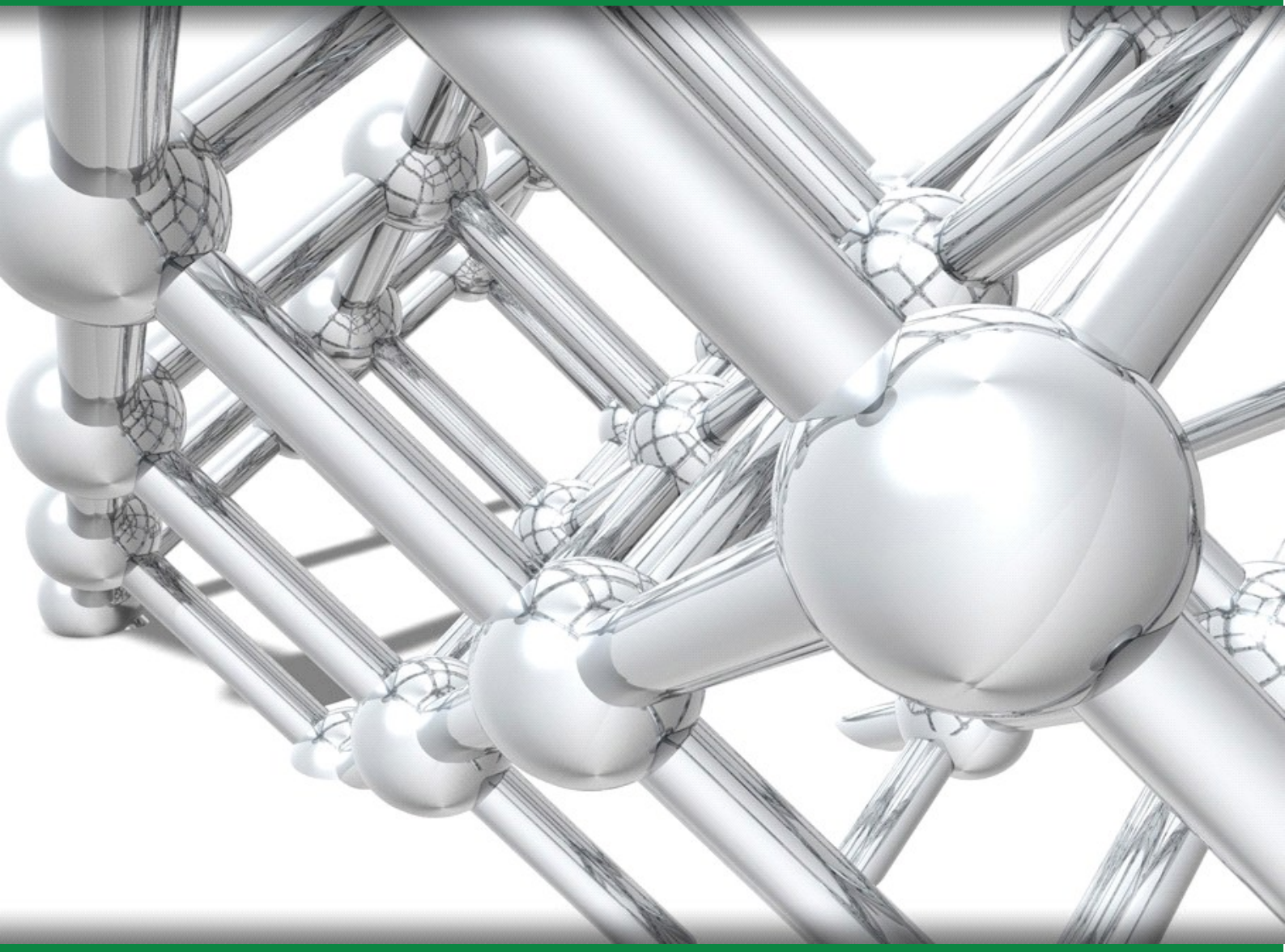
RAFAEL KANDIYOTI

FUNDAMENTALS OF REACTION ENGINEERING



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CHAPTER 1

INTRODUCTION TO CHEMICAL REACTOR DESIGN

1.1 Introduction

We seek to design reaction vessels, i.e. chemical reactors, where a particular chemical reaction (or set of reactions) is carried out. The first decision we take involves the configuration of the reactor and its mode of operation. This means we must decide what reactor type (and reactor shape) to select and whether it would be advantageous to operate in batch or continuous mode.

Other design decisions regarding the new reactor will be affected by a multiplicity of factors. To arrive at an appropriate design, we need information on the reaction kinetics and the required daily output. For relatively small daily production rates, we need to choose between batch and continuous operation, while, large throughputs usually require operation in continuous mode. If the reaction is rapid, we would need short residence times in the reactor. This might imply the use of high fluid velocities or small reactor dimensions, or a combination of the two.

If we choose continuous operation, we still need to select the type of reactor to design and use. We will primarily focus on tubular reactors and continuous stirred tank reactors (CSTR). We will then need to size the reactor. Together with the throughput requirement and available flow rates, the data will allow us to calculate the residence time and help us decide on the shape of the reactor calculate the required size.

The operating temperature and pressure are usually selected on the basis of the kinetics of the reaction and whether the reaction gives off heat (exothermic) or requires a heat input to proceed (endothermic). We will also need to know initial reactant concentrations available to us. Depending on how the problem is presented, some of these operating conditions may have already been specified or we may have to specify these parameters as part of the design process.

Criteria for choosing between batchwise and continuous operation: Batch operation

For small production rates (like pharmaceuticals, dyestuffs etc) of say a few tons/day, batch operations are generally more flexible and economical. Batch operations tend to require smaller capital expenditure than corresponding continuous processes, especially when the required production is of relatively low tonnage. However, quality control may be a problem, as replicating identical conditions in each batch may prove problematic. It is commonly said that no two vats of dye have exactly the same colour.

Criteria for choosing between batchwise and continuous operation: Continuous operation

Continuous operation is eventually adopted in most large-scale chemical processes. Its advantages include the ease of using on-line control systems and diminished labour costs owing to the elimination of many operations such as emptying and filling of reaction vessels. Whilst the use of advanced control systems usually requires greater capital outlay, it enables greater constancy in reaction conditions and improved product quality control. However, designing a continuous reactor requires accounting for the state of flow. Not all molecules going through a reactor will necessarily have the same residence time, or the same time-temperature or concentration histories. Compared to a corresponding batch process, this may lead to significant differences in average reaction rates and overall yields. To summarize, the “right” set of decisions for designing a chemical reactor will depend on numerous technical factors as well as the interplay between capital costs and operating costs. Many other factors may have a role including extraneous factors such as company design habits, supplier preferences, etc.

1.2 General mass balance for isothermal chemical reactors

In order to introduce the basic types of chemical reactors, their modes of operation and basic flow patterns, we will first consider them under isothermal conditions. This means that we will, at first, neglect heat release (or uptake) by the reaction. We will also neglect heat transfer between parts of the reactor and/or heat exchange with the surroundings.

The material balance for a reactant can be written in a general form applicable to any type of reactor. For a time element Δt and a volume element (of the reactor) ΔV_R the principle of the conservation of mass may be formulated as:

$$\left\{\begin{matrix}\text{Mass of Reactant}\\ \text{fed to the Volume}\\ \text{Element per unit time}\end{matrix}\right\} - \left\{\begin{matrix}\text{Mass of Reactant}\\ \text{leaving the Volume}\\ \text{Element, per unit time}\end{matrix}\right\} - \left\{\begin{matrix}\text{Mass of Reactant}\\ \text{converted in the}\\ \text{Volume Element}\\ \text{per unit time}\end{matrix}\right\} = \left\{\begin{matrix}\text{Accumulation of}\\ \text{reactant in the}\\ \text{volume element}\\ \text{per unit time}\end{matrix}\right\}$$

(Eq. 1.1)

The third term of Eq. 1, involving "Mass of reactant converted…" will have the form "$r\ (\Delta V_R)\ (\Delta t)$" . In this expression, "r" is defined as the rate of disappearance of a given reactant per unit volume of reactor, per unit time. It is useful to check each time whether you are given the rate in terms of *formation* or *disappearance* of a particular component. ΔV_R is defined as the "volume element" and Δt, the time element being considered.

We will next consider how this equation applies to particular reactor types. If concentrations and the temperature are uniform throughout the reactor, the volume element can be taken as the whole reactor. This is the case for stirred batch and continuous stirred tank reactors (CSTR) described below. If however, concentrations change as a function of position within an isothermal reactor, then the mass balance equation would take the form of a differential equation. We will encounter this type of analysis, when we examine mass balances of tubular reactors.

1.3 Mass balances for isothermal batch reactors

Batch reactor operation is fundamentally an unsteady state process; we expect all variables to change with time. All materials are charged into a batch reactor at the outset and no withdrawal is made until the reaction has reached the degree of completion desired. The mixture in the reactor volume, V_R, is generally well stirred. This means that concentrations and the temperature may be assumed to be uniform at every point within the reactor. We will initially only consider isothermal reactors. However, we note that, in an actual reactor, the temperature may also change with time. The volume may be kept fixed (constant volume), or may be varied during the reaction to keep the pressure constant.

If the reactor volume V_R is filled with reactant "A", the mass balance for component "A" over the volume V_R, over the time period t to $(t + \Delta t)$ is given by:

$$\underset{\textbf{mass of A at } t}{(M_A N_A)_t} - \underset{\textbf{mass of A at } t+\Delta t}{(M_A N_A)_{t+\Delta t}} = \underset{\textbf{conversion by reaction during } \Delta t}{(M_A r_A V_R)\ \Delta t} \qquad \textbf{(Eq. 1.2)}$$

In this equation

$N_A = N_A(t) \equiv$ number of moles of reactant "A" within the system at time t,
$M_A \equiv$ the molecular weight of "A", and,
$r_A = r_A(t) =$ net reaction rate of component "A",
[=] moles of A disappearing / (unit of time) (unit of volume)

Here the symbol ≡ denotes "defined by" and the symbol [=] denotes "has units of". In Eq. 1.2, we may divide every term by M_A. Taking the limit as $\Delta t \rightarrow 0$, we get

$$-r_A V_R = \frac{dN_A}{dt} \text{ and } r_A = -\frac{1}{V_R}\frac{dN_A}{dt}. \qquad \textbf{(Eq. 1.3)}$$

This is the mass balance equation for a batch reactor expressed in terms of the disappearance of a *reactant*. Eq. 1.3 is sometimes also called the 'design equation'. If the rate is defined in terms of a *product* B

$$r_B = \frac{moles\ of\ B\ formed}{(unit\ time)(unit\ volume)} \text{ and } r_B = \frac{1}{V_R}\frac{dN_B}{dt}. \qquad \textbf{(Eq. 1.4)}$$

In this introductory treatment, we will assume that the volume of the reactor does not change as a function of time. Normally, the reactant concentration falls off as a function of time.

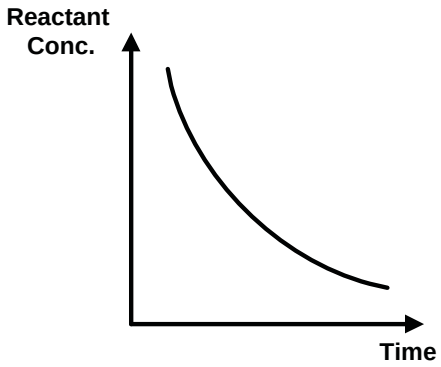


Figure 1.1 The change of reactant concentration in a batch reactor as a function of time.

A few things to remember

Unless externally arrested (say by quenching), a homogeneous chemical reaction would be expected to proceed either (a) until equilibrium is reached, or, (b) in the case of an irreversible reaction, until the reactants are exhausted. The time necessary for achieving a given degree of reaction, say from $N_{AO} \rightarrow N_A$ is found from integrating the mass balance equation.

$$r_A = -\frac{1}{V_R}\frac{dN_A}{dt} \qquad \textbf{(Eq. 1.5a)}$$

Transposing and integrating

$$t = -\int_{N_{A0}}^{N_A} \frac{1}{V_R}\frac{dN_A}{r_A} \qquad \textbf{(Eq. 1.5b)}$$

The conversion x_A at any time t is defined as:

$$x_A = \frac{N_{A0} - N_A}{N_{A0}}; \quad dx_A = -\frac{dN_A}{N_{A0}} \qquad \textbf{(Eq. 1.6a)}$$

Transposing,

$$N_A = N_{A0}(1 - x_A); \quad dN_A = -N_{A0}\, dx_A \qquad \textbf{(Eq. 1.6b)}$$

The time required for achieving conversion x_A may be calculated from

$$t = \int_0^t dt = \int_0^{x_A} \frac{N_{A0}}{V_R} \frac{dx_A}{r_A} \qquad \textbf{(Eq. 1.7)}$$

We consider the case where a first order irreversible reaction, $A \rightarrow B$, with rate expression $r_A = kC_A$, is carried out in a batch reactor. The rate constant has the value: $k = 0.02\ s^{-1}$. We can calculate the time required to reach a fractional conversion of 0.4, as follows:

$$r_A = kC_A = \frac{kN_A}{V_R} = \frac{kN_{A0}(1 - x_A)}{V_R}.$$

Then,

$$t = \int_0^{x_A} \frac{dx_A}{k(1 - x_A)} = \left\{ -\frac{1}{k} ln(1 - x_A) \right\}_0^{0.4} = 25.5\ s. \qquad \textbf{(Eq.1.8)}$$

1.4 Continuous operation: Tubular reactors & the plug flow assumption

Tubular reactors are mostly used for gas phase reactions although liquid phase applications are also common. The NO-oxidation reaction, a step in the production of HNO_3 from NH_3,

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

is an example of reactions carried out in tubular reactors. Tubular reactions are also widely used for catalytic reactions, where the reactor is filled with catalyst. The syntheses of methanol and ammonia are common examples.

$$CO + 2H_2 \rightleftharpoons CH_3OH$$
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

In such reactors, there is a steady movement of reagents along the length of the tubular vessel. During steady state operation, concentrations at any given point in the reactor may be assumed not to change with time. In this type of reactor, no attempt is normally made to induce mixing between elements of fluid.

Mass balances for tubular reactors in steady state operation: Once again, we will first consider the material balance for an *isothermal* reactor. A formal mass balance over a differential volume element requires that we know (or assume) patterns of fluid behaviour within the reactor. The simplest set of

assumptions about the behaviour of the fluid in a tubular reactor is the 'Plug Flow Assumption' (PFA), also known as 'piston flow'.

The plug flow assumption: The flow rate and fluid properties (P,T, composition) are assumed to be uniform over any cross section normal to the motion of the fluid, leading to the term "piston flow". We assume that axial mixing by convection or diffusion may be neglected.

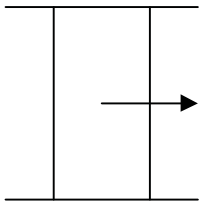


Figure 1.2 A "plug" of fluid in a tubular reactor

Good radial mixing may in fact be obtained when operating at relatively high flow rates, for example at Reynold's Number values of Re ~ 10^4. *Axial* mixing may be realistically neglected when the length/diameter ratio approaches ~ 50. At this stage we will assume the reactor to be isothermal so we can describe reactor performance through the material balance alone. In the analysis of non-isothermal reactors, which will be examined later on in this book, the material balance equation is coupled with the energy balance equation.

Implications of the Plug Flow Assumption ('PFA'): Over any cross-section normal to the reactor axis, i.e. within any piston or 'plug' of fluid, all properties of the reacting mixture are assumed to be uniform. These properties include the mass flow rate, the flow velocity, the pressure, the temperature and the composition. Each plug of fluid is assumed to spend the same length of time as all others, in passing through the reactor. Each plug of fluid is similarly assumed to go through the same temperature, pressure and concentration histories. Thus, a plug of fluid may be viewed as a small batch reactor, passing through the tubular reactor without interacting with the preceding or succeeding plug of fluid. Diffusion relative to bulk flow is neglected. It is also important to remember that axial temperature gradients do not in themselves violate the PFA. However, we will postpone the treatment of non-isothermal reactors to a little later in the book.

The tubular reactor mass balance using the plug flow assumption: It is convenient to perform the material balance over the reactor on a mass basis. Volume or moles are not necessarily conserved. At steady state, the mass balance over a single reactant A is given as follows. [Holland & Anthony, 1979]

$$(M_A n_A)_V \quad - \quad (M_A n_A)_{V+\Delta V} \quad - \quad M_A r_A \Delta V_R \quad = \quad 0 \qquad \textbf{(Eq. 1.9)}$$

$$\left\{\begin{matrix} \textit{inflow of A} \\ \textit{per unit time} \\ \textit{into} \\ \textit{volume element} \end{matrix}\right\} - \left\{\begin{matrix} \textit{outflow of A} \\ \textit{per unit time} \\ \textit{into} \\ \textit{volume element} \end{matrix}\right\} - \left\{\begin{matrix} \textit{loss of A} \\ \textit{per unit time} \\ \textit{through} \\ \textit{reaction} \end{matrix}\right\} = \left\{\begin{matrix} \textit{rate of} \\ \textit{accumulation} \end{matrix}\right\} \qquad \textbf{(Eq. 1.10)}$$

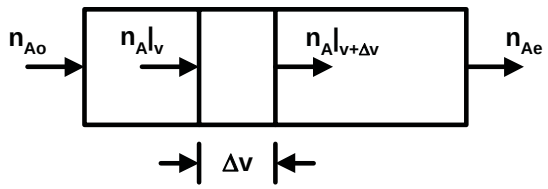


Figure 1.3 The mass balance of a ("plug") volume element in a tubular reactor

As before, the term r_A has units of 'moles/[(volume)(time)]'. In this equation, each term has units of 'mass/time'. Dividing by M_A (the molecular weight) and taking the limit as $\Delta V \rightarrow 0$:

$$-\frac{dn_A}{dV_R} - r_A = 0$$

leads to

$$r_A = -\frac{dn_A}{dV_R} . \qquad \textbf{(Eq. 1.11a)}$$

This is the material balance equation for a tubular reactor assumed to be operating in plug flow. It is also sometimes called the "design equation". Many students forget the (-) sign in this equation. Care must be taken not to! Clearly for the case where the mass balance is carried out over a *product* component "B":

$$r_B = \frac{dn_B}{dV_R} . \qquad \textbf{(Eq. 1.11b)}$$

A convenient way of looking at the plug flow assumption (PFA) is to visualise each plug as travelling through the tubular reactor as a small batch reactor. Equation 1.11a may be compared with the batch reactor mass balance equation.

$$r_A = -\frac{dC_A}{dt} . \qquad \textbf{(Eq. 1.12)}$$

Equation (1.11a) allows sizing a tubular reactor necessary for converting an initial molar flow rate of reactant n_{A0} to an eventual molar flow rate $n_{A,\,Exit}$

$$\int_0^V dV_R = -\int_{n_{A0}}^{n_{Ae}} \frac{dn_A}{r_A} .$$

Integrating the left side, we get

$$V_R = -\int_{n_{A0}}^{n_{Ae}} \frac{dn_A}{r_A} \qquad \textbf{(Eq. 1.13)}$$

Note that the calculation of the reactor volume using the plug flow assumption gives no information about the corresponding length/diameter ratio.

Similar expressions can readily be derived for fixed bed catalyst reactors (FCBR), where the volume of reactor is replaced by the weight of catalyst. In such cases, the reaction rate is expressed in terms of "moles/(wt-cat) (time)". Note, again, that the use of both expressions (i.e. empty tube & FBCR) is limited by the applicability of the PFA.

The fractional conversion: In flow reactors, the fractional conversion is defined by the equation

$$n_A = n_{A0}(1 - x_A) . \qquad \textbf{(Eq 1.14)}$$

The molar flow rate, n_A, is related to the concentration through the equation $n_A = C_A v_T$ and carries units of [moles/time]. Thus if (and only if) the total volumetric flow rate v_T is constant throughout the reactor, we can write

$$\frac{n_A}{v_T} = \frac{n_{A0}}{v_T}(1 - x_A) \;\; and \;\; C_A = C_{A0}(1 - x_A) \qquad \textbf{(Eq. 1.15)}$$

Where more than one reaction is in progress, a set of ordinary differential equations of the form

$$\frac{dn_i}{dV} = -r_i \qquad \textbf{(Eq. 1.16)}$$

may have to be solved simultaneously. However, for the time being, we will deal with single reactions. There are several points to consider before we can perform the integration indicated by Equation (1.13)

$$V_R = -\int_{n_{A0}}^{n_{Ae}} \frac{dn_A}{r_A}$$

can be performed. To explain this fully, a few new elements must be introduced into the discussion. The *rate expression* is usually given in terms of the concentrations or partial pressures of the reactants. Consider the chemical reaction:

$$aA \rightarrow bB + dD \qquad \textbf{(Eq. 1.17)}$$

and the associated simple reaction rate expression:

$$r_A = kC_A^n . \qquad \textbf{(Eq.1.18)}$$

The algebraic form of the reaction rate expression [reaction order etc.] is usually obtained experimentally for each reaction. Whether the reaction rate can be deduced from the stoichiometry directly can only be ascertained empirically. For example, in Eq. 1.18 the exponent '*n*' is not necessarily equal to the stoichiometric coefficient '*a*'of Eq. 1.17.

1.4.1 Integration of the tubular reactor mass balance equation (plug flow assumption)

Step 1: Consider a case where the reaction rate expression is written in terms of concentrations. The rate expression must be re-cast in terms of molar flow rates (n_A, n_B etc) rather than concentrations. The equation

$$n_A = C_A v_T$$

is well worth remembering. It will come up time and again. In this equation, n_A is the molar flow rate with units of "moles sec^{-1}", C_A the concentration of "A" with units of "moles vol^{-1}" and v_T is defined as the total volumetric flow rate through the reactor, with units of vol s^{-1}. The mass balance equation can now be written as:

$$V_R = -\int_{n_{A0}}^{n_{Ae}} \frac{dn_A}{k\left(\frac{n_A}{v_T}\right)^n} = -\int_{n_{A0}}^{n_{Ae}} \frac{v_T^n}{k}\frac{dn_A}{n_A^n} \qquad \textbf{(Eq.1.19)}$$

Step 2: We have already seen that for continuous reactors, the equation

$$n_A = n_{A0}(1-x_A) \qquad \textbf{(Eq. 1.14)}$$

defines the fractional conversion, x_A. When the total volumetric flow rate, v_T, is constant throughout the reactor, i.e. when the density or molar volume of the reacting mixture can be assumed constant as it travels down the reactor, we can write:

$$\frac{n_A}{v_T} = \frac{n_{A0}}{v_T}\left(1-x_A\right) \qquad \Rightarrow \qquad C_A = C_{A0}(1-x_A) \qquad \textbf{(Eq. 1.20)}$$

Clearly, if v_T is not constant, $\frac{n_{A0}}{v_T} \neq C_{A0}$ and the equation "$C_A = C_{A0}(1-x_A)$" is no longer valid.

In general, changes in v_T may be safely neglected when dealing with liquid phase reactions. However, for gas phase reactions where the number of moles changes (as in the reaction $A \rightarrow B + C$) and/or when the axial temperature, and therefore the molar volume changes, the change in v_T as a function of position must be taken into account. In fact, v_T must be expressed in terms of n_A or whatever other variable (such as the conversion, x_A) is selected for tracking the progress of the reaction. We will presently cover that particular case in some detail.

Step 3: If v_T may be assumed constant throughout the reactor, the term involving v_T can be taken out of the integrand.

$$V_R = -v_T^n \int_{n_{A0}}^{n_{Ae}} \frac{dn_A}{kn_A^n} \qquad \textbf{(Eq. 1.21)}$$

Step 4: The rate expression also contains a reaction rate constant 'k', which is a sensitive function of the temperature. Typically, k is proportional to an exponential in the temperature: $e^{-E/RT}$. Thus the integration indicated above cannot be carried out simply, unless we are able to assume "k" to be a constant, that is, unless the system is assumed to be isothermal. When the temperature changes with the conversion, the design equation (i.e. the material balance) must be coupled with an energy balance equation and solved simultaneously. We will see how we deal with such problems a little later in this text. Meanwhile, the assumption of isothermal operation may be considered as valid when the heat evolved during (or absorbed by) the reaction may be neglected.

Let us assume for present purposes that both v_T and k are constant for this reaction, throughout the reactor. For a first order reaction, assuming the exponent n to have a value of unity, the integration is straightforward:

$$V_R = \frac{v_T}{k} ln\left(\frac{n_{A0}}{n_{Ae}}\right) \qquad \textbf{(Eq. 1.22)}$$

For $n \neq 1$, the volume of the reactor may be calculated from the expression:

$$V_R = \frac{v_T^n}{k}\left(\frac{1}{n-1}\right)\left\{\frac{1}{n_{Ae}^{n-1}} - \frac{1}{n_{A0}^{n-1}}\right\} \qquad \textbf{(Eq. 1.23)}$$

1.4.2 Volume Change Upon Reaction in Isothermal Tubular Reactors

In gas phase reactions at constant pressure, changes in the total number of moles with increasing conversion give rise to changes in volume. This affects the gas velocity and the total volumetric flow rate. Consider the reaction,

$$A \rightarrow 2S, \qquad \textbf{(Eq. 1.24)}$$

where "A" and "S" are gases. The total volumetric flow rate, v_T, would change as a function of conversion, and also, as a function of position within the reactor. Postulating a simple reaction rate expression, $r_A = kC_A = kn_A / v_T$, we can write the material balance (design equation) for an isothermal tubular reactor and integrate:

$$V_R = -\int_{n_{A0}}^{n_{Ae}} \frac{v_T^n}{k}\frac{dn_A}{n_A^n} \quad . \qquad \textbf{(Eq. 1.19)}$$

For this type of reaction, v_T is not a constant with respect to n_A and cannot be taken out of the integrand in Eq. (1.19) as a constant. Instead, the molar flow rate, n_A, and the total volumetric flow rate, v_T, are expressed in terms of x_A (the fractional conversion), by using the relationships given below. Allowing that there may be some product S and also some inert gaseous component 'I' in the mixture *entering* the reactor:

n_I	=	n_{I0}	for the inert component	
n_A	=	$n_{A0} - n_{A0}x_A$	for the reactant	**(Eq. 1.25)**
n_S	=	$n_{S0} + 2\,n_{A0}\,x_A$	for the product	
---				
n_T	=	$n_{T0} + n_{A0}x_A$	n_T is the total molar flow rate as a function of the local conversion	

We now need an expression relating the molar flow rate to the total volumetric flow rate. In cases where the pressure is not very high, using the ideal gas law as the thermodynamic equation of state is usually appropriate.

$$Pv_T = n_T RT$$

leads to:

$$v_T = n_T\left(\frac{RT}{P}\right).$$

Replacing n_T with the expression derived in Eq. 1.25 ($n_T = n_{T0} + n_{A0}x_A$) we get:

$$v_T = \left(n_{T0} + n_{A0}x_A\right)\left(\frac{RT}{P}\right). \qquad \textbf{(Eq. 1.26)}$$

Assuming a first order reaction and substituting Eq. (1.26) for v_T in the design equation (Eq. 1.19), we get

$$V_R = -\int_{n_{A0}}^{n_{Ae}} \left(n_{T0} + n_{A0}x_A\right)\left(\frac{RT}{P}\right)\left(\frac{1}{k\,n_A}\right)dn_A \qquad \textbf{(Eq. 1.27)}$$

The defining equation for the fractional conversion was written in Eq (1.14) as $n_A = n_{A0}(1 - x_A)$.
Differentiating, we get:

$$dn_A = -n_{A0}dx\,. \qquad \textbf{(Eq. 1.28)}$$

This expression may now be used for changing variables in Eq. 1.27.

$$V_R = -\int_0^{x_{Ae}} \frac{(n_{T0} + n_{A0}x_A)}{(n_{A0} - n_{A0}x_A)} \left(\frac{RT}{P}\right) \frac{1}{k} (-n_{A0})\, dx_A \qquad \textbf{(Eq. 1.29)}$$

The limits of integration in Eq. 1.29 arise from $n_A = n_{A0}(1\text{-}x_A)$:

When $n_A = n_{A0}$ $\Rightarrow$ $x_A = 0$ **(Eq. 1.30)**

When $n_A = n_{Ae}$ $\Rightarrow$ $x_A = x_{Ae}$

Thus far, we have assumed the pressure drop, ΔP, through the reactor to be negligible. Unless high pressures are used (say above 10 or 20 bar) *and* the pressure drop is significant, pressure effects are usually dwarfed by the effect of variations in the temperature. Neglecting ΔP is not permissible, however, in many catalyst packed reactors, where it constitutes a significant fraction of the total pressure.

We then require another equation relating the internal total pressure either to the conversion or, more usually, to the position variable within the reactor. In this case we need to consider resorting to numerical procedures, to solve the pressure (momentum) equation and the material balance, and eventually the energy balance, simultaneously.

Continuing from Eqs. 1.30 and 1.30 and assuming an isothermal reactor where the pressure drop may be neglected, we get:

$$V_R = \frac{RT}{Pk}\left\{ n_{T0} \int_0^{x_{Ae}} \frac{dx_A}{1-x_A} + n_{A0} \int_0^{x_{Ae}} \frac{x_A dx_A}{1-x_A} \right\} \quad . \qquad \textbf{(Eq. 1.31)}$$

We next define the integrals, I_1 and I_2: $I_1 = \int_0^x \frac{dx}{1-x} = -ln(1-x)$ and $I_2 = \int_0^x \frac{xdx}{1-x}$ **(Eq. 1.32)**

I_1 is integrated easily. There are two equally quick ways of integrating I_2:

$$I_2 = \int_0^x \frac{xdx}{1-x} = -\int_0^x \left(1 - \frac{1}{1-x}\right) dx \qquad \textbf{(Eq. 1.33)}$$

and the integration is then straightforward. Alternatively Eq. 1.32 can be integrated "by parts", as follows: We define $u = x$, and, $dv = dx/(1\text{-}x)$. Then: $du=dx$ and $v= - ln\,(1\text{-}x)$. We then use the expression:

$$\int udv = uv - \int vdu$$

$$I_2 = -x\,ln(1-x) + \int_0^x ln(1-x)dx = -\{(1-x)ln(1-x) + x\} \qquad \textbf{(Eq. 1.34)}$$

$$I_2 = -x\,ln(1-x) - (1-x)ln(1-x) - x = -ln(1-x) - x; \quad so... \qquad \textbf{(Eq. 1.35)}$$

$$V_R = \frac{RT}{Pk} n_{T0} \{-ln(1-x_{Ae}) - y_{A0}\,ln(1-x_{Ae}) - y_{A0}x_{Ae}\} \qquad \textbf{(Eq. 1.36)}$$

where $y_{A0} \equiv n_{A0}/n_{T0}$, the mole fraction of "A" at the inlet. Finally, we get:

$$V_R = \frac{RT}{Pk} n_{T0} \left\{ (1+y_{A0})\,ln\left[\frac{1}{1-x_{Ae}}\right] - y_{A0}x_{Ae} \right\} \qquad \textbf{(Eq. 1.37)}$$

Remember: If the heat of reaction, ΔH_r, is significant, the energy and mass balance equations would have to be solved simultaneously. We will treat such problems later on in this book.

Also remember: In principle, most reactions produce a change in volume. However, it is usually a good first approximation to take $\Delta V = 0$ *for liquid phase reactions*. Clearly $\Delta V = 0$ is also strictly correct for ideal gases reacting with no overall change in the number of moles.

1.5 Continuous operation: Continuous stirred tank reactors & the perfect mixing assumption

A stirred tank reactor can be operated as a steady flow reactor (CSTR), as a batch reactor, or in semi batch mode. The latter is the case of fermenters, where a gas (usually air) is bubbled through liquid in the stirred tank. The common key feature in all these cases is the assumption that mixing is immediate and complete.

In an ideal CSTR, the composition, temperature and pressure of the reaction mixture are all assumed to be uniform everywhere in the vessel. These properties are assumed to be identical to the properties of the reaction mixture at the exit of the reactor. When these assumptions hold, the rate of reaction is expected to be uniform and constant throughout the vessel and may be evaluated at the temperature, pressure and composition of the product stream.

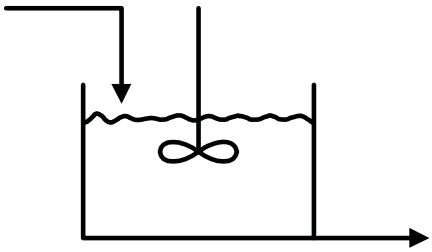


Figure 1.4 Schematic diagram of a continuous stirred tank reactor (CSTR)

Consider the simple case of a CSTR with a *single* feed stream and a *single* product stream. At steady state, the properties of this system will not change with time. The material balance around component "A", over the volume V, at steady state, is given by:

$$n_{A0} \quad - \quad \{n_A + r_A V_R\} \quad = \quad 0 \qquad \textbf{(Eq. 1.38)}$$

input into the reactor per unit time	**output of A by flow and loss through reaction per unit time**	**accumulation**

where n_{A0} the molar flow rate of A into the reactor [=] moles/time
n_A molar flow rate of A out of the reactor [=] moles/time
r_A [=] moles/[(volume) (time)]

Rewriting, we get

$$V_R = \frac{n_{A0} - n_A}{r_A} \qquad \textbf{(Eq. 1.39)}$$

The average residence time in a CSTR is defined as $\tau \equiv V_R/v_T$.

Mixing: A fair approximation to perfect mixing is not difficult to achieve in an ordinary CSTR, provided the fluid phase is not too viscous. In the laboratory, if an injected pulse of dye is distributed uniformly throughout the tank in a time much shorter than the average residence time of fluid in the tank, then the CSTR can probably be considered as 'well mixed'.

Lower overall reaction rates compared to tubular reactors: The "perfect mixing" assumption implies that the inlet reactant concentration rapidly (if the mixing is "perfect", *immediately*) drops to the concentration level of the mixture in the tank and in the outlet stream. In other words, the concentration driving force is quickly reduced to that in the product stream. This stepwise and rapid drop in concentration directly reduces the reaction rate. In general, the average rate of reaction in a CSTR is lower than, say, a tubular reactor with the same inlet concentration of reactants as the CSTR.

For the same reactor volume, therefore, the CSTR would give lower conversions. The relatively lower conversion in CSTRs – compared to tubular reactors – is a fundamental property, arising from the "perfect" mixing. The same phenomenon may also be described in terms of a higher proportion of by-pass of reactant in CSTRs. Clearly, in the absence of adequate mixing, bulk streaming between the inlet and outlet of the CSTR would make losses in conversion even greater.

Conversely, due to relatively lower reactant concentrations in the CSTR, the CSTR volume required for an equal conversion as a tubular reactor would need to be larger than the tubular reactor. As we will see later on, it is sometimes advantageous to have several smaller CSTR's in series, in order to reduce bypass loss and increase conversion.

Some advantages of CSTRs: Despite adverse factors like lower reaction rates, lower conversions and lower product concentrations, CSTRs are frequently used in industry, mostly for liquid phase reactions. They are easy and relatively cheap to construct. The greater volumes necessary for equal conversion, compared to tubular reactors, is comparatively less important as an economic factor, particularly in the case of atmospheric pressure tanks, made of inexpensive materials such as mild steel. Other advantages include easy temperature control due to the large volumes of partially reacted fluid, avoidance of hot spots and ease of maintenance due to their open construction.

Summary: For an isothermal reactor with no volume change on reaction, the design of a CSTR is simple. For A $\rightarrow$ products with rate expression $r_A = k\,C_A$ (irreversible reaction), remembering that $n_A = C_A v_T$, where n_A is the exit molar flow rate of reactant "A",

$$V_R = \frac{(n_{A0} - n_A)}{r_A} = \frac{(n_{A0} - n_A)}{k n_A} v_T \quad . \qquad \textbf{(Eq. 1.40)}$$

The perfect mixing assumption requires that fluid entering the vessel is instantaneously mixed with the fluid already present and that the time during which the new material passes through intermediate concentrations is short, effectively zero. For most types of kinetics, this stepwise dilution results in the average reaction rate being much smaller than if the same feed materials were allowed to react batchwise or in a tubular reactor. As shown in Figure 5, for equal conversions, the reactant concentration within the CSTR would be similar to the concentration at the termination of the process in a batch reactor or at exit of a tubular reactor.

We have already seen that for the same conversion, a larger CSTR volume is required compared to a tubular reactor. Using several tanks in series can diminish the necessary increase in reactor volume and the attendant cost of having several tanks in series is usually acceptable. Where high pressure vessels are involved, the additional cost associated with using large volumes and indeed of having several reactors in series may be significant. We will consider these points in more detail later on.

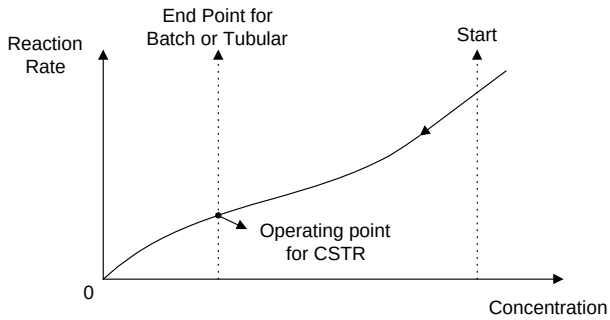


Figure 1.5 The reaction rate versus concentration diagram, showing differences between a CSTR and a tubular reactor.

1.5.1 CSTR design with volume change upon reaction

Consider the gas phase reaction $A \rightarrow 2S$ with the associated rate expression $r_A = k_p\, p_A$. Here, p_A is defined as the partial pressure of "*A*". Note the different form of the rate expression; in this case we have expressed it in terms of the partial pressure of the reactant, rather than the concentration. (There is no rule! Rate expressions can be given in different forms.) Nevertheless, the units of r_A must remain unchanged [mols/(volume×time)]. Accordingly, the reaction rate constant k_p has different units [moles/(time)(volume)(pressure)]. We use the design equation for CSTRs:

$$V_R = \frac{n_{A0} - n_A}{k_p p_A} = \frac{n_{A0} x_A}{k_p p_A} = \frac{n_{T0} y_{A0} x_A}{k_p p_A}, \qquad \textbf{(Eq.1.41)}$$

where y_{A0} is the mole fraction of component A in the feed. From the stoichiometry

$n_A = n_{A0} - n_{A0} x_A$ **(Eq. 1.42)**

$n_S = n_{S0} + 2\, n_{A0} x_A$ since we make two moles of "S" for every mole of "A" that is reacted

$n_I = n_{I0}$ the molar flow rate of inert component, if any, would remain unchanged

---

$n_T = n_{T0} + n_{A0} x_A$ this is the total molar flow rate at the point where the conversion is "x_A"

The partial pressure can now be written in terms of the total pressure and the conversion. Recalling that

$$n_T = n_{T0} + n_{A0} x_A = n_{T0}\,(1 + y_{A0} x_A), \qquad \textbf{(Eq. 1.43)}$$

and using the ideal gas law:

$$p_A = \frac{n_A}{n_T} p_T = \frac{n_{A0}(1 - x_A) p_T}{n_{T0}(1 + y_{A0} x_A)} = \frac{y_{A0} p_T (1 - x_A)}{1 + y_{A0} x_A} \qquad \textbf{(Eq. 1.43)}$$

Substituting back in the design equation

$$V_R = \frac{n_{T0} y_{A0} xA}{k_p}\left[\frac{1}{y_{A0} p_T}\right]\left\{\frac{1 + y_{A0} x_A}{1 - x_A}\right\} = \frac{n_{T0}}{k_p p_T} x_A \left\{\frac{1 + y_{A0} x_A}{1 - x_A}\right\} \qquad \textbf{(Eq. 1.43)}$$

In dealing with CSTR design, when v_T and p_A are known to change, both are mentioned as the properties of the EXIT stream in the design equation. This is because the exit properties are the same as the properties *inside* the reactor.

1.5.2 Comparison of plug flow and CSTR reactors

Example: Consider the first order reaction with constant mass density, A $\rightarrow$ products, with reactor parameters, $\frac{kV_R}{v_T} = 2$. For the plug flow reactor

$V_R = -\int_{n_{A0}}^{n_A} \frac{dn_A}{r_A} = -\int_{C_{A0}}^{C_A} \frac{v_T}{k}\frac{dC_A}{C_A} = -\frac{v_T}{k} ln \frac{C_A}{C_{A0}}$ where $C_A = \frac{n_A}{v_T}$. Then, ln $\frac{C_A}{C_{AO}} = -\frac{kV_R}{v_T}$ and

$\frac{C_A}{C_{AO}} = exp\left\{-\frac{kV_R}{v_T}\right\}$. So if $kV_R/v_T = 2$, $\frac{C_A}{C_{AO}} = 0.1353$ and the conversion is ~ 86.5 %.

Meanwhile, for the CSTR

$V_R = \frac{n_{A0} - n_A}{r_A} = \frac{v_T(C_{A0} - C_A)}{k\, C_A}$; $\frac{kV_R}{v_T} = \frac{C_{A0}}{C_A} - 1$; $\frac{C_{A0}}{C_A} = \left\{\frac{kV_R}{v_T} + 1\right\}$. Therefore

$\frac{C_A}{C_{A0}} = \frac{1}{3} = 0.3333$ and the conversion is ~ 67 %.

So for the same reactor volume the conversion is considerably less in the CSTR [Holland & Anthony, 1979]

1.6 CSTR reactors in cascade

We have seen that, for a comparable level of conversion, the volume of a CSTR may be much greater than that of a tubular reactor. This volume can be reduced by using two or more stirred tanks in series, the volume of each tank being much smaller than for a single CSTR. As an example, if we carry out the same reaction in two CSTR's in series, with reactor volumes equal to one half the original volume, then

$$N_R \equiv \frac{kV_R}{v_T} = 2 \quad , \quad \text{where } N_R = N_{R1} + N_{R2} \text{ and } N_{R1} = N_{R2} = 1. \qquad \textbf{(Eq. 1.44)}$$

$$V_R = \frac{n_{A0} - n_A}{r_A} \; ; \; \left[\frac{kV_A}{v_T}\right]_1 = \frac{C_{A0} - C_{A1}}{C_{A1}} \; ; \; \frac{C_{A0}}{C_{A1}} = N_{R1} + 1 ; \frac{C_{A1}}{C_{A0}} = \frac{1}{2} ; \frac{C_{A1}}{C_{A2}} = N_{R2} + 1 \text{ and } \frac{C_{A2}}{C_{A1}} = \frac{1}{2}$$

(Eq. 1.45)

Then $\dfrac{C_{A2}}{(1/2)C_{A0}} = \dfrac{1}{2}$; $\dfrac{C_{A2}}{C_{A0}} = \dfrac{1}{4}$. The conversion is increased up to 75 %.

We will show that as the number of perfectly mixed reactor stages is increased, the exit concentration from the last reactor tends to approach the outlet concentration of a plug flow reactor, which has a total volume equal to the sum of the volumes of the perfectly mixed reactors. In fact we will show that the conversion in an infinite number of CSTR's in series approaches that of a tubular reactor operating in plug flow.

An expression for the concentration of component A in the effluent stream from the last reactor in a series of N reactors of equal volume is developed as follows. For simplicity, we will assume the mass density and the total volumetric flow rate v_T to be constant. We will also assume a 1st order chemical reaction, that all the reactors have equal volumes V_R and that all the reactors operate at the same temperature. The reaction rate constant k will therefore have the same value in every reactor. The design equation for the 1st reactor can now be written as:

$$V_{R1} = \frac{n_{A0} - n_{A1}}{r_{A1}} = \frac{n_{A0} - n_{A1}}{kC_{A1}} \qquad \textbf{(Eq. 1.46)}$$

where C_{A1} is the exit concentration from the first reactor. Transposing,

$$C_{A1} = \frac{C_{A0} - C_{A1}}{\left(\frac{kV_R}{v_T}\right)}. \qquad \textbf{(Eq. 1.47)}$$

Defining $\frac{kV_R}{v_T} \equiv N_{R1}$ leads to $C_{A1} = \frac{C_{A0}}{1 + N_{R1}}$. **(Eq. 1.48)**

N_{Ri} is constant for all reactors and $N_{Ri} = N_R / N$, where $N_R = \left[k \sum V_{Ri}\right] / v_T$. **(Eq.1.49)**

We have already stated that $V_{R,i} = V_{R,\,i+1}$ for all i; then

$C_{A1} = \frac{C_{AO}}{1+(N_R/N)}$; then $C_{A2} = \frac{C_{A1}}{1+(N_R/N)} = \frac{C_{AO}}{(1+N_R/N)^2}$. **(Eq. 1.50)**

Hence,

$$C_{A,N-1} = \frac{C_{A,\,N-2}}{1+(N_R/N)} = \frac{C_{A,\,N-3}}{(1+N_R/N)^2} = \ldots\ldots = \frac{C_{AO}}{[1+(N_R/N)]^{N-1}} \qquad \textbf{(Eq. 1.51)}$$

and

$$C_{A,N} = C_{AO}/[1+(N_R/N)]^N \qquad \textbf{(Eq. 1.52)}$$

Now we must find the limiting value of $C_{A,N}$ as the number of reactors N is increased without bound (i.e. to infinity) while the total volume of the reactor is held fixed. In other words, we subdivide our original single CSTR into an array of infinitesimally small CSTR's in series. It is convenient to restate the equation

$$C_{A,N} = \frac{C_{A0}}{(1+N_R/N)^N} \quad \text{as} \quad ln\left(\frac{C_{A,\,N}}{C_{AO}}\right) = -\frac{ln(1+N_R/N)}{(1/N)}. \qquad \textbf{(Eq. 1.53)}$$

But

$$\lim_{N\to\infty}\left\{ln\left(\frac{C_{A,\,N}}{C_{A0}}\right)\right\} = \lim_{N\to\infty}\left\{-\frac{ln(1+N_R/N)}{(1/N)}\right\} = \frac{0}{0} \text{ indeterminate} \qquad \textbf{(Eq. 1.54)}$$

REMINDER: l'Hospital's rule states that $\lim_{t\to a} \frac{f(t)}{g(t)} = \lim_{t\to a} \frac{\left\{\frac{df(t)}{dt}\right\}}{\left\{\frac{dg(t)}{dt}\right\}}$ **(Eq. 1.55)**

Differentiating the numerator and the denominator separately,

$$\lim_{N\to\infty}\left(ln\frac{C_{A,N}}{C_{A0}}\right) = -\frac{\left[\frac{1}{1+(N_R/N)}\right]\left(-\frac{N_R}{N^2}\right)}{\left(-\frac{1}{N^2}\right)} = \frac{-\left(\frac{1}{1+0}\right)(-N_R)}{(-1)} = -N_R \quad , \qquad \textbf{(Eq. 1.56)}$$

which brings us to:

$$\lim_{N\to\infty}\left(\ln\frac{C_{A,N}}{C_{A0}}\right)=-N_R \Rightarrow \ln\frac{C_{A0}}{C_{A,out}}=\frac{kV_R}{v_T}\text{, where } V_R=\sum V_{R,i} \quad . \qquad \textbf{(Eq. 1.57)}$$

This is the expression for an isothermal plug flow reactor. Remember that for constant mass density and a first order reaction rate expression, the isothermal tubular reactor design equation is:

$$V_R=-\int_{n_{A0}}^{n_{Ae}}\frac{dn_A}{r_A}=-\int_{C_{A0}}^{C_{Ae}}\frac{v_T\,dC_A}{k\,C_A}=\frac{v_T}{k}\ln\frac{C_{A0}}{C_{Ae}} \qquad \textbf{(Eq. 1.58)}$$

We have thus shown that the concentration $C_{A,N}$ of A in the stream leaving the Nth perfectly mixed reactor approaches the concentration of A in the stream leaving a plug flow reactor, when the number of perfectly mixed reactors is increased without bound.

1.7 The start-up/shutdown problem for a CSTR normally operating at steady state

The dynamic (i.e. non-steady state) behaviour of chemical reactors is an important area of study on its own. This type of analysis provides the basis for the design of control systems for reactors during normal operation as well as during the start-up and shut down stages. As an introduction to the subject, we will study a simple but useful problem: that of a step change in inlet concentration during isothermal steady state operation. We will see that start-up/shut down problems may be handled by using similar methods. Of its kind, this is probably the simplest problem to solve.

CSTR mass balance with an accumulation term: This is no longer a steady-state problem. We carry out a material balance on component *A*, over the volume V_R over the time period Δt:

$$\left\{\bar{n}_{A0}(t)-\bar{n}_A(t)-\bar{r}_A(t)V_R\right\}\ \Delta t = N_A\big|_{t+\Delta t}-N_A\big|_t \qquad \textbf{(Eq. 1.58)}$$

In Eq. 1.58, the bars indicate averaging over the time interval Δt, and $N_A(t)$ is defined as the total number of moles of component A in the reactor at time t. We will work with a simple reaction rate expression: $r_A = k\,C_A$. We will assume V_R and v_T to be constant. Note that in general, it is necessary to write as many material balance equations as there are components with independently changing chemical concentrations. Remember that the inlet flow rates (and/or concentrations) of the various reactants are not necessarily related. For a simple reaction, $A \to Products$, it is possible to get by with a single mass balance equation.

As before $C_A=\frac{n_A}{v_T}=\frac{N_A}{V_R}$ and the average residence time is given by $\tau = V_R / v_T$ **(Eq. 1.59)**

Taking the limit as $\Delta t \to dt$ in the above equation,

$$n_{A0}-n_A-r_AV_R=\frac{dN_A}{dt}\ ,$$

where $N_A \equiv V_R\frac{n_A}{v_T}=V_RC_A$, which leads to

$$n_{A0}-n_A-\frac{kn_AV_R}{v_T}=\tau\frac{dn_A}{dt}\ .$$

Rearranging

$$\frac{dn_A}{dt}+\left[\frac{1}{\tau}+k\right]n_A=\frac{n_{A0}}{\tau} \qquad \textbf{(Eq. 1.60)}$$

The starting point of the problem is a CSTR operating at steady state. At $t = t_0$, a step change is assumed to take place in the inlet concentration from $n_{A0,ss}$ to n_{A0}. Now the question we must ask is: "How will the *outlet* molar flow rate of the reactant change with time?" Defining $\beta \equiv (1/\tau) + k$, we can write,

$$\frac{dn_A}{dt} + \beta n_A = \frac{n_{A0}}{\tau}. \qquad \textbf{(Eq. 1.61)}$$

The solutions are: $n_{A,\,complementary} = C_1 e^{-\beta t}$ and $n_{A,\,particular} = C_2$ *(const)*, where $n_A = n_{A,c} + n_{A,p}$ and C_1 and C_2 are arbitrary constants. Substituting the particular solution into the differential equation, we get: $\beta C_2 = n_{A0}/\tau$ and $C_2 = n_{A0}/\beta\tau$. We can then write

$$n_A = C_1 e^{-\beta\ t} + [n_{A0}/\beta\tau] \ . \qquad \textbf{(Eq. 1.62)}$$

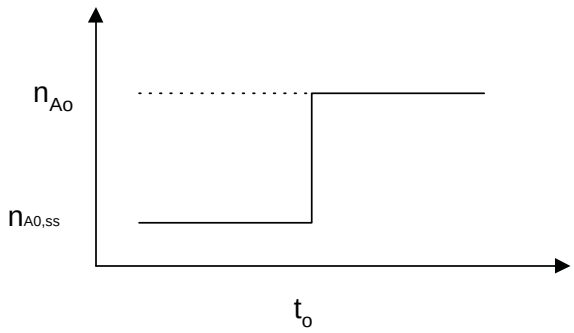


Figure 1.6 Schematic diagram of the step change in inlet concentration of reactant as a function of time

Eq. 1.62 is the "most general" solution. To derive C_1, we substitute the initial condition: $n_A = n_{A,ss}$ at $t=0$, into the general solution:

$$n_{A,ss} = C_1 + \frac{n_{A0}}{\beta\tau}; \qquad \Rightarrow \qquad C_1 = n_{A,ss} - \frac{n_{A0}}{\beta\tau}. \qquad \textbf{(Eq. 1.63)}$$

The solution of the differential equation then becomes

$$n_A = \left\{ n_{A,ss} - \frac{n_{A0}}{\beta\tau} \right\} e^{-\beta\ t} + \frac{n_{A0}}{\beta\tau} \ , \qquad \textbf{(Eq. 1.64)}$$

where $\beta\tau$ has been defined as $1+k\tau$. We next calculate the new steady state value of the exit stream i.e.

$$\lim_{t\to\infty} \quad n_A = \frac{n_{A0}}{\beta\tau} = \frac{n_{A0}}{1+k\tau}, \qquad \textbf{(Eq. 1.65)}$$

which denotes the new steady state exit molar flow rate of A. In fact, we would like to deal with finite lengths of time. The relevant question then becomes, how fast do we approach this steady state value?

For $t = 3\tau$ $\quad e^{-t/\tau} = e^{-3\tau/\tau} \approx 0.05$

$t = 5\tau$ $\quad e^{-t/\tau} = e^{-5\tau/\tau} \approx 0.007$

Hence, after three to five residence times, the outlet stream from the CSTR approaches the steady state values quite closely.

CHAPTER 2

REACTOR DESIGN FOR MULTIPLE REACTIONS

2.1 Consecutive and parallel reactions

In complex mixtures, the reaction leading to the desired product may be one of a number of parallel or consecutive reactions taking place. For example, during the partial oxidation of ethylene, the desired product is ethylene oxide. However, in a *parallel* reaction, ethylene may also directly combust, giving CO_2 and H_2O. In addition, once formed, ethylene oxide may also further oxidize to CO_2 and H_2O, through a *consecutive* reaction. [Holland & Anthony, 1979]

Parallel reactions:

$$A \xrightarrow{k_1} X \qquad r_1 = r_{A1} = k_1 C_A$$

$$A \xrightarrow{k_2} Y \qquad r_2 = r_{A2} = k_2 C_A$$

Consecutive reactions:

$$A \xrightarrow{k_1} X \qquad r_1 = r_A = k_1 C_A$$

$$X \xrightarrow{k_2} Y \qquad r_2 = r_X = k_2 C_X$$

Definitions of Yield, Overall Selectivity and Point Selectivity: Two parameters indicating the extent of desired performance are the production rate of ethylene oxide and its concentration in the reaction products. Since there are several possible outcomes of the set of reactions, we cannot assume the production rate of ethylene oxide to be necessarily *directly* related to the total amount of ethylene consumed.

Yield: The yield of a specific product is defined as the fraction of reactant converted to that product. Defining "*x*" as the conversion, the total fractional conversion of a reactant A would be written as

$$x_{total} = x_X + x_Y,$$

where x_X is the fractional conversion of "*A*" to "*X*" and x_Y is the fractional conversion of "*A*" to "*Y*".

Selectivity: The selectivity needs to be defined for each product separately. In this case, the overall selectivity to form *X* is defined as $S_0 = x_X / (x_X + x_Y)$. When there are more than two products to consider, it is also possible to define the selectivity in terms of a pair of products, or a group of products. For the purposes of this text, we will stay with the simple definitions used above. If our pair of parallel or consecutive reactions is assumed to take place at constant volume, the selectivity can also be defined in terms of the concentrations of the components involved. In this case: $S_0 = C_X / (C_X + C_Y)$

Point selectivity: The point selectivity at a particular point within the reactor refers to the local or instantaneous ratio of the rate of production of one product to the total rate of production of all products. In batch reactors, where we ordinarily assume perfect mixing, reaction related parameters do not vary with position inside the reactor. However, reaction parameters will vary as a function of time. Where we have just two products, *X* and *Y*, we can write the point selectivity in a batch reactor as:

$$S_p = \frac{(dC_X / dt)}{(dC_X / dt) + (dC_Y / dt)} \qquad \textbf{(Eq. 2.1)}$$

These derivatives are evaluated at a specified time during the reaction. In a tubular reactor assumed to be at steady state, however, the point selectivity would be a function of position within the reactor, and not a function of time.

$$S_p = \frac{(dC_X / dV_R)}{(dC_X / dV_R) + (dC_Y / dV_R)} \qquad \textbf{(Eq. 2.2)}$$

This equation represents the expression for the point selectivity at steady state, where the system does not change with time. Instead, the derivatives are evaluated at a specified position within the reactor.

The number of possible combinations of simultaneous (parallel) and consecutive reactions is large. We will consider several simple examples.

2.2 Simple Consecutive reactions: Applications to reactor types

2.2.1 Isothermal batch reactors

Consider the pair of consecutive liquid phase reactions

$$A \rightarrow X \qquad r_1 = r_A = k_1 C_A \qquad \text{(Reaction 1)} \qquad \textbf{(Eq. 2.3)}$$

$$X \rightarrow Y \qquad r_2 = r_X = k_2 C_X \qquad \text{(Reaction 2)} \qquad \textbf{(Eq. 2.4)}$$

In this reaction scheme, "*X*" is produced through Reaction 1 and consumed through Reaction 2. We next write rate expressions for the formation and consumption of the three species involved (i.e. *A*, *X* and *Y*):

$$r_A = k_1 C_A \qquad \textbf{(Eq. 2.5)}$$

$$r_X = k_1 C_A - k_2 C_X \qquad \textbf{(Eq. 2.6)}$$

$$r_Y = k_2 C_X \qquad \textbf{(Eq. 2.7)}$$

The *net* rate of formation/removal of the intermediate product "*X*" is expressed by Eq. 2.6, where the rate of removal of "*X*" from the system (forming the final product "*Y*") is subtracted from its rate of formation of "*X*" by the reaction of "*A*". Let us derive an expression for the number of moles of *A*, *X* and *Y* in the batch reactor, as a function of time. We have already derived:

$$r_A = -\frac{1}{V_R}\frac{dN_A}{dt}; \quad r_A = k_1 C_A = \frac{k_1 N_A}{V_R}, \qquad \textbf{(Eq. 2.8)}$$

reactor mass balance **reaction rate expression**

where $C_A = N_A / V_R$. Integrating the equation: $-\frac{1}{V_R}\frac{dN_A}{dt} = \frac{k_1 N_A}{V_R}$ between the limits $t = 0$ and $t = t$, leads to

$$N_A = N_{A0}\, exp(-k_1 t) \qquad \textbf{(Eq. 2.9)}$$

The *net* rate for the *production* of "*X*" would be

$$r_X = \frac{1}{V_R}\frac{dN_X}{dt}. \qquad \textbf{(Eq. 2.10)}$$

Note that there is no "minus" sign on the right hand side. Using Eq. 2.6:

$$r_X = \frac{1}{V_R}\frac{dN_X}{dt} = r_1 - r_2 = k_1 C_A - k_2 C_X \qquad \textbf{(Eq. 2.11)}$$

Rearranging terms and using $C_A = N_A / V_R$, we can write:

$$\frac{dN_X}{dt} + k_2 N_X = k_1 N_A. \qquad \textbf{(Eq. 2.12)}$$

We have already derived an expression for N_A: $N_A = N_{A0}\, exp(-k_1\, t)$. Substituting in Eq. 2.12,

$$\frac{dN_X}{dt} + k_2 N_X = k_1 N_{A0}\, exp(-k_1\, t). \qquad \textbf{(Eq. 2.13)}$$

This is a first order ordinary differential equation with constant coefficients and a non-homogeneous part. One way of solving it involves picking a "particular solution": $N_X^{part.} = A_p\, exp(-k_1\, t)$. Next, we substitute the "particular solution" in the differential equation (Eq. 2.13) and solve for the constant A_p, as follows:

$$-A_p k_1\, exp(-k_1\, t) + A_p k_2\, exp(-k_1\, t) = k_1 N_{A0}\, exp(-k_1\, t). \qquad \textbf{(Eq. 2.14)}$$

Then,

$$A_p = \frac{k_1 N_{A0}}{k_2 - k_1}. \qquad \textbf{(Eq. 2.15)}$$

The general solution with arbitrary constant *A* can then be written as:

$$N_X(t) = A\, exp(-k_2 t) + \left[\frac{k_1 N_{A0}}{k_2 - k_1}\right] exp(-k_1 t) \qquad \textbf{(Eq. 2.16)}$$

Next, we need to find the value of *A*. The amount of product *X*, at *t=0*, is zero. Solving for *A*, we get:

$$A = -\frac{k_1 N_{A0}}{k_2 - k_1}, \qquad \textbf{(Eq. 2.17)}$$

This allows us to write the full solution as:

$$N_X(t) = \left(\frac{k_1 N_{A0}}{k_2 - k_1}\right)\left[exp(-k_1\, t) - exp(-k_2\, t)\right] \qquad \textbf{(Eq. 2.18)}$$

An expression for N_Y can next be obtained using the overall mass balance equation, which states:

$$N_{A0} = N_A + N_X + N_Y \qquad \textbf{(Eq. 2.19)}$$

$$N_Y = N_{A0}\left[1 - \left(\frac{k_2}{k_2 - k_1}\right) exp(-k_1 t) + \left(\frac{k_1}{k_2 - k_1}\right) exp(-k_2 t)\right] \qquad \textbf{(Eq. 2.20)}$$

Figure 2.1 shows how N_A, N_X, N_Y change as a function of time in an isothermal batch reactor.

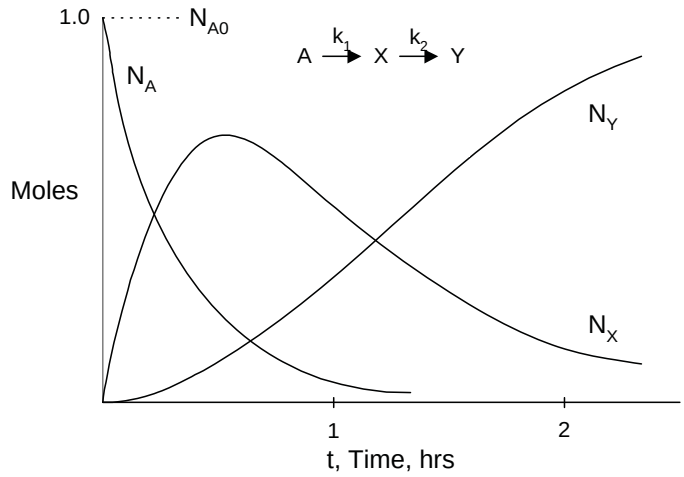


Figure 2.1 Number of moles of reactant A and products X and Y as a function of time; batch reactor

If the intermediate 'X' is the desired product, it would be desirable to maximise its production. Differentiating N_X with respect to time:

$$\frac{dN_X}{dt} = 0 = \left(\frac{k_1 N_{A0}}{k_2 - k_1}\right)\left[-k_1 \exp(-k_1 t_{opt}) + k_2 \exp(-k_2 t_{opt})\right] \qquad \textbf{(Eq. 2.21)}$$

$$\frac{\exp(-k_1 t_{opt})}{\exp(-k_2 t_{opt})} = \frac{k_2}{k_1}; \qquad t_{opt} = \frac{ln\left[\frac{k_2}{k_1}\right]}{k_2 - k_1} = \frac{1}{\left[k_{lm}\right]} \qquad \textbf{(Eq. 2.22)}$$

The 'ln-mean' operation used in this equation is defined as $Z_{lm} \equiv \dfrac{Z_2 - Z_1}{ln\left[\frac{Z_2}{Z_1}\right]}$ **(Eq. 2.23)**

2.2.2 Consecutive reactions: isothermal (plug flow) tubular reactors

$$A \xrightarrow{k_1} X \xrightarrow{k_2} Y$$

Assuming no density change upon reaction (say, for a liquid phase reaction), we can write the mass balance equation for a tubular reactor, operating in plug flow mode, as follows:

$$V_R = -\int_{n_{A0}}^{n_{Ae}} \frac{dn_A}{r_A}. \qquad \textbf{(Eq. 2.24)}$$

In this equation, the reaction rate expression is given by $r_A = k_1 C_A = k_1\, n_A / v_T$. Performing the integration and inserting the limits as indicated by (Eq. 2.24), we get:

$$V_R = -\frac{v_T}{k_1} ln\left(\frac{n_A}{n_{A0}}\right). \qquad \textbf{(Eq. 2.25)}$$

Solving for n_A, we get:

$$n_A = n_{A0}\, exp\left\{-k_1 \frac{V_R}{v_T}\right\}. \qquad \textbf{(Eq. 2.26)}$$

To obtain an expression for n_X, we start with a mass balance over component "X" in a volume element dV:

$$\frac{dn_X}{dV_R} = k_1 C_A - k_2 C_X \;\; ; \;\; \frac{dn_X}{dV_R} = \frac{k_1}{v_T} n_A - \frac{k_2}{v_T} n_X \;\; ; \;\; \frac{dn_X}{dV_R} + \frac{k_2}{v_T} n_X = \frac{k_1}{v_T} n_A \qquad \textbf{(Eq. 2.27)}$$

Note that an expression for n_A has already been derived (Eq. 2.26). Again, we are faced with a first order ordinary differential equation with constant coefficients. Let us solve this equation by a different method than in the previous section. We first define an integrating factor u. Multiplying both sides of the equation by u, we get:

$$u\frac{dn_X}{dV_R} + \frac{k_2}{v_T} u n_X = u \frac{n_{A0}}{v_T} k_1\, exp\left\{-\frac{k_1}{v_T} V_R\right\}. \qquad \textbf{(Eq.2.28)}$$

The left hand side of equation 2.28 can then be written as

$$\frac{d}{dV_R}\{u n_X\} = \frac{u n_{A0}}{v_T} k_1\, exp\left\{-\frac{k_1}{v_T} V_R\right\}, \qquad \textbf{(Eq. 2.29)}$$

where,

$$\frac{du}{dV_R} = \frac{k_2}{v_T} u \,;\; \frac{du}{u} = \frac{k_2}{v_T} dV_R \,;\; ln(u) = \frac{k_2}{v_T} V_R \text{ and } u = exp\left\{\frac{k_2}{v_T} V_R\right\}. \qquad \textbf{(Eq. 2.30)}$$

Eq. 2.29 can be can be integrated and divided by the function "*u*" to give:

$$n_X = \frac{k_1}{uv_T}\int_0^{V_R} un_{A0}\, exp\left\{-\frac{k_1 V_R}{v_T}\right\}dV_R = \left(\frac{n_{A0}k_1}{v_T}\right)exp\left\{-\frac{k_2}{v_T}V_R\right\}\int_0^{V_R} exp\left\{\frac{(k_2-k_1)V_R}{v_T}\right\}dV_R \quad \textbf{(Eq. 2.31)}$$

$$n_X = \left(\frac{k_1 n_{A0}}{v_T}\right)exp\left\{-\frac{k_2 V_R}{v_T}\right\}\left(\frac{v_T}{k_2-k_1}\right)\left\{exp\left[\frac{(k_2-k_1)V_R}{v_T}\right]\right\}_0^{V_R} \quad \textbf{(Eq. 2.32)}$$

$$n_X = \frac{k_1 n_{A0}}{(k_2-k_1)}exp\left\{-\frac{k_2 V_R}{v_T}\right\}\left\{exp\left[\frac{(k_2-k_1)V_R}{v_T}\right]-1\right\}. \quad \textbf{(Eq. 2.33)}$$

Finally

$$n_X = \frac{k_1 n_{A0}}{(k_2-k_1)}\left[\exp\left(-\frac{k_1 V_R}{v_T}\right)-\exp\left(-\frac{k_2 V_R}{v_T}\right)\right] \quad \textbf{(Eq. 2.34)}$$

Now we derive n_Y, by making use of expressions already derived for n_A and n_X and the overall mass balance equation.

$$n_{A0} = n_A + n_X + n_Y \rightarrow n_Y = n_{A0} - n_A - n_X \quad \textbf{(Eq. 2.35)}$$

$$\frac{n_Y}{n_{A0}} = 1-\exp\left\{-\frac{k_1 V_R}{v_T}\right\}-\frac{k_1}{k_2-k_1}\left[\exp\left\{-\frac{k_1 V_R}{v_T}\right\}-\exp\left\{-\frac{k_2 V_R}{v_T}\right\}\right] \quad \textbf{(Eq. 2.36)}$$

Note the similarity between the equations derived for the batch and PFR reactors. This is because, volume elements in plug flow may be thought of as small batch reactors travelling down the length of the tubular reactor.

2.2.3 Consecutive reactions: isothermal CSTR reactors

We have already defined the average residence time in a CSTR as $\tau \equiv V_R / v_T$. The design (isothermal mass balance) equation for component '*A*' can be re-written in terms of τ as follows:

$$V_R = \frac{n_{A0}-n_A}{r_A} = \frac{n_{A0}-n_A}{k_1 C_A} = \frac{n_{A0}-n_A}{k_1 n_A / v_T}; \quad \textbf{(Eq. 2.37)}$$

$$\frac{V_R}{v_T} = \tau = \frac{n_{A0}-n_A}{k_1 n_A}; \qquad n_A = \frac{n_{A0}}{1+k_1\tau} \quad \textbf{(Eq. 2.38)}$$

The isothermal mass balance equation for intermediate component "*X*" is written as:

$$\frac{n_X - n_{X0}}{V_R} = k_1\left[\frac{n_A}{v_T}\right]-k_2\left[\frac{n_X}{v_T}\right] \quad \textbf{(Eq. 2.39)}$$

Assuming $n_{X0} = 0$, *i.e.* that no '*X*' is present in the feed and re-arranging with Eq. 2.38 above,

$$n_X = \frac{k_1\tau n_A}{1+k_2\tau} = \frac{k_1\tau n_{A0}}{(1+k_2\tau)(1+k_1\tau)}. \quad \textbf{(Eq. 2.40)}$$

Eq. 2.40 shows how the conversion to intermediate product "X" in the exit stream changes as a function of the average residence time in the CSTR. Recalling that $n_Y = n_{A0} - n_A - n_X$, the conversion to final product "Y" may be calculated from

$$\frac{n_Y}{n_{A0}} = 1 - \frac{1}{1+k_1\tau} - \frac{k_1\tau}{(1+k_2\tau)(1+k_1\tau)} = \frac{k_1k_2\tau^2}{(1+k_2\tau)(1+k_1\tau)} \qquad \textbf{(Eq. 2.41)}$$

If 'X' is the desired product, we would have to find the residence time, which would maximise its rate of production:

$$\frac{dn_X}{d\tau} = 0 = \frac{d}{d\tau}\left\{\frac{k_1\tau n_{A0}}{(1+k_2\tau)(1+k_1\tau)}\right\}. \qquad \textbf{(Eq. 2.42)}$$

This equation easily simplifies to:

$$k_1k_2\tau^2 = 1 \quad ; \quad \tau = \frac{1}{\sqrt{k_1k_2}} \ . \qquad \textbf{(Eq. 2.43)}$$

2.3 Parallel reactions

Consider the two irreversible first order reactions taking place in parallel:

$$\begin{aligned} A &\xrightarrow{k_1} X\,; && \textit{Reaction 1} \\ A &\xrightarrow{k_2} 2Y && \textit{Reaction 2} \end{aligned} \qquad \textbf{(Eq. 2.44)}$$

Where the rate of Reaction 1 is given by $r_1 = k_1C_A$ and the rate of Reaction 2 is given by $r_2 = k_2C_A$. We define N_1 and N_2 as the number of moles of A reacted through Reaction 1 (rate constant k_1) and Reaction 2 (rate constant k_2) respectively. Then, $N_X = N_{X0} + N_1(t)$ and $N_Y = N_{Y0} + 2N_2(t)$. Note that in general $k_1 \neq k_2$. Indeed, if $k_1 = k_2$ then 2 moles of "Y" would be produced for each mole of "X" formed and "A" consumed and the reaction would be simply written as $2A \rightarrow X + 2Y$. Note that in either case, the net rate of disappearance of "A" is given by $r_A = r_1 + r_2$.

2.3.1 Parallel reactions: Isothermal batch reactors

If both reactions are irreversible, the material balance around reactant "A" remains the same as in the case of a single reaction. For simplicity, we will assume the fluid density to be constant. For a batch reactor, the rate of disappearance of A is given by

$$r_A = -\frac{1}{V_R}\frac{dN_A}{dt} \ , \qquad \textbf{(Eq. 2.45)}$$

and the reaction rate expression takes the form:

$$r_A = k_1C_A + k_2C_A = (k_1 + k_2)C_A = (k_1 + k_2)\frac{N_A}{V_R}. \qquad \textbf{(Eq. 2.46)}$$

Note that the total reactor volume V_R is being assumed constant and that r_A, C_A and N_A are all expected to change with time. Integrating the equation

$$-\frac{1}{V_R}\frac{dN_A}{dt} = (k_1 + k_2)\frac{N_A}{V_R} \qquad \textbf{(Eq. 2.47)}$$

gives

$$N_A = N_{A0}\,exp\left\{-(k_1+k_2)t\right\}. \qquad \textbf{(Eq. 2.48)}$$

In order to calculate the number of moles of each product formed through the two reactions, we go back to

$$\frac{dN_1}{dt} = k_1 N_A \quad , \qquad \frac{dN_2}{dt} = k_2 N_A \ , \qquad \textbf{(Eq. 2.49)}$$

and divide the two equations by one another**:**

$$\frac{dN_1}{dN_2} = \frac{k_1}{k_2} \qquad \textbf{(Eq. 2.47)}$$

We integrate with 'zero' initial conditions (i.e. $N_1 = 0$; $N_2 = 0$). This simply means that the reactions '1' and '2' start at $t=0$; it does not necessarily mean that we assuming zero initial concentration of products. Thus:

$$\frac{N_1}{N_2} = \frac{k_1}{k_2} \qquad \textbf{(Eq. 2.50)}$$

To obtain N_1 as a function of time, we make use of $N_A = N_{A0} - N_1 - N_2$. Combining, we get:

$$N_A = N_{A0} - N_1(1 + k_2/k_1). \qquad \textbf{(Eq. 2.51)}$$

Rearranging,

$$N_1 = k_1 \frac{(N_{A0} - N_A)}{(k_1 + k_2)} \qquad \textbf{(Eq. 2.52)}$$

where N_A has already been given by Eq. 2.46. Similarly,

$$N_2 = k_2 \frac{(N_{A0} - N_A)}{(k_1 + k_2)}. \qquad \textbf{(Eq. 2.53)}$$

Since $N_X = N_{X0} + N_1$ and $N_Y = N_{Y0} + 2\ N_2$, the above two equations allow writing N_X and N_Y as explicit functions of time:

$$N_X = N_{X0} + \frac{k_1}{(k_1 + k_2)}\{N_{A0} - N_{A0}\ exp\ [-\ (k_1\ +\ k_2)\ t]\} \qquad \textbf{(Eq. 2.54)}$$

Leading to

$$\frac{N_X - N_{X0}}{N_{A0}} = \frac{k_1}{(k_1 + k_2)}\{1 - exp\ [-\ (k_1\ +\ k_2)\ t]\} \qquad \textbf{(Eq. 2.55)}$$

and

$$\frac{N_Y - N_{Y0}}{N_{A0}} = \frac{2k_2}{(k_1 + k_2)}\{1 - exp\ [-\ (k_1\ +\ k_2)\ t]\}\ . \qquad \textbf{(Eq. 2.56)}$$

The last two equations allow calculating yields and selectivities to products "*X*" and "*Y*".

2.3.2 Parallel reactions: Isothermal (plug flow) tubular reactors

Consider the same simple parallel reaction system:

$$A \xrightarrow{k_1} X \qquad ; \qquad A \xrightarrow{k_2} 2Y$$

The molar flow rate of "*A*" is given by

$$n_A = n_{A0} - n_1 - n_2 \qquad \textbf{(Eq. 2.57)}$$

where

n_1 = flow rate of component A reacted to form "*X*" through Reaction 1, and,

n_2 = flow rate of component A reacted to form "*Y*" through Reaction 2.

The net rate of reaction will be the sum of r_1 (= k_1C_A) and r_2 (= k_2C_A). The mass balance equation for the reactant "A" is given by the usual expression, $r_A = -\ dn_A / dV_R$. Substituting the rate laws for r_1 and r_2:

$$-\frac{dn_A}{dV_R} = k_1C_A + k_2C_A = (k_1 + k_2)\frac{n_A}{v_T} \qquad \textbf{(Eq. 2.58)}$$

We have already defined the average residence time as $\tau \equiv V_R/v_T$. We will also assume (for simplicity) that we have a liquid phase reaction and that the total volumetric flow rate, v_T, is constant. Substituting τ for V_R/v_T in Eq. 2.56 and integrating the tubular reactor (plug flow) mass balance equation

$$n_A = n_{A0} \exp[-(k_1 + k_2)] \qquad \textbf{(Eq. 2.59)}$$

Note the similarity with the analogous equation for a batch reactor: $N_A = N_{A0} \exp\{-(k_1 + k_2)\, t\}$. We also have the two equations :

$$\frac{dn_X}{dV_R} = \frac{dn_1}{dV_R} = k_1 C_A \text{ and } \frac{dn_Y}{dV_R} = 2\frac{dn_2}{dV_R} = 2\, k_2 C_A \qquad \textbf{(Eq. 2.60)}$$

As in the treatment for the batch reactor, we divide the two equations

$$\frac{dn_1}{dV_R} = k_1 C_A \quad \text{and} \quad 2\frac{dn_2}{dV_R} = 2\, k_2 C_A \qquad \textbf{(Eq. 2.61)}$$

by one another to get $\frac{dn_1}{dn_2} = \frac{k_1}{k_2}$. Integrating we get:

$$\frac{n_1}{n_2} = \frac{k_1}{k_2} \qquad \textbf{(Eq. 2.62)}$$

In this integration, the lower limits n_{10} and n_{20} were assumed to be zero. As in the case of batch reactors, this does not necessarily imply that C_{X0} and C_{Y0} are = 0. Using Eq. 2.62 we can write:

$$n_A = n_{A0} - n_1 - n_2 = n_{A0} - n_1 \{1 + k_2/k_1\} \quad , \qquad \textbf{(Eq. 2.63)}$$

which can be easily solved for n_1 :

$$n_1 = \frac{k_1(n_{A0} - n_A)}{(k_1 + k_2)} \qquad \textbf{(Eq. 2.64)}$$

An expression for n_A was derived above (Eq. 2.59). A similar expression for n_2 can now be derived.

$$n_2 = k_2 \frac{(n_{A0} - n_A)}{(k_1 + k_2)} \qquad \textbf{(Eq. 2.65)}$$

Note the similarity between analogous equations derived for the PFR and batch reactor.

2.3.3 Parallel reactions: Isothermal CSTR reactors

We begin by writing the mass balance equation for a CSTR and the rate expression as defined in Eq. 2.46.

$$r_A = \frac{n_{A0} - n_A}{V_R} = (k_1 + k_2)\frac{n_A}{v_T} \qquad \textbf{(Eq. 2.66)}$$

mass balance **rate expression**

For simplicity, we define ($k_1 + k_2$) as the constant **"a".** We can then write $r_A = a\, n_A / v_T$. Once again, we assume v_T to be constant. Solving for n_A as a function of the average residence time, τ (= V_R/v_T).

$$n_A = \frac{n_{A0}}{1 + a\tau} \qquad \textbf{(Eq. 2.67)}$$

In order to calculate n_X and n_Y we have to go through the same type of calculation as in the case of the Plug Flow Reactor. Taking the CSTR mass balance equation as the point of departure, we can write:

$$r_X = \frac{n_X - n_{X0}}{V_R} = k_1 \frac{n_A}{v_T} \quad \text{and} \quad r_Y = \frac{n_Y - n_{Y0}}{V_R} = 2k_2 \frac{n_A}{v_T} = 2r_{A2} \qquad \textbf{(Eq. 2.68)}$$

Once again we get:

$$\frac{n_1}{n_2} = \frac{k_1}{k_2} \qquad \textbf{(Eq. 2.69)}$$

In order to find the amounts of "*X*" and "*Y*" produced, in a given reactor volume V_R for a given v_T, we eliminate n_A from Eqs. 2.68, by using Eq. 2.67. We can then write:

$$n_X = n_{X0} + n_{A0}\left\{\frac{k_1\tau}{1 + a\tau}\right\} \quad \text{and} \quad n_Y = n_{Y0} + n_{A0}\left\{\frac{2k_2\tau}{1 + a\tau}\right\} \qquad \textbf{(Eq. 2.70)}$$

When the reaction orders are mixed, life is not so simple, since it is no longer possible to rely on Eq. 2.69. In all of these three simple cases, we dealt with first order reactions taking place in isothermal reactors.

2.4 Effect of temperature on relative rates of parallel reactions

We have seen how, for equal reaction rate orders, the ratio of moles formed by any reaction, to the moles of A reacted by the reference reaction is equal to the ratio of the rate constants (See Eqs. 2.50 and 2.69).

$$\frac{N_1}{N_2} = \frac{k_1}{k_2} \quad \text{or} \quad \frac{n_1}{n_2} = \frac{k_1}{k_2}$$

Clearly, these ratios can be changed by changing the temperature.

$$\frac{n_1}{n_2} = \frac{k_1}{k_2} = \frac{A_1 \exp[-E_{A1}/RT]}{A_2 \exp[-E_{A2}/RT]} = \frac{A_1}{A_2} \exp\left\{\frac{E_{A2} - E_{A1}}{RT}\right\}, \qquad \textbf{(Eq. 2.71)}$$

where E_{A1} and E_{A2} denote the energy of activation of Reaction 1 and Reaction 2 respectively. According to Eq. 2.71, if $E_{A1} > E_{A2}$, an increase in temperature will lead to an increase in the rate of Reaction 1 relative to the rate of Reaction 2.

If the temperature is increased and ($\Delta E_1 > \Delta E_2$), then $\frac{n_1}{n_2}$ is expected to increase

It is important to note that this conclusion is independent of the type of reactor employed. In cases where not all reactions are first order, i.e. when "mixed" reaction orders are involved, the yield of one product over the other can be increased by altering the temperature as shown above or by altering the relative concentration of reactants. For a case where

$$A \rightarrow X \quad ; \quad r_1 = k_1 C_A$$
$$2A \rightarrow Y \quad ; \quad r_2 = k_2 C_A^2$$

we can show, by going through a similar derivation that $n_2/n_1 = (k_2/k_1)C_A$. Thus maintaining a high concentration of "*A*" would favour the production of product "*Y*" over product "*X*". It appears therefore that when the "useful" reaction is of higher order than the "wasteful" reaction, improvement of the yield of "useful" product is favoured by increasing the reactant concentration. Conversely, if the useful reaction is of lower order, the yield is favoured by reducing the reactant concentration. The economics of the slowed-down reaction may be such that a higher yield may offset the lower speed of reaction – but this would need to be checked separately.

2.5 How relative rates of reaction can affect the choice of chemical reactors [Denbigh & Turner, 1984]

When the desired reaction is of high order, batch or tubular processes would favour formation of the desired product, compared to reaction in a CSTR. This is because, given similar feed concentrations, batch and tubular reactors operate at higher *average* reactant concentrations. If for quite different reasons, there are grounds for choosing a CSTR, the yield can be improved (although not quite as much as in a batch or tubular reactor) by increasing the number of tanks in the reactor sequence. For a fixed number of tanks, the yield can also be improved by making reactor volumes progressively larger (Figure 2). This has the effect of increasing the average residence time (to allow more conversion) as the concentration driving force diminishes.

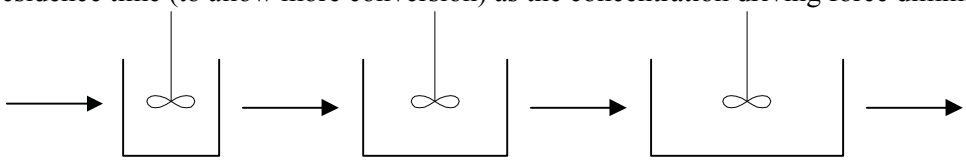


Figure 2 Increasing the number of tanks in the reactor sequence. The yield can also be improved for a fixed number of tanks by making their capacities progressively larger.

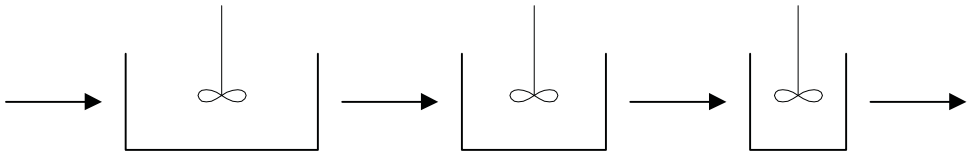


Figure 3 Where the desired reaction is of the lower order, the concentration of reagent should be kept as low as possible. The use of CSTR's has advantages over the use of batch or tubular reactors. Only a small number of tanks in series is used and the first is made relatively large.

If the desired reaction is of the lower order, the concentration of reagent should be kept as low as possible. This can be achieved by the obvious step of reducing the reagent concentration of the feed solution. If outright dilution cannot be practiced due to subsidiary considerations, such as the cost of solvent recovery, the use of CSTR's would have advantages over the use of batch or tubular reactors. In such a case, the reagent concentration is never high, especially if only a small number of tanks in series is used and if the first is made relatively large.

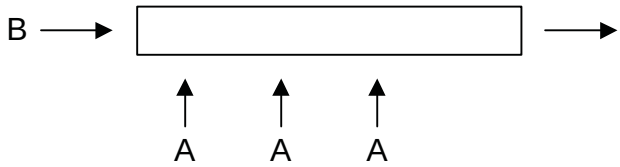


Figure 4a Keeping the reagent concentration low in tubular reactors by small downstream additions of reagent

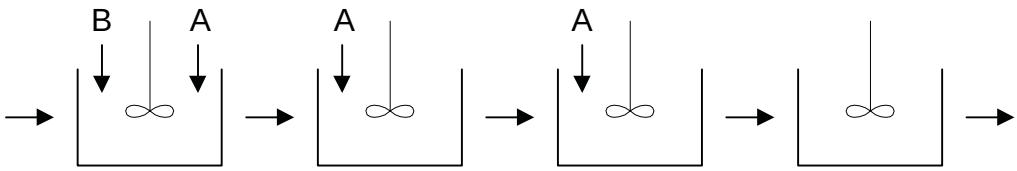


Figure 4b Keeping the reagent concentration low in CSTRs in series, by small additions of reagent further downstream

The same effect may be obtained by operating a type of process in which successive small increments of the reactant are added at a small rate compared to the reaction rate, so as to keep the concentration of reagent low. The method could be applied to batch, tubular, or CSTR reactors.

2.6 Extents of reaction: definitions and simple applications [Alpay, 2001]

We have so far dealt mostly with simple reaction rate expressions and relatively simple reaction schemes, in order to introduce the basic concepts of reactor design without letting complicated rate expressions get in the way. The definition of the fractional conversion serves well enough for tracking the progress of such simple chemical reactions and reaction schemes. Whilst we will continue to use the same terminology in the rest of this text, there is a more general system of definition that enables tracking the progress of complex sets of reactions. The '*extents of reaction*' concept is useful in setting up simultaneous ordinary differential equations, describing the behaviour of more complex systems.

Consider the chemical reaction:

$$aA + bB + cC \ldots \rightarrow xX + yY + zZ \ldots \qquad \textbf{(Eq. 2.72)}$$

In a batch reactor, the fractional conversions would be expressed as

$$x_A = \frac{N_{A0} - N_A}{N_{A0}} \quad ; \quad x_B = \frac{N_{B0} - N_B}{N_{B0}} \quad ; \quad x_C = \frac{N_{C0} - N_C}{N_{C0}} \qquad \textbf{(Eq. 2.73)}$$

According to Eq. 2.73, the fractional conversion calculated for *each reactant* is in fact different. These definitions are adequate so long as the overall reaction scheme is relatively simple. In general, we can use the stoichiometric coefficients to write *for each reaction*

$$\frac{N_{A0}x_A}{a} = \frac{N_{B0}x_B}{b} = \frac{N_{C0}x_C}{c} = ... \qquad \textbf{(Eq. 2.74)}$$

The progress of the same reaction can also be expressed in terms of an 'extent of reaction' defined as

$$\xi \equiv \frac{N_i - N_{i0}}{\nu_i} \qquad \textbf{(Eq. 2.75)}$$

where $\nu_A = -a$; $\nu_B = -b$; $\nu_C = -c$ … $\nu_X = x$; $\nu_Y = y$; $\nu_Z = z$, and ξ has units of moles (or kmols). Thus:

$$\xi = \frac{N_A - N_{A0}}{(-a)} = \frac{N_{A0} - N_A}{a} ; \xi = \frac{N_B - N_{B0}}{(-b)} = \frac{N_{B0} - N_B}{b} ; \xi = \frac{N_C - N_{C0}}{(-c)} = \frac{N_{C0} - N_C}{c} \qquad \textbf{(Eq. 2.76)}$$

The useful feature of the "extents of reaction" notation is that ξ has the same value for every component. For example, given the chemical reaction, $A + 2B \rightarrow 3Y + Z$ and assuming for simplicity that $N_{Y0} = N_{Z0} = 0$, we can write: $\xi = \frac{N_A - N_{A0}}{(-a)} = N_{A0} - N_A$ and $\xi = \frac{N_{B0} - N_B}{2}$ for the reactants. For the products, we write: $\xi = \frac{N_Y - N_{Y0}}{3} = \frac{N_Y}{3}$ has the same value as for the reactants. Finally: $\xi = \frac{N_z - N_{z0}}{1} = N_z$.

The next question we need to tackle is what happens to the design (i.e. material balance) equations for each of the major reactor types we are familiar with.

2.6.1 Extents of reaction: Batch reactors

We have already derived.

$$r_A = -\frac{1}{V_R}\frac{dN_A}{dt} \text{ with } x_A = (N_{A0} - N_A)/N_{A0}\,.$$

Going back to the definition of the "extent of reaction" (Eq. 2.75), and differentiating $\xi \equiv (N_i - N_{i0})/\nu_i$ gives

$$d\xi = \frac{dN_i}{\nu_i} \text{ and } dN_i = \nu_i d\xi\,. \qquad \textbf{(Eq. 2.77)}$$

For reactant "A", the mass balance equation takes the form:

$$r_A = -\frac{\nu_A}{V_R}\frac{d\xi}{dt}\,. \qquad \textbf{(Eq. 2.78)}$$

with analogous expressions for the other reactants. In terms of "extents of reaction", r_A can now be written as

$$r_A = kC_A = k\frac{N_A}{V_R}; \qquad N_A = N_{A0} + \nu_A\xi \qquad \textbf{(Eq. 2.79)}$$

so that

$$r_A = \left(\frac{k}{V_R}\right)\left(N_{A0} + \nu_A\xi\right) = -\frac{\nu_A}{V_R}\frac{d\xi}{dt} \text{ and } \frac{d\xi}{\left(N_{A0} + \nu_A\xi\right)} = -\left(\frac{k}{\nu_A}\right)dt\,. \qquad \textbf{(Eq. 2.80)}$$

Integrating:

$$\frac{1}{\nu_A}ln\left(N_{A0} + \nu_A\xi\right)\Big|_0^{\xi} = \frac{1}{\nu_A}ln\left\{\frac{N_{A0} + \nu_A\xi}{N_{A0}}\right\} = -\frac{k}{\nu_A}t\,. \qquad \textbf{(Eq. 2.81a)}$$

Rearranging:

$$\frac{N_{A0} + \nu_A\xi}{N_{A0}} = exp\{-kt\}\,. \qquad \textbf{(Eq. 2.81)}$$

$$\xi = \frac{N_{A0}}{\nu_A}(e^{-kt} - 1) \qquad \textbf{(Eq. 2.82)}$$

2.6.2 Extents of reaction: Tubular reactors assuming plug flow

The derivation is similar.

$$\xi \equiv \frac{n_i - n_{i0}}{\nu_i} \text{ leads to } d\xi = \frac{dn_i}{\nu_i} \text{ and } dn_i = \nu_i d\xi\,. \qquad \textbf{(Eq. 2.83)}$$

The mass balance over a 'thin-slice' volume element can then be written as

$$r_A = -\nu_A\frac{d\xi}{dV_R},$$

which leads to

$$V_R = -\nu_A\int_0^{\xi}\frac{d\xi}{r_A}\,. \qquad \textbf{(Eq. 2.84)}$$

This is for reactant "*A*". We write analogous expressions for the other reactants. In terms of the extent of reaction, r_A can now be written as $r_A = k\,C_A = k\,n_A/v_T$ and $n_A = n_{A0} + \nu_A\xi$, so that

$$r_A = \underbrace{\left(\frac{k}{v_T}\right)\left(n_{A0} + \nu_A\xi\right)}_{\textbf{from rate expression}} = \underbrace{-\nu_A\frac{d\xi}{dV_R}}_{\textbf{from mass balance}}, \qquad \textbf{(Eq. 2.85)}$$

giving

$$\frac{d\xi}{\left(n_{A0}+\nu_A\xi\right)}=-\left(\frac{k}{\nu_A v_T}\right)dV_R \qquad \textbf{(Eq. 2.86)}$$

Integrating Eq. 2.86, we get

$$\frac{1}{\nu_A}\ln\left(n_{A0}+\nu_A\xi\right)\Big|_0^{\xi}=\frac{1}{\nu_A}\ln\left\{\frac{n_{A0}+\nu_A\xi}{n_{A0}}\right\}=-\left(\frac{k}{\nu_A v_T}\right)V_R \qquad \textbf{(Eq. 2.86)}$$

$$\frac{n_{A0}+\nu_A\xi}{n_{A0}}=\exp\{-k\tau\}, \qquad \textbf{(Eq. 2.87)}$$

where $\tau = V_R / v_T$. Finally

$$\xi=\frac{n_{A0}}{\nu_A}(e^{-k\tau}-1) \quad ; \quad \xi=-\frac{n_{A0}}{\nu_A}(1-e^{-k\tau}) \qquad \textbf{(Eq. 2.88)}$$

This result is for a tubular reactor, assuming plug flow. Note the similarity with the equations we derived for a batch reactor (Eq. 2.82)

$$\xi=-\frac{N_{A0}}{\nu_A}(1-e^{-kt}) \ . \qquad \textbf{(Eq. 2.89)}$$

2.6.3 Extents of reaction: Continuous stirred tank reactors

As before, the defining equation

$$\xi \equiv \frac{n_i-n_{i0}}{\nu_i}$$

leads to $d\xi = dn_i / \nu_i$ and $dn_i = \nu_i d\xi$. For a reactant, "A", the CSTR material balance equation now takes the form:

$$r_A=\frac{n_{A0}-n_A}{V_R}=-\left(\frac{\nu_A\xi}{V_R}\right),$$

which gives

$$V_R=-\left(\frac{\nu_A\xi}{r_A}\right), \qquad \textbf{(Eq. 2. 90)}$$

with analogous expressions for the other reactants. For products, the equation takes the form

$$r_X=\frac{n_X-n_{X0}}{V_R}=\left(\frac{\nu_X\ \xi}{V_R}\right) \qquad \textbf{(Eq. 2. 91)}$$

In terms of extents of reaction, r_A can now be written in the usual form $r_A = k\,C_A = k\,n_A / v_T$, but with the molar flow rate defined in the form $n_A = n_{A0} + \nu_A\xi$. Substituting, we get

$$r_A=\left(\frac{k}{v_T}\right)\left(n_{A0}+\nu_A\xi\right)=-\left(\frac{\nu_A\xi}{V_R}\right) \quad ; \quad \nu_A\xi=-\frac{\nu_A}{k\tau}\xi-n_{A0} \text{ , and,} \qquad \textbf{(Eq. 2. 92)}$$

$$\xi=-\left(\frac{n_{A0}}{\nu_A}\right)\frac{k\tau}{1+k\tau} \qquad \textbf{(Eq. 2. 93)}$$

Note the similarity between the three equations for the three different types of reactors.

2.6.4 Applications to complex reaction schemes:

It is in the treatment of multiple reactions that formulations in terms of "extents of reaction" come into their own. For a single reaction, we had defined ξ by equation Eq. 2.83 as: $n_i - n_{i0} = \nu_i \xi$. For multiple reactions where ξ_j is defined as the extent of reaction "*j*" and where "*J*" is defined as the total number of reactions, this equation takes the form:

$$n_i - n_{i0} = \sum_{j=1}^{J} \nu_{ij} \xi_j \qquad \textbf{(Eq. 2. 94)}$$

For component 'i' we can now write:

$$dn_i = d\left\{\sum_{j=1}^{J} \nu_{ij} \xi_j\right\} = \sum_{j=1}^{J} \nu_{ij} d\xi_j \qquad \textbf{(Eq. 2. 95)}$$

For N components in the reaction mixture, the principle of conservation of mass requires:

$$\sum_{i=1}^{N} \left\{ M_i \sum_{j=1}^{J} \nu_{ij} \xi_j \right\} = 0 \,. \qquad \textbf{(Eq. 2. 96)}$$

This equation allows reducing the number of differential equations by one. To proceed with the calculation, we select a key reactant '*k*' for *each reaction*. Then we can write the mass balance equation for each reaction. For batch reactors, the equation takes the form:

$$\frac{d\xi_j}{dt} = -\left(\frac{V_R r_{k_j}}{\nu_{kj}}\right), \qquad \textbf{(Eq. 2. 97)}$$

For tubular reactors:

$$\frac{d\xi_j}{dV_R} = -\left(\frac{r_{k_j}}{\nu_{kj}}\right), \qquad \textbf{(Eq. 2. 98)}$$

and for continuous stirred tank reactors:

$$\xi_j = -\left(\frac{V_R r_{k_j}}{\nu_{kj}}\right) . \qquad \textbf{(Eq. 2. 99)}$$

2.6.5 Extents of reaction: Example

The following set of chemical reactions is carried out in a tubular reactor operating under plug flow conditions:

$$A \rightarrow B + C \qquad r_{A1} = k_1 C_A$$

$$2A \rightarrow D \qquad r_{A2} = k_2 C_A^2$$

$$C \rightleftarrows D + E \qquad r_C = k_3 C_C - k_{-3} C_D C_E$$

We now make use of the Eq. 2.98. The set of mass balance equations to be solve simultaneously may now be written as:

$$\frac{d\xi_1}{dV_R} = -\frac{r_{A1}}{(-1)} = k_1 C_A = k_1 \frac{n_A}{v_T}$$

$$\frac{d\xi_2}{dV_R} = -\frac{r_{A2}}{(-2)} = \left(\frac{1}{2}\right) k_2 C_A^2 = \left(\frac{1}{2}\right) k_2 \frac{n_A^2}{v_T^2} \qquad \textbf{(Eqs. 2. 100)}$$

$$\frac{d\xi_3}{dV_R} = -\frac{r_{C3}}{(-1)} = k_3 C_C - k_{-3} C_D C_E = k_3 \frac{n_C}{v_T} - k_{-3} \frac{n_D n_E}{v_T^2}$$

Now we make use of the definition of ξ_j, in the equation $n_i - n_{i0} = \sum_{j=1}^{J} \nu_{ij}\xi_j$, where ξ_j is defined as the extent of "reaction *j*" and *J* is defined as the total number of reactions. Then:

$$
\begin{aligned}
n_A &= n_{A0} + \sum_{j=1}^{3} \nu_{Aj}\xi_j = \quad n_{A0} - \xi_1 - 2\xi_2 \\
n_C &= n_{C0} + \xi_1 - \xi_3 \\
n_D &= n_{D0} + \xi_2 + \xi_3 \\
n_E &= n_{E0} + \xi_3
\end{aligned}
\qquad \textbf{(Eqs. 2. 101)}
$$

These molar flow rates may now be substituted in the three differential equations and the system of equations solved for the three unknowns: ξ_1, ξ_2 and ξ_3. The actual molar flow rates can then be calculated from:

$$n_i - n_{i0} = \sum_{j=1}^{J} \nu_{ij}\xi_j \ .$$

Note that if v_T is not constant as the ξ_j change, we would develop an expression for v_T in terms of the ξ_j. This expression would then be inserted into the differential equations, before attempting to solve the set of equations.

CHAPTER 3

NON-ISOTHERMAL REACTORS

3.1 Energy balance equations: Introduction
[Holland & Anthony, 1979]

Except for rare cases where isothermal behaviour may be reasonably assumed, chemical reactions either absorb or release energy, usually in the form of heat. The reaction process thus tends to change the temperature of the reacting medium. Furthermore, rates of reaction change rapidly with changing reaction temperatures.

$$r_A = k\,C_A = k(T)\,C_A \qquad \textbf{(Eq. 3.1)}$$

where $k(T)$ normally depends exponentially on the temperature: $k_0\ exp\{-E_a/RT\}$. In designing reactors, it is important to keep close track of temperature distributions and the release *or* uptake of energy by the reacting system.

In designing non-isothermal reactors, material balance equations derived for isothermal reactors remain unchanged.

However, material balances alone are not sufficient to describe the behaviour of *non-isothermal* reactors.

The reaction rate depends on the local temperature. Energy balance equations must be formulated to keep track of heat exchange and temperature variations. The material balance equations and the energy balance equation must then be solved together.

Due to the exponential dependence of the reaction rate constant on the temperature, the coupling of mass and energy balance equations usually requires the solution of simultaneous *non-linear* differential equations.

The energy balance equation: The energy equivalents of the net heat absorbed by, and the net work done by, the system must be taken into account. The following is a general statement of the energy balance equation, which also applies to unsteady-state operation.

$$\left\{\begin{pmatrix}\text{energy input into}\\ \text{volume element}\\ \text{per unit time}\end{pmatrix}-\begin{pmatrix}\text{energy output from}\\ \text{volume element}\\ \text{per unit time}\end{pmatrix}\right\}\Delta t=\begin{bmatrix}\text{energy within}\\ \text{volume element}\end{bmatrix}_{t_n+\Delta t}-\begin{bmatrix}\text{energy within}\\ \text{volume element}\end{bmatrix}_{t_n}$$

(Eq. 3.2)

We begin by writing the expression for the total internal energy of a unit mass of fluid, U_T^m .

$$U_T^m = U^m + (KE)^m + (PE)^m \qquad \textbf{(Eq. 3.3)}$$

The terms on the right hand side of Eq. 3.3 denote the internal energy, the kinetic energy and the potential energy, respectively; all terms have units of energy/mass. $(KE)^m$ denotes the kinetic energy due to the motion of the fluid and the superscript "*m*" implies that the quantity is expressed on a 'mass' basis. Similarly $(PE)^m$ denotes the work required to raise a unit mass of fluid a given distance above a specified datum level against the force of gravity. The total enthalpy per unit mass of fluid may now be expressed as:

$$H_T^m \equiv U_T^m + PV = U^m + PV + (KE)^m + (PE)^m \ , \qquad \textbf{(Eq. 3.4)}$$

where V is the volume per unit mass. We next need to define *W* as the shaft work done by the system (in our case, the reacting fluid) on the environment, and *w* as the mass flow rate, in units of mass per unit time. The shaft work is defined as positive when work is done *by* the system *on* the environment.

3.2 Energy balance equations for CSTR reactors

Combining the general energy balance (Eq. 3.2) and Eq. 3.4 for the total enthalpy, the general enthalpy balance at steady state for a CSTR can now be written as

$$\underbrace{\left(wH_T^m\right)_0}_{\textbf{at inlet conditions}} - \underbrace{\left[\left(wH_T^m\right)+W\right]}_{\textbf{at exit conditions}} + \underbrace{Q}_{\textbf{heat transfer}} = \underbrace{0}_{\textbf{accumulation (nil at steady state)}} \qquad \textbf{(Eq. 3.5)}$$

Q is negative if heat is *exported* from the system. In its present form, this equation is too general for using in an ordinary reactor design problem. We need to simplify Eq. 3.5 before we can make it work in practice.

> When a quantity of energy is considered to be "negligible", it means the effect is small relative to other energy effects associated with the system. We usually compare these with heat effects associated with the chemical reaction(s).

Changes in kinetic and potential energy: The form of Eq. 3.5 implies that we do not deal in absolute total energies, but in energy *differences*. For example, the kinetic energy related to the motion of mass through the reactor *may* itself be large, e.g., due to the high velocity of the reaction mixture. Generally however, *changes* in kinetic energy, due to *changes* in velocity in the reactor etc., would be relatively small.

Similarly *changes* in potential energy, related to gravity effects of the streams entering and leaving the reactor may usually be neglected. In other words, although the kinetic energy and potential energy related terms themselves may be numerically large, it is usually safe to neglect, i.e. consider the associated *changes* to be *relatively* small. Thus $\Delta(KE) \approx 0$ and $\Delta(PE) \approx 0$.

Shaft work: A system that has work done on it experiences the conversion of mechanical energy to internal energy, U. This is the energy associated with the structures and molecular motions of molecules. In a CSTR, the 'shaft work' done by the system (i.e. fluid) on the environment is normally associated with energy effects involving stirring.

Strictly, we must take account of the mechanical energy that the stirrer imparts to the reaction mixture. In practice however, the amount of energy involved is usually negligible, compared to reaction related heat effects. *Usually*, amounts of energy absorbed or released by chemical reactions are much larger. One exception would be the case of stirring of a very viscous liquid, where large amounts of energy may be involved. The energy equivalent of the work done by the stirrer on ordinary reacting mixtures is therefore *usually* neglected. The energy balance equation *for a CSTR at steady state* now becomes.

$$\left[wH^m\right]_0 - \left[wH^m\right] + Q = 0 , \qquad \textbf{(Eq. 3.6)}$$

where the enthalpy is defined as $H^m = U + PV$ with P denoting the pressure and V the volume per unit mass. Clearly, at steady state, w (the mass flow rate) is constant. Generally it is more practical to work with an equation written in terms of molar flow rates rather than mass flow rates. Also, in thermodynamic tables, enthalpies are usually given on a molar basis, rather than a mass basis. Defining H as the average enthalpy per mole of mixture:

$$wH^m = n_T H$$

$$\left\{\frac{mass}{time}\right\}\left\{\frac{energy}{mass}\right\} = \left\{\frac{moles}{time}\right\}\left\{\frac{energy}{mole}\right\} \qquad \textbf{(Eq. 3.7)}$$

We can now cast our energy balance in the form:

$$\left\{n_{T0}H\right\}_0 - \left\{n_T H\right\} + Q = 0 \qquad \textbf{(Eq. 3.8)}$$

where $\{n_{T0}H\}_0$ is evaluated at reactor inlet conditions and $n_T H$ at reactor outlet conditions. A common way of expressing Q is,

$$Q = U\,A\,(T - T_C), \qquad \textbf{(Eq. 3.9)}$$

where T is the reactor temperature and T_C the temperature of the heat transfer medium. Eventually, depending on the reactor configuration, different formulations of this equation may be required. However, at this stage, what we really need is a way of recasting the terms $\{n_{T0}H\}_0$ and $n_T H$ in a form that is more readily usable. Once again, it is useful to recall that heat coming into the system is defined as positive and heat leaving the system is defined as negative. In what follows, we will assume that heats of mixing and pressure effects on the enthalpy are negligible. In practice, this amounts to assuming that we are dealing with perfect gases and ideal solutions. We can now write

$$n_T = \sum n_i\, H_{fi} \qquad \textbf{(Eq. 3.10)}$$

Now we need to go back to the thermodynamic definition of the enthalpy, as referred to its value at the standard state. For any component 'i', the enthalpy H_{fi} can be calculated by using the equation

$$H_{fi}(T) = H_{fi}^0 + \int_{T^0}^{T} C_p dT \qquad \textbf{(Eq. 3.11)}$$

where H_{fi}^0 is defined as the standard heat of formation of compound "*i*" at temperature T^0; H_{fi}^0 is the standard heat of reaction when the given compound in its standard state is formed from its elements in their standard states at the same temperature T^0 (usually taken as 25 °C). The elements in their standard states are considered as being in the reference state.

We have, thus far, neglected effects due to changes in kinetic and potential energy and shaft work and we have assumed the additivity of energies associated with each component in the reaction mixture. Using the latter concept (i.e. the equation $n_T H = \sum n_i H_{fi}$), the mass balance for a CSTR (Eq. 3.8) may now be written as

$$\underbrace{\sum n_{i0} H_{fi}(T_0)}_{\text{Energy flow in}} - \underbrace{\sum n_i H_{fi}(T)}_{\text{Energy flow out}} + \underbrace{Q}_{\text{Heat exchange}} = \underbrace{0}_{\substack{\text{Accumulation}\\ \text{(nil at steady state)}}}, \qquad \textbf{(Eq. 3.12)}$$

where the *subscript* '0' in Eq. 3.12 refers to the reactor inlet conditions.

In a "non-isothermal CSTR," the temperature is uniform everywhere within the reaction zone. Non-isothermal behaviour in a CSTR refers to differences between the feed temperature (T_0) and the reaction temperature (T), the heat absorbed or released by the chemical reaction and to heat exchange between the reactor and the surroundings.

In Eq. 3.12, the difference between the first two terms on the left hand side implicitly contains information on the sensible energy exchanges due to differences between the feed temperature (T_0) and the reaction temperature (T), as well as any energy absorbed or released by the reaction. We will now recast Eq. 3.12 in a form which distinguishes between these two effects.

We have already seen in Chapter 1 that for any single component "i", the mass balance in a CSTR may be written as $n_{i0} - n_i = V_R\, r_i$, where r_i is defined in terms of the disappearance of component "i". Let us substitute $n_i = n_{i0} - V_R\, r_i$ into the energy balance (Eq. 3.12).

$$\sum n_{i0} H_{fi}(T_0) - \sum \left[n_{i0} - V_R\, r_i \right] H_{fi}(T) + Q = 0 \qquad \textbf{(Eq. 3.13)}$$

Rearranging, we get:

$$n_{i0} \sum \left[H_{fi}(T_0) - H_{fi}(T) \right] + V_R \sum r_i H_{fi}(T) + Q = 0 \qquad \textbf{(Eq. 3.14)}$$

Taken together with the perfect mixing assumption, *for an exothermic reaction*, the first term represents the sensible heat absorbed by the feed stream, to bring it up to the reactor temperature. If the reactor is operating at a temperature *below* that of the feed stream, the first term would represent the heat given off by the feed stream. The reaction mixture would then absorb heat from the feed stream and the material in the feed stream would cool down to the reactor temperature. The second term represents the heat released (or *absorbed* in an endothermic reaction) by the chemical reaction. Q represents the heat added to or withdrawn from the CSTR by heat exchange.

For an *exothermic* reaction, it is thus convenient to look at the first term as heat removed from system by flow. The second term is the heat generated by the reaction and Q is the heat withdrawn from the reactor. Conversely, for an endothermic reaction, it is convenient to look at the first term as heat carried into the reactor by the feed stream (i.e. by flow). The second term then represents the heat absorbed by the reaction and Q is the heat added to the reactor. We can further simplify the energy balance equation by using the equation:

$$\sum n_{i0} \left[H_{fi}(T_0) - H_{fi}(T) \right] = -\sum n_{i0} \int_{T_0}^{T} C_{pi}\, dT \qquad \textbf{(Eq. 3.15)}$$

where the enthalpy difference per mole between the feed stream and reaction mixture can be calculated, if the heat capacity for each component is known. In this approximation, it is assumed that the C_{pi} are functions of the temperature alone. The energy balance equation may now be written as:

$$-\sum n_{i0} \int_{T_0}^{T} C_{pi}\, dT + V_R \sum H_{fi}(T) r_i + Q = 0 \qquad \textbf{(Eq. 3.16)}$$

The case of a single reaction: If we have just one chemical reaction taking place, say,

$$A \rightarrow B + C$$

The heat of reaction term, $V_R \sum H_{fi}(T) r_i$, can be considerably simplified.

$$\sum H_{fi} r_i = H_{fA}\, r_A + H_{fB}\, r_B + H_{fC}\, r_C$$

In this equation $r_A = -r_B = -r_C$, leading to

$$\sum H_{fi} r_i = r_A \left\{ H_{fA} - H_{fB} - H_{fC} \right\} = -r_A\, \Delta H_r \qquad \textbf{(Eq. 3.17)}$$

The energy balance equation for a CSTR can then be written as:

$$-\sum n_{i0} \int_{T_0}^{T} C_{pi} dT - V_R \Delta H_r r_A + Q = 0 \qquad \textbf{(Eq. 3.18)}$$

Equation 3.18 can be further simplified by making two approximations which are not always very accurate. However, they will simplify our task in performing preliminary calculations. We first define an average heat capacity over the temperature interval, i.e. the range of integration in Eq. 3.18.

$$\overline{C}_{pi} \equiv \frac{1}{\Delta T} \int_{T_0}^{T} C_{pi} dT \text{ and } \overline{C}_{pi}\, \Delta T = \int_{T_0}^{T} C_{pi} dT \qquad \textbf{(Eq. 3.19)}$$

The energy balance equation for a CSTR then simplifies to:

$$\sum n_{i0}\overline{C}_{pi}(T_0 - T) - V_R(\Delta H_r)r_A + Q = 0 \qquad \textbf{(Eq. 3.20)}$$

$$(T_0 - T)\sum n_{i0}\overline{C}_{pi} - V_R(\Delta H_r)r_A + Q = 0 \qquad \textbf{(Eq. 3.21)}$$

A second approximation would have us define a constant total heat capacity for the whole of the reaction mixture:

$$\left\{n_{T0}\overline{\overline{C}}_p\right\} = \sum n_{i0}\overline{C}_{pi}\ , \qquad \textbf{(Eq. 3.22)}$$

which reduces the general energy balance equation for a CSTR to:

$$n_{T0}\overline{\overline{C}}_p(T_0 - T) - V_R(\Delta H_r)r_A + Q = 0\ . \qquad \textbf{(Eq. 3.23)}$$

Broadly, the first term in this equation may be viewed as heat removal (or addition) by flow. The second term corresponds to the heat released (or absorbed) by the chemical reaction. Finally the third term, Q, represents heat removal (or addition) to the system by heat exchange. This simplified equation allows rapid preliminary calculations to be carried out in designing non-isothermal CSTRs.

3.3 Multiplicity of steady states in non-isothermal CSTR's [Denbigh & Turner, 1984]

In non-isothermal CSTR calculations, the interplay of heat removal by flow, the heat released by the chemical reaction and the heat added (or removed) by ordinary heat transfer may give rise to a multiplicity of steady states. The analysis requires comparing the magnitudes of the three terms in Eq. 3.23. Consider an irreversible first order chemical reaction carried out in a CSTR, $A \rightarrow R+S$. For ease of discussion, we will assume that the reaction is exothermic.

The heat generation term: The heat generation term is given by

$$Q_g = -V_R(\Delta H_r)r_A = -V_R(\Delta H_r)(kC_A) = -k\left[\frac{V_R}{v_T}\right]n_A(\Delta H_r)$$
$$Q_g = -k\tau n_A(\Delta H_r) \qquad \textbf{(Eq. 3.24)}$$

Where the reaction rate constant is given as $k = k_o\, e^{-E/RT}$ and the average residence time as $\tau = V_R/v_T$. Recalling from Eq. 1.65 that for CSTRs

$$n_A = \frac{n_{A0}}{1+k\tau}\ , \qquad \textbf{(Eq. 3.25)}$$

Q_g can be rewritten as

$$Q_g = -k\tau(\Delta H_r)\frac{n_{A0}}{1+k\tau} = -\frac{n_{A0}(\Delta H_r)}{1+\dfrac{e^{E/RT}}{\tau k_0}} \qquad \textbf{(Eq. 3.26)}$$

For an exothermic reaction ($\Delta H_r < 0$), the heat generation term takes the form shown in Figure 3.1. At high values of T, k is so large that virtually no unreacted reagent remains in the exit stream. Thus a still higher value of T cannot cause Q_g to increase.

The heat removal term: The heat removal term is made up of the sum of two terms: the sensible heat exchange term, Q, and heat removal by flow:

Q_{rem} = Q (due to heat exchange) + Q (due to flow). **(Eq. 3.27)**

For adiabatic operation, Q (due to heat exchange) = 0. Then,

$$Q_{rem} = n_{T0}\overline{\overline{C}}_p(T - T_0) \qquad \textbf{(Eq. 3.28)}$$

which is the "heat removal by flow" term on its own.

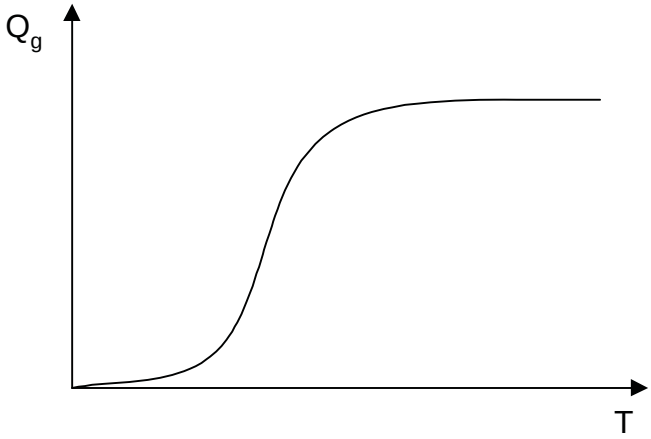


Figure 3.1 The form of heat generation term for a CSTR (Eq. 3.26) as a function of increasing temperature. At high values of T, k is so large that virtually no unreacted reagent remains in the exit stream.

For non-adiabatic operation, using a simple equation to characterize the heat transfer term: $UA(T-T_C)$,

$$Q_{rem} = n_{T0}\overline{\overline{C}}_p(T - T_0) + UA(T - T_c)$$

$$Q_{rem} = \left(n_{T0}\overline{\overline{C}}_p + UA\right) T - \left(n_{T0}\overline{\overline{C}}_p\, T_0 + UAT_c\right) \qquad \textbf{(Eq. 3.29)}$$

In this simplified model of a CSTR, Q_{rem} turns out to be linear as a function of the temperature. We can plot and compare the magnitudes of the heat generation (Eq. 3.26) and heat removal (Eq. 3.29) terms of the energy balance equation (Eq. 3.23):

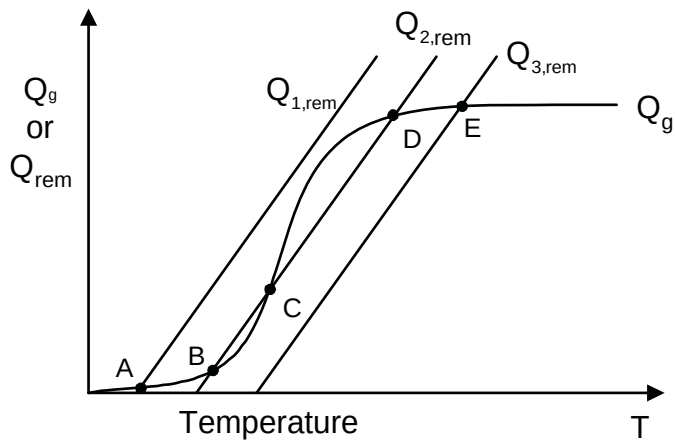


Figure 3.2 Comparing the heat generation, Qg and heat removal Qrem terms in the CSTR energy balance equation (Eq. 3.23).

In Figure 3.2, $Q_{1,rem}$, $Q_{2,rem}$ and $Q_{3,rem}$ represent three different scenarios, distinguished by three different inlet temperatures T_0. Clearly, at steady state, $Q_g = Q_{rem}$; the intersections are thus the only possible steady state operating points. Not all the intersections represent stable steady states.

Points A and B: These two points correspond to low rates of heat generation and removal. This combination may result from one or more of the following factors: (i) Small value of ΔH_r; (ii) Low value of the reaction rate constant, presumably due to a low inlet temperature; (iii) Short average residence time, giving low conversions and therefore relatively little heat generation; (iv) Small value of the feed rate, and finally, (v) Rapid heat removal from the reactor not allowing the temperature to climb to higher values. Both points A and B correspond, however, to stable steady state operation.

Points D and E: The properties of these two points correspond to nearly complete consumption of the reactants. This outcome is favoured by the opposite of the conditions listed for points A and B. (i) A larger value of ΔH_r; (ii) A larger value of the reaction rate constant; (iii) Longer average residence times; (iv) Larger reactant throughput and finally (v) A slower heat removal regime by heat exchange.

Point C: This point has unusual features. A slight *upward* fluctuation of the temperature would make the 'heat generation' term greater than the 'heat removal' term ($Q_g > Q_r$) and the temperature would rise until Point D was reached. Similarly any slight downward drift of the temperature would mean that $Q_g < Q_r$, resulting in a further drop of the temperature until point B were attained. Thus, the system cannot operate in stable manner at Point C. It is termed an unstable steady state of the system.

If an intersection where the heat removal and heat generation rates are matched and no further net heat is supplied to, or removed from, the system, the reaction is said to be capable of being operated 'autothermally'.

Note that, if D is the desired point of operation, the reactor temperature would have to rise to reach that point. This means, the temperature would need to move through the lower steady state point ("B") as well as the unstable steady state point ("C"). This cannot be done when operating auto-thermally (i.e. not adding or withdrawing heat). One straightforward way of achieving the temperatures associated with Point D would be to use a burst of additional heat.

Remember that all this was developed assuming a simple reaction rate expression, $r_A = k\ C_A$. As the characteristics of the reaction changes (i.e. reversible or consecutive or endothermic reactions etc) the shape of the heat generation curve will change and the resulting analysis will need to be accordingly modified. Figure 3.3 presents qualitative forms of the heat generation curve for (a) a reversible reaction, (b) a pair of consecutive exothermic reactions and (c) for two consecutive reactions, where the first is exothermic and the second is endothermic.

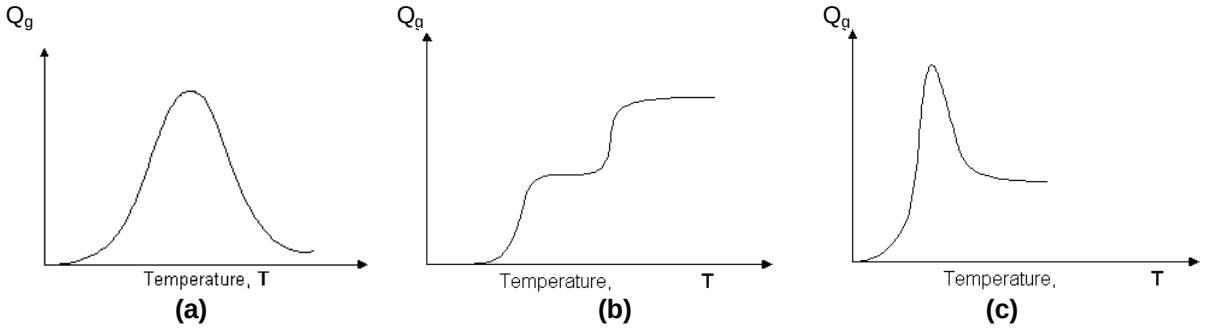


Figure 3.3 The qualitative shape of Q_g, the heat generation term, for (a) a reversible reaction, (b) a pair of consecutive exothermic reactions and (c) for two consecutive reactions, where the first is exothermic and the second is endothermic.

3.4 Non-isothermal CSTR's: The adiabatic operating line

The material balance equation: Let us assume that a first order irreversible reaction $A \rightarrow B$ is taking place in a non-isothermal CSTR and write the material balance equation.

$$V_R = \frac{n_{A0} - n_A}{r_A} = \frac{n_{A0} - n_A}{kC_A} = \frac{n_{A0} - n_A}{k\left(n_A / v_T\right)} \qquad \textbf{(Eq. 3.30)}$$

Recalling the definition of the average residence time, $\tau = V_R / v_T$, the equation takes the form:

$$\tau = \frac{n_{A0} - n_A}{kn_A}\ .$$

Using $n_A = n_{A0}(1 - x_A)$ we can write:

$$\tau = \frac{n_{A0} x_A}{k n_{A0}(1 - x_A)}. \qquad \textbf{(Eq. 3.31)}$$

Solving for the fractional conversion of "*A*", we derive an expression arising from the material balance alone.

$$x_A = \frac{k\tau}{1 + k\tau} = \frac{1}{1 + \dfrac{e^{E/RT}}{\tau k_0}} \qquad \textbf{(Eq. 3.32)}$$

When x_A vs. T is plotted (Eq. 3.32), we get an S-shaped curve; do *not* confuse with the Q_g line in Figure 3.2!

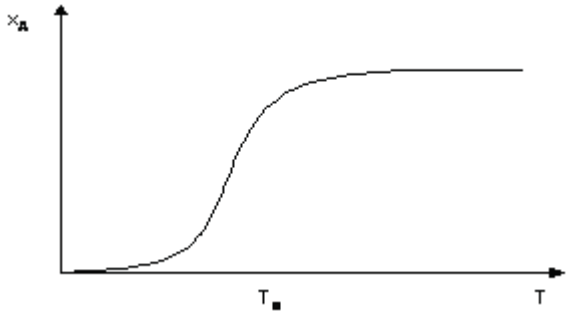


Figure 3.4 The x_A – temperature relationship plotted using Eq. 3.32

The energy balance equation: The corresponding energy balance equation was derived earlier:

$$n_{T0}\overline{\overline{C}}_p(T_0 - T) - V_R(\Delta H_r)r_A + Q = 0 \qquad \textbf{(Eq. 3.23)}$$

When the reactor is operated adiabatically, $Q = 0$ and Eq. 3.23 takes the form:

$$n_{T0}\overline{\overline{C}}_p(T_0 - T) - V_R r_A \Delta H_r = 0, \qquad \textbf{(Eq. 3.33)}$$

where we had already seen that $V_R r_A = n_{A0} - n_A$ and $n_{A0} - n_A = n_{A0}x_A$. Substituting in Eq. 3.33:

$$n_{T0}\overline{\overline{C}}_p(T_0 - T) - n_{A0}x_A \Delta H_r = 0 \qquad \textbf{(Eq. 3.34)}$$

Solving Eq. 3.34 for the fractional conversion, x_A:

$$x_A = -\left\{\frac{n_{T0}\overline{\overline{C}}_p}{n_{A0}\Delta H_r}\right\}(T - T_0) \qquad \textbf{(Eq. 3.35)}$$

and using $y_{A0} \equiv n_{A0} / n_{T0}$, we can write the energy balance equation for a non-isothermal CSTR as:

$$x_A = -\left\{\frac{\overline{\overline{C}}_p}{y_{A0}\Delta H_r}\right\}(T - T_0) \qquad \textbf{(Eq. 3.36)}$$

We can now plot the energy balance equation (Eq. 3.36) together with the mass balance equation (Eq. 3.32)

$$x_A = \frac{1}{1 + \dfrac{e^{E/RT}}{\tau k_0}} \qquad \textbf{(Eq. 3.32)}$$

The intersection of the two lines represents the simultaneous solutions of the mass and energy balance equations. Note that when we plot the energy balance, the slope is positive for exothermic ($\Delta H_r < 0$) reactions and negative for endothermic reactions ($\Delta H_r > 0$). It may also be noted that the shape of the material balance remains unchanged for exothermic and endothermic reactions.

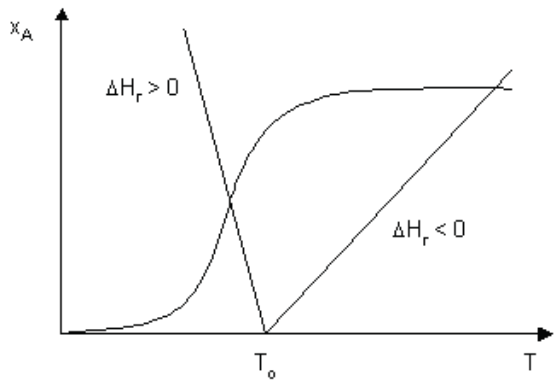


Figure 3.5 The material and energy balance lines for a non-isothermal CSTR. The intersections indicate the position of the simultaneous solution.

The treatment for a simple 1st order irreversible reaction is thus relatively easy. It would get considerably more complicated even for the simple reversible reaction $A \rightleftarrows B$. In any case, the basic design problem consists of finding "the most desirable" intersection of the mass and energy balances. In this simple case the parameters which we can readily modify are y_{A0} $(= n_{A0}/n_{T0})$ and τ $(= V_R/v_T)$

3.5 Mass & energy balances in tubular reactors

The energy balance equation for a tubular reactor – assuming plug flow: At steady state, the energy balance over a volume element in terms of molar flow rates is written as follows:

$$n_T H_T\big|_z - \left\{ n_T H_T\big|_{z+\Delta z} + W \right\} + \int_z^{z+\Delta z} q dz \;=\; 0 \qquad \textbf{(Eq. 3.37)}$$

in - out + in = accumulation

where z is the distance from the reactor inlet and, as before, the accumulation term is zero at steady state. In what follows, we will assume plug flow. In other words, we will not introduce (or take into account) the existence of any radial concentration and/or temperature gradients. Thus, gradients perpendicular to the direction of flow will be neglected. Also neglecting *changes* in kinetic and potential energy and the 'shaft' work W, and rearranging, we can write

$$-\left\{ n_T H\big|_{z+\Delta z} - n_T H\big|_z \right\} + \bar{q}\,\Delta z \;=0 \qquad \textbf{(Eq. 3.38)}$$

Taking the limit as $\Delta z \to dz$ and $\bar{q} \to \; q(z)$ i.e. a point value, Eq. 3.38 can be rewritten as

$$-\frac{d}{dz}(n_T H) + q(z) = 0 \qquad \textbf{(Eq. 3.39)}$$

or, dividing by the cross-sectional area of the tube, πR^2,

$$-\frac{d}{dV_R}(n_T H) + Q = 0 \qquad \textbf{(Eq. 3.40)}$$

In Eq. 3.40, Q denotes conduction heat transfer, in terms of the reactor volume, V_R. As before, we will neglect (i) the enthalpy change upon mixing (perfect solution) and (ii) the effect of pressure changes in enthalpy (perfect gas). The energy balance then takes the form:

$$-\frac{d}{dV_R}\left\{ \sum n_i H_{fi} \right\} + Q(z) = 0 \quad \text{, where } H_{fi} \equiv \Delta H_{fi}^0 + \left\{ \int_{T_0}^{T} dH_i \right\} \qquad \textbf{(Eq. 3.41)}$$

In Eq. 3.41, ΔH_{fi}^0 is the standard heat of formation of compound "*i*" from its elements, at the standard temperature. In order to cast this equation in a form that is readily usable, we need to go through several steps, similar to those we carried out for the energy balance for the CSTR. The first term on the left hand side may be written as:

$$\frac{d}{dV_R}\left\{ \sum n_i H_{fi} \right\} = \underbrace{\sum n_i \frac{dH_{fi}}{dV_R}}_{\textbf{sensible heat}} + \underbrace{\sum H_{fi} \frac{dn_i}{dV_R}}_{\textbf{heat of reaction}} \qquad \textbf{(Eq. 3.42)}$$

Recalling that $dH_{fi} = C_{pi} dT$ and that in a tubular reactor, $r_i = -\, dn_i / dV_R$

$$\frac{d}{dV_R}\left\{ \sum n_i H_{fi} \right\} = \sum n_i C_{pi} \frac{dT}{dV_R} - \sum H_{fi} r_i \;= \frac{dT}{dV_R} \sum n_i C_{pi} - \sum H_{fi} r_i \qquad \textbf{(Eq. 3.43)}$$

This equation can be simplified if only a single reaction is taking place: $A \to B$.

$$\sum H_{fi} r_i = H_{fA} r_A + H_{fB} r_B \qquad \textbf{(Eq. 3.44)}$$

However, $r_A = -\, r_B$, and

$$\sum H_{fi} r_i = H_{fA} r_A - H_{fB} r_A = r_A \left(H_{fA} - H_{fB} \right) = -\Delta H_R r_A \qquad \textbf{(Eq. 3.45)}$$

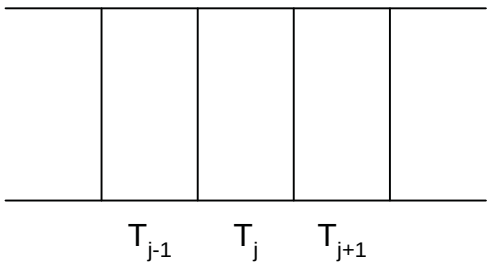
Summarizing, for a single reaction, $\sum H_{fi} r_i = -\Delta H_r r_A$. The energy balance equation Eq. 3.41 may then be rewritten as

$$-\left\{ \frac{dT}{dV_R}\left[\sum n_i \bar{C}_{pi} \right] + r_A \Delta H_r \right\} + Q(x) = 0 \qquad \textbf{(Eq. 3.46)}$$

The general energy balance can thus be cast in the form of an ordinary differential equation, which must be solved simultaneously with the material balance equation(s).

$$\frac{dT}{dV_R} = \frac{Q - r_A \Delta H_r}{\sum n_i \overline{C}_{pi}} \qquad \textbf{(Eq. 3.47)}$$

Clearly $Q = 0$ corresponds to adiabatic operation and $Q = Q_0$ denotes a constant heat flux. More commonly, the heat flux would be formulated as $Q_i = -AU(T_i - T_c)$, where T_j is local reactor temperature and T_c the coolant temperature.



Note that in the solution of the simultaneous ODE's, r_A, ΔH_r and C_{pi} will depend on the local temperature and position within the reactor and n_i will depend on the conversion as a function of position. When calculations are carried out numerically, the variation of ΔH_r and C_{pi} with temperature can be taken into account in straightforward fashion.

For simpler calculations, we will assume, as before that the heat capacity *of the reaction mixture* may be considered as approximately constant over the temperature and concentration changes envisaged.

$$\sum n_i C_{pi} \cong n_{T0} \overline{\overline{C}}_p$$

Assuming plug flow, the tubular reactor energy balance equation for a single reaction (Eq. 3.47) can now be rewritten as

$$\frac{dT}{dV_R} = \frac{Q - r_A \Delta H_r}{(n_{T0} \overline{\overline{C}}_p)} \qquad \textbf{(Eq. 3.48)}$$

The material balance equation for a tubular reactor – assuming plug flow: In the case of a single reaction taking place, the energy balance equation can be solved, coupled to a single material balance equation. Assuming plug flow, the material balance equation (the "design equation") is written as:

$$r_A = -dn_A / dV_R \,.$$

Substituting $n_{A0}(1 - x_A)$ for n_A, we get

$$-\frac{d}{dV_R}\{n_{A0} - n_{A0} x_A\} = n_{A0} \frac{dx_A}{dV_R} \,,$$

which simplifies to

$$\frac{dx_A}{dV_R} = \frac{r_A}{n_{A0}} \qquad \textbf{(Eq. 3.49)}$$

Even for the simplest rate expressions, the simultaneous solution of Eqs. 3.48 and 3.49 usually requires resorting to numerical solution methods. In order to calculate concentration and temperature profiles along the length of the reactor, the equations must be combined with the initial conditions (in this case, the reactor inlet conditions). In the simplest cases, it is easier to work by assuming ΔH_r and C_p to be independent of the temperature.

Dividing the energy balance equation (Eq. 3.48) by the mass balance equation (Eq. 3.49), we derive the equation for the "operating line", on the x_A versus T plane:

$$\frac{dT}{dx_A} = \frac{n_{A0}}{n_{T0}} \left\{ \frac{Q}{r_A \overline{\overline{C}}_p} + \frac{(-\Delta H_r)}{\overline{\overline{C}}_p} \right\}$$

leads to

$$\frac{dT}{dx_A} = y_{A0} \left\{ \frac{Q}{r_A \overline{\overline{C}}_p} + \frac{(-\Delta H_r)}{\overline{\overline{C}}_p} \right\} \qquad \textbf{(Eq. 3.50)}$$

If we assume (i) adiabatic operation and (ii) ΔH_r and C_p to be constant over the temperature range, we can integrate Eq. 3.50 and solve for x_A.

$$x_A = -\frac{\overline{\overline{C}}_p}{y_{A0} \Delta H_r} (T - T_0) \qquad \textbf{(Eq. 3.51)}$$

This is the equation for the operating line, subject to the set of assumptions listed above. It is linear for adiabatic operation. Note that for non adiabatic operation *(Q ≠0)*, the operating line will be curved.

For CSTRs the intersection of the material and energy balance lines allows pinpointing the operating *point*, whereas, in a tubular reactor, temperatures and concentrations change continuously. The operating line shows the conversion-temperature trajectory *along* the length of the reactor.

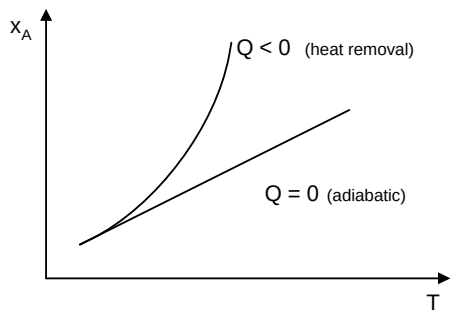


Figure 3.6 The tubular reactor (plug flow) operating lines for adiabatic and non-adiabatic operation.

The fractional conversion and temperature trends resulting from the simultaneous solution of material and energy balance equations as a function of position within the tubular reactor are as follows:

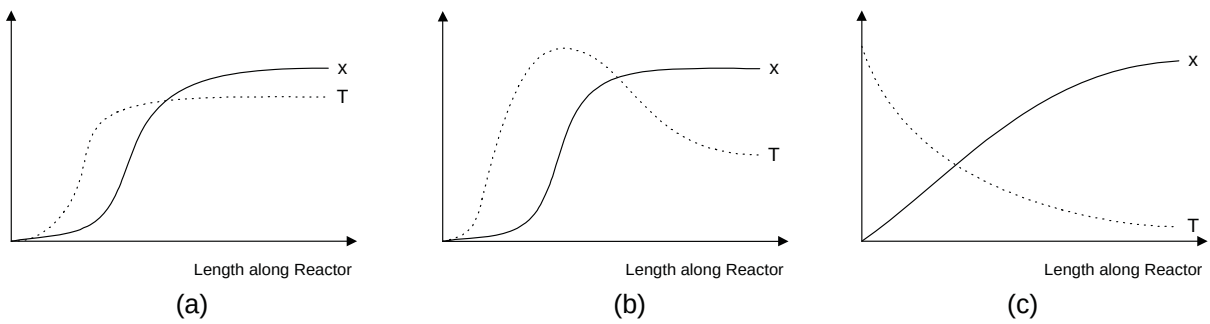


Figure 3.7 Qualitative fractional conversion and temperature trends from the simultaneous solution of material and energy balance equations as a function of position within the tubular reactor. (a) Adiabatic tubular reactor: Conversion and temperature for an exothermic reaction ($\Delta H_r < 0$); (b) Non-adiabatic, non-isothermal tubular reactor: Conversion and temperature for an exothermic reaction ($\Delta H_r < 0$); (c) Adiabatic tubular reactor: Conversion and Temperature for an endothermic reaction ($\Delta H_r > 0$).

CHAPTER 4

REVERSIBLE REACTIONS IN NON-ISOTHERMAL REACTORS

4.1 Reversible reactions

The properties of reversible reactions introduce a number of new elements into the discussion about non-isothermal reactors. Consider the reversible reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B, \qquad \textbf{(Eq. 4.1)}$$

where the rate of disappearance of A is given by the expression

$$r_A = k_1 C_A - k_2 C_B . \qquad \textbf{(Eq. 4.2)}$$

The equilibrium constant for this reaction is defined as

$$K_{eq} = \frac{k_1}{k_2} = \frac{C_{B,eq}}{C_{A,eq}} . \qquad \textbf{(Eq. 4.3)}$$

In this equation, $C_{A,eq}$ and $C_{B,eq}$ denote the equilibrium concentrations of "*A*" and "*B*", respectively. If we start the reaction with pure A:

$$K_{eq} = \frac{k_1}{k_2} = \frac{C_{B,eq}}{C_{A,eq}} = \frac{C_{A0} x_{A,eq}}{C_{A0}(1 - x_{A,eq})} = \frac{x_{A,eq}}{1 - x_{A,eq}} \qquad \textbf{(Eq. 4.4)}$$

leads to

$$x_{A,eq} = \frac{Keq}{1 + Keq} \qquad \textbf{(Eq. 4.5)}$$

Before we proceed further, however, we need to derive a famous old equation.

4.1.1 Deriving the van't Hoff Equation

We know from laboratory experiments that if during a *single* reaction, we plot *ln k* against *1/T*, where *T* denotes the absolute temperature, in the first approximation we obtain an (almost) straight line. If the line bends significantly, it is safe to infer that we do not have a simple, single reaction. The reaction mechanism may be changing with temperature or there may be interference from mass transfer effects. In catalytic reactions, which we will study later on in this book, when the slope decreases at higher temperatures, we look for diffusion limitations.

The activation energy of a chemical reaction is *defined* by the slope of this straight line:

$$\frac{d\,ln\,k}{d\left(1/T\right)} = -\frac{E_a}{R} \qquad \textbf{(Eq. 4.6)}$$

Which can also be written as

$$\frac{d\,ln\,k}{dT} = \frac{E_a}{RT^2} \qquad \textbf{(Eq. 4.7)}$$

Integrating, we get the Arrhenius equation:

$$k(T) = k_0\ exp\left\{-E_a\ /\ RT\right\} \qquad \textbf{(Eq. 4.8)}$$

where *R* denotes the gas constant [= 8.314 J mol^{-1} K^{-1} (or kJ kmol^{-1} K^{-1}) = 0.08314 bar m^3 kmol^{-1} K^{-1}].

The Arrhenius equation is consistent with simple Collision Theory. k_0 is viewed as the product of the collision rate (largely independent of molecular species) and a steric factor, the value of which varies widely with the chemical species being considered. The exponential term $exp\left\{-E_a\ /\ RT\right\}$ is called the 'Boltzmann factor' and is viewed as the fraction of collisions that are energetic enough to lead to reaction. Values of E_a usually range between 4×10^4 and 2×10^5 kJ kmol^{-1}.

For a reversible reaction, we have already seen that $K_{eq} = k_1/k_2$. This may be rewritten as

$$ln\ K_{eq} = ln\ k_1 - ln\ k_2. \qquad \textbf{(Eq. 4.9)}$$

Differentiating

$$d\ ln\ K_{eq} = d\ ln\ k_1 - d\ ln\ k_2\,. \qquad \textbf{(Eq. 4.10)}$$

Starting with the Arrhenius equation, we can also write

$$\frac{d\,ln\,k_1}{d\left(1/T\right)} = -\frac{E_{a1}}{R} \quad \text{and} \quad \frac{d\,ln\,k_2}{d\left(1/T\right)} = -\frac{E_{a2}}{R} \qquad \textbf{(Eq. 4.11)}$$

Subtracting the two equations form one another, we get

$$d\,ln\,k_1 - d\,ln\,k_2 = d(ln\,K_{eq}) = -\left(\frac{E_{a1} - E_{a2}}{R}\right)d(1/T) \qquad \textbf{(Eq. 4.12)}$$

We also know that,

$$E_{a1} - E_{a2} \ = \ \Delta H_r\,, \qquad \textbf{(Eq. 4.13)}$$

Substituting Eq. 4.13 in Eq. 4.12 leads to the van 't Hoff equation:

$$\frac{d\,ln\,K_{eq}}{d(1/T)} = -\frac{\Delta H_r}{R} \qquad \textbf{(Eq. 4.14)}$$

This equation shows the relationship between the change in temperature *T* with the change in the equilibrium constant *K*. It can also be written as:

$$\frac{d(ln\,K_{eq})}{dT} = \frac{\Delta H_r}{RT^2} \qquad \textbf{(Eq. 4.15)}$$

4.1.2 How does the equilibrium constant change with temperature?

When the temperature rises, does K_{eq} increase or decrease? Inspecting the form of the equation reveals straightforward trends. For endothermic reactions ($\Delta H_r > 0$), when the temperature rises, the equilibrium constant K_{eq} increases. Meanwhile, for exothermic reactions ($\Delta H_r < 0$), K_{eq} *decreases* as the temperature rises. Clearly both rate constants increase with increasing temperature. What this means is that for increasing temperatures, when $\Delta H_r < 0$, k_2 increases faster, *relative* to k_1. Note that the van't Hoff equation is entirely independent of reactor related considerations.

We can also test for trends in the value of K_{eq} by integrating the van't Hoff equation:

$$\int_{T_1}^{T_2} d(\ln K_{eq}) = \frac{\Delta H_r}{R}\int_{T_1}^{T_2}\frac{dT}{T^2} = \frac{\Delta H_r}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \qquad \textbf{(Eq. 4.16)}$$

$$\ln\left\{\frac{K_{eq}(T_2)}{K_{eq}(T_1)}\right\} = \frac{\Delta H_r}{R}\left\{\frac{1}{T_1}-\frac{1}{T_2}\right\} \qquad \textbf{(Eq. 4.17)}$$

For increasing temperatures ($T_2 > T_1$):

$$\left(\frac{1}{T_1}-\frac{1}{T_2}\right) > 0 \qquad \textbf{(Eq. 4.18)}$$

For endothermic reactions ($\Delta H_R > 0$), we find once again that as the temperature increases, K_{eq} , the equilibrium constant increases, whereas for exothermic reactions ($\Delta H_R < 0$), K_{eq} *decreases as* the *temperature rises.*

For endothermic reactions	($\Delta H_R > 0$)	as $T \uparrow$	$k_1/k_2 = K_{eq} \uparrow$
For exothermic reactions	($\Delta H_R < 0$)	as $T \uparrow$	$k_1/k_2 = K_{eq} \downarrow$

These trends are entirely independent of chemical reactor design. We next turn to the implications of the van't Hoff equation for the design of chemical reactors.

4.2 Reactor design for reversible endothermic reactions

We have already seen that, for *endothermic* reactions, the rate of the reverse reaction decreases relative to the forward reaction, as the temperature rises.

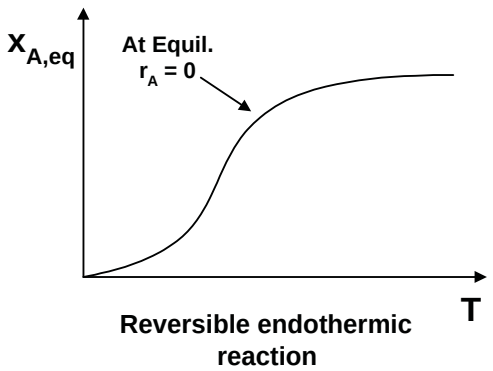


Figure 4.1 Qualitative sketch of the equilibrium conversion $x_{A,,eq}$ vs. T for a reversible endothermic reaction

When considering the cost of atmospheric pressure reactors, the reactor volume is not usually a critical parameter. If, however, we are dealing with high-pressure reactors, it is important to keep to a reasonably small volume in order to limit construction costs. This in turn suggests that we would wish to operate at high reaction rates.

Thus, when carrying out reversible-endothermic reactions (Figure 4.1) and indeed irreversible reactions, it would be sensible to operate at the highest possible temperature that is consistent with the durability of the materials of construction and also staying well clear of excessive by-product formation through accelerating side reactions.

4.3 Reactor design for reversible exothermic reactions

With reversible exothermic reactions, the combination of thermodynamic and kinetic parameters means that increasing temperatures give rise to *decreasing* net forward reaction rates. This may seem a little counter-intuitive. Let us go back to Eq. 4.13:

$$E_{a1} - E_{a2} = \Delta H_r \,. \qquad \textbf{(Eq. 4.13)}$$

For exothermic reactions, "$\Delta H_R < 0$" means that E_{a2} is greater than E_{a1}. Thus, as the temperature rises, the term "$exp\{-E_{a2}/RT\}$" increases in magnitude faster that the term "$exp\{-E_{a1}/RT\}$". This is why the ratio k_1/k_2 ($=K_{eq}$) diminishes with rising temperature. Plotting x_A vs T, we find that the equilibrium conversion decreases with increasing temperature.

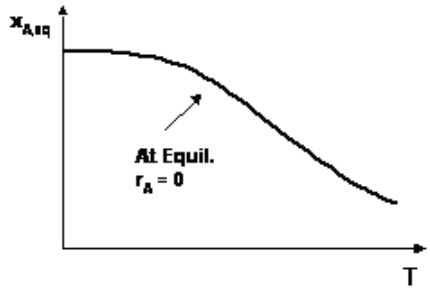


Figure 4.2 Qualitative sketch of the equilibrium conversion $x_{A,eq}$ vs. T for a reversible exothermic reaction

As already discussed, when working with irreversible or reversible-*endothermic* reactions, high reaction rates can be achieved by raising the temperature to as high a level as is safe and practical. But when working with reversible-*exothermic* reactions, the choosing operating conditions is less straightforward. In designing a reactor, it is necessary to take account of two competing effects. First, both the forward and reverse rates of reaction increase with rising temperature, so the kinetics is favoured by increasing the reaction temperature. However, equilibrium limitations are more restrictive at higher temperatures. In other words, the maximum attainable conversion, $x_{A,eq}$ takes on smaller values with increasing temperature. This is because, with increasing temperature, the reverse reaction picks up speed faster than the forward reaction so equilibrium, where the net rate of reaction is zero, is approached sooner. Let us look at the x_A *vs.* T diagram for a reversible exothermic reaction in greater detail.

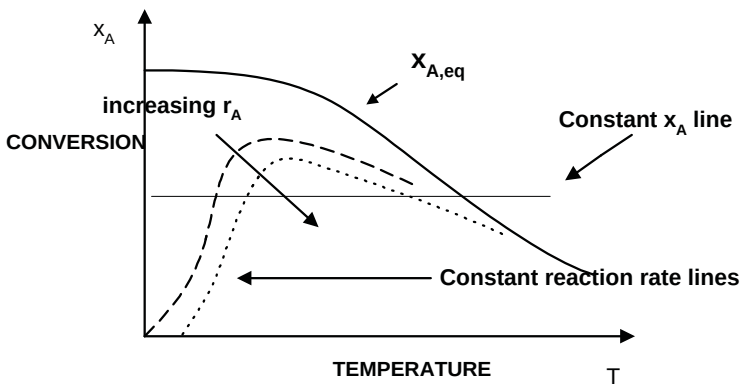


Figure 4.3 Several features of the x_A *vs.* T *diagram*

At constant reaction rate (Figure 4.3), the conversion initially rises rapidly with increasing temperature and then begins to fall – due to the faster rising rate of the reverse reaction. The characteristics of the reversible-exothermic reaction can be better understood by following a horizontal (constant conversion) line in Figure 4.3. At low temperatures, the reaction rate would be low but would initially increase with rising temperature as we move towards the right in Figure 4.3, i.e. towards higher temperatures. At the other extreme, the intersection of the constant x_A-*line* (horizontal line) with the equilibrium line $x_{A,eq}$ represents the point where the net reaction rate r_A is zero. Moving from left to right, between these two extremes, the reaction rate passes through a maximum.

Thus, for reversible exothermic reactions, there exists an 'optimum' operating temperature (corresponding to the maximum reaction rate) for a fixed conversion. The line through these maxima gives a trajectory of maximum reaction rates as a function of the conversion, which we will call "the locus of maximum reaction rates" and discuss in the next section. It is important to remember that the present discussion is independent of the design of any particular type of reaction vessel.

4.3.1 The Locus of Maximum Reaction Rates

We will next derive an equation for the locus of maximum reaction rates for a simple reversible-exothermic reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B,$$

Assuming $C_{B0} = 0$, the rate equation for the *net* consumption of the reactant "*A*" may be written as

$$r_A = k_1 C_{A0}(1 - x_A) - k_2 C_B = C_{A0}\{k_1 - (k_1 + k_2)x_A\} \qquad \textbf{(Eq. 4.19)}$$

where $k_1 = k_{10}e^{-\Delta E_1/RT}$, $k_2 = k_{20}e^{-\Delta E_2/RT}$ and $\Delta E_2 > \Delta E_1$. The maximum reaction rate as a function of temperature can now be found by differentiating Eq. 4.19 with respect to the temperature, at constant conversion:

$$\left(\frac{dr_A}{dT}\right)\bigg|_{x_A} = 0 = C_{A0}\frac{dk_1}{dT} - C_{A0}\left(\frac{dk_1}{dT} + \frac{dk_2}{dT}\right)x_A \qquad \textbf{(Eq. 4.20)}$$

Rearranging

$$\frac{dk_1}{dT} - \left(\frac{dk_1}{dT} + \frac{dk_2}{dT}\right)x_A = 0 \qquad \textbf{(Eq. 4.21)}$$

and solving for x_A

$$x_{A,opt} = \frac{\frac{dk_1}{dT}}{\frac{dk_1}{dT} + \frac{dk_2}{dT}} = \frac{1}{1 + \dfrac{\left(-\frac{\Delta E_2}{R}\right)\left(-\frac{1}{T^2}\right)k_{20}e^{-\Delta E_2/RT}}{\left(-\frac{\Delta E_1}{R}\right)\left(-\frac{1}{T^2}\right)k_{10}e^{-\Delta E_1/RT}}} = \frac{1}{1 + \frac{\Delta E_2}{\Delta E_1}\frac{1}{K_{eq}(T)}} \qquad \textbf{(Eq. 4.22)}$$

Having derived an expression for $x_{A,opt}(T)$ along the locus of maximum reaction rates, the corresponding maximum reaction rates can be derived as a function of temperature, by substituting Eq. 4.22 into

$$r_A = C_{A0}\{k_1 - (k_1 + k_2)x_{A,opt}\}. \qquad \textbf{(Eq. 4.23)}$$

$$r_{A,max} = C_{A0}\left[k_1 - \frac{(k_1 + k_2)}{1 + \left(\frac{\Delta E_2}{\Delta E_1}\right)\frac{1}{K_{eq}}}\right] = k_1 C_{A0}\left[1 - \frac{1 + \frac{1}{K_{eq}}}{1 + \left(\frac{\Delta E_2}{\Delta E_1}\right)\frac{1}{K_{eq}}}\right] \qquad \textbf{(Eq. 4.24)}$$

For a given conversion, the reactor volume would therefore be a minimum if the temperature of operation is selected to be that corresponding to the maximum reaction rate.

Both the constant rate lines in Figure 4.3 *and* the locus of maximum reaction rates are independent of the type of reactor used.

4.4 Reversible reactions: Conversions in a non-isothermal CSTR

Once again, consider the reversible reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B.$$

The mass balance for a CSTR (derived in Chapter I) gives:

$$V_R = \frac{n_{A0} - n_A}{r_A} = \frac{n_{A0} x_A}{k_1 \frac{n_A}{v_T} - k_2 \frac{n_B}{v_T}}. \qquad \textbf{(Eq. 4.25)}$$

Using the equation defining n_A, $n_A = n_{A0}(1 - x_A)$ and $n_B = n_{A0} x_A$, i.e. assuming we start with pure "A" and that $n_{B0} = 0$, we can write

$$\tau = \frac{V_R}{v_T} = \frac{n_{A0} x_A}{\{k_1 - (k_1 + k_2) x_A\} n_{A0}} \quad . \qquad \textbf{(Eq. 4.26)}$$

Solving for x_A we get

$$x_A = \frac{\tau\, k_1}{1 + (k_1 + k_2)\tau}. \qquad \textbf{(Eq. 4.27)}$$

Dividing by $k_2 \tau$

$$x_A = \frac{K_{eq}}{\frac{1}{k_2 \tau} + (K_{eq} + 1)} \quad . \qquad \textbf{(Eq. 4.28)}$$

Alternatively, we can divide by $k_1 \tau$:

$$x_A = \frac{1}{\frac{1}{k_1 \tau} + (1 + \frac{1}{K_{eq}})} \qquad \textbf{(Eq. 4.29)}$$

Note that as the average residence time in the reactor tends to large values (i.e. $\tau \to \infty$), we get back the equation relating x_A to the temperature T at equilibrium.

$$\lim_{\tau \to \infty} x_A = \frac{K_{eq}}{1 + K_{eq}} \qquad \textbf{(Eq. 4.30)}$$

This equation was derived using the mass balance alone. Now let us see how the form of the energy balance equation might affect the design.

4.4.1 CSTR operation with a reversible-endothermic reaction ($\Delta H_r > 0$)

The adiabatic operating line for a CSTR was previously derived (Eq.3.36).

$$x_A = -\left(\frac{\overline{C}_p}{y_{A0} \Delta H_r} \right) (T - T_0) \qquad \textbf{(Eq. 3.36)}$$

For an endothermic reaction, $\Delta H_r > 0$ and the slope of the line is negative. Since a CSTR operates at a single point only, the operating line joins the inlet and operating points.

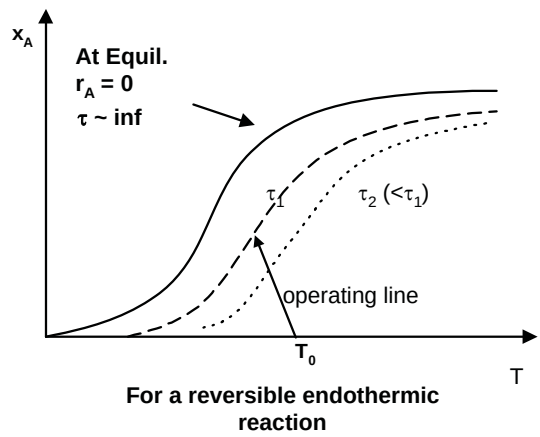


Figure 4.4 Reversible endothermic reaction in a CSTR: Equilibrium and operating lines on the x_A - T plane.

4.4.2 CSTR operation with a reversible-exothermic reaction ($\Delta H_r < 0$)

We have already seen that in the case of reversible-exothermic reactions, the equilibrium conversion, $x_{A,eq}$, decreases with increasing temperature (cf. Figure 4.3). Away from equilibrium, x_A is given by Eq. 4.27 or Eq. 4.28.

$$x_A = \frac{K_{eq}}{\frac{1}{k_2\tau} + (K_{eq} + 1)} \quad \text{or} \quad x_A = \frac{1}{\frac{1}{k_1\tau} + (1 + \frac{1}{K_{eq}})} \qquad \textbf{(Eqs. 4.27 \& 4.28)}$$

and since $\Delta H_r < 0$, the slope of the adiabatic operating line Eq. 3.36 (i.e. the energy balance equation) is positive.

$$x_A = -\left(\frac{\overline{C}_p}{y_{A0}\Delta H_r}\right)(T - T_0) \qquad \textbf{(Eq. 3.36)}$$

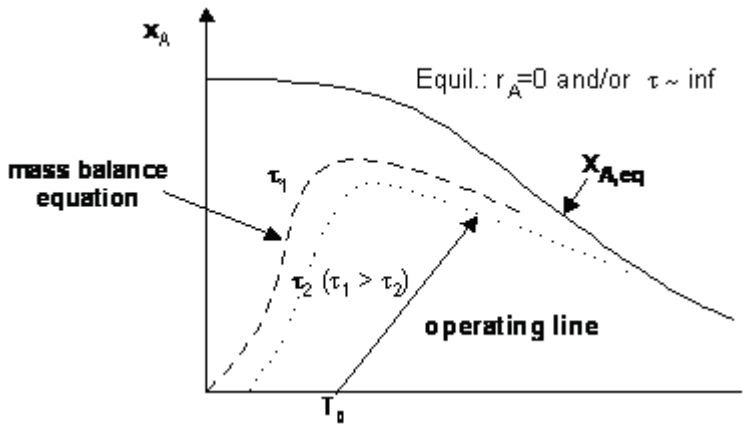


Figure 4.5 Reversible exothermic reaction in a CSTR: Equilibrium and operating lines on the x_A - T plane.

In Figure 4.5, the intersection of the operating line (energy balance equation) and the mass balance equation gives the operating point for the CSTR.

4.5 Reversible-exothermic reaction ($\Delta H_r < 0$): "inter-stage cooling" and "cold-shot cooling"

We would like to take advantage of the fact that at higher temperatures, the reaction rate is higher. We would also like to exploit the fact that at lower temperatures, (while the reaction rate is low) the concentration driving force and attainable conversions are greater compared to operation at higher temperatures. Essentially we would like to operate *on* the locus of maximum reaction rates, moving towards lower temperatures as the conversion increases.

However applying continuous cooling along the optimum reaction path would be impractical. A more practical option is to stage the reaction in such a way that each successive stage operates at a lower temperature to achieve a higher overall conversion. We will discuss two frequently used methods: "inter-stage cooling", and, "cold shot cooling". Both methods are used in industry to tackle problems involving reversible exothermic reactions. Typical applications include the methanol synthesis ($CO + 2H_2 \rightarrow CH_3OH$) and ammonia ($N_2 + 3H_2 \rightarrow 2\,NH_3$) synthesis reactions. These reactions are carried out at high pressure, between 70 – 300 bar depending on the catalyst used. In the following treatment, for simplicity, each stage will be assumed to operate in adiabatic mode. Note that the discussion applies to tubular reactors as well as CSTRs, although we will select our examples from CSTR operation.

4.5.1 Inter-stage cooling

An inter-stage cooled reactor system consists of a series of catalyst chambers. In each of the reactor stages, the temperature rises from inlet to outlet. Heat-exchangers (inter-stage coolers) are placed between the reactor stages, where the temperature is reduced without affecting the composition of the process stream.

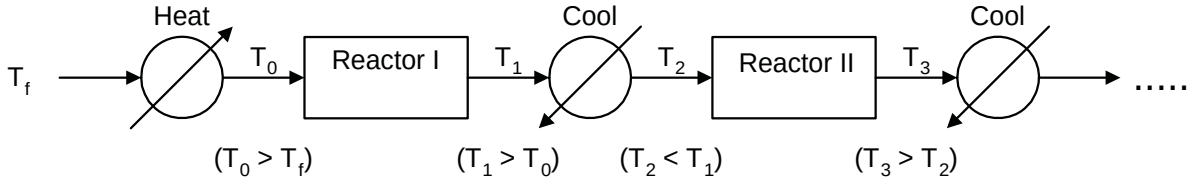


Figure 4.6 Schematic diagram of two reactors in series. The first heat exchanger heats the feed stream from T_f to the reactor inlet temperature T_0. After "Reactor I" the temperature T_1 is dropped to T_2 before entering "Reactor II".

The operating line of a single-reactor does not naturally follow a trajectory that shadows the locus of maximum reaction rates. In fact it cuts across that trajectory. By subdividing the reactor into a number of stages and removing heat from the reaction mixture after each reactor stage, the temperature is forced lower before the stream enters the next vessel. This allows working closer to the locus of maximum rates (see Figure 4.7). Clearly the larger the number of steps, the closer the trajectory of the system would approach the theoretical optimum. An inordinately large increase in the number of inter-stage coolers, however, would tend to increase construction costs. We would need to determine the optimum number of reactor stages.

We have seen in Chapter 3 that the energy balance equation for a CSTR is given by

$$n_{T0}\overline{\overline{C}}_p(T_0 - T) - V_R(\Delta H_r)r_A + Q = 0\,. \qquad \textbf{(Eq. 3.23)}$$

Using $V_R r_A = n_{A0} - n_A$, the CSTR mass balance, and $n_{A0} - n_A = n_{A0}x_A$, the definition of x_A, leads to

$$n_{T0}\overline{\overline{C}}_p(T_0 - T) - n_{A0}x_A\Delta H_r + Q = 0\,. \qquad \textbf{(Eq. 3.34)}$$

When the reactor is operated adiabatically, $Q = 0$ and Eq. 3.34 takes the form:

$$n_{A0}x_A(-\Delta H_r) = n_{T0}\overline{\overline{C}}_p(T - T_0) \qquad \textbf{(Eq. 4.31)}$$

Eq. 3.23 was derived, assuming the total heat capacity of the mixture, $\overline{\overline{C}}_p n_{T0}$, remains constant, although the composition of the reaction mixture may change. The amount of reactant converted in the first stage may be written as $n_{A0}x_A$; for each subsequent stage, '*i*', the fractional conversion may be written as $n_{A0}\,(x_{A,i} - x_{A,i-1})$. Thus for the first stage,

$$x_A = \frac{\overline{\overline{C}}_p n_{T0}}{n_{A0}(-\Delta H_r)}(T - T_0) \qquad \textbf{(Eq. 4.32)}$$

And for each subsequent stage, the conversion is written as

$$(x_{A,i} - x_{A,i-1}) = \frac{\overline{\overline{C}}_p n_{T0}}{n_{A0}(-\Delta H_r)}(T - T_0)\,. \qquad \textbf{(Eq. 4.33)}$$

The form of Eq. 4.33 shows that the slopes of the operating lines for each stage may be assumed to remain constant, to within the accuracy of the equation. Note that we still need to solve the mass and energy balance equations in order to calculate actual size of the reactor or amounts of catalyst to be used.

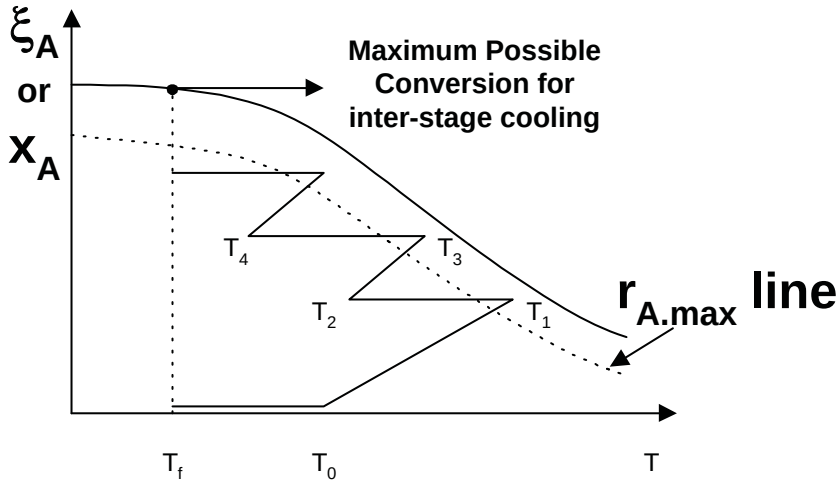


Figure 4.7 An inter-stage cooled reactor system consists of a series of adiabatic catalyst chambers. In each of the reactor stages, the temperature rises from inlet to outlet. Then an interstage cooler cools the reaction stream to a pre-determined temperature.

In designing reactor systems with interstage cooling, one important question that must be addressed is how the reactor stages should be sized. Should all the temperature differences (ΔT) between inlet and outlet be equal? Or is there some optimum distribution of ΔT's? The latter would imply the existence of an optimum in the number of reactor stages and (in the case of catalytic reactions) an optimum distribution of mass of catalyst between the reactor stages.

Usually, the first stage is designed to be smaller than subsequent stages. This is because the concentration driving force is larger, i.e. the conversion is as yet low. A large amount of heat is released in the initial stages of the reaction because rates are fast due to the large concentration driving force. However, there is no single "correct" answer. The system is clearly complex and the optimum to be arrived at would depend on the type of objective function(s) that are adopted.

4.5.2 Cold shot cooling

Inter-stage cooling requires expensive heat exchange equipment and generates low grade energy from high grade energy. Another method of controlling the reaction temperature and conversion in the vicinity of the maximum reaction rate line involves splitting the inlet stream and injecting some of the cold feed into the system further down the line.

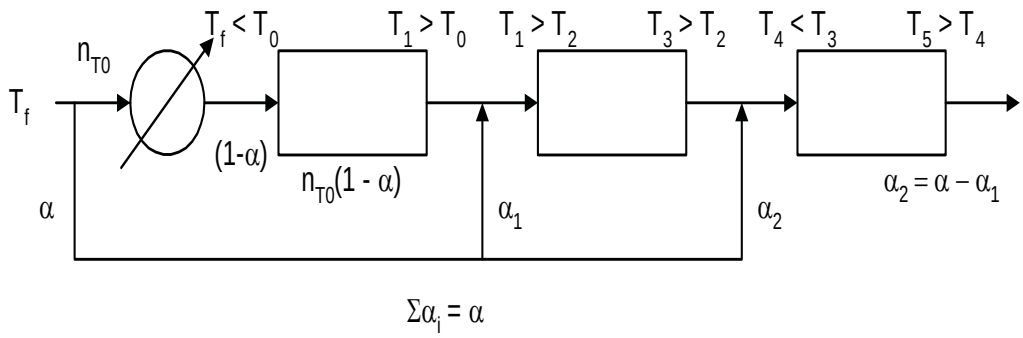


Figure 4.8 Schematic diagram of three reactors in series: Cold-shot cooling.

In Figure 4.8, the heat exchanger before the first stage reactor serves to heat up the feed stream from T_f (feed temperature) to the reactor inlet temperature T_0. The exit stream from the first reactor stage is at temperature

T_1. Before entering the second stage, the temperature of this stream is dropped to T_2 by injecting some of the feed material which is at T_f – in this case the ambient temperature. "Cold shot" injection is repeated after the second stage. α is the fraction of feed stream that is retained for "cold-shot"s. Unlike the case of inter-stage cooling however, mixing cold feed with the inter-stage process stream has the effect of not just cooling the mixture but also adding fresh reactant and changing the process stream composition.

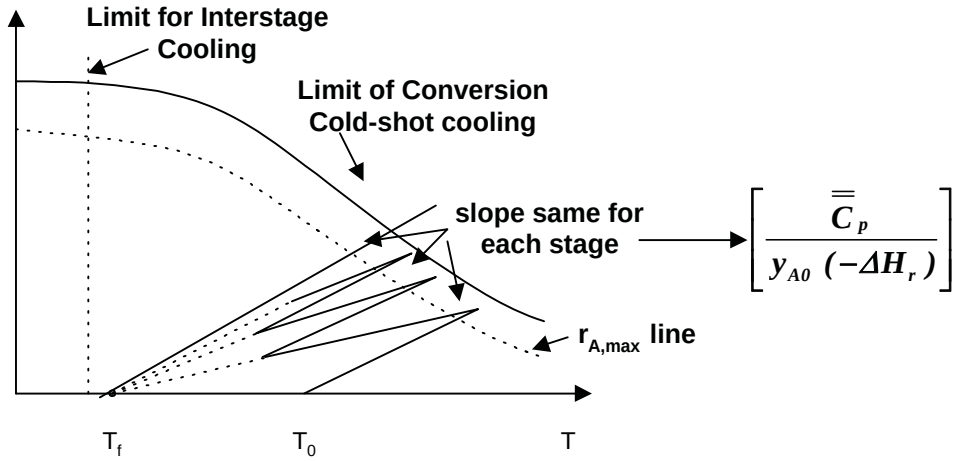


Figure 4.9 A "cold-shot" cooled reactor system consists of a series of adiabatic catalyst chambers. In each of the reactor stages, the temperature rises from inlet to outlet. A cold shot of initial feed material is introduced between stages to cool the reaction stream to a pre-determined temperature.

For the first stage, the operating line still has the form of Eq. 4.32:

$$x_A = -\frac{\overline{\overline{C}}_p}{y_{A0}\Delta H_r}(T - T_0)$$

The *operating* line for each subsequent reactor stage has the same slope. Note that the slope of the limiting line from T_f at the system inlet has the same slope $-\overline{\overline{C}}_p/(y_{A0}\,\Delta H_r)$ as the first adiabatic bed. Clearly, these equations are accurate to within the limits allowed by the approximations made in deriving them.

The adiabatic operating trajectories will rarely be linear but deviations may be ignored at the price of usually small errors. By contrast, in tubular reactors non-adiabatic operating lines cannot be expected to behave linearly.

$$x_A = \frac{\overline{\overline{C}}_p}{y_{A0}(-\Delta H_r)}(T - T_0)$$ Adiabatic operating line for both reactors - linear

$$\frac{dT}{dx_A} = y_{A0}\left[\frac{Q}{r_A\overline{\overline{C}}_p} + \frac{(-\Delta H_r)}{\overline{\overline{C}}_p}\right]$$ Non-adiabatic operating line for tubular reactor – not linear

$$x_A = \frac{n_{T0}\,\overline{\overline{C}}_p\,(T_0 - T) + Q}{n_{A0}\,(\Delta H_r)}$$ Non-adiabatic operating line for CSTR

Many of the approximations made in this introductory text are made for presenting the subject matter - and solving problems - in their simplest form. These assumptions are not needed when it is possible to resort to computer calculations.

4.5.3 Discussion

In actual practice, "cold shot" cooling is a convenient method for carrying our reversible exothermic reactions. There are no costly inter-stage heat exchangers. However, for the same number of stages, it cannot result in quite such a large limiting conversion as can be obtained by the use of inter-stage cooling. The streams entering the second and subsequent stages have shorter average residence times in the reactor system. The price paid for omitting the inter-stage heat-exchangers is some reactant by-pass, which leads to lower possible overall conversions.

The x_A vs T graphs for the two modes of operation do not contain information on reactor volumes or catalyst bed sizes. Calculating reactor volumes requires the simultaneous solution of the material balance equation(s) and the energy balance equation.

Generally, with a reasonable choice for values of the inlet temperatures into the various stages, one can considerably lower the reactor volume from that which would have been necessary for a single stage. Does this necessarily make multistage operation always preferable to simple, single stage operation? Not always. There is no single, simple solution to reactor optimisation in reversible exothermic reaction-reactor design. One would usually work with an economic objective function. But economic data [price forecasting, size of markets, elasticity of demand etc] are fickle guides at best. If equipment costing is to be made the important determinant in the objective function, multi– bed reactor systems enter the scales with complicated control equipment, added costs of inter-stage cooling etc.

The minimum amount of catalyst alone is an unsuitable objective function. Choice of the minimum mass of catalyst for a fixed number of stages is a reasonable objective but inter-stage cooling comes at a cost.

For CSTRs it is possible to operate each stage ON the locus of maximum reaction rates. For tubular reactors, every point on the operating line corresponds to a point within the reactor.

In tubular reactors, the decision about where to stop [i.e. end] each reactor stage must be taken carefully. Either side of the maximum-line corresponds to lower reaction rates than the maximum. Generally half way between the "optimum" line and the equilibrium line turns out to be a reasonable place to stop. Clearly one must avoid approaching the equilibrium line very closely, where the reaction rate dwindles down to zero.

CHAPTER 5

EFFECT OF FLOW PATTERNS ON CONVERSION

5.1 Introduction

The plug flow and continuous stirred tank models represent the two extremes in idealised flow regimes. The plug flow regime assumes total segregation between fluid elements, while the CSTR model represents total and instantaneous mixing. In CSTRs, the assumed ("ideal") total and rapid mixing gives rise to a broad distribution of residence times of the fluid elements in the reactor. In this Chapter, we will derive an equation for such residence time distributions. Elements of "non-ideal" flow, such as fluid by-pass and stagnant pockets give rise to further broadening of the residence time distribution. Clearly, conversions within fluid elements are affected by the time available for reaction. Differences in conversion between fluid elements leaving the reactor will result from differences in residence time. A spread of residence times is not an advantage and tends to require, for the same conversion, a larger reactor than would otherwise be the case.

In many industrial reactors, flow distributions do not necessarily approximate to either one of the two idealised models (PFR or CSTR). However, such reactors can sometimes be modelled by borrowing elements from both. For example, simple fluidised-bed reactor models borrow from the CSTR model for the emulsion phase and from PFRs for the bubble phase.

5.2 Discussing the plug flow assumption

Radial velocity profiles: The plug flow assumption implies that all fluid elements move through the reactor at the same velocity. All fluid elements are therefore assumed to have the same residence time (τ) in the reactor. In reality, when fluids flow through pipes, radial velocity profiles range from parabolic (in laminar flow) to a flatter profile for turbulent flow. The distribution of velocities causes different fluid elements to travel through the reactor at different residence times, leading to a distribution. The plug flow assumption entirely ignores these velocity profiles. Nevertheless, in many instances, the PFA may be used with small corrections or modifications, particularly when length/diameter rations are large.

Radial *temperature* profiles: Since reaction rates are very sensitive to the temperature, the plug flow assumption (PFA) breaks down completely, if radial *temperature* gradients are set up during the operation of a tubular reactor. It is then no longer possible to assume that "concentrations and reaction rates are uniform everywhere within the plug of fluid". In such cases, deviations from the PFA are great and use of the PFA is no longer tenable. In such cases, two dimensional reactor models, taking account of radial variations, must be used.

In themselves, *axial* temperature gradients do not violate the plug flow assumption, although it is usually difficult to retain the plug flow assumptions in the relatively realistic modelling of non-isothermal reactors. *Possible* cases where the PFA may be retained are (a) when the reactor diameter is small enough that radial gradients may be neglected *or* (b) adiabatic reactors, in cases where *radial* velocity profiles do not necessarily give rise to radial temperature gradients. In any case, caution is advised before plug flow assumptions are retained for non-isothermal reactors.

5.3 Defining residence time distributions

Residence time distributions (RTD) provide a method for evaluating the effect of flow patterns within reactors on levels of chemical conversion. This section discusses how residence time distributions can be determined and used to estimate reactor performance. Experimentally, the most common way to determine the RTD of a reactor is by injecting an inert tracer material into the reactor as a 'pulse-signal' or as a "step change" or as "periodic-signal". The concentration of the tracer leaving the reactor can then be measured at the outlet, to provide a measurement of the residence time distribution inside the reactor.

Choosing a tracer is not simple. The tracer should not affect the flow and should be inert but totally miscible within the reaction mixture. Typical materials used as tracers include dyes in organic solutions, which are distinguishable by visible colour or by UV-absorption, salt solutions, distinguishable by electrical conductivity in aqueous streams or radioactive materials such as ^{14}C-tagged compounds. Helium has been used as tracer for the gas stream in a catalytic cracking plant of an oil refinery. During the same batch of experiments, radioactive tracers were used for the catalyst flowing from the reactor to the generator and back again. Radioactive tracers would now be considered a safety hazard and be no longer acceptable.

5.3.1 RTD in an ideal CSTR [Metcalfe 1997]

"Total and instantaneous stirring" in a CSTR implies that as soon as a fluid element (or pulse of tracer) is injected into the reactor, we expect it to distribute itself uniformly throughout the reaction zone. In "ideal" CSTRs, the exit stream is assumed to have the same composition as the reaction mixture within the reaction zone. It follows that the exit stream will have the highest possible concentration of material from the tagged fluid element (or pulse of tracer) at the outset of the experiment (i.e. $t = 0$). Thereafter, the tracer concentration in the main reactor would be diluted with the inlet stream and the concentration of tracer in the exit stream would be expected to gradually decay to zero.

Consider N moles of tracer introduced as a pulse into the reactor inlet at time, $t = 0$. The perfect ('total and instantaneous') mixing assumption requires that at $t = 0$, the tracer should be uniformly distributed inside the reactor. The initial concentration of tracer at $t = 0$ is given by

$$C_{TR,0} = \frac{N_{TR}}{V_R} \qquad \textbf{(Eq. 5.1)}$$

The decay of tracer concentration in the reactor is an unsteady state process. We have already derived an equation for a non-steady-state mass balance in a CSTR:

$$\frac{dn_A}{dt} + \left[\frac{1}{\tau} + k\right] n_A = \frac{n_{A0}}{\tau} \qquad \textbf{(Eq. 1.60)}$$

In the case of an inert tracer, the rate constant $k = 0$ and since there is no more tracer being put in, $n_{A0} = 0$. Eq. 1.60 can then be rewritten as

$$\frac{dn_A}{dt} + \left[\frac{1}{\tau}\right] n_A = 0 \qquad \textbf{(Eq. 5.2)}$$

This is similar to a "shut-down' problem, where from time $t = 0$, only inert (unreactive) material is pumped into the reactor. The general solution to the problem has been derived.

$$n_A = \left\{ n_{A,ss} - \frac{n_{A0}}{\beta\tau} \right\} e^{-\beta\ t} + \frac{n_{A0}}{\beta\tau} \qquad \textbf{(Eq. 1.64)}$$

This equation can be simplified using $n_{A0} = 0$ and $k = 0$, to give

$$n_A(t) = (n_{A,steady\ state})\ e^{-\beta t} = (n_{A,steady\ state})\ e^{-t/\tau} \qquad \textbf{(Eq. 5.3)}$$

$n_{A,ss}$ refers to the initial value of the exit molar flow rate. In this context, it refers to the exit molar flow rate at $t=0$, after which it begins to decay since there is no fresh A coming in. In terms of molar concentrations, dividing through by v_T

$$C_A(t) = C_{A,ss} \quad e^{-t/\tau}, \qquad \textbf{(Eq. 5.3)}$$

where $C_{A,ss}$ is the initial concentration of tracer in the reactor. In terms of tracer flow rate:

$$C_{TR}(t) = C_{TR,0} \quad e^{-t/\tau} \qquad \textbf{(Eq. 5.4)}$$

where $C_{TR}(t)$ represents the concentration of tracer at the reactor exit, as a function of time.

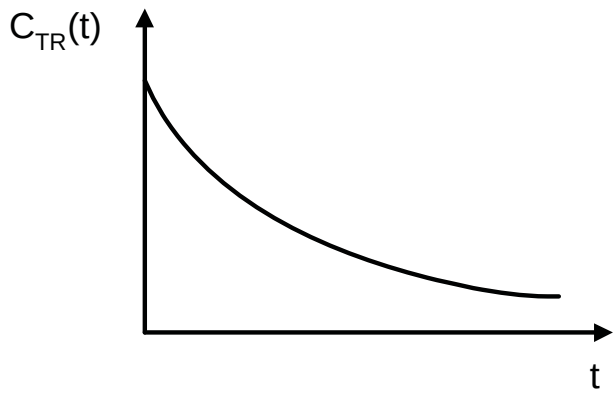


Figure 5.1 Qualitative sketch of the decay of tracer concentration at the exit of a CSTR

The 'normalised' residence time distribution is now defined as:

$$E(t) = \frac{C_{TR}(t)}{\int_0^\infty C_{TR}(t)dt}, \qquad \textbf{(Eq. 5.5)}$$

where,

$$\int_0^\infty C_{TR}(t)dt = \int_0^\infty \frac{n_{TR}(t)}{v_T}dt = \frac{1}{v_T}\int_0^\infty n_{TR}(t)dt = \frac{N_{TR}}{v_T} \qquad \textbf{(Eq. 5.6)}$$

In Eq. 5.6, $n_{TR}(t)$ is defined as the molar flow rate of tracer in the outlet stream. Then,

$$\int_0^\infty C_{TR}(t)dt = \frac{N_{TR}}{v_T} = \frac{V_R C_{TR,0}}{v_T} = \tau\, C_{TR,0} \qquad \textbf{(Eq. 5.7)}$$

Combining with Eq. 5.4, $C_{TR}(t) = C_{TR,0}\ e^{-t/\tau}$, we get

$$E(t) = \frac{C_{TR}(t)}{\int_0^\infty C_{TR}(t)dt} = \frac{C_{TR,0}\, e^{-t/\tau}}{\tau\, C_{TR,0}} = \frac{1}{\tau} e^{-t/\tau} \qquad \textbf{(Eq. 5.8)}$$

The RTD decays exponentially with time. However, the area under the curve is always equal to unity because of the normalization. The residence time distribution: the fraction of the total stream that has a residence time between t and $t+\Delta t$ is $E(t)dt$.

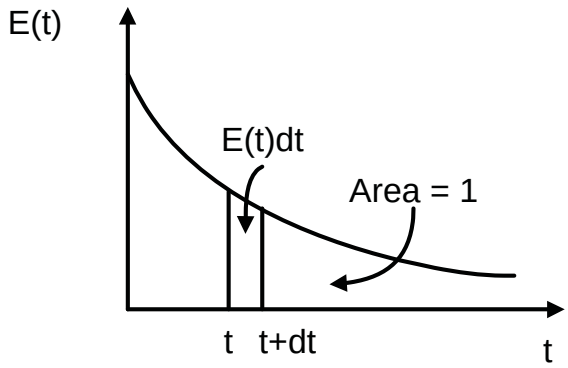


Figure 5.2 The residence time distribution E(t) in a CSTR and the time interval from t to t+dt.

This derivation of the RTD assumes perfect mixing.
We have not (yet) introduced flow non-idealities into the treatment.

5.3.2 The ideal PFR [Metcalfe 1997]

The plug flow assumption requires that a fluid element, or a pulse of tracer, entering the reactor at time $t=0$, exit from the reactor at exactly $t=\tau$ $(=V_R/v_T)$. This corresponds to a pulse of tracer, which is introduced during an infinitesimally short time ('instantaneously') and does not mix with fluid elements running ahead or behind it, within the reactor.

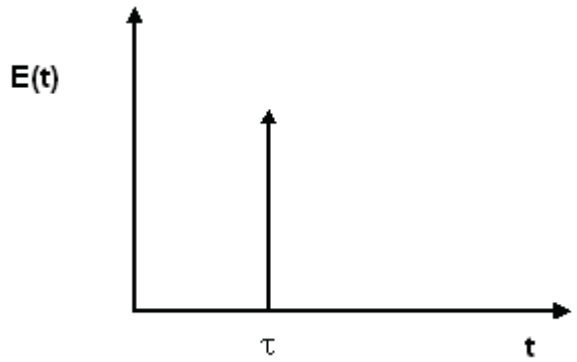


Figure 5.3 The residence time distribution E(t) in an ideal plug flow reactor.

5.4

The normalised residence time distribution is written down in terms of a Dirac "delta-function"

$$E(t) = \delta(t-\tau) \qquad \textbf{(Eq. 5.9)}$$

where $\delta(t-\tau)=0,$ for $t \neq \tau$, and $\delta(t-\tau)=1,$ for $t=\tau$. The integral of the Dirac δ-function is given as:

$$\int_0^\infty \delta\ (t-\tau\ )\ dt = 1 \text{ and } \int_0^\infty a\delta\ (t-\tau\ )\ dt = a, \qquad \textbf{(Eq. 5.10)}$$

where 'a' is any constant.

In actual tubular reactors, not all fluid elements travel at the same speed. This is due to a number of factors. In the case of laminar flow, the parabolic velocity distribution causes dispersion around the spike shown in Figure 5.4. In turbulent flow, a narrower velocity distribution also causes dispersion around the average residence time. Tracer mass exchange with stagnant pockets also tends to broaden the residence time distribution. In packed beds, the fluid holdup causes a delay for some of the fluid elements. Mass transfer between stagnant pockets and the main flow stream contributes to dispersion. Straightforward diffusion between 'plugs' of fluid also contributes to the broadening of the residence time distribution.

Calculation of average residence times (τ): In complicated reactor systems, where modelling the residence time distribution can be difficult (and possibly inaccurate), the RTD can always be measured experimentally. Once we derive the RTD theoretically or determine it experimentally, the average residence time for any system may be calculated from:

$$\bar{t} = \int_0^\infty tE(t)dt \qquad \textbf{(Eq. 5.11)}$$

Mathematically, this is defined as "the first moment of the distribution". The average residence time is simply the individual residence time for each fluid element multiplied by the fraction of the total amount of dye present in that element, summed over all elements. For an 'ideal' CSTR:

$$\bar{t}_{CSTR} = \int_0^\infty t\left(\frac{1}{\tau}\ \ e^{-t/\tau}\right)dt \qquad \textbf{(Eq. 5.12)}$$

Integrating by parts:

$$\bar{t}_{CSTR} = \left[-t\,exp\left(-\frac{t}{\tau}\right)\right]_0^\infty + \int_0^\infty exp\left(-\frac{t}{\tau}\right)dt \qquad \textbf{(Eq. 5.13)}$$

$$\bar{t}_{CSTR} = \left[-t\,exp\left(-\frac{t}{\tau}\right) - \tau\,exp\left(-\frac{t}{\tau}\right)\right]_0^\infty = [0-(-\tau)] = \tau = \frac{V_R}{v_T} \qquad \textbf{(Eq. 5.14)}$$

we arrive at the expected result for an ideal CSTR. For an 'ideal' PFR:

$$\bar{t}_{PFR} = \int_0^\infty t \quad \delta(t-\tau) \quad dt = \tau = \frac{V_R}{v_T} \qquad \textbf{(Eq. 5.15)}$$

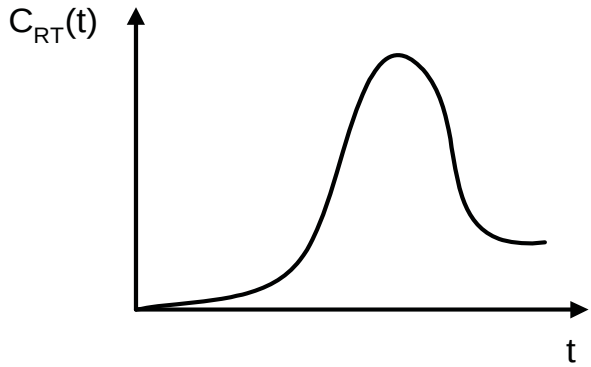


Figure 5.4 The residence time distribution E(t) in a tubular flow reactor with non-ideal flow.

5.4 Calculation of conversions from the residence time distribution

At constant temperature, the conversion in a fluid element depends on the length of time the fluid element spends in the reaction zone. Any spread of residence times of the fluid elements in the reaction zone would therefore give rise to a distribution of conversions between fluid elements leaving the reactor. The average outlet concentration of reactant is given by

$$\overline{C}_A = \int_0^\infty C_A(t)E(t)dt \qquad \textbf{(Eq. 5.16)}$$

In this approach, each fluid element will be treated as a *batch* reactor. So long as they are defined to be sufficiently small, we can consider them to be internally well mixed. For a first-order, irreversible reaction, the design equation for a well-mixed batch reactor is,

$$\frac{dC_A}{dt} = -r_A = -kC_A \qquad \textbf{(Eq. 5.17)}$$

For any single fluid element,

$$C_A = C_{AO}\, exp(-kt) \qquad \textbf{(Eq. 5.18)}$$

The average outlet concentration of reactant may then be given by

$$\overline{C}_A = C_{AO} \int_0^\infty exp(-kt)\, E(t)\, dt \qquad \textbf{(Eq. 5.19)}$$

For an 'ideal' PFR ,

$$\overline{C}_{A,PFR} = C_{AO} \int_0^\infty exp(-kt)\, E(t)\, dt = C_{A0}\, exp(-k\tau) \qquad \textbf{(Eq. 5.20)}$$

where E(t) is the Dirac δ-function. For a CSTR the equations would take the following form:

$$\overline{C}_{A,CSTR} = C_{AO} \int_0^\infty exp(-kt) \frac{1}{\tau} exp\left(-\frac{t}{\tau}\right) dt \qquad \textbf{(Eq. 5.21)}$$

$$\overline{C}_{A,CSTR} = C_{AO} \int_0^\infty \frac{1}{\tau} exp\left(-kt - \frac{t}{\tau}\right) dt \qquad \textbf{(Eq. 5.22)}$$

$$\overline{C}_{A,CSTR} = C_{AO}\left[-\frac{1}{1+k\tau}exp\left(-kt-\frac{t}{\tau}\right)\right]_0^{\infty} = \frac{C_{A0}}{1+k\tau} \qquad \textbf{(Eq. 5.23)}$$

However, the significance of the technique becomes more clearly apparent when arbitrary RTDs are used. We will see an example of this in the solved problems section.

CHAPTER 6

THE DESIGN OF FIXED BED CATALYTIC REACTORS-I

6.1 Introduction

Catalysts are used for increasing the speed or altering the course of chemical reactions. To slow down a rate of reaction, what we use is called an "inhibitor". Ideally, a catalyst remains unchanged, whilst enhancing the speed of a chemical reaction. In practice, however, catalysts may be altered by "poisoning", which is the strong chemical adsorption of species that block active sites. Catalysts may also be altered physically, by "sintering", which causes loss of surface area within the porous structure. Catalysts may also be deactivated by "fouling", that is by depositing semi-inert (e.g. carbonaceous) solids on active sites.

The useful lives of catalysts are determined by the intensity of these effects. A naphtha hydro-desulphurization catalyst, commonly used in oil refineries, may retain sufficient activity to be kept on line for months or, at times, for one or several *years*. Meanwhile, fouling in fluid catalytic crackers is rapid and the catalyst would need to be regenerated on a time scale of usually less than a minute.

Catalysts are used to increase the rate of a reaction by providing reaction pathways with lower energies of activation. In the context of multiple reactions, enhancing some pathways over others is capable of altering the overall selectivity of the process.

Many common catalysts consist of an active component (e.g. nickel oxide) that is impregnated onto a porous matrix such as alumina or silica. The internal (pore) surface area of such catalysts is far greater than the external surface area. For example, ordinary non-porous sand may have a surface area of 1 m^2/gm, whereas typical catalysts would have surface areas in the range of 50 – 300 m^2/gm. Some specialized active carbons have surface areas as high as 1,000 m^2/gm.

It is important that reactants are able to diffuse into catalyst pores and products diffuse back out again. As the effective diffusivity of many species in catalyst pores is low, catalyst pellets are usually quite small. Characteristic dimensions are of the order of millimetres or, rarely, up to 1 cm in diameter. Most pellets are prepared in the form of cylindrical or spherical pellets, due to the relative ease of extrusion; however, the pellets may adopt any shape at all.

A fixed bed catalytic reactor (FBCR) is commonly a tubular reactor packed with catalyst pellets. For reaction to take place, reactants must diffuse from the stream of fluid flowing through the reactor, towards the catalyst pellets. Reaction takes place, mostly on internal (pore) surfaces. Product molecules diffuse back into the bulk fluid stream. In any given volume element of the reactor, therefore, there are concentration gradients that drive reactants towards catalyst pellet surfaces and similarly move products away from catalyst pellets. In calculating – or deriving expressions for – the overall reaction rate, these concentration driving forces and diffusion resistances must be taken into account, alongside the intrisic (i.e. surface) reaction rate.

In this Chapter, we will first discuss the design of *isothermal* fixed bed catalytic reactors (FBCR). As a flow model, "plug flow" may still apply in designing FBCRs, if we can reasonably assume that we have radially uniform temperature and concentration profiles.

The rate expressions for catalytic reactions can still be expressed in terms of "kmol/(time × volume)". However, what we are really interested in is the volume *filled with catalyst* and more specifically the actual amount of catalyst used in the reactor. The catalyst packing density is usually known and the rate expression can be, and usually is, recast in terms of

$$r_A \text{ [=] kmol/(time} \times \text{mass of cat.)} \qquad \textbf{(Eq. 6.1)}$$

The major difference between isothermal homogeneous reactors and isothermal packed catalytic reactors is that concentrations may vary between the bulk of the fluid stream and external catalyst particle surfaces. Concentrations may also vary *within* catalyst pellets, often continuously, giving rise to *intra*-pellet concentration gradients. Unlike homogeneous reactors, therefore, we can no longer assume that concentrations are uniform within small volume elements. Instead we need new ways of developing mass balance equations.

The use of catalysts to enhance reversible reactions does not affect or shift the equilibrium point. It simply enables approaching equilibrium more rapidly.

6.2 Mass transport between the bulk fluid phase and external catalyst surfaces in isothermal reactors [Smith, 1981]

In a FBCR, the "bulk" stream of reactant-bearing fluid moves from inlet to exit, through a matrix of packed catalyst. In order to model mass transport processes around a catalyst pellet, we assume the pellet to be surrounded by a stagnant film of gas (or liquid). Initially, we will assume the catalyst pellet to be isothermal.

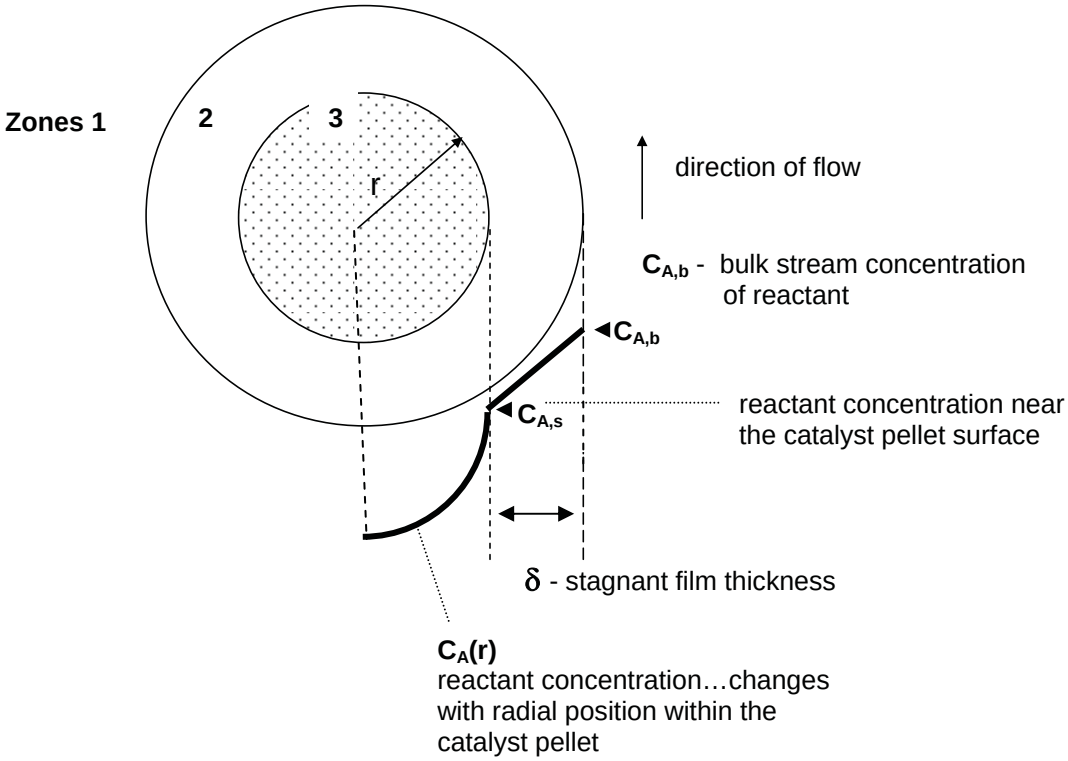


Figure 6.1 Three contiguous zones are defined, to help formulate reaction rate expressions in catalyst beds: (1) bulk fluid phase, (2) stagnant film surrounding the catalyst pellet, and, (3) the catalyst pellet.

Transport resistances may give rise to appreciable differences in concentration between the bulk fluid stream and catalyst particle surfaces. These gradients usually result from continuous changes. However, defining a stagnant film enables assigning the concentration differences to a specific location.

We postulate the following steps for an isothermal chemical reaction occurring in the presence of a catalyst pellet. In Table 1, Steps 3,4 and 5 (above) are usually lumped together as the surface reaction rate ($r_{surface}$) or the intrinsic reaction rate. This is to be distinguished from the rate of reaction at external pellet conditions, r_s (the intrinsic reaction rate at external surface conditions). The two are not always equal.

Step 1	Diffusion of reactants from the bulk fluid stream, through the stagnant film, to external surfaces of the pellet.
Step 2	Transport of reactants from external pellet surfaces to the interior of the catalyst pellet by pore diffusion.
Step 3	Adsorption of reactants onto active sites within the pores of the catalyst pellet.
Step 4	Chemical reaction on internal pellet surfaces, between adsorbed molecules or between adsorbed molecules and molecules in the gas phase. Surface migration (surface diffusion) is possible but usually difficult to characterize.
Step 5	Desorption of products from internal catalyst pellet surfaces
Step 6	Outward pore diffusion of products from the interior of catalyst pellet to external pellet surfaces.
Step 7	Film diffusion of products from external surfaces of the pellet to the flowing bulk fluid stream.

Table 1. Successive diffusion and reaction near and within catalyst pellets

The mass flux of reactant *"A"* from the bulk fluid stream to external catalyst pellet surfaces, N_A, is defined as

$$N_A = k_m a_m (C_{A,b} - C_{A,s}) \quad , \qquad \textbf{(Eq. 6.2)}$$

where k_m is the mass transfer coefficient and a_m the external surface area of the catalyst. $C_{A,b}$ is defined as the bulk concentration of reactant and $C_{A,s}$ the external pellet surface concentration. A similar expression defines the mass flux *from* external pellet surfaces to the bulk fluid stream. A little further on, we will describe methods for estimating mass transfer coefficients from existing correlations.

When a sequence of events takes place in several successive steps, the overall process can proceed no faster than the rate of the slowest step. At steady state, the rate of each of the seven steps will be equal to each other. If the slowest step is very much slower than the rest, it is called the "rate limiting step"; *its* rate determines the overall rate.

6.3 Defining effectiveness factors – for isothermal pellets [Smith, 1981]

Figure 6.1 shows the concentration profile *within* the catalyst pellet, $C_A(r)$, in schematic form. As reactants diffuse towards the centre of the pellet, they are gradually consumed and their concentrations decrease. The reaction rate within the pellet is, therefore, not uniform; it is a function of position.

The rate of chemical reaction per pellet is needed in order to integrate over the reactor; this enables calculating the reactor volume and the conversion. However, when we try to calculate the rate of chemical reaction per pellet, the distribution of reaction rates over the pellet radius gives rise to mathematical complications. To simplify the problem, we define an "effectiveness factor", as a global measure of intra-particle diffusion resistance within the pellet.

$$\eta = \frac{[\textit{actual rate of reaction for the whole pellet: the "global" reaction rate}]}{[\textit{rate of reaction evaluated at external pellet surface conditions}]} = \frac{r_p}{r_s} \qquad \textbf{(Eq. 6.3)}$$

$$\eta = r_p / r_s \qquad \textbf{(Eq. 6.4)}$$

In Equation 6.4, r_p is defined as the "global" reaction rate; it is the rate per unit mass of pellet. r_s is the rate of reaction rate evaluated at external pellet surface conditions. These definitions allow us to express the rate per pellet in terms of external pellet surface conditions and an effectiveness factor.

$$r_p = \eta\, r_s \qquad \textbf{(Eq. 6.5)}$$

Later on in this chapter, we will introduce methods for deriving expressions for calculating effectiveness factors. We will also show how external pellet surface conditions can be expressed in terms of bulk fluid stream conditions. Combined with the effectiveness factor, this information will enable deriving expressions for the *overall* chemical reaction rate per pellet, r_p, in terms of local bulk stream conditions. The global rate can then be integrated over the whole reactor, to calculate the total conversion in the reactor, or (given the conversion) the reactor volume.

More formally, the effectiveness factor is defined in the form of an integral over the particle volume, of the ratio of the real reaction rate over the rate of reaction at surface conditions.

$$\eta = \frac{1}{V_p} \int \frac{r_A(C_i, C_j, \ldots, T)\, dV_P}{r_A(C_{is}, \ldots T_s)} \qquad \textbf{(Eq. 6.6)}$$

6.3.1 Deriving the global reaction rate expression

Consider a simple intrinsic reaction rate expression: $r_A = k\,C_A$. At external pellet surface conditions, we can write $r_{A,s} = k\,C_{A,s}$. Having defined η in Eq. 6.4 makes it possible to write the global reaction rate in terms of the external pellet surface concentration:

$$r_{A,p} = \eta\, r_{A,s} = \eta\, k\, C_{A,s} \;\; [=] \;\; [kmoles/(time \times kg\text{-}catalyst)]\,. \qquad \textbf{(Eq. 6.7)}$$

In Equation 6.7, $C_{A,s}$ denotes the concentration of reactant *near* the external surface of the catalyst pellet. It is *not* the surface concentration of reactant, in the sense of being the concentration of an *adsorbed* species. Also note that while we have initially assumed isothermal behaviour, the implicit dependence of *k* on the temperature is clear.

At steady state, the overall rate of reaction, r_p, is equal to the net flux of reactant reaching the pellet surface. In other words, at steady state, $r_p = N_A$. Here we set the reaction rate per unit weight of catalyst particle, called the "global reaction rate", (in Equation 6.7) equal to the mass flux to catalyst pellets, $k_m a_m (C_b - C_s)$ (cf. Equation 6.2).

$$r_p = k_m a_m (C_{A,b} - C_{A,s}) = \eta k C_{A,s}\,, \qquad \textbf{(Eq. 6.8)}$$

Note that $C_{A,s}$ cannot be measured readily, but it is possible to measure $C_{A,b}$ directly. Eq. 6.8 is useful in allowing us to solve for $C_{A,s}$ in terms of $C_{A,b}$.

$$k_m a_m (C_{A,b} - C_{A,s}) = \eta k C_{A,s} \qquad \textbf{(Eq. 6.9)}$$

Solving for $C_{A,s}$, we get:

$$C_{A,s} = \frac{k_m a_m}{\eta\, k + k_m a_m} C_{A,b}\,. \qquad \textbf{(Eq. 6.10)}$$

Substituting this result into $r_p = \eta k C_{A,s}$ and rearranging, we get:

$$r_p = \frac{1}{\left\{ \dfrac{1}{k\eta} + \dfrac{1}{k_m a_m} \right\}} C_{A,b}\,. \qquad \textbf{(Eq. 6.11)}$$

Eq. 6.11 is important in showing the separate kinetic and diffusional contributions to the global reaction rate expression, for a simple first order reaction rate expression.

When chemical reaction is much faster than the diffusion process,

$$\frac{1}{k_m a_m} \gg \frac{1}{k\eta}\,. \qquad \textbf{(Eq. 6.12)}$$

The resulting rate expression represents overall "diffusion control".

$$r_p = k_m a_m C_{A,b}\,. \qquad \textbf{(Eq. 6.13)}$$

Conversely, when diffusion is much faster than chemical reaction, the overall process is controlled by the rate of the chemical reaction.

$$\frac{1}{k_m a_m} \ll \frac{1}{k\eta} \qquad \textbf{(Eq. 6.14)}$$

The global rate expression then represents "kinetic control".

$$r_p = k\eta\, C_{A,b} \qquad \textbf{(Eq. 6.15)}$$

6.3.2 How does $r_{A,p}$ fit into the overall design problem?

In Chapter 1, we derived the isothermal mass balance (design) equation for a homogeneous reaction, assuming plug flow in a tubular reactor.

$$V_R = -\int \frac{dn_A}{r_A} \qquad \textbf{(Eq. 1.13)}$$

When the reactor is packed with catalyst and plug flow is assumed, we can use a modified form of this equation. In designing a catalytic reactor, we keep track of the *catalyst packed volume*, or the total *weight of catalyst*, and *not* the total volume of the reactor. This last statement assumes that no homogeneous reaction is taking place in the unpacked spaces of the reactor. It is usually a good working assumption, although there are exceptions. The volume of catalyst packed reactor is directly related to the *weight* of catalyst through the relationship:

$$W_{cat} = V_R / \rho_{cat,bulk} \quad , \qquad \textbf{(Eq. 6.16)}$$

where W_{cat} is the total weight of catalyst used, V_R the volume of reactor packed with catalyst and $\rho_{cat,bulk}$ the bulk density of the catalyst. Assuming plug flow, we can carry out the mass balance in terms similar to those of a homogeneous reactor (cf. Chapter 1)

$$(M_A n_A)_W \quad - \quad (M_A n_A)_{W+\Delta W} \quad - \quad M_A r_{A,p} \Delta W_{cat} = 0 \qquad \textbf{(Eq. 6.17)}$$

$$\left\{\begin{matrix} \text{inflow of } A \\ \text{per unit time} \\ \text{into} \\ \text{volume element} \end{matrix}\right\} - \left\{\begin{matrix} \text{outflow of } A \\ \text{per unit time} \\ \text{into} \\ \text{volume element} \end{matrix}\right\} - \left\{\begin{matrix} \text{loss of } A \\ \text{per unit time} \\ \text{through} \\ \text{reaction} \end{matrix}\right\} = \left\{\begin{matrix} \text{rate of} \\ \text{accumulation} \end{matrix}\right\} \qquad \textbf{(Eq. 6.18)}$$

Taking the limit as $\Delta W_{cat} \to dW_{cat}$,

$$-\frac{dn_A}{dW_{cat}} = r_{A,p} \qquad \textbf{(Eq. 6.19)}$$

The material balance equation for a catalyst packed bed operating in plug flow is then given by:

$$W_{cat} = -\int \frac{dn_A}{r_P} = -\int \frac{d(C_{A,b}\, v_T)}{r_P} \qquad \textbf{(Eq. 6.20)}$$

In Eq. 6.20, v_T is the total volumetric flow rate, n_A is the molar flow rate of reactant "*A*" in the bulk fluid stream and $C_{A,b}$ is the concentration of reactant "*A*" in the bulk fluid stream. Note that the units of r_P, the global reaction rate, are given as

$$r_p \triangleq \text{kmoles}/(\text{unit time} \times \text{kg} - \text{catalyst}), \qquad \textbf{(Eq. 6.21)}$$

while the units for the rate of a homogeneous reaction are expressed in terms of

$$r_A \triangleq \text{kmoles}/(\text{unit time} \times \text{volume}). \qquad \textbf{(Eq. 6.22)}$$

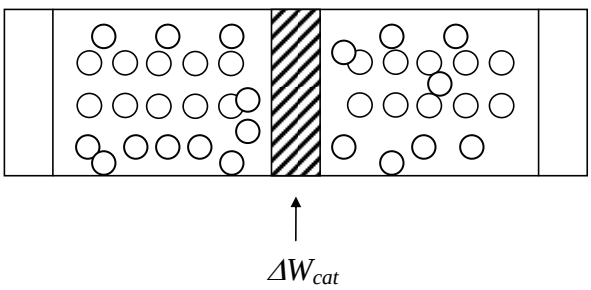


Figure 6.2 Schematic diagram showing a volume element in a fixed bed catalytic reactor. The plug flow assumption is assumed to be valid over the volume element.

Eqs. 6.19 and 6.20 implicitly ignore the presence of catalyst pellets as discreet particles. It assumes that reaction intensity is uniform within particular *volume* elements. Thus, it is implicitly assumed that the reaction takes place in "pseudo-homogeneous" mode. This is a simplifying assumption.

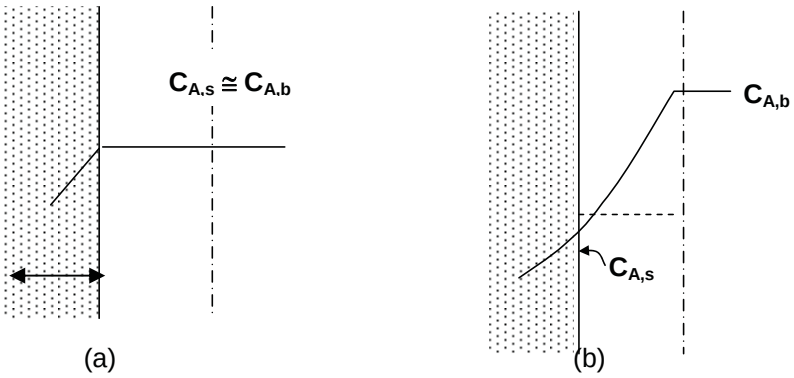


Figure 6.3 (a) When the process is controlled kinetically, i.e. when reaction is slower than diffusion, the concentration gradient across the external stagnant film tends to flatten. (b) When external diffusion is slower than chemical reaction, a concentration gradient is set up across the stagnant film. This is called external diffusion control.

Resistance to mass transfer within a porous catalyst matrix is normally greater than diffusion resistance through the stagnant film, which is a gaseous (or liquid) medium. When diffusion from the bulk fluid to the external catalyst surface is limiting, the stagnant film concept would have all external resistance to diffusion concentrated in the stagnant film. If external diffusion is limiting, intra-particle diffusion would also be slow and provide the limiting step, in respect of the overall reaction rate. In these cases, the designer must take both external and internal diffusion resistances into account. The possibility of a system where external diffusion is controlling, in coexistence with negligible "internal" diffusion resistance (i.e. an effectiveness factor $\eta \cong 1$) may be discounted. Note that the algebra of the equation

$$r_{A,p} = \eta\, r_{A,s} = k_m a_m (C_{A,b} - C_{A,s}) \qquad \textbf{(Eq. 6.23)}$$

gets progressively more complicated as the reaction rate expressions get more realistic.

In order to relate the isothermal effectiveness factor to the overall reactor design problem,
1. We equate net mass transfer to/from the catalyst pellet with the amount of reaction taking place within the pellet
2. Express the result in terms of the *bulk* concentration(s) of reactant(s)
3. Use a flow model (e.g. plug flow) to integrate over the whole reactor

6.3.3 What happens if we ignore external diffusion resistances?

Activation energies of chemical reactions are usually larger than activation energies for diffusive processes, often by a factor of four or more. Reaction rate constants are normally exponentially dependent on the temperature. Compared to reaction rate constants, mass transfer coefficients (k_m) are less sensitive to changes in temperature; often they turn out to be approximately linearly dependent on the temperature.

If resistance to diffusion between the bulk stream and external particles surfaces is (wrongly) neglected, the calculated activation energy for the lumped reaction-diffusion process would inevitably not solely reflect the activation energy of the chemical reaction. If the measured kinetic constant also contains a diffusional contribution, and this was overlooked, what we would in effect be doing is lumping together two contributions with differing activation energies. In other words, we would write the rate expression as $r_p = k_{apparent}\, C_{A,b}$ instead of

$$r_p = \frac{1}{\left\{\frac{1}{k\eta} + \frac{1}{k_m a_m}\right\}} C_{b,A} \qquad \textbf{(Eq. 6.24)}$$

Then $k_{apparent}$ is given by

$$k_{apparent} = \frac{1}{\frac{1}{a_m k_m} + \frac{1}{\eta\, k_0 \exp\{-\Delta E_a / RT\}}}. \qquad \textbf{(Eq. 6.25)}$$

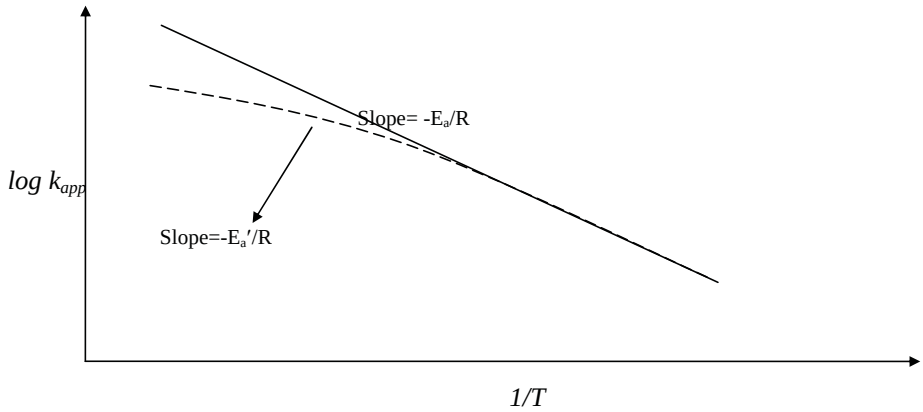


Figure 6.4 Arrhenius type plot showing the effect of external diffusion on the overall process.

If external transport is thus erroneously ignored, the *log k* versus *1/T* plot does not give a straight line. The slope begins to diminish and the line bends at higher temperatures, where the overall rate is increasingly controlled by the rate of diffusion.

6.4 Isothermal effectiveness factors [Smith, 1981; Froment & Bischoff, 1990]

Catalyst pellets may be prepared in any shape or size. The mathematical expressions derived for effectiveness factors depend on the geometry of the pellet. In this section, we will show how such expressions are derived for the effectiveness factor of a "flat-plate" catalyst pellet in detail. The more common derivation for spherical pellets is found in most textbooks; that derivation will also be summarized.

6.4.1 The isothermal effectiveness factor for a flat-plate catalyst pellet

Consider the chemical reaction $A \xrightarrow{k} B$ taking place within a "flat slab" catalyst pellet with intrinsic reaction rate $r_A = k\, C_A$. We will assume (i) ideal gas behaviour, (ii) a two-component (i.e. binary) system and (iii) equimolar counter diffusion, where the molar flux of component "A" is denoted by N_A. Fick's law of diffusion is then given by:

$$N_A = -D_e \frac{\partial C_A}{\partial z}, \qquad \textbf{(Eq. 6.26)}$$

where D_e denotes the effective diffusivity of the reactant A through the porous matrix. In the following derivation, we postulate a "no flux" boundary condition. This is used to express axial symmetry; i.e. the other side of the boundary would show the mirror image of the concentration profile.

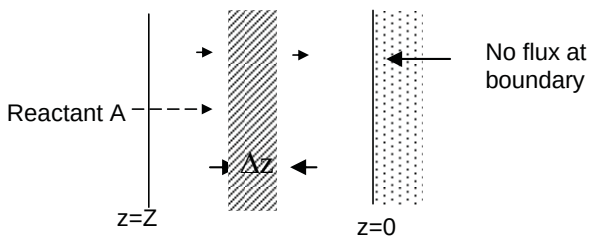


Figure 6.5 Schematic diagram of flat-plate catalyst pellet with volume element $\alpha\, \Delta z$; α is the surface area.

We assume the surface area of the flat plate "α", normal to the plane of diffusion, to be large, so that edge effects do not affect the material balance.

$$\alpha\, N_A = -D_e \alpha \frac{\partial C_A}{\partial z} \qquad \textbf{(Eq. 6.27)}$$

We perform a mass balance over the volume element "$\alpha\, \Delta z$". Note that C_A is the concentration of reactant "A" in the gas layer *near* the internal catalyst pellet surfaces; it is not the *surface* concentration of reactant, in the sense of adsorbed species. We may view C_A as an "in flight" concentration. At steady state, the material balance takes the form:

$$N_A \alpha\big|_z - \left\{ N_A + \frac{\partial N_A}{\partial z} dz \right\} a \Bigg|_{z+dz} - k\, C_A \alpha\, dz = 0 \qquad \textbf{(Eq. 6.28)}$$

Rearranging and dividing by α, we get

$$-\frac{dN_A}{dz} - kC_A = 0 \qquad \textbf{(Eq. 6.29)}$$

Substituting Fick's law (Eq. 6.24) for N_A, we get a second order ordinary differential equation:

$$D_e \frac{d^2 C_A}{dz^2} - kC_A = 0 \qquad \textbf{(Eq. 6.30)}$$

with boundary conditions: $C_A = C_{A,s}$ at $z=Z$ and

$$dC_A / dz = 0 \text{ at } z=0. \qquad \textbf{(Eq. 6.31)}$$

It is convenient to recast these equations in dimensionless form. We define $y \triangleq C_A / C_{A,s}$ and $\xi \triangleq z/Z$ and substitute in Eq. 6.28.

$$\left(\frac{D_e C_{A,s}}{Z^2}\right) \frac{d^2 y}{d\xi^2} - k\, C_{A,s} y = 0\,. \qquad \textbf{(Eq. 6.32)}$$

Simplifying, we get:

$$\frac{d^2 y}{d\xi^2} - \frac{kZ}{D_e} y = 1\,. \qquad \textbf{(Eq. 6.33)}$$

We now define the Thiele modulus. This is the characteristic geometry-dependent variable in terms of which we derive expressions for effectiveness factors. It contains the ratio of the kinetic constant to the effective diffusivity:

$$\Phi_c = Z\left[k / D_e\right]^{1/2} \qquad \textbf{(Eq. 6.34)}$$

Recast using Φ , Equation 6.32 takes the form

$$\frac{d^2 y}{d\xi^2} - \Phi_c{}^2 y = 0\ , \qquad \textbf{(Eq. 6.35)}$$

The boundary conditions are now recast as y=1 at ξ=1 and $dy / d\xi = 0$ at ξ=0. Solving the equation in the standard way and using the boundary conditions, we get:

$$y = \frac{e^{\Phi_c \xi} + e^{-\Phi_c \xi}}{e^{\Phi_c} + e^{-\Phi_c}} = \frac{cosh(\Phi_c\ \ \xi\ )}{cosh(\Phi_c\ )} \qquad \textbf{(Eq. 6.36)}$$

In terms of the original variables, the solution becomes

$$C_A = C_{A,s} \frac{cosh\left\{z\sqrt{k/D_e}\right\}}{cosh\left\{Z\sqrt{k/D_e}\right\}} \qquad \textbf{(Eq. 6.37)}$$

The rate of reaction for the catalyst pellet can then be calculated from:

$$r_{A,p} = \frac{\int_0^Z kC_A(z)\alpha\, dz}{\int_0^Z \alpha\, dz} \qquad \textbf{(Eq. 6.38)}$$

Substituting C_A from Eq. 6.35 into Eq. 6.36

$$r_p = \frac{k}{Z} \frac{C_{A,s}}{cosh\,\Phi_c} \int_0^Z cosh \frac{\Phi_c\, z}{Z} dz\,. \qquad \textbf{(Eq. 6.39)}$$

Integrating, we get

$$r_p = k\, C_{A,s} \frac{tanh\,\Phi_p}{\Phi_p} \qquad \textbf{(Eq. 6.40)}$$

Recalling that $\eta = r_p/r_s$ and that $r_s = k\, C_{A,s}$ we arrive at an expression for the effectiveness factor for a flat plate catalyst pellet:

$$\eta = \frac{tanh\,\Phi_p}{\Phi_p} \qquad \textbf{(Eq. 6.41)}$$

where $\Phi_p = Z\left[k / D_e\right]^{1/2}$. The same result can be obtained by calculating the flux at the boundary $z = Z$. The *net* flux of reactant "*A*" into the pellet equals the amount consumed, since we assume steady state. In these derivations we assume that D_e to be independent of concentration and position within the pellet.

6.4.2 The isothermal effectiveness factor for a spherical catalyst pellet

In outline, the derivation of the effectiveness factor for spherical catalyst pellets is similar to that of the flat plate pellet. We will give it in outline. Assuming a spherical isothermal pellet and a first order irreversible reaction, the mass balance for the reactant A leads to

$$\frac{D_e}{r^2}\frac{d}{dr}\left\{r^2\frac{dC_A}{dr}\right\} - k\,C_A = 0 \qquad \textbf{(Eq. 6.42)}$$

with the symmetry boundary condition

$$\frac{dC_A}{dr} = 0 \;\; at \;\; r = 0 \qquad \textbf{(Eq. 6. 43)}$$

and the surface concentration boundary condition

$$C_A = C_s \;\; at\; r = R_s\,. \qquad \textbf{(Eq. 6.44)}$$

Following a similar procedure as for the derivation of η for the "flat plate" catalyst pellet, we can derive the following expression for the effectiveness factor of a spherical catalyst pellet.

$$\eta = \frac{3}{\Phi_s}\left\{\frac{1}{tanh\,\Phi_s} - \frac{1}{\Phi_s}\right\} \qquad \textbf{(Eq. 6.45)}$$

where, the Thiele modulus Φ_S is given by

$$\Phi_s = R_s\left[k\,/\,D_e\right]^{1/2} \qquad \textbf{(Eq. 6.46)}$$

6.4.3 The isothermal effectiveness factor for a cylindrical catalyst pellet

For an infinitely long cylindrical pellet of radius R_c, we define our dimensionless variables as follows.

Dimensionless radius: $$\xi \triangleq \frac{r}{R_c} \qquad \textbf{(Eq. 6.47a)}$$

Dimensionless concentration: $$\varphi \triangleq \frac{C_A(r)}{C_{A,s}} \qquad \textbf{(Eq. 6.47b)}$$

Thiele modulus: $$\Phi_c \triangleq R_c\left[k\;\;/\;D_e\;\right]^{1/2} \qquad \textbf{(Eq. 6.47c)}$$

The mass balance equation then takes the form

$$\frac{1}{r}\frac{d}{dr}\left[r\frac{d\varphi}{dr}\right] - \Phi_c^2\,\varphi = 0 \qquad \textbf{(Eq. 6.48)}$$

With analogous boundary conditions:

$$\frac{d\varphi\,(0)}{dr} = 0 \text{ (symmetry); } \varphi\,(1) = 1 \qquad \textbf{(Eq. 6.49)}$$

The solution turns out in the form of Bessel functions. While at this introductory level, students would not necessarily be expected to have studied Bessel functions, it may be useful to remember that these functions turn up in solutions of differential equations set up in cylindrical coordinates. Solving for the dimensionless concentration:

$$\varphi = \frac{J_0(ir\,\Phi_c)}{J_0(i\,\Phi_c)} \qquad \textbf{(Eq. 6.50)}$$

leads to

$$\eta_c = \frac{2}{\phi_c}\frac{iJ_1(i\Phi_c)}{J_0(i\Phi_c)} \qquad \textbf{(Eq. 6.51)}$$

where the Bessel function of the first kind, of order ν, is defined by:

$$J_\nu(z) = \sum_{r=0}^{\infty}\frac{(-1)^r(\tfrac{1}{2}z)^{\nu+2r}}{r!\Gamma(\nu+r+1)} \qquad \textbf{(Eq. 6.52)}$$

And $\Gamma(\nu+r+1)$, is called a Gamma function, where $\Gamma(n)=(n-1)!$. For more information on Bessel functions the student may wish to consult a standard mathematical text dealing with differential equations.

6.4.4 Discussion: Isothermal effectiveness factors for different pellet geometries

	Effectiveness factor η	Thiele modulus Φ
Flat plate pellets	$\eta_p = \dfrac{\tanh \Phi_p}{\Phi_p}$	$\Phi_p = Z\left[k / D_e\right]^{1/2}$
Cylindrical pellets	$\eta_c = \dfrac{2}{\Phi_c}\dfrac{iJ_1(i\Phi_c)}{J_0(i\Phi_c)}$	$\Phi_c \triangleq R_c\left[k / D_e\right]^{1/2}$
Spherical pellets	$\eta_s = \dfrac{3}{\Phi_s}\left\{\dfrac{1}{\tanh \Phi_s} - \dfrac{1}{\Phi_s}\right\}$	$\Phi_s = R_s\left[k / D_e\right]^{1/2}$

Table 2. Effectiveness factors and Thiele moduli for three catalyst pellet geometries

For non-zero order reactions in isothermal pellets, examination of the forms of η in Table 2 shows that the value of the effectiveness factor changes between zero and unity.

$$0 \le \eta \le 1 \qquad \textbf{(Eq. 6.53)}$$

In all three cases (Table 2), the Thiele modulus turns out to be proportional to $\left[k / D_e\right]^{1/2}$; the ratio of reaction rate constant over the effective diffusivity is repeated. When $D_e >> k$, diffusive processes are far faster than the rate at which reactant is being consumed by the reaction. When reaction processes are much slower than diffusive processes, the process is said to be "kinetically controlled". For an isothermal pellet, this is the case where Φ is small and η tends to unity ($\eta \approx 1$). In this case, we expect to observe reactant concentrations and reaction rates to be relatively uniform over the pellet radius *and* close to values observed at external particle surfaces.

Conversely, when $k >> D_e$, Φ tends to large values and η becomes much smaller than unity ($\eta << 1$). When reaction processes are much faster than diffusive processes, the process is said to be "diffusion controlled". This is the case when reactive processes are far faster than rates at which diffusive processes can replenish the supply of reactant. In this case, much of the reactant is consumed, immediately it contacts the catalyst pellet. Most reaction takes place, therefore, near the periphery of the catalyst pellet. Concentration gradients within the pellet are sharp, and most reactant molecules are consumed near the periphery of the pellet.

For isothermal pellets and non-zero order chemical reaction, η varies between zero and unity ($0 \le \eta \le 1$).
When D_e **>>** k then Φ has small values and η tends to 1; the process is kinetically controlled (i.e. no diffusion limitation).
When k **>>** D_e then Φ takes on large values and η tends to zero; the process is then said to be diffusion-controlled.

When the temperature of an (isothermal) catalyst pellet rises, we expect the intrinsic reaction rate at external surface temperatures ($r_s = k\ C_s$) to increase. We have seen in Table 2 that the effectiveness factor for any geometry is proportional to $\left[k / D_e\right]^{1/2}$. Since k rises exponentially with the temperature but D_e increases more slowly, an increase in temperature signals an increase in the Thiele modulus (irrespective of catalyst geometry) and a corresponding decrease in the effectiveness factor (see Figure 6.5). The global rate of reaction, r_p, would also be expected to increase with the rising temperature but less rapidly than r_s, since $r_p=(\eta\downarrow)\times(r_s\uparrow)$ with increasing temperature.

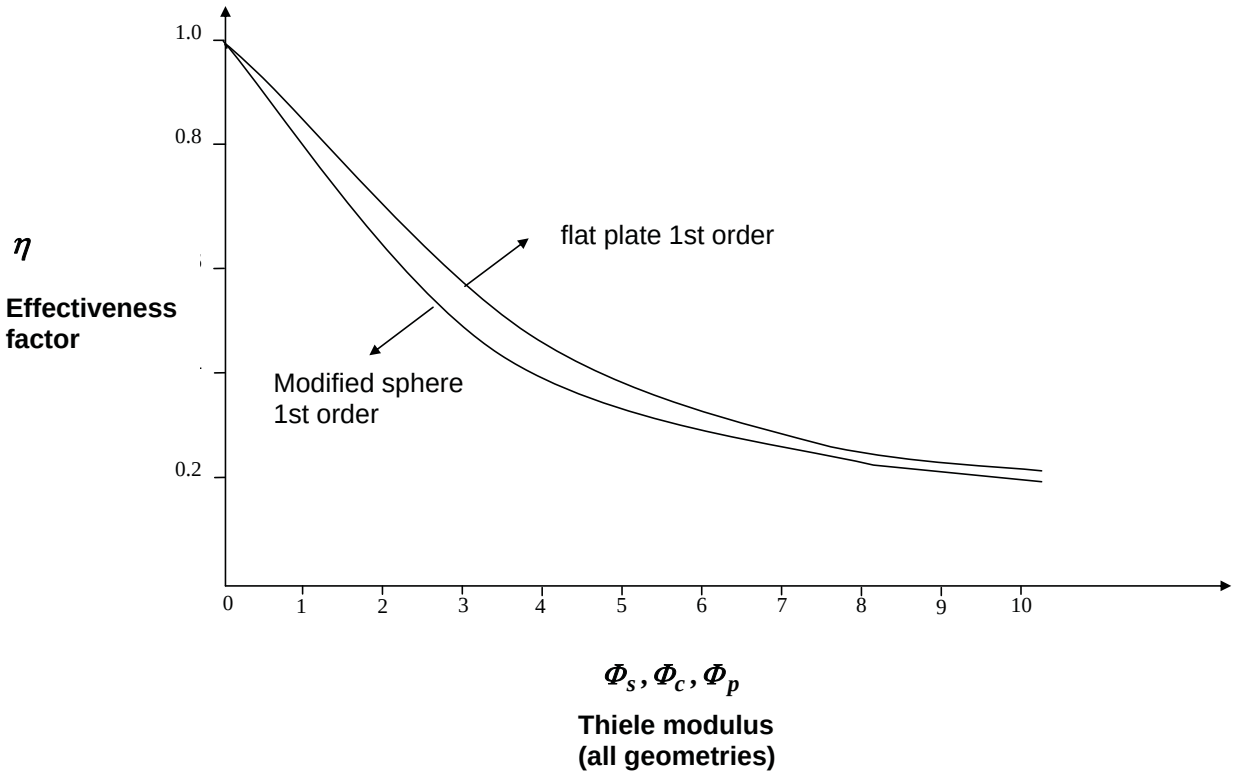


Figure 6.6 The effectiveness factor as a function of Thiele modulus, showing small differences between effectiveness factors for different geometries, at similar Thiele modulus values.

For similar values of the Thiele modulus, the values of η based on different geometries are quite close. This gives rise to a simplified approach. Let us first inspect the asymptotic values of η, as Φ tends to large values. For a flat plate, from Eq. 6.39 (above) we have

$$\eta_p = \frac{\tanh \Phi_p}{\Phi_p} \qquad \textbf{(Eq. 6.39)}$$

In general, the function $\tanh(x)$ tends to unity for large values of the argument x. For large values of the Thiele modulus, therefore,

$$\lim_{\Phi_p \to \infty} \eta_p = \frac{1}{\Phi_p} \qquad \textbf{(Eq. 6.54)}$$

In fact, to a good approximation, $\tanh \Phi_p$ rapidly tends to unity for values of Φ_p above a value of 3. In general therefore, we can consider $\eta_p \cong 1/\Phi_p$ for values of $\Phi_p > 3$. For a spherical catalyst pellet, η has the form (Eq. 6. 45),

$$\eta = \frac{3}{\Phi_s}\left\{\frac{1}{\tanh \Phi_s} - \frac{1}{\Phi_s}\right\} \quad , \qquad \textbf{(Eq. 6.45)}$$

which for values of $(\Phi_s / 3) > 3$ leads to

$$\eta_s \cong \frac{3}{\Phi_s} \qquad \textbf{(Eq. 6.55)}$$

Similarly, for a cylindrical pellet geometry, for values of $(\Phi_c / 2) > 3$

$$\eta_c = \frac{2}{\Phi_c} \qquad \textbf{(Eq. 6.56)}$$

Can we make the three curves coincide by making an appropriate change of variable? This would be useful, when we tackle catalyst pellets of other geometries, in particular when dealing with awkward catalyst geometries, such as randomly shaped (e.g. crushed) pellets. We would also like to handle different and in particular awkward reaction rate orders and expressions with the same approach.

6.4.5 Discussion: Unifying isothermal effectiveness factors for different pellet geometries

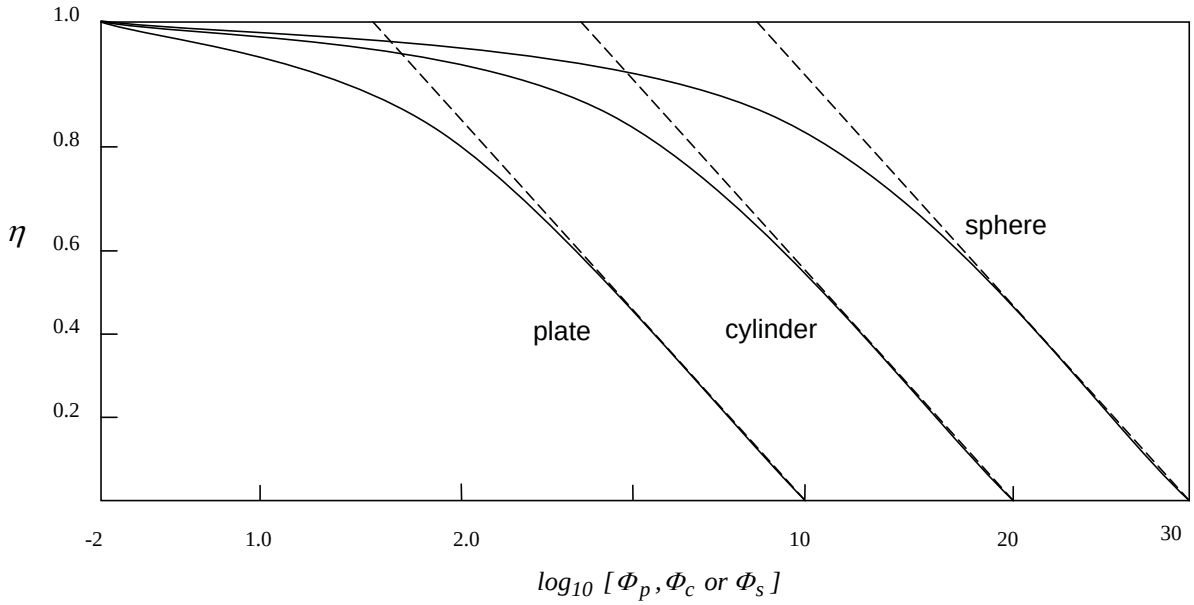


Figure 6.7 The isothermal effectiveness factor η vs. $log_{10}\ \Phi$ for three distinct geometries.

For small values of Φ (any geometry), the isothermal effectiveness factor η tends to unity. Meanwhile, for large values of Φ, the asymptotic values tend to ($1/\Phi_p$) for a flat plate pellet, to ($2/\Phi_c$) for a cylindrical pellet and ($3/\Phi_s$) for a cylindrical pellet. Is there a pattern? The three curves can be brought closer together if we define a generalized modulus that can cover all shapes, including irregularly shaped pellets.

$$\Phi = \left(V_p/S_x\right)[k/D_e]^{1/2} \qquad \textbf{(Eq. 6.57)}$$

where, V_p is defined as the pellet volume and S_x as the external pellet surface area. For pellets of specific shapes, this geometric factor in the Thiele modulus simply gives back the original form. For example, for a spherical pellet:

$$\frac{V_p}{S_x} = \frac{(4/3)\pi R_s^3}{4\pi R_s^2} = \frac{R_s}{3} \qquad \textbf{(Eq. 6.58)}$$

With the Thiele modulus defined as $\Phi = \left(V_p/S_x\right)[k/D_e]^{1/2}$, the effectiveness factor, η, can be expressed in a form that is not directly dependent on the pellet geometry.

The resulting curves for plate, cylindrical and spherical pellets shown in Figure 6.8 converge for small ($\rightarrow 0$) as well as for large (≈ 10) values of the generalized Thiele modulus.

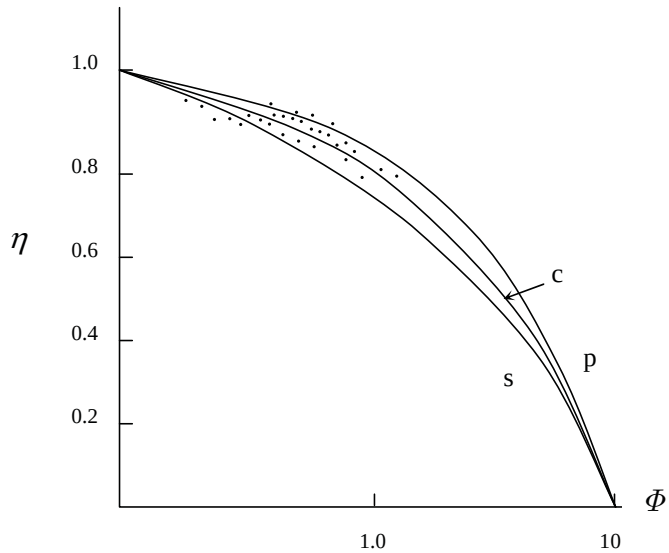


Figure 6.8 Isothermal effectiveness factor for three geometries plotted against the generalized Thiele modulus. The dots indicate some of the empirical findings. Note that the scatter is of the same order of magnitude as the divergence between the lines.

When the speed of the reaction is significantly greater than the speed of diffusion within a catalyst pellet, $k > D_e$, and the Thiele Modulus is large (> 5-10), the effectiveness factor can be approximated by, $\eta \cong (1/\Phi)$.

This treatment was formulated only for first order reaction rate orders. The difference between values of η for different pellet shapes is larger in the intermediate zone $\Phi \cong 1$ for non-first order reactions and particularly with Langmuir-Hinshelwood type reaction rate equations.

6.5 Effectiveness factors for reaction rate orders other than unity [Froment & Bischoff, 1990]

One way to deal with non-first order reaction rate expressions is to run through similar sets of derivations each time. In other words, we would solve differential equations analogous to Eqs. 6.30 and 6.31 for each case. To simplify matters, we will show, instead, how a generalized or normalized modulus can be defined, which attempts to account for all non-first order cases.

We have already seen that different pellet geometries can be handled by defining a new modulus:

$$\Phi = \left(V_p/S_x\right)[k/D_e]^{1/2} \qquad \textbf{(Eq. 6.57)}$$

Consider a slab symmetric about z=0. The isothermal mass balance at steady state would give

$$\frac{d}{dz}\left\{D_e(C_A)\frac{dC_A}{dz}\right\} = r_v(C_A) \qquad \textbf{(Eq. 6.59)}$$

where $r_v = \rho_B\, r_A$ is the reaction rate per unit of volume packed with pellets and ρ_B the density of the catalyst bed. The boundary conditions involve the concentration of reactant "*A*" at the external boundary

$$C_A(Z) = C_{A,s} \qquad \textbf{(Eq. 6.60)}$$

and the absence of mass flux at the axis of symmetry:

$$\frac{dC_A(0)}{dz} = 0\ . \qquad \textbf{(Eq. 6.61)}$$

We then multiply both sides of Eq. 6.59 by the factor $D_e\left[dC_A/dz\right]$, we get

$$\left[D_e\frac{dC_A}{dz}\right]\frac{d}{dz}\left\{D_e\frac{dC_A}{dz}\right\} = \left[D_e\frac{dC_A}{dz}\right]r_{A,V} \qquad \textbf{(Eq. 6.62)}$$

The left hand side of Eq. 6.62 can be reduced to: $\frac{1}{2}\frac{d}{dz}\left[D_e\left(dC_A/dz\right)^2\right]$. Integrating both sides of Eq. 6.62

$$D_e(C_A)\frac{dC_A}{dz} = \left\{2\int_{C_{A0}}^{C_A} D_e(C_A')\ r_{A,V}(C_A')\ dC_A'\right\}^{1/2} \qquad \textbf{(Eq. 6.63)}$$

Where C_{A0}, the concentration at the centreline (i.e. the no flux boundary), is not defined as yet. Integrating again:

$$Z = \int_{C_{A,0}}^{C_{A,s}} \frac{D_e(C_A'')\,dC_A''}{\left\{2\int_{C_{A0}}^{C_A''} D_e(C_A')\ r_{A,V}(C_A')\ dC_A'\right\}^{1/2}} \qquad \textbf{(Eq. 6.64)}$$

If Z, C_{As}, D_e & $r_{A,V}$ are known, Eq. 6.64 allows the calculation of C_{A0}. Returning to the effectiveness factor, the definition

$$\eta = \frac{\textit{rate of reaction with pore diffusion resistance}}{\textit{rate of reaction at surface condititions}}$$

leads to

$$\eta = \frac{\frac{1}{V_p}\int r_{A,V}(C_A)\,dV_p}{r_{A,V}(C_{As})} \qquad \textbf{(Eq. 6.65)}$$

Integrating the mass balance (Eq. 6.59) once, we get

$$\int_0^Z r_{A,V}\ dz = \int_0^Z \frac{d}{dz}\left\{D_e \frac{dC_A}{dz}\right\} dz\ . \qquad \textbf{(Eq. 6.66)}$$

Integrating the right hand side, we have from Eq. 6.61 that $D_e \frac{dC_A}{dz} = 0\ at\ z = 0$. This leaves us with

$$\int_0^Z r_{A,V}\ dz = D_e(C_{A,S})\frac{dC_A(z)}{dz} \qquad \textbf{(Eq. 6.67)}$$

and

$$\eta\ =\ \frac{D_e(C_{AS})\frac{dC_A}{dz}}{Z \times r_{A,V}(C_{AS})} \qquad \textbf{(Eq. 6.68)}$$

Combining with Eq. 6.63

$$\eta = \frac{\sqrt{2}}{Z \times r_V(C_{A,s})}\left\{\int_{C_{A0}}^{C_{A,s}} D_e(C_A^{'})r_{A,V}(C_A^{'})d\,C_A^{'}\right\}^{\frac{1}{2}} \qquad \textbf{(Eq. 6.69)}$$

where C_{A0} is found from Eq. 6.64. For diffusion limited systems, the penetration of reactant molecules is limited and it may be practical to test whether C_{A0} is effectively zero. Unlike first order reaction rates, Eq. 6.69 shows that η changes with concentration for non-first order reaction rates. For a first order reaction, Eq. 6.69 easily reduces to

$$\eta = \frac{tanh\,\Phi}{\Phi}.$$

Eq. 6.69 is valid for any form of $r_{A,V}$ and D_e . For a binary mixture of ideal gases,

$$\frac{1}{D_{eA}} = \frac{1 - y_A(1 + N_B/N_A)}{D_{AB}} + \frac{1}{D_{KA}} \qquad \textbf{(Eq. 6.70)}$$

where $D_{K,A}$ is the Knudsen diffusivity of component of "*A*" within the pores of the given catalyst. For equimolar counter-diffusion:

$$\frac{1}{D_{eA}} = \frac{1}{D_{AB}} + \frac{1}{D_{KA}}. \qquad \textbf{(Eq. 6.71)}$$

It is also possible to arrive at Eq. 6.69 by using

$$C_A = C_{AS}\frac{cosh\left[z\sqrt{k/D_e}\right]}{cosh\left[Z\sqrt{k/D_e}\right]} \qquad \textbf{(Eq. 6.72)}$$

for the flux (which at steady state indicates the rate of reaction), rather than starting with

$$r_p = \frac{\int_0^Z kC_A(z)\alpha\ dz}{\int_0^Z \alpha\ dz}$$

In the case where diffusion is controlling, $\Phi \rightarrow \infty$, the concentration of reactant at the symmetry boundary, would be close to zero or close to C_{eq}.

$$\eta_\infty \sim \frac{\sqrt{2}}{Z \times r_{A,V}(C_{S,A})}\left\{\int_{0\ or\ C_{eq}}^{C_{A,s}} D_e(C'_A)\,r_{A,V}(C'_A)\,d\,C'_A\right\}^{1/2} \qquad \textbf{(Eq. 6.73)}$$

A generalized or normalized modulus can now be defined for $\eta_\infty \approx 1/\Phi$. This definition would lead to approximating the same curve for *any pellet geometry*, *any reaction rate form* and *any* diffusivity relationship:

$$\Phi = \frac{V_p}{S_x}\frac{r_{A,V}(C_{A,s})}{\sqrt{2}}\left\{\int_{\substack{C_{A,eq}\\ or\ zero}}^{C_{A,s}} D_e(C'_A)r_{A,V}(C'_A)dC'_A\right\}^{-1/2} \qquad \textbf{(Eq. 6.74)}$$

6.6 Criteria for determining the significance of intra-particle diffusion resistances [Froment & Bischoff]

When the reaction rate constant is (or constants are) not known from laboratory kinetic experiments, Φ cannot be calculated. Developing criteria, therefore, for the significance of pore diffusion limitations independent of reaction rate constants would be useful. One simple test involves performing experiments with two sizes of catalysts. Using Eq. 6.74 and assuming that k and D_e are similar for the two cases and that $Z=V_P/S_x$, we get

$$\frac{\Phi_1}{\Phi_2} = \frac{Z_1}{Z_2} \qquad \textbf{(Eq. 6.75)}$$

Note that D_e may not be the same for the two cases, if he smaller pellet is made by cutting a larger one, as it usually is. The reason for this difference is that most pellets are prepared by impregnation of the active material. For large pellets the process is not necessarily uniform over the pellet radius. Ignoring this potential mishap for the time being and using Eq. 6.4 (i.e. that $\eta = r_p/r_s$), we can write:

$$\frac{(r_{obs})_1}{(r_{obs})_2} = \eta_1/\eta_2 \qquad \textbf{(Eq. 6.76)}$$

From Eq. 6.75, the two Thiele moduli will be different and their ratio equal to Z_1/Z_2 . If the two observed rates are the similar, $\eta_1 \cong \eta_2$ and the process would be taking part in the initial "nearly-horizontal" part of the $\eta(\Phi)$ curve. This would imply that Φ -values were small and that resistances due to diffusion could be neglected. At the other extreme η_∞ would tend to $1/\Phi$ and

$$\frac{(r_{obs})_1}{(r_{obs})_2} = \eta_1 / \eta_2 \approx \Phi_2 / \Phi_1 = Z_2 / Z_1 \qquad \textbf{(Eq. 6.77)}$$

i.e. the rates would turn out to be inversely proportional to pellet size.

$$\frac{(r_{obs})_1}{(r_{obs})_2} \approx Z_2 / Z_1 \qquad \textbf{(Eq. 6.78)}$$

6.6.1 The Weisz-Prater criterion

Let us derive the Weisz-Prater criterion for a flat catalyst pellet, where $V_P/S_x = Z$, and a first order reaction. Starting with $\Phi = (V_p / S_x)(k / D_e)^{1/2}$ and $r_{V,obs} = \eta\, kC_{A,s}$, we can write

$$k = \frac{\Phi^2}{Z^2} D_e \text{ and } r_{V,obs} = \eta \frac{\Phi^2}{Z^2} D_e C_{AS} \qquad \textbf{(Eq. 6.79)}$$

Transposing all observable variables to one side, we get

$$\frac{\left[r_{V,obs}\right] Z^2}{D_e C_{A,s}} = \eta\ \Phi^2 \qquad \textbf{(Eq. 6.80)}$$

There are now two limiting cases that must be examined. First, let us look at the case where $\Phi << 1$, $\eta = 1$ *and* $\eta\phi^2 << 1$. When intraparticle diffusion limitations are negligible, the ratio of observed variables is much smaller than unity.

$$\frac{r_{V,obs}\ Z^2}{D_e C_{A,s}} << 1 \qquad \textbf{(Eq. 6.81)}$$

If on the other hand, $\phi >> 1$, η tends to $1/\Phi$ and $\eta\phi^2$ *tends to* Φ; thus

$$\Phi = \frac{r_{v,obs} Z^2}{D_e C_{A,s}} >> 1 \qquad \textbf{(Eq. 6.82)}$$

for pore diffusion limitation controlling.

6.7 Simultaneous mass & energy transport from the bulk fluid phase to external catalyst surfaces [Smith, 1981; Froment & Bischoff, 1990]

Let us now examine situations where we have temperature as well as concentration gradients between the bulk stream and pellet surfaces. We will also examine the case of non-isothermal catalyst pellets. In what follows, we will define the temperature and concentration gradients between the bulk fluid phase and external catalyst pellet surfaces as ΔT_{EXT} and ΔC_{EXT}. If these gradients are significant, equations describing external and intra-pellet transport rates will be coupled and solved together.

We will also assume that the external surface of a catalyst pellet is uniformly accessible to heat and mass transport, to and from the bulk fluid phase. Strictly – no real system totally conforms to the assumption of uniform accessibility, but this assumption considerably simplifies the problem at hand. We will also assume that the thickness of the concentration and thermal boundary layers have constant values over the entire catalyst pellet surface. In such a system, the transport behaviour determined in the absence of chemical

reaction may be utilized to predict the performance of similar systems in which catalytic reactions are taking place. These assumptions may appear restrictive; however, the accuracy and quality of kinetic information usually has a more critical effect on resulting predictions.

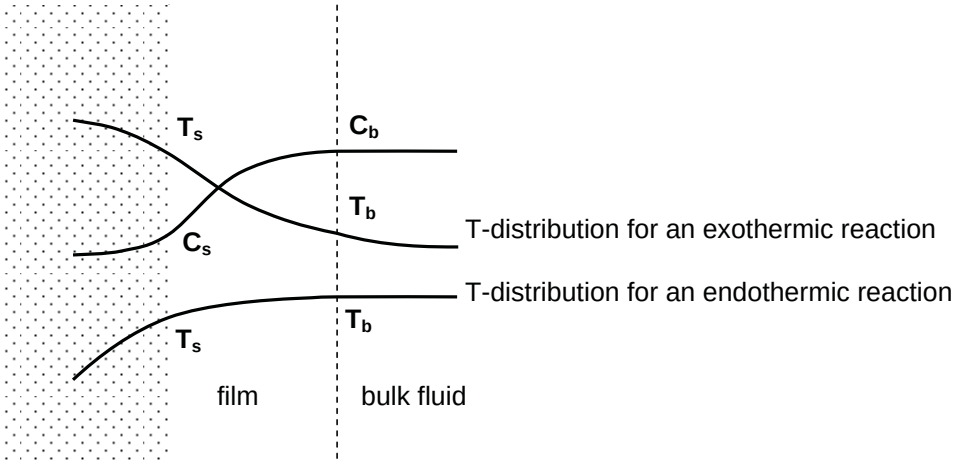


Figure 6.9 Temperature and concentration gradients between the bulk fluid phase and the catalyst pellet.

We have seen in Eq. 6.2 above, that at steady state, the mass flux N_A may be set equal to the net global reaction rate r_p.

$$N_A = r_p = k_m a_m (C_b - C_s) \qquad \textbf{(Eq. 6.2)}$$

In this equation, k_m denotes the mass transfer coefficient (length/time), a_m denotes the external particle surface area (area/weigh), C_b denotes the reactant concentration in the bulk phase and C_s the (in flight) reactant concentration near the external surface of the catalyst pellet. The heat flux equation may be written in similar terms:

$$Q = r_p(-\Delta H_r) = h a_m (T_s - T_b), \qquad \textbf{(Eq. 6.83)}$$

where ΔH_r denotes the heat of reaction, h the local heat transfer coefficient, T_s the temperature near the external surface of the catalyst pellet and T_b the temperature in the bulk fluid phase.

6.7.1 External heat and mass transfer coefficients

For most practical applications, data is presented in the form of correlations, typically against the Reynolds number.

$$j_D = \frac{k_m \rho}{G}\left\{\frac{\mu}{\rho D}\right\}^{2/3} = f\left(\frac{d_P G}{\mu}\right) \qquad \textbf{(Eq. 6.84)}$$

$$j_H = \frac{h}{C_p G}\left\{\frac{C_p \mu}{\lambda}\right\}^{2/3} = f'\left(\frac{d_p G}{\mu}\right) \qquad \textbf{(Eq. 6.85)}$$

In Eqs. 6.84 and 6.85, j_D and j_H denote the mass and heat fluxes, respectively. In these equations, the functions f and f' depend on the configuration of the physical system, e.g. packed bed, fluidized bed, etc. Also, $d_P G/\mu = Re$, defines the Reynolds number with d_p denoting the particle diameter, G the mass velocity based on superficial area, and μ and ρ the fluid viscosity and density, respectively. D denotes the molecular bulk diffusivity of the component being transported, as defined by Fick's Law or the Stefan Maxwell equations. The latter provide the analogue of Fick's Law for multicomponent mixtures. However, we will not study Stefan Maxwell equations at the present level. For packed beds of solids, there are many correlations for

$j_D = f(Re)$ and $j_H = f'(Re)$; these are usually presented in the form of graphs, of type qualitatively sketched in Figure 6.10. They may be found in any standard text.

Figure 6.10 Sketches showing the variation of the mass flux j_D and heat flux j_H as a function of the Reynolds number, Re.

Heat and mass transfer coefficient values arrived at in this manner are open to error, typically of the order of ± 30 %. It is important for the designer to run sensitivity analyses to check what effect variations in heat and mass transfer coefficients might have on the overall design.

6.7.2 Estimating the maximum temperature gradient across the stagnant film [Smith, 1981]

Let us assume for simplicity that the global reaction rate for a catalyst pellet can be written as:

$$r_p = k\,\eta\, C_s^n\,, \qquad \textbf{(Eq. 6.86)}$$

where "*n*" indicates the order of the chemical reaction. Defining Q_g as the heat generated (or absorbed) by the reaction, per unit mass of catalyst, we can write:

$$Q_g = (-\Delta H_r)\, r_p = (-\Delta H_r)\,\eta\, k_0\,(C_s^n)\, exp(-E_a / RT_s) \qquad \textbf{(Eq. 6.87)}$$

The heat transferred to (or from) the bulk fluid across the stagnant film surrounding the pellet is written as:

$$Q_R = h\, a_m (T_s - T_b)\,. \qquad \textbf{(Eq. 6.88)}$$

When a fixed bed reactor operates at steady state, the exact amount of heat released (or absorbed) by the reaction, must be transported to (or form) the catalyst pellet to the bulk fluid.

$$(-\Delta H_r)\,\eta\, k_0\,(C_s^n)\, exp^{-E_a/RT_s} = h\, a_m (T_s - T_b) \qquad \textbf{(Eq. 6.89)}$$

At steady state, there is no mass accumulation in and around the catalyst pellet. The amount of reactant consumed by the reaction (expressed as $\eta\, k_0\,(C_s^n)\, exp^{-E_a/RT_s}$) will therefore be equal to the *net* mass flux of reactant from the bulk fluid phase to the external catalyst surface:

$$\eta\, k_0\,(C_s^n)\, exp^{-E_a/RT_s} = k_m a_m (C_b - C_s) \qquad \textbf{(Eq. 6.90)}$$

Combining Eqs. 6.89 and 6.90, we can write:

$$k_m a_m (C_b - C_s)(-\Delta H_r) = h a_m (T_s - T_b)\,. \qquad \textbf{(Eq. 6.91)}$$

We solve Eqs. 6.84 and 6.85 for k_m and h respectively and substitute in Eq. 6.91. The temperature gradient across the stagnant film is then given by:

$$T_s - T_b = (C_b - C_s)\left(\frac{-\Delta H_r}{C_p\,\rho}\right)\left\{\frac{C_p\;\mu/\lambda}{\mu/\rho\, D}\right\}^{2/3}\frac{j_D}{j_H} \qquad \textbf{(Eq. 6.92)}$$

Considering that numerically both $\frac{j_D}{j_H} \sim 1$ and $\left\{\frac{C_p\;\mu/\lambda}{\mu/\rho\, D}\right\} \sim 1$, Eq. 6.91 may be simplified:

$$T_s - T_b \cong \left[\frac{-\Delta H_r}{C_p\,\rho}\right](C_b - C_s) \qquad \textbf{(Eq. 6.93)}$$

The maximum temperature rise corresponds to *total* conversion. For an irreversible 1st order reaction, this would imply: $(C_b - C_s) \cong C_b$. Then:

$$\Delta T_{max,ext} = \left[\frac{-\Delta H_r}{\rho C_p}\right] C_b \qquad \textbf{(Eq. 6.94)}$$

For a *reversible* first order reaction $\Delta T_{max,ext}$ would take the form

$$\Delta T_{max,ext} = \left[\frac{-\Delta H_r}{\rho C_p}\right] (C_b - C_{s,eq}) \qquad \textbf{(Eq. 6.95)}$$

The external temperature gradient for any level of conversion may then be estimated by combining Eqs. 6.89 and 6.90:

$$T_s - T_b \cong \Delta T_{max,ext} \left[\frac{C_b - C_s}{C_b}\right] \qquad \textbf{(Eq. 6.96)}$$

Eq. 6.96 can be used for an initial estimate of whether the external temperature gradient around the pellet is significant. If the pellet surface temperature is greater (or smaller) than the bulk temperature by 5-8 °C or more, it is necessary to use the pellet temperature (and not the bulk temperature, which is easier to measure) in calculating reaction rates.

In the extreme case of the highly exothermic reaction, forming water from hydrogen and oxygen, $H_2 + (1/2)O_2 \rightarrow H_2O$, on a Pt/$Al_2O_3$ catalyst, $\Delta T_{max,ext}$ turns out to be large: ~200 °C. Note also that for an exothermic reaction, the external ΔT would increase with increasing external ΔC:

$$\Delta T_{ext} \uparrow \Rightarrow \Delta C_{ext} \uparrow$$

If the mass flow rate, G, is low, it would cause the mass transfer coefficient, k_m, to be relatively small, which in turn would cause the external concentration gradient, ΔC_{ext}, to be large:

$$G \downarrow k_m \downarrow \Delta C_{ext} \uparrow .$$

In laboratory experiments designed for measuring kinetic constants, it is essential for the data be independent of external diffusional resistances. (Internal diffusion resistances are minimized by using the smallest possible pellet size.) This requires $C_b \sim C_s$ at the highest temperature of the range where the kinetic constant is required. One way of realizing such conditions is to keep the mass flow rate, G, large. This causes turbulence in the system, enhancing mass transfer to and from catalyst surfaces.

$$G \uparrow (k_m a_m) \uparrow$$

The ($C_b \sim C_s$) condition must be achieved at the highest temperature because, as the temperature is increased, the rate of reaction increases faster than the rate of diffusion. That is why diffusional control usually kicks in at higher temperatures. If diffusional resistances are negligible at the highest operating temperature, they would be even less severe at lower temperatures.

> If ($C_b \sim C_s$) is achieved at the highest experimental temperature, then measurements of the kinetic constants may be considered independent of external diffusional resistances over the whole of the temperature range.

6.8 Effectiveness factors for non-isothermal catalyst pellets [Smith, 1981]

For the simple chemical reaction $A \rightarrow B$, neglecting the temperature dependence of D_e, the material balance equation for a spherical shell of (spherical) catalyst pellet can be written as:

$$\left\{-4\pi r^2 D_e \frac{dC_A}{dr}\right\}_r - \left\{-4\pi r^2 D_e \frac{dC_A}{dr}\right\}_{r+\Delta r} = 4\pi r^2 \, \Delta r \, \rho_P \, k_1 C_A \qquad \textbf{(Eq. 6.97)}$$

Dividing by $4\pi r^2 \Delta r$ and taking the limit as $\Delta r \rightarrow 0$,

$$\frac{d^2 C_A}{dr^2} + \frac{2}{r}\frac{dC_A}{dr} - \frac{k_1 \rho_p C_A}{D_e} = 0 \qquad \textbf{(Eq. 6.98)}$$

with boundary conditions $dC_A/dr = 0$ at $r=0$ and $C_A = C_{As}$ at $r = R_s$. The energy balance over the same spherical shell volume element can be written as:

$$\left\{-4\pi r^2 \lambda_e \frac{dT}{dr}\right\}_r - \left\{-4\pi r^2 \lambda_e \frac{dT}{dr}\right\} = 4\pi r^2 \, \Delta r \, \rho_P \, k_1 C_A \, \Delta H_r \qquad \textbf{(Eq. 6.99)}$$

In the last three equations, ρ_P is the density of the pellet itself. Neglecting the temperature dependence of λ_e, the effective thermal conductivity, dividing by $4\pi r^2 \Delta r$ and taking the limit as $\Delta r \rightarrow 0$, we get:

$$\frac{d^2 T}{dr^2} + \frac{2}{r}\frac{dT}{dr} - \frac{k_1 \rho_P}{\lambda_e} C_A \Delta H_r = 0 . \qquad \textbf{(Eq. 6.100)}$$

with $dT/dr = 0$ at $r=0$ and $T = T_s$ at $r = R_s$. Note that the exponential dependence of the reaction rate on the temperature makes the pair of equations non-linear.

$$k_1 = k_{1,0} \, exp\{-E_a/RT\} \qquad \textbf{(Eq. 6.101)}$$

6.8.1 Calculating the maximum temperature rise

To find an analytical relationship between the reactant concentration and the temperature at any point in the pellet, we eliminate $k_1\rho_p C_A$ from the two equations.

$$D_e\left\{\frac{d^2C_A}{dr^2}+\frac{2}{r}\frac{dC_A}{dr}\right\}=\frac{\lambda_e}{\Delta H_r}\left\{\frac{d^2T}{dr^2}+\frac{2}{r}\frac{dT}{dr}\right\}. \qquad \textbf{(Eq. 6.102)}$$

This equation can be re-written as

$$\frac{1}{r^2}D_e\frac{d}{dr}\left\{r^2\frac{dC_A}{dr}\right\}=\frac{\lambda_e}{\Delta H_r}\frac{1}{r^2}\frac{d}{dr}\left\{r^2\frac{dT}{dr}\right\}. \qquad \textbf{(Eq. 6.103)}$$

We then integrate both sides, twice. For the first integration, we use the symmetry boundary condition: $dC_A/dr=0$ and $dT/dr=0$ at $r=0$. That makes the lower bound of the integration equal to zero, for both sides of the equation. We integrate again using the surface boundary conditions.

$$(T-T_s)_p=\frac{\Delta H_r D_e}{\lambda_e}(C_A-C_{A,s})_p \qquad \textbf{(Eq. 6.104)}$$

The maximum temperature rise would occur when all reactant has been consumed.

$$(T-T_s)_{max}=\frac{-\Delta H_r D_e}{\lambda_e}C_{A,s} \qquad \textbf{(Eq. 6.105)}$$

This result is valid for any particle geometry at steady state and is not limited to first order kinetics.

6.8.2 Effectiveness factors for non-isothermal catalyst pellets

The two differential equations (Eqs. 6.100 and 6.102) must be solved numerically. We will illustrate the nature of the problem for a spherical geometry. The problem is usually presented by defining three new parameters.

1. Thiele – type modulus, evaluated at surface conditions:

$$3(\Phi_s)_s=r_s\sqrt{(k_1)_s\rho_p/D_e} \qquad \textbf{(Eq. 6.106)}$$

2. The Arrhenius number

$$\gamma=E/R_gT_s\text{, and,} \qquad \textbf{(Eq. 6.107)}$$

3. The heat of reaction parameter

$$\beta=\frac{(-\Delta H_R)D_eC_{A,s}}{\lambda_eT_s} \qquad \textbf{(Eq. 6.108)}$$

The solution of the system of equations shows contours [cf. Smith, 1981, p. 502, Fig. 11-13] for the effectiveness factor for a non-isothermal pellet plotted against the modified Thiele modulus, for a range of values of β and γ = 20. Clearly, β = 0 traces the line for an isothermal pellet; values of β < 0 trace contours for endothermic reactions.

The contours indicate that the value of η no longer ranges simply between zero and unity. During exothermic reactions, heat generated inside the pellet may give rise temperature increases inside the pellet; thermal conduction rates are never instantaneous, so temperatures may rise compared to the surface. Values of η >1 represent higher rates of reaction inside the pellet compared to the surface. Since reactant concentrations are higher at the surface of the pellet, η >1 arises due to higher temperatures boosting the rate inside the pellet. Large increases in internal temperatures due to highly exothermic reactions may cause deactivation by sintering; they may also give rise to undesired side reactions which would reduce selectivity.

The contours also show that for certain values of the parameters, three possible values of η can be calculated; in other words, multiple solutions are possible due to the non-linear heat generation curve. Only the highest

and lowest states, corresponding to large and small temperature gradients respectively, represent stable states, whilst the middle value corresponds to a meta-stable state.

In Eq. 6.108, we defined β as $\beta = (-\Delta H_r) D_e C_{A,s} / \lambda_e T_s$. Combining with $\Delta T_{max} = -\Delta H_r D_e C_{A,s} / \lambda_e$ in Eq. 6.105, we get $\beta = \Delta T_{max} / T_s$. For many industrial applications β is a small number; typically $\beta \leq 0.1$. Since the thermal conductivities of solids, including porous solid matrices are high, for standard catalysts at steady state conditions, ΔT_{max} in catalyst pellets is *usually* not very large. *Usually* external heat and mass transfer resistances have a more significant effect on reaction rates. The multiple steady-state behaviour deduced from the calculations is therefore not likely to be observed in common catalytic reactions.

For highly exothermic reactions such as hydrogenation, however, ΔT_{max} may be quite significant. In one example, the hydrogenation of benzene, which has a heat of reaction of about -210 kJ mol^{-1} gives rise to a maximum temperature rise of about 35 °C from the centre to the surface of the pellet. This is a gradient that would affect the reaction rate quite significantly, without giving rise to pellet instability.

CHAPTER 7

THE DESIGN OF FIXED BED CATALYTIC REACTORS-II

7.1 Introduction

In Chapters 1 and 3, we derived the material and energy balances, respectively, for homogeneous reactions taking place in tubular reactors.

The material balance equation: $$r_A = -\frac{dn_A}{dV_R} \qquad \textbf{(Eq. 1.11a)}$$

The energy balance equation: $$\frac{dT}{dV_R} = \frac{Q - r_A \Delta H_r}{\sum n_i \overline{C}_{pi}} \qquad \textbf{(Eq. 3.47)}$$

To derive these equations, (i) plug flow was assumed, (ii) changes in kinetic and potential energy and shaft work were neglected, and, (iii) the enthalpies of mixing and the effect of pressure changes on the enthalpy were also neglected. Qualitative temperature and concentration profiles in isothermal, adiabatic and "non-adiabatic/non-isothermal" tubular reactors have been presented in Figure 3.9.

For fixed bed *catalytic* reactors (FBCRs), the mass balance equation takes the form

$$r_p = -\frac{dn_A}{dW} \qquad \textbf{(Eq. 7.1)}$$

where r_p is the global rate of reaction of reactant "*A*" per unit mass of catalyst, with units of $kmol/(kg-cat \times unit-time)$. Using our previous notation and expressing the rate as

$$r_V = \rho_B\, r_p\, [\,=\,]\, \frac{kg\text{-}cat}{m^3_{cat\text{-}bed}} \times \frac{kmol}{(kg.cat) \times unit\text{-}time} = \frac{kmol}{m^3_{cat\text{-}bed} \times unit\text{-}time} \quad . \qquad \textbf{(Eq. 7.2)}$$

When the pressure drop across the catalyst bed is significant (e.g. ~10 % of total pressure), Δp needs to be taken into account. In that case, the position variable is usually defined as the distance from the inlet rather than the reactor volume or catalyst bed volume. We will see below how we can account for changes in pressure along the length of the reactor.

7.1.1 Energy balance equation for FBCR [Denbigh & Turner, 1984; Froment & Bischoff, 1990]

For catalytic reactors, the energy balance equation (Eq. 3.47), may be rewritten as:

$$\frac{dT}{dW} = \frac{Q - r_p \Delta H_r}{\sum n_{i0} \overline{C}_{pi}} \ , \qquad \textbf{(Eq. 7.3)}$$

where $r_p\,[\,=\,]\ kmol/(kg\text{-}cat \times unit\text{-}time)$ and $\overline{C}_{pi}$ the average heat capacity of component "i" over the relevant temperature range. We also saw in Chapter 3 that we can usually simplify the energy balance equation by assuming that the total heat capacity of the reacting mixture is approximately constant, i.e. that it is a weak function of the conversion. For simplicity, we can assume the total heat capacity over the relevant conversion interval to be approximately constant:

$$\left\{ n_{T0} \overline{\overline{C}}_p \right\} \cong \sum n_{i0} \overline{C}_{pi} \quad . \qquad \textbf{(Eq. 3.22)}$$

Recalling that $W = \rho_B \times \alpha \times reactor\ length$, where α is the cross-sectional area of the reactor tube, the energy balance for a FBCR assumed to operate in plug flow (Eq. 7.3) may be written as:

$$\left\{n_{T0}\overline{\overline{C}}_p\right\}\frac{1}{\alpha}\frac{dT}{dz}=(-\Delta H_r)(\rho_B\, r_A)+\rho_B\, Q \qquad \textbf{(Eq. 7.4)}$$

In this equation Q takes on the units: $Q\,[=]\ kJ/(m_b^3 \times unit\text{-}time)$. For adiabatic operation, $Q = 0$. When the reaction is exothermic, it is often necessary to remove heat. In Chapter 3 we saw that heat can be removed from the reaction mixture by inter-stage cooling and that the temperature rise may be controlled by means of cold-shot cooling. Another common way is to remove heat through the external walls of the tubular reactor. The temperature rise may also be controlled by adding an inert diluent, such as nitrogen or steam, to the reaction stream to serve as a heat sink. Conversely the diluent may be used as a source of heat in endothermic reactions. To control the temperature rise during highly exothermic reactions, e.g. the oxidation of SO_2, or the partial oxidation of phthalic anhydride, reactor tubes are designed with relatively small diameters (2 – 5 cm).

7.1.2 The material balance equation for FBCR: The analogous formulation of the mass balance equation takes the form:

$$-\frac{1}{\alpha}\frac{dn_A}{dz}=\rho_B\, r_p=r_V\,, \qquad \textbf{(Eq. 7.5)}$$

where each term has units of "$kmol/(m_b^3 \times unit-time)$". If the total volumetric flow rate is (or can be assumed) constant, the mass balance equation may be formulated in terms of the superficial bulk stream velocity:

$$-\frac{1}{\alpha}\frac{dn_A}{dz}=-\frac{1}{\alpha}\frac{d(C_A v_T)}{dz}=-\frac{v_T}{\alpha}\frac{dC_A}{dz}=\rho_B\, r_p=r_V$$

$$-u_s\frac{dC_A}{dz}=\rho_B\, r_A \qquad \textbf{(Eq. 7.6)}$$

where u_s is the superficial velocity of gas, in units of "m/unit-time" and ρ_B is the catalyst bed density kg-cat/m^3.

7.1.3 The pressure drop (momentum balance) equation: Formally, this is where a momentum balance would fit into the set of equations describing the reactor. For packed beds, in practice, semi-empirical equations are used to calculate the pressure drop Δp. If the pressure drop is relatively small, a mean value for the total pressure is used in calculations.

To calculate the pressure drop, we will introduce the Ergun equation here which has two terms corresponding to slow and fast flow. There are many equations which can be used for estimating pressure drops in packed beds. For a packed bed with void fraction ε, the Ergun equation may be written as

$$\frac{dP}{dz}=\underbrace{\frac{150\mu G}{\rho_g D_p^2}\frac{(1-\varepsilon)^2}{\varepsilon^3}}_{\text{laminar}}+\underbrace{\frac{1.75G^2}{D_p\,\rho_g}\frac{(1-\varepsilon)^2}{\varepsilon^2}}_{\text{turbulent}}, \qquad \textbf{(Eq. 7.7)}$$

where G, the mass flux, has units of "mass/(area × unit-time)" and D_p is defined as the equivalent particle diameter $(D_p = 6V_p/S_x)$. The gas density, ρ_g, may be a function of pressure if pressure drops are large. If the flow is laminar, the first term on the right hand side of Eq. 7.7 turns out to be numerically larger than the second term. For turbulent flow, the second term tends to predominate.

SUMMARY: Equations 7.4, 7.6 and 7.7 describe a 1-dimensional reactor model, where we account for temperature and concentration changes in a single (axial) dimension. The model implicitly assumes plug flow: radial temperature and concentration gradients have been neglected. For adiabatic reactors, Q=0. When Q ≠ 0, the reactor is said to operate in "non-isothermal/non-adiabatic" (NI-NA) mode. To take radial temperature and concentration gradients into account, we need to consider the radius as a second independent variable, in addition to axial distance from the reactor inlet. The material and energy balances then become partial differential equations.

When a reactor operates in "non-isothermal/non-adiabatic" (NI-NA) mode and heat is removed from the walls, it is almost impossible to suppress radial temperature gradients. In these cases, setting up 1-dimensional (i.e. plug flow) models may still provide a useful first approximation to modeling more complicated reactors. In these cases, the temperature gradient is assumed to be concentrated in a thin film near the outside edge of the catalyst bed.

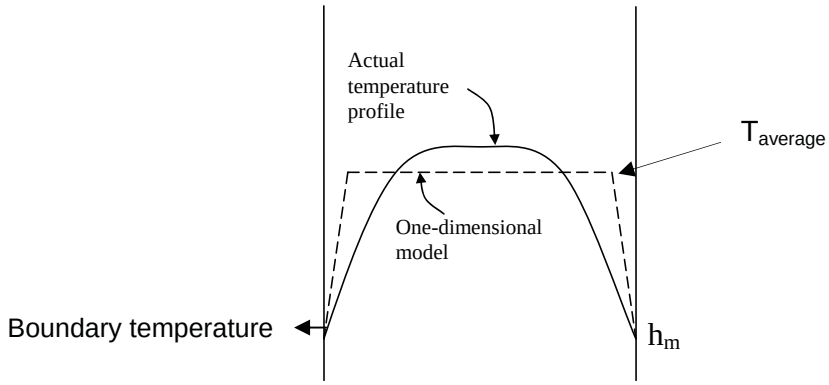


Figure 7.1 Schematic diagram of temperature distribution assumed for 1-dimensional, NI-NA reactor.

7.2 "Pseudo-Homogeneous" FBCR models

The reactor model described by equations 7.4, 7.6 and 7.7 contains a global reaction rate expression such as

$$r_p = \frac{1}{\left\{\frac{1}{k\eta} + \frac{1}{k_m a_m}\right\}} C_{A,b} \,. \qquad \textbf{(Eq. 6.11)}$$

This equation gives the rate per unit mass of catalyst, or in the case of r_V the rate per reactor volume. It does not account for the presence of discreet catalyst particles as a separate domain, with its own boundary conditions etc. In fact the model equations are analogous to those of a homogeneous model. The set of equations [6.11, 7.14, 7.16 and 7.17] is said to describe a "pseudo-homogeneous reactor model". We will next describe more complex reactor models formulated using the same "pseudo-homogeneous" behaviour assumption for FBCR models. "Heterogeneous" models for FBCR design are beyond the scope of this text.

		A	B	C	D	E	F
Type	With...	Isothermal 1-D	Isothermal 2-D	Adiabatic 1-D	Adiabatic 2-D	NI-NA 1-D	NI-NA 2-D
1	HEAT REMOVAL FROM WALL	NO	NO	NO	NO	YES	YES
2	AXIAL HEAT FLOW	NO	NO	YES	YES	YES	YES
3	RADIAL HEAT FLOW	NO	NO	NO	YES	NO	YES
4	AXIAL PRESSURE DROP, ΔP	YES/NO	YES/NO	YES/NO	YES/NO	YES/NO	YES/NO
5	AXIAL MASS DISPERSION	YES/NO	YES/NO	YES/NO	YES/NO	YES/NO	YES/NO
6	RADIAL MASS DISPERSION	NO	YES/NO	NO	YES/NO	NO	YES/NO

Table 7.1 Common "pseudo-homogeneous" reactor model types classified according to aspects of reactor behaviour included in calculations. NI-NA refers to non-isothermal, non-adiabatic reactors.

Table 7.1 summarizes some of the basic types of FBCR models that can be formulated, depending on the phenomena included in the calculations. In general, it may appear tempting to formulate models that take into account all the multiple phenomena we are aware of. However, some of these may not affect the behaviour of the reactor significantly; axial mass dispersion is usually one such effect. Others, such as radial mass dispersion in contexts where radial temperature gradients are significant, may play a crucial role in estimating conversions in the reactor. However, in all cases, care must be taken to quantify the considered effect with a level of accuracy that would help in arriving at a more realistic result. If we are unable to quantify a certain effect, we may still keep it in our model, for sensitivity analysis. Let us briefly review the meaning of each element in Column I of Table 7.1.

7.3 Elements of Column I in Table 7.1

Each of the listed elements refers to a phenomenon that might be significant for predicting/estimating the performance of the reactor.

Heat removal from the wall: An important parameter in non-isothermal, non-adiabatic reactors. When modeling 1-dimensional NI-NA reactors, radial temperature uniformity *must* be assumed. In these cases, as indicated in Figure 1, an average reactor temperature is assumed and the remaining temperature variation is ascribed to the heat transfer boundary.

Axial heat flow: As may be inferred from Eq. 7.4, this term refers to heat axially transported by the flowing reaction mixture. It does *not* refer to heat conduction due to the axial temperature gradient, which is a second order effect. If included, the latter effect would be expressed in terms of Fourier's law of heat conduction.

Radial heat conduction: Is relevant to 2(or more)-dimensional models, which we will briefly introduce below. It's inclusion serves to even out radial temperature gradients. Neglecting this effect would lead to the overestimation of radial temperature gradients, which may distort reaction rates, particularly for highly exothermic reactions.

The axial pressure drop, ΔP: High pressures are normally used in chemical reactors to enhancing the reactivity of gaseous reactants, by increasing the concentration driving force. When the packed catalyst bed is long or pellet sizes are small, the pressure drop across segments of the reactor bed may be significant. This has the effect of changing the reaction rate. To a first approximation, ΔP may be calculated using the Ergun equation (Eq. 7.7) or similar semi-empirical equations.

Axial mass dispersion: This term refers to diffusion of reactant, caused by axial concentration gradients. Strictly, this effect violates the plug flow assumption, although, the magnitude of the effect is minor. We usually expect reactor sizing calculations to be thrown off target by probably less than 10 %. Effects relating to inaccuracies in the kinetic constants would have a more important effect. In reactor modeling, this effect would be characterized by Fick's law type terms and an effective diffusivity which is determined empirically.

Radial mass dispersion: This effect is relevant to 2(or more)-dimensional models, which we will briefly introduce below. Its inclusion serves to even out radial concentration gradients, which become significant when temperature inequalities along the radius give rise to faster depletion of reactants in high temperature zones. Neglecting this effect would lead to the underestimation of reaction rates in hotter zones, since *radial mass dispersion* helps replenish reactant by diffusion from cooler zones with higher reactant concentrations.

As an example of how we can relate to Table 7.1, let us have a brief look at the set of equations we derived above for a non-isothermal reactor: Eq. 7.4 (energy balance), Eq. 7.6 (mass balance) and Eq. 7.7 (momentum balance – pressure drop). Within the framework of Table 7.1, this reactor model would be classed as either 4C or 4E, depending on whether Q is assumed to be zero (adiabatic) or non-zero (NI-NA).

Taking account of axial mass dispersion, the mass balance equation for a 1-dimensional reactor, may be written as:

$$\frac{\partial}{\partial z}\{-uc\}+\frac{\partial}{\partial z}\left\{(D_{e,L})\frac{\partial c}{\partial z}\right\}-r_p \quad \rho_B=0, \qquad \text{(Eq. 7.8)}$$

where $D_{e,L}$ is defined as the effective axial diffusivity of the reactant in the packed bed. Eq. 7.8 reduces to Eq. 7.6, if the superficial velocity "*u*" is assumed to be constant and axial dispersion is neglected (i.e. $D_{e,L}$ =0). In terms of the matrix shown in Table 7.1, Eq. 7.8 corresponds to the mass balance equation of (i) 5A if the reactor is isothermal, (ii) 5C if the reactor is adiabatic, and, (iii) 5E, if the reactor is NI-NA.

7.4 Two-dimensional FBCR models

So far we have only considered 1-dimensional FBCR models, where the only independent variable considered is the axial distance from the reactor inlet. With a single independent variable, the resulting material and energy balances are *ordinary* differential equations. In order to take radial temperature and concentration gradients into account, we would need to consider the radius as a second independent variable. This leads to the formulation of *partial* differential equations.

1-dimensional NI-NA reactor models require considerably less numerical effort compared to 2-dimensional models. As we have seen, however, once heat removal from the reactor wall is introduced, we have to make some rather crude approximations regarding the radial temperature profile, in order to use 1-dimensional models. In highly exothermic reactions such as partial oxidation of hydrocarbons or the oxidation of SO_2, where wall cooling is used, radial temperature and concentration gradients cannot be ignored.

As a relatively extreme but relevant example, during the oxidation of SO_2 (to SO_3 – to eventually make sulphuric acid) a central hot-spot temperature in the catalyst bed was observed as 520 °C whilst the reactor wall was maintained at 197 °C. For a quick calculation, taking 500 °C as the hot spot temperature and the energy of activation E_a as -8×10^7 J kmol^{-1}, the ratio of the reaction rate constants at the two temperatures is calculated as

$$\frac{k_c}{k_w} = \frac{exp\left\{-8\times10^7 / 770\,R\right\}}{exp\left\{-8\times10^7 / 470\,R\right\}} \cong 3000 \qquad \textbf{(Eq. 7.9)}$$

7.4.1 Co-ordinate system for 2-dimensional FBCRs

When radial temperature and or concentration gradients significantly affect FBCR reactor behaviour, we normally assume axial symmetry, and use a 2-dimensional coordinate system.

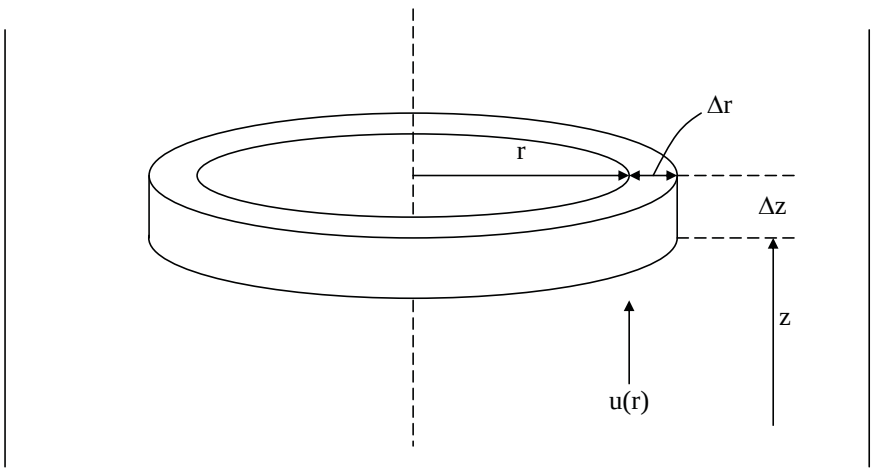


Figure 7.2 Annular volume element in a fixed-bed catalytic reactor. Axial symmetry has been assumed

Inclusion of radial heat and mass transfer phenomena in the calculations requires us to define effective radial thermal conductivity and radial diffusivity coefficients: $\lambda_{e,r}$ and $D_{e,r}$. The use of the term "effective" here means that the coefficients are not inherent properties of the fluids flowing through the reactor. Instead, they characterize the effect (i.e. heat or mass transfer) that arises from the combination of the fluid and the porous catalyst bed built up of stacked pellets. Clearly, using erroneous values of these coefficients would lead us to error. Thus, the inclusion of additional phenomena into our model requires that we know the values of the coefficients that characterize these phenomena to a degree of accuracy that would allow us to simulate reactor behaviour to a level that constitutes an improvement compared to entirely ignoring the phenomenon.

The 2-dimensional material balance equation, which takes radial and axial mass dispersion as well as variations in axial fluid motion into account, is a partial differential equation:

$$\frac{1}{r}\frac{\partial}{\partial r}\left\{(D_{e,r})\ r\frac{\partial C_A}{\partial r}\right\}+\frac{\partial}{\partial z}\left\{-u(z)C_A+(D_{e,z})\frac{\partial C_A}{\partial z}\right\}-r_p\rho_B=0 \qquad \textbf{(Eq. 7.10)}$$

Note that in Eq. 7.10, the concentration $C_A(z,r)$ is a function of radius as well as axial distance from the reactor inlet. However, in this formulation, the axial superficial velocity is a function of axial distance only: $u=u(z)$. Together with its boundary conditions (not discussed), this form of the material balance equation may be formulated for an isothermal reactor, and would represent elements "5,6 – B" in Table 7.1. Alternatively, the material balance equation may be coupled with an energy balance equation and solved simultaneously for an adiabatic reactor ("5 and 6 – D in Table 7.1) or for a NI-NA reactor ("5 and 6 – F"). Such equation systems need to be solved numerically. As an exercise, it may be useful to derive these equations from first principles, using the co-ordinate system in Figure 7.2.

It may be noted that radial temperature gradients may occur without necessarily removing heat from the walls. This may happen if fluid near the central axis of an adiabatic reactor travels faster than fluid elements nearer the wall. Thus, at any reactor cross-section, the residence time of fluid traveling near the central axis would be less than material nearer the walls. Less reaction would have occurred in the central region. This means that a colder plume could travel down the center of the reactor, setting up radial temperature and concentration gradients. Heat would diffuse inwards whilst reactants would diffuse outwards ("3 and 5 – D" in Table 7.1).

7.4.2 Example of full set of equations for a 2-dimensional NI-NA FBCR

For a single reacting component and a single reaction taking place, a NI-NA, 2-dimensional fixed bed catalytic reactor, where the effects of axial thermal and energy dispersion are significant ("1,2,3,6-F" in Table 7.1), the material balance equation can be written as follows:

$$\varepsilon D_{e,r}\left\{\frac{\partial^2 C_A}{\partial r^2}+\frac{1}{r}\frac{\partial C_A}{\partial r}\right\}-u_s\frac{\partial C_A}{\partial z}-\rho_B\, r_A=0 \qquad \textbf{(Eq. 7.11)}$$

In this equation, ε is the void fraction, $D_{e,r}$ the effective radial diffusivity and u, the axial superficial velocity. The energy balance equation in the same co-ordinate system, again assuming axial symmetry is given by:

$$\lambda_{e,r}\left\{\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right\}-u_s\ \rho_g\, C_p\frac{\partial T}{\partial z}+\rho_B(-\Delta H_r)r_A=0 \qquad \textbf{(Eq. 7.12)}$$

where $\lambda_{e,r}$ is defined as the effective radial thermal conductivity. The boundary conditions for this system of equations are given as follows:

At the inlet: $z=0$, $C_A=C_{A0}$; $T=T_0$ (T_0 not necessary equal to T_{wall}) [for $0 \geq r \geq R_t$]

$\frac{\partial C}{\partial r}=0$ (i.e. no flux) at $r=0$ and at $r = R_t$, where R_t is the reactor tube diameter.

$\frac{\partial T}{\partial r}=0$ at $r=0$ for all z.

This is the temperature symmetry boundary condition. Heat transfer at the reactor wall is described by:

$$-\lambda_{e,r}\frac{\partial T}{\partial r}=\alpha_W\,(T_R-T_W)\ \text{ at } r = R_t\,,$$

where the wall temperature can be a function of the axial position: $T_R = T(R_t, z)$.

The role of *radial* mass diffusion in evening out radial concentration and (indirectly) temperature gradients has already been outlined. As radial temperature gradients are set up by heat removal from the reactor through the reactor walls, we expect faster depletion of reactant in the central higher temperature zone of the reactor. Inward radial diffusion is caused by the resulting concentration gradient. *Axial* dispersion effects are less significant and are usually ignored.

Assigning numerical values to *effective* mass diffusivities and thermal conductivities is an inexact science, usually dealt with by means of existing correlations. (cf. textbooks cited in the "References" section.)

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