CHAPTER 1

Reactor Design—General Principles

1.1. BASIC OBJECTIVES IN DESIGN OF A REACTOR

In chemical engineering physical operations such as fluid flow, heat transfer, mass transfer and separation processes play a very large part; these have been discussed in Volumes 1 and 2. In any manufacturing process where there is a chemical change taking place, however, the chemical reactor is at the heart of the plant.

In size and appearance it may often seem to be one of the least impressive items of equipment, but its demands and performance are usually the most important factors in the design of the whole plant.

When a new chemical process is being developed, at least some indication of the performance of the reactor is needed before any economic assessment of the project as a whole can be made. As the project develops and its economic viability becomes established, so further work is carried out on the various chemical engineering operations involved. Thus, when the stage of actually designing the reactor in detail has been reached, the project as a whole will already have acquired a fairly definite form. Among the major decisions which will have been taken is the rate of production of the desired product. This will have been determined from a market forecast of the demand for the product in relation to its estimated selling price. The reactants to be used to make the product and their chemical purity will have been investigated, and information about the composition of the products from the reaction, including any byproducts, should be available.

On the other hand, a reactor may have to be designed as part of a modification to an existing process. Because the new reactor has then to tie in with existing units, its duties can be even more clearly specified than when the whole process is new. Naturally, in practice, detailed knowledge about the performance of the existing reactor would be incorporated in the design of the new one.

As a general statement of the basic objectives in designing a reactor, we can say therefore that the aim is to produce a *specified product* at a *given rate* from *known reactants*. In proceeding further however a number of important decisions must be made and there may be scope for considerable ingenuity in order to achieve the best result. At the outset the two most important questions to be settled are:

(a) The type of reactor to be used and its method of operation. Will the reaction be carried out as a batch process, a continuous flow process, or possibly as a hybrid of the two? Will the reactor operate isothermally, adiabatically or in some intermediate manner?

(b) The physical condition of the reactants at the inlet to the reactor. Thus, the basic processing conditions in terms of pressure, temperature and compositions of the reactants on entry to the reactor have to be decided, if not already specified as part of the original process design.

Subsequently, the aim is to reach logical conclusions concerning the following principal features of the reactor:

- (a) The overall size of the reactor, its general configuration and the more important dimensions of any internal structures.
- (b) The exact composition and physical condition of the products emerging from the reactor. The composition of the products must of course lie within any limits set in the original specification of the process.
- (c) The temperatures prevailing within the reactor and any provision which must be made for heat transfer.
- (d) The operating pressure within the reactor and any pressure drop associated with the flow of the reaction mixture.

1.1.1. Byproducts and their Economic Importance

Before taking up the design of reactors in detail, let us first consider the very important question of whether any byproducts are formed in the reaction. Obviously, consumption of reactants to give unwanted, and perhaps unsaleable, byproducts is wasteful and will directly affect the operating costs of the process. Apart from this, however, the nature of any byproducts formed and their amounts must be known so that plant for separating and purifying the products from the reaction may be correctly designed. The appearance of unforeseen byproducts on start-up of a full-scale plant can be utterly disastrous. Economically, although the cost of the reactor may sometimes not appear to be great compared with that of the associated separation equipment such as distillation columns, etc., it is the composition of the mixture of products issuing from the reactor which determines the capital and operating costs of the separation processes.

For example, in producing ethylene⁽¹⁾ together with several other valuable hydrocarbons like butadiene from the thermal cracking of naphtha, the design of the whole complex plant is determined by the composition of the mixture formed in a tubular reactor in which the conditions are very carefully controlled. As we shall see later, the design of a reactor itself can affect the amount of byproducts formed and therefore the size of the separation equipment required. The design of a reactor and its mode of operation can thus have profound repercussions on the remainder of the plant.

1.1.2. Preliminary Appraisal of a Reactor Project

In the following pages we shall see that reactor design involves all the basic principles of chemical engineering with the addition of chemical kinetics. Mass transfer, heat transfer and fluid flow are all concerned and complications arise when, as so often is the case, interaction occurs between these transfer processes and the reaction itself. In designing a reactor it is essential to weigh up all the

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various factors involved and, by an exercise of judgement, to place them in their proper order of importance. Often the basic design of the reactor is determined by what is seen to be the most troublesome step. It may be the chemical kinetics; it may be mass transfer between phases; it may be heat transfer; or it may even be the need to ensure safe operation. For example, in oxidising naphthalene or o-xylene to phthalic anhydride with air, the reactor must be designed so that ignitions, which are not infrequent, may be rendered harmless. The theory of reactor design is being extended rapidly and more precise methods for detailed design and optimisation are being evolved. However, if the final design is to be successful, the major decisions taken at the outset must be correct. Initially, a careful appraisal of the basic role and functioning of the reactor is required and at this stage the application of a little chemical engineering common sense may be invaluable.

1.2. CLASSIFICATION OF REACTORS AND CHOICE OF REACTOR TYPE

1.2.1. Homogeneous and Heterogeneous Reactors

Chemical reactors may be divided into two main categories, homogeneous and heterogeneous. In homogeneous reactors only one phase, usually a gas or a liquid, is present. If more than one reactant is involved, provision must of course be made for mixing them together to form a homogenous whole. Often, mixing the reactants is the way of starting off the reaction, although sometimes the reactants are mixed and then brought to the required temperature.

In heterogeneous reactors two, or possibly three, phases are present, common examples being gas-liquid, gas-solid, liquid-solid and liquid-liquid systems. In cases where one of the phases is a solid, it is quite often present as a catalyst; gas-solid catalytic reactors particularly form an important class of heterogeneous chemical reaction systems. It is worth noting that, in a heterogeneous reactor, the chemical reaction itself may be truly heterogeneous, but this is not necessarily so. In a gas-solid catalytic reactor, the reaction takes place on the surface of the solid and is thus heterogeneous. However, bubbling a gas through a liquid may serve just to dissolve the gas in the liquid where it then reacts homogeneously; the reaction is thus homogeneous but the reactor is heterogeneous in that it is required to effect contact between two phases—gas and liquid. Generally, heterogeneous reactors exhibit a greater variety of configuration and contacting pattern than homogeneous reactors. Initially, therefore, we shall be concerned mainly with the simpler homogeneous reactors, although parts of the treatment that follows can be extended to heterogeneous reactors with little modification.

1.2.2. Batch Reactors and Continuous Reactors

Another kind of classification which cuts across the homogeneous-heterogeneous division is the mode of operation—batchwise or continuous. Batchwise operation, shown in Fig. 1.1a, is familiar to anybody who has carried out small-scale preparative reactions in the laboratory. There are many situations, however,

especially in large-scale operation, where considerable advantages accrue by carrying out a chemical reaction continuously in a flow reactor.

Figure 1.1 illustrates the two basic types of flow reactor which may be employed. In the *tubular-flow reactor* (b) the aim is to pass the reactants along a tube so that there is as little intermingling as possible between the reactants entering the tube and the products leaving at the far end. In the *continuous stirred-tank reactor* (C.S.T.R.) (c) an agitator is deliberately introduced to disperse the reactants thoroughly into the reaction mixture immediately they enter the tank. The product stream is drawn off continuously and, in the ideal state of perfect mixing, will have the same composition as the contents of the tank. In some ways, using a C.S.T.R., or *backmix reactor* as it is sometimes called, seems a curious method of conducting a reaction because as soon as the reactants enter the tank they are mixed and a portion leaves in the product stream flowing out. To reduce this effect, it is often advantageous to employ a number of stirred tanks connected in series as shown in Fig. 1.1d.

The stirred-tank reactor is by its nature well suited to liquid-phase reactions. The tubular reactor, although sometimes used for liquid-phase reactions, is the natural choice for gas-phase reactions, even on a small scale. Usually the temperature or catalyst is chosen so that the rate of reaction is high, in which case a comparatively small tubular reactor is sufficient to handle a high volumetric flowrate of gas. A few gas-phase reactions, examples being partial combustion and certain chlorinations, are carried out in reactors which resemble the stirred-tank reactor; rapid mixing is usually brought about by arranging for the gases to enter with a vigorous swirling motion instead of by mechanical means.



FIG. 1.1. Basic types of chemical reactors

- (a) Batch reactor
- (b) Tubular-flow reactor
- (c) Continuous stirred-tank reactor (C.S.T.R.) or "backmix reactor"
- (d) C.S.T.R.s in series as frequently used

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1.2.3. Variations in Contacting Pattern — Semi-batch Operation

Another question which should be asked in assessing the most suitable type of reactor is whether there is any advantage to be gained by varying the contacting pattern. Figure 1.2a illustrates the *semi-batch* mode of operation. The reaction vessel here is essentially a batch reactor, and at the start of a batch it is charged with one of the reactants A. However, the second reactant B is not all added at once, but continuously over the period of the reaction. This is the natural and obvious way to carry out many reactions. For example, if a liquid has to be treated with a gas, perhaps in a chlorination or hydrogenation reaction, the gas is normally far too voluminous to be charged all at once to the reactor; instead it is fed continuously at the rate at which it is used up in the reaction. Another case is where the reaction is too violent if both reactants are mixed suddenly together. Organic nitration, for example, can be conveniently controlled by regulating the rate of addition of the nitrating acid. The maximum rate of addition of the second reactant in such a case will be determined by the rate of heat transfer.

A characteristic of semi-batch operation is that the concentration C_B of the reactant added slowly, **B** in Fig. 1.2, is low throughout the course of the reaction. This may be an advantage if more than one reaction is possible, and if the desired reaction is favoured by a low value of C_B . Thus, the semi-batch method may be chosen for a further reason, that of improving the yield of the desired product, as shown in Section 1.10.4.

Summarising, a semi-batch reactor may be chosen:

- (a) to react a gas with a liquid,
- (b) to control a highly exothermic reaction, and
- (c) to improve product yield in suitable circumstances.

In semi-batch operation, when the initial charge of A has been consumed, the flow of **B** is interrupted, the products discharged, and the cycle begun again with a fresh charge of A. If required, however, the advantages of semi-batch operation may be retained but the reactor system designed for continuous flow of both reactants. In



FIG. 1.2. Examples of possible variations in reactant contacting pattern

- (a) Semi-batch operation
- (b) Tubular reactor with divided feed
- (c) Stirred-tank reactors with divided feed
- (in each case the concentration of **B**, C_B , is low throughout)

the tubular flow version (Fig. 1.2b) and the stirred-tank version (Fig. 1.2c), the feed of **B** is divided between several points. These are known as *cross-flow* reactors. In both cases C_B is low throughout.

1.2.4. Influence of Heat of Reaction on Reactor Type

Associated with every chemical change there is a heat of reaction, and only in a few cases is this so small that it can be neglected. The magnitude of the heat of reaction often has a major influence on the design of a reactor. With a strongly exothermic reaction, for example, a substantial rise in temperature of the reaction mixture will take place unless provision is made for heat to be transferred as the reaction proceeds. It is important to try to appreciate clearly the relation between the enthalpy of reaction, the heat transferred, and the temperature change of the reaction mixture; quantitatively this is expressed by an enthalpy balance (Section 1.5). If the temperature of the reaction mixture is to remain constant (isothermal operation), the heat equivalent to the heat of reaction at the operating temperature must be transferred to or from the reactor. If no heat is transferred (adjabatic operation), the temperature of the reaction mixture will rise or fall as the reaction proceeds. In practice, it may be most convenient to adopt a policy intermediate between these two extremes; in the case of a strongly exothermic reaction, some heat-transfer from the reactor may be necessary in order to keep the reaction under control, but a moderate temperature rise may be quite acceptable, especially if strictly isothermal operation would involve an elaborate and costly control scheme.

In setting out to design a reactor, therefore, two very important questions to ask are:

- (a) What is the heat of reaction?
- (b) What is the acceptable range over which the temperature of the reaction mixture may be permitted to vary?

The answers to these questions may well dominate the whole design. Usually, the temperature range can only be roughly specified; often the lower temperature limit is determined by the slowing down of the reaction, and the upper temperature limit by the onset of undesirable side reactions.

Adiabatic Reactors

If it is feasible, adiabatic operation is to be preferred for simplicity of design. Figure 1.3 shows the reactor section of a plant for the catalytic reforming of petroleum naphtha; this is an important process for improving the octane number of gasoline. The reforming reactions are mostly endothermic so that in adiabatic operation the temperature would fall during the course of the reaction. If the reactor were made as one single unit, this temperature fall would be too large, i.e. either the temperature at the inlet would be too high and undesired reactions would occur, or the reaction would be incomplete because the temperature near the outlet would be too low. The problem is conveniently solved by dividing the reactor into three sections. Heat is supplied externally between the sections, and the intermediate temperatures are raised so that each section of the reactor will operate adiabatically.



FIG. 1.3. Reactor system of a petroleum naphtha catalytic reforming plant. (The reactor is divided into three units each of which operates *adiabatically*, the heat required being supplied at intermediate stages via an external furnace)

Dividing the reactor into sections also has the advantage that the intermediate temperature can be adjusted independently of the inlet temperature; thus an optimum temperature distribution can be achieved. In this example we can see that the furnaces where heat is transferred and the catalytic reactors are quite separate units, each designed specifically for the one function. This separation of function generally provides ease of control, flexibility of operation and often leads to a good overall engineering design.

Reactors with Heat Transfer

If the reactor does not operate adiabatically, then its design must include provision for heat transfer. Figure 1.4 shows some of the ways in which the contents of a batch reactor may be heated or cooled. In a and b the jacket and the coils form part of the reactor itself, whereas in c an external heat exchanger is used with a recirculating pump. If one of the constituents of the reaction mixture, possibly a



FIG. 1.4. Batch reactors showing different methods of heating or cooling

- (a) Jacket
- (b) Internal coils
- (c) External heat exchangers

solvent, is volatile at the operating temperature, the external heat exchanger may be a reflux condenser, just as in the laboratory.

Figure 1.5 shows ways of designing tubular reactors to include heat transfer. If the amount of heat to be transferred is large, then the ratio of heat transfer surface to reactor volume will be large, and the reactor will look very much like a heat exchanger as in Fig. 1.5b. If the reaction has to be carried out at a high temperature and is strongly endothermic (for example, the production of ethylene by the thermal cracking of naphtha or ethane—see also Section 1.7.1, Example 1.4), the reactor will be directly fired by the combustion of oil or gas and will look like a pipe furnace (Fig. 1.5c).



FIG. 1.5. Methods of heat transfer to tubular reactors

- (a) Jacketed pipe
- (b) Multitube reactor (tubes in parallel)
- (c) Pipe furnace (pipes mainly in series although some pipe runs may be in parallel)

Autothermal Reactor Operation

If a reaction requires a relatively high temperature before it will proceed at a reasonable rate, the products of the reaction will leave the reactor at a high temperature and, in the interests of economy, heat will normally be recovered from them. Since heat must be supplied to the reactants to raise them to the reaction temperature, a common arrangement is to use the hot products to heat the incoming feed as shown in Fig. 1.6a. If the reaction is sufficiently exothermic, enough heat will be produced in the reaction to overcome any losses in the system and to provide the necessary temperature difference in the heat exchanger. The term *autothermal* is used to describe such a system which is completely self-supporting in its thermal energy requirements.

The essential feature of an autothermal reactor system is the feedback of reaction heat to raise the temperature and hence the reaction rate of the incoming reactant stream. Figure 1.6 shows a number of ways in which this can occur. With a tubular reactor the feedback may be achieved by external heat exchange, as in the reactor shown in Fig. 1.6a, or by internal heat exchange as in Fig. 1.6b. Both of these are catalytic reactors; their thermal characteristics are discussed in more detail in Chapter 3, Section 3.6.2. Being catalytic the reaction can only take place in that part of the reactor which holds the catalyst, so the temperature profile has the form



FIG. 1.6. Autothermal reactor operation

indicated alongside the reactor. Figure 1.6c shows a continuous stirred-tank reactor in which the entering cold feed immediately mixes with a large volume of hot products and rapid reaction occurs. The combustion chamber of a liquid fuelled rocket motor is a reactor of this type, the products being hot gases which are ejected at high speed. Figure 1.6d shows another type of combustion process in which a laminar flame of conical shape is stabilised at the orifice of a simple gas burner. In this case the feedback of combustion heat occurs by transfer upstream in a direction opposite to the flow of the cold reaction mixture.

Another feature of the autothermal system is that, although ultimately it is self-supporting, an external source of heat is required to start it up. The reaction has to be ignited by raising some of the reactants to a temperature sufficiently high for the reaction to commence. Moreover, a stable operating state may be obtainable only over a limited range of operating conditions. This question of stability is discussed further in connection with autothermal operation of a continuous stirredtank reactor (Section 1.8.4).

1.3. CHOICE OF PROCESS CONDITIONS

The choice of temperature, pressure, reactant feed rates and compositions at the inlet to the reactor is closely bound up with the basic design of the process as a whole. In arriving at specifications for these quantities, the engineer is guided by knowledge available on the fundamental physical chemistry of the reaction. Usually he will also have results of laboratory experiments giving the fraction of the reactants converted and the products formed under various conditions. Sometimes he may have the benefit of highly detailed information on the performance of the process from a pilot plant, or even a large-scale plant. Although such direct experience of reactor conditions may be invaluable in particular cases, we shall here be concerned primarily with design methods based upon fundamental physico-chemical principles.

1.3.1. Chemical Equilibria and Chemical Kinetics

The two basic principles involved in choosing conditions for carrying out a reaction are thermodynamics, under the heading of chemical equilibrium, and chemical kinetics. Strictly speaking, every chemical reaction is reversible and, no matter how fast a reaction takes place, it cannot proceed beyond the point of chemical equilibrium in the reaction mixture at the particular temperature and pressure concerned. Thus, under any prescribed conditions, the principle of chemical equilibrium, through the equilibrium constant, determines how far the reaction can possibly proceed given sufficient time for equilibrium to be reached. On the other hand, the principle of chemical kinetics determines at what rate the reaction will proceed towards this maximum extent. If the equilibrium constant is very large, then for all practical purposes the reaction may be said to be *irreversible*. However, even when a reaction is claimed to be *irreversible* an engineer would be very unwise not to calculate the equilibrium constant and check the position of equilibrium, especially if high conversions are required.

In deciding process conditions, the two principles of thermodynamic equilibrium and kinetics need to be considered together; indeed, any complete rate equation for a reversible reaction will include the equilibrium constant or its equivalent (see Section 1.4.4) but complete rate equations are not always available to the engineer. The first question to ask is: in what temperature range will the chemical reaction take place at a reasonable rate (in the presence, of course, of any catalyst which may have been developed for the reaction)? The next step is to calculate values of the equilibrium constant in this temperature range using the principles of chemical thermodynamics. (Such methods are beyond the scope of this chapter and any reader unfamiliar with this subject should consult a standard textbook⁽²⁾.) The equilibrium constant K_p of a reaction depends only on the temperature as indicated by the relation:

$$\frac{\mathrm{dln}K_p}{\mathrm{d}T} = \frac{\Delta H}{\mathbf{R}T^2} \tag{1.1}$$

where $-\Delta H$ is the heat of reaction. The equilibrium constant is then used to determine the limit to which the reaction can proceed under the conditions of temperature, pressure and reactant compositions which appear to be most suitable.

1.3.2. Calculation of Equilibrium Conversion

Whereas the equilibrium constant itself depends on the temperature only, the conversion at equilibrium depends on the composition of the original reaction mixture and, in general, on the pressure. If the equilibrium constant is very high, the reaction may be treated as being irreversible. If the equilibrium constant is low, however, it may be possible to obtain acceptable conversions only by using high or low pressures. Two important examples are the reactions:

$$C_2H_4 + H_2O \rightleftharpoons C_2H_5OH$$
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

both of which involve a decrease in the number of moles as the reaction proceeds, and therefore high pressures are used to obtain satisfactory equilibrium conversions.

Thus, in those cases in which reversibility of the reaction imposes a serious limitation, the equilibrium conversion must be calculated in order that the most advantageous conditions to be employed in the reactors may be chosen; this may be seen in detail in the following example of the styrene process. A study of the design of this process is also very instructive in showing how the basic features of the reaction, namely equilibrium, kinetics, and suppression of byproducts, have all been satisfied in quite a clever way by using steam as a diluent.

Example 1.1

A Process for the Manufacture of Styrene by the Dehydrogenation of Ethylbenzene

Let us suppose that we are setting out from first principles to investigate the dehydrogenation of ethylbenzene which is a well established process for manufacturing styrene:

$$C_6H_5 \cdot CH_2 \cdot CH_3 = C_6H_5 \cdot CH \cdot CH_2 + H_2$$

There is available a catalyst which will give a suitable rate of reaction at 560°C. At this temperature the equilibrium constant for the reaction above is:

$$\frac{P_{\rm SL} \times P_{\rm H}}{P_{\rm EL}} = K_p = 100 \text{ mbar} = 10^4 \text{ N/m}^2 \tag{A}$$

where $P_{\rm Et}$, $P_{\rm St}$ and $P_{\rm H}$ are the partial pressures of ethylbenzene, styrene and hydrogen respectively.

Part (i)

Feed pure ethylbenzene: If a feed of pure ethylbenzene is used at 1 bar pressure, determine the fractional conversion at equilibrium.

Solution

This calculation requires not only the use of the equilibrium constant, but also a material balance over the reactor. To avoid confusion, it is as well to set out this material balance quite clearly even in this comparatively simple case.

First it is necessary to choose a basis; let this be 1 mole of ethylbenzene fed into the reactor: a fraction α_e of this will be converted at equilibrium. Then, from the above stoichiometric equation, α_e mole styrene and α_e mole hydrogen are formed, and $(1 - \alpha_e)$ mole ethylbenzene remains unconverted. Let the total pressure at the outlet of the reactor be P which we shall later set equal to 1 bar.

$C_6H_5 \cdot C_2H_5 \longrightarrow \mathbb{R}E$	ACTO	$\begin{array}{c} C_6 H \\ \hline R \\ \hline \end{array} \longrightarrow \begin{array}{c} C_6 H \\ H_2 \end{array}$	Η ₅ • C₂H5 Η ₅ • C₂H3	Temp Press	perature 560°C = 833 K ure P (1 bar = $1.0 \times 10^5 $ N/m ²)
	IN		a		<i>c</i>
	mole		mole	mole traction	partial pressure
$C_6H_5 \cdot C_2H_5$	1		$1 - \alpha_e$	$\frac{1-\alpha_e}{1+\alpha_e}$	$\frac{1-\alpha_e}{1+\alpha_e}P$
$C_6H_5 \cdot C_2H_3$			α	$\frac{\alpha_e}{1+\alpha_e}$	$\frac{\alpha_e}{1+\alpha_e}P$
H ₂			α,	$\frac{\alpha_e}{1+\alpha_e}$	$\frac{\alpha_e}{1+\alpha_e}P$
		TOTAL	$1 + \alpha_e$		

Since for 1 mole of ethylbenzene entering, the total number of moles increases to $1 + \alpha_e$, the mole fractions of the various species in the reaction mixture at the reactor outlet are shown in column b above. At a total pressure P, the partial pressures are given in column c (assuming ideal gas behaviour). If the reaction mixture is at chemical equilibrium, these partial pressures must satisfy equation A above:

$$K_p = \frac{P_{\text{St}} \times P_{\text{H}}}{P_{\text{El}}} = \frac{\frac{\alpha_e}{(1 + \alpha_e)} P \frac{\alpha_e}{(1 + \alpha_e)} P}{\frac{(1 - \alpha_e)}{(1 + \alpha_e)} P} = \frac{\alpha_e^2}{1 - \alpha_e^2} P$$

i.e.:

$$\frac{\alpha_e^2}{1-\alpha_e^2}P = 1.0 \times 10^4 \,\mathrm{N/m^2} \tag{B}$$

Thus, when P = 1 bar, $\alpha_e = 0.30$; i.e. the maximum possible conversion using pure ethylbenzene at 1 bar is only 30 per cent; this is not very satisfactory (although it is possible in some processes to operate at low conversions by separating and recycling reactants). Ways of improving this figure are now sought.

Note that equation B above shows that as P decreases α_e increases; this is the quantitative expression of Le Chatelier's principle that, because the total number of moles increases in the reaction, the decomposition of ethylbenzene is favoured by a reduction in pressure. There are, however, disadvantages in operating such a process at sub-atmospheric pressures. One disadvantage is that any ingress of air through leaks might result in ignition. A better solution in this instance is to reduce the partial pressure by diluting the ethylbenzene with an inert gas, while maintaining the total pressure slightly in excess of atmospheric. The inert gas most suitable for this process is steam: one reason for this is that it can be

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condensed easily in contrast to a gas such as nitrogen which would introduce greater problems in separation.

Part (ii)

Feed ethylbenzene with steam: If the feed to the process consists of ethylbenzene diluted with steam in the ratio 15 moles steam: 1 mole ethylbenzene, determine the new fractional conversion at equilibrium α'_{e} .

Solution

Again we set out the material balance in full, the basis being 1 mole ethylbenzene into the reactor.

$$C_{e}H_{3} \cdot C_{2}H_{5} \longrightarrow REACTOR \longrightarrow C_{e}H_{5} \cdot C_{2}H_{5} \qquad Temperature 560^{\circ}C = 833 \text{ K}$$

$$Pressure P (1 \text{ bar } = 1.0 \times 10^{5} \text{ N/m}^{3})$$

$$H_{2}O$$

$$IN \qquad OUT \qquad b \qquad ressure P (1 \text{ bar } = 1.0 \times 10^{5} \text{ N/m}^{3})$$

$$H_{2}O$$

$$C_{e}H_{5} \cdot C_{2}H_{5} \qquad 1 \qquad 1 - \alpha'_{e} \qquad \frac{1 - \alpha'_{e}}{16 + \alpha'_{e}} \qquad \frac{1 - \alpha'_{e}}{16 + \alpha'_{e}} P$$

$$C_{e}H_{5} \cdot C_{2}H_{5} \qquad 1 \qquad 1 - \alpha'_{e} \qquad \frac{1 - \alpha'_{e}}{16 + \alpha'_{e}} \qquad \frac{1 - \alpha'_{e}}{16 + \alpha'_{e}} P$$

$$C_{e}H_{5} \cdot C_{2}H_{5} \qquad - \qquad \alpha'_{e} \qquad \frac{\alpha'_{e}}{16 + \alpha'_{e}} \qquad \frac{\alpha'_{e}}{16 + \alpha'_{e}} P$$

$$H_{2} \qquad - \qquad \alpha'_{e} \qquad \frac{\alpha'_{e}}{16 + \alpha'_{e}} \qquad \frac{\alpha'_{e}}{16 + \alpha'_{e}} P$$

$$H_{2}O \qquad 15 \qquad 15 \qquad \frac{15}{16 + \alpha'_{e}} P$$

$$K_{p} = \frac{P_{31} \times P_{H}}{P_{E1}} = \frac{\frac{\alpha'_{e}}{(16 + \alpha'_{e})} P \frac{\alpha'_{e}}{(16 + \alpha'_{e})} P}{\frac{\alpha'_{e}}{(16 - \alpha'_{e})} P}$$

$$i.e.: \qquad \frac{\alpha'_{e}^{2}}{(16 + \alpha'_{e})(1 - \alpha'_{e})} P$$

Thus when P = 1 bar, $\alpha'_e = 0.70$; i.e. the maximum possible conversion has now been raised to 70 per cent. Inspection of equation C shows that the equilibrium conversion increases as the ratio of steam to ethylbenzene increases. However, as more steam is used, its cost increases and offsets the value of the increase in ethylbenzene conversion. The optimum steam: ethylbenzene ratio is thus determined by an economic balance.

Part (iii)

Final choice of reaction conditions in the styrene process:

Solution

The use of steam has a number of other advantages in the styrene process. The most important of these is that it acts as a source of internal heat supply so that the reactor can be operated adiabatically. The dehydrogenation reaction is strongly endothermic, the heat of reaction at 560°C being $(-\Delta H) = -125,000 \text{ kJ/kmol.}$ It is instructive to look closely at the conditions which were originally worked out for this process (Fig. 1.7). Most of the steam, 90 per cent of the total used, is heated separately from the ethylbenzene stream, and to a higher temperature (710°C) than is required at the inlet to the



FIG. 1.7. A process for styrene from ethylbenzene using 15 moles steam : 1 mole ethylbenzene. Operating pressure 1 bar. Conversion per pass 0.40. Overall relative yield 0.90

reactor. The ethylbenzene is heated in the heat exchangers to only 520°C and is then rapidly mixed with the hotter steam to give a temperature of 630°C at the inlet to the catalyst bed. If the ethylbenzene were heated to 630°C more slowly by normal heat exchange decomposition and coking of the heat transfer surfaces would tend to occur. Moreover, the tubes of this heat exchanger would have to be made of a more expensive alloy to resist the more severe working conditions. To help avoid coking, 10 per cent of the steam used is passed through the heat exchanger with the ethylbenzene. The presence of a large proportion of steam in the reactor also prevents coke deposition on the catalyst. By examining the equilibrium constant of reactions involving carbon such as:

$$C_6H_5 \cdot CH_2 \cdot CH_3 \rightleftharpoons 8C + 5H_2$$

 $C + H_2O \rightleftharpoons CO + H_2$

it may be shown that coke formation is not possible at high steam: ethylbenzene ratios.

The styrene process operates with a fractional conversion of ethylbenzene per pass of 0.40 compared with the equilibrium conversion of 0.70. This actual conversion of 0.40 is determined by the *rate* of the reaction over the catalyst at the temperature prevailing in the reactor. (Adiabatic operation means that the temperature falls with increasing conversion and the reaction tends to be quenched at the outlet.) The unreacted ethylbenzene is separated and recycled to the reactor. The overall yield in the process, i.e. moles of ethylbenzene transformed into styrene per mole of ethylbenzene supplied, is 0.90, the remaining 0.10 being consumed in unwanted side reactions. Notice that the conversion per pass could be increased by increasing the temperature at the inlet to the catalyst bed beyond 630° C, but the undesirable side reactions would increase, and the overall yield of the process would fall. The figure of 630° C for the inlet temperature is thus determined by an economic balance between the cost of separating unreacted ethylbenzene (which is high if the inlet temperature and conversion per pass are low), and the cost of ethylbenzene consumed in wasteful side reactions (which is high if the inlet temperature is high).

1.3.3. Ultimate Choice of Reactor Conditions

The use of steam in the styrene process above is an example of how an engineer can exercise a degree of ingenuity in reactor design. The advantages conferred by the steam may be summarised as follows:

- (a) it lowers the partial pressure of the ethylbenzene without the need to operate at sub-atmospheric pressures;
- (b) it provides an internal heat source for the endothermic heat of reaction, making adiabatic operation possible; and
- (c) it prevents coke formation on the catalyst and coking problems in the ethylbenzene heaters.

As the styrene process shows, it is not generally feasible to operate a reactor with a conversion per pass equal to the equilibrium conversion. The rate of a chemical reaction decreases as equilibrium is approached, so that the equilibrium conversion can only be attained if either the reactor is very large or the reaction unusually fast. The size of reactor required to give any particular conversion, which of course cannot exceed the maximum conversion predicted from the equilibrium constant, is calculated from the kinetics of the reaction. For this purpose we need quantitative data on the rate of reaction, and the rate equations which describe the kinetics are considered in the following section.

If there are two or more reactants involved in the reaction, both can be converted completely in a single pass only if they are fed to the reactor in the stoichiometric proportion. In many cases, the stoichiometric ratio of reactants may be the best, but in some instances, where one reactant (especially water or air) is very much cheaper than the other, it may be economically advantageous to use it in excess. For a given size of reactor, the object is to increase the conversion of the more costly reactant, possibly at the expense of a substantial decrease in the fraction of the cheaper reactant converted. Examination of the kinetics of the reaction is required to determine whether this can be achieved, and to calculate quantitatively the effects of varying the reactant ratio. Another and perhaps more common reason for departing from the stoichiometric proportions of reactants is to minimise the amount of byproducts formed. This question is discussed further in Section 1.10.4.

Ultimately, the final choice of the temperature, pressure, reactant ratio and conversion at which the reactor will operate depends on an assessment of the overall economics of the process. This will take into account the cost of the reactants, the cost of separating the products and the costs associated with any recycle streams. It should include all the various operating costs and capital costs of reactor and plant. In the course of making this economic assessment, a whole series of calculations of operating conditions, final conversion and reactor size may be performed with the aid of a computer, provided that the data are available. Each of these sets of conditions may be technically feasible, but the one chosen will be that which gives the maximum profitability for the project as a whole.

1.4. CHEMICAL KINETICS AND RATE EQUATIONS

When a homogeneous mixture of reactants is passed into a reactor, either batch or tubular, the concentrations of the reactants fall as the reaction proceeds. Experimentally it has been found that, in general, the rate of the reaction decreases as the concentrations of the reactants decrease. In order to calculate the size of the reactor required to manufacture a particular product at a desired overall rate of

production, the design engineer therefore needs to know how the rate of reaction at any time or at any point in the reactor depends on the concentrations of the reactants. Since the reaction rate varies also with temperature, generally increasing rapidly with increasing temperature, a *rate equation*, expressing the rate of reaction as a function of concentrations and temperature, is required in order to design a reactor.

1.4.1. Definition of Reaction Rate, Order of Reaction and Rate Constant

Let us consider a homogeneous irreversible reaction:

$$\nu_A \mathbf{A} + \nu_B \mathbf{B} + \nu_C \mathbf{C} \rightarrow \text{Products}$$

where A, B, C are the reactants and ν_A , ν_B , ν_C the corresponding coefficients in the stoichiometric equation. The rate of reaction can be measured as the moles of A transformed per unit volume and unit time. Thus, if n_A is the number of moles of A present in a volume V of reaction mixture, the rate of reaction with respect to A is defined as:

$$\mathfrak{R}_{\mathcal{A}} = -\frac{1}{V} \frac{\mathrm{d}n_{\mathcal{A}}}{\mathrm{d}t} \tag{1.2}$$

However, the rate of reaction can also be measured as the moles of B transformed per unit volume and unit time, in which case:

$$\Re_B = -\frac{1}{V} \frac{\mathrm{d}n_B}{\mathrm{d}t} \tag{1.3}$$

and $\mathfrak{R}_{B} = (\nu_{B}/\nu_{A})\mathfrak{R}_{A}$; similarly $\mathfrak{R}_{C} = (\nu_{C}/\nu_{A})\mathfrak{R}_{A}$ and so on. Obviously, when quoting a reaction rate, care must be taken to specify which reactant is being considered, otherwise ambiguity may arise. Another common source of confusion is the units in which the rate of reaction is measured. Appropriate units for \mathfrak{R}_{A} can be seen quite clearly from equation 1.2; they are kmol of A/m^{3} s or lb mol of A/ft^{3} s.

At constant temperature, the rate of reaction \Re_{λ} is a function of the concentrations of the reactants. Experimentally, it has been found that often (but not always) the function has the mathematical form:

$$\mathfrak{R}_{A}\left(=-\frac{1}{V}\frac{\mathrm{d}n_{A}}{\mathrm{d}t}\right)=kC_{A}^{\ \ p}C_{B}^{\ \ q}C_{C}^{\ \ r}$$
(1.4)

 $C_A(=n_A/V)$ being the molar concentration of A, etc. The exponents p, q, r in this expression are quite often (but not necessarily) whole numbers. When the functional relationship has the form of equation 1.4, the reaction is said to be of order p with respect to reactant A, q with respect to B and r with respect to C. The order of the reaction overall is (p + q + r).

The coefficient k in equation 1.4 is by definition the *rate constant* of the reaction. Its dimensions depend on the exponents p, q, r (i.e. on the order of the reaction); the units in which it is to be expressed may be inferred from the defining equation 1.4. For example, if a reaction:

$A \rightarrow Products$

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behaves as a simple first-order reaction, it has a rate equation:

$$\mathfrak{R}_{\mathcal{A}} = \mathbf{k}_{1}C_{\mathcal{A}} \tag{1.5}$$

If the rate of reaction $\mathcal{R}_{\mathcal{A}}$ is measured in units of kmol/m³ s and the concentration $C_{\mathcal{A}}$ in kmol/m³, then k_1 has the units s⁻¹. On the other hand, if the reaction above behaved as a second-order reaction with a rate equation:

$$\Re_A = k_2 C_A^{2} \tag{1.6}$$

the units of this rate constant, with \Re_A in kmol/m³ s and C_A in kmol/m³, are m³(kmol)⁻¹ s⁻¹. A possible source of confusion is that in some instances in the chemical literature, the rate equation, for say a second order gas phase reaction may be written $\Re_A = k_p P_A^2$, where P_A is the partial pressure of A and may be measured in N/m², bar or even in mm Hg. This form of expression results in rather confusing hybrid units for k_p and is not to be recommended.

If a large excess of one or more of the reactants is used, such that the concentration of that reactant changes hardly at all during the course of the reaction, the effective order of the reaction is reduced. Thus, if in carrying out a reaction which is normally second-order with a rate equation $\Re_A = k_2 C_A C_B$ an excess of **B** is used, then C_B remains constant and equal to the initial value C_{B0} . The rate equation may then be written $\Re_A = k_1 C_A$ where $k_1 = k_2 C_{B0}$ and the reaction is now said to be *pseudo-first-order*.

1.4.2. Influence of Temperature. Activation Energy

Experimentally, the influence of temperature on the rate constant of a reaction is well represented by the original equation of Arrhenius:

$$\boldsymbol{k} = \mathcal{A} \exp\left(-\mathbf{E}/\mathbf{R}T\right) \tag{1.7}$$

where T is the absolute temperature and **R** the gas constant. In this equation **E** is termed the activation energy, and \mathcal{A} the frequency factor. There are theoretical reasons to suppose that temperature dependence should be more exactly described by an equation of the form $k = \mathcal{A}'T^m \exp(-E/RT)$, with m usually in the range 0 to 2. However, the influence of the exponential term in equation 1.7 is in practice so strong as to mask any variation in \mathcal{A} with temperature, and the simple form of the relationship (equation 1.7) is therefore quite adequate. E is called the activation energy because in the molecular theory of chemical kinetics it is associated with an energy barrier which the reactants must surmount to form an activated complex in the transition state. Similarly, \mathcal{A} is associated with the frequency with which the activated complex breaks down into products; or, in terms of the simple collision theory, it is associated with the frequency of collisions.

Values of the activation energy E are in J/kmol in the SI system but are usually quoted in kJ/kmol (or J/mol); using these values **R** must then be expressed as kJ/kmol K. For most reactions the activation energy lies in the range 50,000-250,000 kJ/kmol, which implies a very rapid increase in rate constant with temperature. Thus, for a reaction which is occurring at a temperature in the region of 100°C and has an activation energy of 100,000 kJ/kmol, the reaction rate will be doubled for a temperature rise of only 10°C.

Thus, the complete rate equation for an irreversible reaction normally has the form:

$$\mathfrak{R}_{A} = \mathscr{A} \exp\left(-\mathbf{E}/\mathbf{R}T\right) C_{A}{}^{p}C_{B}{}^{q}C_{C}{}^{r}$$
(1.8)

Unfortunately, the exponential temperature term $\exp(-E/RT)$ is rather troublesome to handle mathematically, both by analytical methods and numerical techniques. In reactor design this means that calculations for reactors which are not operated isothermally tend to become complicated. In a few cases, useful results can be obtained by abandoning the exponential term altogether and substituting a linear variation of reaction rate with temperature, but this approach is quite inadequate unless the temperature range is very small.

1.4.3. Rate Equations and Reaction Mechanism

One of the reasons why chemical kinetics is an important branch of physical chemistry is that the rate of a chemical reaction may be a significant guide to its mechanism. The engineer concerned with reactor design and development is not interested in reaction mechanism *per se*, but should be aware that an insight into the mechanism of the reaction can provide a valuable clue to the kind of rate equation to be used in a design problem. In the present chapter, it will be possible to make only a few observations on the subject, and for further information the excellent text of MOORE and PEARSON⁽³⁾ should be consulted.

The first point which must be made is that the *overall* stoichiometry of a reaction is *no guide whatsoever* to its rate equation or to the mechanism of reaction. A stoichiometric equation is no more than a material balance; thus the reaction:

$$KClO_3 + 6FeSO_4 + 3H_2SO_4 \rightarrow KCl + 3Fe_2(SO_4)_3 + 3H_2O_4$$

is in fact second order in dilute solution with the rate of reaction proportional to the concentrations of ClO_3^- and Fe^{2+} ions. In the general case the stoichiometric coefficients ν_A , ν_B , ν_C , are not necessarily related to the orders p, q, r for the reaction.

However, if it is known from kinetic or other evidence that a reaction $M + N \rightarrow$ Product is a simple *elementary reaction*, i.e., if it is known that its mechanism is simply the interaction between a molecule of M and a molecule of N, then the molecular theory of reaction rates predicts that the rate of this elementary step is proportional to the concentration of species M and the concentration of species N, i.e. it is second order overall. The reaction is also said to be *bimolecular* since two molecules are involved in the actual chemical transformation.

Thus, the reaction between H_2 and I_2 is known to occur by an elementary bimolecular reaction:

$$H_2 + I_2 \rightarrow 2HI$$

and the rate of the forward reaction corresponds to the equation:

$$\mathcal{R}_{l_2} = \mathbf{k}_f C_{H_2} C_{l_2}$$

For many years the hydrogen-iodine reaction was quoted in textbooks as being virtually the only known example of a simple bimolecular reaction. There is now evidence⁽⁴⁾ that in parallel to the main bimolecular transformation, some additional reactions involving iodine atoms do occur.

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Whereas in the hydrogen-iodine reaction, atomic iodine plays only a minor part, in the reaction between hydrogen and bromine, bromine and hydrogen atoms are the principal intermediates in the overall transformation.

The kinetics of the reaction are quite different from those of the hydrogen-iodine reaction although the stoichiometric equation:

$$H_2 + Br_2 \rightarrow 2HBr$$

looks similar. The reaction actually has a chain mechanism consisting of the elementary steps:

$$Br_{2} \rightleftharpoons 2Br \cdot chain initiation and termination$$
$$Br \cdot + H_{2} \rightleftharpoons HBr + H \cdot$$
$$H \cdot + Br_{2} \rightarrow HBr + Br \cdot$$

The rate of the last reaction, for example, is proportional to the concentration of $H \cdot$ and the concentration of Br_2 , i.e. it is second order. When the rates of these elementary steps are combined into an overall rate equation, this becomes:

$$\mathcal{R}_{Br_2} = \frac{k' C_{H_2} C_{Br_2}^{1/2}}{1 + k'' \frac{C_{HBr}}{C_{Br_2}}}$$
(1.9)

where k' and k'' are constants, which are combinations of the rate constants of the elementary steps. This rate equation has a different form from the usual type given by equation 1.4, and cannot therefore be said to have any order because the definition of order applies only to the usual form.

We shall find that the rate equations of gas-solid heterogeneous catalytic reactions (Chapter 3) also do not, in general, have the same form as equation 1.4.

However, many reactions, although their mechanism may be quite complex, do conform to simple first or second-order rate equations. This is because the rate of the overall reaction is limited by just one of the elementary reactions which is then said to be rate-determining. The kinetics of the overall reaction thus reflect the kinetics of this particular step. An example is the pyrolysis of ethane⁽⁴⁾ which is important industrially as a source of ethylene⁽¹⁾ (see also Section 1.7.1; Example 1.4). The main overall reaction is:

$$C_2H_6 \rightarrow C_2H_4 + H_2$$

Although there are complications concerning this reaction, under most circumstances it is first order, the kinetics being largely determined by the first step in a chain mechanism:

$$C_2H_6 \rightarrow 2CH_3$$
.

which is followed by the much faster reactions:

$$\begin{array}{ccc} CH_3 \cdot + C_2H_6 \rightarrow C_2H_5 \cdot + CH_4 \\ C_2H_5 \cdot & \rightarrow C_2H_4 + H \cdot \\ H \cdot + C_2H_6 & \rightarrow C_2H_5 \cdot + H_2 \end{array} \\ \end{array} \\ \left. \begin{array}{c} chain \ propagation \\ chain \ pro$$

Eventually the reaction chains are broken by termination reactions. Other free radical reactions also take place to a lesser extent leading to the formation of CH_4 and some higher hydrocarbons among the products.

1.4.4. Reversible Reactions

For reactions which do not proceed virtually to completion, it is necessary to include the kinetics of the reverse reaction, or the equilibrium constant, in the rate equation.

The equilibrium state in a chemical reaction can be considered from two distinct points of view. The first is from the standpoint of classical thermodynamics, and leads to relationships between the equilibrium constant and thermodynamic quantities such as free energy and heat of reaction, from which we can very usefully calculate equilibrium conversion. The second is a kinetic viewpoint, in which the state of chemical equilibrium is regarded as a dynamic balance between forward and reverse reactions; at equilibrium the rates of the forward reactions and of the reverse reaction are just equal to each other, making the net rate of transformation zero.

Consider a reversible reaction:

$$\mathbf{A} + \mathbf{B} \stackrel{k_f}{\underset{k_r}{\rightleftharpoons}} \mathbf{M} + \mathbf{N}$$

which is second order overall in each direction, and first order with respect to each species. The hydrolysis of an ester such as ethyl acetate is an example

$$CH_3COOC_2H_5 + NaOH \Rightarrow CH_3COONa + C_2H_5OH$$

The rate of the forward reaction expressed with respect to A, \Re_{+A} is given by $\Re_{+A} = k_f C_A C_B$, and the rate of the reverse reaction (again expressed with respect to A and written \Re_{-A}) is given by $\Re_{-A} = k_r C_M C_N$. The net rate of reaction in the direction left to right is thus:

$$\mathfrak{R}_{\mathcal{A}} = \mathfrak{R}_{+\mathcal{A}} - \mathfrak{R}_{-\mathcal{A}} = \mathbf{k}_{f} C_{\mathcal{A}} C_{\mathcal{B}} - \mathbf{k}_{r} C_{\mathcal{M}} C_{\mathcal{N}}$$
(1.10)

At equilibrium, when $C_A = C_{Ae}$ etc., \Re_A is zero and we have:

$$\boldsymbol{k}_{f}C_{Ae}C_{Be} = \boldsymbol{k}_{r}C_{Me}C_{Ne}$$

or:

$$\frac{C_{Me}C_{Ne}}{C_{Ae}C_{Be}} = \frac{k_f}{k_r} \tag{1.11}$$

But $C_{Me}C_{Ne}/C_{Ae}C_{Be}$ is the equilibrium constant K_c and hence $k_f/k_r = K_c$. Often it is convenient to substitute for k_r , in equation 1.10 so that we have as a typical example of a rate equation for a reversible reaction:

$$\mathfrak{R}_{A} = k_{f} \left(C_{A} C_{B} - \frac{C_{M} C_{N}}{K_{c}} \right)$$
(1.12)

We see from the above example that the forward and reverse rate constants are not completely independent, but are related by the equilibrium constant, which in turn is related to the thermodynamic free energy, etc. More detailed examination of the kinds of kinetic equations which might be used to describe the forward and reverse reactions shows that, to be consistent with the thermodynamic equilibrium constant, the form of the rate equation for the reverse reaction cannot be completely independent of the forward rate equation. A good example is the formation of phosgene:

$$CO + Cl_2 \rightleftharpoons CO Cl_2$$

The rate of the forward reaction is given by $\Re_{+CO} = k_f C_{CO} C_{Cl_2}^{y_2}$. This rate equation indicates that the chlorine concentration must also appear in the reverse rate equation. Let this be $\Re_{-CO} = k_r C_{COCl_2} C_{Cl_2}^{q}$; then at equilibrium, when $\Re_{+CO} = \Re_{-CO}$, we must have:

$$\frac{\mathcal{R}_{-CO}}{\mathcal{R}_{+CO}} = 1 = \frac{k_r}{k_f} \left(\frac{C_{\text{COCI}_2} C_{\text{CI}_2}^{q}}{C_{\text{CO}} C_{\text{CI}_2}^{3/2}} \right)_{\text{eq}}$$
(1.13)

But we know from the thermodynamic equilibrium constant that:

$$K_{c} = \left(\frac{C_{\text{COCl}_{2}}}{C_{\text{CO}}C_{\text{Cl}_{2}}}\right)_{\text{eq}}$$
(1.14)

Therefore it follows that p = 1 and q = 1/2. The complete rate equation is therefore:

 $\Re_{\rm CO} = \mathbf{k}_f C_{\rm CO} C_{\rm Cl_2}^{3/2} - \mathbf{k}_r C_{\rm COCl_2} C_{\rm Cl_2}^{1/2}$

or:

$$\mathcal{R}_{\rm CO} = k_f \left(C_{\rm CO} C_{\rm Cl_2}^{3/2} - \frac{C_{\rm COCl_2} C_{\rm Cl_2}^{1/2}}{K_c} \right)$$
(1.15)

1.4.5. Rate Equations for Constant-Volume Batch Reactors

In applying a rate equation to a situation where the volume of a given reaction mixture (i.e. the density) remains constant throughout the reaction, the treatment is very much simplified if the equation is expressed in terms of a variable χ , which is defined as the number of moles of a particular reactant transformed per unit volume of reaction mixture (e.g. $C_{A0} - C_A$) at any instant of time *t*. The quantity χ is very similar to a molar concentration and has the same units. By simple stoichiometry, the moles of the other reactants transformed and products generated can also be expressed in terms of χ , and the rate of the reaction can be expressed as the rate of increase in χ with time. Thus, by definition,

$$\Re_A = -\frac{1}{V} \frac{\mathrm{d}n_A}{\mathrm{d}t} \tag{1.16}$$

and if V is constant this becomes:

$$\mathfrak{R}_{\mathcal{A}} = -\frac{\mathrm{d}(n_{\mathcal{A}}/V)}{\mathrm{d}t} = -\frac{\mathrm{d}C_{\mathcal{A}}}{\mathrm{d}t} = \frac{\mathrm{d}\mathcal{X}}{\mathrm{d}t}$$
(1.17)

x being the moles of A which have reacted. The general rate equation 1.4 may then be written:

$$\frac{\mathrm{d}\boldsymbol{\chi}}{\mathrm{d}t} = \boldsymbol{k} (C_{A0} - \boldsymbol{\chi})^{p} \left(C_{B0} - \frac{\nu_{B}}{\nu_{A}} \boldsymbol{\chi} \right)^{q} \left(C_{C0} - \frac{\nu_{C}}{\nu_{A}} \boldsymbol{\chi} \right)^{r}$$
(1.18)

where $C_{\lambda 0}$ etc. are the initial concentrations. This equation may then in general, at constant temperature conditions, be integrated to give χ as a function of time, so that the reaction time for any particular conversion can be readily calculated.

The equations which result when these integrations are carried out for reactions of various orders are discussed in considerable detail in most texts dealing with the physico-chemical aspects of chemical kinetics^(3, 4). Table 1.1 shows a summary of some of the simpler cases; the integrated forms can be easily verified by the reader if desired.

One particular point of interest is the expression for the *half-life* of a reaction $t_{1/2}$; this is the time required for one half of the reactant in question to disappear. A first order reaction is unique in that the *half-life* is independent of the initial concentration of the reactant. This characteristic is sometimes used as a test of whether a reaction really is first order. Also since $t_{1/2} = \frac{1}{k_1} \ln 2$, a first-order rate constant can be readily converted into a *half-life* which one can easily remember as characteristic of the reaction.

A further point of interest about the equations shown in Table 1.1 is to compare the shapes of graphs of χ (or fractional conversion $\chi/C_{A0} = \alpha_A$) vs. time for reactions of different orders p. Figure 1.8 shows a comparison between first and second-order reactions involving a single reactant only, together with the straight line for a zeroorder reaction. The rate constants have been taken so that the curves coincide at 50 per cent conversion. The rate of reaction at any time is given by the slope of the curve (as indicated by equation 1.17). It may be seen that the rate of the secondorder reaction is high at first but falls rapidly with increasing time and, compared with first-order reactions, longer reaction times are required for high conversions. The zero-order reaction is the only one where the reaction rate does not decrease with increasing conversion. Many biological systems have apparent reaction orders between 0 and 1 and will have a behaviour intermediate between the curves shown.



FIG. 1.8. Batch reactions at constant volume: Comparison of curves for zero, first and second-order reactions

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Reaction type	Rate equation	Integrated form
	Irreversible reac	tions
First order $\mathbf{A} \rightarrow \text{products}$	$\frac{\mathrm{d}\boldsymbol{\chi}}{\mathrm{d}t} = \boldsymbol{k}_1 (\boldsymbol{C}_{A0} - \boldsymbol{\chi})$	$t = \frac{1}{k_1} \ln \frac{C_{A0}}{(C_{A0} - \chi)}$
		$t_{1/2} = \frac{\ln 2}{k_1}$
Second order $\mathbf{A} + \mathbf{B} \rightarrow \text{products}$	$\frac{\mathrm{d}\chi}{\mathrm{d}t} = k_2 (C_{A0} - \chi) (C_{B0} - \chi)$	$t = \frac{1}{k_2(C_{B0} - C_{A0})} \ln \frac{C_{A0}(C_{B0} - \chi)}{C_{B0}(C_{A0} - \chi)}$
		$C_{A0} \neq C_{B0}$
$2\mathbf{A} \rightarrow \text{products}$	$\frac{\mathrm{d}\boldsymbol{\chi}}{\mathrm{d}t} = \boldsymbol{k}_2 (C_{A0} - \boldsymbol{\chi})^2$	$t = \frac{1}{k_2} \left(\frac{1}{C_{A0} - \chi} - \frac{1}{C_{A0}} \right)$
		$t_{1/2} = \frac{1}{k_2 C_{A0}}$
Order p, one reactant	$\frac{\mathrm{d}\chi}{\mathrm{d}t} = k \left(C_{A0} - \chi\right)^p$	$t = \frac{1}{k(p-1)} \left[\frac{1}{(C_{A0} - \chi)^{p-1}} - \frac{1}{C_{A0}^{p-1}} \right]$
$\mathbf{A} \rightarrow \mathbf{products}$		$t_{1/2} = \frac{2^{p-1} - 1}{k(p-1)C_{A0}^{p-1}} p \neq 1$
	Reversible react	ions
First order both directions	$\frac{\mathrm{d}\chi}{\mathrm{d}t} = k_f (C_{A0} - \chi) - k_r (C_{M0} + \chi)$	$t = \frac{1}{(k_f + k_r)} \ln \frac{k_f C_{A0} - k_r C_{M0}}{k_f (C_{A0} - \chi) - k_r (C_{M0} + \chi)}$
$A \stackrel{k_{f}}{\underset{k_{f}}{\leftrightarrow}} M$		or since $K_c = k_f / k_r$
		$t = \frac{K_c}{k_f (1 + K_c)} \ln \frac{K_c C_{A0} - C_{M0}}{K_c (C_{A0} - \chi) - (C_{M0} + \chi)}$
		If $C_{M0} = 0$
		$t = \frac{1}{(k_f + k_r)} \ln \frac{\chi_e}{(\chi_e - \chi)}$
Second order both directions	If $C_{A0} = C_{B0}$ and $C_{M0} = C_{N0} = 0$	
$\mathbf{A} + \mathbf{B} \stackrel{\mathbf{x}_{f}}{\underset{k}{\leftrightarrow}} \mathbf{M} + \mathbf{N}$	$\frac{\mathrm{d}\chi}{\mathrm{d}t} = k_f \left(C_{A0} - \chi\right)^2 - k_r \chi^2$	$t = \frac{\sqrt{K_c}}{2k_f C_{A0}} \ln \frac{C_{A0} + \chi[1/(\sqrt{K_c}) - 1]}{C_{A0} - \chi[1/(\sqrt{K_c}) + 1]}$

TABLE 1.1. Rate Equations for Constant Volume Batch Reactors

1.4.6. Experimental Determination of Kinetic Constants

The interpretation of laboratory scale experiments to determine order and rate constant is another subject which is considered at length in physical chemistry texts^(3, 4). Essentially, it is a process of fitting a rate equation of the general form given by equation 1.4 to a set of numerical data. The experiments which are carried out to obtain the kinetic constants may be of two kinds, depending on whether the rate equation is to be used in its original (differential) form, or in its integrated form (see Table 1.1). If the differential form is to be used, the experiments must be designed so that the rate of disappearance of reactant A, \Re_A , can be measured without its concentration changing appreciably. With batch or tubular reactors this has the disadvantage in practice that very accurate measurements of C_4 must be made so that, when differences in concentration ΔC_A are taken to evaluate \Re_A (e.g. for a batch reactor, equation 1.17 in finite difference form is $\Re_A = -\Delta C_A/\Delta t$, the difference may be obtained with sufficient accuracy. Continuous stirred-tank reactors do not suffer from this disadvantage; by operating in the steady state, steady concentrations of the reactants are maintained and the rate of reaction is determined readily.

If the rate equation is to be employed in its integrated form, the problem of determining kinetic constants from experimental data from batch or tubular reactors is in many ways equivalent to taking the design equations and working backwards. Thus, for a batch reactor with constant volume of reaction mixture at constant temperature, the equations listed in Table 1.1 apply. For example, if a reaction is suspected of being second order overall, the experimental results are plotted in the form:

$$\frac{1}{C_{B0} - C_{A0}} \ln \left\{ \frac{C_{A0}(C_{B0} - \chi)}{C_{B0}(C_{A0} - \chi)} \right\} \text{ versus } t$$

If the points lie close to a straight line, this is taken as confirmation that a secondorder equation satisfactorily describes the kinetics, and the value of the rate constant k_2 is found by fitting the best straight line to the points by linear regression. Experiments using tubular and continuous stirred-tank reactors to determine kinetic constants are discussed in the sections describing these reactors (Sections 1.7.4 and 1.8.5).

Unfortunately, many of the chemical processes which are important industrially are quite complex. A complete description of the kinetics of a process, including byproduct formation as well as the main chemical reaction, may involve several individual reactions, some occurring simultaneously, some proceeding in a consecutive manner. Often the results of laboratory experiments in such cases are ambiguous and, even if complete elucidation of such a complex reaction pattern is possible, it may take several man-years of experimental effort. Whereas ideally the design engineer would like to have a complete set of rate equations for all the reactions involved in a process, in practice the data available to him often fall far short of this.

1.5. GENERAL MATERIAL AND THERMAL BALANCES

The starting point for the design of any type of reactor is the general material balance. This material balance can be carried out with respect to one of the reactants

or to one of the products. However, if we are dealing with a single reaction such as:

$$\nu_A \mathbf{A} + \nu_B \mathbf{B} = \nu_M \mathbf{M} + \nu_N \mathbf{N}$$

then, in the absence of any separation of the various components by diffusion, it is not necessary to write separate material balance equations for each of the reactants and products. The stoichiometric equation shows that if ν_A moles of A react, ν_B moles of B must also have disappeared, ν_M moles of M must have been formed together with ν_N moles of N. In such a case the extent to which the reaction has proceeded at any stage can be expressed in terms of the fractional conversion α of any selected reactant, for example A. (See also Section 1.4.5 where similarly the rate of the reaction could be expressed by considering one reactant only.) Alternatively, one of the products M or N could be chosen as the entity for the material balance equation; however, it is usual to use one reactant as a basis because there may be some uncertainty about just what products are present when the procedure is extended to more complex reactions in which several byproducts are formed, whereas usually the chemical nature of the reactants is known for certain.

Basically, the general material balance for a reactor follows the same pattern as all material and energy balances, namely:

but with the important difference that the reactant in question can disappear through chemical reaction. The material balance must therefore be written:

In setting out this equation in an exact form for any particular reactor, the material balance has to be carried out

- (a) over a certain element of volume, and
- (b) over a certain element of time.

If the compositions vary with position in the reactor, which is the case with a tubular reactor, a differential element of volume δV_r must be used, and the equation integrated at a later stage. Otherwise, if the compositions are uniform, e.g. a well-mixed batch reactor or a continuous stirred-tank reactor, then the size of the volume element is immaterial; it may conveniently be unit volume (1 m³) or it may be the whole reactor. Similarly, if the compositions are changing with time as in a batch reactor, the material balance must be made over a differential element of time. Otherwise for a tubular or a continuous stirred-tank reactor operating in a steady state, where compositions do not vary with time, the time interval used is immaterial and may conveniently be unit time (1 s). Bearing in mind these considerations the general material balance may be written:

Rate of flow of reactant into volume element	Rate of flow of - reactant out of volume element	Rate of reactant - removal by reaction within volume element	Rate of accumulation = of reactant within volume element	(1.19)
(1)	(2)	(3)	(4)	

For each of the three basic types of chemical reactor this equation may be reduced to a simplified form. For a *batch reactor* terms (1) and (2) are zero and the *Rate of accumulation*, i.e. the rate of disappearance of the reactant, is equal to the rate of



FIG. 1.9. Continuous stirred-tank reactor showing steady state operation (a) and two modes of unsteady state operation (b) and (c)

reaction. For a tubular reactor or a continuous stirred-tank reactor, if operating in a steady state, the Rate of accumulation term (4) is by definition zero, and the Rate of reactant removal by reaction is just balanced by the difference between inflow and outflow.

For unsteady state operation of a flow reactor, it is important to appreciate the distinction between the Reaction term (3) above and the Accumulation term (4), which are equal for a batch reactor. Transient operation of a flow reactor occurs during start-up and in response to disturbances in the operating conditions. The nature of transients induced by disturbances and the differences between terms (3) and (4) above can best be visualised for the case of a continuous stirred-tank reactor (Fig. 1.9). In Fig. 1.9a, the reactor is operating in a steady state. In Fig. 1.9b it is subject to an increase in the input of reactant owing to a disturbance in the feed composition. This results in a rise in the concentration of the reactant within the reaction vessel corresponding to the Accumulation term (4) which is guite distinct from, and additional to, the Reactant removal by the reaction term (3). Figure 1.9c shows another kind of transient which will cause compositions in the reactor to change, namely a change in the volume of reaction mixture contained in the reactor. Other variables which must be controlled, apart from feed composition and flowrates in and out, are temperature and, for gas reactions particularly, pressure. Variations of any of these quantities with time will cause a change in the composition levels of the reactant in the reactor, and these will appear in the Accumulation term (4) in the material balance.

The heat balance for a reactor has a form very similar to the general material balance, i.e.

Rate of heat	Rate of heat	Rate of absorption of	Rate of heat	(1.20)
inflow into	- outflow from	- heat by chemical reaction =	accumulation in	
volume element	volume element	in volume element	volume element	
(1)	(2)	(3)	(4)	

In the *Inflow* and *Outflow* terms (1) and (2), the heat flow may be of two kinds: the first is transfer of sensible heat or enthalpy by the fluid entering and leaving the element; and the second is heat transferred to or from the fluid across heat transfer surfaces, such as cooling coils situated in the reactor. The *Heat absorbed in the chemical reaction*, term (3), depends on the rate of reaction, which in turn depends on the concentration levels in the reactor as determined by the general material balance equation. Since the rate of reaction depends also on the temperature levels

in the reactor as determined by the heat balance equation, the material balance and the heat balance interact with each other, and the two equations have to be solved simultaneously. The types of solutions obtained are discussed further under the headings of the various types of reactor—batch, tubular and continuous stirred-tank.

1.6. BATCH REACTORS

There is a tendency in chemical engineering to try to make all processes continuous. Whereas continuous flow reactors are likely to be most economic for large scale production, the very real advantages of batch reactors, especially for smaller scale production, should not be overlooked. Small batch reactors generally require less auxiliary equipment, such as pumps, and their control systems are less elaborate and costly than those for continuous reactors, although manpower needs are greater. However, large batch reactors may sometimes be fitted with highly complex control systems. A big advantage of batch reactors in the dyestuff, fine chemical and pharmaceutical industries is their versatility. A corrosion-resistant batch reactor such as an enamel or rubber-lined jacketed vessel (Fig. 1.4a) or a stainless steel vessel with heating and cooling coils (Fig. 1.4b) can be used for a wide variety of similar kinds of reaction. Sometimes only a few batches per year are required to meet the demand for an unusual product. In some processes, such as polymerisations and fermentations, batch reactors are traditionally preferred because the interval between batches provides an opportunity to clean the system thoroughly and ensure that no deleterious intermediates such as foreign bacteria build up and spoil the product. Moreover, it must not be forgotten that a squat tank is the most economical shape for holding a given volume of liquid, and for slow reactions a tubular flow reactor with a diameter sufficiently small to prevent backmixing, would be more costly than a simple batch reactor. Although at present we are concerned mainly with homogeneous reactions, we should note that the batch reactor has many advantages for heterogeneous reactions; the agitator can be designed to suspend solids in the liquid, and to disperse a second immiscible liquid or a gas.

In calculating the volume required for a batch reactor, we shall be specifying the volume of liquid which must be processed. In designing the vessel itself the heights should be increased by about 10 per cent to allow freeboard for waves and disturbances on the surface of the liquid; additional freeboard may have to be provided if foaming is anticipated.

1.6.1. Calculation of Reaction Time; Basic Design Equation

Calculation of the time required to reach a particular conversion is the main objective in the design of batch reactors. Knowing the amount of reactant converted, i.e. the amount of the desired product formed per unit volume in this reaction time, the volume of reactor required for a given production rate can be found by simple scale-up as shown in the example on ethyl acetate below.

The reaction time t_r is determined by applying the general material balance equation 1.19. In the most general case, when the volume of the reaction mixture is not constant throughout the reaction, it is convenient to make the material balance over the whole volume of the reactor V_b . For the reactant A, if n_{A0} moles are charged initially, the number of moles remaining when the fraction of A converted is α_{λ} is $n_{\lambda 0}(1 - \alpha_{\lambda})$ and, using a differential element of time, the rate at which this is changing, i.e. the Accumulation term (4) in equation 1.19 is:

$$\frac{\mathrm{d}}{\mathrm{d}t} \left[n_{A0} (1 - \alpha_A) \right] = - n_{A0} \frac{\mathrm{d}\alpha_A}{\mathrm{d}t} \tag{1.21}$$

The rate at which A is removed by reaction term (3) is $\Re_A V_b$ and, since the Flow terms (1) and (2) are zero, we have:

$$-\Re_A V_b = -n_{A0} \frac{\mathrm{d}\alpha_A}{\mathrm{d}t}$$
(1.22)

Reaction Accumulation

Thus, integrating over the period of the reaction to a final conversion α_{Af} , we obtain the basic design equation:

$$t_r = n_{A0} \int_0^{\alpha_{A/}} \frac{\mathrm{d}\alpha_A}{\Re_A V_b}$$
(1.23)

For many liquid phase reactions it is reasonable to neglect any change in volume of the reaction mixture. Equation 1.23 then becomes:

$$t_r = \frac{n_{A0}}{V_b} \int_0^{\alpha_{Af}} \frac{\mathrm{d}\,\alpha_A}{\Re_A} = C_{A0} \int_0^{\alpha_{Af}} \frac{\mathrm{d}\,\alpha_A}{\Re_A} \tag{1.24}$$

This form of the equation is convenient if there is only one reactant. For more than one reactant and for reversible reactions, it is more convenient to write the equation in terms of χ , the moles of A converted per unit volume $\chi = C_{A0} \alpha_A$, and obtain:

$$t_r = \int_0^{\chi_f} \frac{\mathrm{d}\chi}{\Re_A} \tag{1.25}$$

This is the integrated form of equation 1.17 obtained previously; it may be derived formally by applying the general material balance to unit volume under conditions of constant density, when the *Rate of reaction* term (3) is simply $\mathfrak{R}_{\mathcal{A}}$ and the *Accumulation* term (4) is: $\frac{dC_{\mathcal{A}}}{dt}, \quad i.e. \quad -\frac{d\chi}{dt}$

Thus:

$$-\mathcal{R}_{A}=-\frac{\mathrm{d}\chi}{\mathrm{d}t}$$

which is equation 1.17.

1.6.2. Reaction Time — Isothermal Operation

If the reactor is to be operated isothermally, the rate of reaction \mathcal{R}_A can be expressed as a function of concentrations only, and the integration in equation 1.24 or 1.25 carried out. The integrated forms of equation 1.25 for a variety of the simple rate equations are shown in Table 1.1 and Fig. 1.8. We now consider an example with a rather more complicated rate equation involving a reversible reaction, and show also how the volume of the batch reactor required to meet a particular production requirement is calculated.

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Example 1.2

Production of Ethyl Acetate in a Batch Reactor

Ethyl acetate is to be manufactured by the esterification of acetic acid with ethanol in an isothermal batch reactor. A production rate of 10 tonne/day of ethyl acetate is required.

$$CH_3 \cdot COOH + C_2H_5OH \rightleftharpoons CH_3 \cdot COOC_2H_5 + H_2O$$

$$A \qquad B \qquad M \qquad N$$

The reactor will be charged with a mixture containing 500 kg/m³ ethanol and 250 kg/m³ acetic acid, the remainder being water, and a small quantity of hydrochloric acid to act as a catalyst. The density of this mixture is 1045 kg/m³ which will be assumed constant throughout the reaction. The reaction is reversible with a rate equation which, over the concentration range of interest, can be written:

$$\mathfrak{R}_{A} = \mathbf{k}_{f} C_{A} C_{B} - \mathbf{k}_{F} C_{M} C_{N}$$

At the operating temperature of 100°C the rate constants have the values:

$$k_f = 8.0 \times 10^{-6} \text{ m}^3/\text{kmol s}$$

 $k_r = 2.7 \times 10^{-6} \text{ m}^3/\text{kmol s}$

The reaction mixture will be discharged when the conversion of the acetic acid is 30 per cent. A time of 30 min is required between batches for discharging, cleaning, and recharging. Determine the volume of the reactor required.

Solution

After a time *t*, if $\chi \text{ kmol/m}^3$ of acetic acid (A) has reacted, its concentration will be $(C_{A0} - \chi)$ where C_{A0} is the initial concentration. From the stoichiometry of the reaction, if $\chi \text{ kmol/m}^3$ of acetic acid has reacted, $\chi \text{ kmol/m}^3$ of ethanol also will have reacted and the same number of moles of ester and of water will have been formed. The rate equation may thus be written:

$$\mathfrak{R}_{\mathcal{A}} = \mathbf{k}_{f}(C_{\mathcal{A}0} - \boldsymbol{\chi})(C_{\mathcal{B}0} - \boldsymbol{\chi}) - \mathbf{k}_{r}\boldsymbol{\chi}(C_{\mathcal{N}0} + \boldsymbol{\chi}).$$

From the original composition of the mixture, its density, and the molecular weights of acetic acid, ethanol and water which are 60, 46 and 18 respectively, $C_{A0} = 4.2 \text{ kmol/m}^3$; $C_{B0} = 10.9 \text{ kmol/m}^3$; $C_{N0} = 16.4 \text{ kmol/m}^3$. Thus, from equation 1.25, t_r in seconds is given by:

$$l_r = \int_0^{\chi_r} \frac{\mathrm{d}\chi}{8.0 \times 10^{-6} (4.2 - \chi) (10.9 - \chi) - 2.7 \times 10^{-6} \chi (16.4 + \chi)}$$

This integral may be evaluated either by splitting into partial fractions, or by graphical or numerical means. Using the method of partial fractions, we obtain after some fairly lengthy manipulation:

$$t_r = 16,200 \left[\log_{10} \frac{29 - \chi_f}{2.4 - \chi_f} - 1.082 \right]$$

Since the final conversion of acetic acid is to be 30 per cent, $\chi_f = 0.30 \times C_{A0} = 1.26 \text{ kmol/m}^3$: whence the reaction time t_r is, from the above equation, 4920 s.

Thus 1 m³ of reactor volume produces 1.26 kmol of ethyl acetate (molecular weight 88) in a total batch time of 6720 s, i.e. in 4920 s reaction time and 1800 s shut-down time. This is an average production rate of:

$$1.26 \times 88 \times \frac{24 \times 60^2}{6720}$$

i.e. 1420 kg/day per m³ of reactor volume. Since the required production rate is 10,000 kg/day the required reactor volume is $10,000/1420 = \frac{7.1 \text{ m}^3}{2}$.

Example 1.2 on ethyl acetate is useful also in directing attention to an important point concerning reversible reactions in general. A reversible reaction will not normally go to completion, but will slow down as equilibrium is approached. This progress towards equilibrium can, however, sometimes be disturbed by continuously removing one or more of the products as formed. In the actual manufacture of ethyl

acetate, the ester is removed as the reaction proceeds by distilling off a ternary azeotrope of molar composition ethyl acetate 60.1 per cent, ethanol 12.4 per cent and water 27.5 per cent. The net rate of reaction is thereby increased as the rate equation above shows; because C_M is always small the term for the rate of the reverse reaction $k_r C_M C_N$ is always small and the net rate of reaction is virtually equal to the rate of the forward reaction above, i.e. $k_r C_A C_B$.

1.6.3. Maximum Production Rate

For most reactions, the rate decreases as the reaction proceeds (important exceptions being a number of biological reactions which are autocatalytic). For a reaction with no volume change, the rate is represented by the slope of the curve of χ (moles converted per unit volume) versus time (Fig. 1.10), which decreases steadily with increasing time. The maximum reaction rate occurs at zero time, and, if our sole concern were to obtain maximum output from the reactor and the shutdown time were zero, it appears that the best course would be to discharge the reactor after only a short reaction time t_r , and refill with fresh reactants. It would then be necessary, of course, to separate a large amount of reactant from a small amount of product. However, if the shut-down time is appreciable and has a value t_s then as we have seen in the example on ethyl acetate above, the average production rate per unit volume is:

$$\frac{\chi}{t_r+t_s}$$

The maximum production rate is therefore given by the maximum value of:

$$\frac{\chi}{t_r+t_s}$$

This maximum can be most conveniently found graphically (Fig. 1.10). The average production rate is given by the slope of the line ZA; this is obviously a maximum when the line is tangent to the curve of χ versus *t*, i.e. ZT as shown. The reaction time obtained t_{rmax} is not necessarily the optimum for the process as a whole,



FIG. 1.10. Maximum production rate in a batch reactor with a shut-down time t_s

however. This will depend in addition upon the costs involved in feed preparation, separation of the products, and storage.

1.6.4. Reaction Time --- Non-isothermal Operation

If the temperature is not constant but varies during the course of the reaction, then the rate of reaction \Re_4 in equation 1.24 or 1.25 will be a function of temperature as well as concentration (equation 1.8). The temperature at any stage is determined by a heat balance, the general form of which is given by equation 1.20. Since there is no material flow into or out of a batch reactor during reaction, the enthalpy changes associated with such flows in continuous reactors are absent. However, there may be a flow of heat to or from the reactor by heat transfer using the type of equipment shown in Fig. 1.4. In the case of a jacketed vessel or one with an internal coil, the heat transfer coefficient will be largely dependent on the agitator speed, which is usually held constant. Thus, assuming that the viscosity of the liquid does not change appreciably, which is reasonable in many cases (except for some polymerisations), the heat transfer coefficient may be taken as constant. If heating is effected by condensing saturated steam at constant pressure, as in Fig. 1.11b, the temperature on the coil side T_c is constant. If cooling is carried out with water (Fig. 1.11c), the rise in temperature of the water may be small if the flowrate is large, and T_c again taken as constant. Thus, we may write the rate of heat transfer to cooling coils of area A_t as:

$$Q = UA_l(T - T_c) \tag{1.26}$$

where T is the temperature of the reaction mixture. The heat balance taken over the whole reactor thus becomes:

$$- UA_t(T - T_c) + (-\Delta H_A) V_b \Re_A = \left(\sum m_j c_j\right) \frac{\mathrm{d}T}{\mathrm{d}t}$$
(1.27)

Rate of heat flow out by heat transfer Rate of heat release by chemical reaction Rate of heat accumulation

where ΔH_A is the enthalpy change in the reaction per mole of A reacting, and $(\Sigma m_i c_i)$ is the sum of the heat capacities (i.e. mass \times specific heat) of the reaction



FIG. 1.11. Methods of operating batch reactors

- (a) Isothermal operation of an exothermic reaction; heating to give required initial temperature, cooling to remove heat of reaction
- (b) and (c) non-isothermal operation; simple schemes

mixture and the reactor itself, including all the various internal components such as the agitator, whose temperatures also change.

Finding the time required for a particular conversion involves the solution of two simultaneous equations, i.e. 1.24 or 1.25 for the material balance and 1.27 for the heat balance. Generally, a solution in analytical form is unobtainable and numerical methods or analogue simulation must be used. Taking, for example, a first-order reaction with constant volume:

$$\mathfrak{R}_{A} = \frac{\mathrm{d}\chi}{\mathrm{d}t} = k(C_{A0} - \chi) \tag{1.28}$$

and:

$$k = \mathcal{A} \exp\left(\frac{-\mathbf{E}}{\mathbf{R}T}\right) \tag{1.29}$$

we have for the material balance:

$$\frac{\mathrm{d}\boldsymbol{\chi}}{\mathrm{d}t} = \mathcal{A} \exp\left(\frac{-\mathbf{E}}{\mathbf{R}T}\right) (C_{A0} - \boldsymbol{\chi}) \tag{1.30}$$

and for the heat balance:

$$(-\Delta H_A) \ V_b \ \mathcal{A} \ \exp\left(\frac{-\mathbf{E}}{\mathbf{R}T}\right) (C_{A0} - \chi) - UA_t (T - T_C) = \left(\sum m_j c_j\right) \frac{\mathrm{d}T}{\mathrm{d}t} \qquad (1.31)$$

With t as the independent variable, the solution will be:

- (a) χ as f(t)
- (b) T as F(t).

A typical requirement is that the temperature shall not rise above T_{mx} in order to avoid byproducts or hazardous operation. The forms of the solutions obtained are sketched in Fig. 1.12.



FIG. 1.12. Non-isothermal batch reactor: Typical curves for an exothermic reaction with just sufficient cooling (constant U and T_c) to prevent temperature rising above T_{mx}

1.6.5. Adiabatic Operation

If the reaction is carried out adiabatically (i.e. without heat transfer, so that Q = 0), the heat balance shows that the temperature at any stage in the reaction can be expressed in terms of the conversion only. This is because, however fast or slow the

reaction, the heat released by the reaction is retained as sensible heat in the reactor. Thus, for reaction at constant volume, putting Q = 0 and $\Re_A = d\chi/dt$ in equation 1.27:

$$(-\Delta H_{\lambda}) V_{b} d\chi = \left(\sum m_{j} c_{j}\right) dT$$
(1.32)

Equation 1.32 may be solved to give the temperature as a function of χ . Usually the change in temperature $(T - T_0)$, where T_0 is the initial temperature, is proportional to χ , since $\sum m_j c_j$, the total heat capacity, does not vary appreciably with temperature or conversion. The appropriate values of the rate constant are then used to carry out the integration of equation 1.24 or 1.25 numerically, as shown in the following example.

Example 1.3

Adiabatic Batch Reactor

Acetic anhydride is hydrolysed by water in accordance with the equation:

 $(CH_3 \cdot CO)_2O + H_2O \rightleftharpoons 2CH_3 \cdot COOH$

In a dilute aqueous solution where a large excess of water is present, the reaction is irreversible and pseudo first-order with respect to the acetic anhydride. The variation of the pseudo first-order rate constant with temperature is as follows:

Temperature	(°C)	15	20	25	30
-	(K)	288	293	298	303
Rate Constant	(s ⁻¹)	0.00134	0.00188	0.00263	0.00351

A batch reactor for carrying out the hydrolysis is charged with an anhydride solution containing 0.30 kmol/m³ at 15°C. The specific heat and density of the reaction mixture are 3.8 kJ/kgK and 1070 kg/m³, and may be taken as constant throughout the course of the reaction. The reaction is exothermic, the heat of reaction per kmol of anhydride being 210,000 kJ/kmol. If the reactor is operated adiabatically, estimate the time required for the hydrolysis of 80 per cent of the anhydride.

Solution

For the purposes of this example we shall neglect the heat capacity of the reaction vessel. Since the anticipated temperature rise is small, the heat of reaction will be taken as independent of temperature. Because the heat capacity of the reactor is neglected, we may most conveniently take the adiabatic heat balance (equation 1.32) over the unit volume, i.e. 1 m^3 of reaction mixture. Thus, integrating equation 1.32 with the temperature T_0 when $\chi = 0$:

	$(-\Delta H_A)\chi = mc(T-T_0)$
i.e.:	$210,000 \ \chi = 1070 \times 3.8(T - T_0)$
<i>:</i>	$(T-T_0)=52\chi$
Writing:	$\chi = C_{A0}\alpha = 0.3\alpha$
	$(T - T_0) = 15.6\alpha$

Thus, if the reaction went to completion ($\alpha = 1$), the adiabatic temperature rise would be 15.6°C. For a pseudo first-order reaction, the rate equation is:

$$\mathfrak{R}_{\mathcal{A}} = \boldsymbol{k}_{1}(\boldsymbol{C}_{\mathcal{A}0} - \boldsymbol{\chi}) = \boldsymbol{C}_{\mathcal{A}0}\boldsymbol{k}_{1}(1-\boldsymbol{\alpha})$$

and from equation 1.24:

$$t_r = \int_0^{0.8} \frac{\mathrm{d}\,\alpha}{k_1(1-\alpha)}$$

To evaluate this integral graphically, we need to plot:

$$\frac{1}{k_1(1-\alpha)} \text{ versus } \alpha$$

remembering that k_1 is a function of T (i.e. of α). Interpolating the values of k_1 given, we evaluate:

$$\frac{1}{k_1(1-\alpha)}$$

for various values of α , some of which are shown in Table 1.2.

Fractional conversion α	Temperature rise $(T - T_0) \text{ deg } K$	Temperature K	Rate constant $k_1(s^{-1})$	$\frac{1}{k_1(1-\alpha)}$
0	0	288	0.00134	740
0.2	3.1	291.1	0.00167	750
0.4	6.2	294.2	0.00205	810
0.6	9.4	297.4	0.00253	990
0.8	12.5	300.5	0.00305	1630

TABLE 1.2. Evaluation of Integral to Determine t_r

From the area under the graph up to $\alpha = 0.80$, we find that the required reaction time is approximately $\frac{720 \text{ s} = 12 \text{ min.}}{12 \text{ min.}}$

1.7. TUBULAR-FLOW REACTORS

The tubular-flow reactor (Fig. 1.1b) is chosen when it is desired to operate the reactor continuously but without back-mixing of reactants and products. In the case of an *ideal* tubular reactor, the reaction mixture passes through in a state of *plug flow* which, as the name suggests, means that the fluid moves like a solid plug or piston. Furthermore, in the ideal reactor it is assumed that not only the local mass flowrate but also the fluid properties, temperature, pressure, and compositions are uniform across any section normal to the fluid motion. Of course the compositions, and possibly the temperature and pressure also, change between inlet and outlet of the reactor in the longitudinal direction. In the elementary treatment of tubular reactors, *longitudinal dispersion*, i.e. mixing by diffusion and other processes in the direction of flow, is also neglected.

Thus, in the idealised tubular reactor all elements of fluid take the same time to pass through the reactor and experience the same sequence of temperature, pressure and composition changes. In calculating the size of such a reactor, we are concerned with its volume only; its shape does not affect the reaction so long as plug flow occurs.

The flow pattern of the fluid is, however, only one of the criteria which determine the shape eventually chosen for a tubular reactor. The factors which must be taken into account are:

- (a) whether plug flow can be attained,
- (b) heat transfer requirements,
- (c) pressure drop in the reactor,
- (d) support of catalyst, if present, and
- (e) ease and cheapness of construction.

Figure 1.13 shows various configurations which might be chosen. One of the cheapest ways of enclosing a given volume is to use a cylinder of height approximately equal to its diameter. In Fig. 1.13*a* the reactor is a simple cylinder of this kind. Without packing, however, swirling motions in the fluid would cause serious

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FIG. 1.13. Various configurations for tubular reactors

- (a) Simple cylindrical shell: suitable only if packed with catalyst
- (b) Shallow cylinder giving low pressure drop through catalyst bed
- (c) Tubes in parallel: relatively low tube velocity
- (d) Tubes in series: high tube velocity

departures from plug flow. With packing in the vessel, such movements are damped out and the simple cylinder is then quite suitable for catalytic reactions where no heat transfer is required. If pressure drop is a problem, the depth of the cylinder may be reduced and its diameter increased as in Fig. 1.13b; to avoid serious departures from plug flow in such circumstances, the catalyst must be uniformly distributed and baffles are often used near the inlet and outlet.

When heat transfer to the reactor is required, a configuration with a high surface to volume ratio is employed. In the reactors shown in Fig. 1.13c and 1.13d the reaction volume is made up of a number of tubes. In c they are arranged in parallel, whereas in d they are in series. The parallel arrangement gives a lower velocity of the fluid in the tubes, which in turn results in a lower pressure drop, but also a lower heat transfer coefficient (which affects the temperature of the reactant mixture and must be taken into account in calculating the reactor volume). The parallel arrangement is very suitable if a second fluid outside the tubes is used for heat transfer; parallel tubes can be arranged between tube sheets in a compact bundle fitted into a shell, as in a shell and tube heat exchanger. On the other hand, with tubes in series, a high fluid velocity is obtained inside the tubes and a higher heat transfer coefficient results. The series arrangement is therefore often the more suitable if heat transfer is by radiation, when the high heat transfer coefficient helps

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