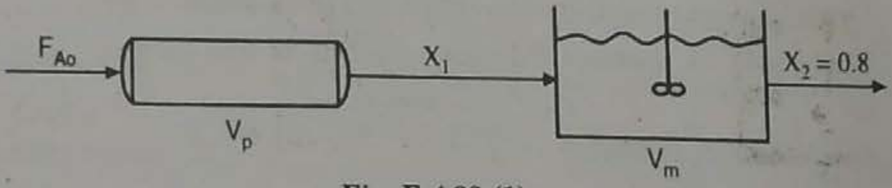


Fig. E 4.23 (1)

2. Mixed flow reactor followed by plug flow reactor

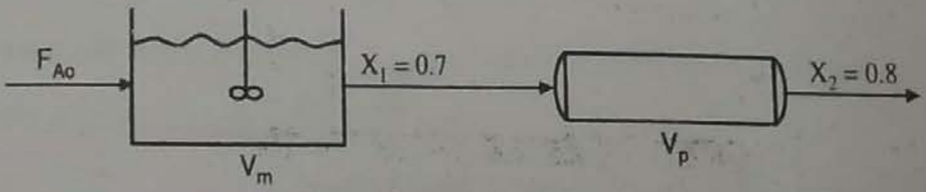


Fig. E 4.23 (2)

In order to find which reactor should be placed first for obtaining total minimum volume of reactors i.e. to select the best scheme out of cited above we have to plot $1/(-r_A)$ versus X_A with the help of which we can get the volume of reactors.

X_A	$-r_A$	$\frac{1}{(-r_A)}$
0	0.0053	188.67
0.1	0.0052	192.3
0.2	0.0050	200
0.3	0.0045	222.2
0.4	0.0040	250
0.5	0.0033	303
0.6	0.0025	400
0.7	0.0018	555.6
0.8	0.00125	800
0.85	0.001	1000

From Fig. E 4.23 (3)

(i)

$$\tau_p = \text{Area a - b - c - d} \times \text{Scale x-axis} \times \text{Scale y -axis}$$

$$= 19 \times \frac{0.1}{1} \times \frac{100}{1}$$

$$= 190$$

$$\frac{V_p}{F_{Ao}} = \tau_p = 190$$

$$V_p = 190 \times 0.083 = 15.77\, l$$

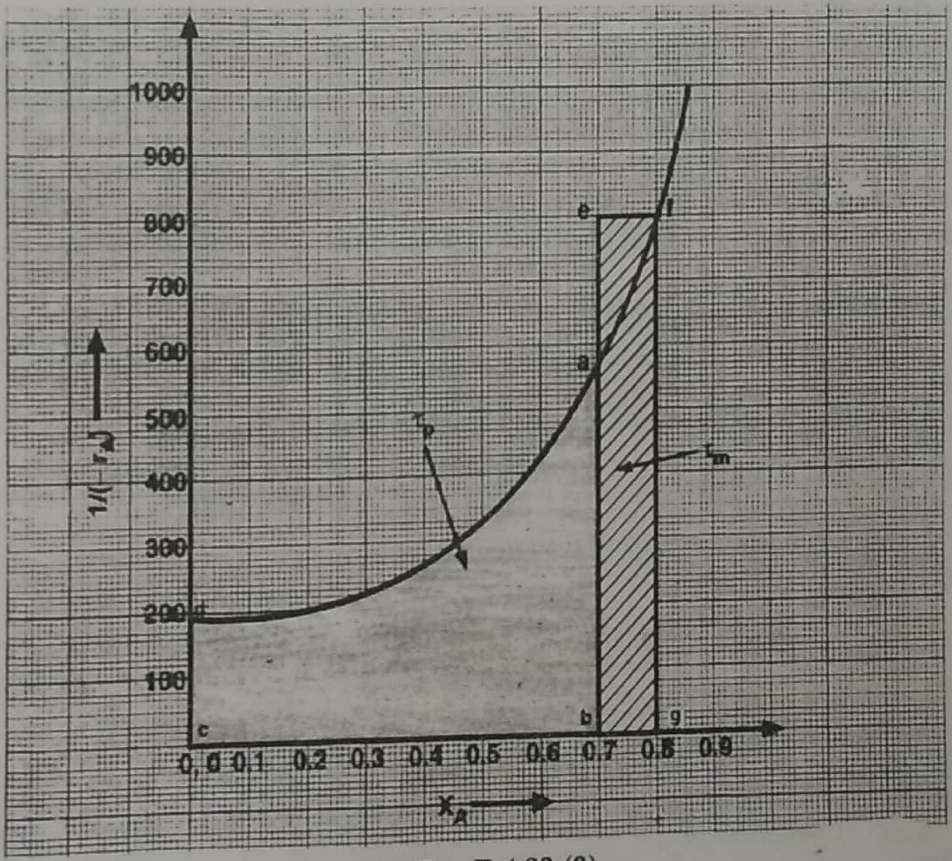


Fig. E 4.23 (3)

(ii)

$$\tau_m = \text{Area b - e - f - g} \times \text{Scale x-axis} \times \text{Scale y-axis}$$

$$= 8 \times \frac{0.1}{1} \times \frac{100}{1}$$

$$= 80$$

$$\frac{V_m}{F_{Ao}} = \tau_m$$

$$V_m = \tau_m F_{Ao}$$

$$= 80 \times 0.083$$

$$= 6.64\, l$$

Total volume for plug flow followed by mixed flow reactor in series is

$$V = 15.77 + 6.64$$

$$V = 22.41\, l$$

From Fig. E 4.23 (4)

(i)

$$\tau_m = \text{Area a - b - c - d} \times \text{Scale x-axis} \times \text{Scale y-axis}$$

$$= 38.5 \times \frac{0.1}{1} \times \frac{100}{1}$$

$$= 385$$

$$\frac{V_m}{F_{Ao}} = \tau_m$$

$$V_m = 385 \times 0.083 = 31.96\, l$$

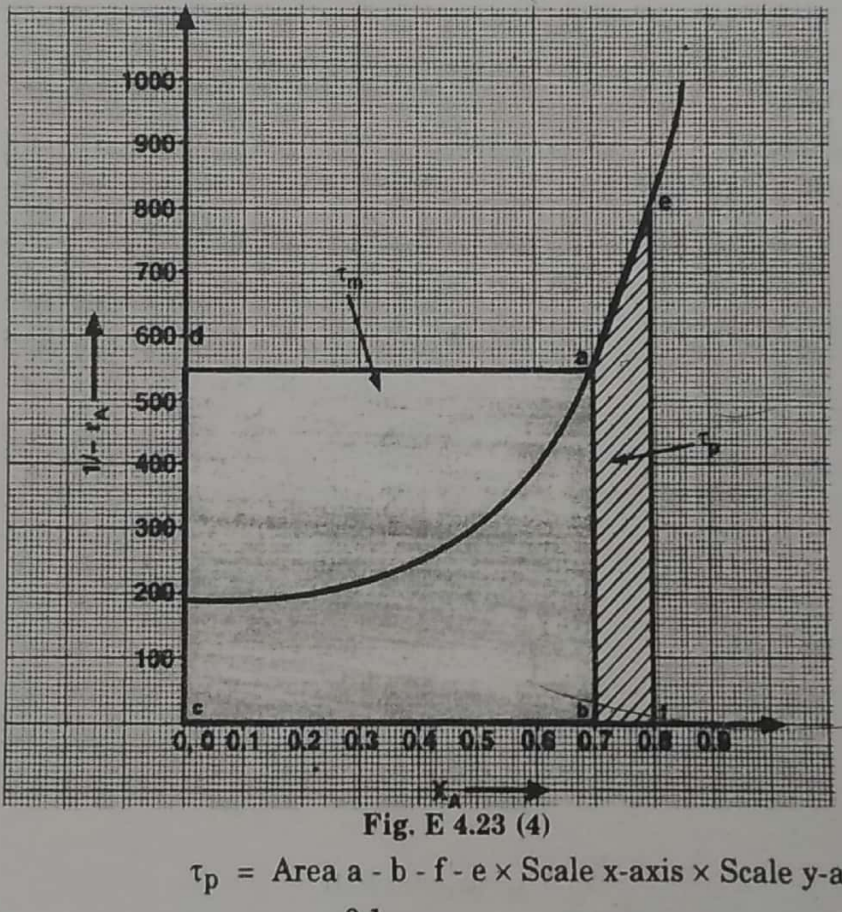


Fig. E 4.23 (4)

(ii)

$$\tau_p = \text{Area a - b - f - e} \times \text{Scale x-axis} \times \text{Scale y-axis}$$

$$= 6.7 \times \frac{0.1}{1} \times 100$$

$$= 67$$

$$\frac{V_p}{F_{Ao}} = \tau_p = 67$$

$$V_p = 67 \times 0.083 = 5.6\, l$$

Total volume for mixed flow reactor followed by plug flow reactor in series is $V = 31.96 + 5.6 = 37.56\, l$

For total volume to be **smaller**, use the arrangement – plug flow reactor followed by mixed flow reactor. ... **Ans.**

Ex. 4.24 : Liquid phase elementary reaction

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

with $-r_A = 500\ [l/(\text{mol.min})]\ C_A\, C_B$

is carried out in experimental tubular reactor (assume plug flow) under following conditions :

Volume of reactor, $V = 0.1$ litre

Volumetric feed rate, $v = 0.05\ l/\text{min}$.

Concentration of reactants in feed, $C_{Ao} = C_{Bo} = 0.01\ \text{mol}/l$

(a) What fractional conversion of reactants can be expected ?

(b) For the same conversion as in part (a), what size of stirred tank reactor (assume mixed flow) is needed ?

(c) What conversion can be expected in a mixed reactor equal in size to the plug flow reactor ?

Solution : $A + B \rightarrow \text{products}$

For equimolar feed, we may treat this as a second order reaction of the type

$2A \rightarrow$ products, $\quad -r_A = k.C_A^2$

$$\frac{V}{v_0} = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

$$-r_A = k.C_A^2 = k.C_{Ao}^2\,(1 - X_A)^2, \text{ for } \varepsilon_A = 0$$

$$k = 500\ l/(\text{mol.min})$$

$$\frac{V}{v_0} = C_{Ao} \int_0^{X_A} \frac{dX_A}{k \cdot C_{Ao}^2\,(1 - X_A)^2}$$

$$\frac{V}{v_0} = \frac{1}{k.C_{Ao}} \left[\frac{X_A}{1 - X_A}\right]$$

$$\frac{X_A}{1 - X_A} = k.C_{Ao} \cdot \frac{V}{v_0}$$

$$= \frac{500 \times 0.01 \times 0.1}{0.05}$$

$$\frac{X_A}{1 - X_A} = 10$$

$\therefore \quad X_A = 0.91$ ... **Ans. (a)**

For stirred tank reactor, $\dfrac{V}{v_0} = \dfrac{C_{Ao} \cdot X_A}{(-r_A)}$

$$\frac{V}{v_0} = \frac{C_{A_0} \cdot X_A}{k.C_{A_0}^2 (1-X_A)^2}$$

$$V = \frac{X_A \cdot v_0}{k.C_{A_0} (1-X_A)^2}$$

$$X_A = 0.91,\ k = 500\ l/(\text{mol.min}),\ C_{A_0} = 0.01\ \text{mol}/l,\ v_0 = 0.05\ l/\text{min}$$

$$V = \frac{0.91 \times 0.05}{500 \times 0.01\,(1-0.91)^2}$$

$$= 1.12\ l$$ ... **Ans. (b)**

For mixed flow reactor,

$$\frac{V}{v_0} = \frac{X_A}{k.C_{A0}(1-X_A)^2}$$

Volume of mixed flow, V = Volume of plug flow = 0.1 l

$$v_0 = 0.05\ l/\text{min}$$

$$C_{A_0} = 0.01\ \text{mol}/l$$

$$k = 500\ l/(\text{mol.min})$$

$$\therefore \quad \frac{X_A}{(1-X_A)^2} = \frac{0.10}{0.05} \times 500 \times 0.01$$

$$\therefore \quad 10X_A^2 - 21X_A + 10 = 0$$

$$X_A = \frac{21 \pm \sqrt{(21)^2 - 4 \times 10 \times 10}}{2 \times 10}$$

$$= 0.73$$ ... **Ans. (c)**

(only feasible root of X_A is to be taken).

Ex. 4.25 : It is desired to produce 4000 kmol/day of ethylene glycol. The reactor is operated isothermally. A 16.05 kmol/m³ solution of ethylene oxide in water is fed to the CSTR together with an equal volumetric solution of water containing 90% by weight H_2SO_4. If 80% conversion is to be achieved, find the volume of reactor. How many CSTRs, each having volume of 3 m³, would be required if they are arranged in parallel ? What is the corresponding conversion ? How many CSTRs, each with volume 3 m³, would be required if they are arranged in series ? What is the corresponding conversion ? The first order reaction rate constant is 0.311 (min)⁻¹.

Solution : $C_2H_4O + H_2O \xrightarrow{H_2SO_4} CH_2OH - CH_2OH$

$$A + B \xrightarrow{\text{cat.}} C$$

Production rate of ethylene glycol = F_C = 4000 kmol/day

$$F_C = \frac{4000}{24 \times 60} = 2.78\ \text{kmol/min}$$

From stoichiometry of reaction,

$$F_C = F_{A_0} \cdot X_A$$

$\therefore$ F_{A_0} = molar flow rate of ethylene oxide

$\therefore$ F_{A_0} = 2.78/0.80 = 3.475 kmol/min, (given $X_A = 0.80$)

For single CSTR :

$$V = \frac{F_{A_0} X_A}{(-r_A)}$$

Rate of reaction is

$$-r_A = k\,C_A$$

For liquid phase reaction, $\varepsilon_A = 0 \quad \therefore\ v = v_o$

$$\therefore \quad -r_A = k\, C_{Ao}(1 - X_A)$$

$$V = \frac{F_{Ao}\, X_A}{k\, C_{Ao}(1 - X_A)}$$

C_{Ao1} = concentration of A in ethylene oxide stream before mixing
= 16.05 kmol/m^3

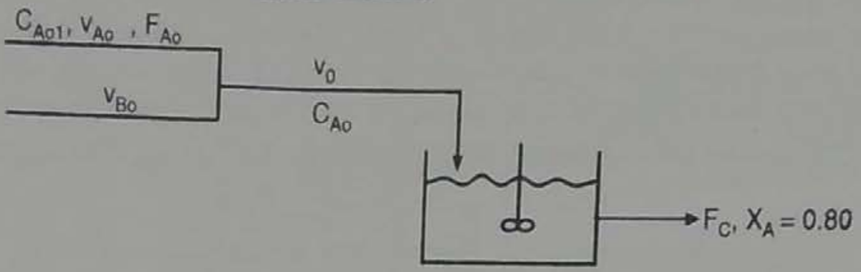


Fig. E 4.25

The entering volumetric flow rate of stream A, before mixing, is

$$v_{Ao} = \frac{F_{Ao}}{C_{Ao1}} = \frac{3.475}{16.05} = 0.2165 \text{ m}^3/\text{min}$$

The volumetric flow rate of water solution containing H_2SO_4 is equal to that of ethylene oxide stream (given).

$$v_{Bo} = v_{Ao} = 0.2165 \text{ m}^3/\text{min}$$

$$v_o = v_{Ao} + v_{Bo} = 0.2165 + 0.2165 = 0.433 \text{ m}^3/\text{min}$$

$$C_{Ao} = F_{Ao}/v_o = 3.475/0.433 = 8.025 \text{ kmol/m}^3$$

$$V = \frac{F_{Ao} \cdot X_A}{k\, C_{Ao}(1 - X_A)} = \frac{3.475}{8.025} \times \frac{0.80}{(1 - 0.80) \times 0.311}$$

$$= 5.57 \text{ m}^3 \qquad \text{... Ans.}$$

For CSTRs in parallel :

Consider two CSTRs in parallel each with volume of 3 m^3.

The flow is equally distributed in case of CSTRs in parallel.

$$\text{Molar flow rate of A to each unit} = F_{oi} = F_{Ao}/2 = \frac{3.475}{2} = 1.7375 \text{ kmol/min}$$

or

$$\text{Volumetric flow rate to each unit, } v_{oi} = v_o/2 = \frac{0.433}{2} = 0.2165 \text{ m}^3/\text{min}$$

$$\tau_i = \frac{V}{v_{oi}} = \frac{3}{0.2165} = 13.86 \text{ min}$$

or

$$\tau_i = \frac{V}{F_{oi}/C_{oi}} = \frac{3}{1.7375/8.025} = 13.86 \text{ min}$$

Conversion achieved in each reactor is same for equal-size CSTRs in parallel.

$$\tau_i = \frac{C_{oi}\, X_i}{k\, C_{oi}(1 - X_i)}$$

$$\tau = \frac{C_o\, X}{k\, C_o(1 - X)}$$

$$\therefore \qquad X = \frac{\tau\, k}{1+\tau\, k}$$

$$X = \frac{13.86 \times 0.311}{1+(13.86 \times 0.311)}$$

$$= 4.31/5.31 = 0.81$$

So conversion achieved with two equal-size CSTRs is 0.81.

If we use three equal size CSTRs in parallel, then

$$\tau = \frac{V}{v_o/3}$$

$$= \frac{3}{(0.433/3)} = 20.78$$

$$\therefore \qquad X = \frac{20.78 \times 0.311}{1+(20.78 \times 0.311)} = 0.866$$

For four CSTRs in parallel :

$$\tau = V/(v_o/4) = 3/(0.433/4) = 27.71$$

$$X = 0.896$$

So we may recommend the use of two CSTRs in parallel and conversion from two CSTRs in parallel is 0.81. ... **Ans.**

Equal-size CSTRs in series :

$$V_1 = V_2 = 3 \text{ m}^3$$

For CSTR-1 :

$$\tau_1 = \frac{C_o (X_1)}{k\, C_o\, (1-X_1)}$$

$$\therefore \qquad X_1 = \frac{\tau_1 k}{1+\tau_1 k}$$

$$\tau_1 = \frac{V\, C_{Ao}}{F_{Ao}}$$

$$= \frac{3 \times 8.025}{3.475} = 6.93 \text{ min}$$

$$X_1 = \frac{6.93 \times 0.311}{1+(6.93 \times 0.311)} = 0.683$$

For calculating conversion exiting the second reactor, we have

$$V = V_1 = V_2 \text{ and } v_{o1} = v_{o2}$$

$$\therefore \qquad \tau_1 = \tau_2 = \tau$$

For CSTR-2 :

$$\tau_2 = \frac{C_o (X_2 - X_1)}{k\, C_o\, (1-X_2)}$$

$$\tau_2\, k = \frac{X_2 - X_1}{(1-X_2)}$$

$$\tau_2 = \tau_1 = 6.93 \text{ min} = \tau$$

$$6.93 \times 0.311 = \frac{X_2 - X_1}{(1-X_2)} = \frac{X_2 - 0.683}{(1-X_2)}$$

Solving, for X_2, we get $X_2 = 0.90$

or
$$X_2 = \frac{X_1 + \tau k}{1 + \tau k} \quad \left[\text{as } \tau k = \frac{X_2 - X_1}{(1 - X_2)}\right]$$

$$X_2 = \frac{0.683 + (6.93 \times 0.311)}{1 + (6.93 \times 0.311)} = 0.90$$

For 3 CSTRs in series,

$$\tau_1 = \tau_2 = \tau_3 = \tau$$

$$\tau_3 = \tau = \frac{C_o (X_3 - X_2)}{k\, C_o (1 - X_3)}$$

$$X_3 = \frac{X_2 + \tau k}{1 + \tau k} = \frac{0.90 + (6.93 \times 0.311)}{1 + (6.93 \times 0.311)} = 0.968$$

So we recommend use of two CSTRs in series as volume is 6 m^3 and conversion is 90%.

$\therefore$ 4000 kmol/day of ethylene glycol can be produced by using two CSTRs in series (each of volume 3 m^3). ... **Ans.**

Ex. 4.26 : A harmful A present in industrial waste water degrades into harmless chemicals in presence of an enzyme E that acts as a homogeneous catalyst. Following laboratory results are obtained using mixed flow reactor for a given enzyme concentration.

C_{Ao}, mmol/m^3	2	5	6	6	11	14	16	24
C_A, mmol/m^3	0.5	3	1	2	6	10	8	4
τ, min	30	1	50	8	4	20	20	4

It is desired to treat 0.1 m^3/min of waste water with C_{Ao} = 10 mmol/m^3 to 90% conversion with enzyme E at concentration C_E.

(a) What arrangement of plug flow and mixed flow reactors would you use to minimise the total volume of reactors needed and determine the size of each unit required ?

(b) Determine the total volume of two CSTRs used in series and show how it is better than using one (single) CSTR ?

Solution : $A \xrightarrow{E}$ products.

Data is collected by using CSTR. For CSTR, we have,

$$\tau = \frac{C_{Ao} - C_A}{(-r_A)} \quad \text{for } \varepsilon_A = 0$$

$$\therefore \quad (-r_A) = \frac{C_{Ao} - C_A}{\tau} \quad \therefore \frac{1}{(-r_A)} = \frac{\tau}{C_{Ao} - C_A}$$

Calculate the rate using above equation. For data given, tabulate $1/(-r_A)$ at the measured C_A and plot $1/(-r_A)$ v/s C_A.

C_{Ao}, mmol/m^3	2	5	6	6	11	14	16	24
C_A, mmol/m^3	0.5	3	1	2	6	10	8	4
τ, min	30	1	50	8	4	20	20	4
$(-r_A)$, mmol/(m^3.min)	0.05	2	0.1	0.5	1.25	0.2	0.4	5
$1/(-r_A)$, (m^3.min)/mmol	20	0.5	10	2	0.8	5	2.5	0.2

Sample calculation : $C_{Ao} = 2$, $C_A = 0.5$ and $\tau = 30$

$$(-r_A) = (2 - 0.5)/30 = 0.05 \text{ mmol/(m}^3\text{.min)}$$

$$\frac{1}{(-r_A)} = \frac{1}{0.05} = 20 \text{ (m}^3\text{.min)/mmol}$$

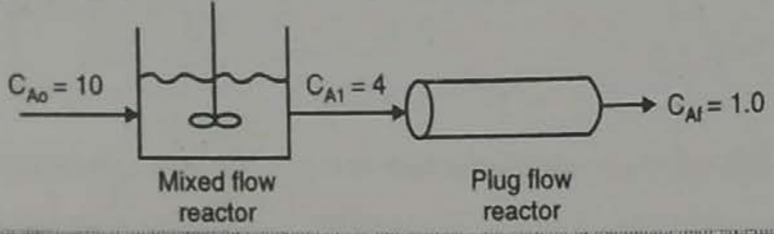
We have, C_{A_0} = 10 mmol/m^3 and $X_A = 0.90$

$C_{Af} = C_{A_0}(1-X_A) = 10\,(1-0.9) = 1$ mmol/m^3

As we are interested in area between $C_{A_0} = 10$ and $C_{Af} = 1.0$ plot a graph of $1/(-r_A)$ v/s C_A with minimum $C_A = 1.0$.

(a) We have to use CSTR and PFR in series. We have concentration range from C_{A_0} = 1 to $C_{Af} = 1.0$. We should operate the first reactor in series upto concentration of A, $C_A = 4$ (the point at which the rate is maximum = 5 mmol/(m^3.min) and second reactor from $C_A = 4$ to $C_A = 1.0$. I is clear from shape of rate-concentration curve that we should use mixed flow reactor followed by plug flow reactor to have minimum total volume of reactor system.

Reactor arrangement : Mixed flow followed by plug flow reactor.



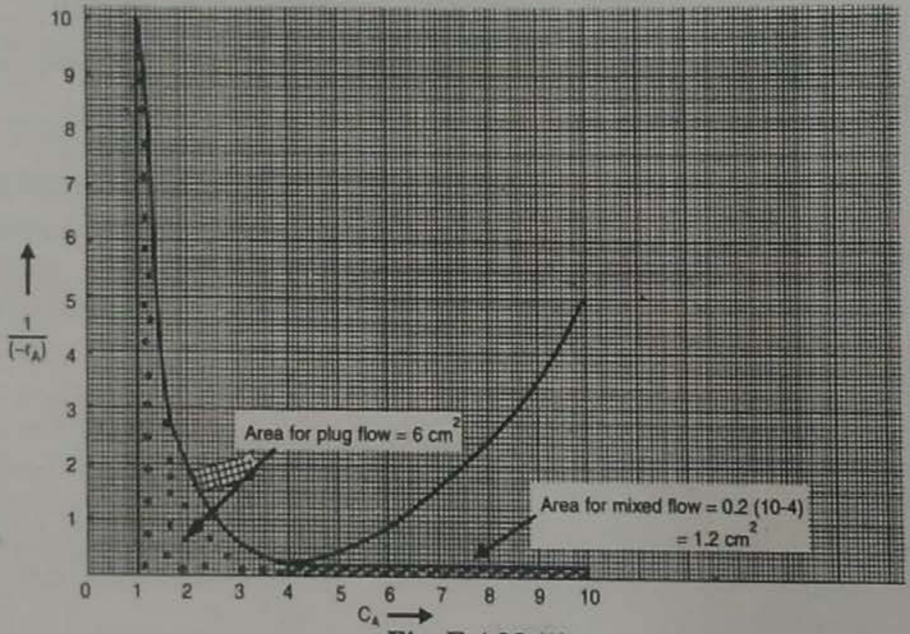


Fig. E 4.26 (1)

From Fig. E 4.26 (1)

Rectangular area for mixed flow = 1.2 cm^2

$$\therefore \quad \tau_m = \text{Area} \times \text{Scale x-axis} \times \text{Scale y-axis}$$

$$= 1.2 \times \frac{1}{1} \times \frac{1}{1} = 1.2 \text{ min}$$

Area under the curve for plug flow = 6 cm^2

$$\therefore \quad \tau_p = 6 \times \frac{1}{1} \times \frac{1}{1} = 6 \text{ min}$$

We have, $v = 0.1$ m^3/min

For MFR :

$$\tau_m = V_m/v$$

$$V_m = \tau_m \cdot v = 1.2 \times 0.1 = 0.12 \text{ m}^3$$ ... Ans.

For PFR :

$$\tau_p = V_p/v$$

$$V_p = \tau_p v = 6 \times 0.10 = 0.60 \text{ m}^3$$ ... Ans.

Total volume of system of reactors = 0.12 + 0.60 = 0.72 m^3 ... Ans

(b) CSTR or Two CSTRs in series :

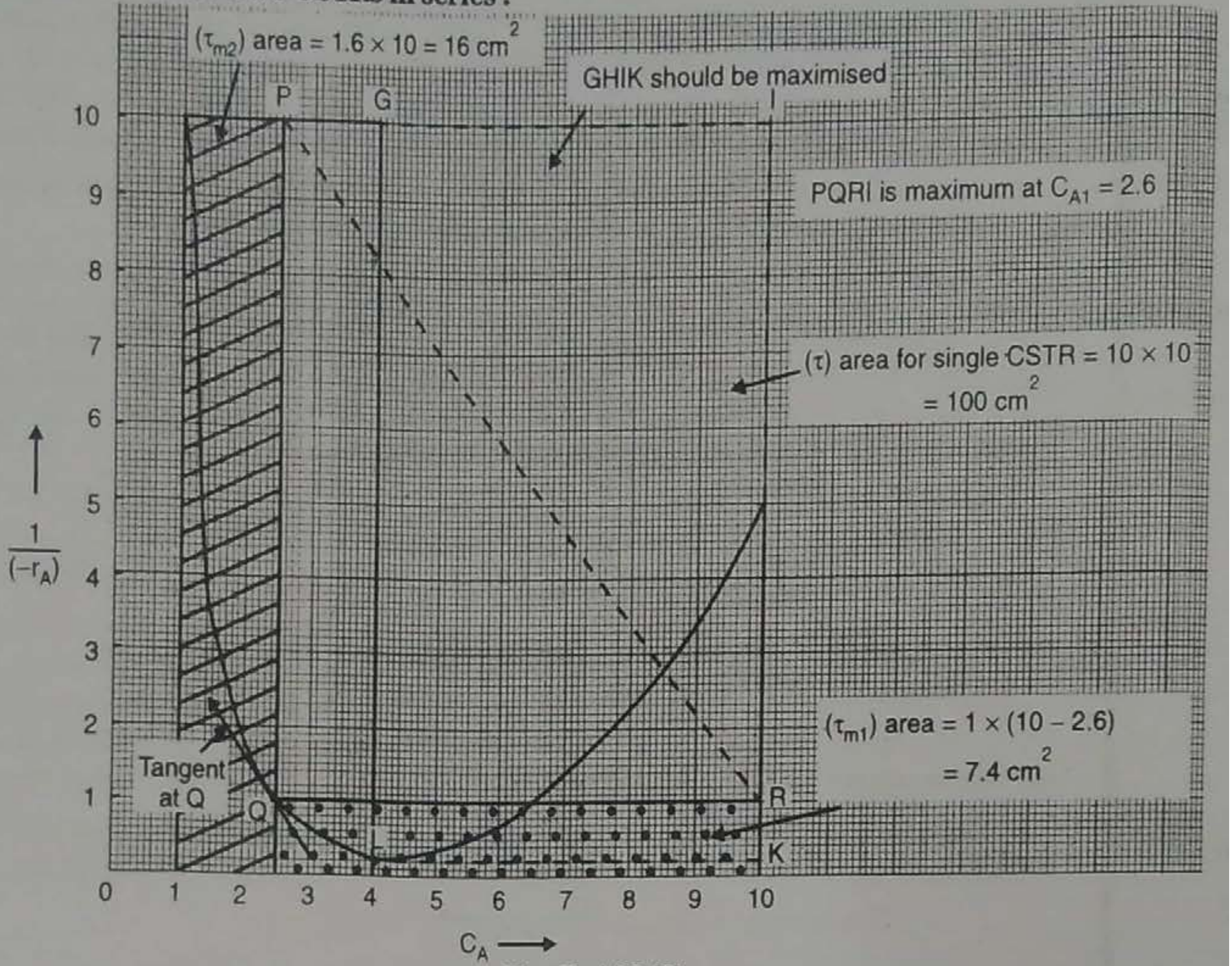


Fig. E 4.26 (2)

(i)For single CSTR/MFR for 90% conversion of A with C_{A_0} = 10 mmol/m^3 :

Refer Fig. E 4.26 (2).

Rectangular area for single MFR between $C_A - C_{A_0}$ = 10 and C_{Af}= 1.0 is 100 cm^2.

$$\tau = 100 \times \text{Scale y-axis} \times \text{Scale x-axis}$$

$$= 100 \times \frac{1}{1} \times \frac{1}{1} = 100 \text{ min}$$

$$\tau = V/v$$

$$V = \tau \cdot v = 100 \times 0.1 = 10 \text{ m}^3$$

... **Ans.**

(ii)For two CSTRs in series :

From graph, for CSTR-1 :

$$A_1 = 7.4 \text{ cm}^2$$

$$\therefore \quad \tau_1 = 7.4 \times \frac{1}{1} \times \frac{1}{1} = 7.4 \text{ min}$$

$$V_1 = \tau_1 v = 7.4 \times 0.1 = 0.74 \text{ m}^3$$

From graph, for CSTR-2 : A_2 = 16 cm^2

$$\tau_2 = 16 \times \frac{1}{1} \times \frac{1}{1} = 16 \text{ min}$$

$$V_2 = \tau_2 v = 16 \times 0.1 = 1.6 \text{ m}^3$$

Total volume of two CSTRs in series required to achieve 90% conversion of A

$$= 0.74 + 1.6 = 2.34 \text{ m}^3$$

... **Ans.**

Here we have to find the minimum volume required by using a concept of maximisation of rectangle. If we take for example, $C_{A1} = 4$ then area for first CSTR is 1.2 cm^2 and that for CSTR-2 is 30 cm^2.

$$\therefore \quad \tau_1 = 1.2 \text{ min and } \tau_2 = 30 \text{ min}$$

$$\text{Total volume} = (1.2 + 30) \times 0.1 = 3.12 \text{ m}^3$$

In this case, area of rectangle GLKI is 58.8 cm^2.

We have to make this area of GLKI maximum.

The area of rectangle will be maximum when the diagonal of rectangle and tangent to the curve at certain point are parallel to each other.

The tangent to the curve at point Q is parallel to diagonal PR of rectangle PQRI (area of PQRI = 66.6 cm^2).

The concentration of A corresponding to point P is $C_{A1} = 2.6$ mmol/m^3.

So operate first CSTR from $C_{A_0} = 10$ to $C_{A1} = 2.6$ mmol/m^3 and second one from $C_A = 2.6$ to $C_{Af} = 1.0$ mmol/m^3.

In this case, total volume of CSTRs in series = 2.34 m^3

The volume of single CSTR = 10 m^3.

∴ Two CSTRs in series are always preferred to single CSTR for a given job as they require smaller total volume than the volume of single CSTR.

❐❐❐

Chapter ... ⑤

DESIGN FOR MULTIPLE REACTIONS

In this chapter we will deal with multiple reactions. There are three basic types of multiple reactions, namely, parallel, series, and independent.

In case of parallel reactions, the reactant is consumed by two different reactions to form different reactions. They are also called competing reactions.

$$A \xrightarrow{k_1} R$$

$$A \xrightarrow{k_2} S$$

Example of parallel reaction of industrial importance is :

(i) $C_2H_4 + \frac{1}{2} O_2 \longrightarrow C_2H_4O$ (desired)

(ii) $C_2H_4 + 3\,O_2 \longrightarrow 2\,CO_2 + 2\,H_2O$ (undesired)

Oxidation of ethylene to ethylene oxide occurs along with formation of CO_2.

In case of series reactions (also called as consecutive reactions), the reactant forms an intermediate product, that reacts further to form another product.

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

In this case, the desired product may be R or S depending upon the situation.

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$

$$C_6H_5NO_2 + HNO_3 \xrightarrow{H_2SO_4} C_6H_4(NO_2)_2$$

i.e. $C_6H_6 \longrightarrow C_6H_5NO_2 \longrightarrow C_6H_4(NO_2)_2$

$$CH_4 \xrightarrow{Cl_2} CH_3Cl \xrightarrow{Cl_2} CH_2Cl_2 \xrightarrow{Cl_2} CHCl_3 \xrightarrow{Cl_2} CCl_4$$

In nitration of benzene, nitrobenzene is the desired product and dinitrobenzene is the undesired product.

In case of independent reactions, different reactants react to form different products.

$$A \rightarrow R$$

$$B \rightarrow T$$

Such reactions occur in feed-stock containing more than one reactant.

The cracking of crude oil to form gasoline is an example where independent reactions occur.

The multiple reactions represented by more than one stoichiometric equation require more than one kinetic expression (rate equation) to represent the progress of reaction i.e. to follow the changing composition of all the reaction components.

In discussion to follow we will use concentration rather than conversion as a primary variable to develop necessary equations for determining reactor size and for study of product distribution we will eliminate time variable by dividing one rate equation with another that gives equation relating the rate of change of one component with respect to other component of the system. We also take $\varepsilon = 0$ i.e. neglect the expansion effect throughout our discussion.

For multiple reactions two natural requirements are : small reactor size and maximum yield of the desired product (optimum solution for multiple reactions).

The small reactor size and maximisation of formation of desired product may run counter to each other and in such cases an economic analysis will give the best compromise. The reactor system selected will influence the economics of the process by dictating the reactor size needed and product distribution. For single reactions as the product distribution is fixed important factor in comparing designs is the reactor size while in case of multiple reactions primary consideration in design is the product distribution.

Reactions in parallel :

Qualitative Discussion about Product Distribution :

For the parallel/competing reactions,

$$A \xrightarrow{k_1} R \text{ (desired)}$$

$$A \xrightarrow{k_2} S \text{ (undesired)}$$

the rate equations for formation of R and S are

$$r_R = \frac{dC_R}{dt} = k_1 C_A^{n1} \quad \text{... (5.1)}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A^{n2} \quad \text{... (5.2)}$$

The rate of disappearance of A for this reaction scheme is sum of the rates of formation of R and S.

$$-r_A = r_R + r_S$$

$$-r_A = k_1 C_A^{n1} + k_2 C_A^{n2} \quad \text{... (5.3)}$$

Dividing equation (5.1) by equation (5.2), we get

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} C_A^{n1-n2} \quad \text{... (5.4)}$$

Equation (5.4) gives a measure of the relative rates of formation of R and S.

The ratio r_R/r_S is called the rate selectivity parameter (R with respect to S).

We want the rate of formation of R, r_R to be high with respect to the rate of formation of S, r_S. i.e. we wish the ratio r_R/r_S to be as high as possible.

Referring to equation (5.4) we can see that C_A is the only factor which we can adjust and control (k_1, k_2, n_1 and n_2 are all constant for a specific reaction system at a given temperature).

We can keep C_A low by any of the following means :

Using mixed flow reactor, maintaining high conversion, increasing inerts in the feed or decreasing the pressure in gas phase reactions.

We can keep C_A high by any of the following means :

Using a batch or plug flow reactor, maintaining low conversion, removing inerts from the feed, or increasing pressure in case of gas phase reactions.

Now we will see whether to keep C_A high or low for the reactions in parallel given above.

(i) If $n_1 > n_2$ i.e. the case where the desired reaction is of higher order than the undesired reaction.

Let $n_1 - n_2 = \alpha$ (where α is a positive number)

Then equation (5.4) becomes

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^{\alpha} \qquad \text{... (5.5)}$$

To make the ratio R/S as large as possible, we have to carry out the reaction in a manner that will keep the concentration of reactant A as high as possible during the reaction (high concentration of A is desirable). With the high concentration of A we see from equation (5.5) that the ratio of the desired product to the undesired product (R/S) will also be high.

So in order to keep C_A high, we have to carry a gas phase reaction without presence of inerts and at high pressure. In case of liquid phase reaction, use of diluent should be kept at minimum for keeping C_A high.

A batch or plug flow reactor should be used as it favours the formation of R and would require a minimum reactor size. The reason for use of either of these reactors is that the concentration of A in these reactors start at high value and drops progressively during the course of reaction. In case of CSTR, the concentration of reactant within the reactor is always at its lowest value (i.e. that of exit concentration).

(ii) If $n_1 < n_2$ i.e. when the desired reaction is of lower order than the undesired reaction (i.e. reaction order of undesired product is greater than that of the desired product).

$$n_2 - n_1 = \alpha' \text{ (where } \alpha' \text{ is a positive number)}$$

then

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^{n_1 - n_2}$$

$$\frac{r_R}{r_S} = \frac{k_1}{k_2}\left(\frac{1}{C_A^{n_2 - n_1}}\right) = \frac{k_1}{k_2 \cdot C_A^{\alpha'}} \qquad \text{... (5.6)}$$

It is clear from equation (5.6) that for the ratio r_R/r_S to be high, the concentration of A should be as low as possible.

So we need a low concentration of A to favour i.e. to maximise the formation of R. This low concentration may be accomplished by diluting the feed with inerts and running the reactor at low concentrations of A. In such cases, CSTR should be used because the concentration of reactant is maintained at a low level. Also the recycle reactor in which the product stream acts as a diluent could be used to keep the entering concentration of A at a low value.

(iii) If $n_1 = n_2$ i.e. the two reactions are of same order then

$$n_1 - n_2 = 0$$

$$\frac{r_R}{r_S} = \frac{dC_R}{dt} = \frac{k_1}{k_2} C_A^{0} = \frac{k_1}{k_2} = \text{constant}$$

Therefore, the product distribution is fixed by k_1/k_2 alone and it will not be affected by the type of reactor used.

The product distribution may also be controlled by varying the ratio k_1/k_2. This can be done by following ways :

(i) By changing the temperature of reaction system. If the activation energies of two reactions are different, k_1/k_2 can be made to vary.

(ii) By using a catalyst. One of the most important features of the catalyst is that, it selectively depresses or accelerates specific reactions (selectivity of catalyst). Use of catalyst is much more effective way of controlling the product distribution than the methods given above.

The ratio of amount of desired product R to the amount of undesired product S formed can also vary with temperature. The sensitivity of this ratio to temperature can be determined from the ratio of the reaction rate constants (k_1/k_2).

$$k_1 = k_{o1} \cdot e^{-E_1/RT}$$

$$k_2 = k_{o2} \cdot e^{-E_2/RT}$$

$$\frac{k_1}{k_2} = \frac{k_{o1}}{k_{o2}} \cdot e^{-(E_1 - E_2)/RT} \qquad \text{... (5.7)}$$

where k_o is the frequency factor and E is the activation energy (E_1 is of desired reaction and E_2 of undesired reaction).

(i) If $E_1 > E_2$ then the rate constant of desired reaction (k_1) and therefore the rate (r_R) increases more rapidly with increase in temperature than the rate constant (k_2) of undesired reaction. Hence, the reaction should be carried out at the highest possible temperature to maximise the formation of R.

(ii) If $E_1 < E_2$ then the reaction should be carried out at low temperature to maximise the formation of R, but not so low that the desired reaction does not proceed to any significant extent.

We summarise our **qualitative findings** for single reactant as follows :

(i) For reactions in parallel, the concentration level of reactant is the key to proper control of product distribution at a given temperature.

(ii) A high concentration of reactant favours the reaction of higher order.

(iii) A low concentration of reactant favours the reaction of lower order.

(iv) The concentration level of reactant has no effect on the product distribution for reactions of the same order.

(v) A high reaction temperature favours the reaction with high activation energy and vice-versa.

Now we will consider reactions in parallel for two reactants :

For the parallel reactions :

$$A + B \xrightarrow{k_1} R \qquad \text{(desired)}$$

$$A + B \xrightarrow{k_2} S \qquad \text{(undesired)}$$

The rate of formation of R is

$$r_R = k_1 \, C_A^{\alpha_1} \cdot C_B^{\overset{\beta_1}{\alpha_2}} \qquad \text{... (5.8)}$$

The rate of formation of S is

$$r_S = k_2 \, C_A^{\beta_1} \cdot C_B^{\beta_2} \qquad \text{... (5.9)}$$

Dividing equation (5.8) by equation (5.9), we get,

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} C_A^{\alpha_1 - \alpha_2} \cdot C_B^{\beta_1 - \beta_2}$$

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^a \cdot C_B^b \quad \text{... (5.10)}$$

where $a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$.

As R is the desired product which we wish to maximise

$$\frac{dC_R}{dC_S} \text{ or } \frac{k_1}{k_2} \cdot C_A^a \cdot C_B^b$$

Hence, we have to examine whether a and b are positive or negative and this will determine whether to keep A or B at low or high concentration.

When we have two or more reactants, combinations of high and low concentrations are desirable depending upon the kinetics of the competing reactions. One can obtain these combinations of high and low concentrations by controlling the concentration of feed materials, by taking certain component in excess, and by using the correct contacting pattern of reacting fluids. Figs. 5.1 and 5.2 show methods for contacting two reacting fluids in continuous and non-continuous operation that keep the concentrations of these components both high, both low, or one high and other low. For obtaining a favourable product distribution for multiple reactions, the use of proper contacting pattern/scheme is the critical factor.

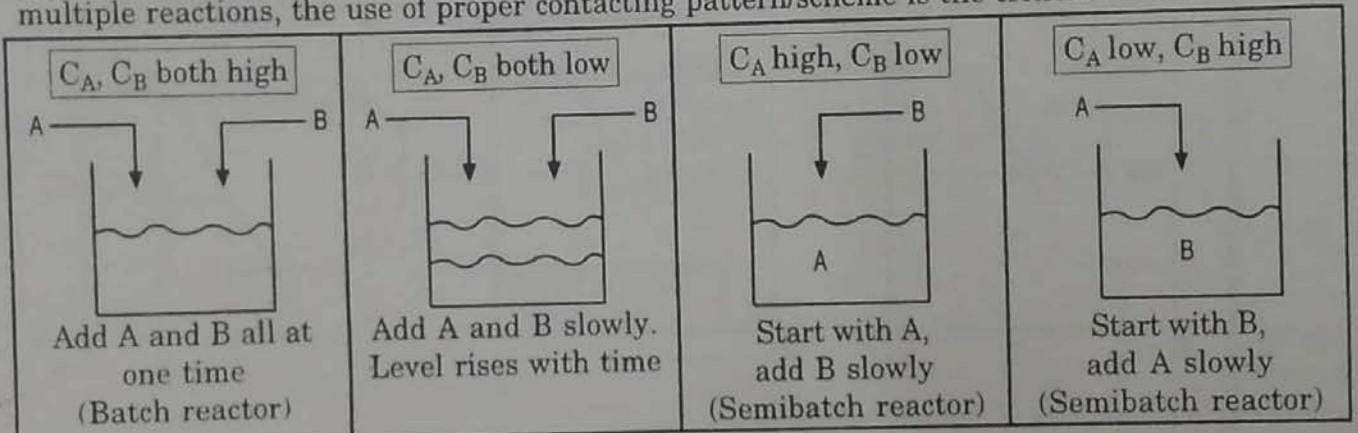
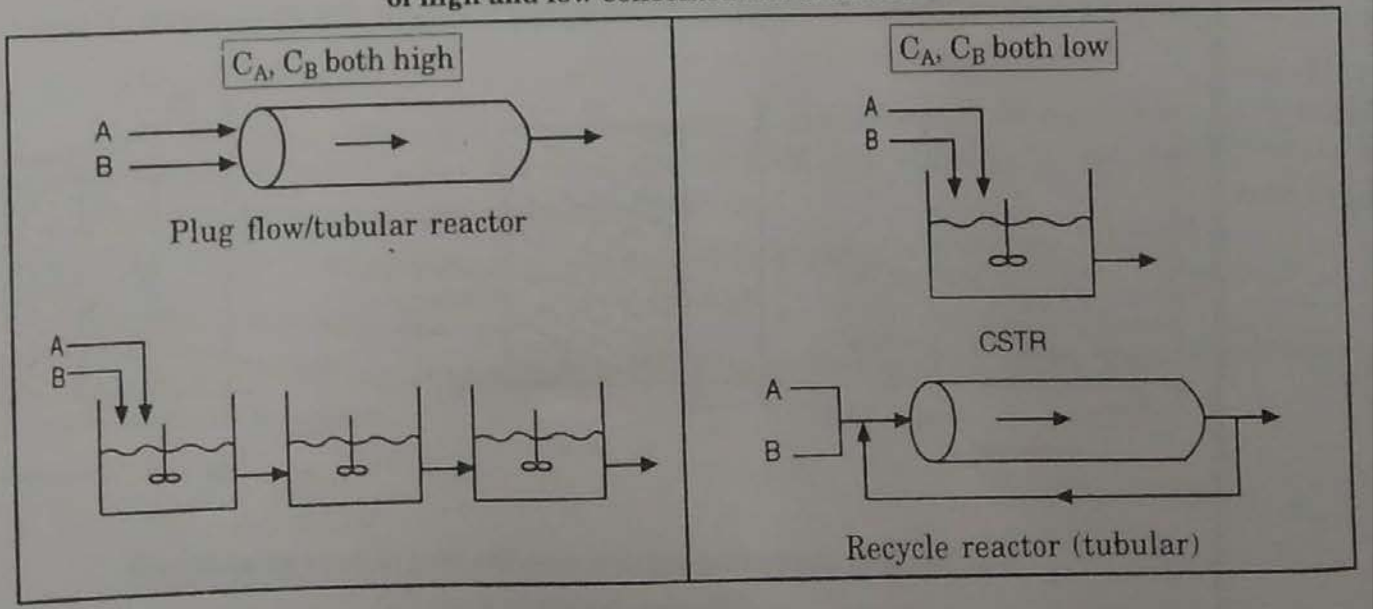


Fig. 5.1 : Contacting patterns/schemes in non-continuous operations for various combinations of high and low concentration of reactants



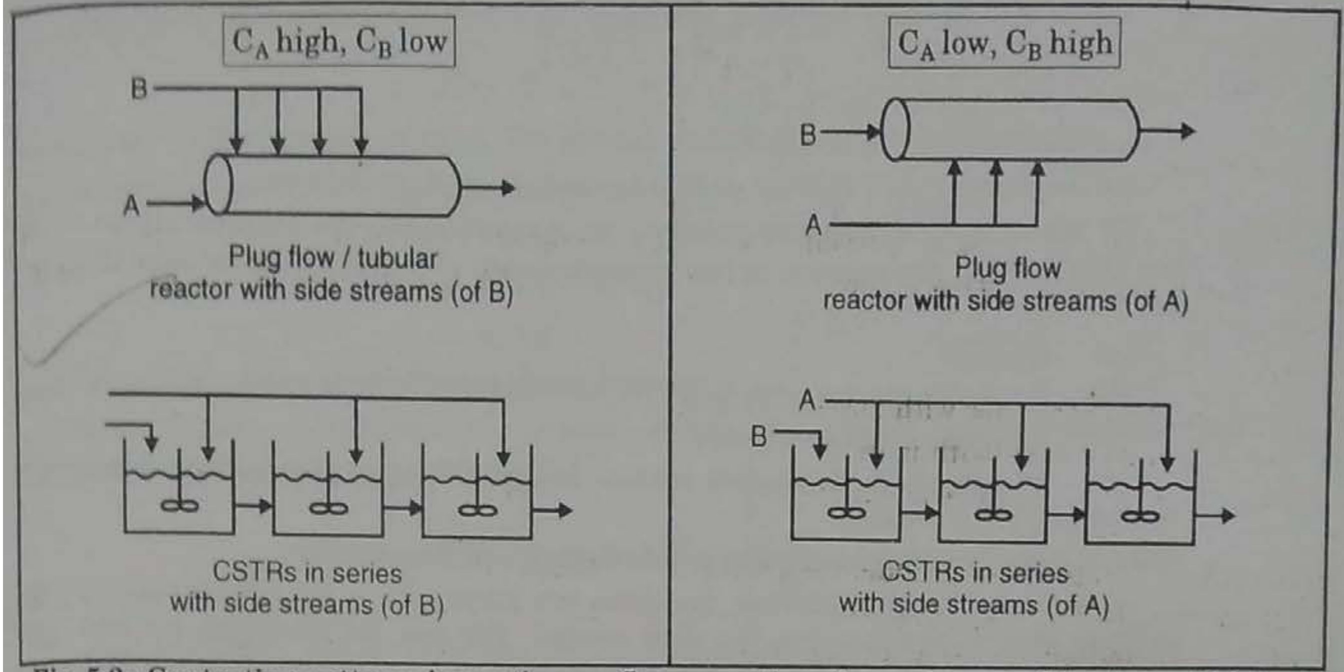


Fig. 5.2 : Contacting patterns in continuous flow operations for various combinations of high and low concentration of reactants

We have, $$\frac{r_R}{r_S} = \frac{k_1}{k_2} C_A^a \cdot C_B^b$$

where $a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$

(i) If $\alpha_1 > \alpha_2$ and $\beta_1 > \beta_2$ then both a and b are positive numbers.

So to maximise the ratio r_R/r_S i.e. to maximise the formation of R, we have to maintain the concentrations of both A and B as high as possible.

And for doing this, we have to use batch reactor, a plug flow/tubular reactor, and high pressures in case of gas phase reaction.

(ii) If $\alpha_1 > \alpha_2$ and $\beta_1 < \beta_2$

$a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$ where a and b are positive constants

then $$\frac{r_R}{r_S} = \frac{k_1}{k_2} \cdot C_A^a \cdot C_B^{-b} = \frac{k_1}{k_2} \frac{C_A^a}{C_B^b} \qquad \text{... (5.11)}$$

To maximise the formation of R as large as possible, we should have the concentration of A high and the concentration of B low.

For making the concentration of A high and that of B low, use :

(a) A semibatch reactor containing large amount of A to which B is fed slowly.

(b) A plug flow reactor with side streams of B continually fed to the reactor.

(c) Small CSTRs in series with A fed only to the first reactor and B fed to each reactor.

(iii) $\alpha_1 < \alpha_2$ and $\beta_1 > \beta_2$

$a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$, where a and b are positive constants

$$\therefore \quad \frac{r_R}{r_S} = \frac{k_1}{k_2} \cdot \frac{C_B^b}{C_A^a} \qquad \text{... (5.12)}$$

To maximise r_R/r_S we have to carry out reaction at high concentrations of B and low concentrations of A.

For achieving high concentration of B and low concentration of A, use :

(a) A semibatch reactor in which A is slowly fed to a large amount of B in it.

(b) A tubular reactor with side streams of A with B fed at the inlet.

(c) A series of small CSTRs with B fed only to the first reactor and A fed to each reactor.

(iv) If $\alpha_1 < \alpha_2$ and $\beta_1 < \beta_2$

$a = \alpha_1 - \alpha_2$ and $b = \beta_1 - \beta_2$, where both a and b are positive constants.

$$\therefore \qquad \frac{r_R}{r_S} = \frac{k_1}{k_2} \cdot \frac{1}{C_A^a \cdot C_B^b} \qquad \text{... (5.13)}$$

as $a = \alpha_1 - \alpha_2$ and $\alpha_1 < \alpha_2$

$-a = \alpha_2 - \alpha_1 \quad \therefore$ a is –ve

$b = \beta_1 - \beta_2$ and $\beta_1 < \beta_2 \quad \therefore$ b is –ve

To make r_R/r_S as large as possible, we want to make the concentrations of both A and B low. To carry out the reaction at low concentrations of A and B to maximise the formation of R, use :

(a) A CSTR

(b) A tubular reactor with large recycle ratio

(c) A diluted feed (with inerts)

(d) Low pressure of reaction system in case of gas phase reaction (carry the gas phase reaction at low pressure).

Quantitative Treatment of Product Distribution and Reactor Size :

If the kinetics of individual reactions are known then we can quantitatively determine product distribution and reactor size needed. For our convenience, we will introduce two terms, ψ and ϕ to evaluate the product distribution.

Consider the decomposition of A according to the following reactions :

$$A \rightarrow R \text{ (desired)}$$
$$A \rightarrow S \text{ (undesired)}$$

Let ψ be the fraction of A disappearing at any instant that is transformed into the desired product R. We term this as the instantaneous fractional yield of R.

Therefore at any C_A,

$$\psi = \frac{\text{moles R formed}}{\text{moles A reacted}} = \frac{dC_R}{dC_A} \qquad \text{... (5.14)}$$

For given set of reactions and rate equations, ψ is a function of C_A. As C_A varies through the reactor, ψ will also change with position in the reactor. So we will define ϕ, the overall fractional yield of R, as the fraction of all the reacted A that has been transformed into desired product R. The overall fractional yield is then the mean of instantaneous fractional yields at all points within the reactor.

$$\phi = \left(\frac{\text{all R formed}}{\text{all A reacted}}\right) = \frac{C_{Rf}}{C_{Ao} - C_{Af}} = \frac{C_{Rf}}{(-\Delta C_A)} = \bar{\psi} \text{ in reactor} \qquad \text{... (5.15)}$$

The overall fractional yield represents the product distribution at the reactor outlet. We are so concerned with ϕ and proper averaging for ψ depends upon the flow within the reactor.

For **plug flow reactor** :

C_A changes progressively through the reactor (along the length of reactor), we have from equation (5.14)

$$\phi_p = \frac{-1}{C_{Ao} - C_{Af}} \int_{C_{Ao}}^{C_{Af}} \psi \, dC_A = \frac{1}{\Delta C_A} \int_{C_{Ao}}^{C_{Af}} \psi \, dC_A \qquad \text{... (5.16)}$$

For **mixed flow reactor** :

C_{Af} is same everywhere, so ψ is likewise constant throughout the reactor.

$$\therefore \qquad \phi_m = \psi_{\text{evaluated at } C_{Af}} \qquad \text{... (5.17)}$$

For mixed flow and plug flow reactors processing A from C_{Ao} to C_{Af}, the overall fractional yields are related by

$$\phi_m = \left(\frac{d\phi_p}{dC_A}\right)_{at\ C_{Af}} \quad \text{and} \quad \phi_p = \frac{1}{\Delta C_A}\int_{C_{Ao}}^{C_{Af}} \phi_m \, dC_A \qquad \text{... (5.18)}$$

For N mixed flow reactors in series, the overall fractional yield is obtained by summing the fractional yields in each of the N mixed flow reactors [CSTRs] and weighing these values by the amount of reaction occurring in each reactor. Hence,

$$\psi_1 (C_{Ao} - C_{A1}) + \ldots + \psi_N (C_{A,N-1} - C_{A,N}) = \phi_{N\ mixed} (C_{Ao} - C_{A,N}) \qquad \text{... (5.19)}$$

$$\therefore \quad \phi_{N\ mixed} = \frac{\psi (C_{Ao} - C_{A1}) + \ldots + \psi_N (C_{A,N-1} - C_{A,N})}{(C_{Ao} - C_{A,N})} \qquad \text{... (5.20)}$$

where C_{A1}, C_{A2} ... C_{AN} concentrations of A in mixed flow reactors 1, 2, ... N i.e. at exit of reactors 1, 2 ... N.

For any reactor type, the exit concentration of R is given by

$$C_{Rf} = \phi (C_{Ao} - C_{Af}) \qquad \text{... (5.21)}$$

The instantaneous fractional yield, ψ, as a function of C_A for plug flow reactor, mixed flow reactor and mixed flow reactors in series, is shown in Fig. 5.3.

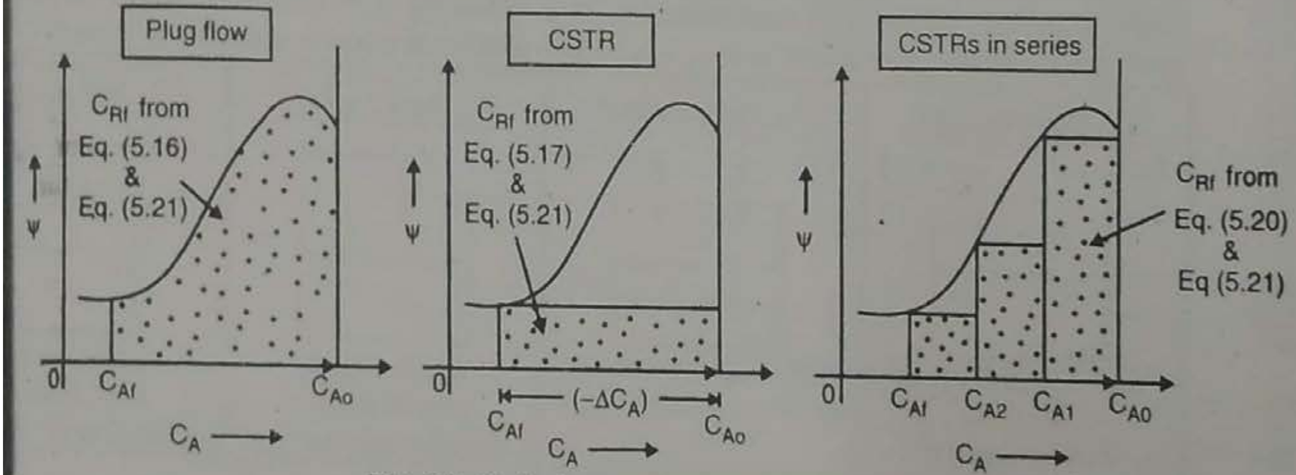


Fig. 5.3 : Dotted area gives total R formed

Such curves help to find C_R for different types of reactor. The type of flow (type of reactor) that gives the best product distribution depends upon the shape of ψ v/s C_A curve (Fig. 5.4).

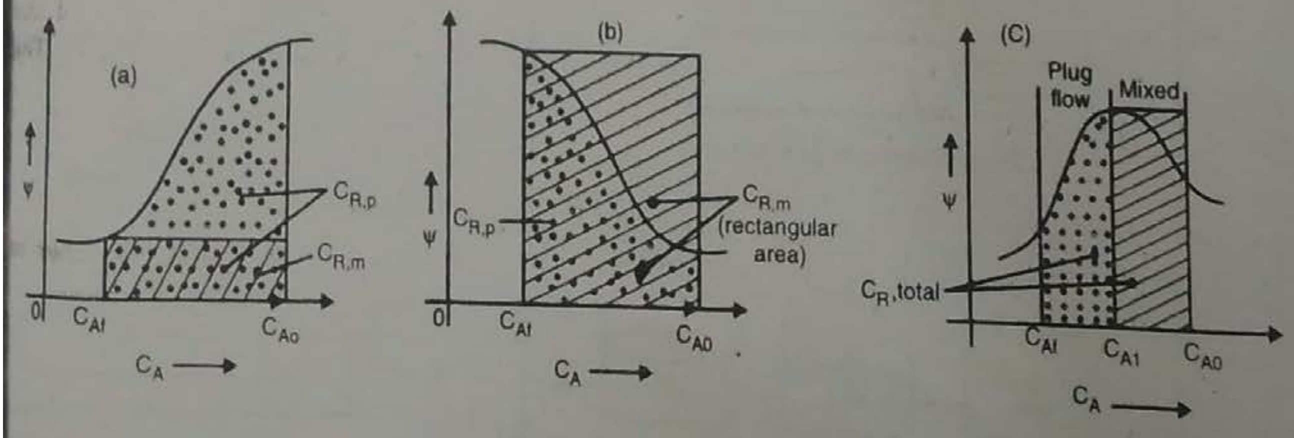


Fig. 5.4 : The contacting pattern with the largest area gives most R (different shapes of ψ v/s C_A)

(a) Plug flow is best. (b) Mixed flow is best. (c) Mixed flow followed by plug flow is best.

Note : For plug flow reactor, it is the area under curve and for mixed flow reactor (CSTR), it is the area of rectangle (rectangular area).

The fractional yield expressions cited above help in calculation of the product distributio from different types of reactors and to select the best reactor set up for given reaction system.

In above discussion, the fractional yield of R has been taken as a function of C_A (only one reactant is considered). When two or more reactants are involved, one can define the fractional yield based on one of the reactants consumed or on all the reactants consumed or products formed. It is simply a matter of convenience to use any particular basis. Hence, in general, we define ψ (P/Q) as the instantaneous fractional of P based on the disappearance or formation of Q.

Selectivity : It is defined as *the ratio of moles of desired product formed to moles of undesired product formed*. It may be used in place of fractional yield.

For batch system :

$$\text{Selectivity} = \frac{\text{moles of desired product formed}}{\text{moles of undesired product formed}}$$

$$= \frac{N_R}{N_S}$$

For flow system :

$$\text{Selectivity} = \frac{\text{molar flow rate of desired product at the exit of reactor}}{\text{molar flow rate of undesired product at the exit of reactor}}$$

$$= \frac{F_R}{F_S}$$

where R is desired and S is the undesired product.

Consider reaction scheme

$$A \rightarrow R \text{ (desired)}$$

$$A \rightarrow S \text{ (undesired)}$$

Overall fractional yield of R is the fraction of A converted to R = $\phi(R/A)$.

Overall fractional yield of S = $\phi(S/A)$

If total conversion of A is X consisting of conversion X_1 of reactant A to R and th conversion X_2 to C ($X = X_1 + X_2$), the fractional yield of R is simply X_1 and that of S is X_2. T amount of product produced is proportional to yield.

$$\therefore \quad (\text{Selectivity})_{RS} = X_1/X_2 = \text{Ratio of yields of R and S.}$$

Reactions in Series :

In such reactions, reactants form the intermediate product which then reacts further form another product.

For example :

(i) $A \rightarrow R \rightarrow S$

(ii) $A + B \rightarrow R$

$R + B \rightarrow S$

$S + B \rightarrow T$

Irreversible First Order Reactions in Series :

Consider unimolecular type first order reactions in series, such as

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \qquad \text{... (5.22)}$$

proceed only in the presence of light. The instant the light is turned off, they stop.

For given intensity of radiation, they proceed with the following rate equations :

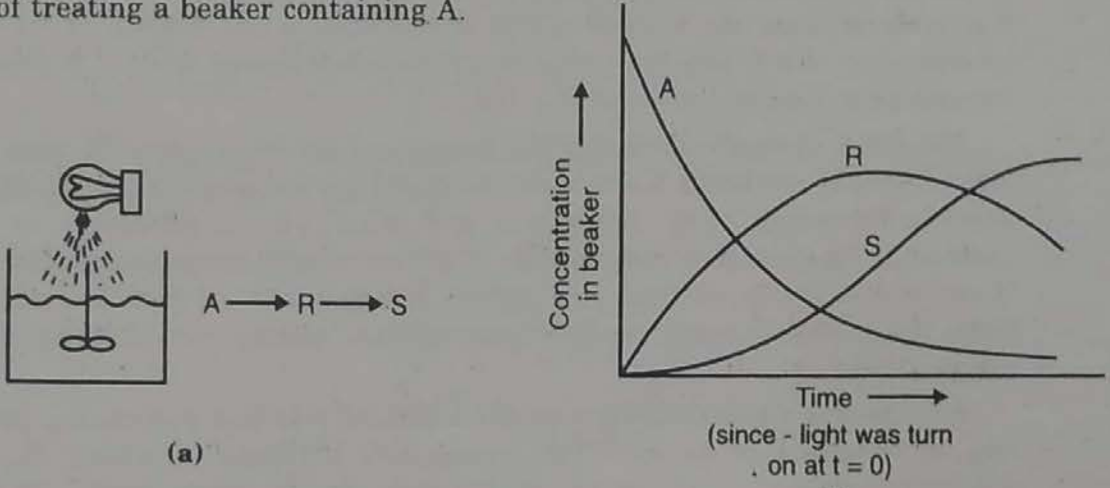
$$-r_A = k_1 C_A \qquad \text{... (5.23)}$$

$$r_R = k_1 C_A - k_2 C_R \qquad \text{... (5.24)}$$

$$r_S = k_2 C_R \qquad \text{... (5.25)}$$

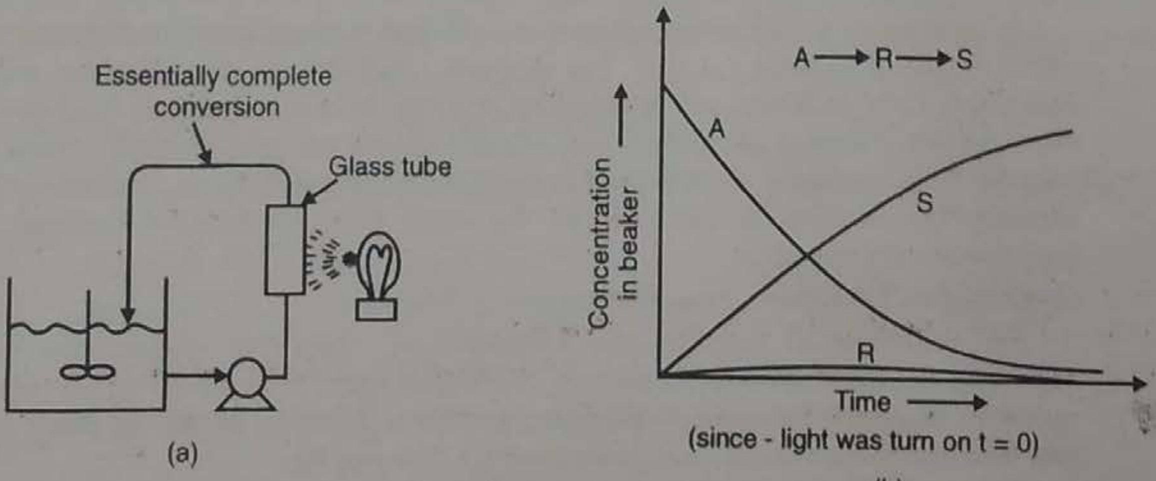
Qualitative Discussion about Product Distribution :

For qualitative discussion about product distribution, let us consider the following two methods of treating a beaker containing A.



(a) (b)

Fig. 5.5 : Concentration v/s time curves for contents of the beaker irradiated uniformly



(a) (b)

Fig. 5.6 : Concentration v/s time curves for the contents of the beaker when only small portion of the fluid is irradiated at any instant

Method 1 : Refer to Fig. 5.5. The contents are uniformly irradiated.

Method 2 : Refer to Fig. 5.6. A small portion of fluid is continuously withdrawn from the beaker, irradiated, and returned to the beaker.

Note that the rate of absorption of radiant energy is same in both the cases. During the process, A disappears and products are formed.

In method-1, the contents in the beaker are irradiated all at the same time. As only A is present at the start, a first bit of light will attack A alone and results in formation of R. The next bit of light will attack both A and R, both will compete, however, as A is in large excess it will preferentially absorb the radiant energy and gets decomposed to form more R. Hence, concentration of R will rise and that of A will decrease. This will continue until R is present in enough concentration to compete favourably with A for the radiant energy. When this happens, a maximum concentration of R is reached and afterwards the conversion of R into S becomes more rapid that its formation from A and its concentration decreases. This is shown in concentration v/s time curve of Fig. 5.5.

In method-2, small fraction of the contents of beaker is continuously removed, irradiated and returned to the beaker. Though the total absorption rate is small in the two cases, the intensity of radiation received by the fluid removed from beaker is greater, so the fluid being irradiated reacts essentially to completion when the flow rate is not too high. In this case, then, A is removed from the beaker and S is returned to the beaker. So as the time passes the concentration of A slowly falls, that of S rises in the beaker while R is absent. This is shown in concentration v/s time curve of Fig. 5.6.

These two methods of reacting the contents of the beaker give different product distribution. These methods represent the two extreme conditions in possible operation, one with maximum possible formation of R (method-1) and other with a minimum or no formation of R (method-2). In method-1, the contents of beaker remain homogeneous throughout all changing slowly with time. In method-2, a stream of highly reacted fluid is continuously mixed with fresh fluid, that means, in this case we are mixing two streams of fluid of different compositions.

So with this discussion, we conclude a general rule that governs the product distribution in case of reactions in series – For irreversible reactions in series, the mixing of fluid of different compositions is the key to the formation of intermediate. The maximum possible amount of intermediate is formed if fluid streams of different compositions are not allowed to mix.

In most cases as the intermediate is the desired product, this rule helps us in evaluating the effectiveness of various reactors. For example, plug flow as well as batch reactor should give maximum yield of R because in these reactors there is no mixing of fluid streams of different compositions whereas the mixed flow reactor should not give as high a yield of R as possible because in this reactor a fresh stream containing pure A is being continuously mixed with an already reacted fluid in the reactor. To verify these qualitative findings, we present the quantitative treatment.

Quantitative Treatment, Plug Flow or Batch Reactor :

For reactions in parallel the formation of undesired product can be minimised by adjusting the reaction conditions (e.g. concentration) and by choosing the proper reactor. For reactions in series the most important variable is the time needed to carry out the reaction : real time for batch reactor and space time for flow reactor.

For unimolecular type first order reactions in series such as

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

with rate equations,

$$r_A = \frac{-dC_A}{dt} = k_1 C_A$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R$$

Starting with a feed containing A of concentration C_{Ao} and no R and S present in it, we have derived the equations for change in concentrations of A, R and S i.e. C_A, C_R and C_S as a function of time for batch reactor [Refer chapter -2].

For batch reactor :

The concentration of A varies with time as per the following equation :

$$\frac{C_A}{C_{Ao}} = e^{-k_1t}$$

The concentration of R varies with time according to the following equation :

$$\frac{C_R}{C_{Ao}} = \frac{k_1}{(k_2-k_1)}\left(e^{-k_1t}-e^{-k_2t}\right)$$

The concentration of S varies with time as per the following equation :

$$\frac{C_S}{C_{Ao}} = \left(1+\frac{k_2}{k_1-k_2}\,e^{-k_1t}+\frac{k_1}{k_2-k_1}\,e^{-k_2t}\right)$$

The concentration of S is also found from

$$C_S = C_{Ao}-C_A-C_R$$

If the reaction time (t) in the above equations is replaced by the space time (τ) then these equations are equally applicable to the plug flow reactors.

∴ For plug flow reactor :

$$\frac{C_A}{C_{Ao}} = e^{-k_1\tau} \qquad \ldots (5.25)$$

$$\frac{C_R}{C_{Ao}} = \frac{k_1}{k_2-k_1}\left(e^{-k_1\tau}-e^{-k_2\tau}\right) \qquad \ldots (5.26)$$

$$C_S = C_{Ao}-C_A-C_R \qquad \ldots (5.27)$$

The maximum concentration of intermediate product (R) and the time at which it occurs is given by (Refer chapter-2)

$$\frac{C_{R\,max}}{C_{Ao}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)} \qquad \ldots (5.28)$$

$$\tau_{p,\,opt.} = \frac{1}{k_{log\,mean}} = \frac{\ln(k_2/k_1)}{k_2-k_1} \qquad \ldots (5.29)$$

At this τ_p value, the rate of formation of S is also most fast.

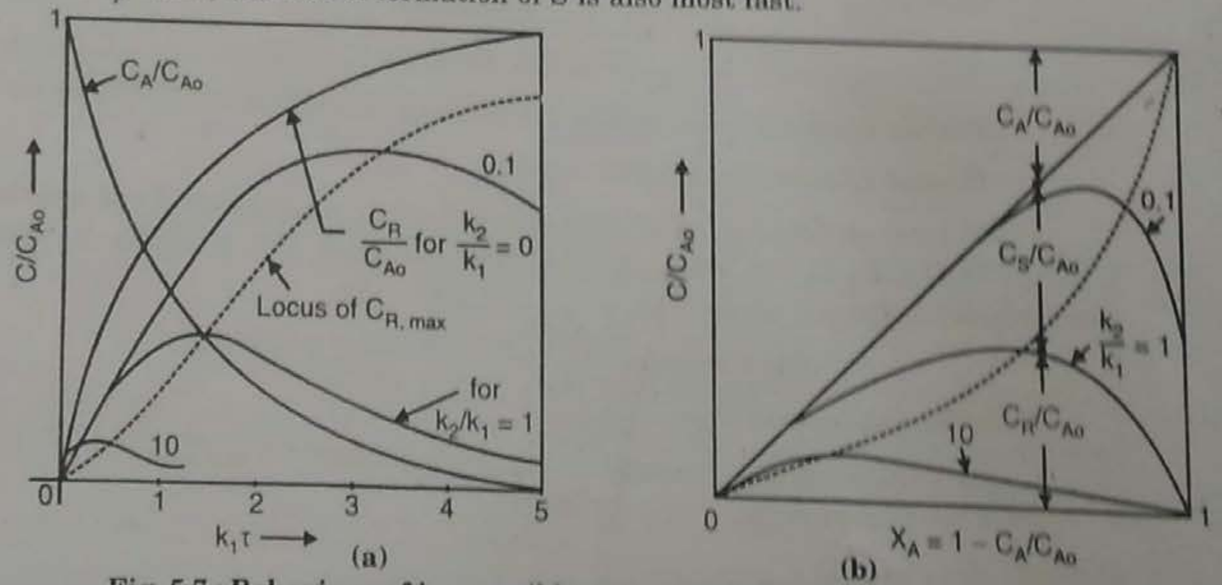


Fig. 5.7 : Behaviour of irreversible unimolecular type first order reactions

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \text{ with } C_{Ro} = C_{So} = 0$$

in plug flow reactor (a) concentration v/s time curves and (b) relative concentrations of the reaction components.

Fig. 5.7 (a) shows the relationship between the concentration of intermediate product R and time for various values of k_2/k_1. This plot thus gives us idea regarding how this ratio k_2/k_1 governs the relationship between C_R and t. Fig. 5.7 (b) is a time independent plot relating the concentrations of all reaction components.

Quantitative Treatment, Mixed Flow Reactor :

Find optimum space time for MFR
in series
for
19M

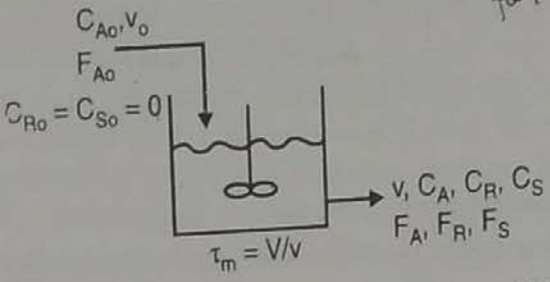


Fig. 5.8 : Variables for series reactions in mixed flow reactor

Consider irreversible unimolecular type first order reactions in series such as

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S \text{ (with first order rate constants } k_1 \text{ and } k_2\text{)}$$

occurring in a mixed flow reactor. For this case now we will develop concentration - time relationships.

Here we are assuming that feed stream contains no R and S.

Steady-state material balance for component A over mixed flow reactor is :

$$\begin{matrix}\text{input of A} \\ \text{(moles/time)}\end{matrix} = \begin{matrix}\text{output of A} \\ \text{(moles/time)}\end{matrix} + \begin{matrix}\text{disappearance of A by reaction} \\ \text{(moles/time)}\end{matrix}$$

(as accumulation term is zero at steady state)

$$F_{Ao} = F_A + (-r_A)\, V$$

$$v_o C_{Ao} = v\, C_A + (-r_A)\, V$$

$$v\, C_{Ao} = v\, C_A + (-r_A)\, V \quad \text{(for constant density, } v_o = v\text{)}$$

$$-r_A = k_1 C_A \quad \text{(for first order reaction)} \qquad \dots (5.30)$$

$$\therefore \quad v\, C_{Ao} = v\, C_A + k_1 C_A V$$

$$\tau_m = \bar{t} = \frac{V}{v} \qquad \dots (5.31)$$

$$C_{Ao} = C_A + k_1 C_A (\tau_m)$$

$$C_{Ao} = C_A (1 + k_1 \tau_m)$$

$$\therefore \quad \frac{C_A}{C_{Ao}} = \frac{1}{1 + k_1 \tau_m} \qquad \dots (5.32)$$

For component R :

Steady-state material balance of R over reactor is :

$$\begin{matrix}\text{Input of R} \\ \text{(moles/time)}\end{matrix} + \begin{matrix}\text{Generation of R} \\ \text{(moles/time)}\end{matrix} = \begin{matrix}\text{Output of R} \\ \text{(moles/time)}\end{matrix} \qquad \dots (5.33)$$

$$v\, C_{Ro} + (r_R)\, V = v\, C_R$$

$$v\, C_{Ro} + (k_1 C_A - k_2 C_R)\, V = v\, C_R$$

$$C_{Ro} = 0$$

$$\therefore \quad (k_1 C_A - k_2 C_R)\, V = v\, C_R$$

$$k_1 C_A V - k_2 C_R V = v\, C_R$$

As $$\tau_m = \frac{V}{v}$$

$$C_R = k_1 C_A \tau_m - k_2 C_R \tau_m$$

$$C_R(1 + k_2 \tau_m) = k_1 C_A \tau_m \quad \text{... (5.34)}$$

We have from equation (5.32),

$$C_A = C_{Ao}/(1 + k_1 \tau_m)$$

$\therefore$ Putting this value of C_A into equation (5.34),

$$C_R(1 + k_2 \tau_m) = \frac{k_1 C_{Ao} \tau_m}{(1 + k_1 \tau_m)}$$

$$\therefore \quad C_R = \frac{k_1 C_{Ao} \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)} \quad \text{... (5.35)}$$

$$\frac{C_R}{C_{Ao}} = \frac{k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)} \quad \text{... (5.36)}$$

At any time,

As there is no change in total number of moles, the stoichiometry relates the concentrations of the reacting components by the relation

$$C_A + C_R + C_S = C_{Ao} = \text{constant}$$

$$C_S = C_{Ao} - C_A - C_R$$

$$C_S = C_{Ao} - \frac{C_{Ao}}{(1 + k_1 \tau_m)} - \frac{k_1 C_{Ao} \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)}$$

$$\frac{C_S}{C_{Ao}} = \frac{(1 + k_1 \tau_m)(1 + k_2 \tau_m) - (1 + k_2 \tau_m) - k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)}$$

$$\frac{C_S}{C_{Ao}} = \frac{k_1 k_2 \tau_m^2}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)} \quad \text{... (5.37)}$$

The maximum concentration of the intermediate product R (desired) and the corresponding space time are found out determining $dC_R/d\tau_m$ and setting it equal to zero.

$$C_R = \frac{C_{Ao} k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)}$$

$$\frac{dC_R}{d\tau_m} = 0 = \frac{C_{Ao} k_1 (1 + k_1 \tau_m)(1 + k_2 \tau_m) - C_{Ao} k_1 \tau_m [k_1(1 + k_2 \tau_m) + k_2(1 + k_1 \tau_m)]}{(1 + k_1 \tau_m)^2 (1 + k_2 \tau_m)^2}$$

$$C_{Ao} k_1 (1 + k_1 \tau_m)(1 + k_2 \tau_m) - C_{Ao} k_1 \tau_m [k_1 (1 + k_2 \tau_m) + k_2 (1 + k_1 \tau_m)] = 0$$

$$C_{Ao} k_1 (1 + k_1 \tau_m)(1 + k_2 \tau_m) = C_{Ao} k_1 \tau_m [k_1 (1 + k_2 \tau_m) + k_2 (1 + k_1 \tau_m)]$$

$$(1 + k_1 \tau_m)(1 + k_2 \tau_m) = \tau_m [k_1 (1 + k_2 \tau_m) + k_2 (1 + k_1 \tau_m)]$$

$$1 + k_2 \tau_m + k_1 \tau_m + k_1 k_2 \tau_m^2 = k_1 \tau_m + k_1 k_2 \tau_m^2 + k_2 \tau_m + k_1 k_2 \tau_m^2$$

$$1 = k_1 k_2 \tau_m^2$$

$$\tau_m^2 = 1/k_1 k_2$$

$$\tau_{m,\,opt.} = \frac{1}{\sqrt{k_1 k_2}} \quad \text{... (5.38)}$$

This is the space time at which maximum concentration of R occurs.

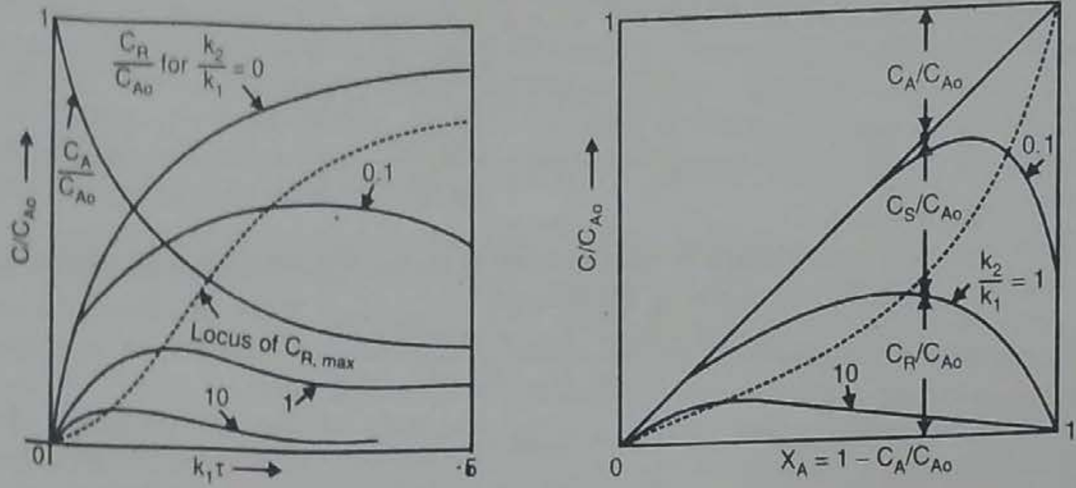
The maximum concentration of R is obtained by putting τ_m from equation (5.38) into equation (5.36).

$$\frac{C_{R\,max}}{C_{A_0}} = \frac{k_1 (k_1 k_2)^{-1/2}}{[1 + k_1 (k_1 k_2)^{-1/2}]\ [1 + k_2 (k_1 k_2)^{-1/2}]}$$

$$= \frac{(k_1/k_2)^{1/2}}{[1 + (k_1/k_2)^{1/2}]\ [1 + (k_2/k_1)^{1/2}]}$$

$$= \frac{(k_1/k_2)^{1/2}}{(k_1/k_2)^{1/2}\ [(k_2/k_1)^{1/2} + 1]\ \ [1 + (k_2/k_1)^{1/2}]}$$

$$\therefore \quad \frac{C_{R\,max}}{C_{A_0}} = \frac{1}{[(k_2/k_1)^{1/2} + 1]^2} \qquad \dots (5.39)$$



(a) Concentration v/s time curves for A→ R→ S (unimolecular) in mixed flow reactor

(b) Relative concentrations of the reaction components for A → R → S (unimolecular) in mixed flow reactor

Fig. 5.9

The time-concentration behaviour for first order reactions in series for plug flow and mixed flow reactors shown in Figs. 5.7 (a) and 5.9 (a) respectively are helpful in visualising the actual progress of the reaction.

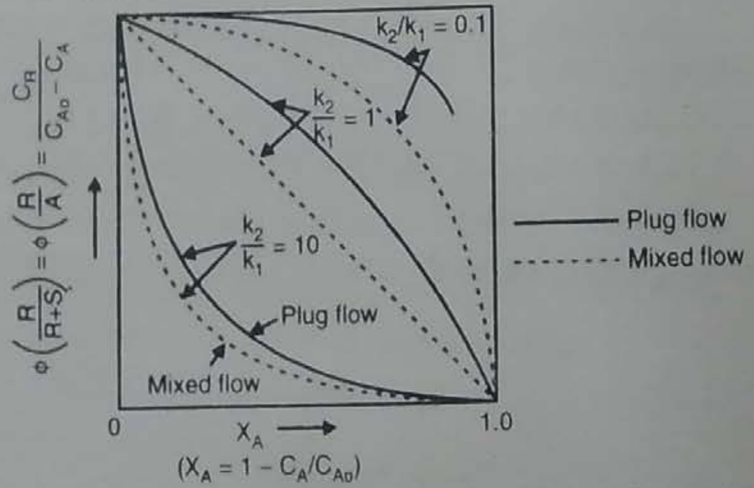


Fig. 5.10 : Comparison of the fractional yields of R in plug flow and mixed flow reactors for irreversible unimolecular first order reactions $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

(i) Comparing these two figures we conclude that except for $k_1 = k_2$, the plug flow reactor needs a smaller time than required by mixed flow reactor to achieve maximum concentration of R and the time difference $(\tau_p - \tau_m)$ becomes progressively larger as the ratio k_2/k_1 departs from unity [Refer equations (5.29) and (5.38)].

(ii) For any reaction, the maximum attainable concentration of desired product, R, in a plug flow reactor is always higher than that it in mixed flow reactor.

The fractional yields of desired product R as a function of the concentration level and the rate constant ratio (as a parameter) for plug flow and mixed flow reactors are plotted in Fig. 5.10.

From the curves of Fig. 5.10, we conclude that (i) the fractional yield of R is always higher in plug flow reactor than in mixed flow reactor for any conversion level, (ii) if k_2/k_1 is smaller than unity we should design a reactor for high conversion of A and if k_2/k_1 is greater than unity we should design a reactor for a very small conversion of A per pass, separation of R, and recycle of unused reactant (to avoid formation of unwanted S as the fractional conversion decreases sharply even at low conversion).

Irreversible first order reaction followed by zero-order reaction :

Consider reactions in series such as $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

Reaction – A to R follows the first order kinetics and reaction – R to S follows zero order kinetics.

So the rate of disappearance of A is given by

$$-r_A = k_1 C_A \qquad \ldots (5.40)$$

and the net rate of formation of R is given by

$$r_R = k_1 C_A - k_2 C_A^0$$

$$r_R = k_1 C_A - k_2 \qquad \ldots (5.41)$$

For batch or plug flow reactor with

$$C_{Ro} = C_{So} = 0$$

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A$$

$$\frac{-dC_A}{C_A} = k_1\, dt$$

Integrating, we get,

$$-\ln (C_A/C_{Ao}) = k_1 t$$

$$\therefore \quad \frac{C_A}{C_{Ao}} = e^{-k_1 t} \qquad \ldots (5.42)$$

$$\frac{dC_R}{dt} = k_1 C_A - k_2$$

$$\frac{dC_R}{dt} = k_1 C_{Ao} e^{-k_1 t} - k_2$$

$$\int_{C_{Ro}}^{C_R} dC_R = \int_0^t (k_1 C_{Ao} e^{-k_1 t} - k_2)\, dt$$

$$C_R - C_{Ro} = k_1 C_{Ao} \int_0^t e^{-k_1 t}\, dt - \int_0^t k_2\, dt$$

$$= k_1 C_{Ao} \left[\frac{1}{-k_1} e^{-k_1 t}\right]_0^t - k_2 t$$

$$C_R - C_{Ro} = -C_{Ao}\, e^{-k_1 t} + C_{Ao} - k_2 t$$

But

$$C_{Ro} = 0$$

$$\therefore \quad C_R = C_{Ao}(1 - e^{-k_1 t}) - k_2 t$$

$$\frac{C_R}{C_{Ao}} = 1 - e^{-k_1 t} - \frac{k_2 t}{C_{Ao}} \qquad \dots (5.43)$$

For plug flow, replace t by τ and use above equations.

The maximum concentration of R, $C_{R,\,max}$, and the time at which it occurs is obtained by differentiating C_R with respect to t and setting $dC_R/dt = 0$.

$$C_R = C_{Ao}\left[1 - e^{-k_1 t} - \frac{k_2 t}{C_{Ao}}\right]$$

$$\frac{dC_R}{dt} = 0 = C_{Ao}\left[0 - (-k_1)\, e^{-k_1 t} - \frac{k_2}{C_{Ao}}\right]$$

$$\therefore \quad k_1\, e^{-k_1 t} = \frac{k_2}{C_{Ao}}$$

$$e^{-k_1 t} = \frac{k_2/C_{Ao}}{k_1}$$

Let

$$\frac{k_2/C_{Ao}}{k_1} = K$$

$$e^{-k_1 t} = K$$

t is time at which $C_R = C_{R,\,max}$. So denoting it by $t_{R,\,max}$

$$-k_1 \cdot t_{R,\,max} = \ln K$$

$$t_{R,\,max} = \frac{1}{k_1} \ln\left(\frac{1}{K}\right) \qquad \dots (5.44)$$

Put the value of t from equation (5.44) into equation (5.43) to get $C_{R,\,max}$.

$$C_{R,\,max} = C_{Ao}\left[1 - \exp.\left[-k_1 \cdot \frac{1}{k_1} \cdot \ln\left(\frac{1}{K}\right)\right] - k_2 \cdot \frac{1}{k_1 C_{Ao}} \ln\left(\frac{1}{K}\right)\right]$$

$$\frac{C_{R,\,max}}{C_{Ao}} = 1 - K - K \ln(1/K), \text{ as } K = \frac{k_2/C_{Ao}}{k_1}$$

$$= 1 - K + K \ln K$$

$$= 1 - K(1 - \ln K) \qquad \dots (5.45)$$

$$\therefore \quad \frac{C_{R,\,max}}{C_{Ao}} = 1 - K(1 - \ln K)$$

Product distribution for these reactions in series is shown in Fig. 5.11.

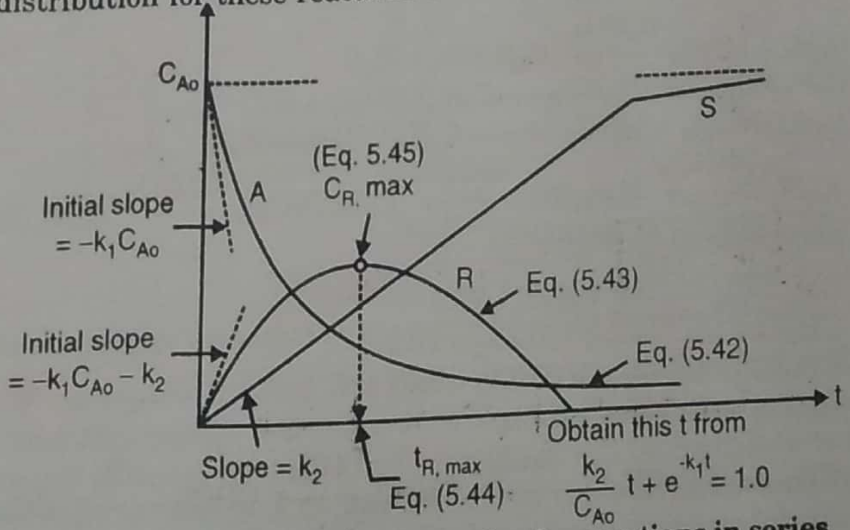


Fig. 5.11 : Product distribution for reactions in series

$$A \xrightarrow{n\,=\,1} R \xrightarrow{m\,=\,0} S$$

Zero order reaction followed by first order reaction :

Consider reactions in series such as

$$A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_2=1]{k_2} S$$

Rate equations with respect to A and R are

$$-r_A = k_1$$

$$r_R = k_1 - k_2\,C_R, \qquad \text{when A is present}$$

$$r_R = -k_2\,C_R, \qquad \text{when A is absent}$$

For batch or plug flow with $C_{Ro} = C_{So} = 0$ and $K = \dfrac{k_2}{k_1/C_{Ao}}$,

$$-r_A = k_1$$

$$\frac{-dC_A}{dt} = k_1$$

$$C_{Ao} - C_A = k_1 t$$

$$C_A = C_{Ao} - k_1 t$$

$$\frac{C_A}{C_{Ao}} = 1 - \frac{k_1 t}{C_{Ao}} \qquad \text{... (5.46)}$$

$$r_R = \frac{dC_R}{dt} = k_1 - k_2\,C_R$$

$$\frac{dC_R}{dt} + k_2\,C_R = k_1$$

It is first order differential equation of the form

$$\frac{dy}{dx} + Py = Q$$

Integrating factor is $e^{\int P dx}$

By multiplying through with integrating factor, the solution is

$$y\,e^{\int P\,dx} = \int Q \cdot e^{\int P dx} \cdot dx + I$$

$$y\,e^{\int P\,dx} = e^{\int k_2\,dt} = e^{k_2 t}$$

$$Q = k_1$$

$$\int Q\,e^{\int P dx} \cdot dx = \int k_1 \cdot e^{k_2 t}\,dt = \frac{k_1}{k_2}\,e^{k_2 t}$$

$$y\,e^{\int P\,dx} = C_R \cdot e^{k_2 t}$$

$$\therefore \quad C_R\,e^{k_2 t} = \frac{k_1}{k_2}\,e^{k_2 t} + I$$

At $t = 0$, $\quad C_R = C_{Ro} = 0$

$$\therefore \quad I = \frac{-k_1}{k_2}$$

∴ $$C_R e^{k_2 t} = \frac{k_1}{k_2} e^{k_2 t} - \frac{k_1}{k_2}$$

$$C_R = \frac{k_1}{k_2} - \frac{k_1}{k_2} e^{-k_2 t}$$

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

Let, $$K = \frac{k_2}{k_1/C_{A0}}$$

∴ $$\frac{k_1}{k_2} = \frac{C_{A0}}{K}$$

$$C_R = \frac{C_{A0}}{K} (1 - e^{-k_2 t})$$

$$\frac{C_R}{C_{A0}} = \frac{1}{K}(1 - e^{-k_2 t}) \qquad \text{for } t < \frac{C_{A0}}{k_1} \qquad \ldots (5.47)$$

We have, $$C_A = C_{A0} - k_1 t$$

$$\text{for } t = C_{A0}/k_1, \quad C_A = 0$$

The time at which the concentration of A is zero and that of C_R is maximum is the $t_{R\,max}$.

$$t_{R\,max} = C_{A0}/k_1 \qquad \ldots (5.48)$$

$$\frac{C_{R\,max}}{C_{A0}} = \frac{1}{K} (1 - e^{-k_2 \cdot C_{A0}/k_1})$$

$$\frac{C_{R,\,max}}{C_{A0}} = \frac{1}{K} (1 - e^{-K}), \quad \text{where } K = \frac{k_2}{k_1/C_{A0}} \qquad \ldots (5.49)$$

After $t = C_{A0}/k_1$ i.e. $t_{R\,max}$, A is absent

∴ $$r_R = -k_2 C_R$$

$$\frac{dC_R}{dt} = -k_2 C_R$$

$$\frac{dC_R}{C_R} = -k_2 \, dt$$

$$\int_{C_{R,\,max}}^{C_R} \frac{dC_R}{C_R} = -k_2 \int_{C_{A0}/k_1}^{t} dt$$

$$\ln\left(\frac{C_R}{C_{R,\,max}}\right) = -k_2\left[t - \frac{C_{A0}}{k_1}\right]$$

$$= -k_2 t + \frac{k_2 C_{A0}}{k_1}$$

$$\ln\left(\frac{C_R}{C_{R,\,max}}\right) = K - k_2 t$$

$$\frac{C_R}{C_{R,\,max}} = e^{K - k_2 t}$$

Putting $C_{R,\,max}$ value in above equation from equation (5.49)

$$\frac{C_R}{\frac{C_{A0}(1 - e^{-K})}{K}} = e^{K - k_2 t}$$

$$\frac{C_R}{C_{Ao}} = \frac{1}{K}(1-e^{-K})\cdot e^{K-k_2t}$$

$$\frac{C_R}{C_{Ao}} = \frac{1}{K}\left[e^{K-k_2t} - e^{-K+K-k_2t}\right]$$

$$\frac{C_R}{C_{Ao}} = \frac{1}{K}\left[e^{K-k_2t} - e^{-k_2t}\right] \quad \text{for } t > C_{Ao}/k_1 \qquad \dots (5.50)$$

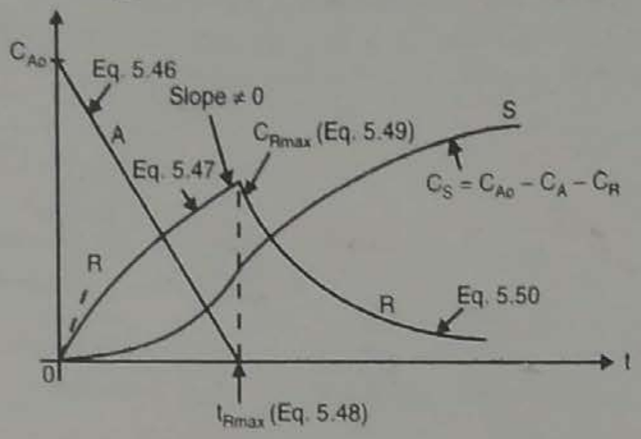


Fig. 5.12 : Product distribution for reactions $A \xrightarrow[n_1=0]{k_1} R \xrightarrow[n_1=1]{k_2} S$

Two-step Irreversible Series - Parallel Reactions :

Multiple reactions consisting of steps in series and in parallel are called series-parallel reactions. For such reactions, these is a greater choice of contacting yielding wider differences in product distribution.

General representation of such reactions is

$$A + B \xrightarrow{k_1} R$$
$$R + B \xrightarrow{k_2} S$$
$$S + B \xrightarrow{k_3} T$$

or $A \xrightarrow{+B,\,k_1} R \xrightarrow{+B,\,k_2} S \xrightarrow{+B,\,k_3} T$

where A is the compound to be converted, B is the reactive material, and R, S, and T are the polysubstituted products formed during the reaction.

Some examples of such reactions : The substitution reactions such as :

(i) Nitration of benzene :

$$C_6H_6 + HNO_3 \xrightarrow{H_2SO_4} C_6H_5NO_2 + H_2O$$
$$C_6H_5NO_2 + HNO_3 \longrightarrow C_6H_4(NO_2)_2 + H_2O$$
$$C_6H_4(NO_2)_2 + HNO_3 \longrightarrow C_6H_3(NO_2)_3 + H_2O$$
$$C_6H_6 \xrightarrow{+HNO_3} C_6H_5NO_2 \xrightarrow{+HNO_3} C_6H_4(NO_2)_2 \xrightarrow{+HNO_3} C_6H_3(NO_2)_3$$

(ii) Chlorination of methane :

$$CH_4 + Cl_2 \xrightarrow{U.V.} CH_3Cl + HCl$$
$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$
$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$
$$CHCl_3 + Cl_2 \longrightarrow CCl_4$$
$$CH_4 \xrightarrow{+Cl_2} CH_3Cl \xrightarrow{+Cl_2} CH_2Cl_2 \xrightarrow{+Cl_2} CHCl_3 \xrightarrow{+Cl_2} CCl_4$$

Now we will consider the two-step reaction in which the first substitution product is desired. In reality, for an n-step reaction, steps third onwards do not occur to any appreciable extent and may be ignored if the ratio (moles of A/moles of B) is high.

Consider reaction set such as :

$$\begin{aligned} A + B &\xrightarrow{k_1} R \\ R + B &\xrightarrow{k_2} S \end{aligned} \qquad \text{... (5.51)}$$

Assume that the reactions are irreversible, bimolecular and of constant density ($\varepsilon = 0$).

The rate equations are :

$$-r_A = \frac{-dC_A}{dt} = k_1 C_A C_B \qquad \text{... (5.52)}$$

$$-r_B = \frac{-dC_B}{dt} = k_1 C_A C_B + k_2 C_R C_B \qquad \text{... (5.53)}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A C_B - k_2 C_R C_B \qquad \text{... (5.54)}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R C_B \qquad \text{... (5.55)}$$

Refer octave also

Qualitative Discussion about Product Distribution :

To get idea regarding difference in the product distribution based upon how we mix A and B, consider the following methods of mixing the reactants.

(i) Add A slowly to B. (ii) Add B slowly to A. (iii) Mix A and B together rapidly.

(i) Add A slowly to B : Add A a little at a time (from beaker containing A) to the beaker containing B, stirr thoroughly, and make sure that all the A is consumed and that reaction stops before we add the next bit of A. With each bit of A added, a bit of R is produced and this R find itself in excess of B so it reacts further with B to produce S. So during slow addition of A to B, A and R will not be present in an appreciable amount. As we go on adding A, the mixture becomes progressively richer in S and poorer in B and this will continue till the beaker contains only S (Refer Fig. 5.13).

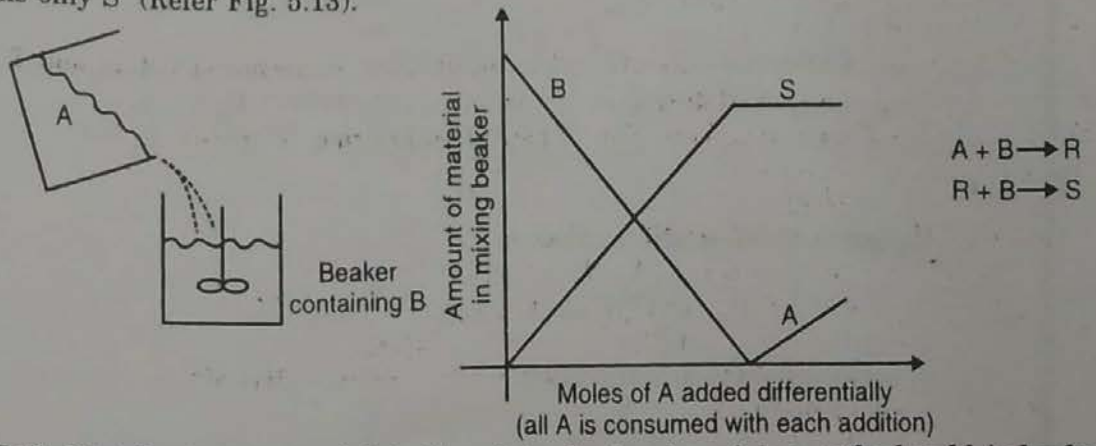


Fig. 5.13 : Distribution of materials in the mixing beaker for-mixing method : add A slowly to B

(ii) Add B slowly to A : Add B a little at a time (differential addition) to the beaker containing A, stirr thoroughly, and make sure that all the B is consumed and that the reaction stops before we add the next bit of B. The first bit of B will be consumed to produce R and this R will not react further to form S as no B is present in the mixing beaker. For the addition of the next bit of B, both A and R will compete with each other to undergo reaction with B added. As A is in large excess in the mixing beaker (compared to R), it will react with most A resulting in more formation of R. This process of progressive build up of R and depletion of A will be continued (along with some formation of S) until the concentration of R reaches such a value that it can compete favourably with A for each bit of B added. When this happens, the concentration of R reaches a maximum and then decreases progressively and that of S increases.

Ultimately, after adding 2 moles of B for each mole of A, we get a solution containing only S (Refer Fig. 5.14).

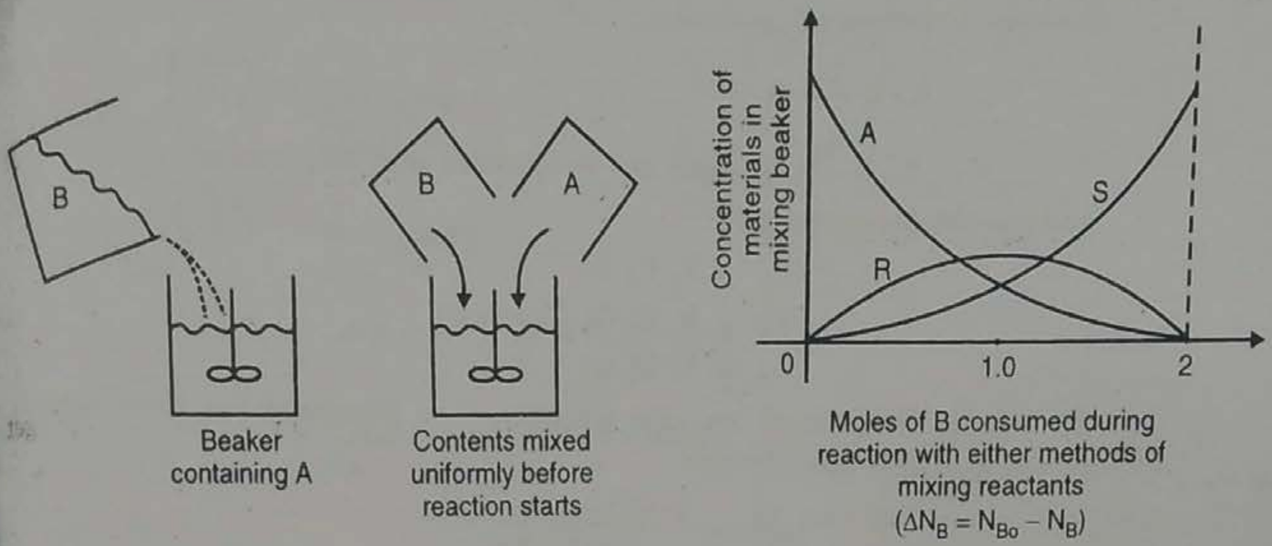


Fig. 5.14 : Distribution of materials in the mixing beaker for either of mixing method of reactants (i) Add B slowly to A and (ii) Mix A and B rapidly

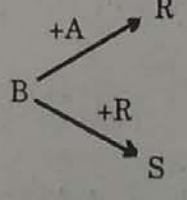
(iii) Mix A and B rapidly : In this case, the contents of the two beakers are rapidly mixed together. The reaction does not proceed to any appreciable extent unless the mixture is uniform throughout. During first few reaction increments, R also competes with a large excess of A for B. So there is formation of R, with some S and depletion of A till concentration of R reaches a maximum and then decreases. For this method, we get thus the same type of distribution curve as for the mixture in which B is added slowly to A (Refer Fig. 5.14).

The product distributions shown in Figs. 5.13 and 5.14 are totally different. When A is kept uniform in composition during the course of reaction (as it reacts), as shown in Fig. 5.14, then R is formed. However, when fresh A is mixed with partly reacted mixture, as shown in Fig. 5.13 then no R is formed.

This is precisely the behaviour of reactions in series. Hence as far as A, R and S are concerned, we may view the reactions of equation (5.50) as

$$A \xrightarrow{+B} R \xrightarrow{+B} S$$

As seen from Fig. 5.14 the concentration of B high or low has no effect on the reaction path and on the distribution of products. This is precisely the behaviour of parallel reactions of the same order. Hence as far as B is concerned, we may view the reactions of equation (5.51) as



So we can analyse the irreversible series-parallel reactions in terms of their constituent series reactions and parallel reactions in that optimum contacting for favourable product distribution.

So for reactions of equation (5.51) when intermediate R is the desired product, the best of contacting A and B is to keep A uniform in composition as it reacts and B in any convenient way.

Quantitative Treatment – Plug Flow or Batch Reactor :

Consider a reaction set, such as

$$A + B \xrightarrow{k_1} R$$

$$R + B \xrightarrow{k_2} S \quad \text{(both are irreversible and bimolecular)}$$

and R is the desired product.

$$-r_A = k_1 C_A C_B$$

$$r_R = k_1 C_A C_B - k_2 C_R C_B$$

$$r_S = k_2 C_R C_B$$

By taking the ratio of two rate equations, we eliminate the time variable and get information of product distribution.

$$\frac{r_R}{r_A} = \frac{k_1 C_A C_B - k_2 C_R C_B}{-k_1 C_A C_B}$$

$$\frac{r_R}{r_A} = -1 + \frac{k_2 C_R}{k_1 C_A} \qquad \text{... (5.56)}$$

$$\frac{r_R}{r_A} = \frac{dC_R}{dC_A} = -1 + \frac{k_2 C_R}{k_1 C_A}$$

$$\frac{dC_R}{dC_A} - \frac{k_2 C_R}{k_1 C_A} = -1 \qquad \text{... (5.57)}$$

Equation (5.57) is the first order linear differential equation.

With no R present in the feed, the limits of integration are C_{A_0} to C_A and $C_{R_0} = 0$ for R.

Now we will obtain solution of this differential equation.

$$\frac{dy}{dx} + Py = Q \quad \text{and} \quad \frac{dC_R}{dC_A} - \frac{k_2}{k_1 C_A} \cdot C_R = -1$$

$$\therefore \quad P = -k_2/k_1 C_A, \quad Q = -1 \quad \text{and} \quad y = C_R.$$

$$\int P\,dx = \int \frac{-k_2}{k_1 C_A}\,dC_A = \frac{-k_2}{k_1} \ln C_A = \ln C_A^{-k_2/k_1}$$

$$\text{Integrating factor} = \text{I.F.} = e^{\int P\,dx} = e^{\ln C_A^{-k_2/k_1}} = C_A^{-k_2/k_1}$$

Solution is

$$C_R \times \text{I.F.} = \int Q \times \text{I.F.} \times dC_A + I$$

$$C_R \cdot C_A^{-k_2/k_1} = \int -1\,(C_A)^{-k_2/k_1}\,dC_A + I \qquad \text{... (5.58)}$$

$$= -\int (C_A)^{-k_2/k_1} + I = \frac{C_A^{(-k_2/k_1)+1}}{\frac{-k_2}{k_1} + 1} + I$$

$$C_R \cdot C_A^{-k_2/k_1} = \frac{C_A^{(-k_2/k_1)+1}}{\frac{-k_2}{k_1}+1} + I \qquad \dots (5.59)$$

At $t=0$, $C_A = C_{Ao}$ and $C_{Ro} = 0$

Putting this condition in equation (5.59), find I.

$$\therefore \qquad 0 = \frac{-C_{Ao}^{(-k_2/k_1)+1}}{\frac{-k_2}{k_1}+1} + I$$

$$\therefore \qquad I = \frac{-(C_{Ao})^{(-k_2/k_1)+1}}{\frac{-k_2}{k_1}+1}$$

Putting this value of I (constant of integration) in equation (5.59),

$$C_R C_A^{-k_2/k_1} = -\frac{C_A^{(-k_2/k_1)+1}}{\frac{-k_2}{k_1}+1} + \frac{C_{Ao}^{(-k_2/k_1)+1}}{\frac{-k_2}{k_1}+1}$$

$$= \frac{1}{\frac{-k_2}{k_1}+1}\left[(C_{Ao})^{(-k_2/k_1)+1} - (C_A)^{(-k_2/k_1)+1}\right]$$

$$C_R = \frac{1}{\frac{-k_2}{k_1}+1}\left[\frac{C_{Ao}^{(-k_2/k_1)+1}}{C_A^{-k_2/k_1}} - \frac{C_A^{(-k_2/k_1)+1}}{C_A^{-k_2/k_1}}\right]$$

$$= \frac{1}{1-\frac{k_2}{k_1}}\left[\frac{C_{Ao}^{(-k_2/k_1)+1}}{C_A^{-k_2/k_1}} - C_A\right] \qquad \dots (5.60)$$

Dividing both sides of above equation by C_{Ao} we get,

$$\frac{C_R}{C_{Ao}} = \frac{1}{\left(1-\frac{k_2}{k_1}\right)}\left[\frac{C_{Ao}^{-k_2/k_1}}{C_A^{-k_2/k_1}} - \frac{C_A}{C_{Ao}}\right]$$

$$\therefore \qquad \frac{C_R}{C_{Ao}} = \frac{1}{\left(1-\frac{k_2}{k_1}\right)}\left[\left(\frac{C_A}{C_{Ao}}\right)^{k_2/k_1} - \frac{C_A}{C_{Ao}}\right], \quad \frac{k_2}{k_1} \neq 1 \qquad \dots (5.61)$$

Equation (5.58) is also written as

$$C_R \cdot C_A^{-k_2/k_1} = -\int (C_A)^{-k_2/k_1} dC_A + I_1$$

I_1 is the constant of integration.

$$\text{If } \frac{k_2}{k_1} = 1$$

$$C_R \cdot C_A^{-1} = -\int (C_A)^{-1}\, dC_A + I_1$$

$$= -\int \frac{dC_A}{C_A} + I_1$$

$$\frac{C_R}{C_A} = -\ln C_A + I_1 \qquad \dots (5.62)$$

$$\text{If } C_A = C_{A_0} \text{ and } C_{R_0} = 0$$

$$0 = -\ln C_{A_0} + I_1$$

$$\therefore \quad I_1 = \ln C_{A_0}$$

Putting this value of I_1 in equation (5.61),

$$\frac{C_R}{C_A} = -\ln C_A + \ln C_{A_0}$$

$$\frac{C_R}{C_A} = \ln\left(\frac{C_{A_0}}{C_A}\right)$$

Multiplying both the sides of above equation by C_A/C_{A_0}, we get,

$$\frac{C_R}{C_{A_0}} = \frac{C_A}{C_{A_0}} \ln\left[\frac{C_{A_0}}{C_A}\right] \quad \text{for } \frac{k_2}{k_1} = 1 \qquad \dots (5.63)$$

For obtaining $C_{R,\,max}$, set $dC_R/dC_A = 0$

We have,

$$\frac{C_R}{C_{A_0}} = \frac{C_A}{C_{A_0}} \ln \frac{C_{A_0}}{C_A}$$

$$\therefore \quad C_R = C_A [\ln C_{A_0} - \ln C_A]$$

$$\frac{dC_R}{dC_A} = C_A\left[0 - \frac{1}{C_A}\right] + 1 \times [\ln C_{A_0} - \ln C_A]$$

$$= -1 + \ln C_{A_0} - \ln C_A$$

$$= -1 + \ln\left(\frac{C_{A_0}}{C_A}\right)$$

$$dC_R/dt = 0 = -1 + \ln (C_{A_0}/C_A)$$

$$\therefore \quad \ln (C_{A_0}/C_A) = 1$$

$$\frac{C_{A_0}}{C_A} = e^1$$

$$C_A = \frac{C_{A_0}}{e} \qquad \dots (5.64)$$

Put the value of C_A from equation (5.64) into equation (5.63) to get $C_{R,\,max}$.

$$\therefore \quad \frac{C_{R\,max}}{C_{A_0}} = \frac{C_{A_0}/e}{C_{A_0}} \ln\left[\frac{C_{A_0}}{C_{A_0}/e}\right]$$

$$= \frac{1}{e} \ln (e)$$

$$= \frac{1}{e} \times 1$$

$$= \frac{1}{e}$$

$$\therefore \quad \frac{C_{R\,max}}{C_{A_0}} = \frac{1}{e} = 0.368, \quad \text{for } \frac{k_2}{k_1} = 1 \qquad \dots (5.65)$$

We have equation (5.60) as :

$$C_R = \frac{1}{1 - \frac{k_2}{k_1}}\left[\frac{C_{A_0}^{(-k_2/k_1)+1}}{C_A^{-k_2/k_1}} - C_A\right]$$

To find $C_{R,\,max}$ for $k_2/k_1 \neq 1$, differentiate above equation w.r.t. C_A and set $dC_R/dC_A = 0$.

$$\frac{dC_R}{dC_A} = \frac{1}{\left(1-\frac{k_2}{k_1}\right)}\left[C_{Ao}^{(-k_2/k_1)+1}\cdot\frac{d}{dC_A}\left[C_A^{k_2/k_1}\right]-1\right]$$

$$= \frac{1}{1-\frac{k_2}{k_1}}\left[(C_{Ao})^{(-k_2/k_1)+1}\cdot\frac{k_2}{k_1}C_A^{(k_2/k_1)-1}-1\right] = 0$$

$$(C_{Ao})^{\left(\frac{-k_2}{k_1}\right)+1}\cdot\left(\frac{k_2}{k_1}\right)C_A^{(k_2/k_1)-1}-1 = 0$$

$$(C_{Ao})^{\left(\frac{-k_2}{k_1}\right)+1}\cdot\frac{k_2}{k_1}\cdot C_A^{(k_2/k_1)-1} = 1.0$$

$$C_A^{(k_2/k_1)-1} = \frac{k_1}{k_2}\left(\frac{1}{C_{Ao}^{(-k_2/k_1)+1}}\right)$$

$$C_A^{(k_2/k_1)-1} = \frac{k_1}{k_2}C_{Ao}^{-1+(k_2/k_1)}$$

$$C_A = \left[\frac{k_1}{k_2}\cdot(C_{Ao})^{(k_2/k_1)-1}\right]^{\frac{1}{\frac{k_2}{k_1}-1}}$$

$$= \left(\frac{k_1}{k_2}\right)^{k_1/k_2-k_1}\cdot C_{Ao}^{\frac{k_2-k_1}{k_1}\cdot\frac{k_1}{k_2-k_1}}$$

$$C_A = \left(\frac{k_1}{k_2}\right)^{k_1/k_2-k_1}\cdot C_{Ao} \qquad \dots(5.66)$$

Put this value of C_A from equation (5.66) into equation (5.61) to get $C_{R,\,max}$.

$$\frac{C_{R,\,max}}{C_{Ao}} = \frac{1}{\left(1-\frac{k_2}{k_1}\right)}\left\{\left[\frac{\left(\frac{k_1}{k_2}\right)^{k_1/k_2-k_1}\cdot C_{Ao}}{C_{Ao}}\right]^{k_2/k_1}-\left(\frac{k_1}{k_2}\right)^{k_1/k_2-k_1}\right\}$$

$$= \frac{k_1}{k_1-k_2}\left\{\left(\frac{k_1}{k_2}\right)^{k_2/k_2-k_1}-\left(\frac{k_1}{k_2}\right)^{k_1/k_2-k_1}\right\}$$

$$= \frac{k_1}{k_1-k_2}\left(\frac{k_1}{k_2}\right)^{k_2/k_2-k_1}\left[1-\frac{\left(\frac{k_1}{k_2}\right)^{k_1/k_2-k_1}}{\left(\frac{k_1}{k_2}\right)^{k_2/k_2-k_1}}\right]$$

$$= \frac{k_1}{k_1-k_2}\left(\frac{k_1}{k_2}\right)^{k_2/k_2-k_1}\left[1-\left(\frac{k_1}{k_2}\right)^{(k_1-k_2)/(k_2-k_1)}\right]$$

$$= \frac{k_1}{k_1-k_2}\left(\frac{k_1}{k_2}\right)^{k_2/k_2-k_1}\left[1-\left(\frac{k_1}{k_2}\right)^{-1}\right]$$

$$= \frac{k_1}{k_1 - k_2}\left(\frac{k_1}{k_2}\right)^{k_2/k_2 - k_1}\left[1 - \frac{k_2}{k_1}\right]$$

$$= \frac{k_1}{k_1 - k_2}\left(\frac{k_1}{k_2}\right)^{k_2/k_2 - k_1}\left(\frac{k_1 - k_2}{k_1}\right)$$

$$\therefore \quad \frac{C_{R\,max}}{C_{Ao}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2 - k_1)} \quad \text{for } \frac{k_2}{k_1} \neq 1 \qquad \dots (5.67)$$

Equations (5.61), (5.63), (5.65) and (5.67) give relationship between C_R and C_A in a batch or in a plug flow reactor.

For finding the concentrations of other components, simply make the material balance. An A balance gives

$$C_{Ao} + C_{So} = C_A + C_R + C_S \qquad \dots (5.68)$$

or $\quad \Delta C_A + \Delta C_R + \Delta C_S = 0$

With the help of this, C_S can be found as a function of C_A and C_R.

A balance about B gives

$$\Delta C_B + \Delta C_R + 2\,\Delta C_S = 0 \qquad \dots (5.69)$$

With the help of this, C_B can be found.

Quantitative Treatment, Mixed Flow :

The performance equation for mixed flow reactor in terms of A and R is :

$$\tau_m = \frac{C_{Ao} - C_A}{(-r_A)} = \frac{-C_R}{(-r_R)}$$

$$\tau_m = \frac{C_{Ao} - C_A}{k_1 C_A C_B} = \frac{-C_R}{k_2 C_R C_B - k_1 C_A C_B}$$

$$\therefore \quad \frac{-C_R}{C_{Ao} - C_A} = \frac{k_2 C_R C_B - k_1 C_A C_B}{k_1 C_A C_B}$$

$$\frac{-C_R}{C_{Ao} - C_A} = -1 + \frac{k_2 C_R}{k_1 C_A}$$

$$\frac{-C_R}{C_{Ao} - C_A} = -1 + \left(\frac{k_2}{k_1}\right)\frac{C_R}{C_A}$$

$$-C_R = -(C_{Ao} - C_A) + \left(\frac{k_2}{k_1}\right)\frac{C_R}{C_A}(C_{Ao} - C_A)$$

$$(C_{Ao} - C_A) = C_R\left[1 + \left(\frac{k_2}{k_1}\right)\frac{(C_{Ao} - C_A)}{C_A}\right]$$

$$C_A(C_{Ao} - C_A) = C_R[C_A + (k_2/k_1)(C_{Ao} - C_A)]$$

$$C_R = \frac{C_A(C_{Ao} - C_A)}{[C_A + (k_2/k_1)(C_{Ao} - C_A)]} \qquad \dots (5.70)$$

and

$$\frac{C_{R,\,max}}{C_{Ao}} = \frac{1}{[1 + (k_2/k_1)^{1/2}]^2} \qquad \dots (5.71)$$

$$C_{Ao} + C_{So} = C_A + C_R + C_S \qquad \dots (5.72)$$

and $\quad \Delta C_B + \Delta C_R + 2\Delta C_S = 0 \qquad \dots (5.73)$

SOLVED EXAMPLES

Ex. 5.1 : What reaction schemes and conditions would you use to have maximum concentration of R for the following parallel reactions ?

$$A + B \rightarrow R \text{ (desired)}, \quad r_R = 15 \cdot e^{-273/T} \cdot C_A^{0.5} C_B$$

$$A + B \rightarrow S \text{ (undesired)}, \quad r_S = 200 \cdot e^{-2000/T} \cdot C_A \cdot C_B$$

Solution : For maximum concentration of R i.e. maximum formation of R, the ratio r_R/r_S has to be maximum.

$$\frac{r_R}{r_S} = \frac{15 \times e^{-273/T} \times C_A^{0.5} C_B}{200 \times e^{-2000/T} \times C_A C_B} = \frac{0.075 \cdot e^{-[273-2000]/T}}{(C_A)^{0.5}}$$

It is clear from above equation :

(i) The activation energy of reaction forming S is more that it for reaction forming R. So to maximise r_R/r_S, the reaction should be carried out at low temperature but not so low that the desired reaction does not proceed to any significant extent.

(ii) The amount of R formed can be maximised (amount of S can be minimised) by carrying out reaction at low concentration (as the concentration term is in denominator).

So to have maximum concentration of R (i.e. to maximise the conversion of A to R), we have to operate reactor at (1) low temperatures, and (2) at low concentration of A, which can be achieved by (a) adding inerts – diluting feed with inerts, (b) using low pressures (in case of gas phase reactions) and (c) by using CSTR or a recycle reactor. ... **Ans.**

Ex. 5.2 : The reactant A decomposes as per the reactions :

$$A \rightarrow R, \quad r_R = 0.0012 \exp\left[26000\left(\frac{1}{300} - \frac{1}{T}\right)\right] \cdot C_A$$

$$A \rightarrow S, \quad r_S = 0.0018 \exp\left[25500\left(\frac{1}{300} - \frac{1}{T}\right)\right] C_A^{1.5}$$

$$A \rightarrow T, \quad r_T = 0.0045 \exp\left[5000\left(\frac{1}{300} - \frac{1}{T}\right)\right] C_A^{0.5}$$

How and under what conditions (e.g. reactor type, temperature, pressure, etc.) should the above reactions be carried out to maximise the formation of R (minimise the formation of S and T) ?

Solution :

$$A \rightarrow R \text{ (desired)}, \quad r_R = 0.0012 \exp\left[26000\left(\frac{1}{300} - \frac{1}{T}\right)\right] \cdot C_A$$

$$A \rightarrow S \text{ (undesired)}, \quad r_S = 0.0018 \exp\left[25500\left(\frac{1}{300} - \frac{1}{T}\right)\right] C_A^{1.5}$$

$$A \rightarrow T \text{ (undesired)}, \quad r_T = 0.0045 \exp\left[5000\left(\frac{1}{300} - \frac{1}{T}\right)\right] C_A^{0.5}$$

As seen from the rate equations of formation of R, S, and T, the activation energies of reactions involving formation of R and S are much greater (26000/R, 25500/R) than the activation energy of reaction forming T. The rate of formation of T will be very negligible with respect to rates of formation of R and S at high temperature.

$$\frac{r_R}{r_T} = \text{very large at high temperature}$$

Hence we need to consider the relative rates of R and S at high temperatures.

$$\frac{r_R}{r_S} = \frac{0.0012}{0.0018}\,\frac{\exp.\,[26000\,(1/300 - 1/T)]\cdot C_A}{\exp.\,[25500\,(1/300 - 1/T)]\cdot C_A^{1.5}}$$

$$\frac{r_R}{r_S} = \frac{0.667\, e^{500\,(1/300\,-\,1/T)}}{C_A^{0.5}}$$

From above equation it is clear that :

For r_R/r_S ratio as high as possible i.e. to maximise the formation of R, one has to carry out the reaction at low concentration of A.

So formation of R can be maximised by carrying out reactions at low concentration of A (as $C_A^{0.5}$ is there in the numerator).

Therefore, to maximise the formation of R, we have to operate reactor at high temperature (to minimise the formation of T) and at low concentration of A (to minimise the formation of S).

So carry out the reactions at

(i) High temperature.

(ii) Low concentration of A that can be accomplished by

  (a) Adding inerts i.e. diluting feed with inerts.

  (b) Using low pressures in case of gaseous reactions.

  (c) Using CSTR or recycle reactor. ... **Ans.**

Ex. 5.3 : The desired liquid phase reaction :

$$A + B \rightarrow R + T, \qquad \frac{dC_R}{dt} = \frac{dC_T}{dt} = k_1\, C_A^{1.5}\, C_B^{0.3}$$

is accompanied by the undesired side reaction

$$A + B \rightarrow S + U, \qquad \frac{dC_S}{dt} = \frac{dC_U}{dt} = k_2\, C_A^{0.5}\, C_B^{1.8}$$

Order the contacting schemes given below from the standpoint of favourable product distribution – from most favourable to least favourable.

Contacting schemes :

(1) plug flow reactor

(2) plug flow reactor with side stream of B

(3) plug flow reactor with side stream of A

(4) CSTR.

Solution :

$$A + B \rightarrow R + T \text{ (desired)}, \qquad \frac{dC_R}{dt} = k_1\, C_A^{1.5}\, C_B^{0.30}$$

$$A + B \rightarrow S + U \text{ (undesired)}, \qquad \frac{dC_S}{dt} = k_2\, C_A^{0.5}\, C_B^{1.8}$$

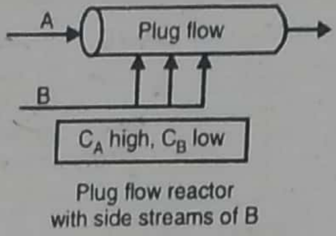
$$\frac{r_R}{r_S} = \frac{k_1 C_A^{1.5} C_B^{0.30}}{k_2 C_A^{0.5} C_B^{1.8}}$$

$$\frac{r_R}{r_S} = \frac{k_1 C_A}{k_2 C_B^{1.5}}$$

For making r_R/r_S as large as possible (for as large formation of R as possible), we have to make concentration of A high (as C_A is in numerator) and concentration of B low (as C_B is in denominator). As the concentration dependency of B is more pronounced than that of A, it is more important to have low C_B than high C_A.

For making high C_A and low C_B which would maximise R we have the scheme :

Plug flow reactor with side stream of B :



C_A high, C_B low

Fig. E 5.3 (1)

(i) With plug flow reactor with side streams of B, we can maintain high C_A and low C_B.

(ii) With CSTR, we can maintain both C_A and C_B low.

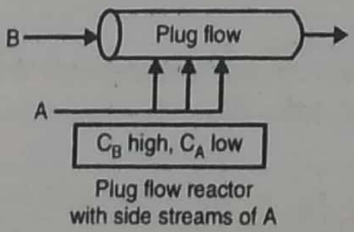
(iii) With plug flow reactor, we can maintain both C_A and C_B high.

(iv) With plug flow reactor with side stream of A, we can maintain C_A low and C_B high.

The least desirable scheme is the one which yields maximum S and minimum R that requires the maximisation of r_S/r_R ratio.

$$\frac{r_S}{r_R} = \frac{k_2}{k_1} \frac{C_B^{1.5}}{C_A}$$

From above equation it is clear that we can maximise S (minimum R) by making C_B high (as C_B is in numerator) and C_A low. High C_B and low C_A can be maintained/accomplished only by using plug flow reactor with side streams of A.



C_B high, C_A low

Fig. E 5.3 (2)

The scheme yielding minimum possible R is the least desirable one as we are concerned with getting as large R as possible.

So least desirable scheme : plug flow reactor with side streams of A.

Maximisation of S is opposite of our aim, that this scheme does, so it is least desirable.

The most desirable scheme for getting as large R as possible is the one which can make C_A high and C_B low. High C_A and low C_B can be accomplished by making use of a plug flow reactor with side streams of B.

So the most desirable scheme is a plug flow reactor with side streams of B.

Out of two schemes remaining, one is CSTR and other is plug flow.

(i) With CSTR we can maintain both C_A and C_B low.

(ii) With plug flow we can maintain both C_A and C_B high.

As the concentration dependency of B is more pronounced than that of A and as we require C_A high and C_B low, out of these two schemes, the one maintaining C_B low is superior to the one maintaining C_B high.

So CSTR is preferred to plug flow. i.e. CSTR is more desirable than a plug flow reactor.

Suggested order of contact schemes from stand point of favourable distribution – from most favourable to least favourable is :

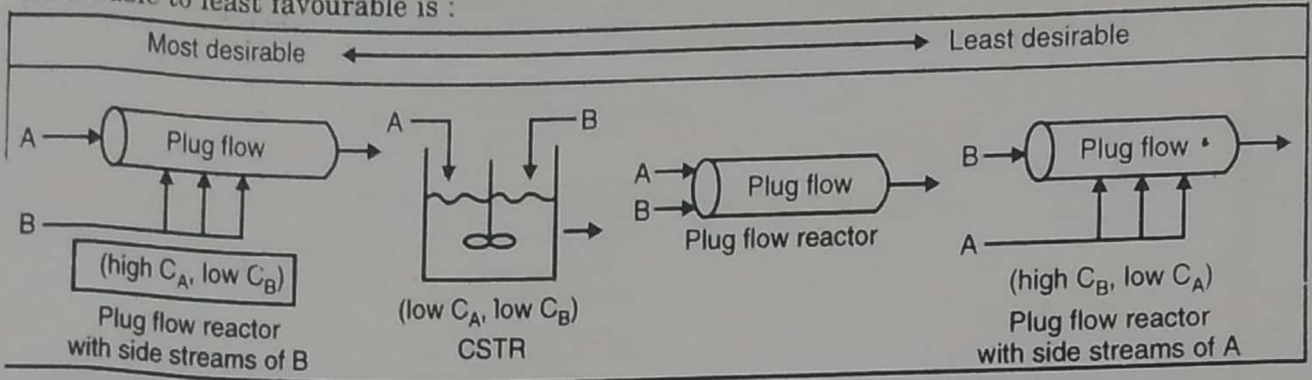
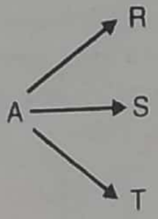


Fig. E 5.3 (3)

Ex. 5.4 : Consider parallel decomposition of A of different orders.



with $r_R = 1$, $r_S = 2\,C_A$ and $r_T = C_A^2$.

Determine the maximum expected C_S for isothermal operations

(i) in mixed flow reactor

(ii) in plug flow reactor

(iii) in any reactor of your choice if unreacted A can be separated from the product stream and returned to feed. In feed, take $C_{Ao} = 2$.

Solution :

$$A \rightarrow R, \qquad r_R = 1.0$$

$$A \rightarrow S, \text{ (desired)} \qquad r_S = 2\,C_A$$

$$A \rightarrow T, \qquad r_T = C_A^2, \quad C_{Ao} = 2$$

As S is the desired product, fractional yield in terms of S is

$$\psi\,(S/A) = \frac{r_S}{r_S + r_R + r_T} = \frac{dC_S}{dC_S + dC_R + dC_T} = \frac{2\,C_A}{1 + 2\,C_A + C_A^2}$$

$$= \frac{2\,C_A}{(1 + C_A)^2}$$

The maximum of the ψ (S/A) v/s C_A curve occurs where $d\psi/dC_A = 0$.

$$\frac{d\psi}{dC_A} = \frac{d}{dC_A}\left[\frac{2\,C_A}{(1 + C_A)^2}\right] = 0$$

$$\therefore \qquad 2\frac{d}{dC_A}\left[\frac{C_A}{(1+C_A)^2}\right] = 0$$

$$\frac{d}{dC_A}\left[\frac{C_A}{(1+C_A)^2}\right] = 0$$

$$\frac{(1+C_A)^2 \times 1 - C_A(2+2C_A)}{(1+C_A)^4} = 0$$

$$\frac{(1+C_A) - 2C_A}{(1+C_A)^3} = 0$$

$$\therefore \qquad (1+C_A) - 2C_A = 0$$

$$\therefore \qquad C_A = 1.0$$

$$\therefore \qquad C_{Af} = 1.0$$

$$\psi\,(S/A) = \frac{2C_A}{(1+C_A)^2}$$

$$= \frac{2\times 1}{(1+1)^2} \quad \text{as } C_{Af} = 1.0$$

$$= 0.50$$

This is the highest (maximum) possible fractional yield ($\psi = 0.50$) which occurs at $C_A = 1.0$

$$\psi\,(S/A) = \frac{2C_A}{(1+C_A)^2}$$

Take $C_A = 0, 0.25, 0.5$ ... upto 2 and evaluate ψ (S/A) and plot a graph of ψ (S/A) v/s C_A.

C_A	0	0.25	0.5	0.75	1.0	1.25	1.5	1.75	2
ψ (S/A)	0	0.32	0.44	0.489	0.50	0.49	0.48	0.46	0.44

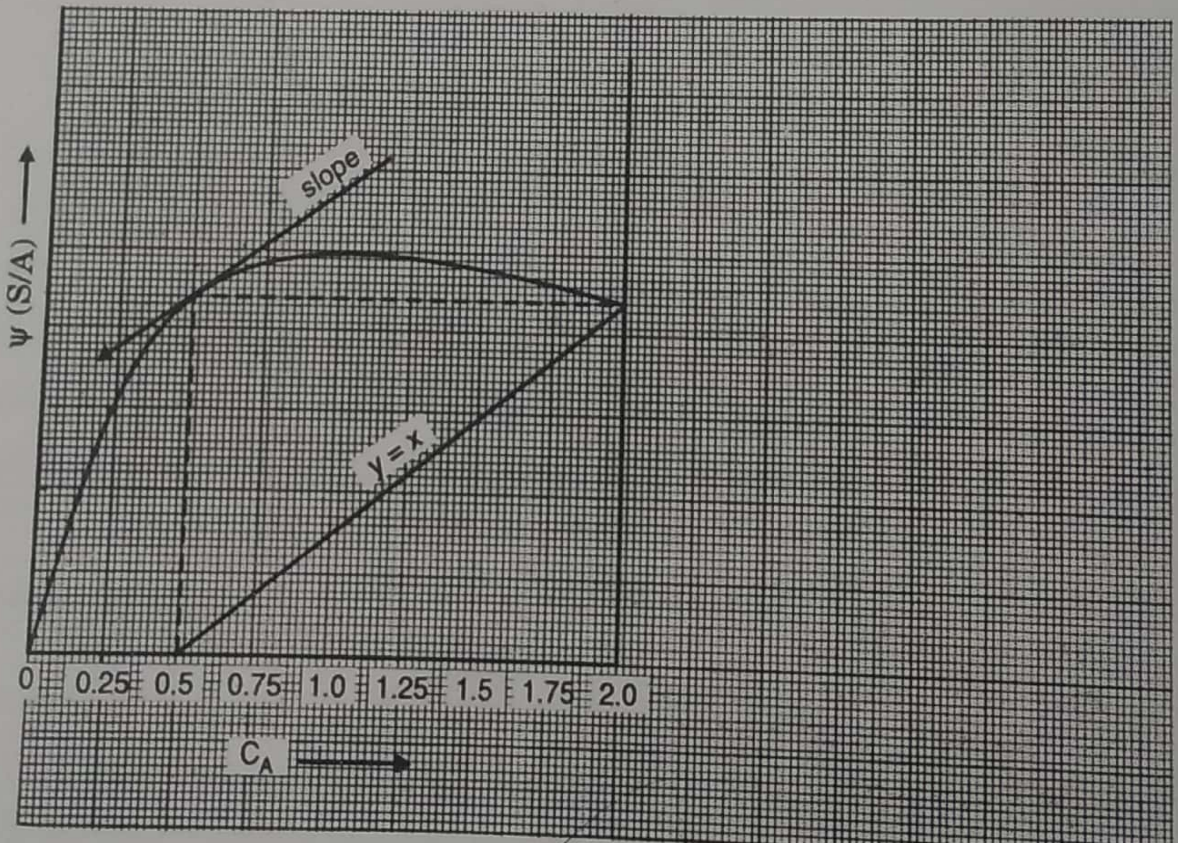


Fig. E 5.4

1. **Mixed flow reactor :** Most S is formed when area under the ψ v/s C_A curve has the largest area (slope = y/x).

For largest area, tangent to the curve should be parallel to diagonal.

This occurs at $C_{Af} = 0.50$.

Area under the curve between $C_{Af} = 0.5$ and $C_{Ao} = 2$, from graph :

$$\text{Area} = 26.4 \text{ cm}^2$$

$$C_{Sf} = \text{Area} \times \text{Scale x-axis} \times \text{Scale y-axis}$$

$$= 26.4 \times \frac{0.25}{1} \times \frac{0.1}{1}$$

$$= 0.66 \text{ mol}/l \qquad \text{... Ans.}$$

Analytically :

$$C_{Sf} = \psi\,(S/A)\,(-\Delta C_A)$$

$$= \frac{2\,C_A}{(1+C_A)^2}\,(C_{Ao} - C_A)$$

Differentiating and setting equal to zero to find the conditions at which most S is formed

$$\frac{dC_{Sf}}{dC_A} = 0 = \frac{d}{dC_A}\left[\frac{2\,C_A(2-C_A)}{(1+C_A)^2}\right]$$

$$= \frac{d}{dC_A}\left[\frac{2\,(2\,C_A - C_A^2)}{(1+C_A)^2}\right]$$

$$= 2\left[\frac{(1+C_A)^2(2-2\,C_A) - (2\,C_A - C_A^2)(2+2\,C_A)}{(1+C_A)^4}\right]$$

$$= 2\left[\frac{2\,(1+C_A)^2(1-C_A) - 2\,(1+C_A)(2\,C_A - C_A^2)}{(1+C_A)^4}\right]$$

$$= 4\left[\frac{(1+C_A)(1-C_A) - (2\,C_A - C_A^2)}{(1+C_A)^3}\right]$$

$$\therefore \quad (1+C_A)(1-C_A) - (2\,C_A - C_A^2) = 0$$

$$1 - C_A^2 - 2\,C_A + C_A^2 = 0$$

$$C_A = \frac{1}{2} = 0.5 \text{ mol}/l$$

$$C_{Sf} = \frac{2\,C_A}{(1+C_A)^2}\,[C_{Ao} - C_A]$$

$$= \frac{2 \times 0.5\,[2-0.5]}{(1+0.5)^2}$$

$$= 0.666 \text{ mol}/l \qquad \text{... Ans.}$$

Graphically obtained C_{Sf} matches with analytically calculated.

2. **Plug flow reactor :** The formation of S is maximum when the area under the curve is maximum. This occurs at 100% conversion of A (i.e. when $C_{Af} = 0$) as seen from Fig. E 5.4.

From graph area under the curve between $C_{Af} = 0$ and $C_A = C_{Ao} = 2$ is

$$\text{Area} = 34.5 \text{ cm}^2$$

$$\therefore \quad C_{Sf} = 34.5 \times \text{Scale y-axis} \times \text{Scale x-axis}$$

$$= 34.5 \times \frac{0.1}{1} \times \frac{0.25}{1}$$

$$= 0.8625 \text{ mol}/l \quad \ldots \text{(graphical)}$$

... **Ans.**

$$C_{Sf} = -\int_{C_{Ao}}^{C_{Af}} \psi\,(S/A)\, dC_A = \int_0^2 \frac{2\,C_A}{(1+C_A)^2}\, dC_A$$

$$= 2\int_0^2 \frac{C_A}{(1+C_A)^2}\, dC_A$$

$1 + C_A = x \quad \therefore \; dC_A = dx$

Limits $x = 1$ at $C_A = 0$ and $x = 3$ at $C_A = 2$.

$$= 2\int_1^3 \frac{(x-1)}{x^2}\, dx$$

$$= 2\left[(\ln x)_1^3 - \left(\frac{-1}{x}\right)_1^3 \right]$$

$$= 0.864 \text{ mol}/l$$

... **Ans.**

Answer by both methods is almost same.

3. Any reactor with separation and recycle of unreacted A : As no reactant leaves the system unconverted, it is important to operate at the conditions of highest fractional yield. Highest fractional yield of S is achieved at $C_A = 1.0$ as shown in Fig. E 5.4. Hence, one should use a mixed flow reactor operating at $C_A = 1.0$. One would then have 50% of reactant A forming product S.

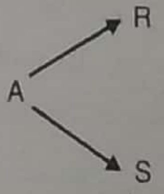
For mixed flow reactor : moles S/moles A fed $= \dfrac{0.666 \text{ mol}/l}{2 \text{ mol}/l} = 0.33$

For mixed flow with recycle : 50% A forming S $\therefore$ S formed $= 2 \times 0.5 = 1.0$ mol/l

: moles S formed/moles A fed = 1/2 = 0.50

Reactor type	moles S formed/moles A fed
Mixed flow reactor	0.33
Plug flow reactor	0.43
Mixed flow with separation and recycle	0.50

Ex. 5.5 : Liquid reactant A decomposes as per reaction scheme :



with rate equations :

$r_R = k_1\, C_A^2, \qquad k_1 = 0.4 \text{ m}^3/(\text{mol.min})$

$r_S = k_2\, C_A, \qquad k_2 = 2 \text{ (min)}^{-1}$

An aqueous feed A ($C_{Ao} = 40$ mol/m^3) enters a reactor, decomposes, and a mixture of A, R, and S leaves. Find the operating condition (X_A, τ, and C_R) which maximises C_R in a mixed flow reactor.

Solution : $A \xrightarrow{k_1} R, \quad r_R = k_1 C_A^2, \quad k_1 = 0.4 \text{ m}^3/(\text{mol.min})$

$$A \xrightarrow{k_2} S, \quad r_S = k_2 C_A, \quad k_2 = 2\ (\text{min})^{-1}$$

$$C_{Ao} = 40 \text{ mol/m}^3$$

$$\psi\ (R/A) = \frac{dC_R}{dC_R + dC_S} = \frac{k_1 C_A^2}{k_1 C_A^2 + k_2 C_A} = \frac{0.40\ C_A^2}{0.40\ C_A^2 + 2\ C_A}$$

$$= \frac{C_A^2}{C_A^2 + 5\ C_A} = \frac{1}{1 + 5/C_A}$$

$$C_{Rf} = \psi\ (R/A)\ (-\Delta C_A) = \frac{1}{\left(1 + \frac{5}{C_A}\right)} \cdot (C_{Ao} - C_A)$$

Differentiating w.r.t. C_A and setting equal to zero to find the conditions at which maximum R is formed.

$$\frac{dC_{Rf}}{dC_A} = \frac{d}{dC_A}\left[\frac{C_{Ao}}{1 + 5/C_A} - \frac{C_A}{1 + 5/C_A}\right] = 0$$

$$\frac{\left[\left(1 + \frac{5}{C_A}\right) \times 0 - C_{Ao}\left(\frac{-5}{C_A^2}\right)\right]}{\left(1 + \frac{5}{C_A}\right)^2} - \frac{\left[\left(1 + \frac{5}{C_A}\right) \times 1 - C_A\left(\frac{-5}{C_A^2}\right)\right]}{\left(1 + \frac{5}{C_A}\right)^2} = 0$$

$$\frac{5\ C_{Ao}}{C_A^2} - 1 - \frac{5}{C_A} - \frac{5}{C_A} = 0$$

$$\frac{5\ C_{Ao}}{C_A^2} - 1 - \frac{10}{C_A} = 0$$

$$5\ C_{Ao} - C_A^2 - 10\ C_A = 0$$

$$C_A^2 + 10\ C_A - 5\ C_{Ao} = 0$$

$$C_A^2 + 10\ C_A - 200 = 0, \quad \text{as } C_{Ao} = 40$$

$$C_A = \frac{-10 \pm \sqrt{(10)^2 - 4 \times 1 \times (-200)}}{2 \times 1}$$

$$= 10 \text{ mol/m}^3$$

Maximum R is formed at $C_{Af} = 10$ mol/m^3

$$C_{Rf} = \frac{1}{\left(1 + \frac{5}{C_A}\right)} \times (C_{Ao} - C_A) = \frac{(40 - 10)}{\left(1 + \frac{5}{10}\right)} = 20 \text{ mol/m}^3 \qquad \text{... Ans.}$$

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao}} = \frac{40 - 10}{40} = 0.75 \qquad \text{... Ans.}$$

For mixed flow :

$$\tau = \frac{C_{Ao}X_A}{(-r_A)}, \quad -r_A = k_1 C_A^2 + k_2 C_A$$

$$\tau = \frac{C_{Ao}X_A}{k_1 C_A^2 + k_2 C_A} = \frac{C_{Ao}X_A}{k_1 C_{Ao}^2 (1-X_A)^2 + k_2 C_{Ao}(1-X_A)}$$

$$= \frac{X_A}{k_1 C_{Ao}(1-X_A)^2 + k_2 (1-X_A)}$$

$$= \frac{0.75}{0.4 \times 40 (1-0.75)^2 + 2(1-0.75)}$$

$$= 0.5 \text{ min.}$$

... Ans.

Ex. 5.6 : The desired liquid phase reaction :

$A + B \rightarrow R + T$, $\quad \frac{dC_R}{dt} = \frac{dC_T}{dt} = k_1 C_A^{1.5} C_B^{0.30}$

is accompanied by the undesired side reaction

$A + B \rightarrow S + U$, $\quad \frac{dC_S}{dt} = \frac{dC_U}{dt} = k_2 C_A^{0.50} \cdot C_B^{1.8}$

What contacting schemes (reactor types) would you use to carry above reactions minimise the concentration of undesired products ?

Solution :

$A + B \rightarrow R + T$ (desired), $\quad \frac{dC_R}{dt} = k_1 C_A^{1.5} C_B^{0.30}$

$A + B \rightarrow S + U$ (undesired), $\quad \frac{dC_S}{dt} = k_2 C_A^{0.50} \cdot C_B^{1.8}$

To minimise the formation of undesired product, means to minimise r_S/r_R ratio.

$$\frac{r_S}{r_R} = \frac{1}{(r_R/r_S)} \quad \text{i.e. to maximise } r_R/r_S \text{ ratio}$$

$$\frac{r_R}{r_S} = \frac{k_1 C_A^{1.5} C_B^{0.30}}{k_2 C_A^{0.50} C_B^{1.8}}$$

$$\frac{r_R}{r_S} = \frac{k_1}{k_2} \cdot \frac{C_A}{C_B^{1.5}}$$

From above equation it is clear that the ratio r_R/r_S can be maximised (i.e. formation of S can be minimised) by using high concentration of A (as C_A is in numerator) and using lo concentration of B (as C_B is in denominator).

Or

$$\frac{r_S}{r_R} = \frac{k_2 C_A^{0.5} C_B^{1.8}}{k_1 C_A^{1.5} C_B^{0.30}}$$

$$\frac{r_S}{r_R} = \frac{k_2}{k_1} \frac{C_B^{1.5}}{C_A^{0.5}}$$

For minimising formation of S we should minimise ratio r_S/r_R and this ratio can be minimised by using low concentration of B (as C_B is in numerator) and high concentration o A (as C_A is in the denominator).

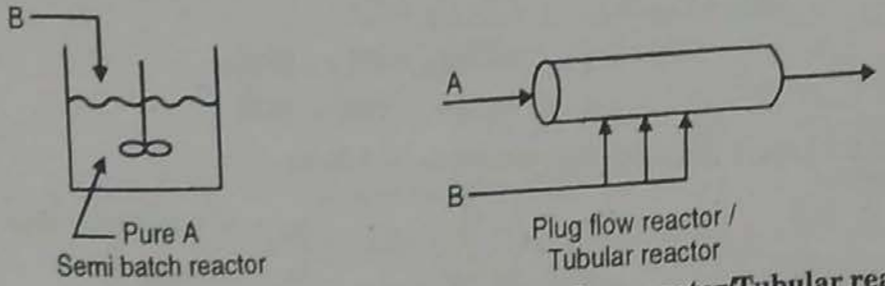
So to minimise the formation of undesired product, we want to make the concentration of A high and the concentration of B low.

To achieve this result, use :

(i) A semibatch reactor in which B is fed slowly into large amount of A.

(ii) A plug flow/tubular reactor with side streams of B continuously fed to the reactor.

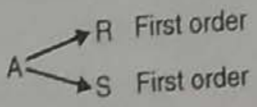
(iii) Series of CSTRs with A fed to first reactor and B fed to each reactor.



(a) Semibatch reactor **(b) Plug flow reactor/Tubular reactor**

Fig. E 5.6

Ex. 5.7 : Substance A in a liquid reacts to produce R and S as follows :



A feed ($C_{A_o} = 1$, $C_{R_o} = C_{S_o} = 0$) enters in two mixed flow reactors in series ($\tau_1 = 2$ min; $\tau_2 = 5$ min). Knowing the composition in the first reactor ($C_{A1} = 0.40$, $C_{R1} = 0.40$ and $C_{S1} = 0.2$), find the composition leaving the second reactor.

Solution : $A \xrightarrow{k_1} R$, first order

$A \xrightarrow{k_2} S$, first order

$$-r_A = k_1 C_A + k_2 C_A = (k_1 + k_2) C_A$$

$$r_R = k_1 C_A$$

$$r_S = k_2 C_A$$

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

$$\therefore \quad \frac{C_R - C_{R_o}}{C_S - C_{S_o}} = \frac{k_1}{k_2}$$

$$C_{R_o} = C_{S_o} = 0$$

$$\frac{C_R}{C_S} = \frac{k_1}{k_2}$$

$$C_{R1} = 0.40, \quad C_{S1} = 0.2$$

$$\therefore \quad \frac{0.40}{0.20} = \frac{k_1}{k_2}$$

$$k_1 = 2 k_2$$

For mixed flow reactor,

$$\tau = \frac{C_{A_0} - C_{A1}}{(-r_A)_1}$$

$$(-r_A)_1 = (k_1 + k_2)\, C_{A1}$$

For reactor-1 :

$$\begin{aligned}
\tau_1 &= \frac{C_{A_0} - C_{A1}}{(k_1 + k_2)\, C_{A1}} \\
2 &= \frac{1 - 0.4}{(k_1 + k_2)\, 0.40}, \quad C_{A1} = 0.4, \; C_{A_0} = 1.0 \\
0.80\,(k_1 + k_2) &= 0.60 \\
k_1 + k_2 &= 0.75 \\
k_1 &= 2\, k_2 \\
\therefore \quad 3\, k_2 &= 0.75 \\
k_2 &= 0.25 \ (\text{min})^{-1} \\
k_1 &= 0.50 \ (\text{min})^{-1}
\end{aligned}$$

For reactor-2 :

For A :

$$\begin{aligned}
\tau_2 &= \frac{C_{A1} - C_{A2}}{(-r_A)_2} \\
\tau_2 &= \frac{C_{A1} - C_{A2}}{(k_1 + k_2)\, C_{A2}} \\
5 &= \frac{C_{A1} - C_{A2}}{0.75\, C_{A2}} \\
3.75\, C_{A2} &= C_{A1} - C_{A2} \\
4.75\, C_{A2} &= C_{A1} \\
C_{A2} &= 0.4/4.75 = 0.0842 \qquad \text{... Ans.}
\end{aligned}$$

For R :

$$\begin{aligned}
\tau_2 &= \frac{C_{R2} - C_{R1}}{(r_R)_2}, \quad C_{R2} - C_{R1} \text{ is written as R is formed} \\
\tau_2 &= \frac{C_{R2} - C_{R1}}{k_1\, C_{A2}} \\
C_{R2} &= C_{R1} + \tau_2\, k_1\, C_{A2} \\
&= 0.40 + 5 \times 0.5 \times 0.0842 = 0.6105 \approx 0.61 \qquad \text{... Ans.}
\end{aligned}$$

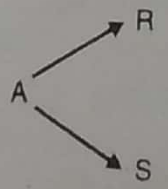
For S :

$$\begin{aligned}
\tau_2 &= \frac{C_{S2} - C_{S1}}{(r_S)_2} = \frac{C_{S2} - C_{S1}}{k_2\, C_{A2}}, \quad C_{S2} - C_{S1} \text{ is written as S is formed} \\
C_{S2} &= C_{S1} + \tau_2\, k_2\, C_{A2} = 0.2 + 5 \times 0.25 \times 0.0842 = 0.30525 \approx 0.305 \ \text{... Ans.}
\end{aligned}$$

Check : From stoichiometry : $C_{A_0} = C_R + C_S + C_A = 0.0842 + 0.6105 + 0.30525$

$1.0 = 0.9995 \quad \therefore \ \text{LHS} = \text{RHS}$

Ex. 5.8 : Substance A in liquid phase produces R and S by the following reactions :



with $r_R = k_1 C_A^2$ and $r_S = k_2 C_A$

The feed ($C_{Ao} = 1.0$, $C_{Ro} = 0$, $C_{So} = 0.30$) enters two mixed flow reactors in series ($\tau_1 = 2.5$ min, $\tau_2 = 10$ min). Knowing the compositions in the first reactor ($C_{A1} = 0.40$, $C_{R1} = 0.20$, $C_{S1} = 0.70$), find the composition leaving the second reactor.

Solution : $A \rightarrow R,\quad r_R = k_1 C_A^2$

$A \rightarrow S,\quad r_S = k_2 C_A$

$$-r_A = k_1 C_A^2 + k_2 C_A$$

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2} C_A$$

$$\therefore \quad \frac{C_R - C_{Ro}}{C_S - C_{So}} = \frac{k_1}{k_2} C_A$$

$$\frac{C_{R1} - C_{Ro}}{C_{S1} - C_{So}} = \frac{k_1}{k_2} C_{A1}$$

$$\frac{(0.20-0)}{(0.70-0.30)} = \frac{k_1}{k_2} \times 0.40$$

$$\frac{k_1}{k_2} = 1.25$$

$$\therefore \quad k_1 = 1.25\, k_2$$

For A : For reactor-1 :

$$\tau_1 = \frac{C_{Ao} - C_{A1}}{(-r_A)_1}$$

$$\tau_1 = \frac{C_{Ao} - C_{A1}}{k_1 C_{A1}^2 + k_2 C_{A1}}$$

$$\tau_1 = \frac{C_{Ao} - C_{A1}}{1.25\, k_2 C_{A1}^2 + k_2 C_{A1}}$$

$$2.5 = \frac{(1-0.40)}{1.25\, k_2 (0.40)^2 + k_2 (0.40)}$$

$$\therefore \quad k_2 = 0.4\ (\text{min})^{-1}$$

$$k_1 = 1.25\, k_2 = 1.25 \times 0.40 = 0.50\ l/(\text{mol.min})$$

For A : For reactor-2 :

$$\tau_2 = \frac{C_{A1} - C_{A2}}{k_1 C_{A2}^2 + k_2 C_{A2}}, \quad \tau_2 = 10 \text{ min}$$

$$10\,[k_1 C_{A2}^2 + k_2 C_{A2}] = 0.40 - C_{A2}$$

$$10\,[0.5\, C_{A2}^2 + 0.4\, C_{A2}] = 0.40 - C_{A2}$$

$$5\, C_{A2}^2 + 5\, C_{A2} - 0.40 = 0$$

$$\therefore \quad C_{A2} = 0.0744$$ ... **Ans.**

For R : For reactor-2 :

$$\tau_2 = \frac{C_{R2} - C_{R1}}{r_{R2}} = \frac{C_{R2} - C_{R1}}{k_1 C_{A2}^2}$$

$$C_{R2} = C_{R1} + \tau_2 k_1 C_{A2}^2$$
$$= 0.20 + 10 \times 0.5 \times (0.0744)^2$$
$$= 0.227$$ ... **Ans.**

For S : For reactor-2 :

$$\begin{aligned}
\tau_2 &= \frac{C_{S2}-C_{S1}}{r_{S2}} = \frac{C_{S2}-C_{S1}}{k_2\,C_{A2}} \\
C_{S2} &= C_{S1} + \tau_2\,k_2\,C_{A2} \\
&= 0.70 + 10 \times 0.40 \times 0.0744 \\
&= 0.9976
\end{aligned}$$

... **Ans.**

Check : From stoichiometry :

$$\begin{aligned}
C_{Ao} + C_{Ro} + C_{So} &= C_A + C_R + C_S \\
1 + 0 + 0.3 &= 0.0744 + 0.227 + 0.9976 \\
1.3 &= 1.299 \quad \therefore \text{ LHS} \approx \text{RHS}
\end{aligned}$$

Ex. 5.9 : Liquid reactant A decomposes as follows :

$A \rightarrow R$, $\quad r_R = k_1\,C_A^2, \quad k_1 = 0.4\ \text{m}^3/(\text{mol.min})$

$A \rightarrow S$, $\quad r_S = k_2\,C_A, \quad k_2 = 2\ (\text{min})^{-1}$

A feed to aqueous A ($C_{Ao} = 40$ mol/m³) enters a reactor, decomposes, and a mixture of A, R, and S leaves. Find C_R, C_S, and τ for $X_A = 0.9$ in a mixed flow reactor.

Solution : $A \xrightarrow{k_1} R, \quad r_R = 0.40\,C_A^2, \quad \text{mol/(m}^3\text{.min)}$

$$A \xrightarrow{k_2} S, \quad r_S = 2\,C_A, \quad \text{mol/(m}^3\text{.min)}$$

$$C_{Ao} = 40\ \text{mol/m}^3$$

For CSTR/mixed flow reactor :

$$\begin{aligned}
\tau &= \frac{C_{Ao}\,X_A}{(-r_A)} \\
(-r_A) &= k_1\,C_A^2 + k_2\,C_A \\
&= 0.4\,C_A^2 + 2\,C_A, \text{ we have } C_A = C_{Ao}(1-X_A) \\
&= 0.4\,C_{Ao}^2\,(1-X_A)^2 + 2\,C_{Ao}\,(1-X_A) \\
\tau &= \frac{C_{Ao}\,X_A}{0.4\,C_{Ao}^2\,(1-X_A)^2 + 2\,C_{Ao}\,(1-X_A)} \\
C_{Ao} &= 40,\ X_A = 0.90 \\
\tau &= \frac{40 \times 0.90}{0.40 \times (40)^2\,(1-0.90)^2 + 2 \times 40\,(1-0.90)} \\
&= 2.5\ \text{min}
\end{aligned}$$

... **Ans.**

$$\begin{aligned}
C_A &= C_{Ao}\,(1-X_A) \\
&= 40\,(1-0.90) = 4\ \text{mol/m}^3
\end{aligned}$$

For R :

$$\begin{aligned}
\tau &= \frac{C_R - C_{Ro}}{r_R} \\
r_R &= 0.4\,C_A^2 \\
\tau &= \frac{C_R - C_{Ro}}{0.4\,C_A^2} \\
C_R &= C_{Ro} + 0.4\,\tau\,C_A^2 \\
&= 0 + 0.4 \times 2.5 \times (4)^2 = 16\ \text{mol/m}^3
\end{aligned}$$

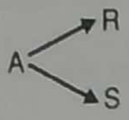
... **Ans.**

For S :
$$\tau = \frac{C_S - C_{So}}{r_S} = \frac{C_S - C_{So}}{k_2 C_A}$$

$$C_S = C_{So} + \tau_2 k_2 C_A$$
$$= 0 + 2.5 \times 2 \times 4 = 20 \text{ mol/m}^3 \quad \text{... Ans.}$$

We have,
$$C_{Ao} = C_A + C_R + C_S \text{ (check)}$$
$$40 = 4 + 16 + 20 = 40$$

Ex. 5.10 : Liquid reactant A decomposes as follows :



with $r_R = k_1 C_A^2$, $k_1 = 0.4 \text{ m}^3/(\text{mol.min})$

$r_S = k_2 C_A$, $k_2 = 2 \text{ (min)}^{-1}$

A feed of aqueous A ($C_{Ao} = 40 \text{ mol/m}^3$) enters a reactor, decomposes, and mixture of A, R and S leaves. Find C_R, C_S, and τ for $X_A = 0.90$ in a plug flow reactor.

Solution :

$A \rightarrow R$, $r_R = 0.40 C_A^2$, $\text{mol/(m}^3\text{.min)}$

$A \rightarrow S$, $r_S = 2 C_A$, $\text{mol/(m}^3\text{.min)}$

$$C_{Ao} = 40 \text{ mol/m}^3$$
$$-r_A = 0.40 C_A^2 + 2 C_A$$
$$= 0.40 C_{Ao}^2 (1 - X_A)^2 + 2 C_{Ao} (1 - X_A)$$

For plug flow reactor,
$$\tau = C_{Ao} \int_0^{X_A} \frac{dX_A}{(-r_A)}$$
$$= C_{Ao} \int_0^{X_A} \frac{dX_A}{0.4 C_{Ao}^2 (1 - X_A)^2 + 2 C_{Ao} (1 - X_A)}$$
$$= C_{Ao} \int_0^{X_A} f(X_A) \cdot dX_A$$

$$f(X_A) = 1/[0.4 C_{Ao}^2 (1 - X_A)^2 + 2 C_{Ao} (1 - X_A)]$$

X_A	$f(X_A)$	$C_{Ao} f(X_A)$
0	1.4×10^{-3}	0.056
0.2	2.10×10^{-3}	0.084
0.4	3.6×10^{-3}	0.144
0.6	7.4×10^{-3}	0.296
0.8	0.024	0.96
0.9	0.069	2.76

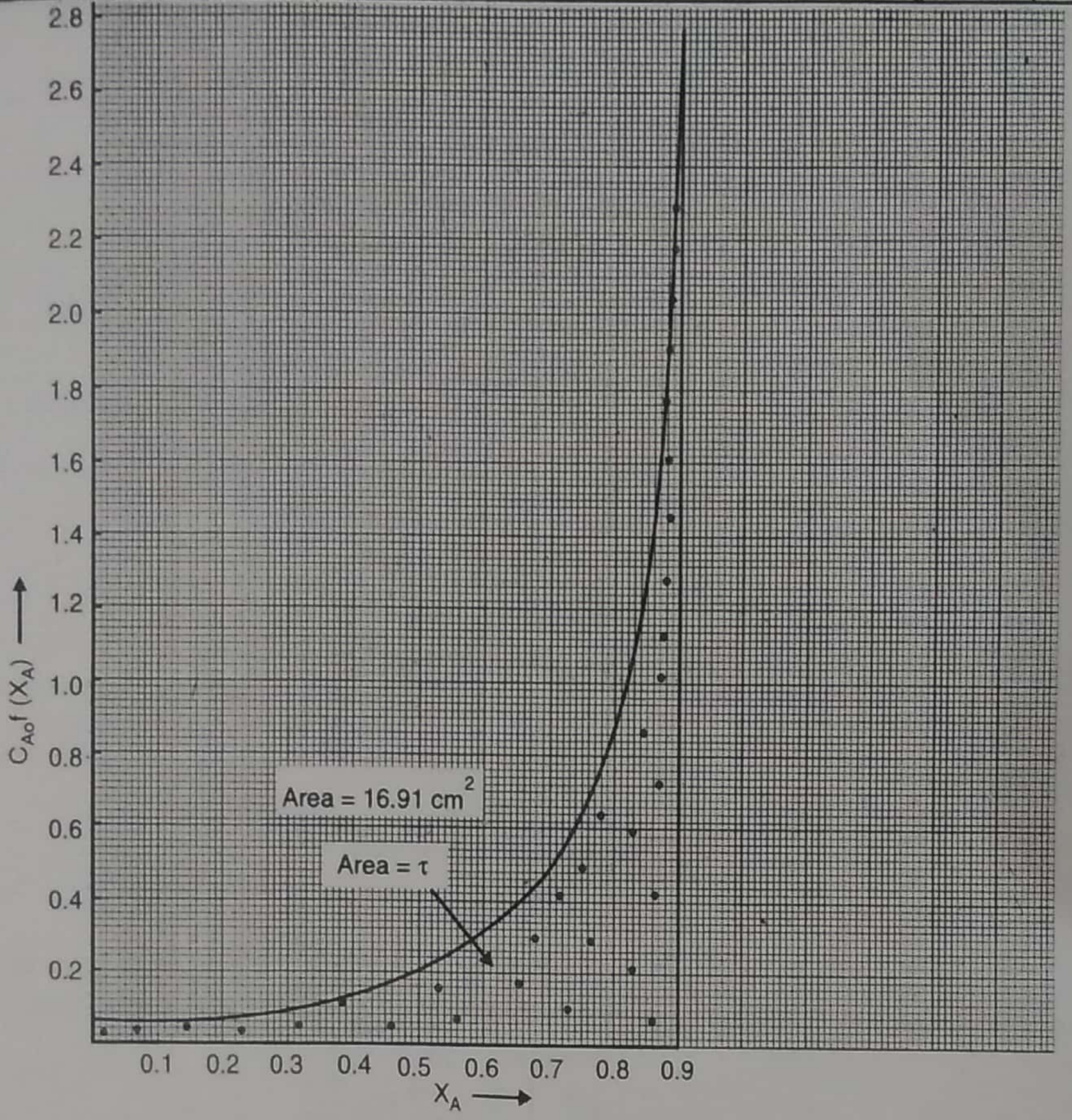


Fig. E 5.10

From graph, area under the curve = 16.91 cm²

$$\tau = 16.91 \times \frac{0.2}{1} \times \frac{0.1}{1}$$

$$= 0.338\ (\text{min})^{-1} \qquad \textbf{... Ans.}$$

$$\psi(R/A) = \frac{dC_R}{dC_R + dC_S}$$

$$= \frac{k_1 C_A^2}{k_1 C_A^2 + k_2 C_A} = \frac{0.4\, C_A^2}{0.4\, C_A^2 + 2\, C_A}$$

$$= \frac{C_A}{5 + C_A}$$

$$\phi_p = \frac{-1}{C_{Ao} - C_{Af}} \int_{C_{Ao}}^{C_{Af}} \psi\, dC_A$$

$$= \frac{-1}{40 - 4} \int_{40}^{4} \left(\frac{C_A}{5 + C_A}\right) dC_A = \frac{-1}{36} \int_{40}^{4} \left(\frac{C_A}{5 + C_A}\right) dC_A$$

$$\int_{40}^{4}\left(\frac{C_A}{5+C_A}\right)dC_A = [y - 5\ln y]_{45}^{9}, \quad \text{Taking } 5 + C_A = y$$

$$= [(9 - 45) - 5\ln 9 + 5\ln 45]$$

$$= [-36 + 5\ln(45/9)] = (27.953)$$

$$\phi_p = \frac{-1}{36}(27.953) = 0.776$$

$$C_{Rf} = \phi_p (C_{Ao} - C_{Af})$$ ... **Ans.**

$$= 0.776\,(40 - 4) = 27.94$$

$$C_{Sf} = (1 - \phi_p)(C_{Ao} - C_{Af})$$ ... **Ans.**

$$= (1 - 0.776)(40 - 4) = 8.064$$

$$\psi(S/A) = \frac{dC_S}{dC_R + dC_S} = \frac{k_2 C_A}{k_2 C_A + k_1 C_A^2}$$

$$= \frac{2\,C_A}{2\,C_A + 0.4\,C_A^2} = \frac{5}{5 + C_A}$$

ϕ_p based on S :

$$\phi_p = \frac{-1}{C_{Ao} - C_{Af}} \int_{C_{Ao}}^{C_{Af}} \psi(S/A)\,dC_A$$

$$= \frac{-1}{(40 - 4)} \int_{40}^{4} \left(\frac{5}{5 + C_A}\right) dC_A \cdot \text{ Let } 5 + C_A = y, \ \therefore\ dy = dC_A$$

$$= \frac{-5}{36} \int_{45}^{9} \frac{dy}{y} = \frac{-5}{36}\left(\ln \frac{9}{45}\right)$$

$$= 0.2235$$

$$C_{Sf} = \phi_p \cdot (C_{Ao} - C_{Af})$$

$$= 0.2235\,(40 - 4) = 8.046$$ ... **Ans.**

$$C_{Rf} = (1 - \phi_p)(C_{Ao} - C_{Af})$$

$$= (1 - 0.2235)(40 - 4) = 27.95$$ ... **Ans.**

Ex. 5.11 : Consider the liquid phase reaction

$$A + B \xrightarrow{k_1} R \text{ (desired)}, \quad dC_R/dt = 1.0\, C_A^{1.5} C_B^{0.30}, \quad \text{mol}/(l.\text{min})$$

$$A + B \xrightarrow{k_2} S \text{ (undesired)}, \ dC_S/dt = 1.0\, C_A^{0.5} C_B^{1.8}, \quad \text{mol}/(l.\text{min})$$

Equal volumetric flow rates of A and B streams with each stream of concentration of 20 mol/*l* of reactant are fed to the reactor.

For 90% conversion of A, find the concentration of R in the product stream if flow in the reactor follows :

(a) plug flow, (b) mixed flow, (c) plug flow with side streams of B and $C_{Bf} = 1$ mol/*l* everywhere in reactor. .

Solution : As equal volumetric flow rates of streams containing A and B are fed to the reactor system and as the concentration of each species (A and B) is 20 mol/*l* in each separate streams, the concentration of A and B in mixed stream entering the reactor is calculated as

Let C'_{Ao} = 20 mol/*l* in stream of A

Let C'_{Bo} = 20 mol/*l* in stream of B

Volumetric flow rate of stream containing A is V *l*/time.

Volumetric flow rate of stream containing B is V *l*/time.

Total volumetric flow rates of mixed stream to reactor = 2 V *l*/time

∴ Concentration of A in mixed stream entering the reactor $= \frac{20}{2V} \times V$

$$C_{Ao} = 10 \text{ mol}/l$$

Similarly, the concentration of B in combined/mixed stream entering the reactor $= \frac{20}{2V} \times V$

$$C_{Bo} = 10 \text{ mol}/l$$

The instantaneous yield of desired component (i.e. R) is :

$$\psi\,(R/A) = \frac{dC_R}{dC_R + dC_S}$$

$$\text{as } -dC_A/dt = dC_R/dt + dC_S/dt$$

$$\therefore \quad \psi\,(R/A) = \frac{k_1 C_A^{1.5}\, C_B^{0.30}}{k_1 C_A^{1.5}\, C_B^{0.30} + k_2 C_A^{0.5} \cdot C_B^{1.8}}$$

$$\text{As } k_1 = k_2 = 1.0$$

$$\psi\,(R/A) = \frac{C_A^{1.5}\, C_B^{0.3}}{C_A^{1.5}\, C_B^{0.3} + C_A^{0.5} \cdot C_B^{1.8}}$$

$$= \frac{C_A}{C_A + C_B^{1.5}}$$

(a) Plug flow :

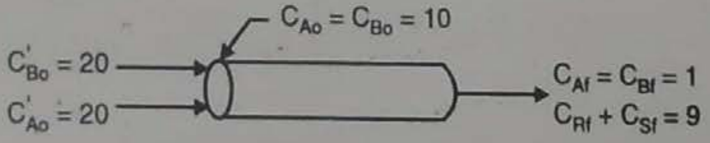


Fig. E. 5.11 (1)

$$C_{Ao} = C_{Bo} = 10 \text{ mol}/l$$

$$\therefore \quad C_A = C_B \text{ everywhere (from stoichiometry)}$$

$$\phi_p = \frac{-1}{C_{Ao} - C_{Af}} \int_{C_{Ao}}^{C_{Af}} \psi\, dC_A$$

$$C_{Af} = C_{Ao}(1 - X_A)$$

and $X_A = 0.90$

∴ $C_{Af} = 10\,(1 - 0.90) = 1 \text{ mol}/l$

$$\phi_p = \frac{-1}{(10-1)} \int_{10}^{1} \left(\frac{C_A}{C_A + C_B^{1.5}} \right) dC_B$$

but $C_B = C_A$ (as $C_{A_0} = C_{B_0}$ and stoichiometric coefficient of A = of B = 1)

From stoichiometry :

$$C_{A_0} X_A = C_{B_0} X_B$$

$$X_B = \frac{10}{10} \times 0.90 = 0.90$$

$$C_B = C_{B_0}(1 - X_B) = 10\,(1 - 0.90)$$

$$= 1.0$$

$$C_A = C_B = 1.0$$

$$\therefore \quad \phi_p = \frac{1}{9} \int_{1}^{10} \left(\frac{C_A}{C_A + C_A^{1.5}} \right) dC_A$$

$$= \frac{1}{9} \int_{1}^{10} \left(\frac{1}{1 + C_A^{0.5}} \right) dC_A$$

Let

$$C_A^{0.5} = x \qquad \therefore\ C_A = x^2 \qquad dC_A = 2x\,dx$$

$$\phi_p = \frac{1}{9} \int_{1}^{\sqrt{10}} \frac{2x\,dx}{1 + x} = \frac{2}{9} \left[\int_{1}^{\sqrt{10}} dx - \int_{1}^{\sqrt{10}} \frac{dx}{(1 - x)} \right]$$

$$= \frac{2}{9} \left[\left(\sqrt{10} - 1 \right) - \ln \left(1 + \sqrt{10} \right) \right]$$

$$= 0.164$$

$$C_{Rf} = \phi_p\,(C_{A_0} - C_{Af}),$$

$$= 0.164\,(10 - 1)$$

$$= 1.47 \text{ mol}/l$$ ... **Ans. (a)**

$$C_{Sf} = (1 - \phi_p)\,(C_{A_0} - C_{Af})$$

$$= (1 - 0.164)\,(10 - 1)$$

$$= 7.53 \text{ mol}/l$$ ... **Ans. (a)**

(b) Mixed flow :

$$C_{A_0} = C_{B_0} = 10 \text{ mol}/l \quad \text{and} \quad C_A = C_B$$

$$\phi_m\,(R/A) = \psi_{\text{at exit}}$$

$$= \frac{C_A}{C_A + C_B^{1.5}} = \frac{C_A}{C_A + C_A^{1.5}}, \quad \text{as } C_B = C_A$$

$$= \frac{1}{1 + C_A^{0.5}}$$

$$C_A = C_{Af} = 1 \text{ mol}/l$$

$$\phi_m\,(R/A) = \frac{1}{1 + (1)^{0.5}} = 0.50$$

$$
\begin{aligned}
C_{Rf} &= \phi_m (C_{Ao} - C_{Af}) \\
&= 0.50\,(10 - 1) \\
&= 4.5 \text{ mol}/l
\end{aligned}
$$

... **Ans. (b)**

$$
\begin{aligned}
C_{Sf} &= (1 - \phi_m)(C_{Ao} - C_{Af}) \\
&= (1 - 0.50)(9 - 1) \\
&= 4.5 \text{ mol}/l
\end{aligned}
$$

... **Ans. (b)**

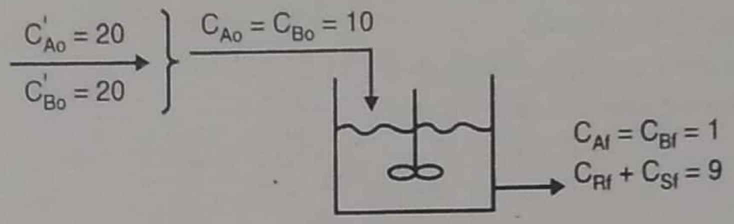


Fig. E 5.11 (2)

(c) Plug flow with side streams of B with $C_{Bf} = 1$ mol/l everywhere in reactor (plug flow of A with mixed flow of B) :

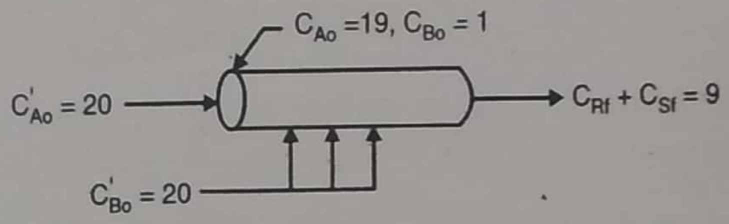


Fig. E 5.11 (3)

In this case, B is introduced into the reactor in such a way that $C_B = 1$ mol/l throughout.

$$\therefore \quad C_{Ao} = 20 - 1 = 19 \text{ mol}/l$$

$$
\begin{aligned}
\phi(R/A) &= \frac{-1}{C_{Ao} - C_{Af}} \int_{C_{Ao}}^{C_{Af}} \psi \, dC_A \\
&= \frac{-1}{19 - 1} \int_{19}^{1} \frac{C_A}{C_A + (C_B)^{1.5}} \, dC_A \\
&= \frac{-1}{18} \int_{19}^{1} \frac{C_A \, dC_A}{C_A + (1)^{1.5}} = \frac{-1}{18} \int_{19}^{1} \frac{C_A}{1 + C_A} \, dC_A \\
&= \frac{1}{18} \left[\int_{1}^{19} dC_A - \int_{1}^{19} \frac{dC_A}{1 + C_A} \right] \\
&= \frac{1}{18} \left[(19 - 1) - \ln (20/2) \right] = 0.87
\end{aligned}
$$

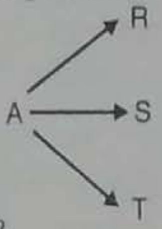
$$
\begin{aligned}
\therefore \quad C_{Rf} &= \phi \cdot (C_{Ao} - C_{Af}) \\
&= 0.87\,(10 - 1) = 7.85 \text{ mol}/l
\end{aligned}
$$

... **Ans. (c)**

$$C_{Sf} = 9\,(1 - 0.87) = 1.15 \text{ mol}/l$$

... **Ans. (c)**

Ex. 5.12 : Consider the parallel decomposition of A of different orders



with $r_R = 1, r_S = 2C_A$ and $r_T = C_A^2$.

Determine the maximum concentration of desired product obtainable in mixed flow reactor and plug flow reactor.

(1) R is desired product and $C_{A_0} = 2$.

(2) S is desired product and $C_{A_0} = 4$.

Solution :

$$A \rightarrow R, \; r_R = 1$$

$$A \rightarrow S, \; r_S = 2C_A$$

$$A \rightarrow T, \; r_T = C_A^2$$

(1) R is desired product and $C_{A_0} = 2$ mol/*l*

$$\psi(R/A) = \frac{dC_R}{dC_R + dC_S + dC_T} = \frac{r_R}{r_R + r_S + r_T}$$

$$= \frac{1}{1 + 2C_A + C_A^2} = \frac{1}{(1 + C_A)^2}$$

$$C_{Rf} = \psi(R/A)(C_{A_0} - C_A)$$

$$\psi(R/A) = \frac{1}{(1 + C_A)^2}$$

Take $C_A = 0, 0.5, 1$ ... upto 2, evaluate ψ (R/A) and plot ψ (R/A) v/s C_A.

C_A	0	0.25	0.5	1	1.5	2
ψ (R/A)	1	0.64	0.44	0.25	0.16	0.11

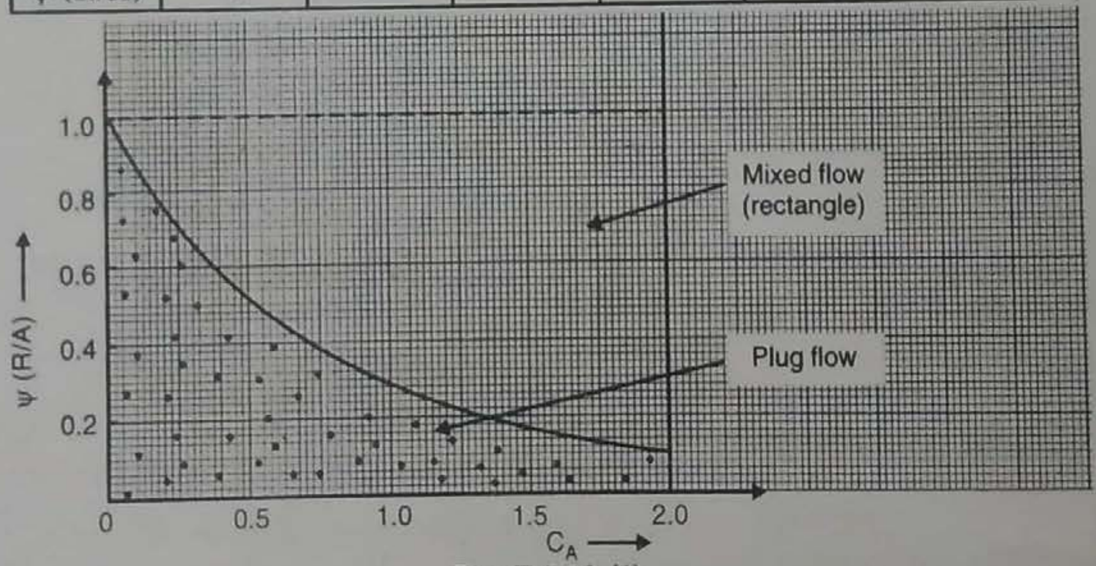


Fig. E 5.12 (1)

(i) For plug flow reactor : The formation of R is maximum when the area under the curve ψ v/s C_A is maximum. This occurs at 100% conversion of A (i.e. at $C_{Af} = 0$).

From graph, area under the curve = 13.25 cm^2

$$C_{Rf} = 13.25 \times \frac{0.5}{2} \times \frac{0.2}{1} = 0.6625 \qquad \text{... Ans.}$$

(ii) For mixed flow reactor : The formation of R is maximum when area of rectangle between C_{Ao} and C_{Af} is maximum. This occurs at $C_{Af} = 0$.

From graph, Area = 40 cm²

$$C_{Rf} = 40 \times \frac{0.5}{2} \times \frac{0.2}{1} = 2$$

For mixed flow reactor :

$$\psi(R/A) = \frac{1}{(1+C_A)^2}$$

$$C_{Rf} = \frac{1}{(1+C_A)^2}(C_{Ao}-C_A)$$

$$= \frac{2-0}{(1+0)^2} = 2.0$$

For plug flow reactor :

$$C_{Rf} = -\int_{C_{Ao}}^{C_{Af}} \psi(R/A)\, dC_A$$

$$= \int_0^2 \frac{1}{(1+C_A)^2} dC_A$$

$1 + C_A = x, \quad dC_A = dx$

$x = 1$ at $C_A = 0$ and $x = 3$ at $C_A = 2$

$$= \int_1^3 \frac{dx}{(x)^2} = \left[-\frac{1}{x}\right]_1^3$$

$$= -\frac{1}{3} + 1 = \frac{2}{3} = 0.67$$

Graphical value is almost same as the analytical one.

(2) S is the desired product and $C_{Ao} = 4$.

$$\psi(S/A) = \frac{dC_S}{dC_S + dC_R + dC_T} = \frac{2C_A}{1 + 2C_A + C_A^2} = \frac{2C_A}{(1+C_A)^2}$$

$$C_{Sf} = \psi(S/A)(-\Delta C_A)$$

$$= \frac{2C_A}{(1+C_A)^2}(C_{Ao}-C_A)$$

$$= \frac{2C_A(4-C_A)}{(1+C_A)^2}, \quad C_{Ao} = 4$$

$$= \frac{2(4C_A - C_A^2)}{(1+C_A)^2}$$

For mixed flow reactor :

Differentiating C_{Sf} w.r.t. C_A and setting $\frac{dC_{Sf}}{dC_A}$ to zero to find the conditions at which most S is formed,

$$\frac{dC_{Sf}}{dC_A} = \frac{d}{dC_A}\left[\frac{2(4C_A - C_A^2)}{(1+C_A)^2}\right] = 0$$

$$\therefore \quad \frac{2d}{dC_A}\left[\frac{4\,C_A - C_A^2}{(1+C_A)^2}\right] = 0$$

$$\frac{d}{dC_A}\left[\frac{4\,C_A - C_A^2}{(1+C_A)^2}\right] = 0$$

$$\frac{(1+C_A)^2(4-2\,C_A) - (4\,C_A - C_A^2)(2+2\,C_A)}{(1+C_A)^4} = 0$$

$$\frac{(1+C_A)(4-2\,C_A) - 2\,(4\,C_A - C_A^2)}{(1+C_A)^3} = 0$$

$$4 - 2\,C_A + 4\,C_A - 2\,C_A^2 - 8\,C_A + 2\,C_A^2 = 0$$

$$4 - 6\,C_A = 0$$

$$C_A = \frac{4}{6} = 0.67$$

$$C_{Sf} = \frac{2\,(4\,C_A - C_A^2)}{(1+C_A)^2}$$

$$= \frac{2\,[4 \times 0.67 - (0.67)^2]}{(1+0.67)^2} = 1.6 \qquad \textbf{... Ans.}$$

$$\psi(S/A) = \frac{2\,C_A}{(1+C_A)^2}$$

Take $C_A = 0,\ 0.5,\ 1$ ... upto 2, evaluate ψ (S/A), and plot ψ (S/A) v/s C_A.

C_A	0	0.25	0.5	1	1.5	2	2.5	3	3.5	4
ψ(S/A)	0	0.32	0.44	0.50	0.48	0.44	0.41	0.375	0.345	0.32

For mixed flow reactor :

The formation of S is maximum possible when area of rectangle is the largest.

$C_{Af} = 1$, Area $= 30\ \text{cm}^2$

$C_{Af} = 0.5$, Area $= 30.8\ \text{cm}^2$

$C_{Af} = 0.67$, Area $= 31.50\ \text{cm}^2$ [from Fig. E 5.12 (2)]

$$C_{Sf} = 31.50 \times \text{Scale of y-axis} \times \text{Scale of x-axis}$$

$$= 31.50 \times \frac{0.1}{1} \times \frac{0.5}{1}$$

$$= 1.575 \qquad \textbf{... Ans.}$$

$$\approx 1.6$$

For plug flow reactor : The formation of S is maximum when the area under the ψ v/s C_A curve is maximum. This occurs at 100% conversion of A (i.e. at $C_{Af} = 0$) as seen from the curve.

$$C_{Sf} = -\int_{C_{Ao}}^{C_{Af}} \psi\,(S/A)\, dC_A = \int_0^4 \frac{2\,C_A}{(1+C_A)^2}\, dC_A$$

From graph, area under the curve $= 32.54\ \text{cm}^2$

$$C_{Sf} = 32.54 \times \frac{0.1}{1} \times \frac{0.5}{1}$$

$$= 1.627 \qquad \textbf{... Ans.}$$

For plug flow reactor, we have :

$$C_{Sf} = -\int_{C_{Ao}}^{C_{Af}} \frac{2\,C_A}{(1+C_A)^2}\,dC_A$$

$$= 2\int_0^4 \frac{C_A}{(1+C_A)^2}\,dC_A$$

$$1 + C_A = x, \quad dC_A = dx$$

$$x = 1 \text{ at } C_A = 0, \; x = 5 \text{ at } C_A = 4$$

$$= 2\int_1^5 \left(\frac{x-1}{x^2}\right) dx$$

$$= 2\left[\int_1^5 \frac{dx}{x} - \int_1^5 \frac{dx}{x^2}\right] = 2\left[(\ln x)_1^5 - \left(\frac{-1}{x}\right)_1^5\right]$$

$$= 2\left[\ln 5 - \ln 1 + \frac{1}{5} - 1\right]$$

$$= 1.62$$

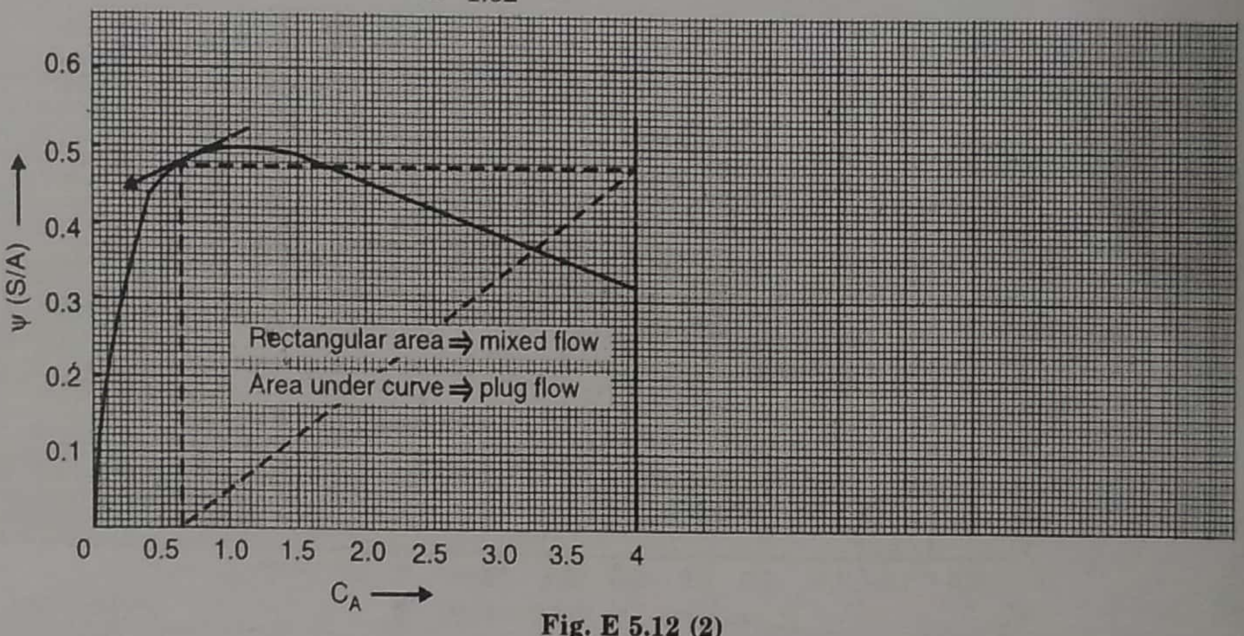


Fig. E 5.12 (2)

Ex. 5.13 : For the reaction of Ex. 5.12 determine the arrangement of reactors which would produce most S in a flow system where recycle of unreacted feed is not possible. Find $C_{S,\,total}$ for this arrangement.

Solution : The maximum of plot of $\psi(S/A)$ v/s C_A occurs at $C_{Af} = 1$ where $\psi(S/A) = 0.50$

$$\psi(S/A) = \frac{dC_S}{dC_S + dC_R + dC_T} = \frac{2\,C_A}{(1+C_A)^2}$$

Maxima occurs at

$$\frac{d\psi\,(S/A)}{dC_A} = 0 = \frac{d}{dC_A}\left[\frac{2\,C_A}{(1+C_A)^2}\right]$$

$$\frac{(1+C_A)^2(2)-2\,C_A(2+2\,C_A)}{(1+C_A)^4} = 0$$

$$\frac{2\,(1+C_A)-4\,C_A}{(1+C_A)^3} = 0$$

$$2+2C_A-4\,C_A = 0$$

$$\therefore \quad 2\,C_A = 2$$

$$C_A = 1.0$$

At $C_{Af} = 1.0$

$$\psi(S/A) = \frac{2\times 1}{(1+1)^2} = 0.5$$

The best reactor arrangement would be mixed followed by plug flow reactor. Operate mixed flow reactor from $C_{A_0} = 4$ upto $C_A = 1.0$ (condition of highest fractional yield) and then followed by plug flow reactor from $C_A = 1$ upto $C_A = 0.0$.

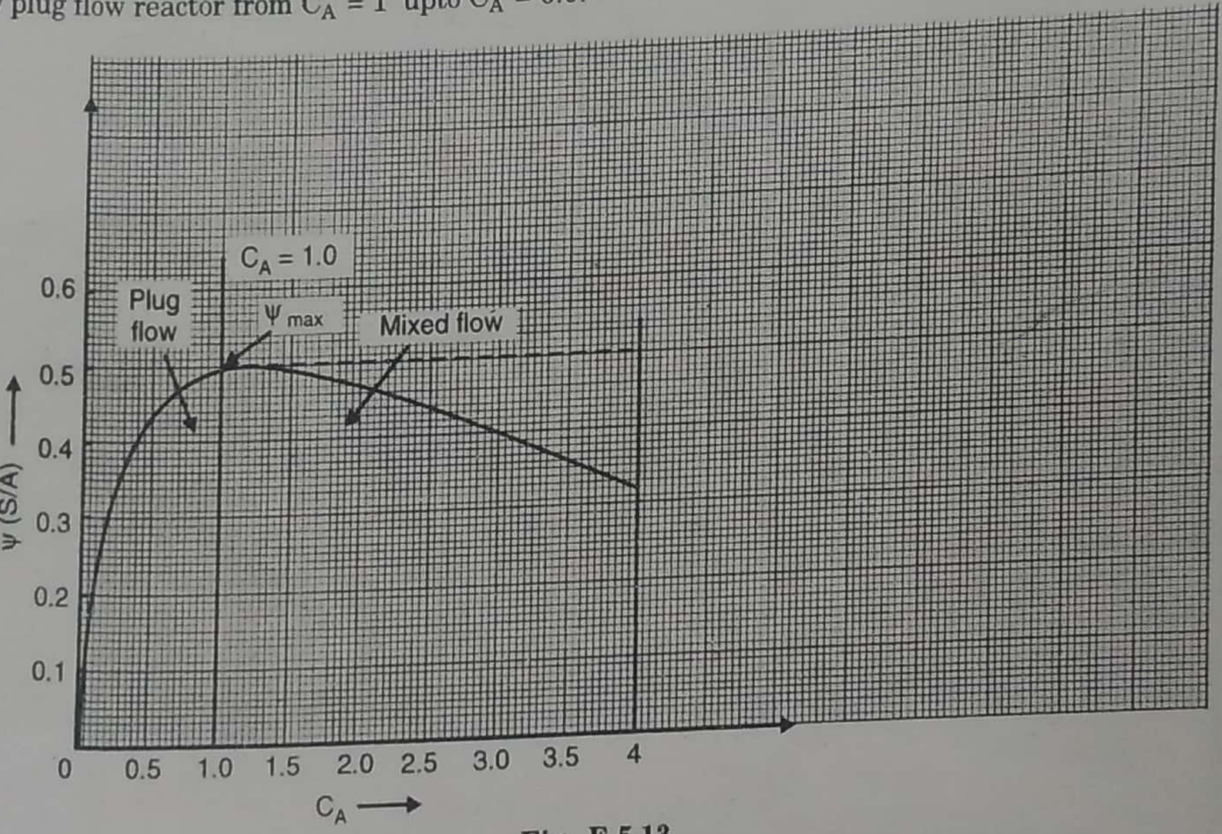


Fig. E 5.13

For mixed flow reactor :

$$C_A = 1.0, \quad \psi = 0.5$$

$$\therefore \quad C_S = 0.5\,(4-1) = 1.5$$

From plot of ψ (S/A) v/s C_A, area of rectangle i.e. rectangular area between $C_A = 4$ and $C_A = 1.0$ is 30 cm^2.

$$C_S = 30\times\frac{0.1}{1}\times\frac{0.5}{1} = 1.5$$

For plug flow reactor :

Area under the curve between $C_A = 1$ and $C_A = 0$ is 7.7 cm^2.

$$C_S = 7.7 \times \frac{0.1}{1} \times \frac{0.5}{1} = 0.385$$

$$C_S = -\int_1^0 \psi \, dC_A = \int_0^1 \frac{2\,C_A}{(1+C_A)^2}\, dC_A$$

$$= 2\int_0^1 \frac{C_A}{(1+C_A)^2}\, dC_A$$

$$= 2\left[(\ln x)_1^2 + \left[\frac{1}{x}\right]_1^2\right]$$

$$= 2\left[\ln 2 - \ln 1 + \frac{1}{2} - 1\right]$$

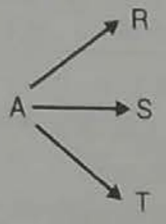
$$= 0.386$$ ... **Ans.**

Therefore, the total amount of S formed

$$C_{S,\,total} = 1.5 + 0.386$$

$$= 1.886$$ ... **Ans.**

Ex. 5.14 : Consider the parallel decomposition of A of different orders



with $r_R = 1.0$, $r_S = 2\,C_A$ and $r_T = C_A^2$.

Determine the maximum concentration of desired product (T) in (i) plug flow and (ii) mixed flow. Take $C_{Ao} = 5$.

Solution : $A \rightarrow R$, $r_R = 1.0$

$A \rightarrow S$, $r_S = 2\,C_A$

$A \rightarrow T$ (desired), $r_T = C_A^2$

$$\psi(T/A) = \frac{r_T}{r_T + r_R + r_S} = \frac{C_A^2}{1 + 2\,C_A + C_A^2} = \frac{C_A^2}{(1+C_A)^2}$$

Take C_A = 0, 0.5, 1, 1.5, 2 ... 5, evaluate ψ (T/A) and plot ψ (T/A) v/s C_A.

C_A	0	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
ψ (T/A)	0	0.11	0.25	0.36	0.44	0.51	0.56	0.60	0.64	0.67	0.694

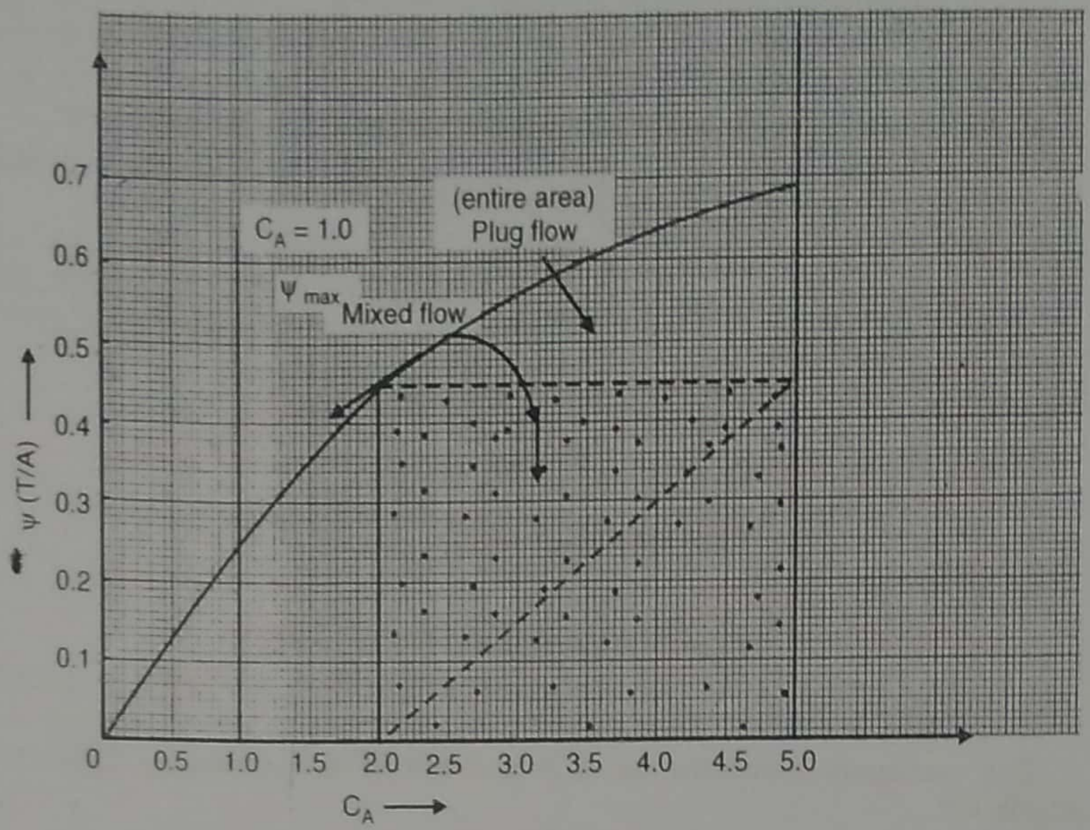


Fig. E 5.14

(1) Plug flow reactor : For plug flow, formation of T is maximum when area under the curve is maximum, which occurs at $C_A = 0.0$ i.e. 100% conversion of A.

From graph, area under the curve between $C_A = 5$ and $C_A = 0$ is :

$$\text{Area} = 44.73 \text{ cm}^2$$

$$C_{Tf} = 44.73 \times \text{Scale x-axis} \times \text{Scale y-axis}$$

$$= 44.73 \times \frac{0.5}{1} \times \frac{0.1}{1} = 2.2365 \approx 2.24 \qquad \text{... Ans.}$$

$$C_{Tf} = -\int_{C_{Ao}}^{C_{Af}} \psi\,(T/A)\, dC_A = \int_0^5 \frac{C_A^2}{(1+C_A)^2}\, dC_A$$

put $1 + C_A = x$, $dC_A = dx$

$x = 1$ at $C_A = 0$, $x = 6$ at $C_A = 5$

$$= \int_1^6 \frac{(x-1)^2}{x^2}\, dx = [x]_1^6 - 2\,[\ln x]_1^6 - \left[\frac{1}{x}\right]_1^6$$

$$= 2.25 \qquad \text{... Ans.}$$

(2) Mixed flow reactor : The formation of T is maximum when the area of rectangle is maximum.

Area of rectangle is maximum at $C_A = 2$.

Area of rectangle between $C_A = 2$ and $C_A = 5$ is 26.6 cm^2.

$$C_{Tf} = \text{Area} \times \text{Scale y-axis} \times \text{Scale x-axis}$$

$$= 26.6 \times \frac{0.1}{1} \times \frac{0.5}{1}$$

$$= 1.33 \text{ mol}/l \qquad \text{... Ans.}$$

$$\begin{aligned}
\phi_{m\,(T/A)} &= \psi_{\text{at exit}} \\
&= \frac{C_A^2}{(1+C_A)^2} \quad \text{at } C_{Af} = 2\ \text{mol}/l \\
&= \frac{(2)^2}{(1+2)^2} = \frac{4}{9} = 0.4444 \\
C_{Tf} &= \phi_m\ (C_{Ao} - C_{Af}) \\
&= 0.4444 \times (5-2) \\
&= 1.33\ \text{mol}/l
\end{aligned}$$

Answer by graphical and analytical method is same :

Ex. 5.15 : Consider the competitive liquid phase reactions :

$$A + B \xrightarrow{k_1} R \text{ (desired)}, \quad \frac{dC_R}{dt} = 1.0\ C_A \cdot C_B^{0.3}, \quad \text{mol}/(l.\text{min})$$

$$A + B \xrightarrow{k_2} S \text{ (undesired)}, \quad \frac{dC_S}{dt} = 1.0\ C_A^{0.5} \cdot C_B^{1.8}, \quad \text{mol}/(l.\text{min})$$

For 90% conversion of A, find the concentration of R in the product stream. Equal volumetric flow rates of A and B are fed to the reactor and each stream has a concentration of 20 mol/l.

The flow in the reactor follows :

(i) plug flow and (ii) mixed flow.

Solution : $A + B \xrightarrow{k_1} R \text{ (desired)}, \quad r_R = 1.0\, C_A \cdot C_B^{0.3}$

$$A + B \xrightarrow{k_2} S \text{ (undesired)}, \quad r_S = 1.0\, C_A^{0.5} \cdot C_B^{1.8}$$

$$X_A = 0.90$$

Equal volumetric flow rates of A and B with one containing A ($C'_{Ao} = 20$ mol/l) and other containing B ($C'_{Bo} = 20$ mol/l) are fed to the reactor, so the starting concentration of each reactant in the combined feed to reactor is

$$C_{Ao} = 20/2 = 10\ \text{mol}/l$$

$$C_{Bo} = 20/2 = 10\ \text{mol}/l$$

90% A is reacted so

$$\begin{aligned}
C_A &= C_{Ao}(1 - X_A) \\
&= 10\,(1 - 0.90) = 1\ \text{mol}/l
\end{aligned}$$

$C_{Af} = 1$ mol/l and $C_{Bf} = 1$ mol/l (as equimolar feed and from stoichiometry of reaction), so $C_A = C_B$ everywhere

$$C_{Bf} = C_{Bo}(1 - X_B) = 10\,(1 - 0.90) = 1\ \text{mol}/l$$

As (from stoichiometry) $C_{Ao} X_A = C_{Bo} X_B$

$$\therefore \quad X_B = \frac{10 \times 0.9}{10} = 0.90$$

(i) **Plug flow :**

$$\phi_p = \frac{-1}{C_{Ao} - C_{Af}} \int_{C_{Ao}}^{C_{Af}} \psi\ (R/A)\ dC_A$$

$$\psi\,(R/A) = \frac{r_R}{r_R + r_S} = \frac{1.0\,C_A C_B^{0.3}}{1.0\,C_A C_B^{0.3} + 1.0\,C_A^{0.5}\,C_B^{1.8}}$$

$$= \frac{1}{1 + C_A^{-0.5}\,C_B^{1.5}}$$

$$\text{as } C_A = C_B$$

$$\psi\,(R/A) = \frac{1}{1 + C_A^{-0.5} \cdot C_A^{1.5}} = \frac{1}{1 + C_A}$$

$$\phi_p = \frac{-1}{(10-1)} \int_{10}^{1} \frac{1}{(1 + C_A)}\, dC_A$$

$$= \frac{-1}{9}\left[\int_{11}^{2} \frac{dx}{x}\right] = \frac{-1}{9}\,[\ln x]_{11}^{2}$$

$$= 0.189 \approx 0.19$$

$$C_{Rf} = \phi_p\,(C_{Ao} - C_{Af})$$

$$= 0.19 \times (10 - 1) = 1.71 \text{ mol}/l \qquad \text{... Ans.}$$

(ii) Mixed flow :

$$\phi_m\;(R/A) = \psi_{\text{at exit}}$$

$$= \frac{1}{1 + C_A} = \frac{1}{1 + C_{Af}} = \frac{1}{1+1} = 0.50$$

$$C_{Rf} = 0.50\,(9) = 4.5 \text{ mol}/l$$

$$C_{Sf} = (1 - 0.5)\,(9) = 4.5 \text{ mol}/l \qquad \text{... Ans.}$$

Ex. 5.16 : Under suitable conditions, A decomposes as follows :

✓

$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

where $k_1 = 0.1\ (\text{min})^{-1}$ and $k_2 = 0.1\ (\text{min})^{-1}$

R is to be produced from 1000 l/h of feed ($C_{Ao} = 1$ mol/l, $C_{Ro} = C_{So} = 0$).

(1) What size of plug flow reactor will maximise the concentration of R ? What is that concentration ($C_{R,\,max}$) in the effluent stream from this reactor ?

(2) What size of mixed flow reactor will maximise the concentration of R ?, and what is that concentration ($C_{R,\,max}$) in the effluent stream from this reactor ?

Solution : $A \xrightarrow{k_1} R \xrightarrow{k_2} S$

$$k_1 = 0.10\ (\text{min})^{-1},\ k_2 = 0.10\ (\text{min})^{-1}$$

$$r_1 = k_1 C_A$$

$$-dC_A/dt = k_1 C_A$$

$$\therefore \quad C_A = C_{Ao}\,e^{-k_1 t}$$

We have, $k_1 = k_2 = 0.1\ (\text{min})^{-1}$

Assume, $k_1 = k_2 = k$

$$\therefore \quad C_A = C_{Ao}\,e^{-kt}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R$$

$$= k\,C_A - k\,C_R$$

$$\therefore \quad \frac{dC_R}{dt} + k\,C_R = k\,C_A$$

$$C_A = C_{Ao}\,e^{-kt}$$

$$\frac{dC_R}{dt} + k\,C_R = k\,C_{Ao}\,e^{-kt}$$

This is a first order differential equation of the form

$$\frac{dy}{dx} + Py = Q$$

By multiplying through with the integrating factor $e^{\int P\,dx}$, the solution is

$$y\,e^{\int P\,dx} = \int Q \cdot e^{\int P\,dx}\,dx + I$$

$$e^{\int P\,dx} = e^{\int k\,dt} = e^{kt}$$

$$Q = k\,C_{Ao}\,e^{-kt}, \quad y = C_R$$

$$C_R\,e^{kt} = \int (k\,C_{Ao}\,e^{-kt} \cdot e^{kt})\,dt + I$$

$$C_R\,e^{kt} = k\,C_{Ao}\int dt + I$$

$$C_R\,e^{kt} = k\,C_{Ao}\,t + I$$

At $t = 0$, $C_R = C_{Ro} = 0$

$\therefore$

$$I = 0$$

$$C_R\,e^{kt} = k\,C_{Ao}\,t$$

$$C_R = \frac{k\,C_{Ao}\,t}{e^{kt}}$$

The maximum concentration of R is found by differentiating C_R w.r.t. t and setting $dC_R/dt = 0$.

$$\frac{dC_R}{dt} = \frac{d}{dt}\left[\frac{kC_{Ao}\,t}{e^{kt}}\right] = 0$$

$$k\,C_{Ao}\frac{d}{dt}\left(\frac{t}{e^{kt}}\right) = 0$$

$\therefore$

$$\frac{d}{dt}\left(\frac{t}{e^{kt}}\right) = 0$$

$$\frac{e^{kt} \cdot 1 - t\,k\,e^{kt}}{(e^{kt})^2} = 0$$

$$e^{kt} - kt\,e^{kt} = 0 \qquad e^{kt} = k\,t\,e^{kt}$$

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

This t is t_{max}.

$$t_{max} = \frac{1}{k}$$

The maximum concentration of R is

$$C_{R\,max} = \frac{k \cdot C_{Ao} \cdot (1/k)}{e^{k\,(1/k)}} = \frac{C_{Ao}}{e}$$

(i) Plug flow reactor :

Only we have to replace t by τ.

$\therefore$

$$\tau_{p,\,opt} = \frac{1}{k}$$

$$C_{R,\,max} = \frac{C_{Ao}}{e}$$

$$\tau_p = \frac{1}{0.10} = 10 \text{ min}$$

$$\tau_p = \frac{V}{v}, \quad v = 1000\ l/\text{h} = 16.67\ l/\text{min}$$

$$V = \tau_p \cdot v = 10 \times 16.67 = 166.7\ l$$

Size of plug flow reactor = 166.7 l ... **Ans.**

$$C_{R,\max} = \frac{C_{Ao}}{e} = \frac{1}{2.7183} = 0.368\ \text{mol}/l \quad \text{... Ans.}$$

(ii) Mixed flow reactor :

For first order followed by first order, we have

$$\frac{C_A}{C_{Ao}} = \frac{1}{1 + k_1 \tau_m}$$

$$\frac{C_R}{C_{Ao}} = \frac{k_1 \tau_m}{(1 + k_1 \tau_m)(1 + k_2 \tau_m)}$$

$$\frac{C_R}{C_{Ao}} = \frac{k\ \tau_m}{(1 + k\ \tau_m)^2}, \quad k_1 = k_2 = k$$

$$\frac{dC_R}{d\tau_m} = \frac{k\ C_{Ao}\ \tau_m}{(1 + k\ \tau_m)^2}$$

Setting $dC_R/d\tau_m = 0$, get $C_{R\max}$ and $\tau_{m,\text{opt}}$

$$\frac{k\ C_{Ao}\ d}{d\tau_m}\left[\frac{\tau_m}{(1 + k\tau_m)^2}\right] = 0$$

$$\frac{d}{d\tau_m}\left[\frac{\tau_m}{(1 + k\tau_m)^2}\right] = 0$$

$$\frac{(1 + k\ \tau_m)^2 \times 1 - \tau_m\,(2k + 2k^2\,\tau_m)}{(1 + k\tau_m)^4} = 0$$

$$\frac{(1 + k\tau_m)^2 - \tau_m\ 2k\ (1 + k\tau_m)}{(1 + k\tau_m)^4} = 0$$

$$\frac{(1 + k\tau_m) - 2k\tau_m}{(1 + k\tau_m)^3} = 0$$

$\therefore \quad 1 + k\tau_m - 2k\tau_m = 0$

$\therefore \quad \tau_m = 1/k$

$$\tau_{m,\text{opt}} = 1/k = \frac{1}{0.1} = 10\ (\text{min})$$

$$\tau_m = \frac{V}{v} \qquad \therefore \quad V = \tau_m \cdot v, \quad v = 16.67\ l/\text{min}$$

$$= 10 \times 16.67 = 166.7\ l$$

Size of mixed flow reactor required = 166.7 l ... **Ans.**

For mixed flow reactor

$$\tau_{m,\text{opt}} = \frac{1}{\sqrt{k_1 k_2}} = \frac{1}{\sqrt{k^2}} = \frac{1}{k} = \frac{1}{0.10} = 10\ \text{min}$$

Maximum concentration of R, $C_{R\max}$ is given by

$$\frac{C_{R\max}}{C_{Ao}} = \frac{1}{[(k_2/k_1)^{1/2} + 1]^2} = \frac{1}{[(0.1/0.1)^{1/2} + 1]^2} = 0.25$$

$$C_{R\max} = 0.25\ C_{Ao} = 0.25 \times 1 = 0.25\ \text{mol}/l \quad \text{... Ans.}$$

TEMPERATURE AND PRESSURE EFFECTS

Now we will first consider the effect of changes in operating temperatures and pressure on rate of reaction, equilibrium conversion, and heat of reaction and then we will focus our attention on heat effects associated with chemical reactions. In the previous chapters we have discussed design of isothermal reactors. The performance equations, rate equations and stoichiometric relationships derived and used for isothermal operations of chemical reactors all are applicable for the design of nonisothermal chemical reactors.

Consider an irreversible first order reaction of the type A → R is carried out adiabatically in a plug flow reactor. Further, consider that it is a liquid phase exothermic reaction. As the reactor is operated adiabatically and reaction is exothermic, the temperature of reaction mixture will increase with conversion along the length of the reactor.

The performance equation for plug flow reactor is

$$\frac{V}{v_o} = C_{Ao} \int_0^{X_A} \frac{dX_A}{-r_A}$$

The rate equation is $-r_A = k\,C_A$

From stoichiometry, $C_A = C_{Ao}(1-X_A)$

$$\therefore \quad -r_A = k\,C_{Ao}\,(1-X_A)$$

$$\therefore \quad \frac{V}{v_o} = \int_0^{X_A} \frac{dX_A}{k\,(1-X_A)} \qquad \dots (6.1)$$

For isothermal operation, we can take k out of integral sign.

$$\frac{V}{v_o} = \frac{1}{k}\int_0^{X_A} \frac{dX_A}{(1-X_A)} \qquad \text{... (for isothermal operation)} \qquad \dots (6.2)$$

We know that k is a function of temperature, T and its variation with T is given by the Arrhenius equation :

$$k = k_o\, e^{-E/RT}$$

$$k_1 = k_o\, e^{-E/RT_1}$$

$$\therefore \quad \frac{k}{k_1} = \frac{e^{-E/RT}}{e^{-E/RT_1}}$$

k as a function of T,

$$k = k_1 \exp.\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_1}\right)\right]$$

As the temperature T varies with conversion X_A along the length of reactor, k will also vary and therefore it cannot be taken out of integral sign [equation 6.1)] as we have done in the case of isothermal plug flow reactor.

$$\therefore \quad \frac{V}{v_o} = \int_0^{X_A} \frac{dX_A}{k_1\left[\exp\left[\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)\right] \times (1-X_A)\right]}$$

$$V = \frac{v_o}{k_1}\int_0^{X_A} \frac{dX_A}{(1-X_A)\exp\left[\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_1}\right)\right]} \quad \ldots (6.3)$$

It is clear that, for performing this integration, we must relate X_A and T and we will do this through energy balance.

Heats of Reaction from Thermodynamics :

When chemical reactions take place, either heat is absorbed or liberated. Three types of reactions are of interest, e.g. combustion, formation, and the reaction of one or more substances to form other compounds.

Standard heat of formation (ΔH_f^o) is the *heat of reaction when one of a compound is formed from its elements when all the reaction species of chemical reaction are in their standard states (25 °C, 1 atm).*

Standard heat of combustion (ΔH_c^o) is the *heat of reaction of one mole of substance with molecular oxygen to yield specified products with both the reactants and products are in their standard states (25 °C, 1 atm).*

Standard heat of reaction (ΔH_R^o or $\Delta H_{R25°C}$) is the *heat of reaction (i.e. enthalpy change resulting from the procedure of reaction) when both the reactants and products are in their standard states (25 °C, 1 atm).* Heat of reaction is the enthalpy change resulting due to reaction wherein (i) the reactants are fed in stoichiometric amounts and the reaction proceeds to completion, (ii) the reactants are fed at temperature T and pressure P, and the products emerge at same temperature and pressure.

When chemical reactions take place either heat is liberated or absorbed. The amount of heat liberated or absorbed during chemical reaction at particular temperature T depends upon (i) the nature of the reacting system, (ii) the amount of material reacting (level of conversion) and (iii) temperature and pressure of the reacting system. It is calculated from the heat of reaction $\Delta H_{R(T)}$ or ΔH_R for a given reaction. When the heat of reaction is not known, it is calculated from the thermochemical data on the heat of formation and heat of combustion of the reacting materials. These data are tabulated for ΔH_f and ΔH_c at T_1 = 25 °C and 1 atm i.e. ΔH_f^o and ΔH_c^o for many chemical compounds.

The standard heat of reaction (ΔH_R^o) can be calculated from data of standard heats of formation of reacting materials as follows :

Consider the chemicals reaction of the type

$$aA + bB \longrightarrow rR + sS$$

$$\begin{aligned}\Delta H_R^o &= \Sigma\,\Delta H^o_{f\,(products)} - \Sigma\,\Delta H^o_{f\,(reactants)} \\ &= \left[r\,\Delta H^o_{f_R} + s\,\Delta H^o_{f_S}\right] - \left[a\,\Delta H^o_{f_A} + b\,\Delta H^o_{f_B}\right] \quad \ldots (6.4)\end{aligned}$$

Standard heat of reaction i.e. the heat of reaction at 25 °C (298 K) and 1 atm pressure can also be calculated from the data of standard heats of combustion of the reacting materials as follows :

$$\begin{aligned}\Delta H_R^o &= \Sigma\,\Delta H^o_{c\,(reactants)} - \Sigma\,\Delta H^o_{c\,(products)} \\ &= (a\,\Delta H^o_{c_A} + b\,\Delta H^o_{c_B}) - (r\,\Delta H^o_{c_R} + s\,\Delta H^o_{c_S}) \quad \ldots (6.5)\end{aligned}$$

Consider the reaction

$$aA \rightarrow rR + sS$$

The heat of reaction at temperature T (by convention) is the heat transferred to the reacting system from the surrounding when 'a' moles of A disappear to form r moles of R and s moles of S with temperature and pressure of the reacting system after and before the change to be same. Therefore,

$$aA \rightarrow rR + sS, \quad \Delta H_{R(T)} \left\} \begin{array}{l} \text{positive : endothermic reaction} \\ \text{negative : exothermic reaction} \end{array} \right.$$

Effect of Temperature on Heat of Reaction :

Standard heat of reaction is the enthalpy change associated with a reaction wherein the reactants and the products are at a temperature of 25 °C and a pressure at 1 atm. In industrial practice, the reactants and products may be at a temperature other than 25 °C. The heat of reaction at 25 °C (298 K) can be calculated by using equations mentioned earlier.

Now, we will develop an equation for evaluating heat of reaction at temperature T_2 knowing heat of reaction at T_1. The heat of reaction at any temperature may be calculated from a known data of heat of reaction provided the heat capacity data are available upto the temperature in question for reactants and products of the reaction.

Consider a general reaction

$$aA + bB \rightarrow rR + sS \qquad \text{... (6.6)}$$

The heat of reaction (enthalpy change) ΔH_{R1} is known for this reaction at pressure of 1 atm and at temperature T_1 and heat of reaction (enthalpy change) ΔH_{R2} is desired at 1 atm and at T_2.

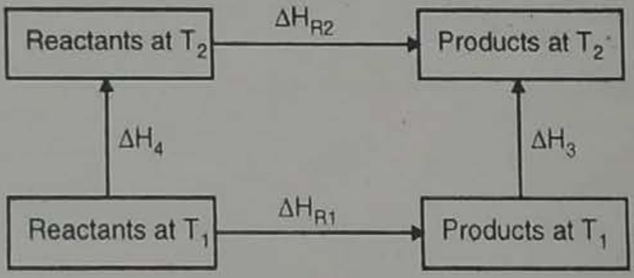


Fig. 6.1 : Effect of temperature on heat of reaction

Let ΔH_3 be the enthalpy change involved in heating all the products from T_1 to T_2 at 1 atm.

Let ΔH_4 be the enthalpy change involved in heating all the reactants from T_1 to T_2 at 1 atm.

As enthalpy is a point function, we can write

$$\Delta H_{R1} + \Delta H_3 = \Delta H_4 + \Delta H_{R2} \qquad \text{... (6.7)}$$

where

$$\Delta H_3 = \int_{T_1}^{T_2} C_p' \, dT \qquad \text{... (6.8)}$$

where C_p' is the total heat capacity of the products.

Also,

$$\Delta H_4 = \int_{T_1}^{T_2} C_p \, dT \qquad \text{... (6.9)}$$

where C_p is the total heat capacity of the reactants.

From Fig. 6.1 it is evident that the enthalpy changes for the following constant pressure paths are equal :

(i) React reactants at T_1 to form products and heat the products from T_1 to T_2.

(ii) Heat the reactants from T_1 to T_2 and then allow them to react isothermally to produce the products.

$$\Delta H_{R_1} + \Delta H_3 = \Delta H_4 + \Delta H_{R_2} \qquad \dots (6.10)$$

Put the values of ΔH_3 and ΔH_4 from equations (6.8) and (6.9) respectively in equation (6.10).

$$\Delta H_{R1} + \int_{T_1}^{T_2} C_p^{'}\, dT = \Delta H_{R2} + \int_{T_1}^{T_2} C_p\, dT$$

$$\Delta H_{R2} = \Delta H_{R1} + \int_{T_1}^{T_2} (C_p^{'} - C_p)\, dT$$

$$\Delta H_{R2} = \Delta H_{R1} + \int_{T_1}^{T_2} (\Delta C_p)\, dT \qquad \dots (6.11)$$

where $\Delta C_p = C_p^{'} - C_p = (rC_{p_R} + s\,C_{p_S}) - (a\,C_{p_A} + b\,C_{p_B})$

Empirical equation for molar heat capacity as a function of temperature is :

$$C_p = \alpha + \beta T + \gamma T^2$$

where α, β, and γ are constants and T is the temperature in K. C_p is the heat capacity at T in J/(mol.K).

$$C_{p_R} = \alpha_R + \beta_R T + \gamma_R T^2$$

$$C_{p_S} = \alpha_S + \beta_S T + \gamma_S T^2$$

$$C_{p_A} = \alpha_A + \beta_A T + \gamma_A T^2$$

$$C_{p_B} = \alpha_B + \beta_B T + \gamma_B T^2$$

$$\begin{aligned}\Delta C_p &= r\,[\alpha_R + \beta_R T + \gamma_R T^2] + s\,[\alpha_S + \beta_S T + \gamma_S T^2] \\ &\quad - a\,[\alpha_A + \beta_A T + \gamma_A T^2] - b\,[\alpha_B + \beta_B T + \gamma_B T^2] \\ &= [r\,\alpha_R + s\,\alpha_S - a\,\alpha_A - b\,\alpha_B] + [r\,\beta_R + s\,\beta_S - a\,\beta_A - b\,\beta_B]\,T \\ &\quad + [r\,\gamma_R + s\,\gamma_S - a\,\gamma_A - b\,\gamma_B]\,T^2\end{aligned}$$

$$\Delta C_p = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 \qquad \dots (6.12)$$

where
$$\Delta\alpha = r\,\alpha_p + s\,\alpha_S - a\,\alpha_A - b\,\alpha_B$$
$$\Delta\beta = r\,\beta_R + s\,\beta_S - a\,\beta_A - b\,\beta_B$$
$$\Delta\gamma = r\,\gamma_R + s\,\gamma_S - a\,\gamma_A - b\,\gamma_B$$

Putting the value of ΔC_p from equation (6.12) in equation (6.11),

$$\Delta H_{R2} = \Delta H_{R1} + \int_{T_1}^{T_2} (\Delta\alpha + \Delta\beta T + \Delta\gamma\, T^2)\, dT$$

$$\Delta H_{R2} = \Delta H_{R1} + \Delta\alpha\,(T_2 - T_1) + \frac{\Delta\beta}{2}\,(T_2^2 - T_1^2) + \frac{\Delta\gamma}{3}\,(T_2^3 - T_1^3) \qquad \dots (6.13)$$

With the help of above equation, we can calculate the heat of reaction at temperature T_2 knowing heat of reaction at temperature T_1 (i.e. ΔH_{R1}) and heat capacity data of reactants and products over temperature range $T_2 — T_1$.

Usually, T_1 is taken as 25 °C (298 K), so the heat of reaction at T_1 (i.e. ΔH_{R1}) is standard heat of reaction, ΔH°_R.

So for calculating ΔH_{R2} i.e. ΔH_R at T_2 using above equation, use ΔH°_R in place of ΔH_{R1} and $T_1 = 298$ K.

In general form, equation (6.13) may also be written as

$$\Delta H_{RT} = \Delta H_{R1} + \Delta\alpha\,(T - T_1) + \frac{\Delta\beta}{2}\,(T^2 - T_1^2) + \frac{\Delta\gamma}{3}\,(T^3 - T_1^3) \qquad \ldots (6.14)$$

where ΔH_{R1} is the heat of reaction at T_1 and ΔH_{RT} is the heat of reaction at any temperature T.

Take $\Delta H_{R1} = \Delta H^{\circ}_R$ (standard heat of reaction) at 25 °C (298 K) and $T_1 = 25$ °C (298 K), evaluate ΔH_{RT}, heat of reaction at any temperature T.

In this case, enthalpy changes ΔH_3, ΔH_4 are the enthalpies of reactants and products over 298 K as $T_1 = 298$ K.

Use of mean molar heat capacities :

If the mean heat capacities $\overline{C}_p$ are known for the reactants and products over the temperature range T_1 to T_2 then it is not necessary to integrate the equation (6.11) and under these conditions we can write the relationship between ΔH_{R2} and ΔH_{R1} as

$$\Delta H_{R2} = \Delta H_{R1} + \Delta\overline{C}_p\,(T_2 - T_1)$$

Here, take $T_1 = 298$ K, so $\Delta H_{R1} = \Delta H^{\circ}_R$ and use the equation to get ΔH_{R2} at any temperature T_2.

$$\Delta H_{RT} = \Delta H^{\circ}_R + \Delta\overline{C}_p\,(T - T_1), \text{ where } T_1 = 298\text{ K} \qquad \ldots (6.16)$$

$$\Delta\overline{C}_p = (r\,\overline{C}_{p_R} + s\overline{C}_{p_S}) - (a\,\overline{C}_{p_A} + b\overline{C}_{p_B}) \qquad \ldots (6.17)$$

The above equations are applicable when reactants and products are at same temperature.

When reactants and products enter and leave the reactor at different temperatures then the calculation of ΔH_{RT} can be bypassed and net enthalpy change accompanying chemical reaction for given conversion can be calculated by using the following equation :

$$Q = \Delta H = \Sigma H_p + \Sigma \Delta H^{\circ}_R - \Sigma H_R \qquad \ldots (6.18)$$

ΣH_p = sum of enthalpies of all the products leaving the reactor, relative to standard state [25 °C (298 K) and 1 atm] i.e. over 298 K.

$$\Sigma H_p = \int_{298}^{T_2} (n_i'\, C_{pi}')\, dT$$

where T_2 is the temperature at which all products leave the reactor (it will contain products formed and reactant unused).

n_i' is the actual number of moles of species i in the product stream from the reactor.

C'_{pi} is the molar heat capacity of the species i in the product stream.

$$\Sigma H_R = \int_{298}^{T_1} (n_i C_{pi})\, dT$$

where T_1 is the temperature at which reactants enter into the reactor.

n_i is the actual number of moles of species i entering the reactor and C_{pi} is its molar heat capacity.

$\Sigma \Delta H^o_R$ = sum of standard heats of reactions based upon actual conversion of reactants or formation of products.

Consider a reaction such as :

$A \rightarrow R + S \qquad \Delta H^o_R = x$ J/mol A

If 10 moles of A are entering at T_1 K and conversion in the reactor is 80% and product leaves at temperature T_2 K then

$$\Sigma H_R = \int_{298}^{T_1} (n_i C_{pi})\, dT = \int_{298}^{T_1} (10\, C_{p_A})\, dT$$

80% conversion,

$$\therefore \quad \text{A reacted} = 10 \times 0.80 = 8 \text{ mol}$$

$$\therefore \quad \Sigma \Delta H^o_R = x \text{ J/mol A} \times 8 = 8x \text{ J}$$

Product stream contains R, S and A unused

$$\text{R in product} = 8 \text{ mol}, \quad \text{S in product} = 8 \text{ mol}$$

$$\text{A in product} = 10 - 8 = 2 \text{ mol}$$

$$\Sigma H_p = \int_{298}^{T_2} \left(8 \times C'_{p_R} + 8\, C'_{p_S} + 2\, C'_{p_A}\right) dT$$

If mean molar heat capacities of reactants and products are given then

$$\Sigma H_p = \Sigma \left(n'_i \bar{C}'_{pi}\right)_{\text{products}} (\Delta T), \quad \Delta T = T_2 - 298$$

$$\Sigma H_R = \Sigma (n_i \bar{C}_{pi}) \cdot \Delta T, \quad \Delta T = T_1 - 298$$

CHEMICAL EQUILIBRIUM

It is a common observation that many chemical reactions do not go to completion. The quantities of reactants left depend on the experimental conditions (temperature, pressure etc.) and the nature of the reaction. The question as to how far a reaction proceeds is very important in chemistry and chemical engineering.

Equilibrium State :

The state in which the measurable properties of a system (such as pressure, density, colour, or concentration of species) do not undergo any noticeable change with time, under a given set of conditions, is said to be a state of equilibrium.

Characteristics of Chemical Equilibrium :

The important characteristics of chemical equilibrium are :

(i) The properties of a system become constant at equilibrium and remain unchanged thereafter.

(ii) The equilibrium can be approached from either direction i.e. starting with pure reactants or pure products, provided enough time is allowed.

(iii) The chemical equilibrium is dynamic in nature (which means that a state of equilibrium is attained and maintained owing to the fact that the forward and reverse processes proceed at same rate). It may be noted that, after the attainment of equilibrium, the reaction does not stop. In fact, both the forward and backward reactions continue at equilibrium but the rates of the two opposing reactions become equal.

(iv) A catalyst can speed up the approach towards equilibrium but it does not change the state of equilibrium.

Equilibrium constants from Thermodynamics :

The Van't Hoff isotherm relates in general form the Gibb's free energy and the equilibrium constant.

$$\Delta G^o = -RT \ln K \qquad \text{... (6.19)}$$

where ΔG^o is the standard Gibb's free energy change for the reaction and K is the thermodynamic equilibrium constant for the reaction.

The standard Gibb's free energy change for the reaction refers to the difference between free energies of products and reactants when each is in a chosen standard state.

Consider the reaction such as

$$aA + bB \longrightarrow rR + sS$$

ΔG^o is given by

$$\Delta G^o = (rG_R^o + sG_S^o) - (aG_A^o + bG_B^o)$$

G^o is the standard Gibb's free energy of formation of a reacting component. The standard Gibb's free energies of formation of many compounds are given in tables of thermodynamic properties and can be found out in handbooks, etc. If such tables are not available, ΔG^o can be found out by the following equation :

$$\Delta G^o = \Delta H^o - T\Delta S^o \qquad \text{... (6.20)}$$

where ΔH^o is the standard enthalpy change of reaction (i.e. ΔH_R at 298 K and 1 atm) and ΔS^o is the standard entropy change of reaction. These two thermodynamic properties are also given in tabulated form in handbooks, etc.

Standard states are chosen so as to make the evaluation of free energy simple and accurate. Commonly chosen standard states at given temperature are.

A standard state is a particular state of a species at temperature T defined by generally accepted reference condition of pressure, composition and state.

With reference to composition, the standard states are states of pure species.

(i) Gases (g) : Pure gas at unit fugacity at given temperature. If the gas is ideal gas, the standard state reduces 1 atm pressure. For ideal gas, fugacity is equal to pressure.

$$\text{Activity } a = f/f^o \text{ and } f^o = 1 \quad \therefore a = f$$

(ii) Liquids (*l*) : Pure liquid at its vapour pressure at given temperature.

(iii) Solids (s) : Pure solid substance at a pressure of 1 atm at given temperature.

(iv) Solute in liquid : 1 molar solution of the solute at 1 atm pressure at given temperature.

The Gibb's free energy function predicts the feasibility and equilibrium conditions at constant temperature and constant pressure and, therefore, is convenient for day-to-day use. It is the magnitude and sign of ΔG^o that predicts whether a chemical reaction is possible or not under given conditions without recourse to direct experiments.

If $\Delta G^0 << 0$, the equilibrium is shifted to right, the yield of product is large and the equilibrium constant is high. On the contrary, if $\Delta G^0 >> 0$, the equilibrium is shifted to the left, the yield is small and $(K << 1)$ equilibrium constant is very low. At chemical equilibrium, $\Delta G^0 = 0$.

The equilibrium constant (K) is defined in terms of the equilibrium activities a_i of the reactants and products. For a general reaction,

$$aA \rightarrow rR + sS$$

the equilibrium constant is

$$K = \frac{a_R^r \cdot a_S^s}{a_A^a} \qquad \text{... (6.21)}$$

The activities refer to equilibrium conditions in a reaction mixture. The activity is the *ratio of fugacity at the equilibrium conditions (i.e. in the equilibrium mixture) to that in the standard state.*

$$a_i = \frac{f_i}{f_i^o}$$

$$K = \frac{(f/f^o)_R^r \cdot (f/f_o)_S^s}{(f/f_o)_A^a} \qquad \text{... (6.22)}$$

For gaseous reactions with a standard state of unit fugacity (i.e. $f^o = 1$) the above equation becomes

$$K = \frac{f_R^r \cdot f_S^s}{f_A^a} \qquad \text{... (6.23)}$$

If the gases follow the ideal gas law, the fugacity is equal to pressure and therefore the equation (6.22) reduces to

$$K = \frac{p_R^r\, p_S^s}{p_A^a} \qquad \text{... (6.24)}$$

p is the partial pressure which is equal to the total pressure P times the mole fraction of the component in the mixture.

$$p_A = y_A \cdot P$$

In gaseous reactions, K_p is defined as

$$K_p = \frac{(y_R\, P)^r\, (y_S\, P)^s}{(y_A\, P)^a} = \left(\frac{y_R^r \cdot y_S^s}{y_A^a}\right) \times P^{\Delta n} = K_y\, P^{\Delta n} \qquad \text{... (6.25)}$$

where $\Delta n = r + s - a$

Comparing equations (6.24) and (6.25), it is clear that

$K = K_p$ for an ideal gas reaction mixture.

For non-ideal systems, equation (6.25) may still be used to calculate K_p from the measured equilibrium compositions (K_y).

In many situations, the assumption of ideal gases is not justified and it becomes necessity to evaluate fugacities. But the fugacity of only pure component is known. Hence, in such cases, it is necessary to make the assumption about the reaction mixture and simplest one being that- the mixture behaves as an ideal solution. The fugacity at equilibrium f, is related to fugacity of pure component, f', at the same temperature and pressure by

$$f_i = f_i\ y_i \qquad \text{... (6.26)}$$

Putting the value of f_i from equation (6.26) in equation (6.23) yields equilibrium constant in terms of pure component fugacities and composition of equilibrium condition.

$$K = \frac{(f_R')^r\,(f_S')^s}{(f_A')^a}\cdot K_y \qquad \ldots (6.27)$$

where
$$K_y = \frac{y_R^r \cdot y_S^s}{y_A^a} \qquad \ldots (6.28)$$

The equilibrium constant in terms of concentrations is given by

$$K_c = \frac{C_R^r\,C_S^s}{C_A^a} \qquad \ldots (6.29)$$

For any component i of an ideal gas,

$$f_i = p_i = y_i P = C_i RT$$

$$\therefore \quad K_f = K_p$$

and
$$K = K_p = K_y P^{\Delta n} = K_c (RT)^{\Delta n}$$

$$K_c = \frac{C_R^r\,C_S^s}{C_A^a}$$

$$K_p = \frac{p_R^r\,p_S^s}{p_A^a} = \frac{y_R^r\,y_S^s}{y_A^a}(P)^{\Delta n} = K_y\,P^{\Delta n}$$

$$= \frac{(C_R RT)^r\,(C_S RT)^s}{(C_A RT)^a} = \frac{C_R^r\,C_S^s}{C_A^a}(RT)^{\Delta n} = K_c (RT)^{\Delta n} \qquad \ldots (6.30)$$

where
$$\Delta n = r + s - a$$

Equilibrium Conversion :

The highest conversion that can be achieved in reversible reactions is equilibrium conversion. This is the only suggested attainable value.

Consider first order reversible reaction.

$$A \rightleftharpoons R$$

For this reaction, equilibrium constant is given by

$$K = K_c = C_{Re}/C_{Ae} = \frac{M + X_{Ae}}{1 - X_{Ae}}, \quad M = C_{Ro}/C_{Ao} \text{ [Refer Chapter 2]}$$

C_{Re}, C_{Ae} – equilibrium compositions of R and A respectively and X_{Ae} is the equilibrium conversion of A.

It is clear from above expression that equilibrium composition and equilibrium conversion are governed by equilibrium constant.

High K means high C_{Re} and X_{Ae} and vice-versa.

The equilibrium constant changes with temperature, so does the equilibrium conversion.

Now we will develop an equation for variation of equilibrium constant and hence equilibrium conversion with temperature.

The variation of equilibrium constant with temperature at constant pressure is quantitatively given by the van't Hoff Isobar (van't Hoff equation for constant pressure process) that relates the rate of change of K to temperature as

$$\frac{d(\ln K)}{dT} = \frac{\Delta H_R}{RT^2} \qquad \ldots (6.31)$$

It follows from equation (6.31) that when ΔH_R takes a +ve sign (i.e. when the reaction is endothermic), $d \ln K/dT > 0$ and K(T) is an increasing function (i.e. equilibrium constant and hence equilibrium conversion increases with increase in T for endothermic reaction). On the contrary, when ΔH_R takes a –ve sign (when the reaction is exothermic), $d \ln K/dT < 0$ and K(T) is a decreasing function (i.e. the equilibrium constant and hence equilibrium conversion decreases for exothermic reaction with increase in T). Hence, analysis of the equation (6.31) shows that it expresses quantitatively the finding that stems from Le-Chatelier's principle – an increase in temperature always shifts the equilibrium in the direction of an endothermic reaction.

When ΔH_R is independent of temperature which is true within the small temperature range then equation (6.31) can be integrated between appropriate limits by considering ΔH_R as a constant as follows :

$$\int_{K_1}^{K_2} d\ln K = \frac{\Delta H_R}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_R}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right] \qquad \ldots (6.32)$$

$$\Delta H_R = \Delta H_R^{\circ} \text{ when } T_1 = 298\text{ K}$$

When ΔH_R varies with temperature then it should be retained within the integral sign.

$$\int_{K_1}^{K_2} d \ln K = \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta H_R}{T^2}\, dT \qquad \ldots (6.33)$$

Variation of ΔH_R with temperature as per equation (6.11) from T_o to T, where T_o is the base temperature, is given by

$$\Delta H_{RT} = \Delta H_{Ro} + \int_{T_o}^{T} \Delta C_p\, dT \qquad \ldots (6.34)$$

$$= \Delta H_{Ro} + \Delta\alpha\,(T - T_o) + \frac{\Delta\beta}{2}(T^2 - T_o^2) + \frac{\Delta\gamma}{3}(T^3 - T_o^3) \qquad \ldots (6.35)$$

Putting the value of ΔH_R from equation (6.35) in equation (6.33), we get,

$$\int_{K_1}^{K_2} d \ln K = \frac{1}{R} \int_{T_1}^{T_2} \frac{[\Delta H_{Ro} + \Delta\alpha\,(T - T_o) + \frac{\Delta\beta}{2}(T^2 - T_o^2) + \frac{\Delta\gamma}{3}(T^3 - T_o^3)]\, dT}{T^2}$$

$$R \ln \frac{K_2}{K_1} = \Delta H_{Ro} \int_{T_1}^{T_2} \frac{dT}{T^2} + \Delta\alpha \int_{T_1}^{T_2} \frac{dT}{T} - \Delta\alpha\, T_o \int_{T_1}^{T_2} \frac{dT}{T^2} + \frac{\Delta\beta}{2} \int_{T_1}^{T_2} dT$$

$$- \frac{\Delta\beta\, T_o^2}{2} \int_{T_1}^{T_2} \frac{dT}{T^2} + \frac{\Delta\gamma}{3} \int_{T_1}^{T_2} T\, dT - \frac{\Delta\gamma}{3} T_o^3 \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$= \Delta\alpha \ln \frac{T_2}{T_1} + \frac{\Delta\beta}{2}(T_2 - T_1) + \frac{\Delta\gamma}{3}(T_2^2 - T_1^2)$$

$$+ \left[-\Delta H_{Ro} + \Delta\alpha T_o - \frac{\Delta\beta\, T_o^2}{2} + \frac{\Delta\gamma}{3} T_o^3\right]\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \qquad \ldots (6.36)$$

Equation (6.36) allows us to find the variation of equilibrium constant, hence, equilibrium conversion, with temperature.

If we take T_o as (25 °C) 298 K then ΔH_{Ro} in equation (6.36) is ΔH_R^o (standard heat of reaction).

The conclusions drawn from thermodynamics can be summarised as follows :

1. Thermodynamic equilibrium constant depends upon the temperature of the system and is independent of pressure of the system, presence of inerts in the system and the kineti of the reaction.

2. K >> 1 implies that practically complete conversion may be possible and that t reaction can be considered to be irreversible. K << 1 implies that reaction will not proceed to any appreciable extent (very low conversion is possible).

3. For endothermic reactions, equilibrium conversion rises with an increase in temperature and for exothermic reactions, the equilibrium conversion decreases with increase in temperature.

4. In case of gas phase reactions taking place with decrease in number of moles of the reaction system, the conversion rises with an increase in pressure of the reaction syste When gas phase reaction takes place with increase in number of moles of the reaction system, the conversion decreases with an increase in pressure of the reaction system.

5. A decrease in inerts for all reactions has the effect same as that of increase in pressure for gas phase reactions.

6. Equilibrium concentration of materials and equilibrium conversions can be affected by pressure of reaction system, presence or absence of inerts and kinetics of the reaction.

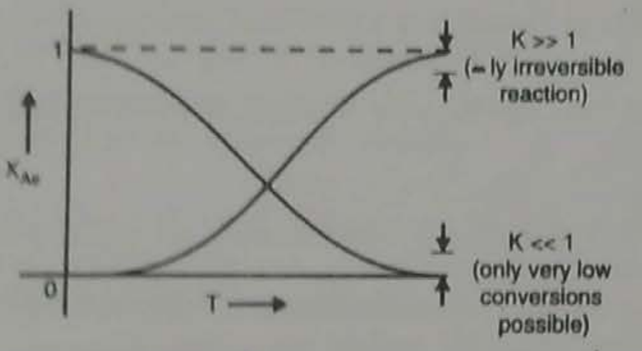
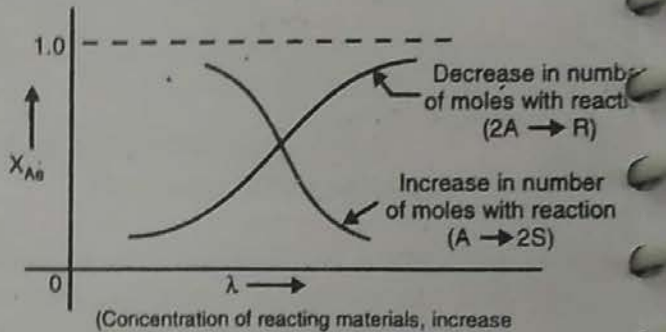


Fig. 6.2 : Effect of temperature on equilibrium conversion at constant pressure as predicted by thermodynamics



(Concentration of reacting materials, increase in pressure for gas phase reaction systems, decrease in inerts for all reaction systems)

Fig. 6.3 : Effect of pressure and inerts on equilibrium conversion at constant temperature as predicted by thermodynamics

General Graphical Design Procedure :

For any single homogeneous reaction, the temperature, composition and rate are uniquely related. The relationship between temperature, composition and rate may be represented graphically in one of the following ways :

(i) the composition v/s temperature plot with rate as a parameter,

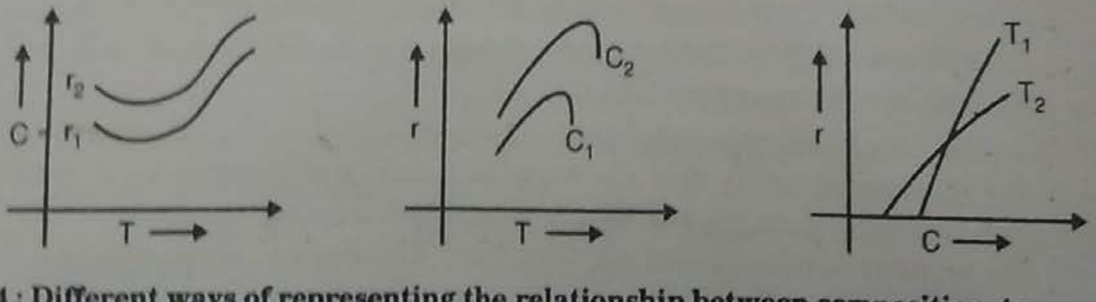


Fig. 6.4 : Different ways of representing the relationship between composition, temperature and rate for a homogeneous reaction

(ii) the rate v/s temperature plot with composition as a parameter,

(iii) the rate v/s composition plot with temperature as a parameter.

Out of these, the composition-temperature plot is the most convenient and we will use it to represent data, to calculate reactor sizes, etc.

For a given feed (fixed C_{Ao}, C_{Bo} ...) and using conversion of component A as a measure of composition and extent of reaction, for irreversible and reversible reactions, the X_A v/s T plot has general shapes as shown in Fig. 6.5.

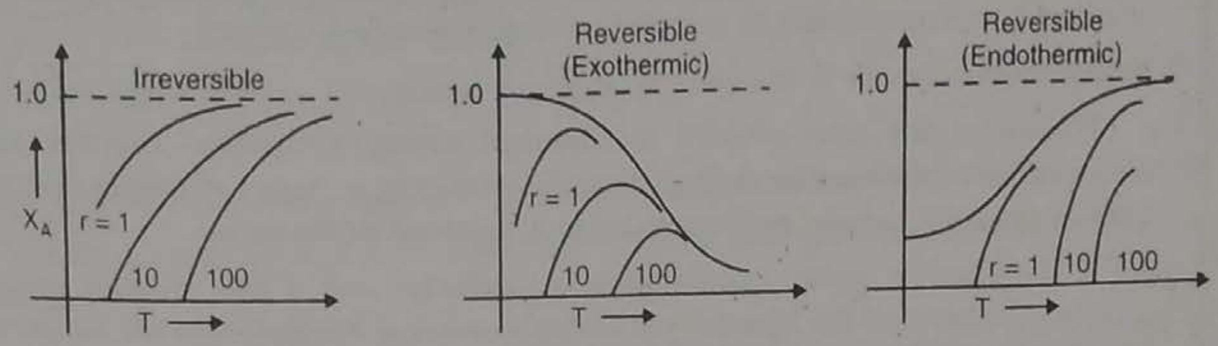


Fig. 6.5 : General shape of temperature-conversion plot for different types of reactions

The reactor size for a given duty (given conversion) and for given temperature, progression is found as follows :

(i) Draw the reaction path on the X_A v/s T plot. This is the operating line for the operation.

(ii) Find the rates at various values of conversion X_A along this path.

(iii) From $-r_A$ and X_A data, plot $1/(-r_A)$ v/s X_A.

(iv) Find the area under the curve which gives V/F_{Ao}.

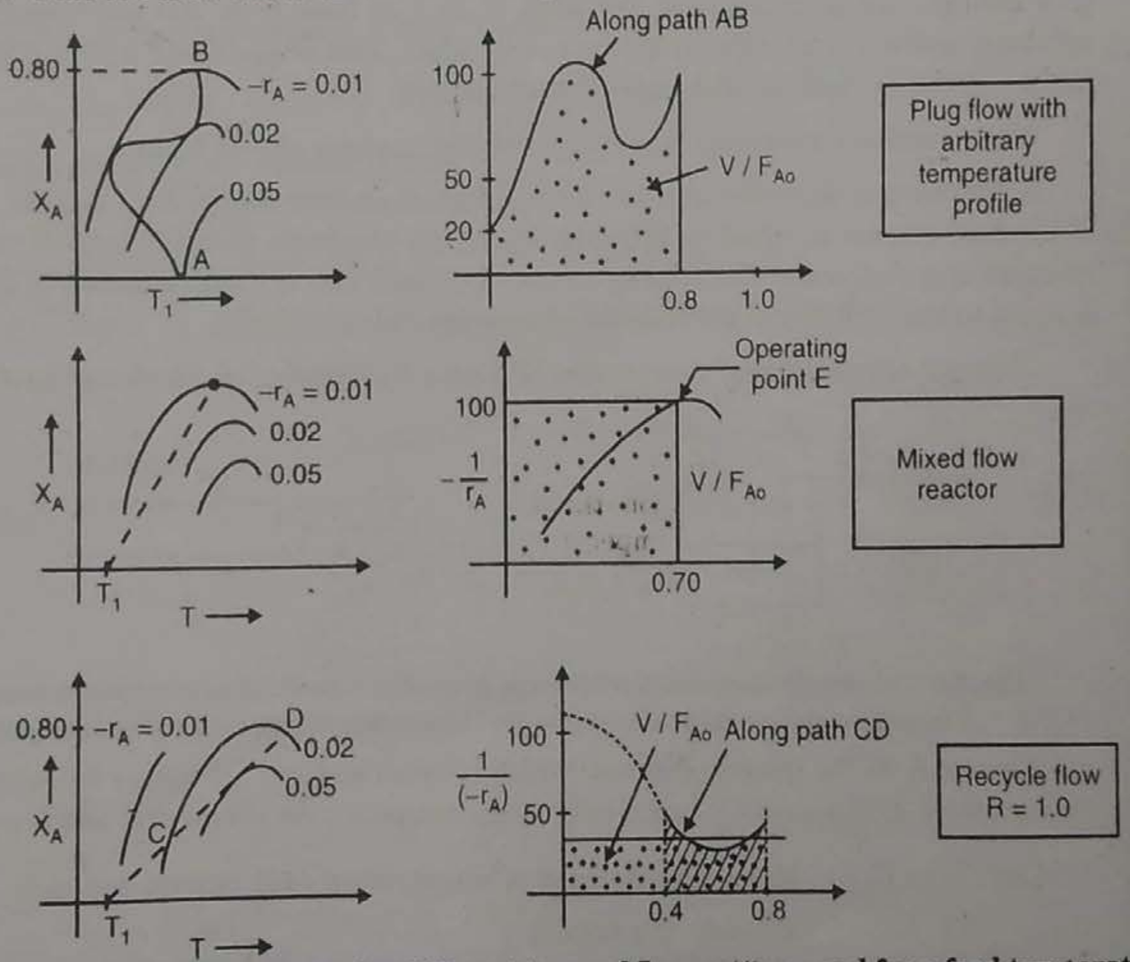


Fig. 6.6 : Finding different size for different types of flow patterns and for a feed temperature T_1

The procedure of determining the size for exothermic reactions for three paths : path AB for plug flow with arbitrary temperature profile, path CD for nonisothermal plug flow with 50% recycle, and point E for mixed flow is shown in Fig. 6.6. Keep in mind that for mixed flow, the operating line reduces to a single point.

Optimum Temperature Progression :

① In case of nonisothermal reactors we have to also find the temperature progression needed for optimum reactor performance. In case of ② multiple reactions this normally means the temperature sequence needed to obtain maximum selectivity for the desired product. ③ In case of single reactions this means the temperature sequence needed to minimise the reactor size of flow reactor for a given conversion or to minimise the time needed for a given conversion.

④ The optimum temperature progression is defined as that temperature progression which minimises V/F_{A_0} (i.e. size) for a given conversion of the reactant A. ⑤ This optimum may be isothermal (constant temperature) or it may be changing, temperature may be along the length of the plug flow reactor, with time in case of batch reactor, or from stage to stage in case of series of CSTRs/mixed flow reactors.

⑥ It is important to know this progression because it is the ideal which we try to approach with a real system and it also helps us to estimate how far any real system departs from this ideal.

The minimum volume will be achieved if the rate is maximum at all points in the reactor. ⑦ The optimum temperature at any point will be the one for which the rate is maximum at any conversion value. The optimum temperature progression in any type of reactor is : at any composition, it will be always at the temperature where the rate is maximum. Therefore, the relation r (T, C) is the basic information needed to determine the optimum temperature progression (say optimum temperatures along the length of plug flow reactor). The locus of maximum rates is found by examining the r (T, C) or r (T, X) curves of Fig. 6.5. Such progression is shown in Fig. 6.7.

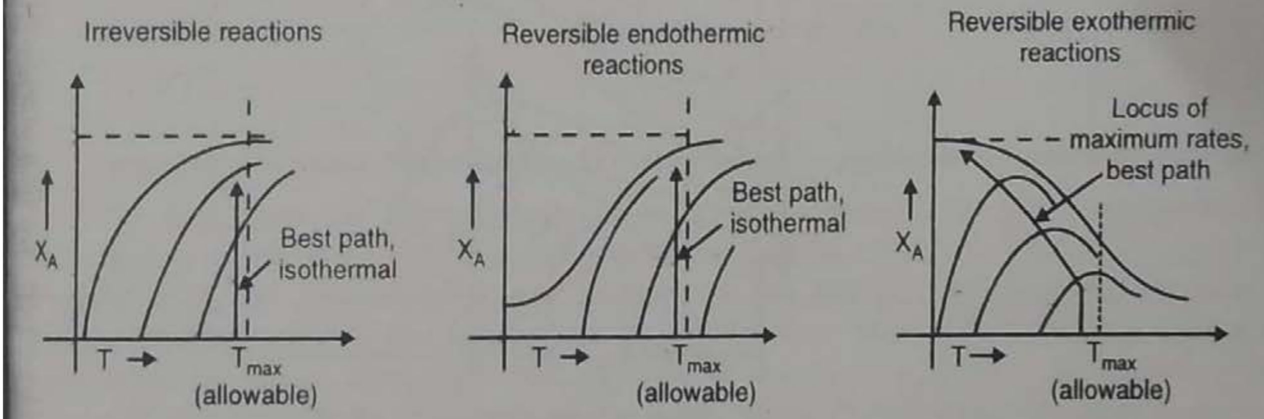


Fig. 6.7 : Operating lines for minimum reactor size

For irreversible reactions we have,

⑨
$$r\ (T, X) = k_o\ e^{-E/RT} \cdot f(X)$$

or

$$r\ (T, C) = k_o\ e^{-E/RT} \cdot f(C)$$

f(X) is the decreasing function of X [e.g. for first order reaction with C_{A_0}, $f(X) = C_{A_0}(1 - X_A)$]. As E is positive, the rate increases with temperature at any composition. The highest rate occurs at the highest allowable temperature. Hence, the optimum temperature progression (sequence) will be the highest temperature that is practical. The materials of constructions and possible increasing importance of side reactions can limit (set) this temperature. This conclusion applies to both exothermic and endothermic reactions.

For a reversible reaction,

$$r(T, X) = k_0 e^{-E/RT} f(X) - k_0' e^{-E'/RT} g(X)$$

where E' and g(X) apply to the reverse reaction. The function g(X) is an increasing function of X as the concentration of products increases with conversion. For endothermic reversible reaction E > E' and hence the rate increases with temperature for any conversion. We therefore conclude that for reversible endothermic reactions, the optimum temperature progression is the highest allowable temperature.

For an exothermic reversible reaction E' > E. Therefore, as temperature is increased, the rate of the reverse reaction increases more rapidly than that of the forward reaction (so the maximum attainable conversion decreases). It is clear from equation cited above that the reverse reaction is slow at low conversions while the forward reaction is fast. So for rate to be maximum at any conversion, the temperature should be high at low conversions in order to take the advantage of the predominant rate of the forward reaction and temperature should be lower at high conversions where the rate of the reverse reaction is high. Therefore, for reversible exothermic reactions the optimum temperature progression will be continually decreasing temperature with conversion. In general, reversible exothermic reaction starts at high temperature that decreases as the conversion rises. Fig.6.8 shows this optimum progression. The optimum temperature progression (i.e. optimum values of temperature at different conversion) is found by the maxima of the different rate curves. The line so obtained is called as the locus of maximum rates.

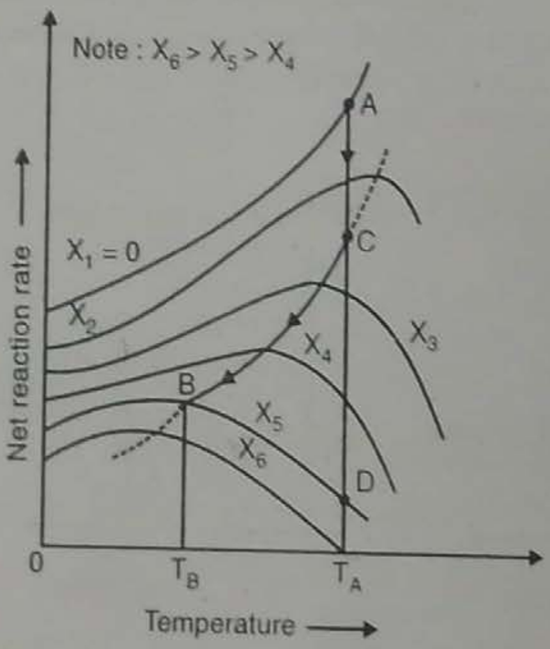


Fig. 6.8 : Optimum temperature progression for an exothermic reversible reaction

r v/s T plot with X as a parameter is given in Fig. 6.8.

- Suppose that a feed to plug flow reactor is unconverted ($X_A = 0$) and at temperature T_A. The rate at the entrance of reactor corresponds to point A. If we require a conversion of X_5 then rate at outlet of reactor would be at point B. The maximum in the rate v/s T curves that is required cannot be achieved in the first part of the reactor because the maximum temperature is T_A. Hence, the best that can be done is to operate isothermally at T_A until the conversion at point C is reached and then onwards follow the dashed line to get the required conversion. The optimum temperature progression path is ACB in Fig. 6.8.

If we operate the reactor isothermally at the feed temperature instead of operating along optimum temperature path, the rate sequence would be that corresponding to vertical line ACD. Such rate would be lower than the rates for the optimum progression for every conversion except from X = 0 to X at point C. Therefore, we would require greater size reactor.

A mixed flow reactor operates at constant temperature and conversion. If the required conversion is X_5, the optimum condition, the condition at which rate is maximum, would require operating at a temperature T_B. The rate at point B is less than that at point A. So the size of mixed flow reactor would be greater than that of plug flow reactor.

Heat Effects :

Whenever the heat evolved or absorbed during a chemical reaction changes the temperature of the reacting fluid, it must be considered in design of reactor and therefore we have to use both material and energy balance equations for the same.

If the reaction under consideration is exothermic and if heat transfer arrangement is unable to remove all the heat evolved during a course of reaction, then the temperature of the reacting fluid will increase as conversion increases. On the other hand, if the reaction under consideration is endothermic on similar lines, the temperature of reacting fluid decreases as the conversion increases. In such cases, we have to relate the temperature with conversion through energy balance.

Adiabatic Operations :

Adiabatic operation (process) is the one in which the system under consideration does not give heat to the surroundings nor does it receive heat from the surroundings. Here the adiabatic process is considered as the one in which heat is contained within a system without loss or addition of heat to or from the outside source.

When adiabatic reactions take place, two observations can be made :

If the reaction is exothermic, the temperature of product stream rises and the total enthalpy of product stream is equal to the enthalpy of the reactants plus the heat of reaction. If the reaction is endothermic, the product stream decreases and the total enthalpy of product stream is equal to the enthalpy of the reactants minus the heat of reaction.

Consider either a mixed flow reactor or a plug flow reactor as shown in Fig. 6.9.

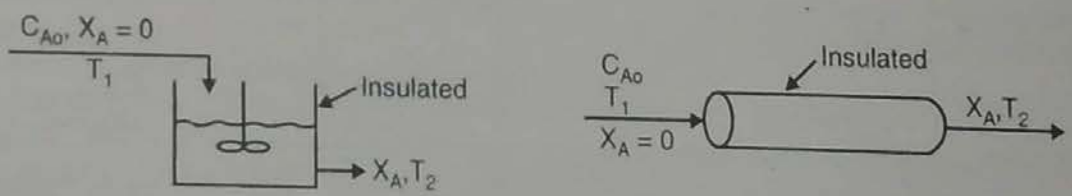


Fig. 6.9 : Adiabatic operations with large heat effect, so there is increase in temperature (exothermic) or decrease in temperature (endothermic) of the reacting fluid

Assume A be the limiting reactant which is taken as basis for energy balance and X_A be the conversion of A. Subscripts 1 and 2 refer to the temperatures of entering and leaving stream.

Let, C_p' : Mean specific heat of unconverted feed stream per mole of reactant A entering the system.

C_p'' : Mean specific heat of completely converted product stream (i.e. of products) per mole of reactant A entering the system.

H' : Enthalpy of unreacted feed stream per mole of reactant A entering the system.

H'' : Enthalpy of completely converted product stream per mole of reactant A entering the system.

ΔH_i : Heat of reaction per mole of reactant A entering the system and at temperature T_i.

Let T_1 be the reference temperature on which enthalpies and heats of reaction are based.

Enthalpy of entering feed to the system (over T_1) i.e. heat content of entering stream to the system over T_1 :

$$H_1' = C_p'(T_2 - T_1) = 0, \quad \text{J/mol A}$$

As X_A is fractional conversion of A,

$$X_A = \frac{\text{moles of A reacted}}{\text{moles of A entering to the system}}$$

$$(1 - X_A) = \frac{\text{moles of A unreacted}}{\text{moles of A entering to the system}}$$

Enthalpy of leaving stream (i.e. heat content of leaving stream at T_2 over T_1) :

$$H_2'' X_A + H_2'(1 - X_A) = C_p''(T_2 - T_1) X_A + C_p'(T_2 - T_1)(1 - X_A), \quad \text{J/mol A}$$

Energy absorbed by reaction :

$$\Delta H_{R1} \cdot X_A \quad \text{J/mol A}$$

The energy balance over system is :

input = output + accumulation + disappearance by reaction.

At steady state we get,

$$0 = [C_p''(T_2 - T_1) X_A + C_p'(T_2 - T_1)(1 - X_A)] + H_{R1} \cdot X_A \quad \text{... (6.37)}$$

$$C_p''(T_2 - T_1) X_A + C_p'(T_2 - T_1) - C_p'(T_2 - T_1) X_A + H_{R1} X_A = 0$$

$$-X_A [\Delta H_{R1} + C_p''(T_2 - T_1) - C_p'(T_2 - T_1)] = C_p'(T_2 - T_1)$$

$$\therefore \quad X_A = \frac{C_p'(T_2 - T_1)}{-\Delta H_{R1} - (C_p'' - C_p')(T_2 - T_1)} = \frac{C_p' \Delta T}{-\Delta H_{R1} - (C_p'' - C_p')\Delta T} \quad \text{... (6.38)}$$

(as $\Delta T = T_2 - T_1$)

We have,

$$\Delta H_{R2} = \Delta H_{R1} + (C_p'' - C_p')\Delta T$$

$$\therefore \quad X_A = \frac{C_p' \Delta T}{-\Delta H_{R2}} = \frac{\text{heat required to raise feed stream to } T_2}{\text{heat released by reaction at } T_2} \quad \text{... (6.39)}$$

For complete conversion, $X_A = 1$ and equation (6.39) reduces to

$$-\Delta H_{R2} = C'_p \, \Delta T \qquad \text{...(6.40)}$$

Equation (6.40) states that the heat released by reaction just balances the heat required to raise the temperature of reactants from T_1 to T_2.

The energy balance relates conversion and temperature through equations (6.38) or (6.39). This relationship between conversion and temperature is shown in Fig. 6.10. For all practical purposes, the resulting lines are straight due to relatively small variation of the denominator term of these equations. When $C''_p - C'_p = 0$, the heat of reaction is independent of temperature and hence equations (6.38) and (6.39) reduce to

$$X_A = \frac{C_p \, \Delta T}{-\Delta H_R} \qquad \text{...(6.41)}$$

Equation (6.41) gives linear relationship between X_A and T and so this energy balance line is a straight line.

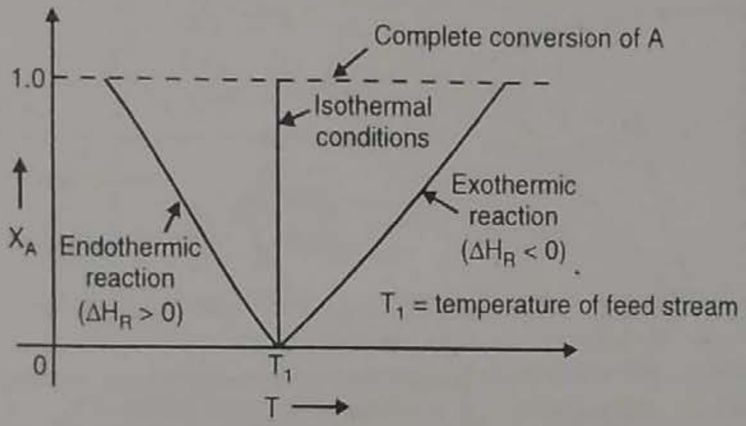


Fig. 6.10 : Graphical representation of energy balance equation for adiabatic operations

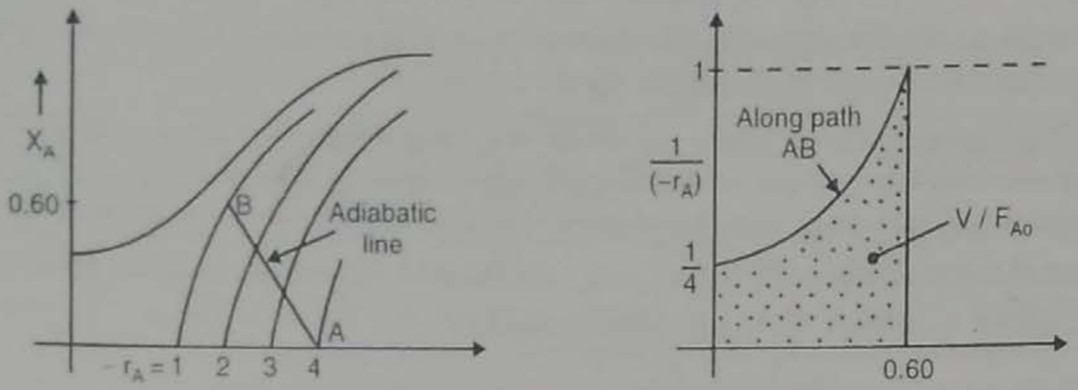
Fig. 6.10 gives the general shape of energy balance curve for both endothermic and exothermic reactions for both mixed flow and plug flow reactors. The 6.10 clearly shows that whatever is the conversion at any location in the reactor, the temperature is at its corresponding point on the curve. In case of plug flow reactor the reacting fluid moves progressively along this curve and in case of mixed flow reactor the reacting fluid immediately jumps to its final value on the curve. These are called the operating lines for the reactor. A vertical line implies that temperature remains unchanged as the reaction proceeds which is the case of reactions carried out isothermally.

The size of reactor required to achieve given conversion is found as follows :

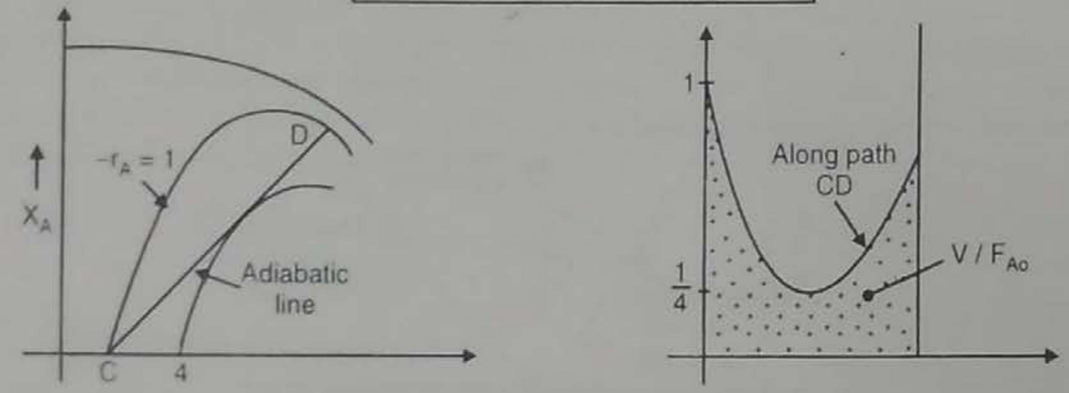
(1) Plug flow reactor : (a) Tabulate the rate for various X_A along this operating line, (b) prepare $1/(-r_A)$ v/s X_A plot and integrate between $X_A = 0$ and $X_A = X_{Af}$ (Measure area under the curve between $X_A = 0$ and $X_A = X_{Af}$) which gives V/F_{A0}.

(2) Mixed flow reactor : Use the rate at the conditions within the reactor and find size (by measuring rectangular area from $X_A = 0$ and $X_A = X_{Af}$) which gives V/F_{A0}.

Endothermic plug flow reactor



Exothermic plug flow reactor



Exothermic mixed flow reactor

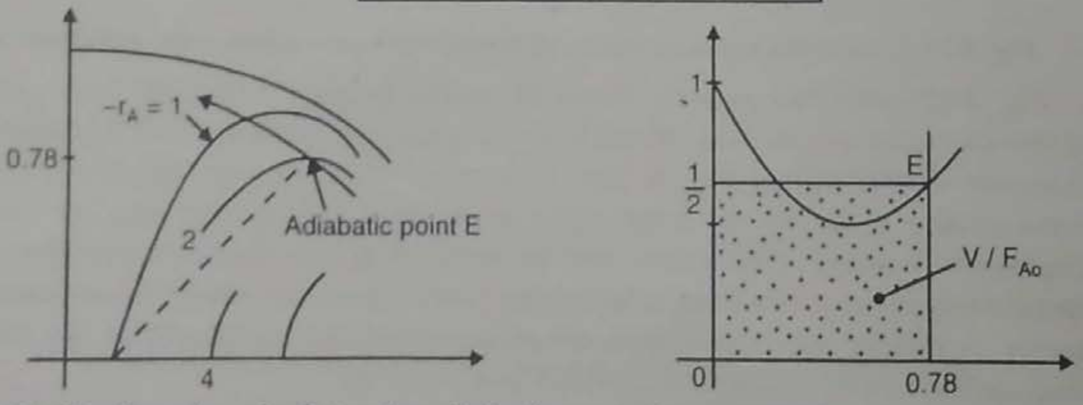


Fig. 6.11 : Finding size of reactor for adiabatic operations of plug flow and mixed flow reactors

The best reactor type (the one which minimises V/F_{Ao}) is found out from X_A v/s T graph. If the rate progressively decreases with conversion then one should use plug flow reactor. This is the case for endothermic reactions. In case of exothermic reactions with large temperature rise during the reaction, the rate rises from a very low value to a maximum at some intermediate conversion and then falls. Such behaviour is the characteristic of autocatalytic reaction and hence in such cases recycle operations are best. Fig. 6.12 shows two situations wherein in one case plug flow is best and in other case the mixed flow is best. The slope of the operating line, $C_p/-\Delta H_R$ will determine the case with which we are dealing.

(a) Mixed flow is best for small $C_p/-\Delta H_R$.

(b) Plug flow is best for large $C_p/-\Delta H_R$.

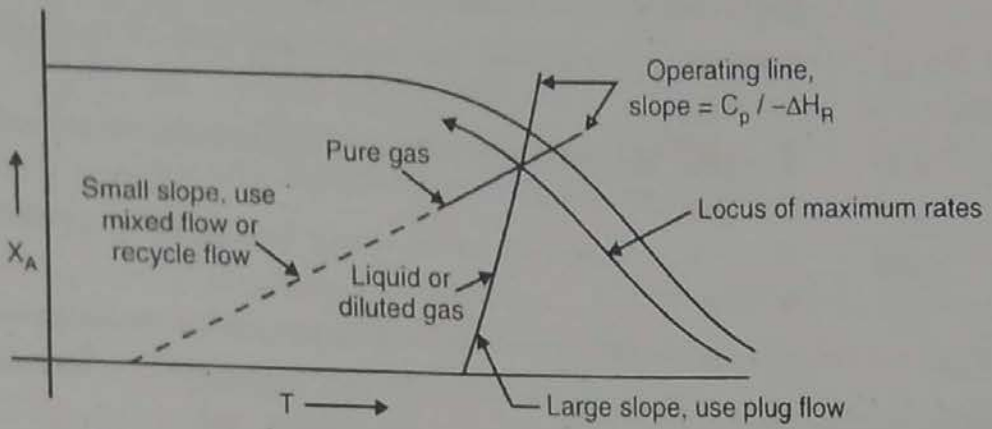


Fig. 6.12 : For exothermic reaction where temperature rise is large mixed flow is best; for close to isothermal systems plug flow is best

Non-adiabatic Operations :

In industrial practice, the reaction temperatures are controlled by either addition or removal of heat depending upon the situation. This is required because of demands from kinetic and thermodynamic considerations. When we provide such type of temperature control, the reaction becomes non-adiabatic.

Let Q be the total heat added to the reactor per mole of reactant A entering the reactor (assume that Q includes heat losses to the surroundings).

The energy balance about the system yields,

$$Q = C_p''(T_2 - T_1)X_A + C_p'(T_2 - T_1)(1 - X_A) + \Delta H_{R1} X_A \qquad \text{... (6.42)}$$

$$Q = C_p''(T_2 - T_1)X_A + C_p'(T_2 - T_1) - C_p'(T_2 - T_1)X_A + \Delta H_{R1} X_A$$

$$-X_A[\Delta H_{R1} + C_p''(T_2 - T_1) - C_p'(T_2 - T_1)] = C_p'(T_2 - T_1) - Q$$

$$X_A = \frac{C_p'(T_2 - T_1) - Q}{-\Delta H_{R1} - (C_p'' - C_p')(T_2 - T_1)} = \frac{C_p'\Delta T}{-\Delta H_{R1} - (C_p'' - C_p')\Delta T} \qquad \text{... (6.43)}$$

We have $\Delta H_{R2} = \Delta H_{R1} + (C_p'' - C_p')\Delta T$

$$\therefore \quad X_A = \frac{C_p'\Delta T - Q}{-\Delta H_{R2}} = \left(\frac{\text{net heat still required after heat transfer to raise feed stream to } T_2}{\text{heat released by reaction at } T_2}\right) \qquad \text{... (6.44)}$$

When $C_p'' = C_p'$, the heat of reaction is independent of temperature and we get,

$$X_A = \frac{C_p\Delta T - Q}{-\Delta H_R} \qquad \text{... (6.45)}$$

With heat input proportional to ΔT, the energy balance line for adiabatic operation rotates about T_1 which is shown in Fig. 6.13.

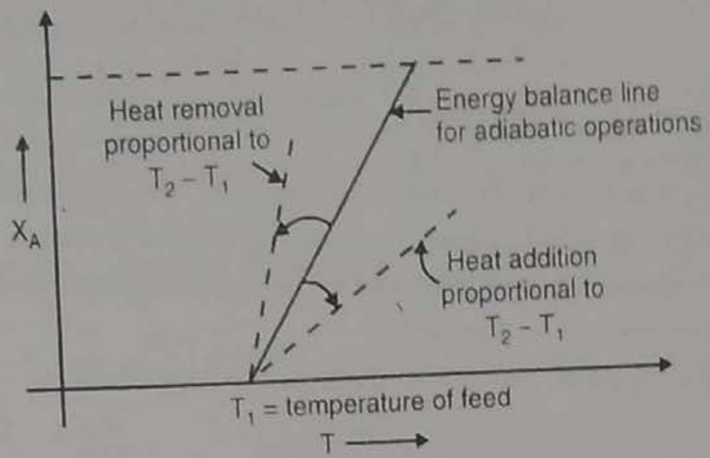


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Fig. 6.13 : Sketch of energy balance equation showing shift in adiabatic line resulted by heat exchange with the surroundings

Equation (6.45) is the operating line for non-adiabatic operation. The procedure for determining the reactor size for adiabatic operation is applicable for non-adiabatic operation.

In case of exothermic reactions carried out in an adiabatic manner, temperature increases with conversion. In such cases, following schemes may be proposed to remove heat in order to achieve ideal temperature profile.

(i) Heat exchange with incoming feed :

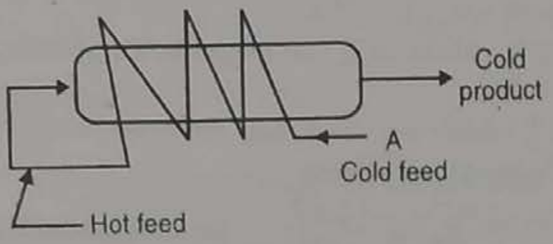


Fig. 6.14

(ii) Multistage operation with interstage cooling between adiabatic sections :

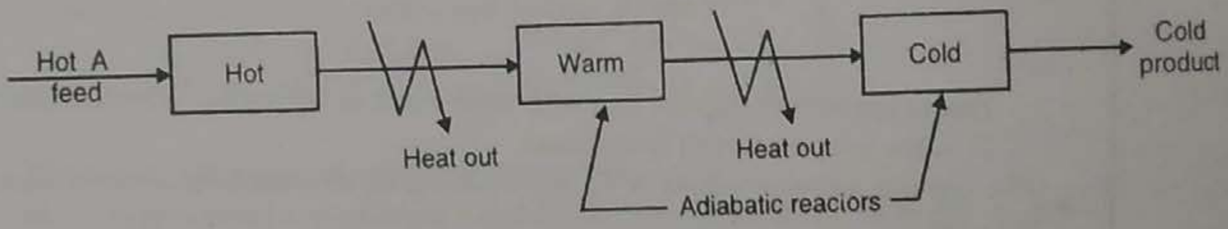


Fig. 6.15

In case of endothermic reaction carried out in adiabatic manner, multistage operatio with reheat between stages is commonly used to keep the temperature falling to low.

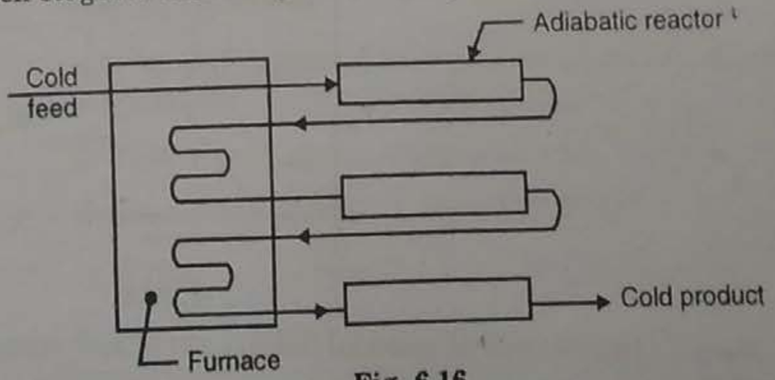


Fig. 6.16

Stable operating conditions in mixed flow reactor :

The permissible or stable operating conditions (temperatures and conversions) can be obtained analytically and graphically by combining the material and energy balances. At a given temperature T_1, the intersection of the energy balance line with material balance line for given τ gives the stable operating conditions within the reactor. Here X is plotted as a function of T for the material and energy balances and intersection gives the solution where both material and energy balance solutions are satisfied. By this graphical method, one can get idea regarding whether there are more than one intersection (i.e. multiple steady state) for which both material and energy balances are satisfied. On this plot virtually straight line corresponds to energy balance and curved line corresponds to material balance. More than one intersection means more than one reactor composition satisfying material and energy balance equations and such type of situation may develop in case of exothermic reactions in mixed flow reactor.

Suppose that exothermic irreversible first order reaction is carried out in an adiabatic mixed flow reactor.

Steady state material balance for a mixed flow reactor yields

$$\tau = \frac{C_{A_0} X_A}{-r_A} = \frac{C_{A_0} X_A}{k\, C_{A_0}(1 - X_A)} = \frac{X_A}{k\,(1 - X_A)}$$

$$X_A = \frac{k\tau}{1 + k\tau}\ ,\quad k = k_o\, e^{-E/RT_2}$$

where T_2 is exit stream temperature from reactor.

In terms of temperature,

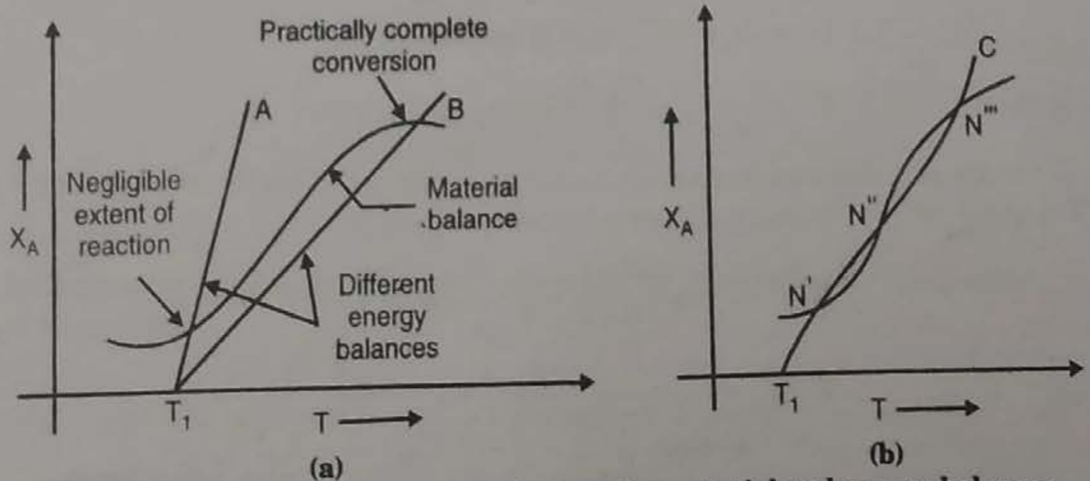
$$X_A = \frac{k_o\, \tau\, e^{-E/RT_2}}{1 + k_o\, \tau\, e^{-E/RT_2}} \qquad \text{... (6.46)}$$

At each reactor temperature there is some particular conversion satisfying this material balance equation (6.46). At low temperature, rate is low and so the conversion is low and at high temperature the conversion rises and approaches unity for irreversible reaction for given τ. The S-shaped curve representing this T v/s X_A relationship is the material balance line shown in Fig. 6.17. Any point on this curve represents the solution of the material balance equation and hence represents the operating point for the mixed flow reactor.

The steady state energy balance for adiabatic operation is

$$X_A = \frac{C_p\, \Delta T}{-\Delta H_R}\ ,\quad \Delta T = T_2 - T_1,\ \ T_1 = \text{feed temperature} \qquad \text{... (6.47)}$$

This energy balance equation shows linear relationship between temperature and conversion and is represented by a straight line in Fig. 6.17.



(a) (b)

Fig. 6.17 : Three types of solutions for material and energy balances for exothermic irreversible reaction in mixed flow reactor

The relative position of the material balance curve and the energy balance line depends upon the properties such as k_o, E, ΔH_R and C_p, and operating conditions τ and C_{Ao} according to equations (6.46) and (6.47). These properties and operating conditions determine whether or not stable operating conditions exist and how many stable operating points exist.

The energy balance line T_1A is steep and represents the situation where insufficient heat is liberated by reaction to raise the temperature to a high enough level for reaction to be self-sustaining. Therefore the conversion is negligible. The energy balance line intersects at a temperature only slightly above the feed temperature. This point is the stable operating condition. If the heat liberated is very large the fluid will be hot and nearly complete conversion occurs (line T_1B). The intersection occurs at nearly complete conversion and the reactor temperature is far above T_1.

The energy balance line T_1C indicates the intermediate situation which has three solutions to material and energy balance equations at three points N', N'' and N'''. Point N'' is an unstable state because with small increase in temperature the heat generated (with rapidly rising material balance curve) is greater than the heat consumed by the reacting fluid (energy balance curve). The excess heat generated will result in rise in temperature until N''' is reached. By similar arguments, if the temperature falls slightly below N'' it will continue to fall until point N' is reached. Hence consider point N'' as the ignition point. If the reaction mixture can be raised above the temperature corresponding to N'' then the reaction will be self-sustaining.

Design procedure for CSTR :

[A] X_A, conversion of A is specified and we have to determine V and T.

Step 1 : Write the rate equation (given). e.g. $-r_A = k\, C_A$.

Step 2 : Express rate equation in terms of conversion. e.g. $-r_A = k\, C_{Ao}(1 - X_A)$.

Step 3 : Write performance equation in any suitable form (based upon whether F_{Ao} or v_o is provided).

e.g. $$V = \frac{F_{Ao}\,X_A}{(-r_A)}$$

Step 4 : Combine steps-2 and 3 to get

$$V = \frac{F_{Ao}\,X_A}{k\,C_{Ao}(1 - X_A)}$$

Step 5 : From given information regarding k as a function of T, express k in terms of T in above equation.

e.g. If we are provided with information of the type :

$$k = k_o\,e^{-E/RT}, \quad k_o, \; E \text{ are known}$$

then $$V = \frac{F_{Ao}\,X_A}{k_o\,e^{-E/RT}\cdot C_{Ao}(1 - X_A)}$$

If we are supplied with k value at known temperature T' and E value of then k as a function of T is given as

$$k = k'\exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)\right], \quad k' \text{ is known value at } T'$$

$$\therefore \quad V = \frac{F_{Ao}\,X_A}{k'\exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)\right]\cdot C_{Ao}\cdot(1 - X_A)}$$

In this equation, only unknown is T. We can obtain this T through energy balance.

Step 6 : Write energy balance

e.g. $$X_A = \frac{C_p \Delta T}{-\Delta H_R} = \frac{C_p (T_2 - T_1)}{-\Delta H_R}, \text{ for adiabatic operation}$$

Here C_p, T_1, $-\Delta H_R$ and X_A are known. T_2 is the temperature within the reactor at X_A.

Get T_2, $T = T_2$

If ΔH_R is not given directly, evaluate it by using appropriate equation from given data.

Step 7 : Use this T in step-5 and get the volume of reactor.

[B] Volume V is specified and we have to determine X_A and T.

Perform steps-1 to 4 as usual.

Step 5 : Express conversion in terms of temperature.

$$V = \frac{F_{A0} X_A}{k\, C_{A0} (1 - X_A)}$$

$$\frac{V\, C_{A0}}{F_{A0}} = \tau = \frac{X_A}{k\,(1 - X_A)}$$

$$\therefore \quad X_A = \frac{\tau k}{1 + \tau k}$$

If k is given as, $k = k_o\, e^{-E/RT}$

$$\therefore \quad X_A = \frac{\tau \cdot k_o\, e^{-E/RT}}{1 + k_o\, e^{-E/RT}}$$

Here we know τ, k_o, E and R.

Take suitable values of T and evaluate X_A starting from $T = T_1$ (given feed temperature) till we get $X_A = 1.0$.

Plot X_A v/s T which is a Q-shaped material balance curve.

Step 6 : Write energy balance

e.g. $$X_A = \frac{C_p \Delta T}{-\Delta H_R}, \text{ for adiabatic operation}$$

C_p, T_1 and ΔH_R are known here. If ΔH_R is not provided directly, calculate it from data given.

$$X_A = \frac{C_p (T_2 - T_1)}{-\Delta H_R}$$

This is the energy balance line with slope equal to $C_p / -\Delta H_R$. Plot this line.

T_1 is the temperature of feed stream.

OR : Assume suitable values of T_2 and evaluate X_A with the help of above equation and plot line as X_A v/s T.

This energy balance line is a straight line.

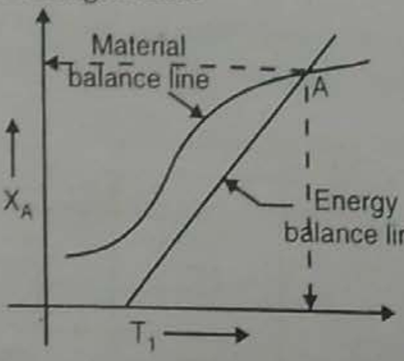


Fig. 6.18

Step 7 : Intersection of material balance curve and energy balance line gives the operating T and X_A.

SOLVED EXAMPLES

Ex. 6.1 : The standard heat of gas phase reaction at 25 °C (298 K)

$$A + B \rightarrow 2R \text{ is } \Delta H_R^o = \Delta H_{R\,(298\ K)} = -50000\ J$$

indicating that the reaction is strongly exothermic. It is planned to run this reaction at 1000 °C. What is the value of heat of reaction at that temperature ? Is the reaction still exothermic at 1000 °C ?

Data : The mean/average C_p values between 25 °C and 1000 °C for various reaction components are :

$$\bar{C}_{p_A} = 35\ J/(mol.K),\quad \bar{C}_{p_B} = 45\ J/(mol.K),\quad \bar{C}_{p_R} = 70\ J/(mol.K)$$

Solution : $A + B \rightarrow 2R$

$$T_1 = 25\,^oC = 298\ K,\quad \Delta H_R^o = \Delta H_{R1} = -50000\ J$$

$$T_2 = 1000\,^oC = 1273\ K,\quad \Delta H_{R2} = ?$$

$$\Delta H_{R2} = \Delta H_{R1} + \Delta\bar{C}_p\,(T_2 - T_1)$$

$$\Delta H_{RT} = \Delta H_R^o + \Delta\bar{C}_p\,(T - 298)$$

$$\Delta\bar{C}_p = r\,\bar{C}_{p_R} - a\,\bar{C}_{p_A} - b\,\bar{C}_{p_B}$$

$$= 2 \times \bar{C}_{p_R} - 1 \times \bar{C}_{p_A} - 1 \times \bar{C}_{p_B}$$

$$= 2 \times 70 - (1 \times 35 + 1 \times 45)$$

$$= 60$$

$$\Delta H_{RT} = \Delta H_{R\ at\ 1000^oC} = -50000 + 60\ (1273 - 298)$$

$$= 8500\ J$$ ... **Ans.**

As ΔH_{R2} i.e. heat of reaction at 1000 °C is +ve, the reaction is endothermic at 1000 °C... **Ans.**

Ex. 6.2 : Calculate the heat of reaction for the synthesis of ammonia from hydrogen and nitrogen at 150 °C in kJ/mol H_2 reacted and kJ/mol N_2 reacted.

$$N_2 + 3H_2 \rightarrow 2NH_3$$

Standard heat of formation of ammonia is – 11020 cal/mol N_2.

Use :

(i) Mean heat capacities of reaction components.

Mean heat capacities of reaction components over the range 25 °C to 150 °C are –

$$\bar{C}_{PH_2} = 6.992\ cal/(mol.K),\quad \bar{C}_{PN_2} = 6.984\ cal/(mol.K)$$

$$\bar{C}_{PNH_3} = 8.92\ cal/(mol.K)$$

(ii) C_p of each reacting component is expressed as a quadratic function of temperature.

$$C_{PH_2} = 6.946 - 0.196 \times 10^{-3}\,T + 0.476 \times 10^{-6}\,T^2$$

$$C_{PN_2} = 6.457 + 1.39 \times 10^{-3}\,T - 0.069 \times 10^{-6}\,T^2$$

$$C_{PNH_3} = 5.92 + 8.963 \times 10^{-3}\,T - 1.764 \times 10^{-6}\,T^2$$

Solution : $N_2 + 3H_2 \rightarrow 2NH_3$

$$\Delta H^o_{f\,NH_3} = -11020\ cal/mol$$

Standard heats for formation of N_2 and H_2 are zero.

$$\Delta H_R^o = \Delta H_{R\ at\ T=298\ K} = \sum \Delta H^o_{f\,(products)} - \sum \Delta H^o_{f\,(reactants)}$$

$$= 2 \times (-11020) - [1 \times 0 + 3 \times 0]$$

$$= -22040\ \text{cal/mol}\ N_2$$

ΔH_{RT} is heat of reaction at temperature T

$$T = 150 + 273 = 423\ K$$

(i) Use of mean molar heat capacities :

Heat of reaction at any temperature T is given by,

$$\Delta H_{R2} = \Delta H_{R1} + \Delta \bar{C}_p (T_2 - T_1)$$

$$\Delta H_{RT} = \Delta H_R^o + \Delta \bar{C}_p (T - 298)$$

$$\Delta \bar{C}_p = 2 \times \bar{C}_{pNH_3} - [1 \times \bar{C}_{p_{N_2}} + 3 \times \bar{C}_{p_{H_2}}]$$

$$= 2 \times 8.92 - [1 \times 6.984 + 3 \times 6.992]$$

$$= -10.12\ \ \text{cal/(mol.K)}$$

$$\Delta H_{RT} = -22040 + (-10.12)\ (423 - 298)$$

$$= -23305\ \text{cal/mol}\ N_2\ \text{reacted}$$

$$= -97.58\ \text{kJ/mol}\ N_2\ \text{reacted}$$ **... Ans.**

$$= -97.58 \times \frac{1}{3} = -32.53\ \text{kJ/mol}\ H_2\ \text{reacted}$$ **... Ans.**

(As 1 mol $N_2 \equiv 3$ mol H_2)

(ii) Use of C_p as a quadratic function of temperature :

$$\Delta H_{RT} = \Delta H_R^o + \Delta\alpha\,(T - 298) + \frac{\Delta\beta}{2}\,(T^2 - 298^2) + \frac{\Delta\gamma}{3}\,(T^3 - 298^3)$$

$$\Delta\alpha = 2\,\alpha_{NH_3} - 1\,\alpha_{N_2} - 3\,\alpha_{H_2}$$

$$= (2 \times 5.92) - (1 \times 6.457 + 3 \times 6.946) = -15.455$$

$$\Delta\beta = [2 \times (8.963) - 1 \times (1.39) - 3 \times (-0.196)] \times 10^{-3} = 15.948 \times 10^{-3}$$

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

$$T = 423\ K$$

$$\Delta H_{RT} = -22040 - 15.455\,(423 - 298) + \frac{15.948 \times 10^{-3}}{2}\,(423^2 - 298^2) - \frac{4.887 \times 10^{-6}}{3}\,(423^3 - 298^3)$$

$$= -23333.4\ \text{cal/mol}\ N_2\ \text{reacted}$$

$$= -97.7\ \text{kJ/mol}\ N_2\ \text{reacted}$$ **... Ans.**

$$= -97.7 \times \frac{1}{3} = -32.57\ \text{kJ/mol}\ H_2\ \text{reacted}$$ **... Ans.**

Ex. 6.3 : Determine the equilibrium conversion for the following elementary reaction between 0 °C and 100 °C.

$$A \rightleftharpoons R$$

At 298 K : $\Delta G^o = -14130$ J/mol, $\Delta H_R^o = -75300$ J/mol, $C_{p_A} = C_{p_R}$ = constant.

(i) Construct a plot of temperature v/s conversion.

(ii) What restrictions should be placed on the reactor operating isothermally if conversion of 75% or highest is desired ?

Solution : $A \rightleftarrows R$

At 298 K : $\Delta G^o = -14130$ J/mol,

$$\Delta H_R^o = -75300 \text{ J/mol}$$

$$C_{p_A} = C_{p_R} = \text{constant}$$

$\therefore$ $\Delta C_p = 0$ and hence heat of reaction is independent of temperature.

$$\therefore \quad \Delta H_R = \Delta H_R^o = -75300 \text{ J/mol}$$

Relation between ΔG^o and K is

At 298 K : $\Delta G^o = -RT \ln K$

$$K_{298} = e^{-\Delta G^o/RT} = \exp.\left(\frac{-\Delta G^o}{RT}\right)$$

$$= \exp.\left(\frac{+14130}{8.314 \times 298}\right)$$

$$= 299.8 \approx 300$$

As the heat of reaction does not change with the temperature, the equilibrium constant at any temperature T is given by

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H_R}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

$$\ln\left[\frac{K}{K_{298}}\right] = \frac{-\Delta H_R}{R}\left[\frac{1}{T} - \frac{1}{298}\right]$$

$$K = K_{298} \exp\left[\frac{-\Delta H_R}{R}\left(\frac{1}{T} - \frac{1}{298}\right)\right]$$

$$K = 300 \exp\left[-\frac{(-75300)}{RT} + \frac{(-75300)}{R \times 298}\right]$$

$$K = 300 \exp\left[\frac{75300}{RT} - 30.40\right]$$

$$K = \exp(5.7) \cdot \exp\left[\frac{75300}{RT} - 30.4\right], \quad 300 = e^{5.7}$$

$$K = \exp\left[\frac{75300}{RT} - 24.7\right] \qquad \text{... (i)}$$

Use T, in K. in this equation.

$$-r_R = k_1 C_A - k_2 C_R$$

$$-r_R = k_1 C_{Ao}(1 - X_A) - k_2 C_{Ao} X_A$$

$$C_R = C_{Ro} + C_{Ao} X_A, \text{ but } C_{Ro} = 0 \quad \therefore C_R = C_{Ao} X_A$$

At equilibrium, net rate is zero.

$$0 = k_1 C_{Ao}(1 - X_{Ae}) - k_2 C_{Ao} X_{Ae}$$

$$\frac{k_1}{k_2} = \frac{X_{Ae}}{1 - X_{Ae}} = K$$

$$\therefore \quad X_{Ae} = \frac{K}{K+1} = \frac{K(T)}{K(T)+1} \qquad \text{... (ii)}$$

as K is function of T.

So put T = 0, 10, 20 ... 100 °C in equation (i) to evaluate K and put it in equation (ii) to evaluate corresponding equilibrium conversion.

$$T = 0\,^{\circ}C = 273\,K$$

$$K = \exp\left[\frac{75300}{8.314 \times 273} - 24.7\right] = 4797.6$$

$$X_{Ae} = \frac{4797.6}{1 + 4797.6} = 0.999^*$$

$$T = 10\,^{\circ}C = 283\,K$$

$$K = \exp\left[\frac{75300}{8.314 \times 283} - 24.7\right] = 1485.6$$

$$X_{Ae} = \frac{1485.6}{1 + 1485.6} = 0.999$$

T, °C	0	10	20	30	40	50	60	70	80	90	100	110
T, K	273	283	293	303	313	323	333	343	353	363	373	383
K	4797.6	1485.6	498.3	179.7	69.10	28.23	12.16	5.5	2.6	1.28	0.658	0.349
X_{Ae}	0.999*	0.999	0.998	0.994	0.986	0.966	0.924	0.846	0.72	0.56	0.397	0.258

... **Ans. (i)**

From graph it is clear that temperature must be below 78 °C for achieving 75% or more than 75% conversion.

... **Ans. (ii)**

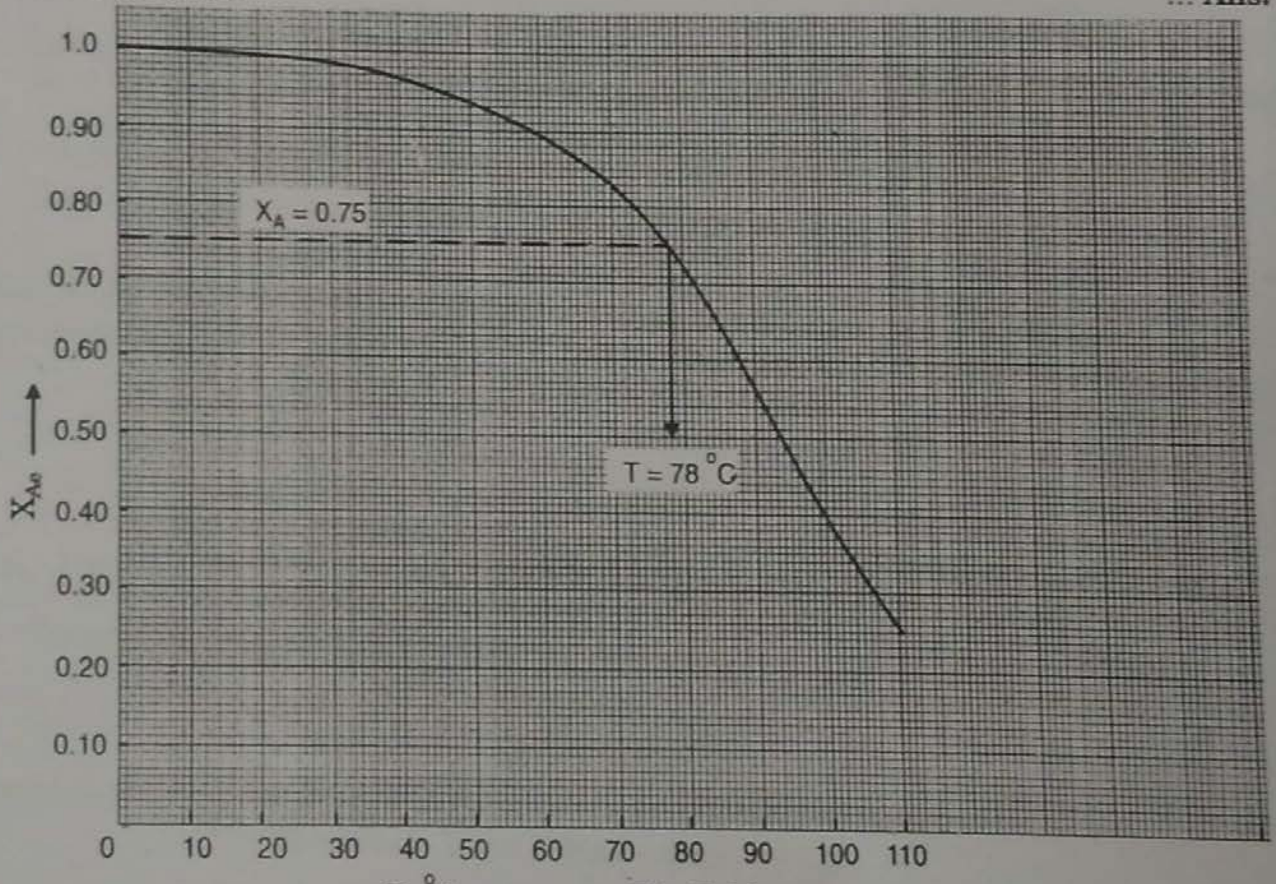


Fig. E 6.3

Ex. 6.4 : For reversible first order aqueous reaction

$$A \rightleftharpoons R$$

starting with pure A, kinetic experiments in a batch reactor give 58.1% conversion in 1 min at 65 °C and 60% conversion in 10.1 min at 25 °C. Find the rate expression for this reaction.

Data : Equilibrium conversion at 65 °C = 0.89

Equilibrium conversion at 25 °C = 0.993

At 298 K, $\Delta G^o = -14130$ J/mol, $\Delta H_R^o = -75300$ J/mol

$$C_{p_A} = C_{p_R} = \text{constant}$$

Solution : $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$, aqueous reaction, $\varepsilon_A = 0$

$$-r_A = k_1 C_A - k_2 C_R$$

$$\Delta G^o = -14130 \text{ J/mol}, \quad \Delta H_R^o = -75300 \text{ J/mol}$$

$$C_{p_A} = C_{p_R} = \text{constant}$$

$$\Delta C_p = C_{p_R} - C_{p_A} = 0$$

∴ Heat of reaction is independent of temperature and is given by

$$\Delta H_R = \Delta H_R^o = -75300 \text{ J/mol}$$

At 298 K, $\Delta G^o = -RT \ln K$

$$K = \exp(-\Delta G^o/RT)$$

$$= \exp[-(-14130)/8.314 \times 298] = 300$$

$$K \text{ at } 298 = 300$$

Since the heat of reaction does not change with temperature, the equilibrium constant at any temperature T is given by

$$\ln\left(\frac{K}{K_{298}}\right) = \frac{-\Delta H_R}{R}\left[\frac{1}{T} - \frac{1}{298}\right]$$

$$K = K_{298} \exp\left[\frac{-\Delta H_R}{RT} + \frac{\Delta H_R}{R \times 298}\right]$$

$$= 300 \exp\left[\frac{-(-75300)}{RT} + \frac{-75300}{8.314 \times 298}\right]$$

$$K = 300 \exp\left[\frac{75300}{RT} - 30.40\right]$$

$$K = \exp\left[\frac{75300}{RT} - 24.7\right], \text{ as } 300 = e^{5.7}$$

For batch reactor :

$$t = C_{Ao} \int \frac{dX_A}{-r_A} = \frac{1}{k_1} \int_0^{X_A} \frac{dX_A}{1 - X_A/X_{Ae}}$$

$$-r_A = k_1 C_A - k_2 C_R$$

$$= k_1 C_{Ao}(1 - X_A) - k_2 C_{Ao} X_A$$

∴ At equilibrium, $-r_A = 0$

∴ $k_1(1 - X_{Ae}) = k_2 X_{Ae}$

$$k_2 = \frac{k_1(1 - X_{Ae})}{X_{Ae}}$$

$$
\begin{aligned}
-r_A &= k_1 C_{A_0}(1-X_A) - k_2 C_{A_0} X_A \\
&= k_1 C_{A_0}(1-X_A) - \frac{k_1(1-X_{Ae})}{X_{Ae}} \cdot X_A C_{A_0} \\
&= C_{A_0} k_1 \left[1 - X_A - \frac{(1-X_{Ae}) X_A}{X_{Ae}} \right] \\
&= C_{A_0} k_1 \left[\frac{X_{Ae} - X_A X_{Ae} - X_A + X_A X_{Ae}}{X_{Ae}} \right] \\
&= C_{A_0} k_1 [1 - X_A/X_{Ae}]
\end{aligned}
$$

For batch reactor, performance equation is

$$
\begin{aligned}
t &= C_{A_0} \int \frac{dX_A}{-r_A} = C_{A_0} \int \frac{dX_A}{C_{A_0} k_1 [1 - X_A/X_{Ae}]} \\
&= \frac{1}{k_1} \int \frac{dX_A}{1 - X_A/X_{Ae}} \\
\frac{k_1 t}{X_{Ae}} &= -\ln \left[1 - \frac{X_A}{X_{Ae}} \right]
\end{aligned}
$$

At 65 °C, $X_{Ae} = 0.892$, $X_A = 0.581$, $t = 1.0$ min

$$
\begin{aligned}
\frac{k_1 \times 1}{0.89} &= -\ln \left[1 - \frac{0.581}{0.89} \right] \\
k_1 &= 0.941\,(\text{min})^{-1} \text{ at } 65\,^{\circ}\text{C (338 K)}
\end{aligned}
$$

At 25 °C, $X_{Ae} = 0.993$, $X_A = 0.6$, $t = 10.1$ min

$$
\begin{aligned}
\frac{k_1 \times 10.1}{0.993} &= -\ln \left[1 - \frac{0.60}{0.993} \right] \\
k_1 &= 0.091 \text{ min}^{-1} \text{ at } 25\,^{\circ}\text{C (298 K)}
\end{aligned}
$$

We have, $k = k_o e^{-E/RT}$

Taking ratio of rate constants, we get,

$$
\therefore \quad \frac{k_1 \text{ at } 338}{k_1 \text{ at } 298} = \frac{0.941}{0.091} = \frac{k_{10}\, e^{-E_1/R \times 338}}{k_{10} \cdot e^{-E_1/R \times 298}}
$$

Solving we get,

$$
\begin{aligned}
E_1 &= 48870 \text{ J/mol} \\
0.941 &= k_{10} \cdot e^{-48870/8.314 \times 338} \\
\therefore \quad k_{10} &= 33.6 \times 10^6 \\
k_1 &= k_o e^{-E/RT} \\
k_1 &= 33.6 \times 10^6 \exp \left[\frac{-48870}{RT} \right] \\
k_1 &= \exp \left[17.33 - \frac{48870}{RT} \right]
\end{aligned}
$$

$$k_2 = \frac{k_1}{K}$$

$$= \frac{\exp\left[17.33 - \frac{48870}{RT}\right]}{\exp\left[\frac{75300}{RT} - 24.7\right]}$$

$$\therefore \quad k_2 = \exp\left[42.03 - \frac{124170}{RT}\right]$$

For reversible first order reaction

$A \rightleftharpoons R$,

$$K = C_{Re}/C_{Ae}$$

$$-r_A = k_1 C_A - k_2 C_R$$

$$k_1 = \exp\left[17.33 - \frac{48870}{RT}\right]$$

$$k_2 = \exp\left[42.03 - \frac{124170}{RT}\right]$$

$$K = \exp\left[\frac{75300}{RT} - 24.7\right]$$

... **Ans.**

Ex. 6.5 : Compute K_y at 10 atm if K_p at this pressure is 0.00381 atm^{-1} for ammonia synthesis reaction from hydrogen and nitrogen at 500 °C. (Assume ideal gas holds good).

Solution : $N_2 + 3 H_2 \rightleftharpoons 2 NH_3$

$$K_p = 0.00381 \text{ atm}^{-1}$$

Relationship between K_p and K_y is

$$K_p = K_y P^{\Delta n}$$

$$K_y = \frac{K_p}{P^{\Delta n}}, \quad \Delta n = 2-(1+3) = -2$$

$$= \frac{0.00381}{(10)^{-2}} = 0.381$$

... **Ans.**

Ex. 6.6 : Estimate the equilibrium constant at 600 K for the reaction

$$C_2H_4\,(g) + H_2O\,(g) \longrightarrow C_2H_5OH\,(g)$$

At 298 K : $\Delta G^o = -2030$ kcal/mol

ΔH^o_f for $H_2O\,(g) = -57798$ cal/mol

$C_2H_5OH\,(g) = -56240$ cal/mol

$C_2H_4\,(g) = 12496$ cal/mol

Solution : $C_2H_4\,(g) + H_2O\,(g) \longrightarrow C_2H_5OH\,(g)$

$$\Delta G^o = -2030 \text{ cal/mol} \quad \text{at } T = 298 \text{ K}$$

$$\Delta H^o_R = \sum \Delta H^o_{f\,products} - \sum \Delta H^o_{f\,reactants}$$

$$= 1 \times \Delta H^o_{f\,C_2H_5OH} - \left[1 \times \Delta H^o_{f\,C_2H_4} + 1 \times \Delta H^o_{f\,H_2O}\right]$$

$$= -56240 - 12496 + 57798$$

$$= -10938 \text{ cal/mol}$$

We have, $$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ_R}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

K_1 is obtained from the data of ΔG^o,

$$\Delta G^o = -RT \ln K$$

$T_1 = 298$ K, $$\Delta G^o = -2030 \text{ cal/mol}$$

$$\ln K_1 = -\Delta G^o/RT$$
$$= -(-2030)/1.987 \times 298$$

∴ $$K_1 = 30.8$$

Now let us find K_2 at $T_2 = 600$ K,

$$\ln\left(\frac{K_2}{30.8}\right) = \frac{-(-10938)}{1.987}\left[\frac{1}{600}-\frac{1}{298}\right]$$

$$K_2 = 2.83 \times 10^{-3}$$

Equilibrium constant at 600 K $= 2.83 \times 10^{-3}$

Ex. 6.7 : In a laborating investigation, ethanol is esterified to produce ethyl acetate and water at 1 atm according to the reaction.

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \longrightarrow CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

What is the equilibrium constant for the reaction at 100 °C ? What is the composition of the mixture if initially 1 mole of acetic acid and 1 mole of ethanol were present ?

Data : ΔG^o at 298 K for the reaction = 1160 cal.

ΔH_R at 298 K for the reaction = 1713 cal.

Solution : $CH_3COOH\,(l) + C_2H_5OH\,(l) \rightarrow CH_3COOC_2H_5\,(l) + H_2O\,(l)$

Moles of acetic acid initially = 1 mol

Moles of ethanol initially = 1 mol

$$\Delta G^o \text{ at } 298 \text{ K} = 1160 \text{ cal}$$
$$\Delta H_R \text{ at } 298 \text{ K} = 1713 \text{ cal}$$
$$T = 100\,^oC = 373 \text{ K}$$

Equilibrium constant at 100 °C (373 K) is determined as :

At $T_1 = 298$ K, equilibrium constant = K_1

At $T_2 = 373$ K, equilibrium constant = K_2

We have, $$\Delta G^o = -RT \ln K$$

$$\Delta G^o = -RT_1 \ln K_1$$

$$\ln K_1 = -\Delta G^o/RT_1 = \frac{-1160}{1.987 \times 298}$$

∴ $$K_1 = 0.14$$

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H_R}{R}\left[\frac{1}{T_2}-\frac{1}{T_1}\right]$$

$$\ln \frac{K_2}{0.14} = \frac{-1713}{1.987}\left(\frac{1}{373}-\frac{1}{298}\right)$$

∴ $$K_2 = 0.25$$

The equilibrium constant for esterification reaction at 100 °C is 0.25

Let x be the moles of alcohol converted to acetate at equilibrium.

Then at equilibrium :

moles of acetate = x mol

moles of acetic acid = 1 – x mol

moles of water = x mol

moles of ethanol = 1 – x mol

$$\text{Total moles} = x + 1 - x + x + 1 - x$$

$$= 2 \text{ mol}$$

$$\text{Mole fraction of acid} = \frac{1-x}{2}$$

$$\text{Mole fraction of ethanol} = \frac{1-x}{2}$$

$$\text{Mole fraction of acetate} = \frac{x}{2}$$

$$\text{Mole fraction of water} = \frac{x}{2}$$

We can express K in terms of molefraction therefore,

$$K_2 = K_y = \frac{x/2 \cdot x/2}{\left(\frac{1-x}{2}\right)\left(\frac{1-x}{2}\right)} = \frac{x^2}{(1-x)^2}$$

$$0.25 = \frac{x^2}{(1-x)^2}$$

$$x^2 = 0.25 + 0.25\,x^2 + 0.5\,x$$

$$0.75\,x^2 + 0.5\,x - 0.25 = 0$$

$$\therefore \quad x = 0.34$$

So at equilibrium, the reaction mixture will consist of

acetic acid = 1 – 0.34 = 0.66 mol

ethanol = 1 – 0.34 = 0.66 mol

ethyl acetate = 0.34 mol

water = 0.34 mol

Ex. 6.8 : Develop a relationship between equilibrium constant K and temperature T for the ammonia synthesis reaction.

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightarrow NH_3$$

Data :

ΔH_R at 298 K = – 46190 J/mol

ΔG^0 at 298 K = – 16635 J/mol

$$\Delta C_p = -31.780 + 35.517 \times 10^{-3}\,T - 9.316 \times 10^{-6}\,T^2$$

C_p is in J/(mol.K) and T is in K.

Solution :

$$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightarrow NH_3$$

ΔH_R at 298 K = – 46190 J/mol

ΔG^0 at 298 K = – 16635 J/mol

Heat of reaction at any temperature T is given by,

$$\Delta H_{RT} = \Delta H_{R1} + \Delta\alpha\,(T - T_1) + \frac{\Delta\beta}{2}(T^2 - T_1^2) + \frac{\Delta\gamma}{3}(T^3 - T_1^3)$$

Putting values of $\Delta\alpha$, $\Delta\beta$ etc. from ΔC_p data

$$\Delta H_{RT} = \Delta H_{R1} - 31.780\,(T - T_1) + \frac{35.517 \times 10^{-3}}{2}\,(T^2 - T_1^2) - \frac{9.316 \times 10^{-6}}{3}\,(T^3 - T_1^3) \quad \ldots (1)$$

If we take base temperature T_1 as 0 K then equation (1) becomes

$$\Delta H_{RT} = \Delta H_{Ro} - 31.780\,T + 17.758 \times 10^{-3}\,T^2 - 3.105 \times 10^{-6}\,T^3 \quad \ldots (2)$$

where ΔH_{Ro} is heat of reaction at 0 K.

At $T = 298$ K, $\Delta H_{RT} = \Delta H_R^0 = -46190$ mol

$$\therefore \quad -46190 = \Delta H_{Ro} - 31.780\,(298) + 17.758 \times 10^{-3}\,(298)^2 - 3.105 \times 10^{-6}\,(298)^3$$

$$\therefore \quad \Delta H_o = -38214$$

Putting value of ΔH_{Ro} in equation (2) we get,

$$\therefore \quad \Delta H_{RT} = -38214 - 31.780\,T + 17.758 \times 10^{-3}\,T^2 - 3.105 \times 10^{-6}\,T^3$$

Relation between K and T is given by,

$$\ln K = \frac{1}{T} \int \frac{\Delta H_R\,(T)}{T^2}\,dT + I$$

$$\ln K = \frac{1}{R} \int \frac{1}{T^2}\,[-38124 - 31.780\,T + 17.758 \times 10^{-3}\,T^2 - 3.105 \times 10^{-6}\,T^3]\,dT + I$$

$$R = 8.314\ \text{J/(mol.K)}$$

$$\ln K = \frac{4596}{T} - 3.822 \ln T + 2.136 \times 10^{-3}\,T - 0.187 \times 10^{-6}\,T^2 + I \quad \ldots (4)$$

$$\Delta G^0 = -RT \ln K$$

AT $T = 298$ K, $\Delta G^0 = -16635$ J/mol

$$\therefore \quad \ln K = -(-16635)/8.314 \times 298 = 6.715$$

Putting ln K value and $T = 298$ K in equation (4) get value of I,

$$6.715 = \frac{4596}{298} - 3.822 \ln (298) + 2.136 \times 10^{-3} \times 298 - 0.187 \times 10^{-6}\,(298)^2 + I$$

$$\therefore \quad I = 12.44$$

Putting value of I in equation (4) we get,

$$\ln K = \frac{4596}{T} - 3.822 \ln T + 2.136 \times 10^{-3}\,T - 0.187 \times 10^{-6}\,T^2 + 12.44 \quad \ldots (5)$$

Equation (5) is the desired relationship between equilibrium constant K and temperature T.

Ex. 6.9 : N_2O_4 gas dissociates according to following reaction

$$N_2O_{4\,(g)} \rightleftharpoons 2\,NO_{2\,(g)}$$

At 27°C and 1 atm, 20 % of N_2O_4 is dissociated. Calculate

(i) Equilibrium constant K_p

(ii) Percent dissociation of N_2O_4 at 27°C when total pressure becomes 0.2 atm.

(iii) What will be the degree of dissociation when we start with 73.6 g of N_2O_4 in 10 litres. vessel at 27°C.

Solution : (i) Basis : 1 mol of N_2O_4 gas

$$N_2O_4 \rightleftharpoons 2\,NO_2$$

20 mole % N_2O_4 is dissociated

∴ At equilibrium,

$$\text{Moles of } N_2O_4 = 1 - 0.2 = 0.8 \text{ mol}$$

$$\text{Moles of } NO_2 = 0.2 \times \frac{2}{1} = 0.4 \text{ mol}$$

Total g moles of mixture $= 0.8 + 0.4 = 1.2$ mol

Mole fraction of $N_2O_4 = y_{N_2O_4} = \frac{0.8}{1.2} = 0.67$

Mole fraction of $NO_2 = y_{NO_2} = \frac{0.4}{1.2} = 0.33$

Now total pressure $= P = 1$ atm.

Partial pressure of $N_2O_4 = p_{N_2O_4} = 0.67 \times 1 \text{ atm.} = 0.67 \text{ atm.}$

Partial pressure of $NO_2 = p_{NO_2} = 0.33 \times 1 \text{ atm} = 0.33 \text{ atm}$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}}$$

$$= \frac{(.33 \text{ atm})^2}{(0.67 \text{ atm})}$$

$$= 0.16 \text{ atm.}$$

(ii) Let x be the g mole N_2O_4 dissociated at 0.2 atm pressure

At equilibrium,

Moles of $N_2O_4 = 1 - x$ mol

Moles or $NO_2 = 2x$ mol

Moles $= 1 + x$ mol

$$= p_{N_2O_4}$$

$$= \frac{1-x}{1+x} \times (0.2)$$

$$= p_{NO_2}$$

$$= \frac{2x}{1+x} \times (0.2)$$

$$K_p = \frac{p_{NO_2}}{p_{N_2O_2}}$$

$$= \frac{\left[\frac{2x}{1+x} \times (0.2)\right]^2}{\left[\frac{1-x}{1-x} \times (0.2)\right]}$$

$$= 0.16$$

$$\frac{0.8\,x^2}{1-x^2} = 0.16$$

solving, $x = 0.41$

% dissociation $= \frac{0.41}{1} \times 100 = 41$ at 27° C and 0.2 atm.

(iii) Moles of N_2O_4 at start = 73.6/92 = 0.8 mol

Let x be fractional dissociation of N_2O_4

At equilibrium

Moles of N_2O_4 = 0.8 (1 – x)

Moles of NO_2 = 1.6 x

$$p_{N_2O_4} = \frac{0.8\,(1-x)\times 0.08206\times 300}{10} = 1.968\,(1-x)\ \text{atm}$$

$$p_{NO_2} = \frac{(1.6\,x)\times 0.08206\times 300}{10} = 3.936\ \text{atm.}$$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{(3.936\,x)^2}{1.968\,(1-x)} = 0.16$$

solving we get x = 0.13

∴ % dissociation = 13

Ex. 6.10 : 10.425 grams of PCl_5 are heated in a 4 lit. flask at 267°C. The equilibrium mixture had a pressure of 1 atm. Calculate K_p, K_c and ΔG^o for the reaction at 267°C.

Solution : On heating PCl_5 dissociates as,

$$PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$$

Initial amount of PCl_5 = 10.425 g

Mol. Wt. of PCl_5 = 208.5

$$\text{Moles of } PCl_5 = \frac{10.425}{208.5} = 0.05$$

Let x be the moles of PCl_5 decomposed or dissociated.

Then, at equilibrium,

Moles of PCl_5 = 0.05 – x mol

Moles of PCl_3 = x mol

Moles of Cl_2 = x mol

Total number of moles = 0.05 – x + x + x = 0.05 + x mol

According to ideal gas equation

$$\text{Number of moles} = \frac{PV}{RT} = \frac{(1\ \text{atm})\,(4\ l)}{\left[\frac{0.08206\ l.\text{atm}}{\text{mol.K}}\times(540\ \text{K})\right]} = 0.0903$$

or

$$0.05 + x = 0.0903$$

$$x = 0.0403$$

$$
\begin{aligned}
y_{PCl_5} &= \frac{0.05 - 0.0403}{0.0903} = 0.107 \\
y_{PCl_3} &= \frac{00403}{0.0903} = 0.446 \\
y_{Cl_2} &= \frac{0.0403}{0.0903} = 0.446 \\
K_p &= K_y\, P^{\Delta n} \\
\Delta n &= (1+1) - 1 = 1 \\
P &= 1 \text{ atm} \\
K_p &= \frac{(0.446) \times (0.446)}{(0.107)} \times (1)^1 \\
K_p &= 1.86 \text{ atm} \\
T &= 267 + 273 = 540 \text{ K} \\
K_c &= \frac{K_p}{(RT)^{\Delta n}} = \frac{1.86 \text{ atm.}}{\left(0.08206 \frac{l.\text{atm}}{\text{mol.K}}\right) \times (540 \text{ K})} \\
K_c &= 0.0418 \text{ mol}/l \\
\Delta G^o &= -RT \ln K_p \;\; = -(1.987)(540)\, ln\,(1.86) \\
\Delta G^o &= -\,665.8 \text{ cal/mol} \\
(R &= 1.987 \text{ cal/(mol.K))}
\end{aligned}
$$

Ex. 6.11 : First order reversible aqueous reaction

$$A \rightleftharpoons R$$

with rate

$$
\begin{aligned}
-r_A &= k_1 C_A - k_2 C_R \\
k_1 &= 34 \times 10^6 \exp.\ (-48900/RT),\ \ \text{min}^{-1} \\
k_2 &= 1.57 \times 10^{18} \exp.\ (-123800/RT),\ \text{min}^{-1}
\end{aligned}
$$

E is in J/mol

is to be carried in plug flow reactor. For maximum permissible feed temperature of 95 °C (368 K) (maximum permissible operating temperature of 95 °C) and feed rate of 1000 mol/min of reactant A, what is the optimum temperature progression in a plug flow reactor ? A conversion of 80% is required and feed concentration of A is $C_{Ao} = 4$ mol/*l* and $C_{Ro} = 0$.

Also calculate the space time and volume needed for 80% conversion of a feed of $F_{Ao} =$ 1000 mol/min with $C_{Ao} = 4$ mol/*l* and $C_{Ro} = 0$.

Solution : $A \rightleftharpoons R$

The rate of disappearance of A is given by

$$(-r_A) = k_1 C_A - k_2 C_R$$

We have,

$$
\begin{aligned}
C_A &= C_{Ao}(1 - X_A) \\
C_R &= C_{Ro} + C_{Ao}X_A,\quad C_{Ro} = 0,\quad \therefore\ C_R = C_{Ao}X_A \\
-r_A &= k_1 C_{Ao}(1 - X_A) - k_2 C_{Ao} X_A \\
k_1 &= 34 \times 10^6 \exp(-48900/RT),\ \ \text{min}^{-1} \\
k_2 &= 1.57 \times 10^{17} \exp\ (-123800/RT),\ \text{min}^{-1} \\
R &= 8.314 \text{ J/(mol.K)} \\
k_1 &= 34 \times 10^6 \exp(-48900/8.314 \times T) = 34 \times 10^6 \exp\ (-5882/T) \\
k_2 &= 1.57 \times 10^{18}\ \exp(-123800/8.314 \times T) = 1.57 \times 10^{18} \exp\ (-14890/T) \\
(-r_A) &= 34 \times 10^6\, C_{Ao}(1 - X_A)\, e^{-5882/T} - 1.57 \times 10^{18}\, C_{Ao} X_A\, e^{-14890/T}
\end{aligned}
$$

If the above equation is differentiated with respect to T (at constant conversion) and the derivative is set equal to zero then we obtain the following requirement for maximum rate.

For conditions of maximum rate at a given conversion, differentiate $-r_A$ with respect to T and set $d(-r_A)/dT = 0$.

$$\frac{d(-r_A)}{dT} = C_{A_0}\left[\frac{34\times10^6(1-X_A)(5882)}{T^2}e^{-5882/T} - \frac{1.57\times10^{18}X_A(14890)}{T_2}\cdot e^{-14890/T}\right]$$

$$\therefore \quad 0 = 34\times10^6(1-X_A)(5882)\ e^{-5882/T} - 1.57\times10^{18}X_A(14890)\ e^{-14890/T}$$

$$\left[\frac{d}{dx}(e^{-m/x}) = \frac{m}{x^2}\ e^{-m/x}\right]$$

As $C_{A_0}/T^2 \neq 0$,

$$34\times10^6(1-X_A)(5882)\ e^{-5882/T} = 1.57\times10^{18}(14890)\ e^{-14890/T}$$

$$\frac{1.57\times10^{18}\times14890}{34\times10^6\times5882}\left[\frac{X_A}{1-X_A}\right] = \frac{e^{-5882/T}}{e^{-14890/T}}$$

$$1.17\times10^{11}\left(\frac{X_A}{1-X_A}\right) = e^{9008/T}$$

$$T = \frac{9008}{\ln\left[\frac{1.17\times10^{11}X_A}{1-X_A}\right]}, \quad T \text{ in K}$$

With this equation, calculate the values of T for various values of X_A (0, 0.1, 0.2, ... upto 0.80)

For $X_A = 0$, $T = -$

For $X_A = 0.10$,

$$T = \frac{9008}{\ln\left[\frac{1.17\times10^{11}\times0.10}{1-0.10}\right]} = 386.8\ \text{K}\ (113.8\ ^\circ\text{C})$$

For $X_A = 0.20$,

$$T = \frac{9008}{\ln\left[\frac{1.17\times10^{11}\times0.2}{1-0.2}\right]} = 374\ \text{K}\ (101\ ^\circ\text{C})$$

Maximum allowable temperature is 95 °C (368 K)

For T = 368 K, calculate X_A. (It is always required to calculate X_A at maximum allowable temperature).

We have,

$$\ln\left[\frac{1.17\times10^{11}X_A}{1-X_A}\right] = \frac{9008}{T}$$

$$\ln\left[\frac{1.17\times10^{11}X_A}{1-X_A}\right] = \frac{9008}{368}$$

$$\therefore \quad X_A = 0.267 \simeq 0.27$$

Find T for other values of X_A upto 0.8 and tabulate.

X_A	0	0.1	0.2	0.27	0.3	0.4	0.5	0.6	0.7	0.8
T, °C	–	113.8	101	95	92.6	86	80.4	75	69	62

These temperature values for given conversion result in maximum rates i.e. these are optimum temperatures.

Here maximum permissible temperature is 95 °C.

As seen from the table the optimum temperature exceeds the limit of maximum allowable temperature of 95 °C until the conversion reaches 0.27. Therefore, the optimum temperature progression will be isothermal path at 95 °C upto 27% conversion followed by decreasing temperatures in the table until 80% conversion. ... **Ans.**

Optimum temperature progression :

Isothermal at 95 °C upto 27% conversion then 92.6 – 86 – 80.4 – 75 – 69 – 62 °C upto 80% conversion.

Now we will calculate the maximum rates,

$$-r_A = 34 \times 10^6 C_{A_0} (1 - X) e^{-5882/T} - 1.57 \times 10^{18} C_{A_0} X_A e^{-14890/T}$$

$$C_{A_0} = 4 \text{ mol}/l$$

In above equation, use T in K and not in °C.

For $X_A = 0$, use $T = 95\,°C$ [368 K]

$$-r_A = 34 \times 10^6 \times 4 (1 - 0) e^{-5882/368} - 1.57 \times 10^{18} \times 4 \times 0 \times e^{-14890/368}$$

$$= 15.56 \text{ mol}/(l.\text{min})$$

Take X_A and corresponding T from the above table and evaluate maximum rate at various data.

For $X_A = 0.10$ and $T = 113.8\,°C$ [386.8 K]

$$-r_A = 34 \times 10^6 \times 4 (1 - 0.1) e^{-5882/386.8} - 1.57 \times 10^{18} \times 4 \times 0.10 e^{-14890/386.8}$$

$$= 18.45 \text{ mol}/(l.\text{min})$$

$X_A = 0.20$ and $T = 101\,°C$ (374 K), $-r_A = 9.65$

X_A	T, °C	Maximum rate	Rate at 95 °C
0	–	15.56	15.56
0.1	113.8	18.45	12.32
0.2	101	9.65	9.10
0.27	95	6.82	6.82
0.30	92.6	5.93	–
0.4	86	3.81	–
0.5	80.4	2.44	–
0.6	75	1.50	–
0.7	69	0.84	–
0.8	62	0.40	–

For isothermal operation upto 95 °C :

Calculate rate at 95 °C (368 K) from $X_A = 0$ to $X_A = 0.27$ by using equation :

$$-r_A = 34 \times 10^6 C_{A_0} (1 - X_A) e^{-5882/368} - 1.57 \times 10^{18} C_{A_0} X_A e^{-14890/368}$$

$$X_A = 0.10$$

$$(-r_A) = 34 \times 10^6 \times 4 (1 - 0.10) e^{-5882/368} - 1.57 \times 10^{18} \times 4 \times 0.10 \times e^{-14890/368}$$

$$= 12.32 \text{ mol}/(l.\text{s})$$

$$X_A = 0.20, \quad (-r_A) = 9.10 \text{ mol}/(l.\text{min})$$

We have to operate reactor isothermally at 95 °C upto $X_A = 0.27$ and then along the locus of maximum rates upto $X_A = 0.80$.

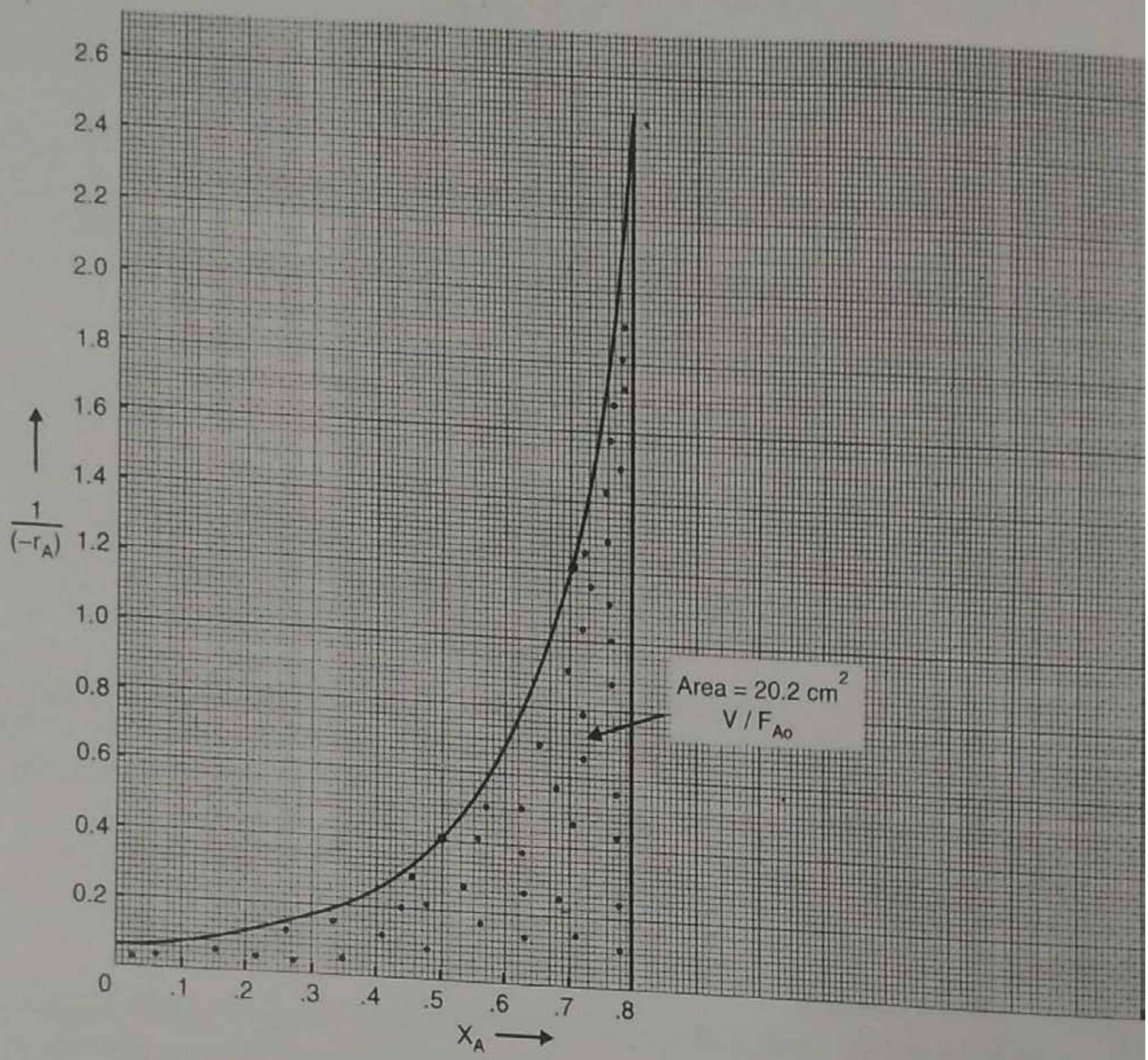


Fig. E 6.11

Upto $X_A = 0.27$ take $-r_A$ calculated at 95 °C and then take $-r_A$ equal to maximum rat various values of X_A upto $X_A = 0.8$ and plot a graph of $1/(-r_A)$ v/s X_A and get the size of plug reactor.

X_A	0	0.1	0.2	0.27	0.3	0.4	0.5	0.6	0.7	0.
$-r_A$	15.56	12.32	9.10	6.82	5.93	3.81	2.44	1.50	0.84	0.
$1/(-r_A)$	0.064	0.081	0.11	0.15	0.17	0.26	0.41	0.67	1.2	2

From graph, area under the curve between $X_A = 0$ and $X_A = 0.8$ is 20.2 cm^2.

$$\begin{aligned} V/F_{Ao} &= \text{Area} \times \text{Scale x-axis} \times \text{Scale y-axis} \\ &= 20.2 \times \frac{0.1}{1} \times \frac{0.2}{1} \\ &= 0.404 \ l/(\text{mol/min}) \\ F_{Ao} &= 1000 \text{ mol/min} \\ V &= 1000 \times 0.404 \\ &= 404 \ l \end{aligned}$$

...

$$\frac{\tau}{C_{Ao}} = \frac{V}{F_{Ao}} = 0.404\left(\frac{l}{\text{mol/min}}\right)$$

$$\tau = 0.404\left(\frac{l.\text{min}}{\text{mol}}\right)\times 4\left(\frac{\text{mol}}{l}\right)$$

$$= 1.616 \approx 1.62 \text{ min}$$

. Ans.

Ex. 6.12 : For same conditions given in Ex. 6.5 is it possible to operate a plug flow reactor isothermally at 95 °C to get conversion of 80% ?

Solution : We have from solution of Ex. 6.5,

$$-r_A = 34\times 10^6\, C_{Ao}(1-X_A)\, e^{-5882/T} - 1.57\times 10^{18}\, C_{Ao} X_A\, e^{-14890/T}$$

For isothermal operation at 95 °C (368 K),

$$-r_A = 34\times 10^6\times 4\,(1-X_A)\;\; e^{-5882/368} - 1.57\times 10^{18}\times 4\times X_A\times e^{-14890/368}$$

$$-r_A = 15.56\,(1-X_A) - 16.81\, X_A$$

At equilibrium, net rate is zero.

$$\therefore \quad 0 = 15.56\,(1-X_{Ae}) - 16.81\, X_{Ae}$$

$$16.81\, X_{Ae} = 15.56 - 15.56\, X_{Ae}$$

$$X_{Ae} = 0.48$$

$\therefore$ At $X_{Ae} = 0.48$, rate at 95 °C = 0

So by operating a plug flow reactor isothermally at 95 °C (368 K) the rate of reaction is zero by the time when conversion reaches 48%. In other words, at 95 °C (368 K) the equilibrium conversion is 48%. Regardless of reactor volume, so it is not possible to achieve the required conversion of 80%. **... Ans.**

Ex. 6.13 : A concentrated aqueous A solution of the Ex. 6.5 (C_{Ao} = 4 mol/l, F_{Ao} =1000 mol/min) is to be 80% converted in a mixed flow reactor. Using optimum temperature progression, find the size of reactor needed.

Solution : $A \rightleftharpoons R$

$$F_{Ao} = 1000 \text{ mol/min}, \quad C_{Ao} = 4 \text{ mol}/l$$

For mixed flow reactor, operating line reduces to a single point representing the condition of fluid leaving the reactor (80% conversion). For 80% conversion i.e. X_A = 0.8, the corresponding optimum temperature is 62 °C and maximum rate is 0.4 mol/(l.min).

$$\therefore \quad -r_A = 0.4 \text{ mol}/(l.\text{min})$$

$$X_A = 0.8$$

For mixed flow reactor,

$$V = \frac{F_{Ao} X_A}{(-r_A)}$$

$$= \frac{1000\times 0.80}{0.40} = 2000\, l$$

... Ans.

Ex. 6.8 : The first order gas phase reversible reaction

$$A \rightleftharpoons R$$

with rate

$$-r_A = k_1 C_A - k_2 C_R, \quad \text{mol/(m}^3\text{.s)}$$

$$k_1 = 0.02 \exp(-29300/RT),\ (s)^{-1}$$

$$k_2 = 0.33 \exp(-46000/RT),\ (s)^{-1}$$

E is given in J/mol

is to be carried out in a plug flow reactor.

For a maximum permissible feed temperature of 600 °C (873 K) and a feed rate of F_{Ao} (kmol/s) of reactant A, what is the optimum temperature progression in a plug flow reactor ? A conversion of 60% is required and the feed concentration of A is C_{Ao} and $C_{Ro} = 0$.

Solution : $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$, gas phase reaction with $\varepsilon_A = 0$.

The rate of disappearance of A is given by

$$(-r_A) = k_1 C_A - k_2 C_R$$

For constant density :

$$C_A = C_{Ao}(1 - X_A)$$

$$C_R = C_{Ro} + C_{Ao}X_A, \quad C_{Ro} = 0$$

$$\therefore \quad C_R = C_{Ao}X_A$$

$$\therefore \quad (-r_A) = k_1 C_{Ao}(1 - X_A) - k_2 C_{Ao} X_A$$

$$= C_{Ao}[k_1(1 - X_A) - k_2 X_A]$$

$$k_1 = 0.02 \exp\ (-29300/RT) \text{ where E is in J/mol}$$

$$= 0.02 \exp\left(\frac{-29300}{8.314\ T}\right) = 0.02 \exp\left(\frac{-3524.2}{T}\right)$$

$$k_2 = 0.33 \exp\ (-46000/RT)$$

$$= 0.33 \exp\ (-46000/8.314 \times T) = 0.33 \exp\ (-5532.8/T)$$

$$(-r_A) = C_{Ao}\ [0.02 \exp\ (-3524.2/T)\ (1 - X_A) - 0.33 \exp\ (-5532.8/T) \cdot X_A]$$

If the above equation is differentiated with respect to T (at constant conversion) and the derivative is set equal to zero then we obtain the following requirement for maximum rate.

For conditions of maximum rate at given conversion, differentiate $-r_A$ (rate) with respect to T and set $d(-r_A)/dT = 0$.

$$\frac{d}{dx}(e^{-m/x}) = \frac{m}{x^2} e^{-m/x}$$

$$\frac{d(-r_A)}{dT} = C_{Ao}\left[0.02 \frac{(+3524.2)}{T^2} e^{-3524.2/T} \cdot (1 - X_A) - 0.33\left(+\frac{5532.8}{T^2}\right) e^{-5532.8/T} \cdot X_A\right]$$

$$0 = \frac{C_{Ao}}{T^2}\ [0.02 \times 3524.2\ (1 - X_A)\ e^{-3524.2/T} - 0.33 \times 5532.8\ X_A\ e^{-5532.8/T}]$$

$$0 = 70.484\ (1 - X_A)\ e^{-3524.2/T} - 1825.82\ X_A\ e^{-5532.8/T}$$

$$\frac{1825.82\ X_A}{70.484\ (1 - X_A)} = e^{(5532.8\ -\ 3524.2)/T}$$

$$\frac{25.9\ X_A}{1 - X_A} = e^{2008.6/T}$$

$$\therefore \quad T = \frac{2008.6}{\ln\left[\dfrac{25.9\ X_A}{1 - X_A}\right]}$$

With this equation calculate the values of T by taking $X_A = 0,\ 0.1,\ 0.2 \ldots$ upto 0.60

For $\quad X_A = 0.0, \quad T = -$

For $\quad X_A = 0.10$

$$T = \frac{2008.6}{\ln\left[\dfrac{25.9 \times 0.1}{1 - 0.10}\right]} = 1900\ \text{K}\ (1627\ ^\circ\text{C})$$

For $X_A = 0.20$

$$T = \frac{2008.6}{\ln\left[\frac{25.9 \times 0.2}{1-0.2}\right]} = 1075\ \text{K}\ (802\ ^\circ\text{C})$$

For $X_A = 0.30$, $T = 834\ \text{K}\ (561\ ^\circ\text{C})$

For $X_A = 0.40$, $T = 705\ \text{K}\ (432\ ^\circ\text{C})$

For $X_A = 0.50$, $T = 617\ \text{K}\ (344\ ^\circ\text{C})$

For $X_A = 0.60$, $T = 549\ \text{K}\ (276\ ^\circ\text{C})$

Feed temperature T = 600 °C (873 K)

$$\ln\left[\frac{25.9\, X_A}{1-X_A}\right] = \frac{2008.6}{T}$$

Put $T = 873$ and get X_A

∴ $X_A = 0.278$

For $X_A = 0.278$, $T = 873\ \text{K}\ (600\ ^\circ\text{C})$

These temperature values for given conversion result in maximum rates. i.e. these are optimum temperatures.

X_A	0	0.10	0.20	0.278	0.30	0.40	0.50	0.60
T, °C	–	1627	802	600	561	432	344	276

As seen from the above table the optimum temperature exceeds the limit of feed temperature 600 °C (873 K) until the conversion reaches 0.278. Therefore, the optimum temperature progression for given reaction will be the isothermal path at 600 °C upto 27.8% conversion followed by decreasing temperatures in the table until 60% conversion.

Optimum temperature progression-isothermal at 600 °C upto 27.8% then

561 – 432 – 344 – 276 °C ... **Ans.**

Ex. 6.14 : For elementary liquid phase reaction

$$A \rightleftharpoons R$$

make a plot of equilibrium conversion as a function of temperature. Determine the adiabatic equilibrium temperature and conversion when pure A is fed to the reactor at 27 °C (300 K).

Data :

$$\Delta H^\circ_{f\,A} = -40000\ \text{cal/mol},\quad \Delta H^\circ_{f\,R} = -60000\ \text{cal/mol}$$

$$C_{p_A} = 50\ \text{cal/(mol.K)},\quad C_{p_R} = 50\ \text{cal/(mol.K)}$$

$$K = 100000\ \text{at}\ 298\ \text{K}$$

Solution : $A \rightleftharpoons R$, liquid phase reaction, $\varepsilon_A = 0$

$$-r_A = k_1 C_A - k_2 C_R$$

$$C_A = C_{A_0}(1-X_A)$$

$$C_R = C_{R_0} + C_{A_0} X_A$$

$$C_R = C_{A_0} X_A \quad \text{as } C_{R_0} = 0 \text{ (pure A)}$$

$$-r_A = k_1 C_{A_0}(1-X_A) - k_2 C_{A_0} X_A$$

At equilibrium, net rate is zero.

$$\therefore \quad 0 = k_1 C_{A_0}(1-X_{Ae}) - k_2 C_{A_0} X_{Ae}$$

$$\frac{k_1}{k_2} = \frac{C_{A_0} X_{Ae}}{C_{A_0}(1-X_{Ae})}$$

$$\frac{X_{Ae}}{1-X_{Ae}} = K$$

$$\therefore \quad X_{Ae} = \frac{K\,(T)}{1+K\,(T)}, \quad \text{K is a function of T}$$

K at 298 K = 100000

$$\Delta C_p = C_{p_R} - C_{p_A} = 50 - 50 = 0 \text{ cal/(mol.K)}$$

When $\Delta C_p = 0$, the heat of reaction is independent of temperature and the equilibrium constant varies with temperature as per the following equation

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-\Delta H_R}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

At 298 K : $\Delta H_R^\circ = 1 \times \Delta H_{f_R}^\circ - 1 \times \Delta H_{f_A}^\circ \; -60000 - (-40000) = -20000$ cal/mol

$$\ln\left(\frac{K_2}{K_1}\right) = \frac{-(-20000)}{1.987}\left[\frac{1}{T_2} - \frac{1}{298}\right]$$

$$= \left[\frac{20000}{1.987\,T_2} - \frac{20000}{1.987 \times 298}\right]$$

$$\ln\left[\frac{K_2}{K_1}\right] = \left[\frac{20000}{1.987\,T_2} - 33.78\right]$$

$$\frac{K_2}{K_1} = \exp\left(\frac{10065}{T_2} - 33.78\right)$$

$$K_2 = K_1 \exp\left(\frac{10065}{T_2} - 33.78\right)$$

For any temperature T above equation can be written as :

$$\therefore \quad K(T) = 100000 \exp\left(\frac{10065}{T} - 33.78\right), \quad \text{K(T) : function of T.}$$

We have, $X_{Ae} = K(T)/[1 + K(T)]$

$$\therefore \quad X_{Ae} = \frac{100000 \exp\left(\frac{10065}{T} - 33.78\right)}{1 + 100000 \exp\left(\frac{10065}{T} - 33.78\right)}$$

So take T = 298, 350, 400 ... upto 500 and calculate X_{Ae} using above equation.

This X_{Ae} calculated is the conversion obtained from material balance. So this is T v/s X_{Ae} for material balance curve.

T	K	X_{Ae}
298	100000	1.0
350	658.6	0.998
400	18.10	0.95
425	4.12	0.80
450	1.1	0.52
475	0.34	0.25
500	0.12	0.11
550	0.0189	0.019

From energy balance :

For reaction carried out adiabatically :

$$X_A = \frac{C_p \Delta T}{-\Delta H_R} \text{ (for } \Delta H_R \text{ independent of temperature as } C_{p_R} - C_{p_A} = 0)$$

$$X_A = \frac{C_p (T - T_o)}{-\Delta H_R} = \frac{50\,(T-300)}{-(-20000)} = \frac{50\,(T-300)}{20000}$$

$$X_A = 2.5 \times 10^{-3}\,(T - 300) \text{ as } T_o = 300 \text{ K (given)}$$

Evaluate X_A for various values of T using energy balance equation.

$$\text{At } T = 300\text{ K}$$

$$X_A = 2.5 \times 10^{-3}\,(300 - 300) = 0$$

$$\text{At } T = 400\text{ K}, X_A = 0.25$$

X_A – T from energy balance

T, K	300	400	500	600
X_A	0	0.25	0.5	0.75

or draw energy balance line through 300 K with slope 50/20000.

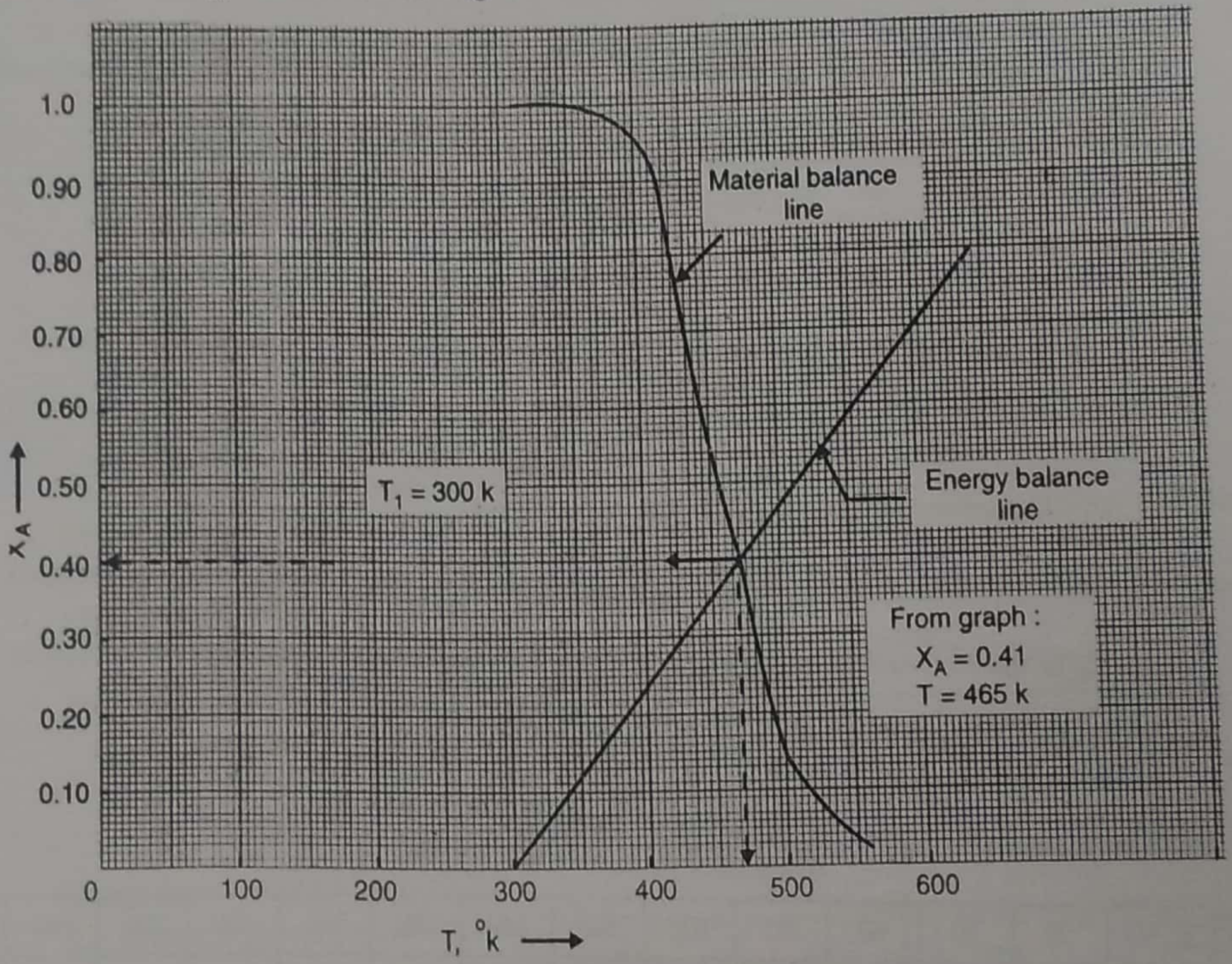


Fig. E 6.14

From graph :

$$X_{Ae} = 0.41 \text{ and } T = 465 \text{ K}$$

For feed temperature of 300 K, the adiabatic equilibrium temperature is 465 K and the corresponding adiabatic equilibrium conversion is 41 %. ... **Ans.**

Ex. 6.15 : A first order liquid phase reaction is carried out in mixed flow reactor. The concentration of reactant in feed is 3 kmol/m^3 and volumetric flow rate is 60×10^{-6} m^3/s. The density and specific heat of reaction mixture are constant at 10^3 kg/m^3 and 4.19×10^3 J/(kg.K). The volume of reactor is 18×10^{-3} m^3. The reactor operates adiabatically. If feed enters at 298 K, what are steady state conversions and temperatures in the product stream ?

Take $\Delta H_R = -2.09 \times 10^8$ J/kmol

and rate $= 4.48 \times 10^6 \exp\left(-\dfrac{62800}{RT}\right) C$, kmol/(m^3.s)

C is the concentration of reactant. T is in K and E is in J/mol.

Solution : $A \rightarrow R$, liquid phase, $\varepsilon_A = 0$

$$C_{A_0} = 3 \text{ kmol/m}^3$$

$$C = \text{Specific heat of reaction mixture} = 4.19 \text{ J/(kg.K)}$$

$$\rho = \text{density of reaction mixture} = 10^3 \text{ kg/m}^3$$

$$\text{Mean specific heat/heat capacity of A} = C\left[\frac{J}{kg.K}\right] \times \rho\left(\frac{kg}{m^3}\right) \times \frac{1}{C_{A_0}}\left(\frac{kmol}{m^3}\right)$$

$$= \frac{4.19 \times 10^3}{3} \times 10^3 = 1396.7 \times 10^3 \text{ J/(kmol.K)}$$

First order reaction :

$$-r_A = k\,C_A = kC_{A_0}(1 - X_A)$$

For mixed flow reactor material balance equation is

$$\tau = \frac{C_{A_0} X_A}{-r_A} = \frac{C_{A_0} X_A}{k\,C_{A_0}(1 - X_A)} = \frac{X_A}{k\,(1 - X_A)}.$$

$$\therefore \quad X_A = \frac{\tau k}{1 + \tau k}$$

$$k = 4.48 \times 10^6 \exp(-62800/RT), \ (s)^{-1}$$

$$\tau = \frac{V}{v_o} = \frac{18 \times 10^{-3}}{60 \times 10^{-6}} = 300 \text{ (s)}$$

$$X_A = \frac{300 \times 4.48 \times 10^6 \exp(-62800/8.314 \times T)}{1 + 300 \times 4.48 \times 10^6 \exp(-62800/8.314\,T)}$$

where X_A is the conversion in exit stream from reactor.

$$X_A = \frac{1.34 \times 10^9 \exp(-7553/T)}{1 + 1.34 \times 10^9 \exp(-7553/T)}$$

This is the material balance equation relating T and X_A.

Feed temperature is 25 °C (298 K).

$$X_A = \frac{1.34 \times 10^9 \exp(-7553/298)}{1 + 1.34 \times 10^9 \exp(-7553/298)} = 0.013 \ (1.3\%)$$

$$T = 40\ ^\circ C \ (313 \text{ K})$$

$$X_A = \frac{1.34 \times 10^9 \exp(-7553/313)}{1 + 1.34 \times 10^9 \exp(-7553/313)} = 0.0425 \quad \text{at } T = 298 \text{ K}$$

In this way, find X_A for various values of T till X_A = 1 and plot material balance curve (X_A v/s T).

X_A	0.013	0.042	0.086	0.16	0.27	0.33	0.40	0.68	0.86	0.94	0.973	0.987	0.991
T, °C	25	40	50	60	70	75	80	100	120	140	160	180	190
T, K	298	313	323	333	343	348	353	373	393	413	433	453	463

Energy balance for adiabatic operation is,

$$X_A = \frac{C_p\,\Delta T}{-\Delta H_R}, \qquad \Delta T = T_2 - T_1$$

where T_2 temperature of exit stream and T_1 is the feed temperature.

$$C_p = 1396.7 \times 10^3 \text{ J/(kmol.K)}, \quad \Delta H_R = -2.09 \times 10^8 \text{ J/kmol}$$

$$X_A = \frac{1396.7 \times 10^3}{-(-2.09 \times 10^8)}\,\Delta T = 6.68 \times 10^{-3}\,\Delta T = 6.68 \times 10^{-3}\,(T_2 - 298)$$

This energy balance line is having slope of 6.68×10^{-3} (1/150). Draw this energy balance line through $T_1 = 298$ with slope equal to (1/150).

OR use $X_A = 6.68 \times 10^{-3}\,(T_2 - 298)$, put T values and evaluate X_A.

T, °C	25	40	60	80	100	120	140	160	170
X_A	0	0.10	0.23	0.37	0.501	0.635	0.77	0.9	0.97

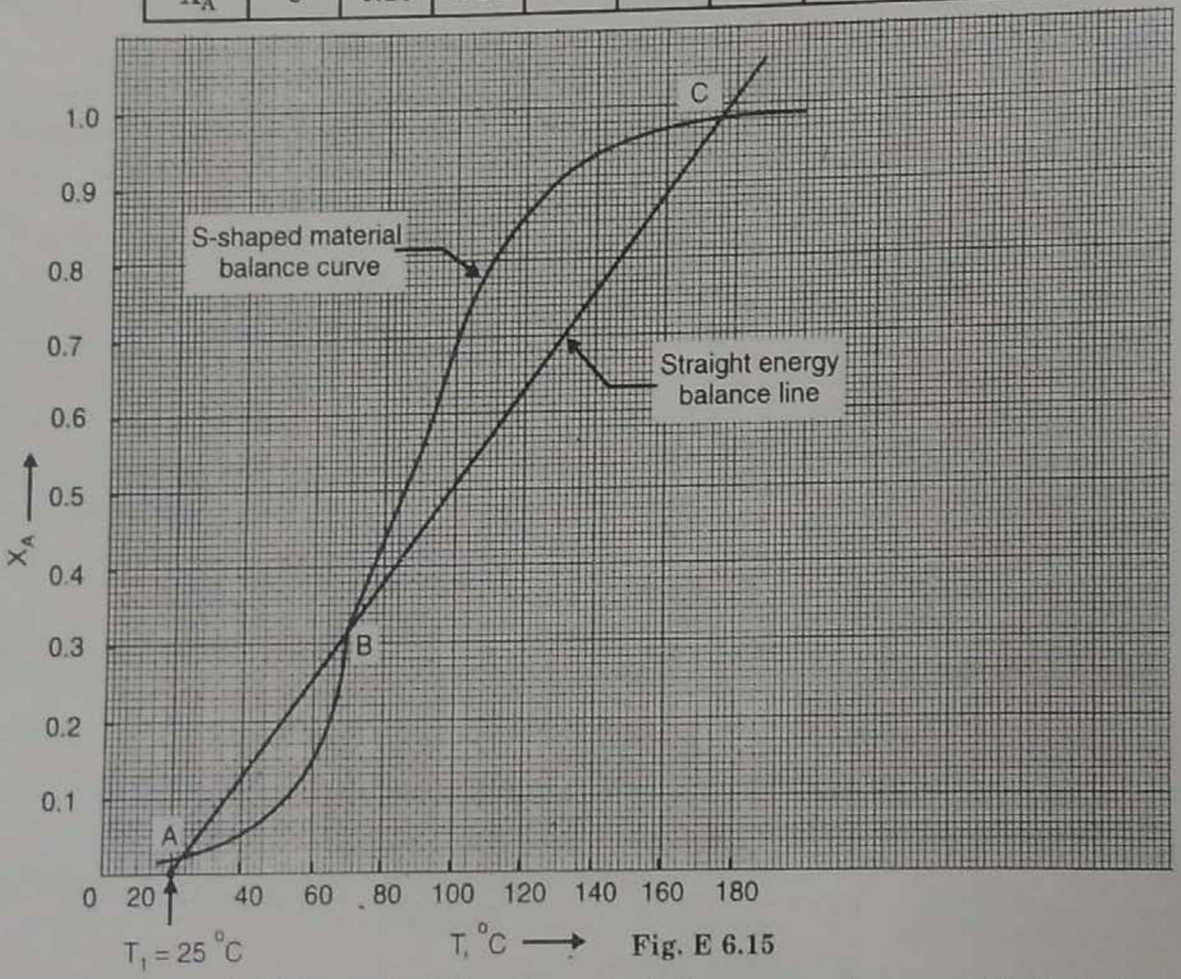


Fig. E 6.15

The plot of X_A v/s T for material and energy balance equations results in intersection at points A, B and C. There are two stable steady state operating conditions (point A and point C). The possible operating temperatures and conversions are :

Intersection	T, °C	X_A	% conversion
A	28.5	0.0175	1.75
C	173	0.985	98.5

The point B is unstable state. It occurs at T = 73 °C. If the reaction is started by adding feed to the reactor at 25 °C the point A will be the steady state operating condition at 28.5 °C and conversion will be 1.75% only. To obtain high conversion the initial temperature would have to be 73 °C (point B). In this case, the reaction temperature will increase to 173 °C and conversion will be 98.5%.

Ex. 6.16 : A first order irreversible liquid phase reaction is carried out in mixed flow reactor. The density of reaction mixture is 1.2 g/cm³ and the specific heat is 0.9 cal/(g. °C). The volumetric flow rate is 200 cm³/s and the reactor volume is 10 litres.

$$k = 1.8 \times 10^5\, e^{-12000/RT},\ s^{-1}$$

If the heat of reaction is –46000 cal/mol and feed temperature is 20 °C, what are possible temperatures and conversions for stable, adiabatic operation for feed concentration of 4 mol/*l* ?

Solution : $A \rightarrow R$

$C_{A_0} = 4$ mol/*l*, c of reaction mixture = 0.9 cal/(g·°C) = 0.9 cal/(g.K)

$\rho = 1.2$ g/cm³

$$\text{Mean specific heat of A} = C_{p_A} = \frac{c\ (\text{cal/g·K}) \cdot \rho\ (g/l)}{C_{A_0}\ (\text{mol}/l)} = \frac{0.9 \times 1.2 \times 10^3}{4} = 270\ \text{cal/(mol.K)}$$

For mixed flow reactor, the material balance yields

$$\tau = \frac{C_{A_0} X_A}{-r_A} = \frac{C_{A_0} X_A}{k\, C_{A_0}\, (1 - X_A)} = \frac{X_A}{k\, (1 - X_A)}$$

$$X_A = \frac{\tau k}{1 + \tau k}\ ,\quad k = k_o e^{-E/RT} = 1.8 \times 10^5\, e^{-12000/RT}$$

$$\tau = \frac{V}{v} = \frac{10 \times 10^3}{200} = 50\ s$$

$$X_A = \frac{50 \times 1.8 \times 10^5\, e^{-12000/RT}}{1 + 1.85 \times 10^5 \times 50\, e^{-12000/RT}}$$

$$= \frac{9.25 \times 10^6\, e^{-6039/T}}{1 + 9.25 \times 10^6\, e^{-6039/T}}\ ,\ \text{as } R = 1.987\ \frac{\text{cal}}{(\text{mol.K})}$$

where X_A is the conversion in the exit stream from reactor/within reactor.

This is the material balance equation relating T and X_A.

Feed temperature = $T_1 = 20\ °C$ (293 K)

$$X_A = \frac{9.25 \times 10^6\, e^{-6039/293}}{1 + 9.25 \times 10^6\, e^{-6039/293}} = 0.01$$

T, °C	20	40	60	80	100	120	140	160	180	200	220	240	250
X_A	0.01	0.04	0.11	0.256	0.46	0.66	0.8	0.89	0.94	0.96	0.98	0.986	0.99

Energy balance for adiabatic operation is

$$X_A = \frac{C_p\, \Delta T}{-\Delta H_R} = \frac{270\ \Delta T}{-(-4600)} = 5.87 \times 10^{-3}\, (T_2 - 293) = \frac{1}{170}\, (T_2 - 293)$$

This energy balance line is having a slope of 1/170 and should be drawn from T_1 = 293 K.

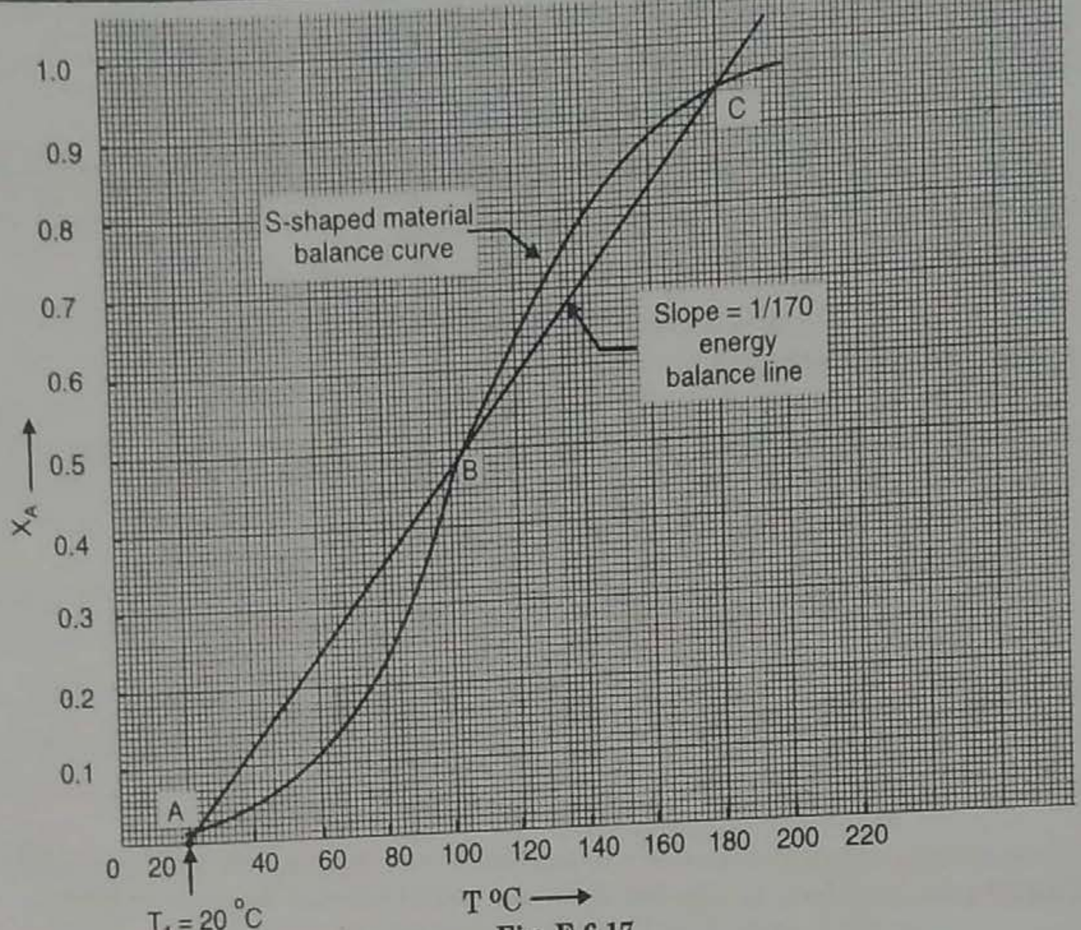


Fig. E 6.17

OR : Take T_2 as 40, 60 ... 250 and evaluate X_A.

T, °C	40	60	80	100	140	180
X_A	0.12	0.235	0.35	0.47	0.70	0.94

This is X_A v/s T for energy balance.

Construct plot of X_A v/s T for energy balance and material balance equations and find the intersections of these two.

From graph, stable operating conditions are given points A and C. Point B is unstable state.

Possible operating temperatures and conversions are :

Intersection	T, °C	X_A	% conversion
A	22	0.015	1.5
B	180	0.94	94

Temperature of point B = 102 °C

To obtain high conversion the initial temperature would have to be 120 °C. In this case reaction temperature would increase to 180 °C and conversion will be 94%.

Ex. 6.17 : An irreversible isomerisation reaction is carried out in liquid phase in mixed flow reactor.

$A \rightarrow R$, first order reaction.

Rate constant at 165 °C = 0.7 $(h)^{-1}$

Activation energy = 120000 J/mol

Heat of reaction = – 350 kJ/kg

Heat capacity of reactants and products = 1.95 kJ/(kg.K)

Volumetric flow rate = 0.33 m^3/h

Feed temperature = 20 °C

Conversion expected = 95%

Calculate the reactor size and temperature of the reaction mixture if the reactor is operated adiabatically.

Solution : $A \rightarrow R,\ \varepsilon_A = 0$

$$-r_A = k\,C_A$$

Material balance over mixed flow reactor yields :

$$\tau = \frac{C_{A0}X_A}{-r_A} = \frac{C_{A0}X_A}{k\,C_{A0}(1-X_A)} = \frac{X_A}{k\,(1-X_A)}$$

$$k = k_o\,e^{-E/RT}$$

$$\therefore \quad k \text{ at } 165\,^{\circ}C = 438\text{ K}$$

k at any T is given by,

$$\ln\frac{k\,(T)}{k\,(438)} = \frac{-E}{R}\left[\frac{1}{T}-\frac{1}{438}\right],\quad E = 120000\text{ J/mol}$$

$$\ln k - \ln(0.7) = \frac{-120000}{8.314}\left[\frac{1}{T}-\frac{1}{438}\right],\quad R = 8.314\text{ J/(mol.K)}$$

$$\ln k = 33.31 - \frac{14433.5}{T}$$

$$k = e^{33.31}\cdot e^{-14433.5/T}$$

$$k = 2.92\times 10^{14}\ e^{-14433.5/T}$$

Energy balance for adiabatic operation :

$$X_A = \frac{C_p\,\Delta T}{-\Delta H_R},\quad \Delta T = T_2 - T_1$$

T_2 = temperature of exit stream, T_1 = feed temperature (20 + 273 = 293 K)

C_p = 1.95 kJ/(kg.K), ΔH_R = 350 kJ/kg

X_A = 0.95

$$0.95 = \frac{1.95\,\Delta T}{-(-350)}$$

$$\Delta T = 170.5\text{ K}$$

$$T_2 = 170.5 + T_1 = 170.5 + 293 = 463.5\text{ K}$$

$T = T_2$ = 463.5 K = temperature within the reactor at 95% conversion.

T obtained from energy balance is to be put into material balance equation to get τ.

$$\tau = \frac{X_A}{k\,(1-X_A)} = \frac{X_A}{2.92\times 10^{14}\,e^{-14433.5/T}\,(1-X_A)}$$

$$= \frac{0.95}{2.92\times 10^{14}\,e^{-14433.5/463.5}\,(1-0.95)}$$

$$= 2.17\ (h)$$

$$\tau = \frac{V}{v_o}$$

$$\therefore \quad V = \tau\,v_o = 2.17\times 0.33 = 0.716\ m^3 = 716\ l$$

... **Ans.**

Under adiabatic conditions, for 95% conversion, temperature of reaction mixture = 190.5 °C (463.5 K)

... **Ans.**

Ex. 6.18 : The elementary liquid phase reaction

$$A + B \rightarrow C$$

is carried out in mixed flow reactor. An equal molar feed in A and B enters the reactor at 27 °C and the volumetric flow rate is 2 *l*/s.

Calculate the volume of reactor to achieve 85% conversion when the reaction is carried out adiabatically.

ΔH_f^o for A = – 20 kcal/mol, for B = – 15 kcal/mol and for C = – 41 kcal/mol

$$C_{Ao} = 0.10 \ \text{kmol/m}^3$$

$$C_{P_A} = C_{P_B} = 15 \text{ cal/(mol.K)}, \ C_{PC} = 30 \text{ cal/(mol.K)}$$

$$k = 0.01\left(\frac{l}{\text{mol.s}}\right) \text{ at } 300 \text{ K}, \ E = 10000 \text{ cal/mol}$$

Solution : $A + B \rightarrow C, \ \varepsilon_A = 0$

$$-r_A = k\, C_A\, C_B$$

$$= k\, C_A^2 \text{ for equimolar feed } (C_{Ao} = C_{Bo})$$

$$= k\, C_{Ao}^2 (1 - X_A)^2$$

Material balance for mixed flow reactor yields :

$$\tau = \frac{C_{Ao} X_A}{(-r_A)} = \frac{C_{Ao} X_A}{k\, C_{Ao}^2 (1 - X_A)^2}$$

$$\tau = \frac{X_A}{k\, C_{Ao} (1 - X_A)^2}$$

k at any T is given by

$$\ln\left[\frac{k(T)}{k\,(300)}\right] = \frac{-E}{R}\left[\frac{1}{T} - \frac{1}{300}\right]$$

$$\ln \frac{k\,(T)}{k\,(300)} = \frac{-10000}{1.987}\left[\frac{1}{T} - \frac{1}{300}\right]$$

As E = – 10000 cal/mol and $R = 1.987 \dfrac{\text{cal}}{(\text{mol.K})}$

$$\ln k - \ln k\,(300) = \frac{-5033}{T} + 16.77$$

$$\ln k - \ln\,(0.01) = \frac{-5033}{T} + 16.77$$

$$\ln k = 12.17 - \frac{5033}{T}$$

$$\therefore \quad k = 1.93 \times 10^5\, e^{-5033/T}$$

where T is the temperature in reactor or at exit of reactor in K.

$$\therefore \quad \tau = \frac{X_A}{1.93 \times 10^5\, e^{-5033/T} \cdot C_{Ao} (1 - X_A)^2}$$

This is material balance equation.

Energy balance equation for adiabatic operation is

$$X_A = \frac{C_p\, \Delta T}{\Delta H_R}, \quad \text{for } C_p'' - C_p' = 0$$

$$C_{P_A} = C_{P_B} = 15 \text{ cal/(mol.K)}, \ C_{P_C} = 30 \text{ cal/(mol.K)}$$

$$\Delta C_p = 30 - (15 + 15) = 0$$

$$\Delta H_{R(T)} = \Delta H_R^o + \Delta C_p\ (T - T_o)$$

$$\Delta H_{R(T)} = \Delta H_R^o \text{ as } \Delta C_p = 0$$

$$\Delta H_R^o = 1 \times \Delta H_{f_C}^o - (1 \times \Delta H_{f_A}^o + 1 \times \Delta H_{f_B}^o)$$

$$= -41 - [(-20) + (-15)]$$

$$= -6 \text{ kcal/mol} = -6000 \text{ cal/mol}$$

$$\Delta H_R = -6000 \text{ cal/mol}$$

Equal molar flow of A and B.

$$C_p \text{ for feed} = C_p \text{ of } A + C_p \text{ of } B \left(\frac{\text{moles of B}}{\text{moles of A}}\right)$$

$$\therefore \quad C_p \text{ for feed} = 15 + 15 \times \frac{1}{1} = 30 \text{ cal/(mol.K)}$$

$$X_A = \frac{C_p\,\Delta T}{-\Delta H_R}, \quad X_A = 0.85$$

$$0.85 = \frac{30\,\Delta T}{-(-6000)} \quad \therefore \quad \Delta T = 170\text{ K}$$

$$\Delta T = T_2 - T_1 \quad \therefore T_2 = \Delta T + T_1 = 170 + 300 = 470\text{ K}$$

$$T_1 = \text{feed temperature} = 27 + 273 = 300\text{ K}$$

Temperature of reaction mixture in reactor/in exit stream from reactor = 470 K = 197 °C. Use this T (obtained from energy balance) in material balance equation to get τ.

$$\tau = \frac{X_A}{1.93 \times 10^5\, e^{-5033/T} \cdot C_{Ao}\,(1 - X_A)^2}$$

$$C_{Ao} = 0.1 \text{ kmol/m}^3 = 0.1 \text{ mol}/l$$

$$\tau = \frac{0.85}{1.93 \times 10^5\, e^{-5033/470} \times 0.10\,(1 - 0.85)^2}$$

$$= 87.56\text{ s}$$

$$\tau = V/v_o, \quad v_o = 2\ l/\text{s}$$

$$V = \tau \cdot v_o = 87.56 \times 2 = 175.12 \approx 175\ l$$

... Ans.

❑❑❑

Chapter ... 7

BASIC ASPECTS OF NON IDEAL FLOW

So far we have treated two ideal flow patterns, namely, plug flow (no axial mixing) and mixed flow (complete mixing). The real reactors always deviate to some degree from these ideal behaviours (two extremes in mixing states). The real reactors never fully follow these flow patterns and the behaviour of a specific reactor will depend upon the extent of mixing. The deviation from ideal flow patterns (existence of non-ideal flow) may be caused (i) by creation of nearly stagnant regions (dead zones) in the vessel, (ii) by bypassing or short-circuiting of the fluid, (iii) by channeling, (iv) by recycling of fluid, (v) due to vortices and turbulence at inlet and outlet.

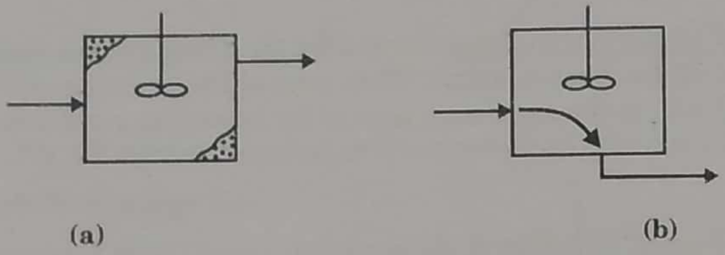


Fig. 7.1 (A) : Deviation from ideal mixed flow performance
(a) stagnant regions, (b) bypassing (short-circuiting)

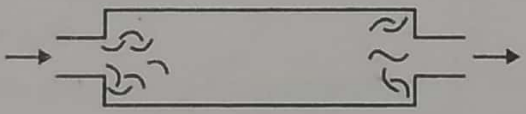


Fig. 7.1 (B) : Deviation from ideal plug flow - longitudinal mixing due to vortices and turbulence

The factors that make up the contacting or flow pattern are :

(i) RTD – residence time distribution of fluid flowing through vessel, (ii) the state of aggregation of fluid and, (iii) the earliness and lateness of fluid mixing in the vessel.

Residence Time Distribution (RTD) Function :

The time it takes a molecule to pass through a reactor is called the residence time of the molecule in the vessel. It is clear that elements of fluid taking different routes/paths through the reactor may take different lengths of time to pass through it. So there is a distribution of residence times of the fluid material within the reactor. The distribution of these times for the stream of fluid leaving the vessel is called the exit age distribution E, or the residence time distribution RTD of fluid. E has units of $(\text{time})^{-1}$.

In an ideal plug flow reactor, all the molecules of material leaving the reactor have been inside it for exactly the same amount of time. Similarly, in ideal batch reactor, all the molecules of material within the reactor have been inside it for same length of time. The ideal plug flow and ideal batch reactors are the only two classes of reactors in which all the fluid elements in the reactors have the same residence time. In all other types, the various molecules in the feed spend different times inside the reactor, that is, there is a distribution of residence times of material within the reactor. For example, consider the mixed flow reactor, the feed introduced into it at any given time gets completely mixed with the material already in the reactor. In other words, some of the molecules entering the mixed flow reactor leave it almost immediately, because the material is continuously removed from the reactor; other molecules remain in the reactor almost for ever because all the material is never withdrawn at one time from the reactor. Many of the molecules, leave the reactor after spending a period of time somewhere close to the mean residence time. The distribution of residence times can significantly affects the performance of reactor. The RTD of a reactor is a characteristic of the mixing that occurs in the reactor.

RTD Measurement :

The RTD is determined experimentally by using an inert chemical called as a tracer. The **characteristics of tracer** are :

(i) It should be non-reactive. (ii) It should be completely soluble in the system fluid. (iii) It should be easily detectable. (iv) It should have physical properties similar to those of the system and (v) It should not adsorb on the walls or other surfaces in the vessel.

Coloured materials (dyes) and radioactive materials are commonly used as a tracer. The tracer is in the form of its concentrated solution.

The RTD is determined experimentally by injecting the tracer at some time t = 0 and then measuring the concentration of tracer, C, in the effluent stream as a function of time.

The most commonly used methods for injecting the tracer are :

(1) Pulse input and (2) Step input.

The Pulse Input Experiment :

In case of pulse input, the known quantity of tracer (M kg or moles) suddenly injected in one shot into the fluid entering the vessel in a as short as time as possible. The tracer concentration in the exit stream is measured as a function of time. The pulse injection (concentration-time curve at inlet of vessel) and pulse response (concentration-time curve at the outlet of the vessel) are shown in Fig. 7.2. In RTD analysis, the effluent concentration - time curve is referred to as C curve.

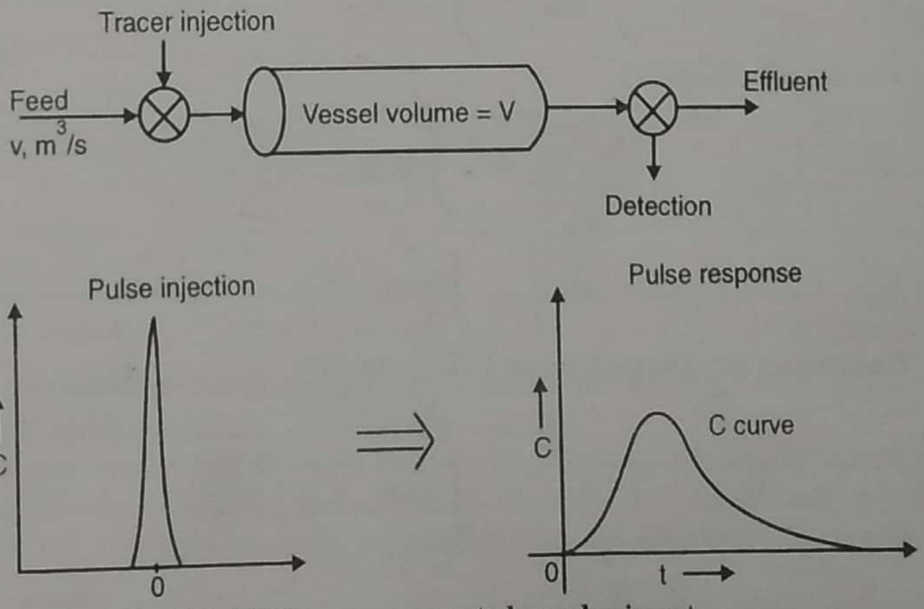


Fig. 7.2 : RTD measurements by pulse input

It can be observed from the pulse response that the concentration of tracer in the effluent stream increases with time, reaches a maximum value and then falls, eventually approaching zero.

The amount of tracer material, ΔM, leaving the vessel between time t and $t + \Delta t$ (by selecting increment Δt sufficiently small so that the tracer concentration, C, exiting between time t and $t + \Delta t$ is essentially constant) is obtained by material balance of tracer.

$$\Delta M = C\,v\,\Delta t \qquad \text{... (7.1)}$$

v is the volumetric flow rate of the effluent stream from vessel.

ΔM is the amount of material that has spent an amount of time between t and $t + \Delta t$ in the vessel.

Dividing equation (7.1) by M, we get,

$$\frac{\Delta M}{M} = \frac{C\,v}{M}\,\Delta t = \frac{C}{M/v}\,\Delta t \qquad \text{... (7.2)}$$

where M is the total amount of tracer injected into the vessel.

$\Delta M/M$ is the fraction of material that has residence time between t and $t + \Delta t$ in the vessel.

Let us define E as,

$$E = \frac{C\,v}{M} = \frac{C}{M/v} \qquad \text{... (7.3)}$$

where E is the residence time distribution function that decreases in a quantitative manner how much time different fluid elements have spent in the vessel.

E has units of time^{-1}.

$$\therefore \quad \frac{\Delta M}{M} = E\,\Delta t \qquad \text{... (7.4)}$$

Whenever M is not known directly, it can be obtained by measuring the tracer concentration in the effluent stream and summing all the amounts of materials, ΔM, between time $t = 0$ and $t = \infty$. For this, write equation (7.1) in the differential form and integrate it.

$$dM = C\,v\,dt$$

$$\int_0^M dM \qquad \int_0^\infty C\,v\,dt$$

v is usually constant.

$$\therefore \quad M = v\int_0^\infty C\,dt \qquad \text{... (7.5)}$$

$$M/v = \int_0^\infty C\,dt \qquad \text{... (7.6)}$$

Combining equations (7.3) and (7.6), we get,

$$E = \frac{C}{\int_0^\infty C\,dt} \qquad \text{... (7.7)}$$

$$\text{Integral} \int_0^\infty C\,dt = \text{Area under C curve} = M/v \left(\frac{\text{kg.s}}{\text{m}^3}\right)$$

E can be obtained from the tracer concentration-time data.

Note that C, E are functions of time and not constant values as they are appearing in equations.

$$\text{We can take,} \quad \int_0^\infty C\,dt \equiv C_i\,\Delta t_i$$

E curve from C curve :

From the data of tracer concentration (in the effluent stream from the vessel) – time, plot C curve and find area of curve graphically or numerically. Then find E for each concentration using equation (7.7) and plot E v/s t which is E curve (Residence time distribution curve).

The residence time distribution function can be interpreted in integral form.

If we consider the time interval as time between $t = t_1$ and $t = t_2$ then,

$$\begin{array}{l}\text{Fraction of material leaving the vessel that has resided in the} \\ \text{vessel between times } t_1 \text{ and } t_2\end{array} = \int_{t_1}^{t_2} E\,dt.$$

Fraction of all the material that has resided for a time t in the vessel between $t = 0$ and $t = \infty$ is 1 (as sum of all fractions is unity). When none of the tracer passes through the vessel in zero time $E = 0$ at $t = 0$. In the same way, none of the tracer can remain indefinitely in the vessel, so $E \to 1$ as $t \to \infty$.

$$\int_0^\infty E\,dt = 1 \qquad \text{... (7.8)}$$

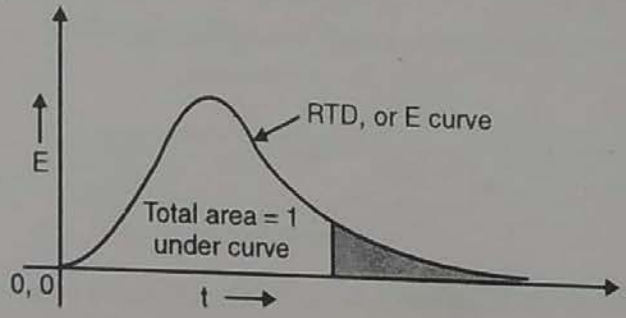


Fig. 7.3 : The exit age distribution curve E

The fraction of the material leaving the vessel (i.e. fraction of the exit stream) of age between t and t + dt is E dt. Age for an element refers to the time spent by the element of the exit stream in the vessel (time it has resided in the vessel).

The fraction of the exit stream of age t_1 is,

$$\int_0^{t_1} E\,dt \qquad \text{... (7.9)}$$

The fraction of the material older than t_1,

$$\int_{t_1}^\infty E\,dt = 1 - \int_0^{t_1} E\,dt \qquad \text{... (7.10)}$$

Fig. 7.3 is the exit age distribution curve E, also called as residence time distribution or RTD for fluid flowing through vessel.

The E curve is the distribution needed to account for nonideal flow.

Mean of the C curve :

$$\bar{t} = \frac{\int_0^\infty t\,C\,dt}{\int_0^\infty C\,dt} \approx \frac{\sum_i t_i C_i \Delta t_i}{\sum_i C_i \Delta t_i} = \frac{V}{v}\ (s) \qquad \ldots (7.11)$$

where $\bar{t}$ is the mean residence time.

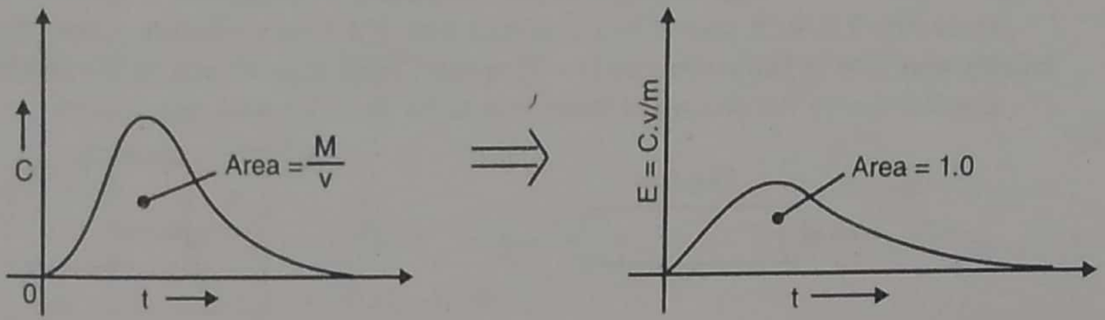


Fig. 7.4 : Transformation of C curve into an E curve

We have another RTD function E_θ.

Frequently, a normalised RTD is used instead of the function E. If we define the paramete

θ as $t/\bar{t}$, a dimensionless function E_θ is defined as,

$$E_\theta = \bar{t}\,E = \frac{V}{v}\frac{C}{M/v} = \frac{V}{M}\,C \qquad \ldots (7.12$$

E_θ is plotted as a function of θ.

The quantity θ represents the number of vessel volumes of fluid that have flowed throug the vessel in time t.

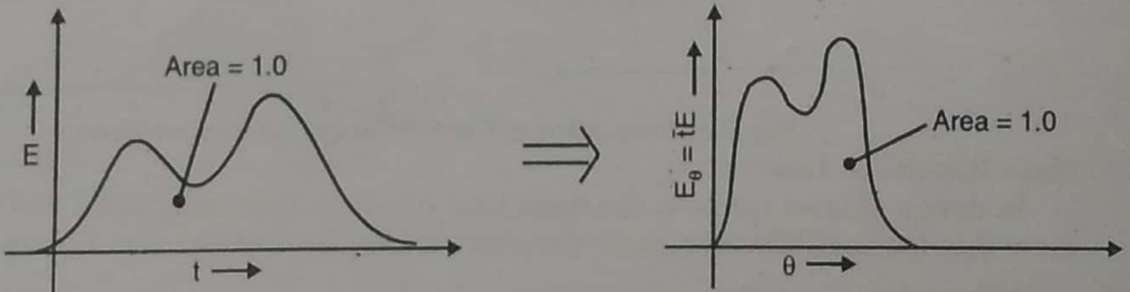


Fig. 7.5 : Transformation of an E curve into an E_θ curve

The Step Input Experiment :

Now we will analyse the step input in tracer concentration for a system of constant volumetric flow rate.

Suppose that v m^3/s of ordinary fluid is flowing through the vessel of volume V m^3 ($t < 0$). At $t = 0$, switch from ordinary fluid to fluid containing tracer with tracer concentration C_o (kg or mol/m^3) and measure the concentration of tracer, C_{step}, in the effluent stream as a function of time.

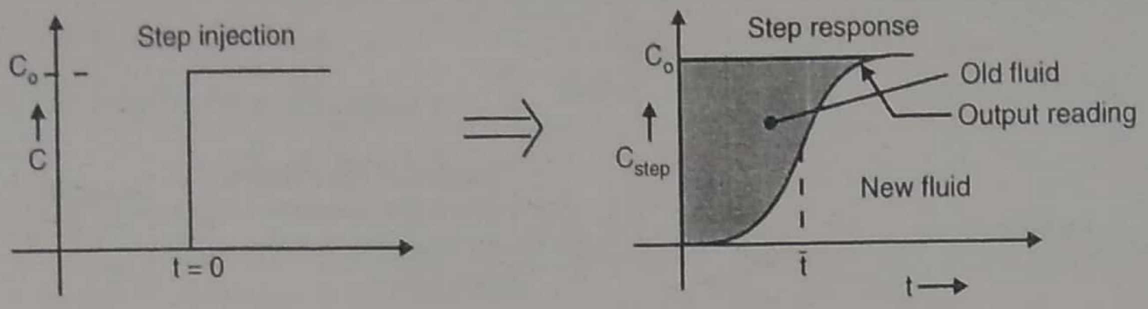


Fig. 7.6 : Response to step input

$\dot m$ is the flow rate of the tracer in the entering fluid in kg/s.

$$C_o = \frac{\dot m}{v} \quad (kg/m^3)$$

Shaded area of Fig. 7.6

$$= C_o \cdot \bar t = \frac{\dot m\ V}{v^2} \quad (kg.s/m^3)$$

$$\bar t = \frac{\int_0^{C_o} t\, dC_{step}}{\int_0^{C_o} dC_{step}} = \frac{1}{C_o}\int_0^{C_o} t\, dC_{step} \quad \dots (7.13)$$

The dimensionless form of C_{step} curve is called as the F curve. It is obtained by plotting C_{step}/C_o v/s time as shown in Fig. 7.7.

The time record of the tracer in the exit stream from the vessel measured as C/C_o for step-input is called as **F curve**.

$$F = \frac{C_{step}}{C_o} = \frac{v \cdot C_{step}}{\dot m}$$

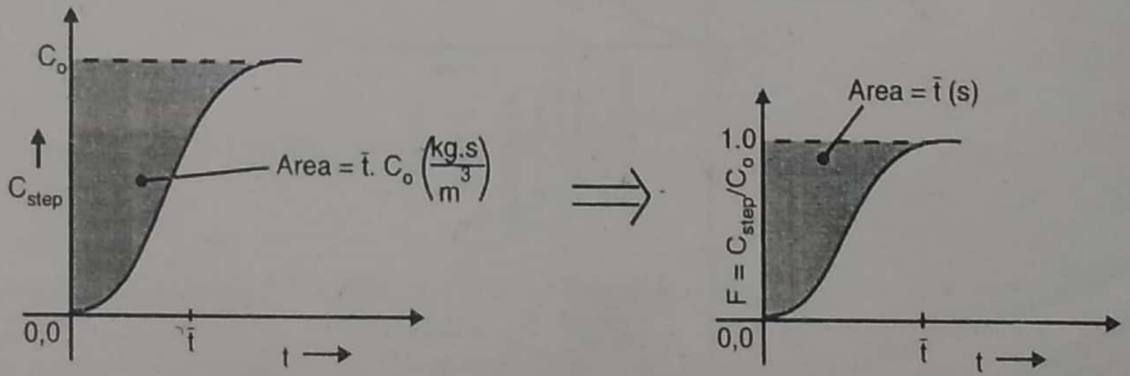


Fig. 7.7 : Transformation of experimental C_{step} curve into an F curve

Relationship between F and E curves :

Consider that there is steady flow of white fluid through the vessel and at time t = 0 we switch to red fluid and measure the rising concentration of red fluid in the effluent stream, the F curve. At any time t > 0, red fluid and only red fluid in the effluent stream is younger than age t. Therefore,

$$\left(\begin{array}{l}\text{fraction of red fluid}\\ \text{in the effluent stream}\end{array}\right) = \left(\begin{array}{l}\text{fraction of the effluent}\\ \text{stream younger}\\ \text{than age t}\end{array}\right) \text{ i.e. } \left(\begin{array}{l}\text{fraction of the effluent}\\ \text{stream that has been}\\ \text{in the vessel for less}\\ \text{than time t}\end{array}\right)$$

LHS is simply F value, while RHS is given by equation (7.9).

$$\therefore \qquad F = \int_0^t E\,dt \qquad \text{... (7.14)}$$

$$\text{Analogously,} \qquad 1 - F = \int_t^{\infty} E\,dt = \left(\begin{array}{l}\text{fraction of the effluent}\\ \text{which has been in}\\ \text{the vessel for longer}\\ \text{then time t}\end{array}\right) \text{ i.e. } \left(\begin{array}{l}\text{fraction of effluent}\\ \text{stream older than}\\ \text{age t}\end{array}\right)$$

$$\text{We have,} \qquad \int_t^{\infty} E\,dt = 1 - \int_0^t E\,dt$$

$$\therefore \qquad \int_t^{\infty} E\,dt = 1 - F \qquad \text{... (7.15)}$$

F is the cummulative RTD function.

On differentiating equation (7.14) with respect to t, we get,

$$\frac{dF}{dt} = E \qquad \text{... (7.15 a)}$$

This relationship is shown in graphical form in Fig. 7.8.

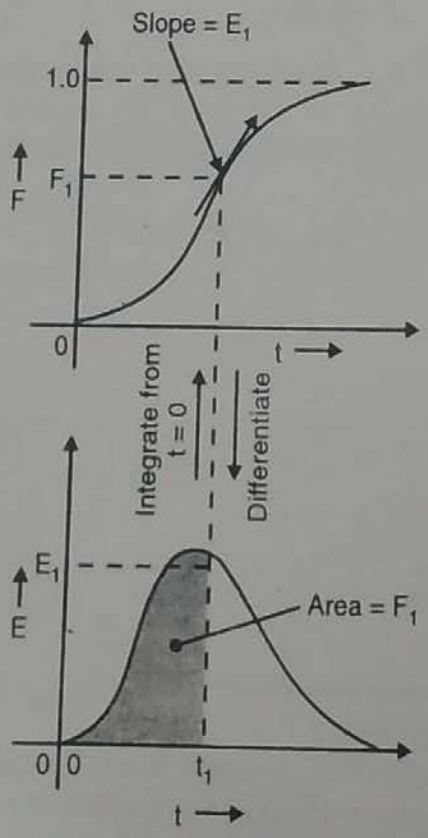


Fig. 7.8 (a) : Relationship between the E and F curves

We can calculate F at various time t from the area under the curve of an E v/s t plot.

Fig. 7.8 (b) shows shape of F curve for a tracer response to a step input.

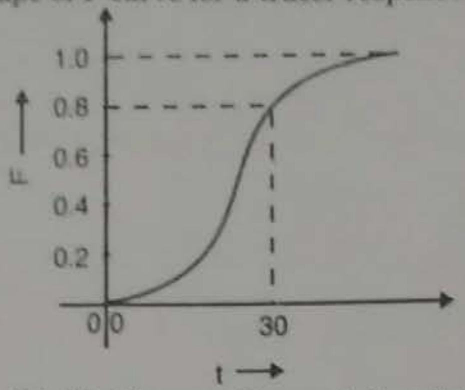


Fig. 7.8 (b) : F curve (Cummulative distribution curve)

From Fig. 7.8 (b) it should be noted that 80% [F] of the molecules spend 30 min or less in t reactor and 20% of the molecules [1 – F] spend longer than 30 min in the vessel.

Fig. 7.9 shows the shapes of these curves for plug flow and mixed flow.

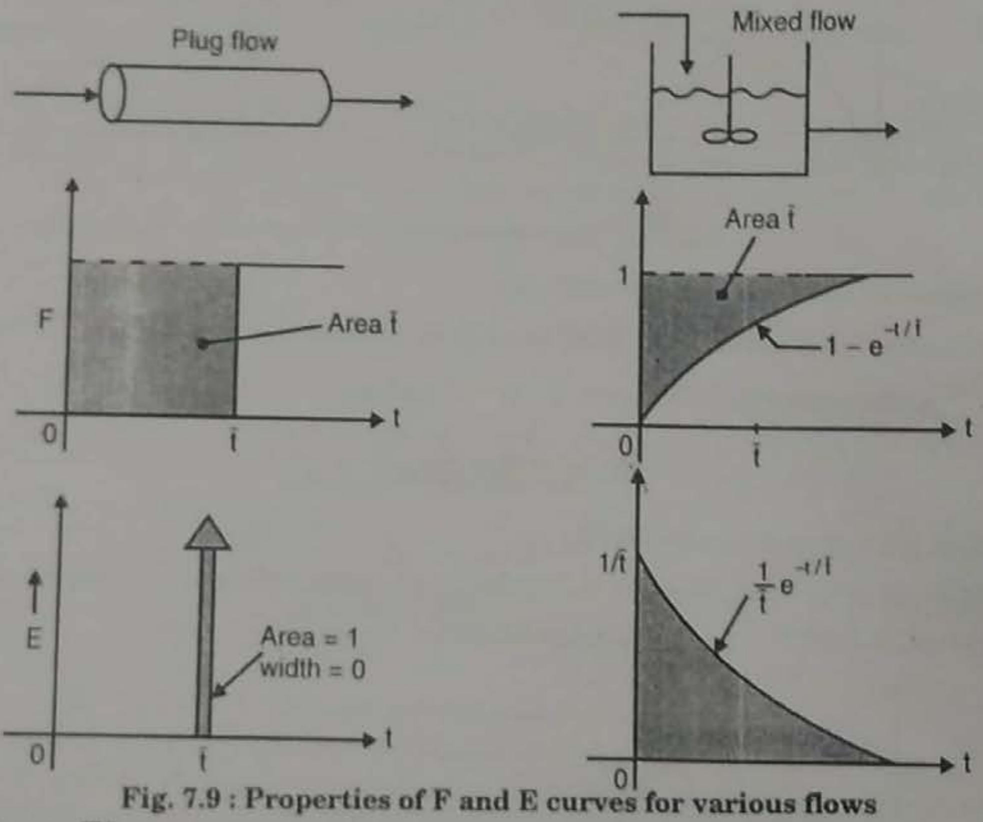


Fig. 7.9 : Properties of F and E curves for various flows

Mean Residence Time :

In design of ideal reactors, the space time was defined as being equal to V/v. Now we will show that for any RTD for a particular reactor, ideal or nonideal, this τ is equal to the mea residence time, $\bar{t}$.

The first moment of RTD function, E, is the mean residence time and is given by,

$$\bar{t} = \frac{\int_0^\infty t\,E\,dt}{\int_0^\infty E\,dt} = \int_0^\infty t\,E\,dt \qquad \dots (7.16)$$

Consider that we have reactor completely filled with white molecules. At time $t = 0$, we start to inject red molecules to replace the white molecules which currently fill the reactor. In time dt, the volume of molecules leaving the reactor is vdt. The fraction of these molecules that have been in the reactor for time t or greater is $1 - F$. As only white molecules have been in the reactor for time t or greater, the volume of white molecules, dV, leaving the reactor in time dt is given as

$$dV = v\,dt\,(1 - F) \quad \text{... (7.17)}$$

By summing up, all the white molecules that have left the reactor in time between 0 and ∞ $(0 < t < \infty)$, we get,

$$V = \int_0^\infty v\,(1 - F)\,dt \quad \text{... (7.18}$$

As the volumetric flow rate is constant,

$$V = v\int_0^\infty (1 - F)\,dt$$

$$\frac{V}{v} = \int_0^\infty (1 - F)\,dt$$

Integrating the above equation by parts,

$$\int x\,dy = xy - \int y\,dx$$

$$\frac{V}{v} = [(1 - F)\,t]_0^\infty + \int_0^1 t\,dF \quad \text{... (7.19}$$

At $t = 0$, $F = 0$, and as $t \to \infty$ then $(1 - F) = 0$ $(F = 1 \text{ as } t \to \infty)$.

$\therefore$ First term on RHS of equation (7.19) is zero.

$$\therefore \quad \frac{V}{v} = \int_0^1 t\,dF$$

Now,

$$\tau = \frac{V}{v}$$

$$\tau = \int_0^1 t\,dF \quad \text{... (7.20)}$$

We have from equation (7.15),

$$\frac{dF}{dt} = E$$

$$\therefore \quad dF = E\,dt$$

Therefore, putting the value of F in terms of E in equation (7.20),

$$\tau = \int_0^\infty t \cdot E\,dt$$

From equation (7.15), we have,

$$\int_0^\infty t\,E\,dt = \bar{t} \quad \therefore \quad \tau = \bar{t} \quad \text{... (7.21)}$$

∴ From equation (7.21), we see that the mean residence time is equal to the space time.

$$\therefore \quad \frac{V}{v} = \tau = \bar{t}$$

The exact reactor volume is given by,

$$V = v \cdot \bar{t} \qquad \text{... (7.22)}$$

Note that above result is true only for no dispersion.

The second moment of RTD function, E, is taken about the mean and is called variance, or square of standard deviation. It is given by,

$$\sigma^2 = \int_0^\infty (t - \bar{t})^2 \, E \, dt \qquad \text{... (7.23)}$$

The magnitude of variance indicates the spread of the residence time distribution. The greater value of variance indicates greater residence time distribution spread.

The RTD in plug flow reactor :

The RTD in plug flow reactor and also in batch reactor are easiest to consider. All the atoms or molecules leaving such reactor have spent precisely the same amount of time within the reactor. The distribution function in such reactor is a spike of infinite height and zero width with area equal to 1. This spike occurs at $t = \tau = V/v$.

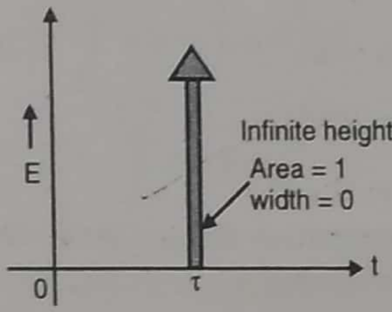


Fig. 7.10 : Ideal plug flow response to a pulse tracer input

Mathematically, this spike is represented as Dirac delta function,

$$E = \delta(t - \tau) \qquad \text{... (7.24)}$$

$$\text{Area under the curve} = \int_0^\infty \delta(t - \tau) = 1$$

$$\text{Any integration with } \delta \text{ function} = \int_0^\infty \delta(t - \tau) \, f(t) \, dt = f(\tau)$$

It is easier to integrate with δ function than any other.

e.g. $\int_0^\infty \delta(t-4)\, t^6 \, dt = 4^6$ (just replace τ by 4 i.e. just replace t of f(t) by τ i.e. by 4)

In above case $f(t) = t^6 \quad \therefore \; f(\tau) = 4^6$

$$\int_0^2 \delta(t-4)\, t^6 \, dt = 0$$

The RTD in mixed flow reactor :

In mixed flow reactor, the concentration of any substance in the effluent stream is identical to the concentration throughout the reactor. By making the material balance of tracer we can determine E.

Consider a steady flow v m³/s of fluid into and out of the reactor of volume V. At t = 0, inject the pulse of tracer into the reactor which will be evenly get distributed and has concentration C_o.

A material balance of tracer at any time t after the tracer is injected is

$$\text{in} - \text{out} = \text{accumulation}$$

$$0 - vC = +V\frac{dC}{dt} \qquad \dots (7.25)$$

C is the concentration of the tracer in the effluent stream or within the reactor as the reactor is perfectly mixed.

$$\frac{dC}{C} = \frac{-v}{V}\,dt = \frac{-1}{(V/v)}\,dt$$

We have,

$$V/v = \tau$$

$$\int_{C_o}^{C}\frac{dC}{C} = \frac{-1}{\tau}\int_0^t dt$$

$$\ln(C/C_o) = -t/\tau$$

$$\frac{C}{C_o} = e^{-t/\tau}$$

$$C = C_o e^{-t/\tau} \qquad \dots (7.26)$$

Equation (7.26) gives the concentration of tracer in the effluent at any time t.

To find E for ideal mixed flow reactor :

We have for pulse input,

$$E = \frac{C}{\int_0^\infty C\,dt}$$

Putting the value of C from equation (7.26) in above equation, we get,

$$E = \frac{C_o e^{-t/\tau}}{\int_0^\infty C_o e^{-t/\tau}\,dt}$$

$$\therefore \quad E = \frac{e^{-t/\tau}}{\tau} \qquad \dots (7.27)$$

Earlier it was shown that $\tau = \bar{t}$. This relationship can be shown in a simpler manner for mixed flow reactor. The mean residence time $\bar{t}$ is defined as,

$$\bar{t} = \int_0^\infty t \cdot E\,dt$$

$$E \text{ for mixed flow reactor} = \frac{e^{-t/\tau}}{\tau}$$

$$\bar{t} = \int_0^\infty t \cdot \frac{e^{-t/\tau}}{\tau} dt$$

$$= \frac{1}{\tau}\left[\frac{t \cdot e^{-t/\tau}}{(1-1/\tau)} - \frac{1}{(1/\tau)^2} e^{-t/\tau}\right]_0^\infty = \tau$$

Hence, the space time, $\tau = V/v$, is equal to the mean residence time ($\bar{t}$) that the material spends in the reactor.

Conversion in non-ideal flow reactors :

For evaluating the reactor behaviour in general we should know the kinetics of the reaction (complete rate equation), the RTD of fluid in the reactor, the earliness or lateness of fluid mixing the reactor and state of aggregation of fluid (micro or macrofluid).

States of aggregation of the flowing stream :

Two extreme states of aggregation of the flowing material based upon its nature are :

(i) microfluid, and (ii) macrofluid.

A fluid in which molecules are free to move everywhere, collide, and intermix is called as microfluid. For example, gases and thin liquids.

A fluid in which globules or aggregates, each containing large number of molecules, of given age do not mix with other globules is called as macrofluid. For example, very viscous liquids, noncoalescing droplets.

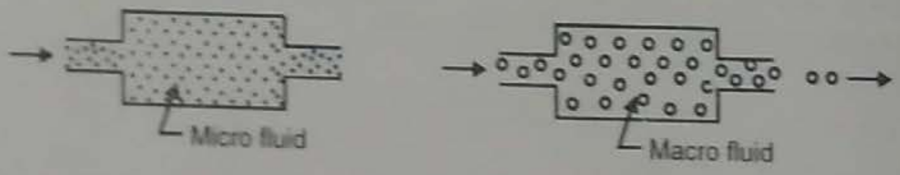


Fig. 7.11 : Micro and macrofluid

A macrofluid exhibits complete segregation and a microfluid exhibits no segregation. A fluid that does not exhibits these extremes in behaviour is called a partially segregated fluid.

Early and late mixing of fluid :

The fluid elements of a single flowing stream can mix each other either early or late in their flow through the vessel.

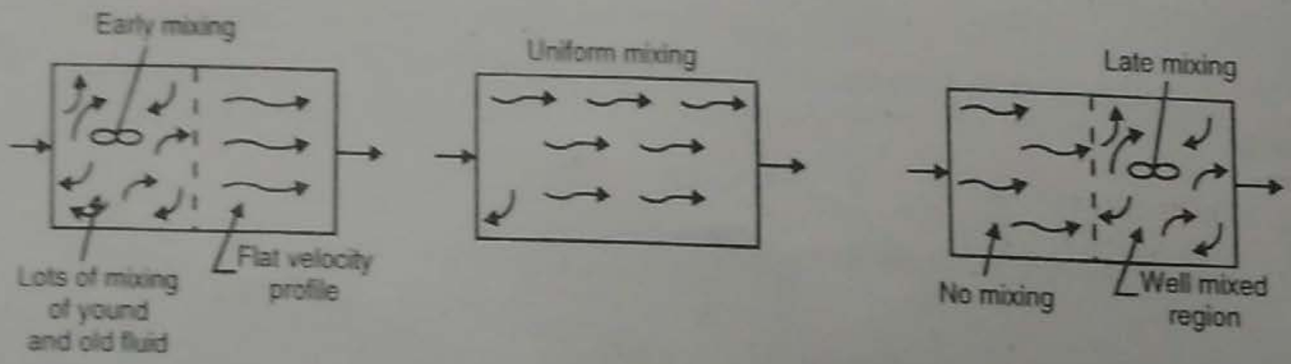


Fig. 7.12 : Examples of early and late mixing

Now we will consider the effect of early and late mixing of a microfluid on extent of reaction. In situation where plug flow is followed by mixed flow unit, we have latest mixing and with mixed flow followed by plug flow unit we have earliest mixing.

Consider a second order reaction is carried out in these two setups. For first set up, the reactant starts at high concentration and react away rapidly as $n > 1$. In second set-up, the fluid drops immediately to low concentration. As the rate of reaction drops more rapidly than drop in concentration it results in lower conversion ($-r_A = k\,C_A^2$). Hence, we can conclude for microfluids;

Late mixing favours reactions with $n > 1$.

Early mixing favours reactions with $n < 1$.

For $n = 1$ the conversion is unaffected by mixing as for first order reactions conversion is independent of concentration $dX_A/dt = k\,(1 - X_A)$.

The normally accepted state of liquid or gas is that of microfluids. In previous chapters, we have developed desired equations for microfluids in plug flow and mixed flow reactors.

For macrofluids, imagine little aggregates/globules of fluid residing for different lengths of time in the reactor (given by E function). Each aggregate of macrofluid acts as its own little/tiny batch reactor and reacts accordingly and therefore the fluid elements (globules) have different compositions. The reaction time in any one of these tiny batch reactors is equal to the time that aggregate spends in the reaction environment. So in order to determine the mean composition in the exit stream from reactor we have to take into account these factors namely kinetics and the RTD function E.

$$\left(\begin{array}{l}\text{Mean/average}\\\text{concentration of}\\\text{reactant in}\\\text{exit stream}\end{array}\right) = \sum_{\substack{\text{all elements}\\\text{of exit stream}}} \left[\begin{array}{l}\text{concentration of}\\\text{reactant remaining}\\\text{in an element of}\\\text{age between t}\\\text{and t + dt}\end{array}\right] \left[\begin{array}{l}\text{fraction of exit}\\\text{stream which is of}\\\text{age between t and t + dt}\\\text{i.e. fraction that}\\\text{spends between}\\\text{t and t + dt in reactor}\end{array}\right]$$

It can be written in symbolic form as,

$$\left(\frac{\bar{C}_A}{C_{Ao}}\right)_{\text{at exit}} = \int_0^\infty \left(\frac{C_A}{C_{Ao}}\right)_{\text{for element/batch of fluid of age t}} \cdot E\,dt \qquad \text{... (7.28)}$$

In terms of conversion above equation becomes,

$$\bar{X}_A = \int_0^\infty (X_A)_{\text{element}} \cdot E\,dt \qquad \text{... (7.29)}$$

$$\left[\text{as } \frac{C_{Ao} - C_A}{C_{Ao}} = X_A\right]$$

We can also write equation (7.28) in a form suitable for numerical integration as :

$$\frac{\bar{C}_A}{C_{Ao}} = \sum_{\substack{\text{all age}\\\text{intervals}}} \left(\frac{C_A}{C_{Ao}}\right)_{\text{element}} \cdot E\,\Delta t \qquad \text{... (7.30)}$$

In above equations note that C_A and X_A are functions of time.

For batch reactor we have,

$$(C_A/C_{Ao})_{\text{element}} = e^{-kt}, \quad \text{... for first order reactions}$$

$$(C_A/C_{Ao})_{\text{element}} = \frac{1}{1 + k\,C_{Ao}\,t}, \quad \text{... for second order reactions}$$

$$(C_A/C_{Ao})_{\text{element}} = [1 + (n-1)\,C_{Ao}^{n-1}\,kt]^{1/1-n} \quad \text{... for } n^{\text{th}} \text{ order reaction, } n \neq 1$$

Special Case : First Order Reactions :

Consider first order reaction of the type :

$$A \rightarrow \text{products}$$

For batch reactor we have,

$$-\frac{dC_A}{dt} = k\,C_A$$

$$C_A = C_{Ao}(1-X_A)$$

$$\therefore \quad -dC_A/dt = C_{Ao}\,dX_A$$

$$C_{Ao}\,dX_A = k\,C_{Ao}(1-X_A)\,dt$$

$$\frac{dX_A}{1-X_A} = k\,dt$$

$$-\ln(1-X_A) = kt, \quad \ln(1-X_A) = -kt$$

$$\therefore \quad X_A = 1-e^{-kt}$$

We have from equation (7.29),

$$\bar{X}_A = \int_0^\infty X_A \cdot E\,dt = \int_0^\infty (1-e^{-kt})\,E\,dt$$

$$\bar{X}_A = \int_0^\infty E\,dt - \int_0^\infty e^{-kt}\,E\,dt$$

$$\bar{X}_A = 1-\int_0^\infty e^{-kt}\,E\,dt \qquad \ldots (7.31)$$

1. **Plug flow reactor :**

For plug flow reactor, the RTD function is given by :

$$E = \delta(t-\tau)$$

$$\bar{X}_A = \int_0^\infty X_A\,E\,dt = 1-\int_0^\infty e^{-kt}\,E\,dt$$

$$\bar{X}_A = 1-\int_0^\infty (e^{-kt})\ \delta(t-\tau)\,dt = 1-\int_0^\infty \delta(t-\tau)\,e^{-kt}\,dt$$

We have,

$$\int_0^\infty \delta(t-\tau)\,f(t)\,dt = f(\tau) \quad \text{[only replace t from f(t) by } \tau\text{]}$$

Here $f(t) = e^{-kt} \quad \therefore \quad f(\tau) = e^{-k\tau}$

$$\therefore \quad \bar{X}_A = 1-e^{-k\tau} \quad \text{for macrofluid} \qquad \ldots (7.32)$$

For plug flow we have,

$$\tau = C_{Ao}\int_0^{X_A} \frac{dX_A}{(-r_A)} = \int_0^{X_A} \frac{dX_A}{k\,(1-X_A)}$$

$$k\tau = -\ln(1-X_A)$$

$$\therefore \quad X_A = 1-e^{-k\tau} \quad \ldots \text{for microfluid} \qquad \ldots (7.33)$$

Equation (7.32) obtained for macrofluid in a plug flow is identical to the equation (7.33) obtained for microfluid. So the degree of segregation does not have any effect on conversion for first order reactions. This occurs because the rate of change of conversion of the reacting molecules for first order reaction does not depend on the concentration of the reacting molecules.

2. For CSTR :

The RTD function is, $E = \frac{1}{\tau} e^{-t/\tau}$

$$\bar{X}_A = 1 - \int_0^\infty e^{-kt}\, E\, dt$$

$$\bar{X}_A = 1 - \int_0^\infty \frac{e^{-(1/\tau + k)t}}{\tau}\, dt$$

$$\bar{X}_A = 1 + \left(\frac{1}{k + 1/\tau}\right)\frac{1}{\tau}\ [e^{-(k + 1/\tau)}]_0^\infty$$

$$\bar{X}_A = \frac{\tau k}{1 + \tau k} \quad \text{... for macrofluid} \qquad \text{... (7.34)}$$

For CSTR, the design equation is

$$\tau = \frac{C_{A_0} X_A}{(-r_A)}$$

$$\tau = \frac{C_{A_0} X_A}{k\, C_{A_0}(1 - X_A)} = \frac{X_A}{k\,(1 - X_A)}$$

Rearranging we get,

$$X_A = \frac{\tau k}{1 + \tau k} \quad \text{... for microfluid} \qquad \text{... (7.35)}$$

Here also τ for macrofluid $= \tau$ for microfluid

So for the first order reactions information regarding only RTD is sufficient.

SOLVED EXAMPLES

✓ **Ex. 7.1 :** The data given below represent a continuous response to a pulse input into a closed vessel which is to be used as a chemical reactor. Calculate the mean residence time of fluid in the vessel $\bar{t}$, and tabulate and construct E curve.

1 2 3 4 5 6 7

t, min	0	5	10	15	20	25	30	35
C_{pulse}, g/*l* (tracer output concentration)	0	3	5	5	4	2	1	0

Solution : The mean residence time is given by,

$$\bar{t} = \frac{\Sigma\, t_i C_i \Delta t_i}{\Sigma\, C_i \Delta t_i}$$

As $\Delta t = \text{constant} = 5 \text{ min}$

$$\bar{t} = \frac{\Sigma\, t_i C_i}{\Sigma\, C_i}$$

$$= \frac{5 \times 3 + 10 \times 5 + 15 \times 5 + 20 \times 4 + 25 \times 2 + 30 \times 1}{0 + 3 + 5 + 5 + 4 + 2 + 1 + 0}$$

$$= 15 \text{ min}$$

... Ans.

Area under the concentration-time curve is given by :

$$\text{Area} = \Sigma\, C_i \Delta t_i = (3 + 5 + 5 + 4 + 2 + 1) \times 5 = 100 \text{ (g.min)}/l$$

Area under C curve is given by,

$$\int_0^\infty C\,dt = \int_0^{25} C\,dt + \int_{25}^{35} C\,dt$$

We can calculate area by numerical integration.

Using Simpson's 1/3 and 3/8th rule,

$$\int_0^{25} C\,dt = \frac{5}{3}\,[0 + 4\,(3) + 5 + 5 + 4\,(5) + \overset{4}{2}]$$

$$= 76.67$$

$$\int_{25}^{35} C\,dt = \frac{3}{8} \times 5\,[4 + 3\,(2) + 3\,(1) + 0]$$

$$\therefore \quad \int_{25}^{35} C\,dt = 24.37$$

$$\text{Area under C curve} = \int_0^\infty C\,dt = 76.67 + 24.37 = 101.04 \ (\text{g.min})/l$$

So area by two methods is almost same. This gives us the total amount of tracer introduced.

$$E = \frac{C}{\int_0^\infty C\,dt} = \frac{C}{\text{Area}}, \ (\text{min})^{-1}, \ \ldots \text{ for pulse input}$$

$$\text{At} \quad t = 5 \text{ min}, \quad C = C_{\text{pulse}} = 3 \text{ g}/l$$

$$\therefore \quad E = \frac{3}{100} = 0.03 \text{ min}^{-1}$$

Evaluate E at various C values and tabulate :

t, min	0	5	10	15	20	25	30	35
E, min^{-1}	0	0.03	0.05	0.05	0.04	0.02	0.01	0

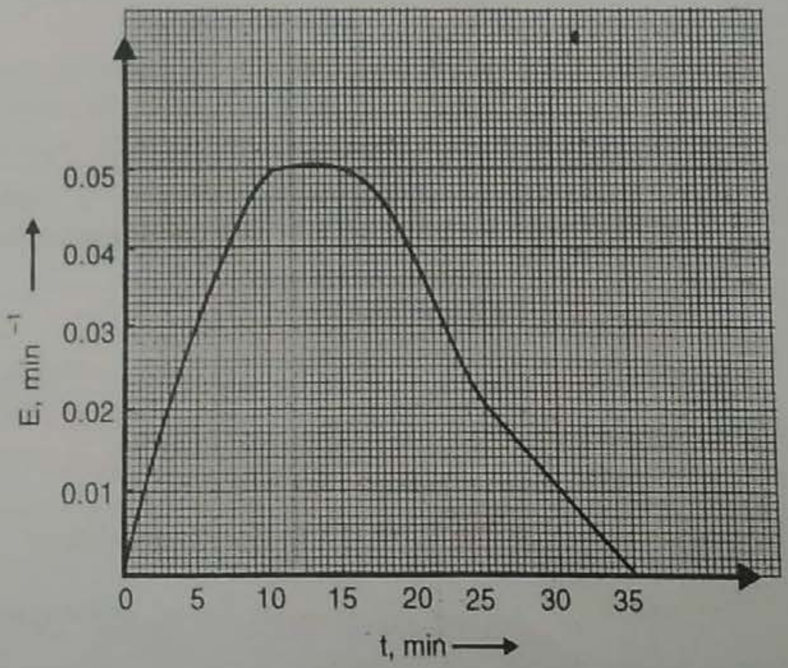


Fig. E 7.1 : E curve from pulse experiment

Ex. 7.2 : A sample of tracer hytane was injected as pulse into a vessel to be used as reactor and the effluent concentration is measured as a function of time. The data collected is given below :

0 1 2 3 4 5 6

t, min	0	1	2	3	4	5	6	7	8	9	10	12	14
C (g/m³)	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0

Construct C and E curves and determine the fraction of material leaving the reactor that has spent between 3 and 6 min in the vessel and the fraction of material leaving that has spent between 7.75 and 8.25 min in the vessel.

Solution : For C curve, plot the concentration of tracer in the effluent (C) as a function of time from the given data.

To obtain E curve from C curve, just divide C by the integral, $\int_0^{\infty} C\,dt$

$$E = \frac{C}{\int_0^{\infty} C\,dt}$$

$$\bar{t} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i}$$

$$\sigma^2 = \sum (t-\bar{t})^2 \cdot C_i \Delta t_i$$

$\int_0^{\infty} C\,dt$ is the area under the C curve.

Now we will find this area using Simpson's one-third rule (three point) as it gives more accurate evaluation of the integral numerically.

$$\int_{x_0}^{x_2} f(x)\,dx = \frac{h}{3}\,[f(x_0) + 4\,f(x_1) + f(x_2)]$$

where $h = (x_2 - x_0)/2, \quad x_1 = x_0 + h$

$$\int_0^{\infty} C\,dt = \int_0^{10} C\,dt + \int_{10}^{14} C\,dt$$

t =	10	12	14
C =	1.5	0.6	0

$$h = 12 - 10 = 2, \quad f(x_0) = 1.5, \quad f(x_1) = 0.6 \text{ and } f(x_2) = 0$$

$$\int_{10}^{14} C\,dt = \frac{2}{3}\,[1.5 + 4 \times 0.6 + 0] = 2.6 \text{ (g.min)/m}^3$$

$$h = 1 - 0 = 1$$

$$\int_0^{10} C\,dt = \frac{1}{3}\,[0 + 4\,(1) + 5 + 5 + 4\,(8) + 10 + 10 + 4\,(8) + 6 + 6 + 4\,(4) + 3 + 3 + 4\,(2.2) + 1.5]$$

$$= 47.4 \text{ (g.min)/m}^3$$

$$\int_0^{\infty} C\,dt = \int_0^{10} C\,dt + \int_{10}^{14} C\,dt$$

$$= 47.4 + 2.6 = 50 \text{ (g.min)/m}^3$$

$$E = \frac{C}{\int_0^\infty C\,dt} = \frac{C}{50} \ (\text{min})^{-1}$$

Find E for values of C given.

$$t = 1 \text{ min}, \quad C = 1 \text{ g/m}^3$$

$$E = \frac{1}{50} = 0.02 \text{ min}^{-1}$$

t	0	1	2	3	4	5	6	7	8	9	10	12	14
C	0	1	5	8	10	8	6	4	3	2.2	1.5	0.60	0
E	0	0.02	0.10	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Plot E curve : The shaded area represents the fraction of the material leaving the reactor that has resided in the vessel between 3 and 6 min.

$$\int_3^8 E\,dt = \text{shaded area}$$

Simpson's $\frac{3}{8}$th rule (four point),

$$\int_{x_0}^{x_3} f(x)\,dx = \frac{3}{8} h \left[f(x_0) + 3\,f(x_1) + 3\,f(x_2) + f(x_3)\right]$$

where $h = \frac{x_3 - x_0}{3}$, $x_1 = x_0 + h$, $x_2 = x_0 + 2h$

$$h = \Delta t$$

In our case : $h = \frac{6-3}{3} = 1$, $f(x_0) = 0.16$, $f(x_1) = 0.20$

$$f(x_2) = 0.16 \quad \text{and} \quad f(x_3) = 0.12$$

$$\int_3^8 E\,dt = \text{shaded area}$$

$$= \frac{3}{8} \times 1 \ [0.16 + 3 \times 0.20 + 3 \times 0.16 + 0.12] = 0.51$$

So 51% of the material leaving the reactor spends between 3 and 6 min in the vessel.

As the time between 7.75 and 8.25 min is small vessel to time scale of 14 min we will use average E between these two.

Average E between 7.75 and 8.25 = $(0.065 + 0.055)/2 = 0.06 \text{ min}^{-1}$

$\therefore$ $E\,dt = 0.06 \times 0.5 = 0.03$

So 3% of the fluid leaving the vessel has been in the reactor between 7.75 and 8.25 min.... **Ans.**

Now we will consider the fraction of the material that has been in the vessel for time t or less. It is the fraction that has spent between 0 and t min in the vessel. This fraction is equal to the area under the curve from t = 0 upto t = t min.

For example, for t = 3 min.

$$\int_0^3 E\,dt = \text{shaded area upto 3 min}$$

$$= \frac{3}{8} \times 1 \ [0 + 3 \times 0.02 + 3 \times 0.1 + 0.16] = 0.195$$

i.e. 19 5% of the material leaving the reactor has spent 3 min or less in the reactor.

The long time portion of the E curve is called tail. In this case, the tail is that portion of the curve between say 10 and 14 min.

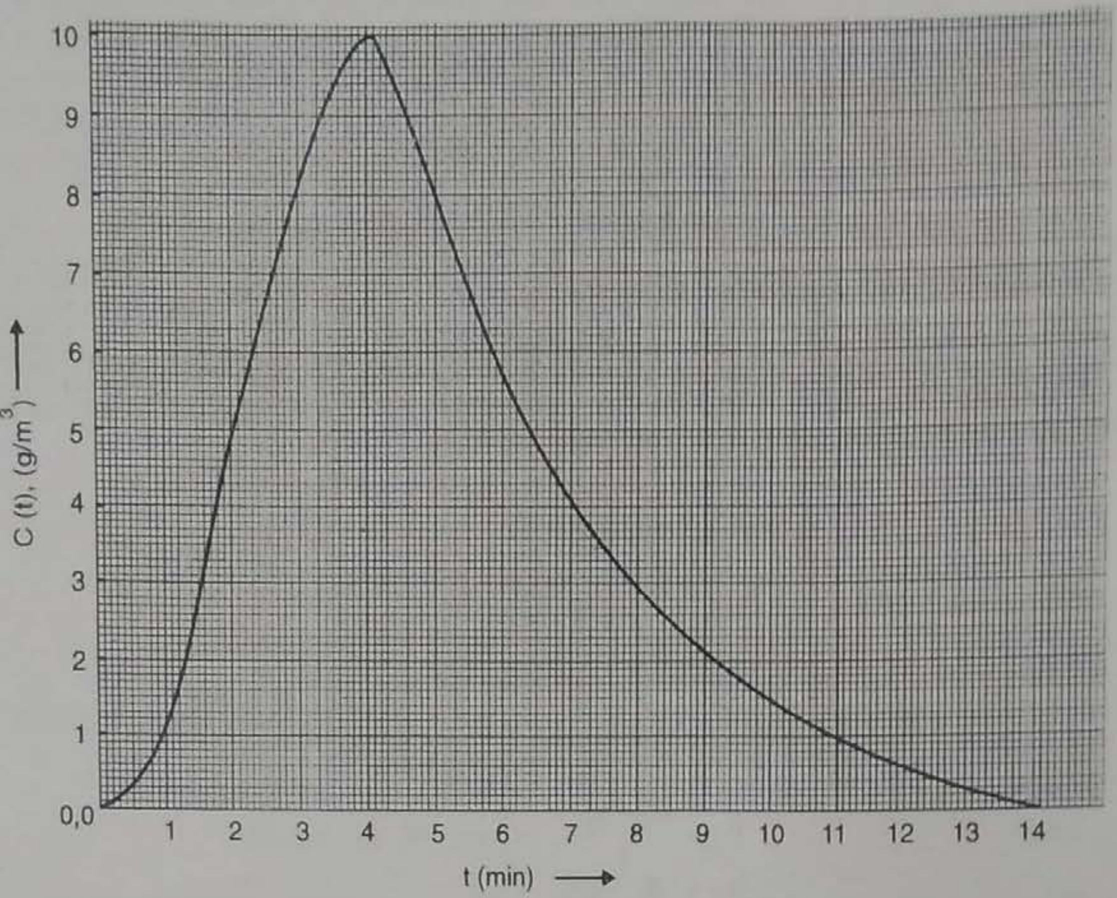


Fig. E 7.2 (1)

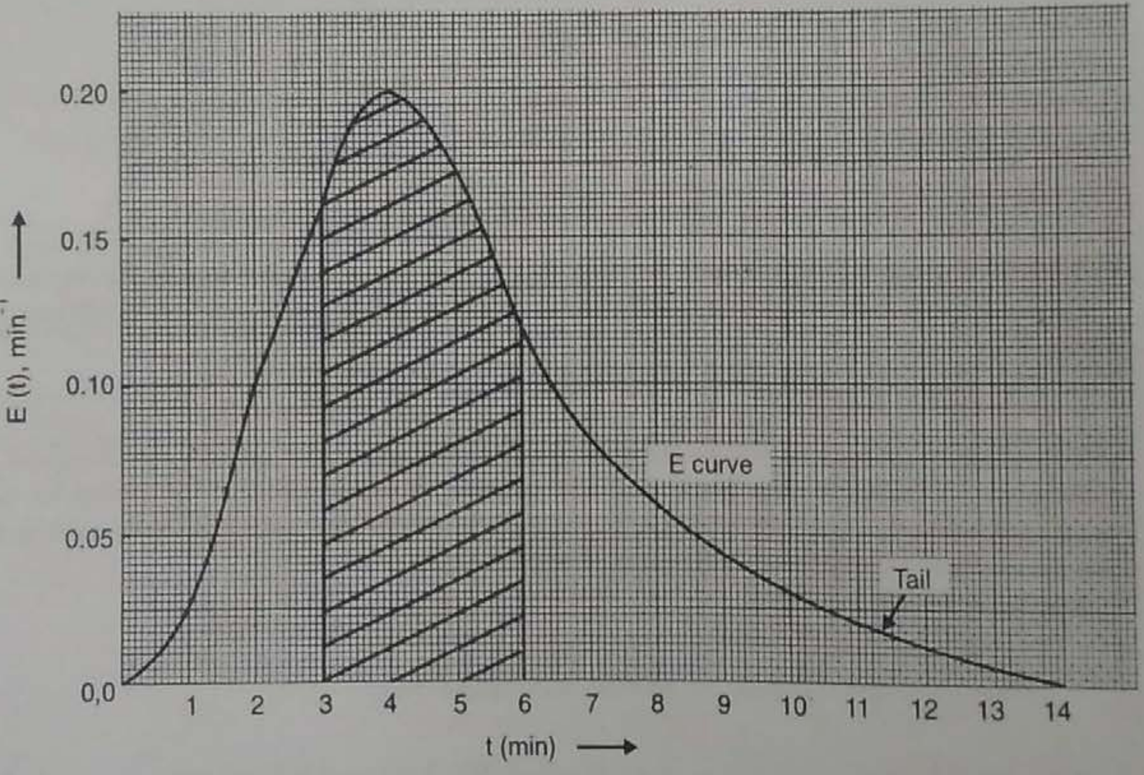


Fig. E 7.2 (2)

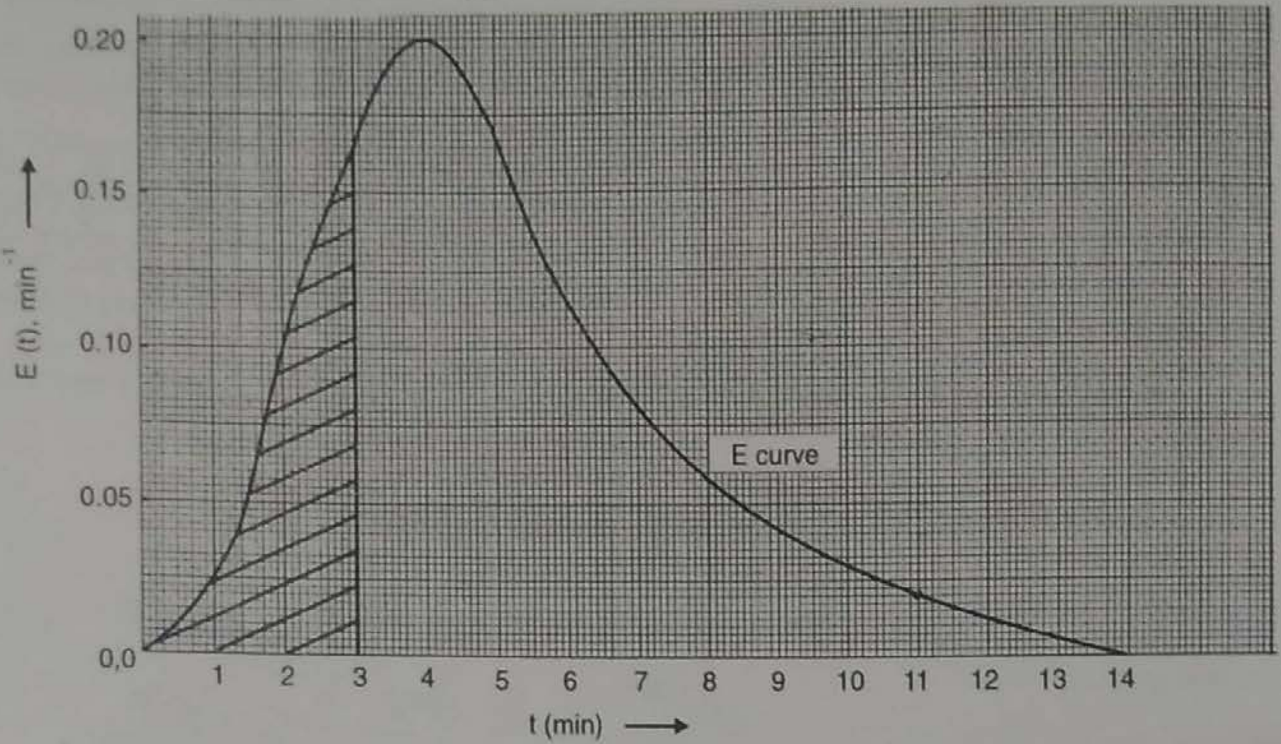


Fig. E 7.2 (3)

Ex. 7.3 : Calculate the mean residence time and the variance for the vessel from the following data :

t, min	0	1	2	3	4	5	6	7	8	9	10	12	14
E, min^{-1}	0	0.02	0.10	0.16	0.20	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

Solution : Mean residence time $\bar{t}$ is given by,

$$\bar{t} = \int_0^\infty t\,E\,dt$$

(i) Area under the curve of t E as a function of t will give $\bar{t}$.

(ii) For calculating $\bar{t}$ one can use numerical integration formulas.

The variance is given by, $\sigma^2 = \int_0^\infty (t - \bar{t})^2\,E\,dt$

Area under the curve of $(t - \bar{t})^2$ E v/s t gives σ^2 or it can also be calculated by numerical integration formulas.

t	E	tE	$t - \bar{t}$	$(t - \bar{t})^2 E$
0	0	0	−5.15	0
1	0.02	0.02	−4.15	0.344
2	0.10	0.20	−3.15	0.992
3	0.16	0.48	−2.15	0.74
4	0.20	0.80	−1.15	0.265
5	0.16	0.80	−0.15	0.004
6	0.12	0.72	0.85	0.087
7	0.08	0.56	1.85	0.274
8	0.06	0.48	2.85	0.487
9	0.044	0.40	3.85	0.652
10	0.03	0.30	4.85	0.706
12	0.012	0.14	6.85	0.563
14	0	0	8.85	0

$$\overline{t} = \int_0^\infty (t\,E)\,dt$$

$$= \int_0^{10} (t\,E)\,dt + \int_{10}^{14} (t\,E)\,dt$$

Using Simpson's $\frac{1}{3}$ rd rule,

$h_1 = 1$ and $h_2 = 2$

$$\overline{t} = \frac{1}{3}\,[0 + 4\,(0.02) + 0.20 + 0.20 + 4\,(0.48) + 0.8 + 0.8$$

$$+ 4\,(0.8) + 0.72 + 0.72 + 4\,(0.56) + 0.48 + 0.48 + 4\,(0.4) + 0.3]$$

$$+ \frac{2}{3}\,[0.3 + 4\,(0.14) + 0]$$

$$= 4.58 + 0.573 = 5.15 \text{ min}$$ ... **Ans.**

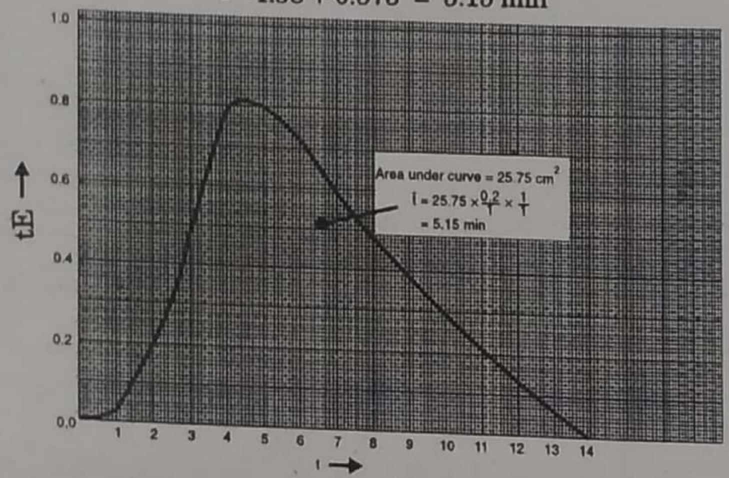


Fig. E 7.3 (1)

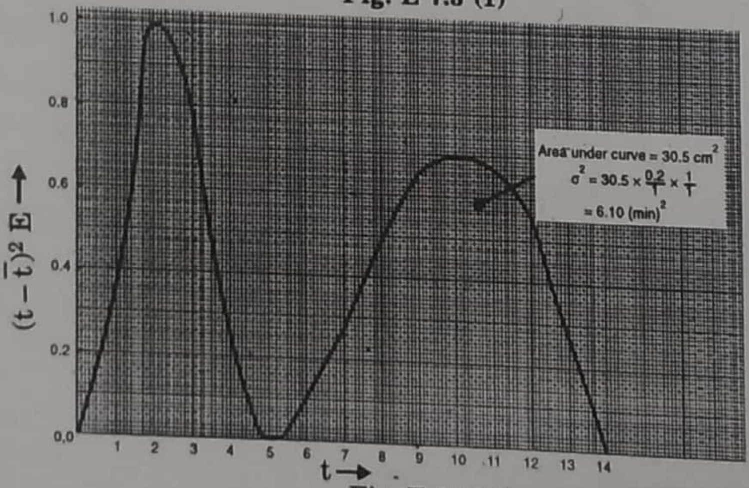


Fig. E 7.3 (2)

$$\sigma^2 = \int_0^\infty (t - \overline{t})^2\,E\,dt$$

Using Simpson's $\frac{1}{3}$rd rule,

$h_1 = 1, \quad h_2 = 2$

$$\sigma^2 = \frac{1}{3}[0 + 4(0.344) + 0.992 + 0.992 + 4(0.74) + 0.265 + 0.265 + 4(0.004) + 0.087 + 0.087 + 4(0.274) + 0.487 + 0.487 + 4(0.652) + 0.706] + \frac{2}{3}[0.706 + 4(0.563) + 0]$$

$$= 6.1 \text{ min}^2$$

The square of the standard deviation is $\sigma^2 = 6.1 \text{ min}^2$.

So $\sigma = 2.47$ min ... **Ans.**

Ex. 7.4 : The concentration readings given below represent a continuous response to a pulse input into a closed vessel.

t, min	0	5	10	15	20	25	30	35
C_{pulse}, g/l (tracer output concentration)	0	3	5	5	4	2	1	0

This vessel is to be used as a reactor for decomposition of a liquid A,

$$A \rightarrow \text{products}$$

with rate $-r_A = k\,C_A, \quad k = 0.307 \text{ min}^{-1}$

Estimate the fraction of the reactant unconverted in the real reactor and compare this with the fraction unconverted in a plug flow reactor of same size.

Solution : $A \rightarrow \text{products}$

$$-r_A = k\,C_A, \quad k = 0.307 \text{ min}^{-1}$$

From the data of tracer concentration v/s t, determine E.

$$E = \frac{C}{\int_0^\infty C\,dt} \approx \frac{C}{\Sigma C_i\,\Delta t_i}$$

$$\Sigma C_i\,\Delta t_i = [3\times5 + 5\times5 + 5\times5 + 4\times5 + 2\times5 + 1\times5]$$

$$= 100 \text{ (g.min)}/l$$

$$E = \frac{C}{\Sigma C_i\,\Delta t_i}$$

At $t = 5$ min, $C = 3$ g/l

$\therefore \quad E = 3/100 = 0.03 \text{ min}^{-1}$

Evaluate E for data provided.

t, min	0	5	10	15	20	25	30	35
E, min^{-1}	5	0.03	0.05	0.05	0.04	0.02	0.01	0

Mean residence time $\bar{t}$ can be calculated by,

$$\bar{t} = \frac{\Sigma t_i C_i \Delta t_i}{\Sigma C_i \Delta t_i} \xrightarrow{\text{for } \Delta t \text{ const.}} = \frac{\Sigma t_i C_i}{\Sigma C_i}$$

$$= \frac{5\times3 + 10\times5 + 15\times5 + 20\times4 + 25\times2 + 30\times1}{3+5+5+4+2+1}$$

$$= 15 \text{ min}$$

The performance equation for plug flow reactor is,

$$\tau = C_{Ao}\int_{0}^{X_A}\frac{dX_A}{(-r_A)} = -\int_{C_{Ao}}^{C_A}\frac{dC_A}{-r_A}$$

We have, $$-r_A = k\,C_A$$

$$\therefore \qquad \tau = -\frac{1}{k}\int_{C_{Ao}}^{C_A} dC_A/C_A$$

$$k\tau = -\ln\,[C_A/C_{Ao}]$$

$$\frac{C_A}{C_{Ao}} = e^{-k\tau}$$

We have, $$\tau = \bar{t} \quad \therefore \quad \tau = 15\text{ min}$$

$$\frac{C_A}{C_{Ao}} = e^{-(0.307)\times 15} = 0.01$$

Hence, the fraction of reactant unconverted in a **plug flow reactor** equals to 1%. ... **Ans.**

$$\frac{C_A}{C_{Ao}} = 0.01$$

$$1 - C_A/C_{Ao} = X_A$$

$$\therefore \qquad X_A = 1 - 0.01 = 0.99$$

Fraction of A converted is 99% and unconverted is 1% (in percent).

For the **real reactor** the fraction unconverted is given by,

$$\left(\frac{\bar{C}_A}{C_{Ao}}\right) = \int_0^{\infty}\left(\frac{C_A}{C_{Ao}}\right)_{\text{element}}\cdot E\,dt$$

$$= \sum\left(\frac{C_A}{C_{Ao}}\right)_{\text{element}}\cdot E\,\Delta t\ldots \text{ for macrofluids} \qquad \ldots(1)$$

For first order reaction,

$$-r_A = k\,C_A$$

$$-dC_A/dt = k\,C_A$$

$$\therefore \qquad \frac{dC_A}{C_A} = -k\,dt \quad \therefore \quad \frac{C_A}{C_{Ao}} = e^{-kt} \qquad \ldots(2)$$

Putting equation (2) in equation (1), we get,

$$\left(\frac{\bar{C}_A}{C_{Ao}}\right) = \sum e^{-kt}\,E\,\Delta t$$

Calculate the terms and tabulate :

t	E	kt	e^{-kt}	$e^{-kt}\,E\,\Delta t$	k
5	0.03	1.53	0.2165	0.0325	0.307
10	0.05	3.07	0.0464	0.0116	–
15	0.05	4.6	0.010	0.0025	–
20	0.04	6.14	0.00215	0.00043	–
25	0.02	7.68	0.00462	4.62×10^{-4}	–
30	0.01	9.21	0.0001	5×10^{-6}	–
				Total = 0.0475	

$$\Delta t = 5 \text{ min}$$

$$\frac{\bar{C}_A}{C_{Ao}} = \sum e^{-kt}\, E\, \Delta t$$

$$= 0.0475$$

∴ The fraction of reactant unconverted in the real reactor = 0.0475.

The fraction of reactant unconverted (in percent) in real reactor = 4.75% ... **Ans.**

Since the reaction is first order we can treat as a microfluid, or a macrofluid. Here we have solved plug flow case as a microfluid and nonideal case as a macrofluid.

Ex. 7.5 : The concentration readings given below represent a continuous response to a pulse input into a closed vessel.

t, min	0	1	2	3	4	5	6	7	8	9	10	12	14
C_{pulse}, g/m^3	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0

This vessel is to be used as a reactor for decomposition of liquid A.

$$A \rightarrow \text{products}$$

with rate $-r_A = k\, C_A, \quad k = 0.10 \text{ min}^{-1}$

Calculate the conversion of reactant A in the real reactor.

Solution : $A \rightarrow \text{products}$

$$-r_A = k\, C_A\,, \quad k = 0.10 \text{ min}^{-1}$$

From the data of tracer concentration v/s t, determine E.

$$E = \frac{C}{\int_0^\infty C\, dt}$$

$$\int_0^\infty C\, dt = \int_0^{10} C\, dt + \int_0^{14} C\, dt, \quad \text{using Simpson's } \frac{1}{3}\text{rd rule,}$$

$$h_2 = 12 - 10 = 2 \quad \text{and} \quad h_1 = 1 - 0 = 1$$

$$\int_0^\infty C\, dt = \frac{1}{3}\,[0 + 4\,(1) + 5 + 5 + 4\,(8) + 10 + 10 + 4\,(8) + 6$$

$$+\ 6 + 4\,(4) + 3 + 3 + 4\,(2.2) + 1.5$$

$$+ \frac{2}{3}\ [1.5 + 4\,(0.6) + 0]$$

$$= 47.4 + 2.6 = 50 \text{ (g.min)/m}^3$$

At $t = 1$ min, $C = 1$ g/m^3

$$\therefore \quad E = \frac{1}{50} = 0.02 \text{ min}^{-1}$$

Tabulate E for various C values.

t	0	1	2	3	4	5	6	7	8	9	10	12	14
C	0	1	5	8	10	8	6	4	3	2.2	1.5	0.6	0
E	0	0.02	0.10	0.16	0.20	0.16	0.12	0.08	0.06	0.044	0.03	0.012	2

For first order reaction in batch reactor we have,

$$-r_A = k\, C_A = k\, C_{Ao}\,(1 - X_A)$$

$$-dX_A/dt = k(1-X_A)$$

$$\ln(1-X_A) = kt \quad \therefore X_A = 1-e^{-kt}, \quad k = 0.1 \text{ min}^{-1}$$

$$X_A = 1-e^{-0.1t}$$ calculate X_A at various data.

e.g. $t = 0$, $X_A = 1-e^{-0.1\times 0} = 0$

We have,

$$\bar{X}_A = \int_0^\infty (X_A)_{\text{element}} \cdot E\,dt$$

t	E	$X_A = 1-e^{-0.1t}$	$X_A E$
0	0	0	0
1	0.02	0.095	1.9×10^{-3}
2	0.10	0.181	0.0181
3	0.16	0.259	0.0414
4	0.20	0.33	0.0660
5	0.16	0.393	0.0629
6	0.12	0.451	0.0541
7	0.08	0.503	0.0402
8	0.06	0.551	0.0331
9	0.044	0.593	0.0261
10	0.03	0.632	0.0189
12	0.012	0.699	0.0084
14	0	0	0

$$\bar{X}_A = \int_0^\infty X_A E\,dt = \int_0^\infty (X_A E)\,dt$$

Using Simpson's $\frac{1}{3}$rd rule (numerical integration),

$$h_1 = 1-0 = 1, \quad h_2 = 12-10 = 2$$

$$\bar{X}_A = \int_0^{10} (X_A E)\,dt + \int_{10}^{14} (X_A E)\,dt$$

$$= \frac{1}{3}[0 + 4(1.9\times10^{-3}) + 0.0181 + 0.0181 + 4(0.0414) + 0.066$$

$$+ 0.066 + 4(0.0629) + 0.0541 + 0.0541 + 4(0.0402)$$

$$+ 0.0331 + 0.0331 + 4(0.0261) + 0.0189]$$

$$+ \frac{2}{3}[0.0189 + 4(0.0084) + 0]$$

$$= 0.385$$

or plot $X_A E$ v/s t and area under the curve gives $\bar{X}_A$.

Mean conversion = 38.5% ... **Ans.**

⑧ **Ex. 7.6 :** Dispersed noncoalescing droplets [$C_{Ao} = 2$ mol/*l*] react as per the reaction $A \rightarrow R$ with rate $-r_A = k\,C_A^2$, $k = 0.5$ *l*/(mol.min) as they pass through the contactor. Find the average concentration of A remaining in the droplets leaving the contactor.

Use $E = 0.50$ for $1 < t < 3$.

Solution : $A \rightarrow R$, $C_{Ao} = 2$ mol/*l*

$-r_A = k\,C_A^2$, $k = 0.5$ *l*/(mol.min)

So for second order reaction in batch reactor, we have,

$$\frac{C_A}{C_{Ao}} = \frac{1}{1 + k\,C_{Ao}\,t} = \frac{1}{1 + 0.5 \times 2\,t} = \frac{1}{1+t}$$

$$E = 0.5 \text{ for } 1 < t < 3$$

$$\frac{\bar{C}_A}{C_{Ao}} = \int_0^{\infty} \left(\frac{C_A}{C_{Ao}}\right)_{element} E\,dt = \int_1^3 \left(\frac{1}{1+t}\right)(0.5)\,dt = 0.5 \ln 2 = 0.346$$

$$\frac{\bar{C}_A}{C_{Ao}} = 0.346$$

$$\bar{C}_A = 0.346 \times 2 = 0.692 \text{ mol}/l$$ ... **Ans.**

To find the mean conversion,

$$\bar{X}_A = 1 - \frac{\bar{C}_A}{C_{Ao}} = 1 - 0.346 = 0.654 \text{ or } 65.4\%$$

❒❒❒

APPENDIX - I

Models for Non ideal Flow :

Models are useful to represent flow in real reactor. When **single parameter** is used to account for the non ideal flow in the reactor, we have one **parameter model and this parameter** is evaluated by analysing the RTD determined from the tracer test.

Models of nonideal (real) reactors include (i) the dispersion model, (ii) the tanks-in-series model, (iii) segregation model, (iv) the compartment models. These models are used to predict conversion from RTD data. We can find RTD from the tracer concentration (tracer test). The tanks-in-series model is used to model non ideal tubular reactor as a series of equal sized stirred tanks. The dispersion model is used to account for deviation from ideal plug flow and involves a modification of the ideal reactor by imposing axial dispersion on plug flow. In compartment models, we consider real reactor to consists of different regions, namely, plug flow region, mixed flow region, and dead/stagnant region. In this case, we model real reactors using combinations of ideal reactors, dead volume, and bypassing. Here we restrict our discussion to the tanks-in-series model.

The Tanks-in-Series Model :

This is one parameter model, used to represent non ideal flow in tubular reactors. The parameter of this model is the number of tanks, N, in series.

In modeling non ideal tubular reactor as a series of equal sized stirred tanks, we will develop first RTD equation for three tanks in series and then generalise it to N tanks in series to arrive at equation that gives the number of tanks in series that best fits the data. (These number of tanks in series will give approximately the same RTD as the non ideal reactor).

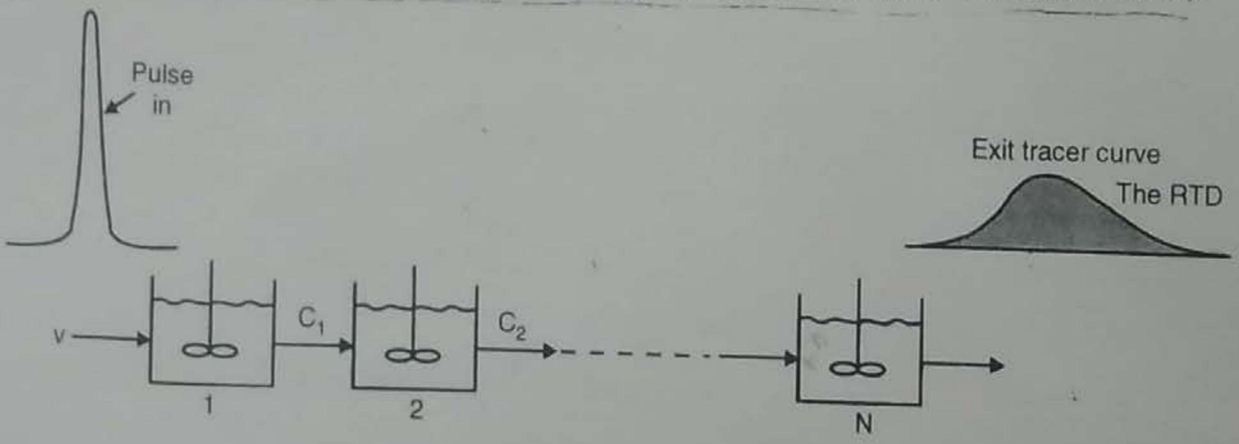


Fig. A : The tanks-in-series model

Consider a steady flow v m³/s of fluid into and out of the **first three** ideal stirred tanks each of volume V_1 m³. At t = 0, inject a pulse of tracer into the first tank.

The tracer balance over the first tank at any time t after introduction of tracer is rate of disappearance of tracer = input rate – output rate.

$$V_1 \frac{dC_1}{dt} = 0 - vC_1 \qquad \dots (1)$$

where C_1 is the concentration of tracer in the exit stream from the **first tank**.

$$\bar{t}_1 = V_1/v$$

$$\frac{dC_1}{C_1} = -\frac{v}{V_1}\,dt = -\frac{1}{\bar{t}_1}\,dt$$

Integrating with limits $t = 0$, $C_1 = C_o$; $t = t$, $C_1 = C_1$, we get,

$$\frac{C_1}{C_o} = e^{-t/\bar{t}_1}$$

$$C_1 = C_o \cdot e^{-t/\bar{t}_1} \quad \text{... (2)}$$

As the volumetric flow rate is constant ($v = v_o$) and as there are equal sized stirred tanks in series ($V_1 = V_2 = V_i$), the mean residence time of all individual tanks is identical, $\bar{t}_1 = \bar{t}_2 = \bar{t}_i$, where V_i is the volume of single tank in series and $\bar{t}_i$ is the mean residence time in one of the tanks.

The tracer balance over second tank, where C_1 enters and C_2 leaves, gives

$$V_2 \frac{dC_2}{dt} = v\,C_1 - v\,C_2$$

$$V_i \frac{dC_2}{dt} = v\,C_1 - v\,C_2$$

$$\therefore \quad \frac{dC_2}{dt} + \frac{v}{V_i} C_2 = \frac{v}{V_i} C_1$$

$$\frac{dC_2}{dt} + \frac{C_2}{\bar{t}_i} = \frac{C_1}{\bar{t}_i}$$

Putting value of C_1 from equation (2), we get,

$$\frac{dC_2}{dt} + \frac{C_2}{\bar{t}_i} = \frac{C_o\,e^{-t/\bar{t}_i}}{\bar{t}_i} \quad \text{... (3)}$$

Equation (3) is first order differential equation.

Here integrating factor is $e^{-t/\bar{t}_i}$ and initial condition is : at $t = 0$, $C_2 = 0$.

With this, the solution is

$$C_2 = \frac{C_o\,t}{\bar{t}_i}\,e^{-t/\bar{t}_i} \quad \text{... (4)}$$

Using the same procedure for third tank in series, the concentration of the tracer in the effluent from third tank (i.e. in exit stream leaving the system of three tanks in series) is

$$C_3 = \frac{C_o\,t^2}{2\,(\bar{t}_i)^2}\,e^{-t/\bar{t}_i} \quad \text{... (5)}$$

This equation gives tracer concentration as a function of time.

The fraction of tracer material leaving the system of three tanks (i.e. leaving the third tank) that has been in the system between time t and t + Δt is

$$E\,\Delta t = \frac{v\,C_3\,\Delta t}{N_o} = \frac{C_3}{N_o/v}\,\Delta t$$

We have,
$$N_o/v = \int_0^\infty C_3\,dt$$

$$\therefore \quad E\,\Delta t = \frac{C_3}{\int_0^\infty C_3\,dt}\cdot\Delta t$$

Putting value of C_3 from equation (5), we get,

$$E = \frac{t^2}{2\,(\bar{t}_i)^2}\cdot e^{-t/\bar{t}_i} \qquad \dots (6)$$

Generalising this method to a series of N equal-sized stirred tanks in series gives RTD for N tanks in series, E :

$$E = \frac{t^{N-1}\cdot e^{-t/\bar{t}_i}}{(N-1)\,!\,(\bar{t}_i)^N} \qquad \dots (7)$$

Multiplying both sides of equation (7) by $\bar{t}_i$,

$$\bar{t}_i\,E = \frac{t^{N-1}\cdot\bar{t}_i}{(N-1)\,!\,(\bar{t}_i)^N}\;e^{-t/\bar{t}_i}$$

$$\bar{t}_i\,E = \left(\frac{t}{\bar{t}_i}\right)^{N-1}\cdot\frac{1}{(N-1)\,!}\cdot e^{-t/\bar{t}_i} \qquad \dots (8\text{ a})$$

For N tanks in series, total volume is NV_i.

$$\bar{t}_i = \frac{\bar{t}}{N}$$

where $\bar{t}$ represents total tank volume divided by flow rate v.

$$\frac{\bar{t}\,E}{N} = \left(\frac{t}{\bar{t}/N}\right)^{N-1}\cdot\frac{1}{(N-1)\,!}\;e^{-tN/\bar{t}}$$

$$\bar{t}\,E = \left(\frac{t}{\bar{t}}\right)^{N-1}\frac{N^N}{(N-1)\,!}\cdot e^{-tN/\bar{t}} \qquad \dots (8\text{ b})$$

$$E_{\theta i} = \bar{t}_i\,E$$

$$\therefore \quad E_{\theta i} = \bar{t}_i\,E = \frac{(\theta i)^{N-1}}{(N-1)}\,e^{-\theta i} \qquad \dots (8\text{ c})$$

$$E_\theta = N\,\bar{t}_i\,E = \frac{N\,(N\theta)^{N-1}}{(N-1)\,!}\cdot e^{-N\theta} \qquad \dots (8\text{ d})$$

where $\bar{t}_i$ is the mean residence time in one tank.

$\bar{t} = N\bar{t}_i$ is the mean residence time in the N tanks system.

$$\theta_i = t/\bar{t}_i = Nt/\bar{t}$$

$$\theta = t/\bar{t} = t/N\bar{t}_i$$

These curves are shown in Fig. B. Their mean and variance both in time and dimensionless time are

$$\bar{t}_i = \frac{\bar{t}}{N}, \qquad \sigma^2 = N(t_i)^2 \qquad \text{... (9 a)}$$

$$\bar{t} = N\bar{t}_i, \qquad \sigma^2 = N(\bar{t}_i)^2 = \frac{(\bar{t})^2}{N} \qquad \text{... (9 b)}$$

$$\bar{t}_{\theta i} = N, \qquad \sigma^2_{\theta i} = N \qquad \text{... (9 c)}$$

$$\bar{t}_\theta = 1, \qquad \sigma^2_\theta = 1/N \qquad \text{... (9 d)}$$

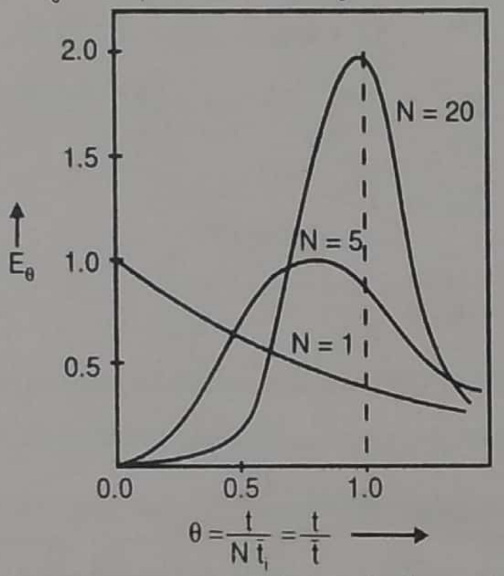


Fig. B : RTD curves for tanks-in-series model

If we connect M tanks to already existing chain of N tanks (all are of same size) then the individual means and variances are additive.

$$\bar{t}_N + \bar{t}_M = \bar{t}_{M+N}$$

and $$\sigma^2_N + \sigma^2_M = \sigma^2_{M+N} \qquad \text{... (10)}$$

If we introduce any one-shot tracer input into N tanks as shown in Fig. C, then

$$\Delta\sigma^2 = \sigma^2_{out} - \sigma^2_{in} = \frac{(\Delta\bar{t})^2}{N} \qquad \text{... (11)}$$

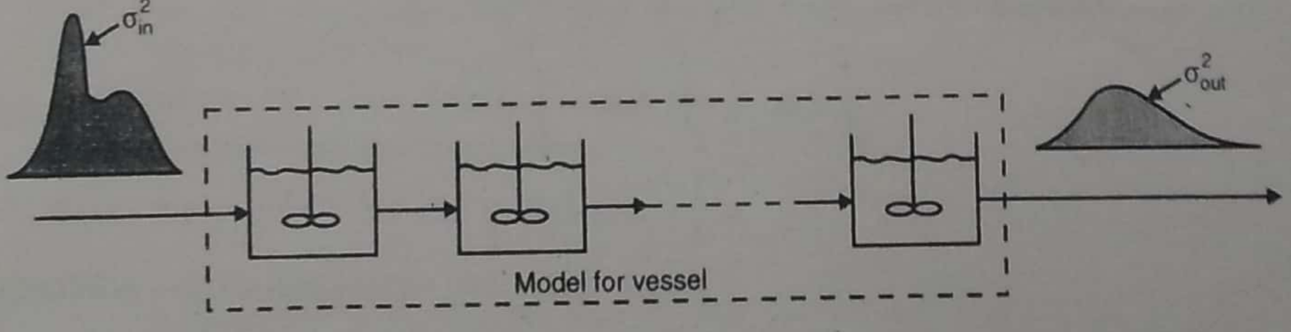


Fig. C : For any one-shot tracer input, equation (10) relates input, output and number of tanks

Therefore, the number of tanks in series is

$$N = \frac{1}{\sigma_\theta^2} = \frac{(\bar{t})^2}{\sigma^2} \quad \ldots (12)$$

Equation (12) represents the number of tanks necessary to model the real reactor as N ideal tanks in series.

Conversion : For first order reaction in one tank, we have,

$$\frac{C_A}{C_{Ao}} = \frac{1}{1 + k\,\bar{t}_i} = \frac{1}{1 + k\,\bar{t}} \quad \ldots (13)$$

Above equation for N equal sized tanks in series becomes

$$\frac{C_A}{C_{Ao}} = \frac{1}{(1 + k\,\bar{t}_i)^N} = \frac{1}{(1 + k\,\bar{t}/N)^N} \quad \ldots (14)$$

We have,

$$X_A = \frac{C_{Ao} - C_A}{C_{Ao}} = 1 - \frac{C_A}{C_{Ao}}$$

$\therefore$

$$X_A = 1 - \frac{1}{(1 + k\,\bar{t}_i)^N} \quad \ldots (15)$$

where

$$\bar{t}_i = \frac{V}{N\,v_o}$$

With the help of equation (15), we can calculate the conversion for first order reaction.

For non first order reaction, sequential mole balance on each tank must be carried out.

$$\bar{t}_i = \frac{C_{Ai-1} - C_{Ai}}{-r_i}$$

Ex. 1 : A first order liquid phase reaction is carried out in a reactor for which the results of (pulse) tracer test are given below :

t, s	0	1	2	3	4	5	6	7	8	9	10	12	14
C, mg/*l*	0	1	5	8	10	8	6	4	3	2.2	1.5	0.60	0

Calculate conversion using (i) ideal plug flow reactor, (ii) ideal mixed flow reactor, and (iii) the tank-in-series model.

Reaction rate constant = 0.25 min^{-1}

Solution : $A \rightarrow R, \quad -r_A = k\,C_A, \quad k = 0.25\ \text{min}^{-1}$

$$\int_0^\infty C\,dt = \int_0^{10} C\,dt + \int_{10}^{14} C\,dt$$

$$= \frac{1}{3}\,[1(0) + 4(1) + 1(5) + 1(5) + 4(8) + 1(10) + 1(10)$$

$$+ 4(8) + 1(6) + 1(6) + 4(4) + 1(3) + 1(3) + 4(2.2) + 1(1.5)]$$

$$+ \frac{2}{3}\,[1(1.5) + 4(0.6) + 1(0)]$$

$$= 50\ \text{mg.min}/l$$

$$E = \frac{C}{\int_0^\infty C\,dt} = \frac{C}{50}$$

Calculate E at various values of C and tabulate.

t	0	1	2	3	4	5	6	7	8	9	10	12	14
C	0	1	5	8	10	8	6	4	3	2.2	1.5	0.60	0
E	0	0.02	0.10	0.16	0.2	0.16	0.12	0.08	0.06	0.044	0.03	0.012	0

We have,

$$\bar{t} = \int_0^\infty t\,E\,dt$$

$$\sigma^2 = \int_0^\infty (t - \bar{t})^2\,E\,dt$$

So to calculate $\bar{t}$ and σ^2 tabulate t, tE, $(t - \bar{t})$ and $(t - \bar{t})^2 E$ and evaluate $\bar{t}$ and σ^2 by using numerical integration.

t	E	tE	$t - \bar{t}$	$(t - \bar{t})^2 E$
0	0	0	– 5.15	0
1	0.02	0.2	– 4.15	0.34
2	0.10	0.2	– 3.15	0.992
3	0.16	0.48	– 2.15	0.74
4	0.20	0.80	– 1.15	0.265
5	0.16	0.80	– 0.15	0.004
6	0.12	0.72	0.85	0.087
7	0.08	0.56	1.85	0.274
8	0.06	0.48	2.85	0.487
9	0.044	0.04	3.85	0.652
10	0.03	0.30	4.85	0.706
12	0.012	0.14	6.85	0.563
14	0	0	8.85	0

$$\bar{t} = \int_0^\infty t\,E\,dt = \int_0^{10} t\,E\,dt + \int_{10}^{14} E\,dt$$

$$= \frac{1}{3}\,[0 + 4\,(0.20) + 0.20 + 0.20 + 4\,(0.48) + 0.80 + 0.80 + 4\,(0.80)$$

$$+ 0.72 + 0.72 + 4\,(0.56) + 0.48 + 0.48 + 4\,(0.04) + 0.30]$$

$$+ \frac{2}{3}\,[0.30 + 4\,(0.14) + 0]$$

$$= 5.15 \text{ min}$$

$$\sigma^2 = \int_0^\infty (t-\bar{t})^2 E\,dt$$

$$= \frac{1}{3}[0 + 4(0.34) + 0.992 + 0.992 + 4(0.74) + 0.265 + 0.265$$

$$+ 4(0.004) + 0.087 + 0.087 + 4(0.274) + 0.487$$

$$+ 0.487 + 4(0.652) + 0.706]$$

$$+ \frac{2}{3}[0.706 + 4(0.563) + 0]$$

$$\sigma^2 = 6.108\ \text{min}^2 \simeq 6.1\ \text{min}^2$$

(i) Conversion using ideal plug flow reactor :

For first order reaction in plug flow, we have,

$$C_A/C_{Ao} = e^{-k\tau}$$

$$\therefore \quad X_A = 1 - e^{-k\tau} = 1 - e^{-k\bar{t}} \qquad (\because\ \bar{t} = \tau)$$

$$X_A = 1 - e^{-(0.25 \times 5.15)}$$

$$= 0.724$$

... **Ans. (i)**

(ii) Conversion using ideal mixed flow reactor :

For first order reaction in mixed flow reactor we have,

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

We have, $\tau = \bar{t}$

$$\therefore \quad X_A = \frac{5.15 \times 0.25}{1 + 5.15 \times 0.25} = 0.563$$

... **Ans. (ii)**

(iii) Conversion using the tanks-in-series model :

Number of tanks in series are calculated as

$$N = \frac{(\bar{t})^2}{\sigma^2} = \frac{(5.15)^2}{6.1} = 4.35$$

For first order reaction for N tanks in series, the conversion is calculated by

$$X_A = 1 - \frac{1}{(1 + \bar{t}_i k)^N}$$

$$= 1 - \frac{1}{\left(1 + \frac{\bar{t}\,k}{N}\right)^N} \quad \text{at } \bar{t} = N\bar{t}_i \quad = 1 - \frac{1}{\left(1 + \frac{5.15 \times 0.25}{4.35}\right)^{4.35}}$$

$$= 0.676$$

Conversion of A = 72.4% ... ideal plug flow reactor

Conversion of A = 56.3% ... ideal mixed flow reactor

Conversion of A = 67.6% ... tanks-in-series model

... **Ans.**

Ex. 2 : Evaluate E as a function of time upto t = 180 s for the vessel using the tanks-in-series model.

Given :

$$C_{in} \text{ with } \bar{t} = 220 \text{ s and } \sigma^2 = 100 \text{ s}^2$$

$$C_{out} \text{ with } \bar{t} = 280 \text{ s and } \sigma^2 = 1000 \text{ s}^2$$

Solution :

$$\Delta\bar{t} = \bar{t}_{out} - \bar{t}_{in} = 280 - 220 = 60 \text{ s}$$

$$\Delta\sigma^2 = \sigma^2_{out} - \sigma^2_{in} = 1000 - 100 = 900 \text{ s}^2$$

Now, calculate the number of tanks in series.

$$\Delta\sigma^2 = \frac{(\Delta\bar{t})^2}{N}$$

$$N = \frac{(\Delta\bar{t})^2}{\Delta\sigma^2} = \frac{(60)^2}{900} = 4$$

For N tanks in series, we have,

$$\bar{t}\,E = \left(\frac{t}{\bar{t}}\right)^{N-1} \cdot \frac{N^N}{(N-1)\,!}\ e^{-tN/\bar{t}}$$

$$E = \frac{t^{N-1}}{(\bar{t})^N} \cdot \frac{N^N}{(N-1)\,!}\ e^{-tN/\bar{t}}$$

$$E = \frac{t^{4-1}}{(60)^4} \cdot \frac{(4)^4}{(4-1)\,!} \cdot e^{-4\,t/60}$$

$$E = 3.29 \times 10^{-6}\, t^3 \cdot e^{-0.067\,t}$$

Now, take t = 0, 20, 40 upto 180 s. Evaluate E and tabulate.

t	0	20	40	60	80	100	120	140	180
E	0	6.89×10^{-3}	0.0144	0.0127	7.9×10^{-3}	4.05×10^{-3}	1.8×10^{-3}	7.6×10^{-4}	2.98×10^{-4}

... **Ans.**

Ex. 3 : A reactor with dividing baffles is to be used to carry the reaction

$A \rightarrow R, \quad -r_A = 0.05\, C_A, \quad \text{mol}/(l.\text{min})$

Pulse test results are :

t, min	0	10	20	30	40	50	60	70
C	35	38	40	40	39	37	36	35

Calculate conversion assuming (i) plug flow, (ii) assuming the tanks-in-series model, and (iii) assuming mixed flow.

Solution : $A \rightarrow R, \quad -r_A = 0.05\, C_A, \quad k = 0.05 \text{ min}^{-1}$.

The mean residence time is given by,

$$\bar{t} = \frac{\int_0^\infty t\,C\,dt}{\int_0^\infty C\,dt}$$

t	0	10	20	30	40	50	60	70
tC	0	380	800	1200	1560	1850	2160	2450

$$\int_0^{\infty} t\,C\,dt = \int_0^{70} t\,C\,dt = \int_0^{40} t\,C\,dt + \int_{40}^{70} t\,C\,dt$$

$$= \frac{10}{3}\,[0 + 4\,(380) + 800 + 800 + 4\,(1200) + 1560]$$

$$+ \frac{3}{8} \times 10\,[1560 + 3 \times 1850 + 3 \times 2160 + 2450] = 91750$$

$$\int_0^{\infty} C\,dt = \int_0^{70} C\,dt = \int_0^{40} C\,dt + \int_{40}^{70} C\,dt$$

$$\int_0^{\infty} C\,dt = \frac{10}{3}\,[35 + 4\,(38) + 40 + 40 + 4\,(40) + 39]$$

$$+ \frac{3 \times 10}{8}\,[39 + 3\,(37) + 3\,(36) + 35]$$

$$= 2651$$

$$\therefore \quad \bar{t} = \frac{91750}{2651} = 34.61 \text{ min}$$ **... Ans.**

$$E = \frac{C}{\int_0^{\infty} C\,dt} = \frac{C}{2651}$$

Evaluate E and tabulate.

t	0	10	20	30	40	50	60	70
E	0.013	0.014	0.015	0.015	0.015	0.014	0.0136	0.013
$t - \bar{t}$	– 34.61	– 24.61	– 14.61	– 4.61	5.39	15.39	25.39	35.39
$(t - \bar{t})^2 \cdot E$	15.57	8.48	3.2	0.32	0.43	3.31	8.75	16.28

$$\sigma^2 = \int_0^{\infty} (t - \bar{t})^2\,E\,dt = \int_0^{40} (t - \bar{t})^2\,E\,dt + \int_{40}^{70} (t - \bar{t})^2\,E\,dt$$

$$= \frac{10}{3}\,[15.57 + 4\,(8.48) + 3.2 + 3.2 + 4\,(0.32) + 0.43]$$

$$+ \frac{3 \times 10}{8}\,[0.43 + 3\,(3.31) + 3\,(8.75) + 16.28]$$

$$= 390.33 \text{ (min)}^2$$

Number of tanks in series are calculated by

$$\sigma^2 = \frac{(\bar{t})^2}{N}$$

$$N = \frac{(\bar{t})^2}{\sigma^2} = \frac{(34.61)^2}{390.33} = 3.07$$ ... **Ans.**

(i) Conversion in ideal plug flow reactor :

For first order reaction in plug flow reactor we have,

$$X_A = 1 - e^{-k\tau} = 1 - e^{-k\bar{t}}$$

$$X_A = 1 - e^{-(0.05) \times 34.61}$$

$$= 0.823$$

Conversion in ideal plug flow reactor = 82.3% ... **Ans.**

(ii) Conversion in ideal mixed flow reactor :

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

$$= \frac{\bar{t}k}{1 + \bar{t}k} = \frac{0.05 \times 34.61}{1 + (0.05 \times 34.61)} = 0.634$$

Conversion in ideal mixed flow reactor = 63.4% ... **Ans.**

(iii) Conversion using the tanks-in-series **model** :

$$X_A = 1 - \frac{1}{(1 + \bar{t}_i\, k)^N}$$

$$= 1 - \frac{1}{\left(1 + \frac{\bar{t}\,k}{N}\right)^N}$$

$$= 1 - \frac{1}{\left(1 + \frac{34.61 \times 0.05}{3.07}\right)^{3.07}}$$

$$= 0.746 \approx 0.75$$

Conversion in tanks-in-series model = 75% ... **Ans.**

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APPENDIX - II

Ex. 1 : The results of the pulse input are shown in Fig. 1.

(i) Check the material balance with the tracer curve to see whether the results are consistent or not.

(ii) If the results are consistent, evaluate $\bar{t}$ and V.

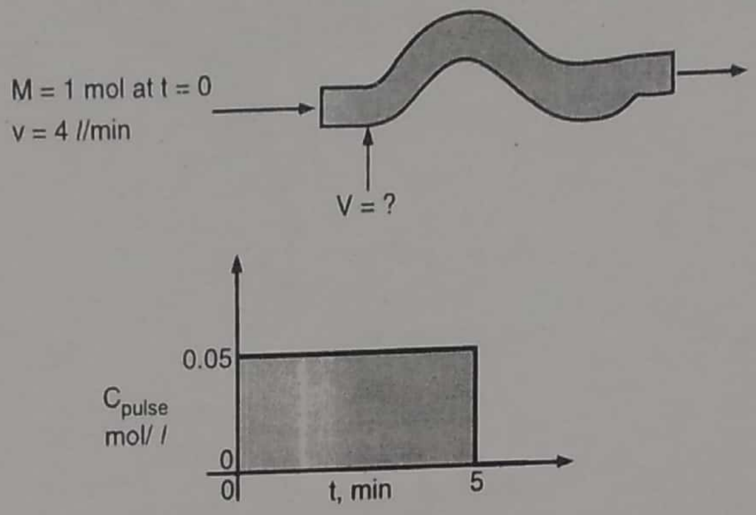

Fig. 1

Solution : M = 1 mol, v = 4 l/min, V = ?

Check material balance against the tracer curve.

(i) From material balance, we should have :

$$\text{Area under curve} = \frac{M}{v} = \frac{1}{4} = 0.25 \text{ mol.min}/l$$

(ii) From the tracer curve, we have :

$$\begin{aligned} \text{Area under curve (Fig. 1)} &= \text{Area of rectangle} \\ &= 0.05 \times 5 \\ &= 0.25 \text{ mol.min}/l \end{aligned}$$

As the values agree, the results are consistent. ... **Ans.** (i)

Mean of the C_{pulse} curve, $\bar{t}$ is given by,

$$\begin{aligned} \bar{t} &= \frac{\sum t_i C_i}{\sum C_i} \\ &= \frac{0 \times 0.05 + 5 \times 0.05}{0.05 + 0.05} \\ &= 2.5 \text{ min} \end{aligned}$$

... **Ans.** (ii)

From Fig. 1 as the concentration is constant from 0 to 5 min, we have,

$$\bar{t} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i}$$

Take t = 0, 1, 2, 3, 4 and 5.

$$\therefore \quad \Delta t_i = 1 \text{ min}$$

$$\therefore \quad \bar{t} = \frac{\Sigma t_i C_i}{\Sigma C_i}$$

$$= \frac{0 \times 0.05 + 1 \times 0.05 + 2 \times 0.05 + 3 \times 0.05 + 4 \times 0.05 + 5 \times 0.05}{0.05 + 0.05 + 0.05 + 0.05 + 0.05 + 0.05}$$

$$= \frac{0.05\,[1 + 2 + 3 + 4 + 5]}{6 \times 0.05}$$

$$= \frac{15}{6} = 2.5 \text{ min} \qquad \text{... Ans.}$$

$$\bar{t} = \frac{V}{v}$$

$$V = \bar{t}\, v$$

$$= 2.5 \times 4$$

$$= 10\, l \qquad \text{... Ans. (ii)}$$

E(t) is obtained by using equation :

$$E = \frac{C_{pulse}}{M/v} = \frac{C}{0.25} = 4C$$

Ex. 2 : Following results were obtained for a pulse test on a piece of reaction equipment. The output concentration rose linearly from zero to 0.5 μmol/dm^3 in 5 min, then fell linearly to zero in 10 min after reaching a maximum value of 0.5 μmol/dm^3.

(i) Calculate the mean residence time.

(ii) Calculate the total reactor volume if the flow rate is 570 l/min.

Solution : At t = 0 min, C = 0

At t = 5 min, C = 0.5 μmol/dm^3

At t = 15 min, C = 0 (in 10 min after maximum)

The output concentration rises linearly first upto 5 min from 0 to 0.5 and then falls linearly from 0.5 to 0 as time passes from 5 to 15 min (in 10 min).

t	C	t	C	t	C
0	0	6	0.45	11	0.20
1	0.1	7	0.40	12	0.15
2	0.2	8	0.35	13	0.10
3	0.3	9	0.30	14	0.05
4	0.4	10	0.25	15	0
5	0.5				

This is linear variation of concentration with time.

t	0	1	2	3	4	5	6	7
tC	0	0.1	0.4	0.9	1.6	2.5	2.7	2.8
t	8	9	10	11	12	13	14	15
tC	2.8	2.7	2.5	2.2	1.8	1.3	0.7	0

$$\bar{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt}$$

$$= \frac{\Sigma t_i C_i \Delta t_i}{\Sigma C_i \Delta t_i}$$

For Δt_i constant,

$$\bar{t} = \frac{\Sigma t_i C_i}{\Sigma C_i}$$

$$= \frac{[0 + 0.1 + 0.4 + 0.9 + 1.6 + 2.5 + 2.7 + 2.8 + 2.8 + 2.7 + 2.5 + 2.2 + 1.8 + 1.3 + 0.7 + 0]}{[0 + 0.1 + 0.2 + 0.3 + 0.4 + 0.5 + 0.45 + 0.4 + 0.35 + 0.3 + 0.25 + 0.2 + 0.15 + 0.1 + 0.05 + 0]}$$

$$= \frac{25}{3.75}$$

$$= 6.67 \text{ min}$$ ... **Ans.** (i)

$$v = 570\ l/\text{min}$$

$$\bar{t} = \frac{V}{v}$$

$$V = \bar{t} \cdot v = 6.67 \times 570 = 3802\ l$$ ... **Ans.**

From graph : Fig. 2

$$\text{Area of } C_{\text{pulse}} \text{ curve} = 37.5 \text{ cm}^2$$

$$= 37.5 \times \frac{0.1}{1} \times \frac{1}{1}$$

$$A = 3.75\ \frac{\mu\text{mol}}{\text{dm}^3} \cdot \text{min}$$

$$A = \text{Area of triangle 1} + \text{Area of triangle 2}$$

$$= \frac{1}{2} \times (5-0) \times 0.5 + \frac{1}{2}\,(15-5) \times 0.5$$

$$= \frac{0.5}{2}\ [5+10]$$

$$= 3.75 \frac{\mu\text{mol}}{\text{dm}^3} \cdot \text{min}$$

$$A = \int_0^\infty C\,dt$$

$$= \int_0^{15} C\,dt = 3.75$$

Area under tC v/s t **curve** : Fig. 3

$$A' = 124 \text{ cm}^2$$

$$= 124 \times \frac{0.2}{1} \times 1$$

$$= 24.8 \frac{\mu\text{mol}}{\text{dm}^3} \cdot (\text{min})^2$$

$$A = \int_0^\infty tC\,dt = \int_0^{15} tC\,dt$$

$$= 24.8$$

∴ $\bar{t}$ = Mean residence time

$$\bar{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt} = \frac{24.8}{3.75}$$

$$= 6.613 \text{ min}$$

... Ans.

So $\bar{t}$ is approximately same by both the methods.

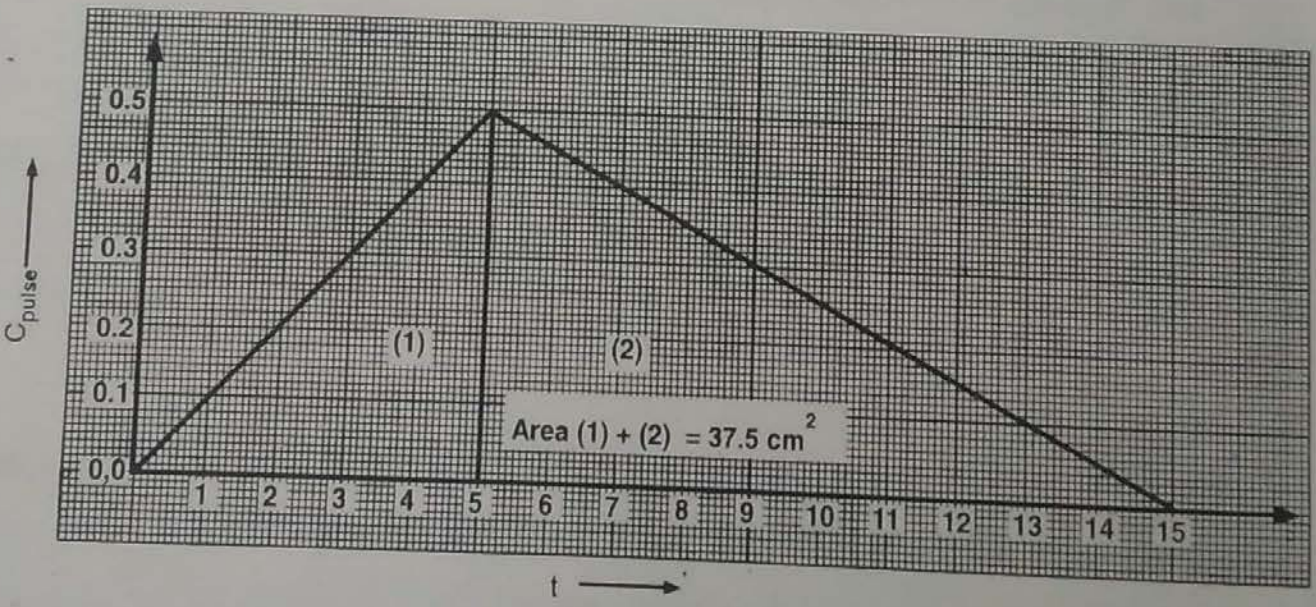

Fig. 2

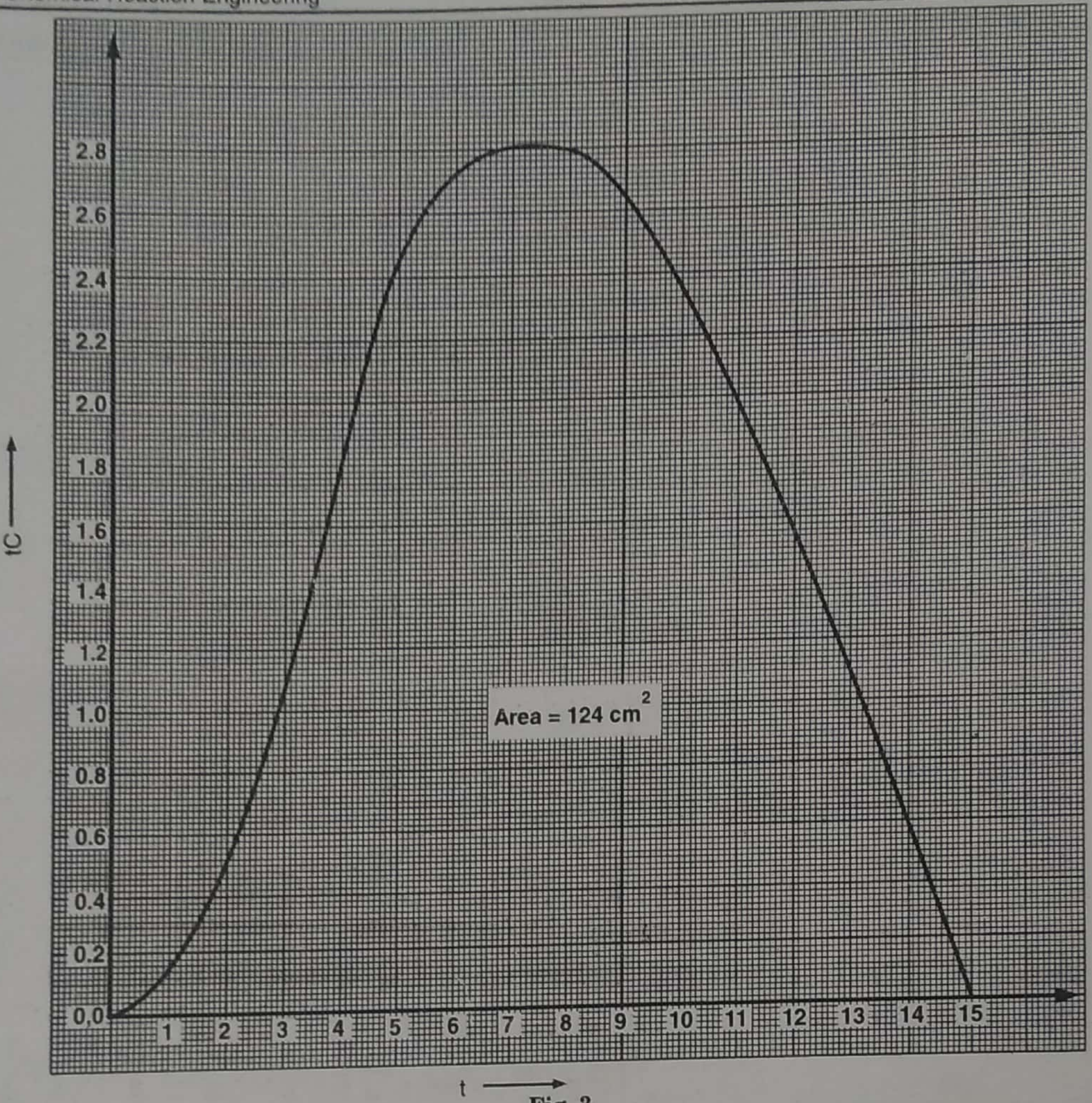

Fig. 3

Ex. 3 : A second order with kC_{Ao} = 1.2 min^{-1} is carried out in a system of Ex. 2. What would be the conversion for the same flow and volume if the reactor is plug flow reactor ? Also calculate the mean conversion in real reactor for data of Ex. 2.

Solution :
$$\tau = C_{Ao} \int_0^{X_A} \frac{dX_A}{-r_A}$$

and
$$-r_A = kC_A^2$$

Integrating we get,
$$X_A = \frac{kC_{Ao}\,\tau}{1 + kC_{Ao}\,\tau}$$

Using τ from Ex. 2,
$$\tau = 6.67 \text{ min}$$

and
$$kC_{Ao} = 1.2 \text{ min}^{-1} \quad \text{(given)}$$

$$X_A = \frac{1.2 \times 6.67}{1 + (1.2 \times 6.67)} = 0.889$$

Conversion in plug flow reactor = 88.9% **... Ans.**

For real reactor : $$E = \frac{C}{\int_0^\infty C\,dt}$$

Now, $$\int_0^\infty C\,dt = 3.75 \text{ (from Ex. 2)}$$

Evaluate E for each value of C from :

$$E = \frac{C}{3.75}$$

$$E = \frac{0.1}{3.75} = 0.0267 \text{ for } t = 1$$

We have for real reactor : $$\frac{\bar{C}_A}{C_{Ao}} = \sum \left(\frac{C_A}{C_{Ao}}\right)_{\text{element}} \cdot E\,\Delta t$$

In our case, $\Delta t = 1$ as $t = 0, 1, 2, 3$ ...

For second order reaction :

$$\left(\frac{C_A}{C_{Ao}}\right)_{\text{element}} = \frac{1}{1 + kC_{Ao}\,t} = \frac{1}{1 + 1.2\,t}$$

t	C	E	1/(1 + 1.2 t)	Δt	[1/(1 + 1.2 t)] E Δt
0	0	0	1	–	–
1	0.1	0.0267	0.45	1	0.012
2	0.2	0.053	0.29	1	0.0154
3	0.3	0.08	0.22	1	0.0176
4	0.4	0.106	0.17	1	0.0180
5	0.5	0.133	0.14	1	0.0186
6	0.45	0.12	0.12	1	0.0144
7	0.40	0.106	0.11	1	0.0117
8	0.35	0.093	0.094	1	0.0087
9	0.30	0.08	0.085	1	0.0068
10	0.25	0.066	0.077	1	0.0051
11	0.2	0.053	0.07	1	0.0037
12	0.15	0.04	0.065	1	0.0026
13	0.10	0.0267	0.06	1	0.0016
14	0.05	0.0133	0.056	1	0.00074
15	0	0	0.053	1	–

$$\frac{\bar{C}_A}{C_{Ao}} = \sum \left(\frac{1}{1 + 1.2\,t}\right) \cdot E\,\Delta t = 0.137$$

$$\frac{\bar{C}_A}{C_{Ao}} = \sum \frac{1}{(1 + 1.2\,t)} \cdot E\,\Delta t = 0.137$$

$$\bar{X}_A = 1 - \bar{C}_A/C_{Ao} = 1 - 0.137 = 0.863\,(86.3\%)$$ ... **Ans.**

Ex. 4 : The results of pulse input to a vessel are shown in the Fig. 4.

(i) Check the material balance with the tracer curve to see whether the results are consistent.

(ii) If the results are consistent, determine the amount of tracer introduced M.

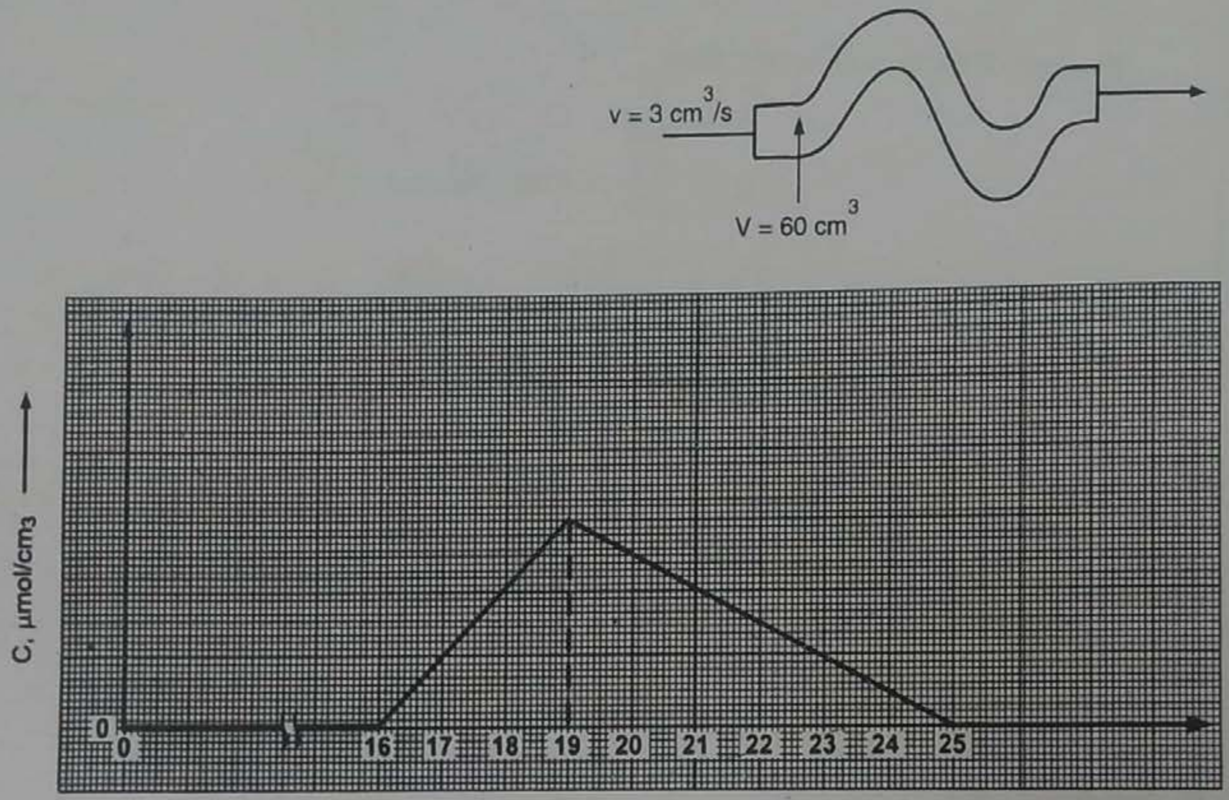

Fig. 4

Solution :

Take scale for time on x-axis and take maximum value of concentration corresponding to t = 19, at 3 cm on y-axis and complete two triangles as shown.

Let the concentration corresponding to time t = 19 s be C μmol/cm^3.

So concentration values at various time from graph are (linear relationship between C and t):

From graph :

t	C	t C
0	0	–
16	0	0
17	1/3 C	17/3 C
18	2/3 C	36/3 C
19	C	19 C
20	5/6 C	100/6 C
21	2/3 C	42/3 C
22	3/6 C	66/6 C
23	1/3 C	23/3 C
24	1/6 C	24/6 C
25	0	0

$$\text{Area under } C_{pulse} \text{ curve} = A = \int_0^{\infty} C\,dt$$

$$A = \int_0^{25} C\,dt = \frac{M}{v}$$

$$A = \text{Area of triangles } (1+2)$$

$$= \frac{1}{2}(19-16)\,C + \frac{1}{2}(25-19)\,C = \frac{9}{2}\,C$$

$$\text{Area under curve} = A = 13.5\ \text{cm}^2 = 13.5 \times \frac{1}{1} \times \frac{1/3\ C}{1} = 4.5\,C = \frac{9}{2}\,C$$

$$A = \sum C_i\,\Delta t_i, \quad \Delta t_i = 1\ \text{min} = \sum C_i$$

$$= \left[\frac{1}{3}C + \frac{2}{3}C + C + \frac{5}{6}C + \frac{2}{3}C + \frac{3}{6}C + \frac{1}{3}C + \frac{1}{6}C\right]$$

$$= \frac{27}{6}\,C = \frac{9}{2}\,C$$

$$\bar{t} = \frac{\int_0^{\infty} tC\,dt}{\int_0^{\infty} C\,dt}$$

$$\int_0^{\infty} tC\,dt = \sum t_i\,C_i\,\Delta t_i$$

$$= \sum t_i\,C_i \qquad \text{as } \Delta t = \text{constant} = 1$$

$$= \left[\frac{17}{3}C + \frac{36}{3}C + 19C + \frac{100}{6}C + \frac{42}{3}C + \frac{66}{6}C + \frac{23}{3}C + \frac{24}{6}C\right]$$

$$= \frac{540}{6}\,C = 90\,C$$

$$\therefore \quad \bar{t} = \frac{90\,C}{9/2\,C} = 20\ \text{s}$$

$$\bar{t} \text{ from } C_{pulse} \text{ curve} = 20\ \text{s}$$

$\bar{t}$ from material balance

$$\bar{t} = \frac{V}{v} = \frac{60}{3} = 20\ \text{s}$$

As the $\bar{t}$ values agree, the results are consistent.

$$A = \frac{9}{2}\,C = \frac{M}{v}$$

$$M = \frac{9}{2} vC$$

$$= \frac{9}{2} \times 3 \times C$$

$$= 13.5\ C\ \mu mol/s \qquad \text{... Ans.}$$

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)\,dt} = \frac{C(t)}{\frac{9}{2}C} = \frac{C(t)}{4.5\ C}$$

Calculate E(t) for various t.

t	C(t)	E(t)
0	–	–
16	0	0
17	1/3 C	0.0741 [(1/3) × 1/4.5]
18	2/3 C	0.1482 [2/3 × 1/4.5]
19	C	0.222 [1/4.5]
20	5/6 C	0.1852 [5/6 × 1/4.5]
21	2/3 C	0.1482 [2/3 × 1/4.5]
22	3/6 C	0.1111 [3/6 × 1/4.5]
23	1/3 C	0.0741 [1/3 × 1/4.5]
24	1/6 C	0.03704 [1/6 × 1/4.5]
25	0	0

$$\text{Area under E curve} = \left[\frac{1}{2} \times 3 \times \frac{1}{4.5}\right] + \left[\frac{1}{2} \times 6 \times \frac{1}{4.5}\right] = 1.0$$

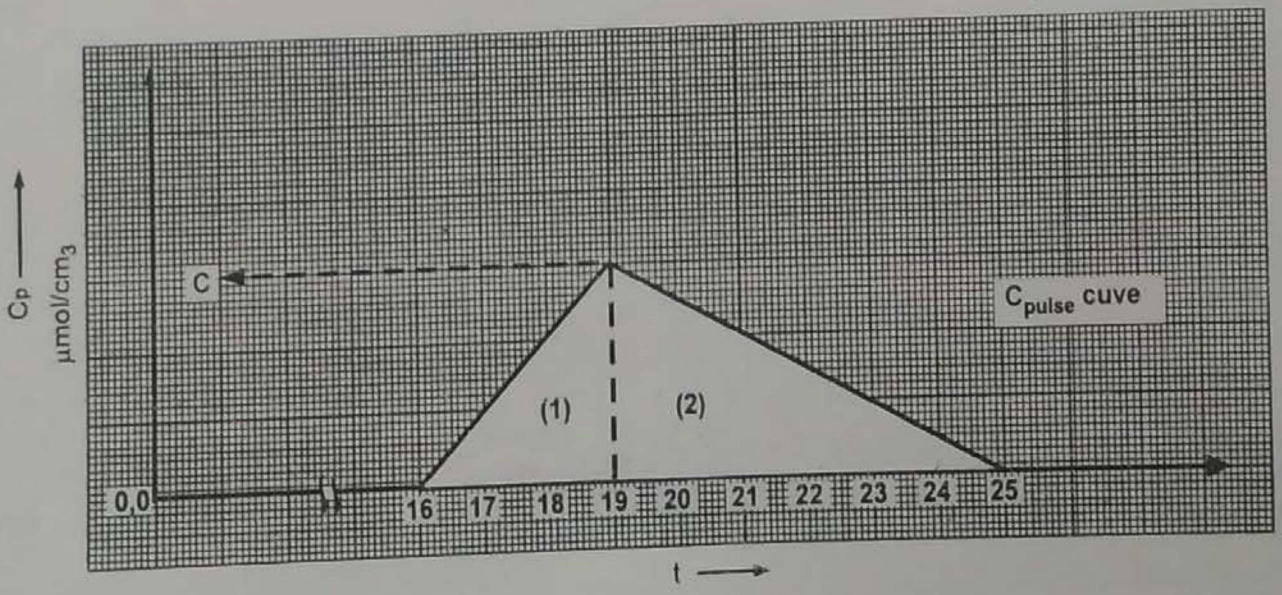

Fig. 5

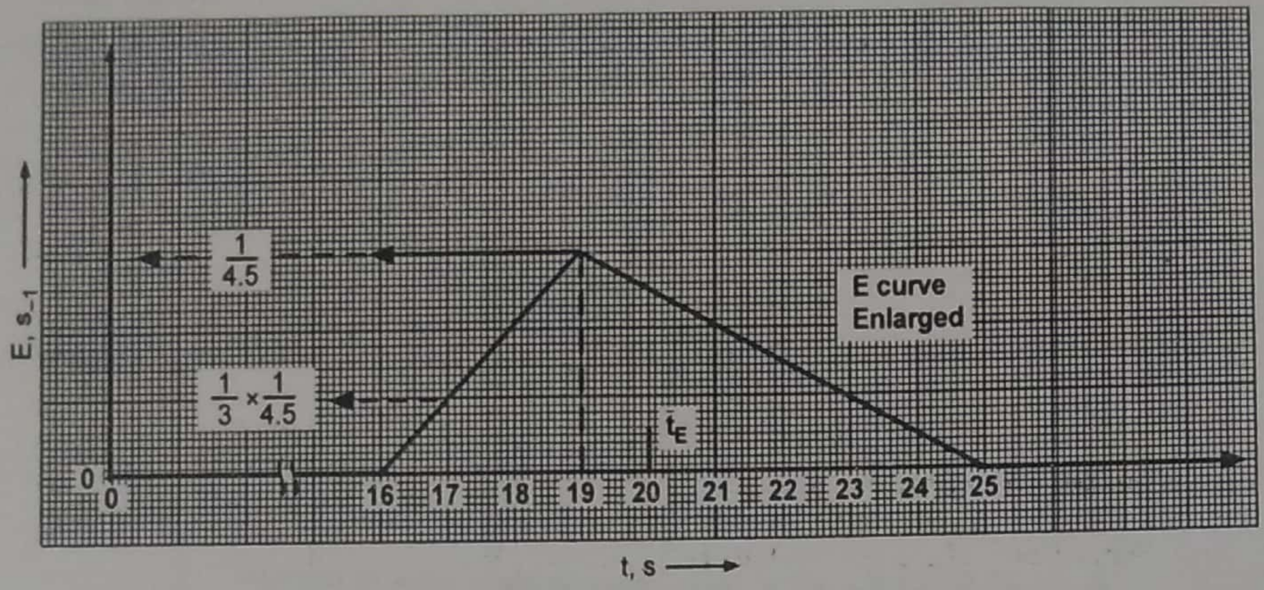

Fig. 6

Ex. 5 : The results of the step experiment made on reactor are shown in the Fig. 7.

Determine the vessel volume V and $\bar{t}$.

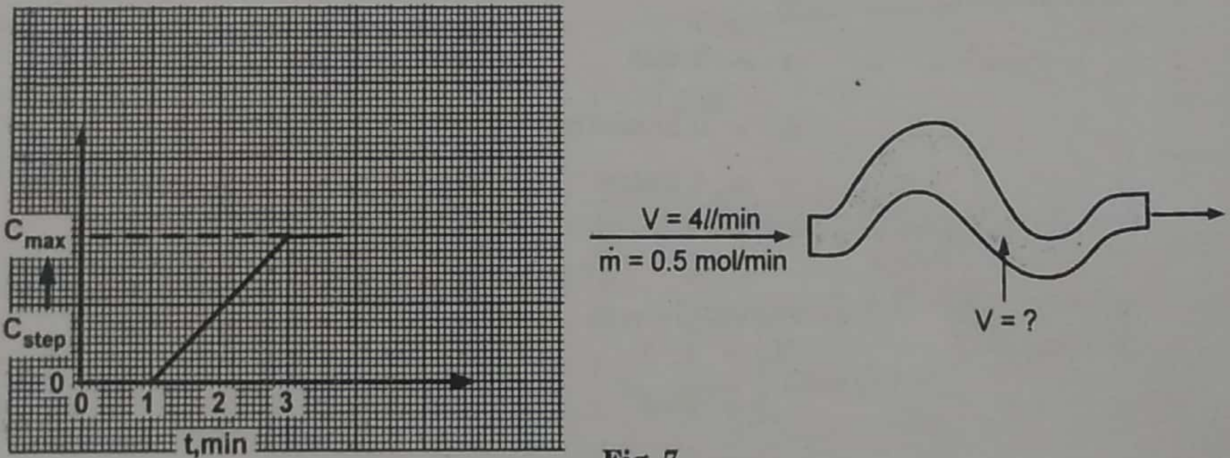

Fig. 7

Solution :

From graph

t	C_{step}
0	0
1	0
2	$C_{max}/2$
3	C_{max}

$$\bar{t} = \frac{1}{C_{max}} \int_0^{C_{max}} t \, dC_{step}$$

Use trapezoidal rule to evaluate integral.

$$\int_{x_0}^{x_1} f(x)\,dx = h/2\,[f(x_0) + f(x_1)] \quad \text{where} \quad h = x_1 - x_0$$

$$\bar{t} = \frac{1}{C_{max}}\left[\frac{C_{max}}{2\times 2}(1+2) + \frac{C_{max}}{2\times 2}(2+3)\right]$$

$$\bar{t} = \frac{1}{C_{max}}\left[\frac{C_{max}}{4}(1+2+2+3)\right]$$

$$= \frac{8\,C_{max}}{4\,C_{max}} = 2\text{ min}$$

$$\text{Shaded area of Fig. 8} = C_{max}\,\bar{t} = \frac{\dot{m}\,V}{v^2}$$

$$\text{Shaded area of Fig. 8} = \text{Area of rectangle + Area of triangle}$$

$$= 1\times C_{max} + \frac{1}{2}\times C_{max}\times 2$$

$$= 2\,C_{max}$$

$$2\,C_{max} = C_{max}\,\bar{t}$$

$$\therefore \quad \bar{t} = 2\text{ min}$$ ... **Ans.**

$$\dot{m} = 0.5\text{ mol/min}$$

$$v = 4\ l\text{/min}$$

$$\bar{t} = \frac{V}{v}$$

$$V = \bar{t}\cdot v$$

$$= 2\times 4$$

$$= 8\,l$$ ... **Ans.**

$$C_{max} = \frac{\dot{m}}{v} = \frac{0.5}{4} = 0.125\text{ mol.min}/l$$

t	C_{step}
1	0
2	0.0625
3	0.125

$$\int_0^{C_{max}} t\,dC_{step} = \frac{0.0625}{2}[1+2] + \frac{0.0625}{2}[2+3]$$

$$= \frac{0.0625\times 8}{2}$$

$$= 0.25$$

$$\text{Shaded area} = 1 \times 0.125 + \frac{1}{2} \times 0.125 \times 2$$

$$= 0.25$$

$$0.25 = C_{max}\,\bar{t}$$

$$\therefore \quad \bar{t} = \frac{0.25}{0.125} = 2 \text{ min.}$$

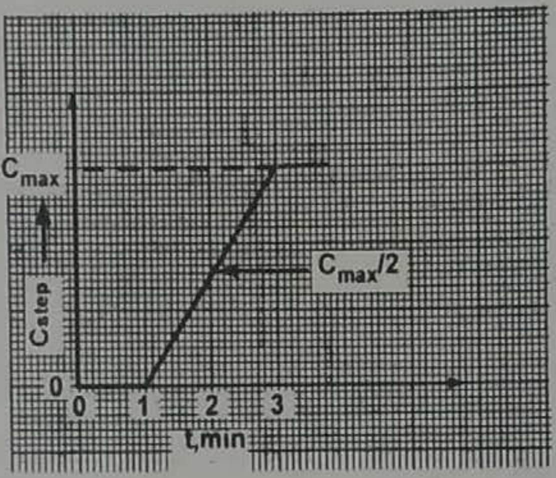

Fig. 8

Ex. 6 : A liquid macrofluid, as it flows through the vessel, reacts as per following reaction

$$A \longrightarrow R$$

$$C_{Ao} = 6 \text{ mol}/l, \quad -r_A = k$$

and $$k = 3 \text{ mol}/(l \cdot \text{min})$$

For flow pattern with $E = 0.333$ for $0 < t < 3$ min determine the conversion of A.

Solution : $A \rightarrow R$, $C_{Ao} = 6 \text{ mol}/l$, $-r_A = k$ (zero order reaction), $k = 3 \text{ mol}/(l \cdot \text{min})$

For zero order reaction, integrated rate equation is

$$C_{Ao} - C_A = kt$$

or $$X_A = \frac{kt}{C_{Ao}}$$

Mean conversion of A is given by,

$$\bar{X}_A = \int_0^\infty (X_A)_{element} \cdot E\,dt$$

$$= \int_0^3 \frac{kt}{C_{Ao}} \cdot E\,dt = \frac{kE}{C_{Ao}} \int_0^3 t\,dt$$

$$= \frac{kE}{C_{Ao}} [t^2/2]_0^3$$

$$= \frac{3 \times 0.333}{6} [9/2] = 0.749 \approx 0.75 \text{ (i.e. } 75\%) \qquad \text{... Ans.}$$

Ex. 7 : The results of pulse input to the vessel are shown in Fig. E 7A (a).

(a) Check material balance with the experimental tracer curve to see whether the results are consistent or not.

(b) If the results are consistent, determine the amount of tracer introduced, M.

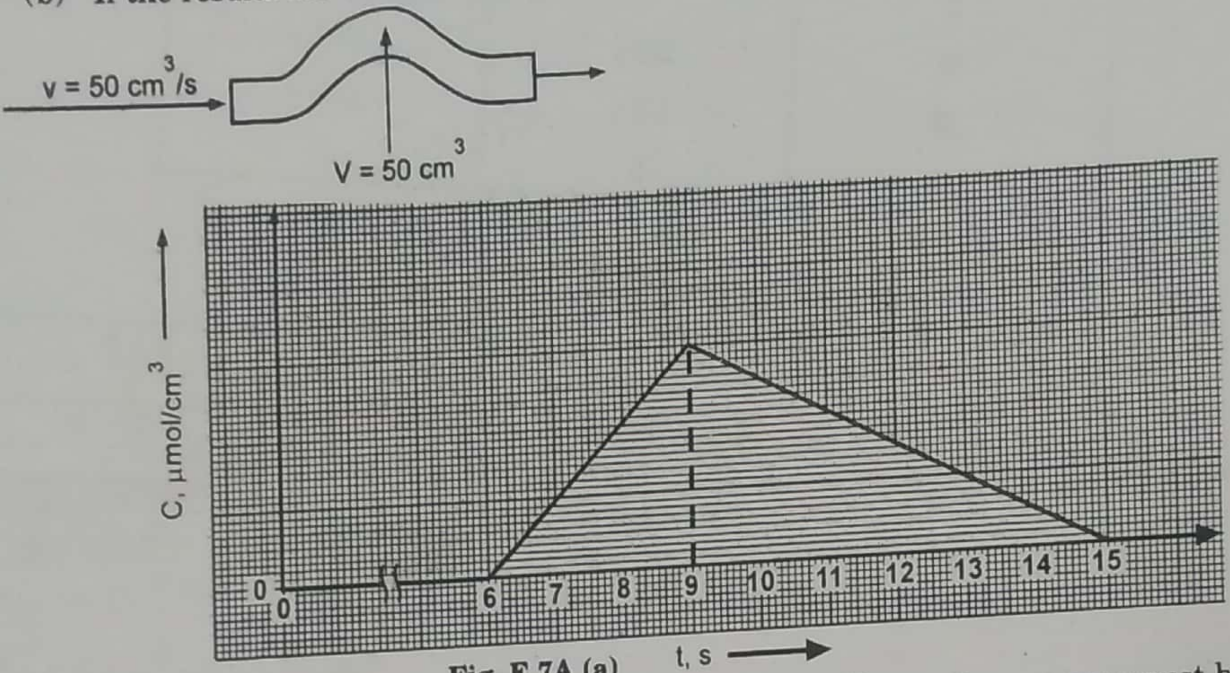

Fig. E 7A (a)

Solution : Please note that for the results to be consistent, $\bar{t}$ from C_{pulse} curve must be equal to $\bar{t}$ from material balance.

Given : $v = 5\ cm^3/s$ and $V = 50\ cm^3$

$$\bar{t} \text{ from material balance } = \frac{V}{v}$$

$$= \frac{50}{5} = 10\ s$$

Now, we will obtain $\bar{t}$ from C_{pulse} curve.

Refer Fig. E 7A (b) :

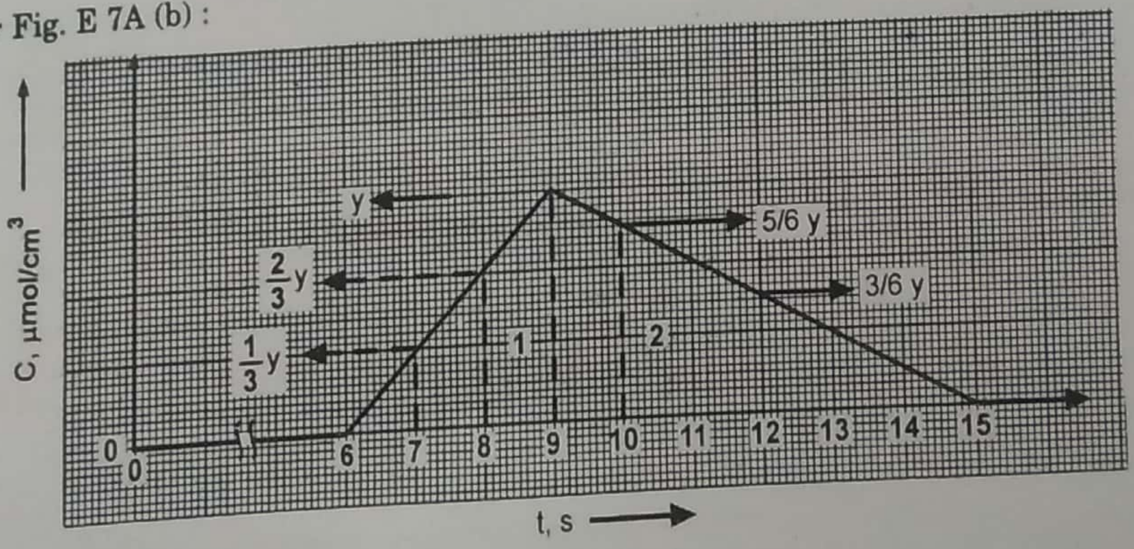

Fig. E 7A (b)

Take scale for time on x-axis and take maximum value of concentration corresponding to time t = 9 s at 3 cm on y-axis and complete two triangles as shown in Fig. E 7A.

Let the concentration corresponding to time t = 9 s be y $\mu mol/cm^3$.

So the concentration values at various values of time in terms of y are :

t	C	tC
0	0	–
6	0	0
7	1/3 y	7/3 y
8	2/3 y	16/3 y
9	y	9 y
10	5/6 y	50/6 y
11	2/3 y	22/3 y
12	3/6 y	36/6 y
13	1/3 y	13/3 y
14	1/6 y	14/6 y
15	0	0

$$\text{Area under } C_{pulse} \text{ curve} = A = \int_0^\infty C\,dt$$

$$A = \int_0^{15} C\,dt = M/v$$

$$A = \text{Area of triangles } (1 + 2)$$

$$= \frac{1}{2}(9-6)\,y + \frac{1}{2}(15-9)\,y$$

$$= \frac{9}{2}\,y$$

OR :

$$A = \Sigma C_i \Delta t_i \quad \text{as} \quad \Delta t_i = 1$$

$$A = \Sigma C_i$$

$$= \left[\frac{1}{3}\,y + \frac{2}{3}y + y + \frac{5}{6}y + \frac{2}{3}y + \frac{3}{6}y + \frac{1}{3}y + \frac{1}{6}y\right]$$

$$= \frac{27}{6}\,y$$

$$= \frac{9}{2}\,y$$

$$\int_0^\infty tC\,dt = \int_0^{15} tC\,dt$$

$$= \Sigma t_i\, C_i\, \Delta t_i$$

$$= \Sigma t_i\, C_i \quad \text{as} \quad \Delta t_i = 1$$

$$= \left[\frac{7}{3}y + \frac{16}{3}y + 9y + \frac{50}{6}y + \frac{22}{3}y + \frac{36}{6}y + \frac{13}{3}y + \frac{14}{6}y\right]$$

$$= \frac{270}{6}y = 45\,y$$

$$\bar{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt}$$

$$= \frac{45\,y}{(9/2)\,y}$$

$$= 10\,\text{s}$$

$\bar{t}$ from C_{pulse} curve = 10 s

$\bar{t}$ from material balance = 10 s

As $\bar{t}$ from C_{pulse} curve is equal to $\bar{t}$ from material balance, the results are consistent.

... **Ans.** (a)

As $\bar{t}$ values agree, the results are consistent. ... **Ans.** (a)

$$A = \text{area under } C_{pulse} \text{ curve} = \frac{9}{2}\,C = M/v$$

$$M = \frac{9}{2}\cdot C\cdot v = \frac{9}{2}\cdot C\cdot 5$$

$$= 22.5\ C\ \mu\text{mol/s}$$ ... **Ans.** (b)

Extra : Use of Simpson's three-eighths rule (four-point) to evaluate $\bar{t}$.

$$\int_{x_0}^{x_3} f(x)\,dx = \frac{3}{8}h\,[f(x_0) + 3f(x_1) + 3f(x_2) + f(x_3)]$$

where, $h = \dfrac{x_3 - x_0}{3}$

For t = 6 to 9s, $\Delta t_i = 1\text{s}$ (time interval of 1s)

For t = 9 to 15s. $\Delta t_i = 2\text{s}$ (time interval of 2s)

t	C	tC
6	0	0
7	1/3 y	7/3 y
8	2/3 y	16/3 y
9	y	9 y
11	2/3 y	22/3 y
13	1/3 y	13/3 y
15	0	0

$$\int_0^\infty C\,dt = \int_0^6 C\,dt + \int_6^9 C\,dt + \int_9^{15} C\,dt, \quad \int_0^6 C\,dt = 0$$

for t = 6 to 9s : $h = \frac{9-6}{3} = 1$

for t = 9 to 15s : $h = \frac{15-9}{3} = 2$

$$= \int_6^9 C\,dt + \int_9^{15} C\,dt$$

$$= \frac{3}{8}\times 1\left[0 + 3\times\frac{1}{3}y + 3\times\frac{2}{3}y + y\right]$$

$$+\frac{3}{8}\times 2\left[y + 3\times\frac{2}{3}y + 3\times\frac{1}{3}y + 0\right]$$

$$= \frac{3}{8}\times 4y + \frac{3}{8}\times 2\times 4y$$

$$= \frac{36y}{8} = \frac{9}{2}y = 4.5\,y$$ … same as previously obtained.

$$\int_0^\infty tC\,dt = \int_0^6 tC\,dt + \int_6^9 tC\,dt + \int_9^{15} tC\,dt$$

$$= \int_6^9 tC\,dt + \int_9^{15} tC\,dt, \quad \int_0^6 tC\,dt = 0$$

$$= \frac{3}{8}\times 1\left[0 + 3\times\frac{7}{3}y + 3\times\frac{16}{3}y + 9y\right]$$

$$+\frac{3}{8}\times 2\left[9y + 3\times\frac{22}{3}y + 3\times\frac{13}{3}y + 0\right]$$

$$= \frac{3}{8}\times 32y + \frac{3}{8}\times 2\times 44\,y$$

$$= 12\,y + 33\,y = 45\,y$$

$\bar{t}$ from C_{pulse} curve :

$$\bar{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt}$$

$$= \frac{45\ y}{9/2\ y}$$

$$= \frac{45\ y}{4.5\ y}$$

$= 10$ s ... same as obtained previously.

(To evaluate $\bar{t}$, you can also adopt above given approach.)

Ex. 8 : The results of pulse input to the vessel are shown in Fig. E 8A (a). Are the results consistent ? (Check the material balance with the experimental tracer curve.)

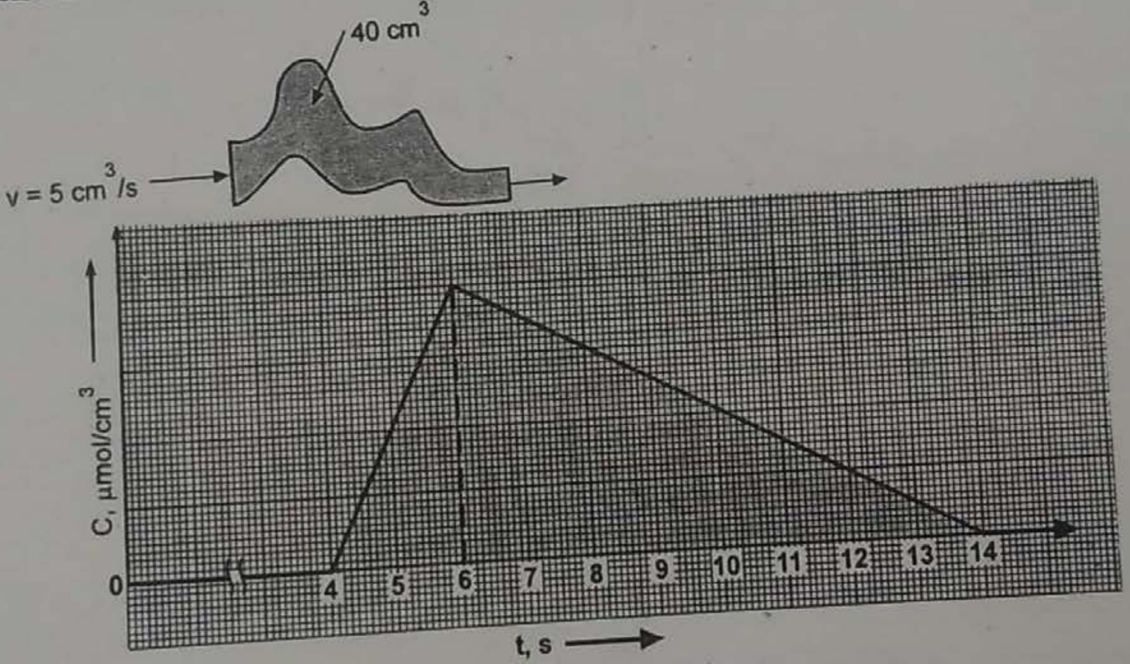

Fig. E 8A (a)

Solution : Please note that for the results to be consistent, $\bar{t}$ from C_{pulse} curve must be equal to $\bar{t}$ from the material balance.

Given : $v = 5\ cm^3/s$, $V = 40\ cm^3$

$$\bar{t} \text{ from material balance} = \frac{V}{v} = \frac{40}{5} = 8\,s$$

Now, we will obtain $\bar{t}$ from the experimental tracer curve.

Refer Fig. E 8A (b) :

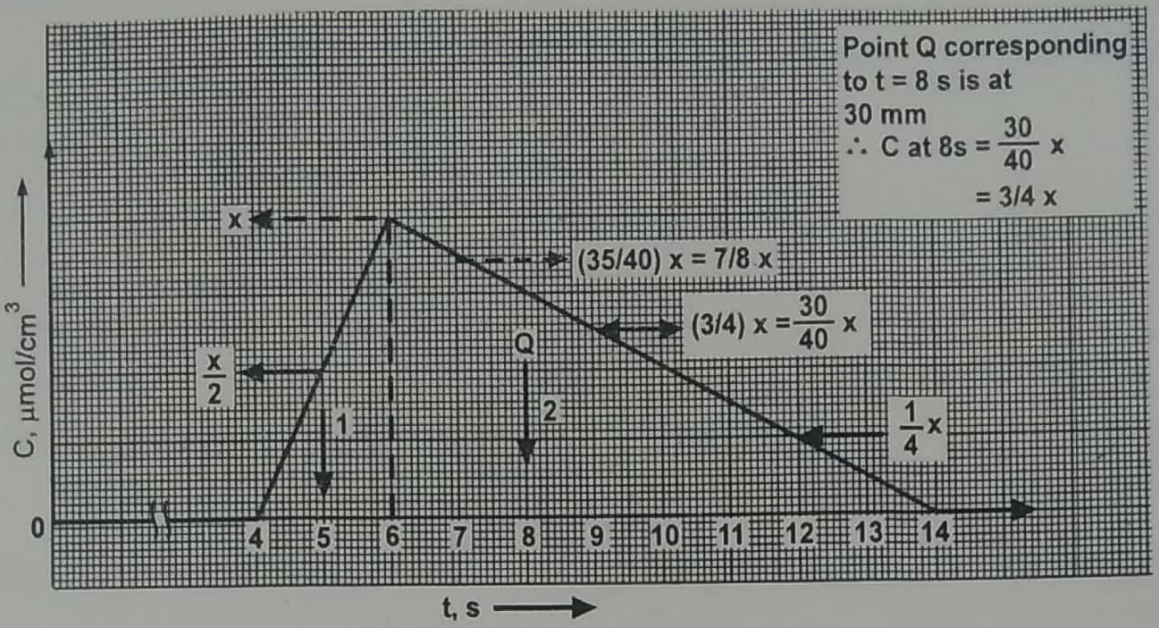

Fig. E 8A (b)

Take scale for time on x-axis and take maximum value of concentration corresponding to time t = 6s at 4 cm on y-axis and complete two triangles as shown in Fig. E 8A (b).

Let the concentration corresponding to time t = 6s be x μmol/cm^3.

So the concentration values at various values of t (assuming linear relationship between t and C) in terms of y are :

For Δt_i = 1 throughout i.e. from 4 to 14s.

t	C	tC
4	0	0
5	1/2 x	5/2 x
6	x	6 x
7	7/8 x	49/8 x
8	3/4 x	24/4 x
9	5/8 x	45/8 x
10	1/2 x	10/2 x
11	3/8 x	33/8 x
12	1/4 x	12/4 x
13	1/8 x	13/8 x
14	0	0

Area under C_{pulse} curve $= A = \int_0^\infty C\,dt$

$=$ Area of triangles (1 + 2)

$$= \frac{1}{2}(6-4)\,x + \frac{1}{2}(14-6)\,x$$

$$= 5x$$

OR :

$$A = \Sigma C_i \Delta t_i$$

$$= \Sigma C_i \quad \text{as} \quad \Delta t_i = 1$$

$$= \left[0 + \frac{1}{2}x + x + \frac{7}{8}x + \frac{3}{4}x + \frac{5}{8}x + \frac{1}{2}x + \frac{3}{8}x + \frac{1}{4}x + \frac{1}{8}x + 0\right]$$

$$= \frac{40}{8}x = 5x$$

$$\int_0^\infty tC\,dt = \Sigma t_i C_i \Delta t_i$$

$$= \Sigma t_i C_i \quad \text{as} \quad \Delta t_i = 1$$

$$= [0 + 5/2\,x + 6x + 49/8\,x + 24/4\,x + 45/8\,x + 10/2\,x + 33/8\,x + 12/4\,x + 13/8\,x + 0]$$

$$= \frac{320}{8}x = 40\,x$$

$$\bar{t} = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt} = \frac{\Sigma t_i C_i \Delta t_i}{\Sigma C_i \Delta t_i} = \frac{\Sigma t_i C_i}{\Sigma C_i}$$

$$= \frac{\Sigma t_i C_i}{A}$$

$$= \frac{40\,x}{5\,x} = 8\,s$$

$\bar{t}$ from C_{pulse} curve = 8 s.

$\bar{t}$ from material balance = 8 s.

As $\bar{t}$ values agree, the results are consistent. ... **Ans.**

Extra : Use of Simpson's $\frac{1}{3}$rd rule :

Let Δt = 1 s from t = 4 to 6 s

and Δt = 2 s from t = 6 to 14 s.

t	C	tC
4	0	0
5	1/2 x	5/2 x
6	x	6 x
8	3/4 x	24/4 x
10	1/2 x	10/2 x
12	1/4 x	12/4 x
14	0	0

We will use Simpson's $\frac{1}{3}$rd rule for evaluation purpose.

$$\int_0^{\infty} C\,dt = \int_0^4 C\,dt + \int_4^6 C\,dt + \int_6^{14} C\,dt$$

$$= \int_4^6 C\,dt + \int_6^{14} C\,dt \qquad \text{as} \quad \int_0^4 C\,dt = 0$$

$$= \frac{1}{3}\left[0 + 4 \times \frac{1}{2}x + x\right] + \frac{2}{3}\left[x + 4 \times \frac{3}{4}x + \frac{1}{2}x + \frac{1}{2}x + 4 \times \frac{1}{4}x + 0\right]$$

$$= x + 4x = 5x$$

[for t = 4 to 6s … h = 1 and for t = 6 to 14 s … h = 2]

$$\int_0^{\infty} tC\,dt = \int_0^4 tC\,dt + \int_4^6 tC\,dt + \int_6^{14} tC\,dt$$

$$= \int_4^6 tC\,dt + \int_6^{14} tC\,dt \quad \text{as} \quad \int_0^4 tC\,dt = 0$$

$$= \frac{1}{3}\left[0 + 4 \times \frac{5}{2}x + 6x\right]$$

$$+ \frac{2}{3}\left[6x + 4 \times \frac{24}{4}x + \frac{10}{2}x + \frac{10}{2}x + 4 \times \frac{12}{4}x + 0\right]$$

$$= \frac{16x}{3} + \frac{104x}{3}$$

$$= \frac{120x}{3} = 40x$$

∴ $\bar{t}$ from C_{pulse} curve :

$$\bar{t} = \frac{\int_0^{\infty} tC\,dt}{\int_0^{\infty} C\,dt}$$

$$= \frac{40x}{5x}$$

$$= 8\,s$$

[You can adopt this method too for evaluating $\bar{t}$ from an experimental tracer curve.]

Ex. 9 : A liquid reactant stream with $C_{Ao} = 1$ mol/l passes through two CSTRs in series. Th concentration of A in the stream leaving the first reactor is 0.5 mol/l. Find the concentration of A in the exit stream from the second reactor. The reaction is second-order with respect to A an $V_2/V_1 = 2$.

Solution : A → product, $-r_A = kC_A^2$

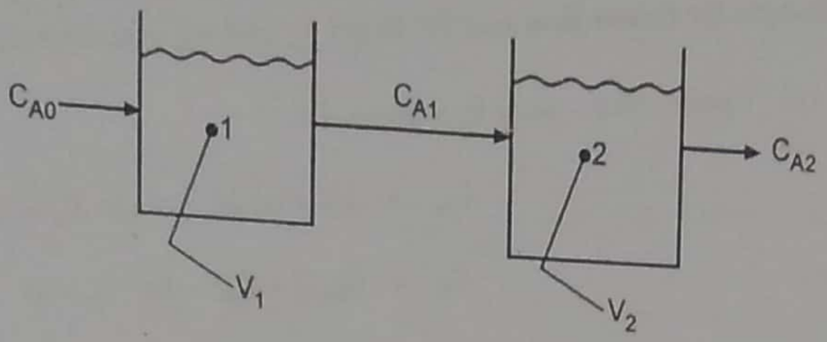

Fig. E 9A : CSTRs in series

Given : $\frac{V_2}{V_1} = 2$, $C_{A0} = 1$ mol/l , $C_{A1} = 0.5$ mol/l

For CSTR-1 :

$$\tau_1 = \frac{C_{A0} - C_{A1}}{(-r_A)_1}$$

$$\tau_1 = \frac{V_1}{v} = \frac{C_{A0} - C_{A1}}{kC_{A1}^2} = \frac{C_0 - C_1}{kC_1^2}, \quad C_{A1} = C_1, \ C_{A0} = C_0$$

$$\frac{V_1}{v} = \frac{1 - 0.5}{k\,(0.5)^2}$$

$$\therefore \quad k = 2v/V_1$$

For CSTR-2 :

$$\tau_2 = \frac{C_{A1} - C_{A2}}{(-r_A)_2} \qquad C_{A1} = C_1 \text{ and } C_{A2} = C_2$$

$$\tau_2 = \frac{V_2}{v} = \frac{C_1 - C_2}{(-r_A)_2}$$

$$\frac{V_2}{v} = \frac{C_1 - C_2}{kC_2^2}$$

$$\frac{V_2}{v} = \frac{0.5 - C_2}{(2v/V_1)\,C_2^2} \qquad \text{as } k = 2v/V_1$$

$$\frac{2V_2}{V_1} = \frac{0.5 - C_2}{C_2^2}$$

$$\frac{V_2}{V_1} = 2$$

$$\therefore \quad 2 \times 2 = \frac{0.5 - C_2}{C_2^2}$$

$$4C_2^2 + C_2 - 0.5 = 0$$

$$C_2 = C_{A2} = \frac{-1 \pm [(1)^2 - 4 \times 4 \times (-0.5)]^{1/2}}{2 \times 4}$$

$$= 0.25$$

The concentration of A in the exit stream of the second reactor = 0.25 mol/l. **... Ans.**

Ex. 10 : An aqueous reactant stream with $C_{A_0} = 4$ mol/l passes through a mixed flow reactor followed by a plug flow reactor. Determine the concentration at the exit of the plug flow reactor if $C_A = 1$ mol/l in the mixed reactor. The reaction is second-order with respect to A and $V_{plug}/V_{mixed} = 3$.

Solution : $A \rightarrow$ product, $-r_A = kC_A^2$

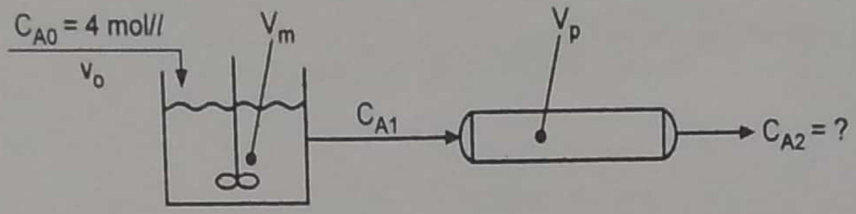

Fig. E 10A (a) : Reactors in series – mixed flow followed by plug flow

Given : $\frac{V_p}{V_m} = 3$ i.e. volume of the plug flow unit is three times that of the mixed flow unit.

$C_{A_0} = C_0 = 4$ mol/l – concentration of A in the stream entering a mixed flow reactor.

The concentration of A in a mixed flow reactor = $C_A = 1$ mol/l.

The concentration of A in the exit of a mixed flow reactor is same as that in the reactor.

$$\therefore \qquad C_{A1} = C_1 = 1 \text{ mol}/l$$

For mixed flow reactor :

$$\tau_m = \frac{V_m}{v_0} = \frac{C_0 - C_1}{(-r_A)_1} = \frac{C_0 - C_1}{kC_1^2}$$

$$k = \left(\frac{C_0 - C_1}{C_1^2}\right)\left(\frac{v_0}{V_m}\right)$$

$$= \frac{(4-1)}{(1)^2}\,\frac{v_0}{V_m} = \frac{3\,v_0}{V_m}$$

We will use this k value for determination of C_{A2} (i.e. C_2) concentration of A in the exit stream from a plug flow reactor.

For plug flow reactor :

$$\frac{V_p}{v_0} = -\int_{C_{A1}}^{C_{A2}} \frac{dC_A}{(-r_A)}$$

$$= -\int_{C_1}^{C_2} \frac{dC}{kC^2}\,, \quad C_A = C,\ C_{A1} = C_1 \text{ and } C_{A2} = C_2$$

$$= -\frac{1}{k}\int_{C_1}^{C_2} \frac{dC}{C^2}$$

$$= -\frac{1}{k}\left[-\left(\frac{1}{C}\right)\right]_{C_1}^{C_2}$$

$$\frac{V_p}{v_0} = \frac{1}{k}\left[\frac{1}{C_2} - \frac{1}{C_1}\right]$$

$$k = 3\ v_o/V_m$$

$$\frac{V_p}{v_0} = \frac{1}{3v_o/V_m}\left[\frac{1}{C_2} - \frac{1}{C_1}\right]$$

$$\frac{3V_p}{V_m} = \frac{1}{C_2} - \frac{1}{C_1}$$

Given : $V_p/V_m = 3$ and $C_1 = C_{A1} = 1$ mol/*l*

$$3 \times 3 = \frac{1}{C_2} - \frac{1}{1}$$

$$C_2 = 0.1 \text{ mol}/l$$

The concentration of A at the exit of a plug flow reactor = $C_2 = C_{A2} = 0.10$ mol/*l* ... **Ans.**

Ex. 10 : The following data on the reaction A → R are obtained by conducting steady-state kinetic runs in a mixed flow reactor.

τ, s	60	35	11	20	11
C_{Ao}, mmol/*l*	50	100	100	200	200
C_A, mmol/*l*	20	40	60	80	100

Determine the space time needed for treating a feed with C_{Ao} = 100 mmol/*l* to 80% conversion

(i) in a plug flow reactor

(ii) in a mixed flow reactor.

Solution : A → R, $\varepsilon_A = 0$

$$\therefore \quad \tau = \frac{C_{Ao} - C_A}{-r_A}$$

$$\frac{1}{-r_A} = \frac{\tau}{C_{Ao} - C_A}$$

Now, calculate and tabulate $1/-r_A$ at the measured C_A using above equation.

C_{Ao}	50	100	100	200	200
C_A	20	40	60	80	100
τ	60	35	11	20	11
$\frac{1}{-r_A} = \frac{\tau}{C_{Ao} - C_A}$	2	0.58	0.275	0.167	0.11

Plot $1/-r_A$ v/s C_A. Measure area under curve for plug flow reactor and measure area of rectangle for mixed flow reactor to get τ_p and τ_m respectively between C_{Ao} and C_{Af}.

(i) Space time – plug flow reactor :

$$C_{Ao} = 100 \text{ mmol}/l \quad \text{and} \quad X_A = 0.80$$

$$C_A = C_{Ao}(1-X_A) \quad \text{for} \quad \varepsilon_A = 0$$

$$= 100\,(1-0.80) = 20 \text{ mmol}/l$$

Refer Fig. E 10A (**b**) :

For plug flow reactor for $\varepsilon_A = 0$

$$\tau = -\int_{C_{Ao}}^{C_{Af}} \frac{dC_A}{-r_A}$$

So space time is the area under the curve $1/-r_A$ v/s C_A between $C_{Ao} = 100$ mmol/l an $C_{Af} = 20$ mmol/l.

$$\text{Area under the curve} = 862 \text{ mm}^2 = 8.62 \text{ cm}^2$$

$$\tau_p = \text{area under the curve} \times \text{scale y-axis} \times \text{scale x-axis}$$

$$= 8.62 \times \frac{0.2}{1} \times \frac{20}{1}$$

$$= 34.48 \approx 34.5 \text{ s}$$

Space time needed in a plug flow reactor = 34.5 s ... **Ans.** (i)

(ii) Space time – mixed flow reactor :

Space time is the area of rectangle of $1/-r_A$ v/s C_A between $C_{Ao} = 100$ mmol/l and $C_A = C_{Af}$ = 20 mmol/l.

From Fig. E 10A : Area of rectangle = 4000 mm^2 = 40 cm^2

$$\tau_m = \text{Area} \times \text{scale of y-axis} \times \text{scale of x-axis}$$

$$= 40 \times \frac{0.2}{1} \times \frac{20}{1} = 160 \text{ s}$$

Space time needed in a mixed flow **reactor** = **160 s** ... **Ans.** (ii) [illegible] ⑦ ⑧

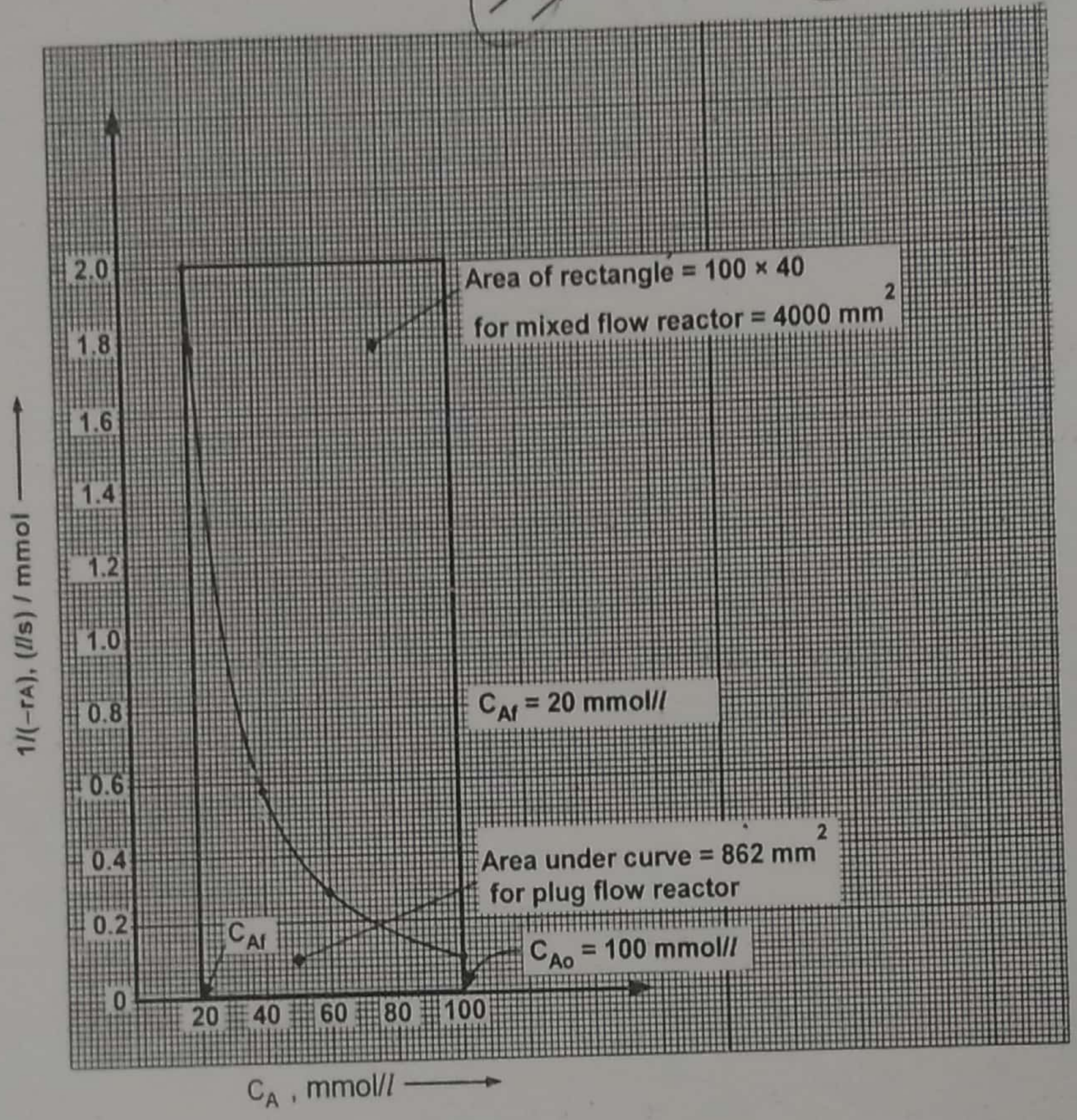

Fig. E 10A (b)

□□□

50 – homo..
56
72
~~[illegible]~~
135
T-pg-7.
~~[illegible]~~ 5
octave-100, 99, 104, 106 +
125
129

[illegible] cuts]

1 to 3

4, 5

1 2, 3 4, 6, ⑦