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SMALL-SCALE MIXING EFFECTS
IN STIRRED REACTORS

by
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CHAPTER I

INTRODUCTION

I.1 Historical Background

The importance of mixing in chemical reactor analysis was first shown by Denbigh [15,16] who compared the performance of batch versus continuous operation. More recently, it has been shown that the study of mixing should include an analysis of small-scale mixing as well as residence time distribution effects. This was most clearly illustrated by Kramers [25], who compared the conversion for a second order reaction for two types of flow having the same residence time distribution. He compared the performance of a system consisting of an ideally stirred tank followed by a plug flow reactor to that of a system containing a plug flow reactor followed by an ideally stirred tank. He found that, for second order reactions, the conversion was always greater in the latter system.

Danckwerts [14] explained this phenomenon in terms of a quantity he called the degree of segregation. As pointed out by Zwietering [50], the upper limit of this quantity is one for any residence time distribution, but a value of zero can only be obtained for a system with an exponential residence time distribution. Zwietering then defines a state of maximum mixedness compatible with a given residence time dis-

tribution which allows the evaluation of the lower limit of the degree of segregation. He uses this, together with Danckwerts' completely segregated case, to obtain bounds on conversion for power-law kinetics. More will be said on this point later.

Several authors have used mathematical models to study the small scale mixing effects discussed above. Curl [12,13] and others [22,36,39] used a coalescence-dispersion model to study segregation effects for zero and second order reactions, and in dominantly first order reactors. Ng and Rippin [31] used a two environment model to study segregation in a partially mixed chemical reactor. Rippin [44] used this model to study second order reactions occurring in a system having the residence time distribution of two ideally stirred tanks hooked up in series. Weinstein and Adler 46 discussed more general kinetic expressions but limited their analysis to cases where the inlet feed is premixed. Some of these works and others related to segregation in chemical reactors have been reviewed by Rietema [32].

For the particular case of stirred tank reactors, experimental work has been carried out [28,29,30,40,47] which shows that good mixing is usually a good assumption. Thus Avery and Hart [2] have analyzed combustor performance assuming that the mixing is instantaneous. Beer and Lee [5] consider the effect of residence time distribution on combustor performance. Experimental work investigating mixedness in jet stirred combustors was carried out by Bartok et al [3] and by Hottel et al [21]. Their work is in general agreement

with those investigators who found good mixing for externally mixed reactors.

The effect of residence time distribution on polymerization systems was considered by Denbigh [16] and Biesenberger and Tadmor [6]. The latter also considered segregation effects [41]. A more complete discussion of their work can be found in the section on polymerization systems.

I.2 Scope of the Thesis

As mentioned above, mixing is made up of two components--the residence time distribution or macro-mixing, and the small-scale or micro-mixing. In the analysis of systems with a fixed residence time distribution, the micro-mixing effect is usually lumped into a single parameter, such as Danckwerts' degree of segregation or Rippin's transfer coefficient. It is the concern of this work to analyze the performance of systems having an exponential residence time distribution as a function of the micro-mixing as determined by a mixing intensity parameter.

Stirred tank reactors are commonly used in industry, but their design based on laboratory or pilot plant data is beset by difficulties in characterizing and scaling up the mixing processes taking place within the reactor. This work will attempt to clarify the scale-up of the mixing processes and, at the same time, to determine the sensitivity of various chemical reaction systems, including combustion and polymerization processes, to departures from ideal mixing.

The analysis begins with the adoption of Curl's coalescence model for mixing in a stirred tank reactor. This one parameter model is shown to predict, in accordance with results obtained through the application of turbulence theory, that the variance of concentration fluctuations decays exponentially in time. The time constant of the decay subsequently turns out to be the mixing intensity parameter in Curl's mixing model, and this fact is then used to relate the mixing intensity to the physical characteristics of the system. This

relation finds application in the study of scale-up of stirred tank reactors, and in the analysis of blowout in mixed combustors.

In Chapter III, the coalescence model is described and the material balance equation is derived. It is shown that the residence time distribution for this model duplicates that of an ideally stirred vessel, and system behavior for the extremes of mixing are presented.

In Chapter IV, several mathematical tracer experiments are performed on the mixing model, and it is shown how the mixing intensity for a real stirred tank might be obtained from such tracer experiments. Also in this chapter, the mixing intensity is related to Danckwerts' measure of micro-mixing, the degree of segregation.

The next two chapters are given over to methods of solution of the material balance equation. The first method considers the area of interest to be high mixing rates, and accordingly proceeds by expanding the concentration distribution into a power series of inverse mixing intensity. The second method assumes a form of distribution, and the free parameters involved are then evaluated from the material balance. Chapter VII compares these two methods, as well as methods reported elsewhere, for some simple kinetic examples.

In Chapter VIII, the expansion method is applied to several reaction systems, and an example of the use of the method is given for one of these systems. In Chapter IX, combustion processes are examined and it is shown that the blowout limit decreases as departures from ideal mixing grow

larger. This analysis shows that there is a critical mixing intensity for a given reaction system below which combustion is impossible.

In Chapter X, the analysis is extended to polymerization systems and it is shown that premixing of the feed always results in a higher conversion of monomer and a narrower distribution of molecular weights.

CHAPTER II

MACRO-MIXING TIMES

II.1 Introduction

The effect of mixing on conversion in a chemical reactor must be studied in terms of the two components of mixing--the macro-mixing and the micro-mixing. The macro-mixing is a large scale phenomenon and has a large effect on conversion. It is characterized by the residence time distribution of a continuous system. The micro-mixing specifies the environment of each molecule in the reactor. The amount of micro-mixing that is possible is limited by the residence time distribution since the latter completely determines the distribution of waiting times in the reactor and entering fluid. The micro-mixing can only affect mixing between molecules or particles having the same waiting time.

Whereas the macro-mixing can be described completely by means of the residence time distribution, there is no analogous way to describe the more complex phenomenon of micro-mixing. Danckwerts [47] lumps the whole effect into a quantity he calls the degree of segregation, but as pointed out by Rippin [33] this quantity together with the residence time distribution is not in general sufficient to determine the conversion in a chemical reactor.

In the present analysis, the mixing model proposed

by Curl [12] is used to describe the micro-mixing in a continuous stirred-tank reactor. In this model, β represents the mixing intensity or inverse micro-mixing time, and α represents the space velocity or inverse mean residence time. The term β/α then is the ratio of macro-mixing time to micro-mixing time. As will be shown later, for this model the variance of concentration fluctuations in a batch-type tracer experiment decays exponentially in time according to

$$\frac{d\sigma^2}{dt} = -\beta\sigma^2 \quad (2.1)$$

In the following analysis, it is first shown that this exponential decay is predicted by turbulent mixing theory, and the mixing intensity parameter β is then related to measurable physical quantities.

II.2 Results from the Theory of Turbulence

The work of Batchelor [4] and Corrsin [10,11] and others on the application of the theory of turbulence to the scale-up of stirred tank reactors leads directly to an estimate of the mixing intensity β in terms of large-scale properties of the turbulence. Accordingly, the basic arguments are recapitulated here and their bearing on the practical estimation of β is discussed. The analysis is all for a homogeneous isotropic turbulence and an incompressible fluid.

The development begins with the standard partial differential equation for Fick's law diffusion superimposed on turbulent convection in a closed system:

$$\frac{\partial c}{\partial t} + u_j \sum_j \frac{\partial c}{\partial x_j} = \mathcal{D} \sum_j \frac{\partial^2 c}{\partial x_j^2} \quad (2.2)$$

where $\mathcal{D}$ is the molecular diffusivity, c is concentration, the x_j are the coordinate directions, and u_j is the velocity component in the direction of x_j . Equation (2.2) holds in the entire region R . On the boundary B , for a closed system

$$u_v c - \mathcal{D} \frac{\partial c}{\partial x_v} = 0 \quad (2.3)$$

where u_v is the velocity component normal to the surface, x_v the direction normal to the surface and pointing outward, and $\partial c / \partial x_v$ the concentration gradient in this direction. In addition to equations (2.2), (2.3), two properties of the velocity vector are noted. First, for an incompressible fluid,

$$\sum_j \frac{\partial u_j}{\partial x_j} = 0 \quad (2.4)$$

throughout the region R . The second property holds only on the boundary B , where, for viscous flow in a closed system,

$$u_j = 0 \quad ; \quad j = 1, 2, 3 \quad (2.5)$$

Using (2.4), (2.2) becomes

$$\frac{\partial c}{\partial t} + \sum_j \frac{\partial}{\partial x_j} (u_j c) = \mathcal{D} \sum_j \frac{\partial^2 c}{\partial x_j^2} \quad (2.6)$$

and with the volume V given by

$$V = \iiint_R dx_1 dx_2 dx_3 \quad (2.7)$$

the mean concentration μ is given as

$$\mu(t) = \frac{1}{V} \iiint_R c(\underline{x}, t) dx_1 dx_2 dx_3 \quad (2.8)$$

Integrating equation (2.6) over the region R then gives

$$\begin{aligned} V \frac{d\mu}{dt} + \iiint_R \sum_j \frac{\partial}{\partial x_j} (u_j c) dx_1 dx_2 dx_3 \\ = \mathcal{D} \iiint_R \sum_j \frac{\partial^2 c}{\partial x_j^2} dx_1 dx_2 dx_3 \end{aligned} \quad (2.9)$$

Using Green's (divergence) theorem, this becomes

$$V \frac{d\mu}{dt} + \iint_B u_v \cdot c dS = \mathcal{D} \iint_B \frac{\partial c}{\partial x_v} dS \quad (2.10)$$

and the surface integrals are seen to cancel with the use of equation (2.3), so that

$$V \frac{d\mu}{dt} = 0 \quad (2.11)$$

or the mean concentration is independent of time,

$$\mu(t) = \mu = \text{a constant} \quad (2.12)$$

A concentration fluctuation c' may now be defined as

$$c' = c - \mu \quad (2.13)$$

and since μ is a constant, (2.6) becomes

$$\begin{aligned} \frac{\partial c'}{\partial t} + \sum_j \frac{\partial}{\partial x_j} (u_j \cdot c) \\ = \mathcal{O} \sum_j \frac{\partial^2 c'}{\partial x_j \partial x_j} \end{aligned} \quad (2.14)$$

Equation (2.3) may also be expressed in terms of concentration fluctuation. Using (2.5) this becomes

$$u_v \cdot c' - \mathcal{O} \frac{\partial c'}{\partial x_v} = 0 \quad (2.15)$$

on the boundary B.

Now, with the variance σ^2 given by

$$\sigma^2(t) = \frac{1}{V} \iiint_R (c')^2 dx_1 dx_2 dx_3 \quad (2.16)$$

equation (2.14) may be multiplied through by c' and integrated over the region R to give

$$\begin{aligned} \frac{V}{2} \frac{d\sigma^2}{dt} + \iiint_R \sum_j c' \frac{\partial}{\partial x_j} (u_j \cdot c) dx_1 dx_2 dx_3 \\ = \mathcal{O} \iiint_R \sum_j c' \frac{\partial^2 c'}{\partial x_j \partial x_j} dx_1 dx_2 dx_3 \end{aligned} \quad (2.17)$$

With the aid of equation (2.4), it can be seen that

$$\sum_j c' \frac{\partial}{\partial x_j} (u_j \cdot c) = \frac{1}{2} \sum_j \frac{\partial}{\partial x_j} (u_j \cdot (c')^2) \quad (2.18)$$

and it is also readily shown that

$$\sum_j c' \frac{\partial^2 c'}{\partial x_j \partial x_j} = \frac{1}{2} \sum_j \frac{\partial^2 (c')^2}{\partial x_j \partial x_j} - \sum_j \frac{\partial c'}{\partial x_j} \frac{\partial c'}{\partial x_j} \quad (2.19)$$

Combining (2.17), (2.18), and (2.19) and using the divergence theorem gives

$$\begin{aligned} \frac{V}{2} \frac{d\sigma^2}{dt} + \frac{1}{2} \iint_B u_v \cdot (c')^2 dS \\ = \frac{\mathcal{D}}{2} \iint_B \frac{\partial (c')^2}{\partial x_v} dS - \mathcal{D} \iiint_R \sum_j \frac{\partial c'}{\partial x_j} \frac{\partial c'}{\partial x_j} dx_1 dx_2 dx_3 \end{aligned} \quad (2.20)$$

The last integral is by definition $V \cdot \overline{(\text{grad } c')^2}$ where the overbar denotes a space average. Since u_v is zero on the boundary (equation (2.5) says that u vanishes on the boundary) and consequently, from equation (2.15), $\partial c' / \partial x_v$ also vanishes on the boundary, equation (2.20) reduces to

$$\frac{d\sigma^2}{dt} = -2\mathcal{D} \overline{(\text{grad } c')^2} \quad (2.21)$$

The mean square gradient in concentration fluctuation is related back to σ^2 by introducing a micro-scale l_m for the turbulent mixing, according to which the mean square components of the concentration gradient all have the common value

$$\frac{1}{2} \left(\frac{\partial c'}{\partial x_1} \right)^2 = \frac{1}{2} \left(\frac{\partial c'}{\partial x_2} \right)^2 = \frac{1}{2} \left(\frac{\partial c'}{\partial x_3} \right)^2 = \sigma^2 / l_m^2 \quad (2.22)$$

so that

$$\overline{(\text{grad } c')^2} = 6 \sigma^2 / l_m^2 \quad (2.23)$$

and

$$\frac{d\sigma^2}{dt} = - \frac{12\mathcal{D}}{l_m^2} \sigma^2 \quad (2.24)$$

This represents a simple exponential decay in variance, and comparing it to (2.1) leads to the conclusion

$$\beta = \frac{12\mathcal{D}}{l_m^2} \quad (2.25)$$

Information about the turbulent velocity field itself is however more naturally expressed in terms of the Taylor (dissipation) micro-scale l_d , and of a corresponding Reynolds number Re . The characteristic velocity appearing in this Reynolds number is the root mean square velocity fluctuation u . For an isotropic turbulence, this root mean square fluctuation is the same in each coordinate direction,

$$u_1 = u_2 = u_3 = u/\sqrt{3} \quad (2.26)$$

and the appropriate Reynolds number is accordingly defined as

$$Re = \frac{1}{\sqrt{3}} \frac{l_d u}{\nu} \quad (2.27)$$

where ν is the (molecular) kinematic viscosity of the working fluid. The two micro-scales are related approximately by the fact that

$$\frac{l_m^2}{l_d} = \frac{2\mathcal{D}}{\nu} \quad (2.28)$$

which is valid for Re large but $\mathcal{D}/\nu$ not too large. (Should $\mathcal{D}/\nu$ be large, ref. (4) shows how the analysis might be modified, but in the examples of interest here--i.e. combustion processes or liquid phase chemical reactions-- $\mathcal{D}/\nu$ is at worst close to unity). Combining (2.28) with (2.25) gives

$$\beta = \frac{6\nu}{l_d^2} \quad (2.29)$$

The Taylor micro-scale may be related to a charac-

teristic linear dimension L of the mixing system as a whole (such as the vessel diameter) by taking

$$\frac{l_d}{L} = \frac{A}{Re} \quad (2.30)$$

or, applying the definition (2.27) of the Reynolds number Re ,

$$\frac{l_d}{L} = \sqrt{3} \frac{Av}{l_d u} \quad (2.31)$$

Here A is an empirical parameter independent of the scale of the mixing system but varying from one mixing configuration to another. The parameter A can be expected to depend, for example, on the physical properties of the working fluid, on the geometry of the vessel, and on the inlet and outlet configurations, but to have the same value for geometrically similar mixing systems working on the same fluid.

The Taylor micro-scale may also be related to the power input to the turbulent fluid. The energy dissipation per unit mass of fluid can be taken approximately as $\frac{10}{3} \nu u^2 / l_d^2$, and with an empirical efficiency factor η , this can be identified as the actual power input ϵ to the mixing system per unit mass of working fluid.

$$\epsilon = \frac{10}{3} \eta \frac{\nu u^2}{l_d^2} \quad (2.32)$$

The efficiency η measures that fraction of the power input to the system which goes directly to the turbulent velocity field (and is only later dissipated as heat) as distinct from that fraction which goes directly to heat. The efficiency η can also be expected to be independent of the scale

of the mixing system, but to vary from one mixing configuration to another.

If u is eliminated between (2.31) and (2.32), l_d can be solved for as

$$l_d = (10A^2\eta)^{1/5} \left(\frac{\nu^3 L^2}{\varepsilon} \right)^{1/5} \quad (2.33)$$

and upon substitution of this relation into (2.29) there results

$$\beta = \left(\frac{21.6}{A^2\eta} \right)^{1/3} \left(\frac{\varepsilon}{L^2} \right)^{1/3} \quad (2.34)$$

The dependence of β on ε shown in (2.34) may also be obtained by a straightforward dimensional argument. The parameter β can be expected to depend on the following variables:

ε	(power input per unit mass)	: cm^2/sec^3
L	(length)	: cm
ρ	(density)	: g/cm^3
μ	(viscosity)	: $\text{g}/\text{cm-sec}$
$\mathcal{D}$	(diffusivity)	: cm^2/sec

So that

$$\beta = F(\varepsilon, L, \rho, \mu, \mathcal{D}) \quad ; \text{sec}^{-1} \quad (2.35)$$

This equation in its function relationship is independent of the units used. If the system of units is changed to a natural system where length is measured in multiples of L , time is measured in units of $(L^2/\varepsilon)^{1/3}$, and mass is measured in units of ρL^3 , equation (2.35) will become

$$\begin{aligned} \beta \cdot \left(\frac{L^2}{\varepsilon} \right)^{1/3} &= F \left(1, 1, 1, \frac{\mu L}{\rho L^2} \left(\frac{L^2}{\varepsilon} \right)^{1/3}, \frac{\mathcal{D}}{L^2} \left(\frac{L^2}{\varepsilon} \right)^{1/3} \right) \\ &= \text{fcn} \left(\frac{L^{-1/3} \varepsilon^{1/3}}{\nu}, \frac{\mathcal{D}}{\nu} \right) \end{aligned} \quad (2.36)$$

The term $L^{4/3} \varepsilon^{1/3} / \nu$ is equal to $L(L\varepsilon)^{1/3} / \nu$, and considering $(L\varepsilon)^{1/3}$ as a velocity, this term can be regarded as a modified Reynolds number. As was mentioned earlier, for large Reynolds numbers, β can be regarded as independent of the Reynolds number. That is, the relation (2.36) as far as Reynolds number is concerned, approaches a limiting value. Also, for D/ν not too large, the diffusion effects are far outweighed by the effects of turbulent mixing and therefore equation (2.36) has a limiting value for D/ν not too large. These are precisely the restrictions on (2.34) and it is obvious that the results agree. The analysis based on turbulence theory has the advantage that it leads also to some idea of the actual numerical magnitudes involved and may serve as a useful guide to practice. From work in wind tunnels and in pipe flows, Corrsin cites the approximate values

$$A \approx 20 \quad ; \quad n \approx 1/2$$

so that (2.34) gives

$$\beta \approx 1/2 \left(\frac{\varepsilon}{L^2} \right)^{1/3} \quad (2.37)$$

II.3 Application to Stirred Tank Reactors

The foregoing analysis applies very generally, regardless of the source of the energy that supports the turbulence. In the case of vessels with mixing of liquid by agitation, both A and η can be expected to depend strongly on agitator design and more accurate studies would be required before prediction of A and η could be made on the basis of the geometrical design of the vessel. Van de Vusse [42] studied the effect of agitator design on overall mixing time by observing the disappearance of large-scale refractive index gradients using the Schlieren method. If this mixing time is taken to be the same as the time required for the decay of the variance of concentration fluctuations, then the mixing time τ_m of van de Vusse can be related to the mixing intensity parameter β through the use of equation (2.1). If, for example, the mixing time measured by van de Vusse is the time necessary for the fluctuations to decrease to 5% of their original value, then (2.1) gives $\beta = 3/\tau_m$, and in general, one may write

$$\beta = h/\tau_m \quad (2.38)$$

where the constant of proportionality h depends on the sensitivity of the method used to determine the time of complete mixing. Since β is the time constant for decay of the variance of concentration fluctuations, then even a rather crude estimate of the mixing time will result in values of h of at least unity. Choosing $h = 1$ then gives a real lower bound on β . From the results of van de Vusse obtained using paddle stirrers, together with (2.38) with $h = 1$, values of

β are predicted which are lower than those given by (2.37). The constant in this equation should perhaps be altered so as to read

$$\beta = 0.1 \left(\frac{\epsilon}{L^2} \right)^{1/3} \quad (2.39)$$

but since this constant depends strongly on agitator design, it is preferable to measure it on small-scale equipment prior to the design of large-scale mixing vessels. In cases where it is necessary to have large values of β , considerable effort should be expended on the design of the agitator. Other factors to be strongly considered are the use of multiple agitators and multiple feed points, and the proper location of the feed pipes.

In the design of stirred tank reactors, the problem of scaling up on the basis of laboratory or pilot plant experiments arises quite often. In cases where the kinetics are complex, product quality is most certain to be affected. For single one path reactions, the only concern is the product yield and this can usually be satisfactorily assured by the use of safety factors. Where product quality can be affected, safety factors cannot make up for the lack of precise knowledge. Cases involving nucleation, such as polymerization or crystallization processes, are very sensitive to local non-uniformities of the reacting mixture and consequently require great care in scale-up. Such factors as molecular weight distribution or product size distribution must be considered.

Maintenance of similarity in the basic flow regime

is a must during scale-up. Shinnar [37] has shown that this criterion can be fulfilled by choosing the size of the pilot plant or bench reactor such that the Reynolds number is large ($>10^4$). This ensures that the average velocity distribution is a function of space coordinates only and fairly independent of Reynolds number, so that, during scale-up, although the Reynolds number changes, geometrically similar reactors will have similarity in their overall velocity distributions. Shinnar also explains that the energy input per unit volume should be held constant as this gives a similarity of the turbulent flow regime in the high wave number range of the turbulent velocity spectrum. It is further seen from (2.37) that in order to keep the same reactor mixing properties on scale-up, it is necessary to hold the ratio ϵ/L^2 constant. Since, in geometrically similar vessels, ϵ is proportional to N^3L^2 where N is agitator speed, this requires keeping N constant during scale-up. But then ϵ being the power input per unit mass of working fluid, this requirement amounts to making the actual power input proportional to the fifth power of L , a demand which easily results in uncommonly high power requirements. In addition, this requirement conflicts with the similarity requirement of maintaining the energy input proportional to L^3 , and therefore a more realistic approach is needed.

What can be done is to use equation (2.37) to estimate β on scale-up and determine, by methods to be described in later chapters, the effect of this value of β on the reaction system under examination. To do this requires of

course a knowledge of the constant $A^2\eta$, but since this is scale-free, it can be estimated economically in small scale tracer experiments to be discussed in a later chapter. That is to say, with β estimated from a tracer experiment in a small-scale reactor with known $\mathcal{E}$ and L , the value of β in a similar large-scale reactor can be estimated by scaling it in proportion to $(\mathcal{E}/L^2)^{1/3}$, where the values of $\mathcal{E}$ and L in the large-scale reactor may be independently specified.

The net profit from such an analysis is a bounding procedure which can be used to determine when it is safe to scale-up from pilot plant or bench-scale experiments. Zwietering [50] has proposed a much simpler bounding procedure which requires no knowledge of the micro-mixing effects at all, but merely knowledge of the residence time distribution. His two bounds correspond to the state of maximum mixedness and complete segregation. Unfortunately, his method works only for one-step power-law kinetics with premixed feed and even then there remains the possibility that the bounds will be too far apart to be of any use.

Other methods to obtain bounds for more complex systems have been proposed [46], and although these methods are not rigorous, they still give a fairly good estimate of the bounds. However, in cases where it matters most, such as complex reactions or systems involving nucleation, the bounds are rather far apart and the methods based on residence time distribution alone are not very useful. It is for these cases that the present analysis offers a useful remedy.

II.4 Application to Gas Combustors

In addition to its use in liquid phase reactions in agitated vessels, the analysis leading up to equation (2.37) finds application also in studying combustion reactions taking place in vessels which are mixed by the injection of fuel and air. Longwell [27] introduced a spherical adiabatic combustor to study the kinetics of fast reactions, and it is assumed in the interpretation of the data from the corresponding kinetic experiments that the reactor is ideally mixed. It has also been observed [5,19,45] that an ideally stirred tank might be a useful simplified description of some industrial combustors. The concept of an ideally stirred reactor has also contributed considerably to the understanding of the stability and control of autothermic reactions [1,45].

It is quite obvious that a perfectly stirred reactor is an ideal concept which can only be approached. In Longwell's spherical reactor, considerable effort is made in the design to approach instantaneous mixing. This is not true in industrial combustors where the mixing is much less intense, and it would be interesting to ascertain what effect imperfect mixing has on the performance of such a reactor. It has also been shown that even for a small spherical reactor as used in kinetic studies, mixing processes are important. Clarke et al [9] in their studies of blowout velocity have suggested empirical correlations based on pressure drop to compensate for the strong effect of injector design. To better understand these effects, the analysis leading up to equation (2.16) is extended here to mixing of a gas reactor

by its feed jets.

If the vessel is fed by a system of jets with inlet velocity v , through a total cross-sectional area S , the energy input per unit mass in the reactor can be written as

$$\mathcal{E} = \frac{SV \cdot \frac{1}{2}v^2}{\frac{1}{6}\pi L^3} \quad (2.40)$$

where L has been taken to be an equivalent spherical diameter of the vessel. Identifying the flow rate per unit volume of reactor as

$$\alpha = \frac{Sv}{\frac{1}{6}\pi L^3} \quad (2.41)$$

leads to

$$\frac{\beta}{\alpha} = \frac{1}{4} \left(\frac{L^2}{S} \right)^{2/3} \quad (2.42)$$

upon elimination of v and $\mathcal{E}$ among equations (2.37), (2.40) and (2.41). Equation (2.42) relates the mixing intensity β directly to the jet design parameter L^2/S .

It is to be noted that in comparing differently sized reactors with the same mean residence time (that is, the same α), constant L^2/S (constant β/α) requires v/L to remain constant. Thus the necessary pressure drop through the injector increases with increasing reactor size.

The constant $1/4$ in equation (2.42) represents some sort of upper bound for optimal placement of the feed jets. This is true because the mixing has been considered to be ideal in the sense that the turbulence was assumed to be

homogeneous and isotropic. This constant then can only be used as an upper bound and when needed, it should be determined for a given mixing configuration by suitable tracer experiments as discussed in a later chapter. If this evaluation leads to a low estimate of this constant, then consideration should be given as to how the feed jet location design can be improved. Such an evaluation of this constant together with knowledge obtained through the use of the mixing model of the next chapter allows quantitative estimates to be made of the effect of incomplete mixing on mixed combustors.

CHAPTER III

THE COALESCENCE MODEL

III.1 Development of the Model

The reactor model used here is one of droplet coalescence and breakup. It was introduced by Curl [12] and used by him and others in studies of mixed reactor performance and of two-phase mixing [13,22,36,39]. The model regards the reacting mass as made up of a large number of uniformly-sized parcels of material ("particles"), which from time to time undergo independent pair collisions, equalize concentrations, and then separate. Between collisions, each parcel of fluid behaves like a little batch reactor. Fresh material is fed at a constant rate, and the output is representative of the vessel contents. While in two-phase mixing studies these particles may have a definite material identity, perhaps for the present purpose they might better be regarded as primitive representations of turbulent eddies.

For a single reaction, the concentration c of reagent behaves in batch according to

$$\frac{dc}{dt} = -r(c) \quad (3.1)$$

where $r(c)$ is the instantaneous reaction rate. Defining $q(c,t)dc$ as the number of particles at time t having concentration in the range $c, c+dc$, it follows that the total number of particles in the reactor at time t is given by

$$Q(t) = \int q(c, t) dc \quad (3.2)$$

the integral being carried out over all allowable values of c . A material balance

$$\begin{aligned} & \text{accumulation} - \text{depletion by chemical reaction} \\ & = \text{inflow} - \text{outflow} + \text{coalescence terms} \end{aligned}$$

leads to

$$\begin{aligned} \frac{\partial q(c, t)}{\partial t} - \frac{\partial}{\partial c} \{r(c) q(c, t)\} \\ = w \left[c - c_0(t) - \frac{q(c, t)}{Q(t)} \right] \\ + K \left[\iint q(c', t) q(c'', t) \delta \left(\frac{c' + c''}{2} - c \right) dc' dc'' \right. \\ \left. - q(c, t) Q(t) \right] \quad (3.3) \end{aligned}$$

where w is the particle inflow-outflow rate, the feed has been taken as pure reagent at concentration $c_0(t)$, and K is of the nature of a collision intensity parameter. The dimensions of K are reciprocal particle number-second. The integrals appearing in equation (3.3) are integrals over all allowable values ($-\infty$ to $+\infty$) of the parameters c' and c'' , which are just dummy concentration variables.

Inherent in (3.3) is the assumption that the probability of collision is independent of the concentration in the particles. Integrating over c in equation (3.3) and using (3.2) gives

$$\begin{aligned} \frac{dQ(t)}{dt} &= w(1-1) + K(Q^2 - Q^2) = 0 \\ Q(t) &= Q = \text{constant} \quad (3.4) \end{aligned}$$

Defining

$$p(c,t) = \frac{q(c,t)}{Q}$$

and letting

$$\alpha = \frac{W}{Q} = \text{space velocity}$$

$$\beta = \frac{QK}{2}$$

equation (3.3) becomes

$$\begin{aligned} \frac{\partial p(c,t)}{\partial t} - \frac{\partial}{\partial c} \{r(c)p(c,t)\} = \alpha \left[\delta(c-c_o(t)) - p(c,t) \right] \\ + 2\beta \left[\int \int p(c',t)p(c'',t) \delta\left(\frac{c'+c''}{2}-c\right) dc'dc'' \right. \\ \left. - p(c,t) \right] \end{aligned} \quad (3.5)$$

where β is the collision intensity parameter with units of reciprocal second, and can be thought of as a mixing intensity. The parameter α is the reciprocal mean residence time, and $p(c,t)$ is the concentration distribution of particles at time t . The function p is a probability density in c , with $\int_{c'}^{c''} p(c,t) dc$ giving the proportion of particles having concentration between c' and c'' at time t .

The mixing model and its associated equation (3.5) are not meant to describe the real mixing processes in a turbulent reactor. These are far more complex and have not yet been described analytically. However, this model has one important similarity to turbulent mixing. That is, as in the case of isotropic turbulence, the variance of the concentration fluctuations for a batch-type tracer experiment decays exponentially in time and with the time constant β . This

will not be shown until the next chapter, but it is mentioned now in order to point out that the β of (3.5) is to be identified with the β of (2.1) and (2.37). Similarly, the α of (3.5) is the same reciprocal residence time as the α of (2.41).

The mean concentration of reagent in the vessel and outlet is simply the first moment of p , and this is the working measure of overall reactor performance for a given kinetic system. The differential equation for the mean concentration is obtained by multiplying through equation (3.5) by c and integrating over the full range $-\infty$ to $+\infty$ on c . It is understood in such an integration that $p(c,t)$ is zero for all values of c outside the allowable range 0 to c_0 .

$$\frac{d\mu}{dt} + \int r(c)p(c,t)dc = \alpha\{c_0(t) - \mu\} \quad (3.6)$$

where the mean is defined as

$$\mu(t) = \int cp(c,t)dc \quad (3.7)$$

Higher moments can be defined similarly

$$\mu_j = \int c^j p(c,t)dc \quad (3.8)$$

and of particular interest is the variance σ^2 which is given by

$$\sigma^2 = \mu_2 - \mu_1^2 \quad (3.9)$$

Note that μ and μ_1 are used interchangeably for the mean concentration. The differential equation for μ_2 is obtained by multiplying through equation (3.5) by c^2 and integrating.

$$\begin{aligned} \frac{d\mu_2}{dt} + 2 \int cr(c)p(c,t)dc &= \alpha(c_0^2 - \mu_2) \\ &+ \beta(\mu_1^2 - \mu_2) \end{aligned} \quad (3.10)$$

from which we obtain, using (3.9),

$$\begin{aligned}
 \frac{d\sigma^2}{dt} + 2 \int (c-\mu) r(c) p(c,t) dc \\
 = \alpha (c_0^2 - \sigma^2 - 2\mu_1 c_0 - 3\mu_1^2) \\
 - \beta \sigma^2
 \end{aligned}
 \tag{3.11}$$

III.2 Generalization

In the development of equation (3.5), the feed stream was assumed to be pure reagent with concentration varying in time. It would be convenient to generalize this equation so that it would incorporate cases where the feed is impure or where there is more than one inlet stream. This is easily done by replacing $\delta(c-c_0(t))$ in equation (3.5) with $p^*(c,t)$, the concentration distribution for the feed. Equation (3.5) then becomes

$$\begin{aligned} \frac{\partial p(c,t)}{\partial t} - \frac{\partial}{\partial c} \{r(c)p(c,t)\} &= \alpha \{p^*(c,t) - p(c,t)\} \\ &+ 2\beta \left[\iint p(c',t)p(c'',t) \delta\left(\frac{c'+c''}{2} - c\right) dc' dc'' - p(c,t) \right] \\ &\left[\right] \end{aligned} \quad (3.12)$$

Equation (3.12) is for a one-dimensional case; that is, only one concentration is being followed. This equation is easily generalized to higher dimensional cases by simply regarding c as a vector quantity. The reaction term is then replaced with a sum of terms, one term for each independent concentration to be followed. Denoting

$$\underline{c} = \{c_1, c_2, \dots, c_s\} \quad (3.13)$$

and generalizing (3.1) to

$$\frac{dc_i}{dt} = r_i(\underline{c}) \quad ; \quad i = 1, 2, \dots, s \quad (3.14)$$

(3.12) becomes

$$\begin{aligned}
\frac{\partial p(\underline{c}, t)}{\partial t} + \sum_{i=1}^s \frac{\partial}{\partial c_i} \{r_i(\underline{c}) p(\underline{c}, t)\} \\
= \alpha \{p^*(\underline{c}, t) - p(\underline{c}, t)\} \\
+ 2\beta \left[\int \int \dots \int p(\underline{c}', t) p(\underline{c}'', t) \delta\left(\frac{\underline{c}' + \underline{c}''}{2} - \underline{c}\right) d\underline{c}' d\underline{c}'' - p(\underline{c}, t) \right]
\end{aligned}
\tag{3.15}$$

where in the last term, the integral is $2s$ -fold, and the shorthand notation

$$\begin{aligned}
\delta(\underline{x}) &= \delta(x_1) \delta(x_2) \dots \delta(x_s) \\
d\underline{x} &= dx_1 dx_2 \dots dx_s
\end{aligned}
\tag{3.16}$$

has been used.

The real significance of using p^* to represent the feed distribution is seen when there is more than one independent concentration and the feeds are not premixed. For example, if two reagents A and B are fed separately in equal volumes the expression for p^* is

$$p^*(\underline{c}, t) = \frac{1}{2} \delta(C_A - C_{Ao}) \delta(C_B) + \frac{1}{2} \delta(C_A) \delta(C_B - C_{Bo})
\tag{3.17}$$

III.3 The Residence Time Distribution

The residence time distribution for the mixing model under consideration is identical to that of an ideally-mixed reactor. This fact can be shown from equation (3.6). The residence time distribution $f(t)$ may in this context be defined as the mean response to an impulse in the absence of chemical reaction. For this case, (3.6) becomes

$$\frac{1}{\alpha} \frac{df}{dt} + f = \delta(t) \quad (3.18)$$

where it is understood that f exists over the whole range $-\infty, \infty$. Since there can be no contribution to $f(t)$ for negative t , equation (3.18) is equivalent to

$$\frac{1}{\alpha} \frac{df}{dt} + f = 0 \quad ; \quad t > 0 \quad (3.19)$$

$$f(0) = \alpha$$

This is easily solved for the residence time distribution

$$f(t) = \alpha e^{-\alpha t} \quad ; \quad t > 0 \quad (3.20)$$

which is identical to that of an ideally-mixed vessel with mean residence time $1/\alpha$. It is independent of the value of β .

III.4 Moments

Equation (3.12) results from a material balance on a rather simple mixing model. Nevertheless, this equation is a nonlinear integro-differential equation for which no analytical solution is known. The difficulty associated with solving it is illustrated by considering it in terms of moments. The i^{th} moment μ_i of p is defined by (3.8) as

$$\mu_i = \int c^i p(c, t) dc \quad (3.8)$$

and similarly, moments of p^* can be defined as

$$\mu_i^* = \int c^i p^*(c, t) dc \quad (3.21)$$

Since p and p^* are probability densities, they integrate to unity, and accordingly

$$\mu_0 = \mu_0^* = 1 \quad (3.22)$$

The fact that $\mu_0 = 1$ is a direct consequence of (3.3), that is, that the total number of particles in the system is invariant in time. This can be further shown by integrating (3.12) over the whole range of c , that is, $-\infty, \infty$. This gives

$$\frac{d\mu_0}{dt} = \alpha(\mu_0^* - \mu_0) \quad (3.23)$$

which agrees with (3.22).

Higher moments can be obtained similarly. Multiplying equation (3.12) by c and integrating gives

$$\frac{d\mu_1}{dt} = -\int r(c) p(c, t) dc + \alpha(\mu_1^* - \mu_1) \quad (3.24)$$

and it is easily seen that for first order reactions, this equation can be solved for μ_1 . In fact, if

$$r(c) = kc$$

then (3.24) gives

$$\frac{d\mu_1}{dt} + (\alpha+k)\mu_1 = \alpha\mu_1^* \quad (3.25)$$

which has the steady state solution

$$\mu_1 = \frac{\alpha}{\alpha+k} \mu_1^* \quad (3.26)$$

and, for an initially reagent-free vessel, (3.25) gives

$$\mu_1 = \frac{\alpha}{\alpha+k} \mu_1^* (1 - e^{-(\alpha+k)t}) \quad (3.27)$$

Equation (3.24) is the mass conservation equation.

It states simply that the accumulation of reagent is equal to the difference between what is fed and what is withdrawn, less that lost by chemical reaction. To obtain equations for higher moments, equation (3.12) is multiplied by powers of c before integrating. In general, multiplying by c^i and integrating yields

$$\begin{aligned} \frac{d\mu_i}{dt} = & -i \int r(c) c^{i-1} p(c,t) dc + \alpha(\mu_i^* - \mu_i) \\ & + 2\beta \left[\frac{1}{2^i} \sum_{j=0}^i \binom{i}{j} \mu_{i-j} \mu_j - \mu_i \right] \\ ; \quad & i = 0, 1, 2, \dots \end{aligned} \quad (3.28)$$

It can be noted from the above equation that for all but first order reactions, there is no finite (closed) set of simultaneous equations for which the calculation of the individual μ_i is possible. Equations for ever higher moments, or endless fractional moments are required. Hulburt and Katz [23] point out the possibility of closing or truncating

this infinite set of equations by approximating the distribution p with a series of special functions. This method will be discussed in detail in a later chapter.

III.5 Behavior for Large and Small β

This section is given over to an analysis of the mixing model for extreme values of β : infinite β , which corresponds to maximum mixedness, and vanishingly small β , which corresponds to complete segregation.

As the condition of maximum mixedness is approached, the contents of the vessel tend toward uniformity and it is easily argued on physical grounds that the distribution takes on the form

$$p(c,t) = \delta(c-\mu(t)) \quad (3.29)$$

where $\mu(t)$, the first moment of p , is not only the mean concentration but the local concentration at every point as well. Equation (3.29) satisfies equation (3.5), for if (3.5) is divided by β , and $\frac{1}{\beta}$ is allowed to approach zero (onset of maximum mixedness condition), then (3.5) becomes

$$p(c,t) = \iint p(c',t)p(c'',t)\delta\left(\frac{c'+c''}{2}-c\right)dc'dc'' \quad (3.30)$$

The time-variation of μ can be obtained from (3.6)

$$\frac{d\mu}{dt} = \alpha\{c_0(t)-\mu\} - \int r(c)p(c,t)dc \quad (3.6)$$

which becomes, upon use of equation (3.29),

$$\frac{d\mu}{dt} = \alpha\{c_0(t)-\mu\} - r(\mu) \quad (3.31)$$

Similarly, the transient response of the variance can be found from (3.11). However, it is easier to begin with the definition of the variance

$$\sigma^2 = \int [c - \mu(t)]^2 p(c, t) dc \quad (3.32)$$

from which it is obvious that, for the ideally-mixed vessel, the variance is identically zero.

Equations (3.29) and (3.31) fully describe the state of the reaction system when the vessel is perfectly mixed. If on the other hand, no micro-mixing took place, equation (3.5) would give

$$\frac{\partial p(c, t)}{\partial t} - \frac{\partial}{\partial c} \{r(c)p(c, t)\} = \alpha \{\delta(c - c_0(t)) - p(c, t)\} \quad (3.33)$$

which is just a partial differential equation for the distribution $p(c, t)$. The transient response for the mean concentration is given by (3.6) and for the variance, (3.11) gives

$$\begin{aligned} \frac{d\sigma^2}{dt} = & \alpha \{c_0^2(t) - \sigma^2 - 2\mu c_0(t) - 3\mu^2\} \\ & - 2 \int (c - \mu) r(c) p(c, t) dc \end{aligned} \quad (3.34)$$

Equation (3.33) describes the state of the reactor system at any time t . At steady state, this equation reduces to an ordinary differential equation, and it may be readily solved for the steady state distribution $p(c)$. At steady state, (3.33) becomes

$$- \frac{d}{dc} \{r(c)p(c)\} = \alpha \{\delta(c - c_0) - p(c)\} \quad (3.35)$$

Since the delta-function is zero except at $c = c_0$, then for $0 < c < c_0$, (3.35) gives

$$\frac{d}{dc} \{r(c)p(c)\} = + \alpha p(c) \quad (3.36)$$

which is readily solved to give

$$p(c)r(c) = p(c')r(c')e^{-\alpha \int_c^{c'} \frac{1}{r(c'')} dc''} \quad (3.37)$$

where $0 \leq c \leq c' \leq c_0$. Straightforward integration of equation (3.33) from $c = c_0^-$ to $c = c_0^+$ gives

$$p(c_0^-)r(c_0^-) - p(c_0^+)r(c_0^+) = \alpha \quad (3.38)$$

where the $-$ and $+$ refer to infinitesimal departures from c_0 .

Since $p(c)$ is zero outside the range $0, c_0$, (3.38) gives

$$p(c_0^-)r(c_0^-) = \alpha$$

and letting c' go to c_0^- in (3.37) gives

$$p(c)r(c) = \alpha e^{-\alpha \int_c^{c_0} \frac{dc''}{r(c'')}} \quad (3.39)$$

Replacement of c' by c_0 in the exponential integral limit is justified since there is no real contribution to this integral in the range c_0^-, c_0 . Equation (3.39) is the solution to (3.33) at steady state. It is only to be used for $0 \leq c \leq c_0$, $p(c)$ vanishing outside this range.

The transient behavior of β can be found if desired from (3.33). This is a linear partial differential equation, and can readily be solved by the method of characteristics.

CHAPTER IV

TRACER EXPERIMENTS ON THE MODEL

IV.1 Introduction

In Chapter II, equations (2.37, 2.42) were developed relating the mixing intensity parameter β to measureable physical quantities. These equations were developed from the theory of turbulence and related to the model through the use of equation (2.1) which shows the exponential decay of variance in a batch-type tracer experiment. This result (i.e. - equation 2.1) stems from a general attempt to attach an empirical interpretation to the mixing intensity parameter β of the model through the analysis of tracer mixing experiments. This analysis begins by writing (3.12) without the kinetic term, in the form

$$\begin{aligned} \frac{\partial (p(c,t))}{\partial t} = & \alpha \{p^*(c,t) - p(c,t)\} \\ & + 2\beta \left\{ \iint p(c',t)p(c'',t) \delta \left[\frac{c'+c''}{2} - c \right] dc' dc'' - p(c,t) \right\} \end{aligned} \quad (4.1)$$

It may immediately be noted that the desired information is contained in the statistical fluctuations of concentration about its mean. As far as mean values are concerned, the mixing system (without reaction) behaves like a completely mixed vessel with input-output time constant α .

Indeed, with the mean concentration denoted as in (3.7)

$$\bar{u} = \int c p(c, t) dc \quad (3.7)$$

equation (4.1) gives

$$\frac{d\bar{u}}{dt} = \alpha (\bar{u}^* - \bar{u}) \quad (4.2)$$

independent of β , with the mean concentration in the inlet $\bar{u}^*$ given by

$$\bar{u}^* = \int c p^*(c, t) dc \quad (4.3)$$

The next few sections of this chapter will describe various tracer experiments which can be used in the estimation and interpretation of the mixing intensity parameter β . Three types of tracer experiments will be described. One is to introduce an amount of tracer and measure the decay of the concentration fluctuations. The second is to introduce a step in tracer concentration and perform the same measurement. The third is in the case of multiple feeds to introduce a tracer in one of the feed streams only and measure the variance of the concentration fluctuations over the vessel at steady state.

In each of the above cases, a method is needed which is able to measure concentration fluctuations on a very small scale. Two methods have been recently developed which should make an important contribution in this area. One developed by Kim and Wilhelm [24] is based on the scattering of light due to gradients in the refractive index. The second by Brodkey [7, 8] uses fiber optics and colored tracers. As yet there have been very few actual studies and perhaps in the near future more measurements will be available, enabling one to correlate β with experimental results.

IV.2 Step Response in a Continuous Mixer

A step tracer experiment is performed by running the mixer without tracer and suddenly (at $t=0$, say) to change the inlet so that it is feeding tracer at concentration c_0 into the vessel. The feed distribution is then given by

$$p^*(c, t) = \delta(c - c_0) \quad t \geq 0 \quad (4.4)$$

and accordingly

$$u^* = c_0 \quad t \geq 0 \quad (4.5)$$

So that equation (4.2) becomes

$$\frac{du}{dt} = \alpha(c_0 - u) \quad ; \quad t \geq 0 \quad (4.6)$$

This, together with the initial condition

$$u(0) = 0 \quad (4.7)$$

shows that the mean tracer concentration in the vessel and its outlet is

$$u(t) = c_0(1 - e^{-\alpha t}) \quad (4.8)$$

the familiar stirred tank exponential response.

The first measure of the concentration fluctuation is given by its variance

$$c^2(t) = \int (c - u(t))^2 p(c, t) dc \quad (4.9)$$

and from (4.1), (4.2) this satisfies the differential equation

$$\frac{dc^2}{dt} = \alpha(u^* - u)^2 + \alpha(u^* \sigma^2 - c^2) - \beta \sigma^2 \quad (4.10)$$

where

$$\sigma^2(t) = \int_0^1 \{c - \mu^*(t)\}^2 p^*(c, t) dc \quad (4.11)$$

is the variance of tracer concentration in the feed. In this tracer experiment, this becomes

$$\sigma^2(t) = 0 \quad (4.12)$$

so that (4.10) gives

$$\frac{d\sigma^2}{dt} + (\alpha + \beta)\sigma^2 = \alpha(\mu^* - \mu)^2 \quad (4.13)$$

With the initial condition

$$\sigma^2(0) = 0 \quad (4.14)$$

and using (4.5), (4.8), solving (4.13) gives

$$\sigma^2(t) = \alpha c_0^2 e^{-\alpha t} \frac{e^{-\alpha t} - e^{-\beta t}}{\beta - \alpha} \quad (4.15)$$

With careful monitoring of an output line, the expression for the variance in (4.15) may serve as a guide to the estimation of the mixing intensity parameter β . This variance rises from zero to a maximum at

$$t = \frac{1}{\beta - \alpha} \ln \frac{\beta + \alpha}{2\alpha} \quad (4.16)$$

before decaying again to zero, and with α known, the bare location of this maximum will give some estimate of β , even without detailed knowledge of the variance history.

IV.3 Batch Mixer

The step input experiments described above furnish perhaps the most convenient means for an empirical determination of β , although the underlying equation (4.1) can readily be made to yield results appropriate to quite different experimental situations. Indeed, the most direct way of visualizing the effect of β is via a batch experiment with no input-output at all. Dropping the input-output terms in (4.1) gives

$$\frac{\partial p(c,t)}{\partial t} = 2\beta \left\{ \iint p(c',t)p(c'',t) \delta \left(\frac{c'+c''}{2} - c \right) dc' dc'' - p(c,t) \right\} \quad (4.17)$$

and it may be seen from equations (3.6) and (3.11) with α and r vanishing that the mean tracer concentration is constant

$$\frac{d\mu}{dt} = 0 \quad (4.18)$$

and that the variance decays according to

$$\frac{d\sigma^2}{dt} = -\beta\sigma^2 \quad (4.19)$$

Thus, in a pure batch experiment, where a quantity of tracer is injected initially into some portion of the vessel, the resulting inhomogeneity in the distribution of tracer in the vessel decays, as far as variance goes, according to

$$\sigma^2(t) = \sigma^2(0)e^{-\beta t} \quad (4.20)$$

that is, simply with the time constant β . This is precisely the result quoted in Chapter II (2.1) and used there to relate β to the characteristics of the turbulent flow in the vessel.

IV. 4 Multiple Feeds

In addition to the aforementioned transient response type tracer experiments, there are also steady-state methods for multiple feeds. At steady state, (4.1) becomes

$$0 = \alpha \{p^*(c) - p(c)\} + 2\beta \left\{ \int \int p(c') p(c'') \delta \left(\frac{c' + c''}{2} - c \right) dc' dc'' - p(c) \right\} \quad (4.21)$$

and (4.2) gives

$$\mu = \mu^* \quad (4.22)$$

For the case where there are two inlet streams, one having tracer concentration c_0 and the other tracer-free, the feed distribution p^* becomes

$$p^*(c) = \phi \delta(c) + (1-\phi) \delta(c - c_0) \quad (4.23)$$

where ϕ is that fraction of the total feed represented by the tracerless stream. The mean concentration in the vessel and in the inlet and outlet streams is then given by

$$\mu = \mu^* = (1-\phi)c_0 \quad (4.24)$$

and the variance of concentration in the feed is

$$*\sigma^2 = (1-\phi)\phi c_0^2 \quad (4.25)$$

Equation (4.21) gives

$$0 = \alpha (\mu^* - \mu)^2 + \alpha (*\sigma^2 - \sigma^2) - \beta \sigma^2 \quad (4.26)$$

so that the variance of tracer concentration in the vessel and its outlet is given by

$$\sigma^2 = \frac{\alpha}{\alpha + \beta} \cdot \phi(1-\phi)c_0^2 \quad (4.27)$$

A single determination of variance in the outlet then is all that is required to give an estimate of the mixing intensity parameter β .

IV.5 Degree of Segregation

It may be noted finally that each value of the mixing intensity β corresponds to a definite value of Danckwerts' degree of segregation [14] in the reactor. This relationship can be established by considering the "particles" of fluid in the reactor to be composed of "subparticles", the distinction being that a subparticle consists of material all of which entered the reactor at the same time. Denoting by θ the age of a subparticle and by $\bar{\theta}$ the mean age of a particle, Danckwerts' degree of segregation, J , becomes

$$J = \frac{\text{variance of } \bar{\theta}}{\text{variance of } \theta} \quad (4.28)$$

The denominator is the total variance so to speak, within the reactor, and the numerator is that part of the total variance contributed by the difference in mean ages of the various particles. The age distribution in the reactor has the same form as the residence time distribution since the latter is equivalent to that of an ideally stirred vessel (see section III.3). Denoting the age distribution by $g(\theta)$, this means

$$g(\theta) = \alpha e^{-\alpha\theta} \quad (4.29)$$

which has mean $1/\alpha$ and the variance is then given by

$$\text{variance of } \theta = \int_0^{\infty} \left(\theta - \frac{1}{\alpha}\right)^2 g(\theta) d\theta \quad (4.30)$$

So that, using (4.29),

$$\text{variance of } \theta = \frac{1}{\alpha^2} \quad (4.31)$$

The numerator of (4.28) cannot be evaluated as easily

until an observation is made. If $\bar{\theta}$ is considered to be a property of a particle which behaves as does concentration during the process of coalescence and breakup with the batch "reaction" rate given by

$$\frac{d\bar{\theta}}{dt} = 1 \quad (4.32)$$

then an equation analogous to (3.5) may be used. With $\psi(\bar{\theta}, t)$ being the distribution of mean ages among the particles, the feed being all at age zero, equation (3.5) becomes, at steady state,

$$\begin{aligned} \frac{d\psi(\bar{\theta})}{d\bar{\theta}} = & \alpha \left[\delta(\bar{\theta}) - \psi(\bar{\theta}) \right] \\ & + 2\beta \left\{ \iint \psi(\bar{\theta}') \psi(\bar{\theta}'') \delta \left(\frac{\bar{\theta}' + \bar{\theta}''}{2} - \bar{\theta} \right) d\bar{\theta}' d\bar{\theta}'' \right. \\ & \left. - \psi(\bar{\theta}) \right\} \end{aligned} \quad (4.33)$$

Integration of (4.33) gives

$$\int \psi(\bar{\theta}) d\bar{\theta} = 1 \quad (4.34)$$

and multiplication of (4.33) by $\bar{\theta}$ and integrating yields

$$\int \bar{\theta} \psi(\bar{\theta}) d\bar{\theta} = 1/\alpha \quad (4.35)$$

Denoting by γ the next such integral

$$\gamma = \int \bar{\theta}^2 \psi(\bar{\theta}) d\bar{\theta} \quad (4.36)$$

and multiplying (4.33) by $\bar{\theta}^2$ and integrating yields the following:

$$-2 \cdot \left(\frac{1}{\alpha} \right) = -\alpha\gamma + 2\beta \left[\frac{1}{2} \left(\frac{1}{\alpha} \right)^2 - \frac{\gamma}{2} \right] \quad (4.37)$$

where whenever $1/\alpha$ appears in parentheses, it arises due to equation (4.35). Solving for γ yields

$$\gamma = \frac{1}{\alpha+\beta} \cdot \left[\frac{\beta}{\alpha^2} + \frac{2}{\alpha} \right] \quad (4.38)$$

With the definition

$$\text{variance of } \bar{\theta} = \int \left(\bar{\theta} - \frac{1}{\alpha} \right)^2 \psi(\bar{\theta}) d\bar{\theta} \quad (4.39)$$

equations (4.34), (4.35), (4.36) give

$$\begin{aligned} \text{variance of } \bar{\theta} &= \gamma - \frac{2}{\alpha^2} + \frac{1}{\alpha^2} \\ &= \gamma - \frac{1}{\alpha^2} \end{aligned} \quad (4.40)$$

which together with (4.38) gives

$$\text{variance of } \bar{\theta} = \frac{1}{\alpha(\alpha+\beta)} \quad (4.41)$$

The degree of segregation J is found by combining (4.28), (4.31), and (4.41) to obtain

$$J = \frac{\alpha}{\alpha+\beta} \quad (4.42)$$

with vanishing β giving complete segregation, and infinite β , complete mixing. Thus an estimate of the degree of segregation, obtained perhaps by studying a particular reaction system (not first order), can be translated directly into an estimate of β .

CHAPTER V

SOLUTIONS AT HIGH MIXING INTENSITY

V.1 The Expansion Method

As was mentioned earlier, equation (3.5) and its higher dimensional analogues such as (3.15) cannot be solved explicitly for the distribution p or its moments. However, since it is departures from ideal mixing which comprise the realm of primary interest, the natural method of analysis is to expand the distribution p in powers of $1/\beta$. What results is a succession of linear integral equations in the successive contributions to the overall p , and while these do not appear to be easily solvable either, they do lead to sets of linear differential equations in the moments of the successive contributions to p . The procedure closes, that is, it gives at each level of approximation a self-contained set of differential equations in a finite number of leading moments, provided the rate expressions (3.1), (3.3) and so on are polynomials. The resulting linear differential equations in the moments can be solved by standard numerical means such as Runge-Kutta routines, with suitable arbitrary starting conditions. The overall average reactor performance at any time t is found finally by adding up the contributions to the first moment of p .

In the following analysis, it may be more convenient to work in terms of a dimensionless variable y in place of

the concentration c . This variable y may stand for mole fraction, percentage yield, or whatever, the only restriction on its choice being that in order to satisfy equation (3.5), the basic property of averaging on agglomeration must be preserved. The rate expression now becomes

$$\frac{dy}{dt} = r(y) \quad (5.1)$$

and for the higher-dimensional case

$$\frac{dy_i}{dt} = r_i(\underline{y}) \quad ; \quad i = 1, 2, \dots, s \quad (5.2)$$

where $\underline{y}$ stands for the vector whose components are the individual y_i .

V.2 The One-Dimensional Case

With the rate expression of (5.1), equation (3.12) becomes

$$\begin{aligned} \frac{\partial p(y,t)}{\partial t} + \frac{\partial}{\partial y} \{r(y)p(y,t)\} \\ = \alpha \{p^*(y,t) - p(y,t)\} \\ + 2\beta \left\{ \int \int p(y',t)p(y'',t) \delta\left(\frac{y'+y''}{2} - y\right) dy' dy'' \right. \\ \left. - p(y,t) \right\} \end{aligned} \quad (5.3)$$

With αt replaced by dimensionless time t , and $R(y) = r(y)/\alpha$, dimensionless reaction rate, this becomes

$$\begin{aligned} \frac{\partial p(y,t)}{\partial t} + \frac{\partial}{\partial y} \{R(y)p(y,t)\} = p^*(y,t) - p(y,t) \\ + \gamma \left\{ \int \int p(y',t)p(y'',t) \delta\left(\frac{y'+y''}{2} - y\right) dy' dy'' \right. \\ \left. - p(y,t) \right\} \end{aligned} \quad (5.4)$$

where

$$\gamma = \frac{2\beta}{\alpha} \quad (5.5)$$

is a dimensionless mixing intensity. With the moments of p given by

$$L_m(t) = \int y^m p(y,t) dy \quad (5.6)$$

and those of p^* by

$$L_m^*(t) = \int y^m p^*(y,t) dy \quad (5.7)$$

an overall average material balance is obtained by multiplying (5.4) through by y and integrating

$$\frac{d\mu_1(t)}{dt} - \int R(y)p(y,t)dy = \mu_1^*(t) - \mu_1(t) \quad (5.8)$$

Also, since $p(y)$ is to be a properly normalized probability density,

$$\int p(y,t)dy = 1 \quad (5.9)$$

If $R(y)$ is a polynomial of degree M , then (5.8) relates the rate of change of μ_1 to the first M moments of p . In particular, for a first order reaction with rate constant k , where y is the concentration of reagent so that $R(y) = -ky/\alpha$, (5.8) gives

$$\frac{d\mu_1}{dt} = \mu_1^*(t) - (1 + \frac{k}{\alpha})\mu_1(t) \quad (5.10)$$

which at steady state gives for the mean reagent concentration in vessel and outlet the standard result

$$\mu = \frac{\mu_1^*}{1 + \frac{k}{\alpha}} \quad (5.11)$$

independent of the mixing intensity β , where μ_1^* is the mean reagent concentration in the feed.

In general, however, p (but not p^*) and its moments depend on the mixing intensity, and the proposed procedure is to expand (5.4), (5.8) and (5.9) in powers of $1/\lambda$.

Formally,

$$p(y,t) = \sum_{j=0}^{\infty} \frac{1}{\lambda^j} p^{(j)}(y,t) \quad (5.12)$$

and

$$\mu_m = \sum_{j=0}^{\infty} \frac{1}{\lambda^j} \mu_m^{(j)}(t) \quad (5.13)$$

so that

$$\mu_m^{(j)}(t) = \int y^m p^{(j)}(y, t) dy \quad (5.14)$$

Bringing (5.12) to (5.4) and equating coefficients in λ gives for $p^{(0)}$

$$p^{(0)}(y, t) - \iint p^{(0)}(y', t) p^{(0)}(y'', t) \delta\left\{\frac{y' + y''}{2} - y\right\} dy' dy'' = 0 \quad (5.15)$$

for $p^{(1)}$

$$\begin{aligned} p^{(1)}(y, t) - 2 \iint p^{(0)}(y', t) p^{(1)}(y'', t) \delta\left\{\frac{y' + y''}{2} - y\right\} dy' dy'' \\ = p^*(y, t) - p^{(0)}(y, t) - \frac{\partial}{\partial y} \{R(y) p^{(0)}(y, t)\} - \frac{\partial}{\partial t} p^{(0)}(y, t) \end{aligned} \quad (5.16)$$

and for the higher $p^{(j)}$

$$\begin{aligned} p^{(j)}(y, t) - 2 \iint p^{(0)}(y', t) p^{(j)}(y'', t) \delta\left\{\frac{y' + y''}{2} - y\right\} dy' dy'' \\ = \sum_{i=1}^{j-1} \iint p^{(i)}(y', t) p^{(j-i)}(y'', t) \delta\left\{\frac{y' + y''}{2} - y\right\} dy' dy'' \\ - p^{(j-1)}(y, t) - \frac{\partial}{\partial y} \{R(y) p^{(j-1)}(y, t)\} - \frac{\partial}{\partial t} p^{(j-1)}(y, t) \\ ; \quad j = 2, 3, \dots \end{aligned} \quad (5.17)$$

Similarly, bringing (5.12), (5.13) to (5.8) and equating coefficients in λ gives in $p^{(0)}$

$$\frac{d}{dt} \mu_1^{(0)} + \mu_1^{(0)} - \int R(y) p^{(0)}(y, t) dy = \mu_1^* \quad (5.18)$$

and in the higher $p^{(j)}$

$$\frac{d\mu_1^{(j)}}{dt} + \mu_1^{(j)} - \int R(y)p^{(j)}(y,t)dy = 0 \quad ; \quad j = 1, 2, \dots \quad (5.19)$$

Finally from (5.9), it is seen that

$$\mu_0^{(0)} = 1 \quad (5.20)$$

while

$$\mu_0^{(j)} = 0 \quad ; \quad j = 1, 2, \dots \quad (5.21)$$

Now the equation (5.15) in $p^{(0)}$ simply represents the behavior of the perfectly mixed reactor (infinite β), and its solution is

$$p^{(0)}(y,t) = \delta(y - \mu_1^{(0)}(t)) \quad (5.22)$$

which satisfies the normalization (5.20). The mean value of $\mu_1^{(0)}(t)$ is determined by the overall material balance (5.18)

$$\frac{d\mu_1^{(0)}}{dt} + \mu_1^{(0)} - R(\mu_1^{(0)}(t)) = \mu_1^*(t) \quad (5.23)$$

which can be solved by a standard Runge-Kutta integration scheme. With $p^{(0)}$ in hand, equation (5.16) in the first correction $p^{(1)}$ may be attacked by taking partial moments (5.14), that is, by multiplying through by successive powers of y and integrating. With (5.21), linear algebraic equations in the $\mu_m^{(1)}$ are found in the form

$$\begin{aligned} \left(1 - \frac{1}{2^{m-1}}\right)\mu_m^{(1)}(t) - \frac{1}{2^{m-1}} \sum_{n=1}^{m-1} \binom{m}{n} \{\mu_1^{(0)}(t)\}^{m-n} \mu_n^{(1)}(t) \\ = \mu_m^*(t) - \{\mu_1^{(0)}(t)\}^{m+m} \{\mu_1^{(0)}(t)\}^{m-1} \left\{ R(\mu_1^{(0)}) - \frac{d\mu_1^{(0)}}{dt} \right\} \end{aligned}$$

; $m = 2, 3, \dots$ (5.24)

there being no new information in the moment equations for $m = 1$. This loss of information is however made up by the overall material balance (5.19) for $j = 1$.

$$\frac{d\mu_1^{(1)}}{dt} + \mu_1^{(1)} - \int R(y) p^{(1)}(y, t) dy = 0 \quad (5.25)$$

At steady state, the equations are all algebraic and their solution will be discussed in a later section. For the transient case, if $R(y)$ is a polynomial of degree M , then (5.25) relates the rate of change of $\mu_1^{(1)}$, the first moment of $p^{(1)}$, to the first M moments of $p^{(1)}$. But, equation (5.24) can be used to relate the higher moments $\mu_2^{(1)}, \mu_3^{(1)}, \dots, \mu_m^{(1)}$ to $\mu_1^{(1)}$, so that what results is a linear first order differential equation in $\mu_1^{(1)}$ which can be solved by standard numerical or algebraic techniques. With $\mu_1^{(1)}(t)$ in hand, as many moments as desired can be generated by taking (5.24) for $m = 2, 3, \dots, m, m + 1, \dots$, etc. in turn. The right hand sides of equation (5.24) offers no difficulty since it depends only on the feed distribution $p^*(y, t)$ and $\mu_1^{(0)}(t)$, both of which are at this point known.

The same procedure applies as well to the higher $p^{(j)}$ of (5.17). Taking moments, one finds a set of algebraic equations very much like (5.24), indeed having the same left-hand sides:

$$\begin{aligned} (1 - \frac{1}{2^{m-1}}) \mu_m^{(j)} - \frac{1}{2^{m-1}} \sum_{n=1}^{m-1} \binom{m}{n} \{\mu_1^{(0)}\}^{m-n} \mu_n^{(j)} \\ = \sum_{i=1}^{j-1} \sum_{n=1}^{m-1} \binom{m}{n} \mu_n^{(i)} \mu_{m-n}^{(j-i)} - \mu_m^{(j-1)} \end{aligned}$$

(cont'd)

$$\begin{aligned}
 & + m \int y^{m-1} R(y) p^{(j-1)}(y, t) dy \\
 & - \frac{d}{dt} u_m^{(j-1)}(t) \quad ; \quad m = 2, 3, \dots \\
 & \quad \quad \quad j = 2, 3, \dots
 \end{aligned}$$

(5.26)

the right hand sides for each j involving moments of the earlier $p^{(j)}$. Again, there is no new information in the moment equations for $m = 1$, but if $R(y)$ is a polynomial of degree M , for each j a closed set of equations in $u_1^{(j)}$, $u_2^{(j)}$, ..., $u_M^{(j)}$ is found by taking (5.26) for $m = 2, 3, \dots, M$ together with (5.19). As before, linear algebraic equations arise for the steady state situation, and for the transient solution, an ordinary differential equation in $u_1^{(j)}$ is found. After solving this differential equation by a standard method, one can generate as many higher moments as desired by taking (5.26) for $m = 2, 3, \dots, M, M+1$, etc. It should be noted that the integral term on the right hand side of (5.26) leads to a certain cascading in the number of earlier moments required as successive values of j are taken. Thus, with $R(y)$ of degree M , $3M-2$ moments of $p^{(1)}$ are needed to find $(2M-1)$ moments of $p^{(2)}$ to find M moments of $p^{(3)}$; etc. But since higher moments can be found at will, this causes no especial difficulty. Finally, having evaluated the partial moments for as many j as desired, one may see the effect of the mixing intensity on the overall performance of the reactor from (5.13).

$$\mu_1(t) = \mu_1^{(0)}(t) + \frac{1}{\lambda} \mu_1^{(1)}(t) + \frac{1}{\lambda^2} \mu_1^{(2)}(t) + \dots$$

(5.27)

And the variance

$$\sigma^2 = \mu_2 - \mu^2 \quad (5.28)$$

is found by suitably combining (5.13) for $m = 1, 2$ to obtain

$$\sigma^2(t) = c_1^2(t) + \frac{1}{\lambda} \sigma_1^2(t) + \frac{1}{\lambda^2} \sigma_2^2(t) + \dots \quad (5.29)$$

It might be noted that similar results can be developed for low mixing intensity by expanding the basic equations in powers of β/α , that is, in powers of the λ of (5.5) rather than of $1/\lambda$. What results is a hierarchy of linear partial differential equations in the successive contributions to p , the leading term being that corresponding to a completely segregated reactor. Moment methods are no longer appropriate, and indeed the successive linear partial differential equations can be readily solved by the method of characteristics. The methods are quite straightforward but of little practical interest, and so no further work has been done in this area.

V.3 Complex Kinetics

In the previous section, solution of the one-dimensional equation (5.4) for large values of the mixing intensity was accomplished by expanding the distribution p in a power series of $1/\lambda$. Entirely similar considerations apply to the higher dimensional versions of (3.12) such as (3.15). For the working equation, we have in place of (5.4)

$$\begin{aligned} \frac{\partial p(\underline{y}, t)}{\partial t} + \sum_{A=1}^s \frac{\partial}{\partial y_A} \{R_A(\underline{y}) p(\underline{y}, t)\} = p^*(\underline{y}, t) - (1+\lambda) p(\underline{y}, t) \\ + \lambda \left[\int p(\underline{y}', t) p(\underline{y}'', t) \delta\left(\frac{\underline{y}' + \underline{y}''}{2} - \underline{y}\right) d\underline{y}' d\underline{y}'' \right] \end{aligned} \quad (5.30)$$

where $\underline{y}$ stands for $(y_1, y_2, \dots, y_s)$, and $d\underline{y}$ for the volume element $dy_1, dy_2, \dots, dy_s$, and the δ -symbol for the appropriate product of δ -functions. The moments of p are now multi-dimensional, and we denote them

$$u_{m_1 m_2 \dots m_s} = \int y_1^{m_1} y_2^{m_2} \dots y_s^{m_s} p(\underline{y}, t) d\underline{y} \quad (5.31)$$

with

$$u_{m_1 m_2 \dots m_s}^* = \int y_1^{m_1} y_2^{m_2} \dots y_s^{m_s} p^*(\underline{y}, t) d\underline{y} \quad (5.32)$$

There are now s overall material balances in place of (5.8)

$$\begin{aligned} \frac{du_{1;A}}{dt} - \int R_A(\underline{y}) p(\underline{y}, t) d\underline{y} = u_{1;A} - u_{1;A} \\ ; \quad A = 1, 2, \dots, s \end{aligned} \quad (5.33)$$

where $\mu_{1;\mathcal{A}}$ is the mean value of the $\mathcal{A}$ -th component in the vessel, that is

$$\mu_{1;\mathcal{A}} = \int y_{\mathcal{A}} p(\underline{y}, t) d\underline{y}$$

$$;\mathcal{A} = 1, 2, \dots, s \quad (5.34)$$

and similarly for the feed

$$\mu_{1;\mathcal{A}}^* = \int y_{\mathcal{A}} p^*(\underline{y}, t) d\underline{y}$$

$$;\mathcal{A} = 1, 2, \dots, s \quad (5.35)$$

Equations (5.33) determine entirely the average behavior of the system for first order kinetics. The single normalization condition (5.9) remains.

The expansion (5.12) applied to (5.30) leads to (5.15) for $p^{(0)}$ with $\underline{y}$ understood to be a vector of dimension s . For $p^{(1)}$, the expansion gives

$$p^{(1)}(\underline{y}, t) - 2 \iint p^{(0)}(\underline{y}', t) p^{(1)}(\underline{y}'', t) \delta \left(\frac{\underline{y}' + \underline{y}''}{2} - \underline{y} \right) d\underline{y}' d\underline{y}''$$

$$= p^*(\underline{y}, t) - p^{(0)}(\underline{y}, t) - \sum_{\mathcal{A}=1}^s \frac{\partial}{\partial y_{\mathcal{A}}} \{ R_{\mathcal{A}}(\underline{y}) p^{(0)}(\underline{y}, t) \}$$

$$- \frac{\partial}{\partial t} p^{(0)}(\underline{y}, t) \quad (5.36)$$

and for the higher $p^{(j)}$,

$$p^{(j)}(\underline{y}, t) - 2 \iint p^{(0)}(\underline{y}', t) p^{(j)}(\underline{y}'', t) \delta \left(\frac{\underline{y}' + \underline{y}''}{2} - \underline{y} \right) d\underline{y}' d\underline{y}''$$

$$= \sum_{i=1}^{j-1} \iint p^{(i)}(\underline{y}', t) p^{(j-i)}(\underline{y}'', t) \delta \left(\frac{\underline{y}' + \underline{y}''}{2} - \underline{y} \right) d\underline{y}' d\underline{y}''$$

$$- p^{(j-1)}(\underline{y}, t) - \sum_{\mathcal{A}=1}^s \frac{\partial}{\partial y_{\mathcal{A}}} \{ R_{\mathcal{A}}(\underline{y}) p^{(j-1)}(\underline{y}, t) \}$$

$$- \frac{\partial}{\partial t} p^{(j-1)}(\underline{y}, t) \quad ; \quad j = 2, 3, \dots \quad (5.37)$$

The moment expansions

$$\mu_{m_1 m_2 \dots m_s}(t) = \sum_{j=0}^{\infty} \frac{1}{j!} \mu_{m_1 m_2 \dots m_s}^{(j)}(t) \quad (5.38)$$

$$\mu_{m_1 m_2 \dots m_s}^{(j)}(t) = \int y_1^{m_1} y_2^{m_2} \dots y_s^{m_s} p^{(j)}(\underline{y}, t) d\underline{y} \quad (5.39)$$

applied to the material balances (5.33) give s equations in $p^{(0)}$

$$\frac{d\mu_{1;\mathcal{A}}^{(0)}}{dt} + \mu_{1;\mathcal{A}}^{(0)} - \int R_{\mathcal{A}}(\underline{y}) p^{(0)}(\underline{y}, t) d\underline{y} = \mu_{1;\mathcal{A}}^* \quad (5.40)$$

$\mathcal{A} = 1, 2, \dots, s$

where the notation is as used in (5.34), and s equations in each of the higher $p^{(j)}$

$$\frac{d\mu_{1;\mathcal{A}}^{(j)}}{dt} + \mu_{1;\mathcal{A}}^{(j)} - \int R_{\mathcal{A}}(\underline{y}) p^{(j)}(\underline{y}, t) d\underline{y} = 0 \quad (5.41)$$

$j = 1, 2, \dots$
 $\mathcal{A} = 1, 2, \dots, s$

Finally, the moment expansions applied to the normalization (5.9) give

$$\mu_{00 \dots 0}^{(0)} = 1 \quad (5.42)$$

and

$$\mu_{00 \dots 0}^{(j)} = 0 \quad ; j=1, 2, \dots \quad (5.43)$$

The equation (5.15) in $p^{(0)}$ is solved just as for one dimension, to give

$$p^{(0)}(\underline{y}, t) = \delta(y_1 - \mu_{1;1}^{(0)}(t)) \dots \delta(y_s - \mu_{1;s}^{(0)}(t)) \quad (5.44)$$

satisfying the normalization (5.42) with the s first moments determined by the s material balances (5.40)

$$\frac{d\mu_{1;\mathcal{A}}^{(0)}}{dt} + \mu_{1;\mathcal{A}}^{(0)} - R_{\mathcal{A}}\{\mu_{1;1}^{(0)}, \mu_{1;2}^{(0)}, \dots, \mu_{1;s}^{(0)}\} = \mu_{1;\mathcal{A}}^* \quad \mathcal{A} = 1, 2, \dots, s \quad (5.45)$$

As for the one-dimensional case, with $p^{(0)}$ in hand, equation (5.36) in the first correction $p^{(1)}$ may be attacked by taking partial moments (5.39). This gives

$$\begin{aligned} \mu_{m_1 m_2 \dots m_s}^{(1)} &= \frac{1}{m_1 + m_2 + \dots + m_s - 1} \sum_{n_1=0}^{m_1} \dots \sum_{n_s=0}^{m_s} \left\{ \pi_{\mathcal{A}=1}^s \left(\begin{matrix} m_{\mathcal{A}} \\ n_{\mathcal{A}} \end{matrix} \right) \{\mu_{1;\mathcal{A}}^{(0)}\}^{m_{\mathcal{A}} - n_{\mathcal{A}}} \right\} \mu_{n_1 n_2 \dots n_s} \\ &= \mu_{m_1 m_2 \dots m_s}^* - \sum_{\mathcal{A}=1}^s \pi_{\mathcal{A}} \{\mu_{1;\mathcal{A}}^{(0)}\}^{m_{\mathcal{A}}} \\ &\quad + m_1 \{\mu_{1;1}^{(0)}\}^{m_1 - 1} \left\{ \sum_{\mathcal{A}=2}^s \pi_{\mathcal{A}} \{\mu_{1;\mathcal{A}}^{(0)}\}^{m_{\mathcal{A}}} \right\} \{R_1(\mu_{1;1}^{(0)}, \mu_{1;2}^{(0)}, \dots, \mu_{1;s}^{(0)}) - \frac{d}{dt} \mu_{1;1}^{(0)}\} \\ &\quad + m_2 \{\mu_{1;2}^{(0)}\}^{m_2 - 1} \left\{ \sum_{\substack{\mathcal{A}=1 \\ \mathcal{A} \neq 2}}^s \pi_{\mathcal{A}} \{\mu_{1;\mathcal{A}}^{(0)}\}^{m_{\mathcal{A}}} \right\} \{R_2(\mu_{1;1}^{(0)}, \mu_{1;2}^{(0)}, \dots, \mu_{1;s}^{(0)}) - \frac{d}{dt} \mu_{1;2}^{(0)}\} \\ &\quad \vdots \\ &\quad + m_s \{\mu_{1;s}^{(0)}\}^{m_s - 1} \left\{ \sum_{\mathcal{A}=1}^{s-1} \pi_{\mathcal{A}} \{\mu_{1;\mathcal{A}}^{(0)}\}^{m_{\mathcal{A}}} \right\} \{R_s(\mu_{1;1}^{(0)}, \mu_{1;2}^{(0)}, \dots, \mu_{1;s}^{(0)}) - \frac{d}{dt} \mu_{1;s}^{(0)}\} \\ &\quad ; m_1 + m_2 + \dots + m_s > 1 \end{aligned} \quad (5.46)$$

where the product symbol π is simply defined by

$$\prod_{A=1}^s Y_A = Y_1 Y_2 \dots Y_s \quad (5.47)$$

Again, the leading term in the sum on the left hand side of equation (5.46) disappears by virtue of the normalization (5.43), and there is no new information in the equations for $m_1 + m_2 + \dots + m_s = 1$. This loss of information is again made up by the overall material balances (5.41) for $j = 1$.

$$\frac{d\mu_{1;A}^{(1)}}{dt} + \mu_{1;A}^{(1)} - \int R_A(\underline{y}) p^{(1)}(\underline{y}, t) d\underline{y} = 0$$

$$A = 1, 2, \dots \quad (5.48)$$

The steady state case, for which the equations are all algebraic, will be discussed in a later section. For the transient case, if the rate expressions R_A are polynomials, each of degree $\leq M$ in each argument, then (5.48) relates the rates of change $d\mu_{1;A}^{(1)}/dt$, to the moments of $p^{(1)}$ with each $m < M$. Taking equation (5.46) for $m_1, m_2, \dots, m_s$ each running from 0 to M , (but excluding $m_1 + m_2 + \dots + m_s = 0, 1$), one can solve this set of equations for these moments in terms of the $\mu_{1;A}^{(1)}$ for $A=1, \dots, s$. Substitution of the resulting expressions into the s material balance equations (5.48) then gives a set of s linear first order differential equations in the $\mu_{1;A}^{(1)}$ which can be solved by standard numerical or algebraic techniques. With the $\mu_{1;A}^{(1)}$ in hand, as many moments as desired can be generated by taking (5.46) for $m_1, m_2, \dots, m_s = 0, 1, 2, \dots$ independently, in turn, excluding $m_1 + m_2 + \dots + m_s = 0, 1$. Again,

the right hand sides of (5.46) depend only on the feed distribution p^* and $p^{(0)}$, the solution at perfect mixing, both of which are in hand at this point.

The same procedure applies as well to the higher $p^{(j)}$ of (5.37). Taking moments, one finds

$$\begin{aligned} \mu_{m_1 m_2 \dots m_s}^{(j)} &= \frac{1}{2^{\sum m_a - 1}} \sum_{n_1=0}^{m_1} \dots \sum_{n_s=0}^{m_s} \prod_{a=1}^s \binom{m_a}{n_a} \{\mu_{n_1 n_2 \dots n_s}^{(0)}\}^{m_a - n_a} \mu_{n_1 n_2 \dots n_s}^{(j)} \\ &= \sum_{i=1}^{j-1} \frac{1}{2^{\sum m_a}} \sum_{n_1=0}^{m_1} \dots \sum_{n_s=0}^{m_s} \prod_{a=1}^s \binom{m_a}{n_a} \mu_{n_1 \dots n_s}^{(i)} \mu_{m_1 - n_1, m_2 - n_2, \dots, m_s - n_s}^{(j-i)} \\ &\quad - \mu_{m_1 m_2 \dots m_s} + \sum_{a=1}^s m_a \int y_1^{m_1} \dots y_a^{m_a - 1} \dots y_s^{m_s} R_a(\underline{y}) p^{(j-1)}(\underline{y}, t) d\underline{y} \\ &\quad - \frac{d}{dt} \mu_{m_1 m_2 \dots m_s}^{(j-1)} \\ &\quad ; m_1 + m_2 + \dots + m_s > 1 \\ j &= 2, 3, \dots \end{aligned} \tag{5.49}$$

and for polynomial R_a , these equations can again be combined with the overall balance (5.41) to give a set of s linear first order differential equations in the $\mu_{1;a}^{(j)}$.

There is again, as successive values of j are taken, a cascading requirement for the number of moments of the earlier $p^{(j)}$, but these can as before be generated in turn once the basic set of differential equations has been solved. Finally, having evaluated the partial moments for as many

j as desired, one can see the effect of the mixing intensity on the overall reactor performances by assembling the s first moments from (5.38)

$$\mu_{1;a} = \mu_{1;a}^{(0)} + \frac{1}{\lambda} \mu_{1;a}^{(1)} + \frac{1}{\lambda^2} \mu_{1;a}^{(2)} + \dots$$

$$; a = 1, 2, \dots, s \quad (5.50)$$

V.4 Steady State Considerations

The foregoing analysis has all been very general, with the feed properties allowed to vary in time, and the output concentration calculated as a function of time. The analysis applies equally well of course under steady state conditions, with some simplifications in the methods required to solve the resulting equations. There are no longer any differential equations to be solved, but the procedure still depends upon having the rate expressions $R(y)$ in polynomial form.

Equation (5.4) becomes, at steady state,

$$\begin{aligned} \frac{d}{dy} \{R(y)p(y)\} &= p^*(j) - (1+\lambda)p(y) \\ &+ \lambda \int \int p(y')p(y'') \delta\left(\frac{y'+y''}{2} - y\right) dy' dy'' \end{aligned} \quad (5.51)$$

and the overall material balance (5.8) becomes

$$- \int R(y)p(y) dy = \mu_1^* - \mu_1 \quad (5.52)$$

After expansion of p in powers of $1/\lambda$, and separation of terms with like coefficients of λ , solving for $p^{(0)}$ gives

$$p^{(0)}(y) = \delta(y - \mu_1^{(0)}) \quad (5.53)$$

with $\mu_1^{(0)}$ determined by (5.52) as

$$\mu_1^{(0)} - R(\mu_1^{(0)}) = \mu_1^* \quad (5.54)$$

Equation (5.24) remains (with $\frac{d\mu_1^{(0)}}{dt} = 0$) but (5.25) becomes

$$\mu_1^{(1)} - \int R(y)p^{(1)}(y) dy = 0 \quad (5.55)$$

so that if $R(y)$ is a polynomial of degree M , then (5.55) is another independent relation among the first M moments of

$p^{(1)}$, and taking it together with (5.24) for $m = 2, 3, \dots, M$, one finds a set of M linear algebraic equations in $\mu_1^{(1)}, \mu_2^{(1)}, \dots, \mu_M^{(1)}$ which can be solved by standard numerical means. With these first M moments in hand, as many further moments as desired can be generated by taking (5.24) for $m = M+1, M+2, \dots$ etc. in turn.

Entirely similar results are obtained for the higher $p^{(j)}$ of (5.17) where now equation (5.26) is combined with the steady state version of (5.25)

$$\mu_1^{(j)} - \int R(y) p^{(j)}(y) dy = 0 \quad (5.56)$$

The cascading requirement of values of moments of the earlier $p^{(j)}$ remains and the partial moments are combined at the end as in (5.27) to show the effect of the mixing intensity on the overall reactor performance.

For the complex kinetics of section V.3, entirely similar considerations apply. Combination of equation (5.46) for $m_1, m_2, \dots, m_s$ each running from 0 to M (but excluding $\sum m_i = 0, 1$) with the steady state version of the s material balance equations (5.48) gives a self-contained set of $Ms+s-1$ linear algebraic equations in the leading moments of $p^{(1)}$. The same is true for the higher $p^{(j)}$ with (5.46), (5.48) replaced by (5.49), (5.41), and the total effect of mixing intensity on reactor performance is obtained as in (5.50).

CHAPTER VI

MOMENT CLOSING PROCEDURES

VI.1 The Method

In the preceding chapter, a method was outlined which permits solution of the moment equations (3.28) for large values of the mixing intensity parameter β when the kinetics are expressible as polynomials in the independent variables. In the present chapter, a method is described which can be used over the whole range of β from zero to infinity. This method, here called moment closing, is of the nature of the Gram-Charlier expansion and involves approximating the distribution p with a series of special functions so as to enable solution of an incomplete set of moment equations. However, this method has the disadvantage that, for systems with more than one independent variable, it is very difficult to arrive at suitable distributional forms to be used in approximating the distribution p . In addition, even for systems with one independent concentration variable, high order kinetics cause numerical complications in the solutions by this method. This is not true in the case of the expansion technique described earlier.

Consider the set of equations (3.28). Being an incomplete set of moment equations, they suggest use of the methods proposed in this chapter. In general, if the set of moment

equations describing a given distribution p is

$$\begin{aligned} f_1(\mu_1, \mu_2, \dots, \mu_r) &= 0 \\ &\vdots \\ f_n(\mu_1, \mu_2, \dots, \mu_r) &= 0 \end{aligned} \tag{6.1}$$

where the functional dependence of f_i on any particular μ_j may also involve the derivatives of that μ_j , then if $n < r$, the set of equations is incomplete and cannot be solved for the μ_j . However, if the distribution p is approximated by a standard type of n -parameter distribution, then the moments $\mu_{n+1}, \mu_{n+2}, \dots, \mu_r$ can be expressed in terms of the first n moments and the set of equations (6.1) will be closed. In general, the n parameters in the distribution may be allowed to vary in time so that a set of differential equations can be solved by this method as well.

For the system of equations (3.28), n can be any number at all, and for rate kinetics $R(y)$ expressed as a polynomial of order M , the r in (6.1) is equal to $M + n - 1$, so that for first order reactions, (3.28) is a closed set. The distributional form taken for p can involve any number of parameters, with the number of equations used being equal to the number of free parameters in the assumed distribution. It is apparent that the more free parameters a proposed distributional form has, the better able it will be to fit the real distribution, and hence the better the results will be.

Another consequence of the fact that the number of equations in (3.28) is unlimited, is that, after the set of equations has been solved for a given n by the above procedure, an

inherent check on the reliability of the results can be easily obtained by writing (3.28) for $i = n + 1$ and comparing the values of μ_{n+1} obtained from this equation to the value predicted by the proposed n -parameter distribution. In fact, as many checks as desired can be made by writing (3.28) for $i = n + 2, \dots$, etc. An alternate checking procedure would be to apply a more refined expression for the distribution in the manner to be described later, and to compare results obtained with the two expressions.

In the following sections, the Gamma distribution as used by Hulburt and Katz [23] and the Beta distribution, which seems to work a little better for the present application, will be presented as proposed moment-closing forms with which to approximate the distribution p .

VI.2 The Gamma Distribution

In outlining the moment closing technique, Hulburt and Katz introduce the Gamma distribution as a suitable basic form for many problems. This form will be used to represent the distribution so that equations (3.28) may be solved for the moments of the concentration distribution, p . Accordingly, the development by Hulburt and Katz for the Gamma distribution is recapitulated here, beginning with the expansion of $p(y)$ in terms of the Gamma distribution and associated Laguerre polynomials, that is, the polynomials which result from orthogonalization of the series $1, z, z^2, \dots$, with respect to the Gamma distribution as a weighting function. With the Gamma weighting function

$$w^{(\gamma)}(z) = \frac{1}{(\gamma-1)!} z^{\gamma-1} e^{-z} \quad ; \quad z > 0 \quad (6.2)$$

the Laguerre polynomials are

$$L_n^{(\gamma)}(z) = \sum_{j=0}^n (-1)^j \binom{n}{j} \binom{n+\gamma-1}{j} j! z^{n-j} \quad ; n = 0, 1, 2, \dots \quad (6.3)$$

These polynomials are orthogonal with respect to $w^{(\gamma)}$. That is,

$$\begin{aligned} & \int_0^\infty L_m^{(\gamma)}(z) L_n^{(\gamma)}(z) w^{(\gamma)}(z) dz \\ &= \begin{cases} 0 & ; m \neq n \\ \frac{n! (n+\gamma-1)!}{(\gamma-1)!} & ; m, n = 0, 1, 2, \dots \end{cases} \end{aligned} \quad (6.4)$$

Now, expanding $p(y)$ as

$$p(y) = \frac{\gamma}{a} w^{(\gamma)} \left(\frac{\gamma y}{a} \right) \sum_{n=0}^{\infty} \phi_n L_n^{(\gamma)} \left(\frac{\gamma y}{a} \right); \quad y > 0 \quad (6.5)$$

one finds

$$\phi_n = \sum_{j=0}^n (-1)^j \frac{\left(\frac{\gamma}{a} \right)^{n-j} (\gamma-1)!}{j! (n+\gamma-1-j)! (n-j)!} \mu_{n-j} \quad ; \quad n = 0, 1, 2, \dots \quad (6.6)$$

which gives for the first few terms

$$\left. \begin{aligned} \phi_0 &= 1 \\ \phi_1 &= \frac{\mu_1}{a} - 1 \\ \phi_2 &= \frac{\gamma \mu_2}{2a^2(\gamma+1)} - \frac{\mu_1}{a} + \frac{1}{2} \\ \phi_3 &= \frac{\gamma^2 \mu_3}{6a^3(\gamma+2)(\gamma+1)} - \frac{\gamma \mu_2}{2a^2(\gamma+1)} + \frac{\mu_1}{2a} - \frac{1}{6} \end{aligned} \right\} \quad (6.7)$$

The equations which relate higher moments to the first few moments can now be established for various approximations to the distribution $p(y)$. The simplest approximation is to take

$$\phi_j = 0 \quad ; \quad j > 0 \quad (6.8)$$

so that $p(y)$ is approximated by the two parameter Gamma distribution

$$\frac{\gamma}{a} w^{(\gamma)} \left(\frac{\gamma y}{a} \right) \quad (6.9)$$

Combining (6.7) with (6.8) gives

$$\begin{aligned}
 a &= \mu_1 \\
 \gamma &= \frac{a^2}{\mu_2 - a^2} \\
 &= \frac{\mu_1^2}{\mu_2 - \mu_1^2} \\
 \mu_3 &= \frac{2\mu_1^2}{\mu_2} - \mu_1 \mu_2
 \end{aligned} \tag{6.10}$$

Higher moments can similarly be expressed in terms of μ_1, μ_2 by successive use of the recurrence relation

$$\frac{\mu_{j+1}}{\mu_j} = j \frac{\mu_1^2}{\mu_2} - (j-1) \mu_1; j=1,2,\dots \tag{6.11}$$

With (6.10) and (6.11), all moments can be expressed in terms of μ_1, μ_2 and equations (3.28) can be solved by taking the equations for $i = 1, 2$ and expressing the right-hand sides in terms of μ_1, μ_2 through (6.10), (6.11) for polynomial kinetics. What results is a pair of differential equations of the form

$$\begin{aligned}
 \frac{d\mu_1}{dt} &= f_1(\mu_1, \mu_2) \\
 \frac{d\mu_2}{dt} &= f_2(\mu_1, \mu_2)
 \end{aligned} \tag{6.12}$$

which can in principle be solved by standard integration techniques given suitable initial conditions. At steady state, these two equations reduce to a pair of algebraic equations which usually require an iterative scheme (such as Newton-Raphson) for numerical solution.

A first refinement of the above procedure would be to take, in place of (6.8),

$$\phi_j = 0, \quad ; \quad j = 1, 2 \quad \text{or} \quad j \geq 4 \tag{6.13}$$

so that $p(y)$ is approximated by the three parameter Gamma

distribution

$$\frac{\gamma}{a} w^{(\gamma)} \left(\frac{\gamma \gamma}{a} \right) \{ 1 + \phi_3 L_3^{(\gamma)} \left(\frac{\gamma \gamma}{a} \right) \} \quad (6.14)$$

with ϕ_3 given as in (6.7). Combining (6.6) with (6.13) gives

$$a = \mu_1 \quad (6.15)$$

$$\gamma = \frac{a^2}{\mu_2 - a^2} = \frac{\mu_1^2}{\mu_2 - \mu_1^2}$$

as in (6.10), and also,

$$\begin{aligned} \mu_4 = & 12 \frac{\mu_2 \mu_3}{\mu_1} - 8 \frac{\mu_2^2 \mu_3}{\mu_1^2} - 18 \frac{\mu_2^3}{\mu_1^2} \\ & + 21 \frac{\mu_2^4}{\mu_1^3} - 6 \mu_1^2 \mu_2 \end{aligned} \quad (6.16)$$

$$\begin{aligned} \mu_5 = & 120 \frac{\mu_2^2 \mu_3}{\mu_1^2} - 170 \mu_2 \mu_3 + 60 \mu_1 \mu_3 \\ & - 216 \frac{\mu_2^4}{\mu_1^3} + 414 \mu_2^2 - 261 \mu_1 \mu_2^2 \\ & + 54 \mu_1^3 \mu_2 \end{aligned} \quad (6.17)$$

and so on. With (6.15), (6.16), (6.17), and higher order analogues, all moments can be expressed in terms of μ_1, μ_2, μ_3 , and equations (3.28) can be solved by taking $i = 1, 2, 3$ and expressing the right hand sides in terms of the first three moments through (6.16), (6.17) for polynomial kinetics. What results is a set of three differential equations of the form

$$\frac{d\mu_1}{dt} = f_1(\mu_1, \mu_2, \mu_3)$$

$$\frac{d\mu_2}{dt} = f_2(\mu_1, \mu_2, \mu_3) \quad (6.18)$$

$$\frac{d\mu_3}{dt} = f_3(\mu_1, \mu_2, \mu_3)$$

which can in theory be solved by standard integration techniques given suitable initial conditions. At steady state, these three equations reduce to three algebraic equations in three unknowns which can be solved Newton-Raphson style.

More refined procedures can be established by leaving more and more of the ϕ_j free. For instance, an m-parameter Gamma distribution can be used to approximate $p(y)$ by taking in place of (6.8) or (6.13)

$$\phi_j = 0 \quad ; \quad j = 1, 2, \quad \text{or} \quad j \geq m+1 \quad (6.19)$$

and it is to be expected that as more ϕ_j are left free, the Gamma distribution will be better able to approximate the actual distribution $p(y)$. Some examples will serve to illustrate the method in a later chapter.

VI.3 The Beta Distribution

In the previous section, it was shown how the Gamma distribution could be used as the basis for the application of the moment closing technique to solve an incomplete set of moment equations such as (3.28). In this section, an entirely similar procedure will be described for the Beta distribution. Again the analysis begins with an orthogonalization of the series $1, y, y^2, \dots$ with respect to a weighting function, this time a Beta distribution weighting function

$$B(a,b)(y) = \frac{y^{a-1}(1-y)^{b-1}}{B(a,b)} \quad ; 0 < y \leq 1 \quad (6.20)$$

where the Beta function $B(a,b)$ is defined as

$$B(a,b) = \int_0^1 z^{a-1}(1-z)^{b-1} dz \quad (6.21)$$

It is to be noticed at once that with the weighting function of (6.20), y is confined to the range $0,1$. This is not really a restriction since y can easily be normalized so that it is confined to this range. Quite to the contrary, since y is naturally confined to be finite, then the Gamma representation (6.5) which allows for the entire positive range of $\gamma y/a$ can only be physically satisfied when γ is infinite (that is zero variance, as in the case of ideal mixing). This is not a serious contradiction, but it is one of the reasons that the Beta distribution is expected to perform better than the Gamma distribution in the present application.

The polynomials that result from orthogonalization of the series $1, y, y^2, \dots$ with respect to the weighting function

$B^{(a,b)}(y)$ are the Jacobi polynomials

$$G_n^{(a,b)}(y) = \sum_{j=0}^n (-1)^j \binom{n}{j} \frac{\binom{a+n-1}{j}}{\binom{a+b+2n-2}{j}} y^{n-j}$$

$$; n = 0, 1, 2, \dots \quad (6.22)$$

These polynomials are orthogonal with respect to $B^{(a,b)}(y)$.

That is,

$$\int_0^1 G_m^{(a,b)}(y) G_n^{(a,b)}(y) B^{(a,b)}(y) dy = \begin{cases} 0 & ; m \neq n \\ H_n(a,b) & ; m=n \end{cases} ; m, n = 0, 1, 2, \dots \quad (6.23)$$

where the normalization is given by

$$H_n(a,b) = \frac{(n!)^2}{(2n)!} \cdot \frac{\binom{a+n-1}{n} \binom{b+n-1}{n}}{\binom{a+b+2n-1}{2n} \binom{a+b+2n-2}{n}} \quad (6.24)$$

Now, expanding $p(y)$ as

$$p(y) = B^{(a,b)}(y) \sum_{n=0}^{\infty} \psi_n G_n^{(a,b)}(y) ; 0 \leq y \leq 1 \quad (6.25)$$

one finds

$$\psi_n = (n+1) \binom{a+b+2n-1}{n+1} B^{(a,b)} \sum_{j=0}^n (-1)^j \binom{n}{j} \binom{a+b+2n-2-j}{b+n-1} \mu_{n-j} ; n = 0, 1, 2, \dots \quad (6.26)$$

which gives, for the first few terms,

$$\psi_0 = 1$$

$$\psi_1 = \frac{(a+b)(a+b+1)}{b} \left(\frac{a+b}{a} \mu_1 - 1 \right)$$

$$\psi_2 = \frac{\frac{1}{2}(a+b+3)(a+b+2)(a+b+1)(a+b)}{b(b+1)} \cdot$$

$$\left(\frac{(a+b+2)(a+b+1)}{(a+1)a} \mu_2 - \frac{2(a+b+1)}{a} \mu_1 + 1 \right)$$

$$\psi_3 = \frac{(a+b+5)(a+b+4)(a+b+3)(a+b+2)(a+b+1)(a+b)}{6(b+2)(b+1)b} \cdot$$

$$\cdot \left\{ \frac{(a+b+4)(a+b+3)(a+b+2)}{(a+2)(a+1)a} \cdot \mu_3 \right.$$

$$\left. - \frac{3(a+b+3)(a+b+2)}{(a+1)a} \mu_2 + \frac{3(a+b+2)}{a} \mu_1 - 1 \right\}$$

(6.27)

Or, using the notation

$$a_j = a(a+1)(a+2) \dots (a+j-1) \quad (6.28)$$

(6.27) becomes

$$\psi_2 = \frac{(a+b)_4}{2b_2} \left\{ \frac{(a+b+1)_2}{a_2} \mu_2 - \frac{2(a+b+1)}{a} \mu_1 + 1 \right\}$$

$$\psi_3 = \frac{(a+b)_6}{6b_3} \left\{ \frac{(a+b+2)_3}{a_3} \mu_3 - \frac{3(a+b+2)_2}{a_2} \mu_2 + \frac{3(a+b+2)}{a} \mu_1 - 1 \right\}$$

(6.29)

As was done for the Gamma distribution, the equations which relate higher moments to the first few moments can now be established for various Beta distribution approximations to the distribution $p(y)$. The simplest approximation is again given by

$$\psi_j = 0 \quad ; \quad j > 0 \quad (6.30)$$

so that $p(y)$ is approximated by the two parameter Beta distribution

$$B(a,b)(y) \quad (6.31)$$

Combining (6.30) with (6.27) gives, after some manipulation,

$$\begin{aligned} a &= \mu_1 (\mu_1 - \mu_2) / (\mu_1 - \mu_1^2) \\ b &= (1 - \mu_1) (\mu_1 - \mu_2) / (\mu_1 - \mu_1^2) \\ \mu &= \frac{2\mu_1 - \mu_1 \mu_2 - \mu_2^2}{\mu_1 + \mu_2 - 2\mu_1^2} \cdot \mu_1 \end{aligned} \quad (6.32)$$

Higher moments can similarly be expressed in terms of μ_1, μ_2 by successive use of the recurrence relation

$$\frac{\mu_{j+1}}{\mu_j} = \frac{\mu_1 (\mu_1 - \mu_2) + j (\mu_2 - \mu_1^2)}{(\mu_1 - \mu_2) + j (\mu_2 - \mu_1^2)} \quad j = 1, 2, \dots \quad (6.33)$$

With (6.32) and (6.33), all moments can be expressed in terms of μ_1, μ_2 and equations (3.28) can be solved by taking

the equations for $i = 1, 2$ and expressing the right hand sides in terms of μ_1, μ_2 through (6.32), (6.33) for polynomial kinetics. What results is a pair of differential equations of the form (6.12) which once more, can be solved in principle by standard integration techniques given suitable initial conditions. At steady state, these two equations reduce to a pair of algebraic equations which can be solved by a Newton-Raphson iterative scheme.

A first refinement of the two parameter Beta distribution approximation is the three parameter approximation obtained by taking, in place of (6.30),

$$\psi_j = 0 \quad ; \quad j = 1, 2 \text{ or } j \geq 4 \quad (6.34)$$

so that $p(y)$ is approximated by the three parameter Beta distribution

$$B(a, b)(y) \{1 + \psi_3 G_3^{(a, b)}(y)\} \quad (6.35)$$

with ψ_3 given as in (6.29). Combining (6.26) with (6.34) gives

$$\begin{aligned} a &= \mu_1 (\mu_1 - \mu_2) / (\mu_2 - \mu_1^2) \\ b &= (1 - \mu_1) (\mu_1 - \mu_2) / (\mu_2 - \mu_1^2) \end{aligned} \quad (6.36)$$

as in (6.32), and also

$$\begin{aligned} \mu_4 &= \frac{4\mu_3(a+3)}{a+b+6} - \frac{3a}{(a+b)_2(a+b+3)(a+b+6)} \\ \mu_5 &= \frac{10\mu_3(a+3)_2}{(a+b+6)_2} - \frac{a_5(3a+3b+13)}{(a+b)_2(a+b+3)_2(a+b+6)_2} \end{aligned} \quad (6.37)$$

and so on, where the notation (6.28) has been used. With (6.36), (6.37), and higher order analogues, all the moments can be expressed in terms of μ_1, μ_2, μ_3 and equations (3.28) can be solved by taking $i = 1, 2, 3$ and expressing the right hand sides in terms of the first three moments through (6.36), (6.37) for polynomial kinetics. What results is a set of three differential equations of the form (6.18) which can in theory be solved by standard integration techniques given suitable initial conditions. At steady state, these three equations reduce to three algebraic equations in three unknowns which can be solved by a Newton-Raphson iterative technique.

More refined procedures can be established by leaving more and more of the ψ_j free. For instance, an m -parameter Beta distribution can be used to approximate $p(y)$ by taking in place of (6.30) or (6.34)

$$\psi_j = 0 \quad ; \quad j = 1, 2 \quad \text{or} \quad j \geq m+1 \quad (6.38)$$

and it is to be expected that as more ψ_j are left free, the Beta distribution will be better able to approximate the actual distribution $p(y)$. Some examples will serve to illustrate the method in a later chapter.

It should be noted that in the present work the moment closing method was not used as a primary source of numerical results, but rather as a means of spot-checking the distribution-free results obtained from the expansions at high mixing intensity.

CHAPTER VII

COMPARISON OF THE METHODS

VII.1 Restatement of the Problem

The general equation describing the effect of mixing in the mathematical model proposed by Curl for continuous stirred reactors was found in Chapter III to be

$$\begin{aligned}
 \frac{\partial p(y, t)}{\partial t} + \frac{\partial}{\partial y} \{R(y)p(y, t)\} \\
 = p^*(y, t) - p(y, t) \\
 + \frac{2\beta}{\alpha} \left\{ \int \int p(y', t) p(y'', t) \delta \left(\frac{y' + y''}{2} - y \right) dy' dy'' - p(y, t) \right\}
 \end{aligned}
 \tag{7.1}$$

where the distribution p depends on the dimensionless time t and the dimensionless concentration y . The parameter y may be, for example, yield or conversion. In equation (7.1), $R(y)$ is the dimensionless reaction rate, $2\beta/\alpha$ the dimensionless mixing intensity, and p^* is the feed distribution. Taking moments on (7.1) gives the set of equations

$$\begin{aligned}
 \frac{d\mu_i}{dt} = i \int R(y) y^{i-1} p(y, t) dy \\
 + (\mu_i^* - \mu_i) \\
 + \frac{2\beta}{\alpha} \left\{ \frac{1}{2^i} \sum_{j=1}^{i-1} \binom{i}{j} \mu_{i-j} \mu_j - \left(1 - \frac{1}{2^{i-1}}\right) \mu_i \right\} \\
 ; i = 1, 2, \dots,
 \end{aligned}
 \tag{7.2}$$

and it is noted that the term multiplied by $2\beta/\alpha$ vanishes for $i = 1$. In equation (7.2), μ_i and μ_i^* are the i^{th} moments of p and p^* respectively.

Equation (7.1), as already noted, can be solved for the distribution p only for the hypothetical perfectly mixed case. Equation (7.2) can be solved for the moments of p only for first order reactions. In the preceding two chapters, two methods were detailed which yield solutions to (7.2) for polynomial kinetics.

This chapter is given over to a comparison of the methods described earlier for a few simple kinetic examples. The inherent checks on third and fourth moments for the moment-closing methods of Chapter VI are incorporated, and where possible, the methods are checked at the extremes of mixing. The conclusions are amply supported and illustrated by graphs.

Although this chapter compares the various methods as equals, it is understood that the main body of results in the later chapters are chiefly obtained through the use of the expansion technique of Chapter V, and only spot-checked with the moment closing methods. The author prefers the expansion technique since it is distribution-free; that is, its use does not rely on the guessing of a suitable form for the distribution p .

For all the examples in this chapter, as well as for those in the later chapters, the calculations are carried out at steady state. The time-derivatives in (7.1) and (7.2) then vanish.

VII.2 First Order Reactions

The easiest example to use to compare the methods of solution is first order reactions. As was mentioned in a previous chapter, for this case (7.2) can be solved explicitly for the moments, so that none of the methods of Chapters V and VI are needed. The comparisons, then, have to be altered slightly for this case.

For first order reactions, with y as fractional conversion, the kinetics are given by

$$R(y) = \frac{k}{\alpha}(1-y) \quad (7.3)$$

and substitution of this expression into (7.2) at steady state yields

$$\begin{aligned} \mu_1 &= \frac{k/\alpha}{1+k/\alpha} \\ \mu_2 &= \frac{\frac{\beta}{\alpha}\mu_1^2 + 2\frac{k}{\alpha}\mu_1}{1 + 2\frac{k}{\alpha} + \frac{\beta}{\alpha}} \\ \mu_3 &= \frac{\frac{3}{2}\frac{\beta}{\alpha}\mu_1\mu_2 + 3\frac{k}{\alpha}\mu_2}{1 + 3\frac{k}{\alpha} + \frac{3}{2}\frac{\beta}{\alpha}} \\ \mu_4 &= \frac{\frac{4}{\alpha}\mu_3 + \frac{\beta}{\alpha}\mu_1\mu_2 + \frac{3}{4}\frac{\beta}{\alpha}\mu_2^2}{1 + 4\frac{k}{\alpha} + \frac{7}{4}\frac{\beta}{\alpha}} \end{aligned} \quad (7.4)$$

and so on, so that the moments may be generated in turn for any pair of values $\frac{k}{\alpha}$, β/α . The variance, σ^2 , is given by

$$\begin{aligned} \sigma^2 &= \mu_2 - \mu_1^2 \\ &= \frac{2\frac{k}{\alpha}\mu_1 - (1 + 2\frac{k}{\alpha})\mu_1^2}{1 + 2\frac{k}{\alpha} + \frac{\beta}{\alpha}} \end{aligned} \quad (7.5)$$

or

$$\frac{\sigma^2}{\mu_1^2} = \frac{1}{1 + 2\frac{k}{\alpha} + \frac{\beta}{\alpha}} \quad (7.6)$$

If one were to apply the methods of Chapter V to the kinetics (7.3), one would first of all find that the mean conversion, μ_1 , is independent of β/α since all the terms in the expansion after the first term vanish. The second result one would obtain is that the variance is given by

$$\begin{aligned} \frac{\sigma^2}{\mu_1^2} &= \frac{1}{\beta/\alpha} - \frac{1 + 2\frac{k}{\alpha}}{(\beta/\alpha)^2} + \frac{(1 + 2\frac{k}{\alpha})^2}{(\beta/\alpha)^3} \\ &= \frac{1}{\beta/\alpha} \sum_{i=0}^{\infty} \left(-\frac{1 + 2\frac{k}{\alpha}}{\beta/\alpha} \right)^i \end{aligned} \quad (7.7)$$

On comparing this result to (7.6), it is clear that the two results are equivalent when the series (7.7) converges. This series converges only if

$$\frac{\beta}{\alpha} > 2\frac{k}{\alpha} + 1 \quad (7.8)$$

so that, even for first order reactions, the expansion method will not yield a convergent series for the variance for values of β/α less than that given by (7.8). However, in the range of convergence of the series, it is clear that the series converges exactly to the proper result.

It is of interest at the present time to see how many terms are needed in the expansion to get a good result for representative values of $\frac{\beta}{\alpha}$ and $\frac{k}{\alpha}$. If, for instance, the second moment is desired for $\frac{k}{\alpha} = 10$ and $\frac{\beta}{\alpha} = 100$, then (7.4) gives

$$\mu_2 = .8333$$

but, from the expansion method, using only the first two corrections (that is, up to terms in $1/(\beta/\alpha)^2$, it is found that

$$\mu_2 = .8330$$

which is sufficiently close to the exact solution for the present purposes. It is noted that, in the example cited, the third correction term (the first unused term in the example) is 21% in absolute value of the preceding term. This fact will be useful later in deciding upon the number of terms in the expansion to be carried.

Expressions such as (7.7), (7.8) can also be found for higher moments. The forms (7.7) are quite complicated for third, fourth and higher moments, but it is noted that, for the expansion for the third moment, the convergence criteria is the same as (7.8).

A very convenient way of comparing the moment closing solutions to the actual solutions for first order reactions is to fix the free parameters in the assumed distribution by using the actual values of the appropriate number of moments, and then to compare higher moments as predicted by the distribution to the actual values of these moments. In using the two parameter distributions (6.9), (6.31), the parameters are fixed by the actual values of μ_1, μ_2 . Then equations (6.10), (6.11) or (6.32), (6.33) can be used to compare the actual third and fourth moments to those predicted by the distributions. For the three parameter distributions (6.14), (6.35), the actual values of μ_1, μ_2, μ_3 are required. Then the predicted values of μ_4 (6.16), (6.37) can be compared to the

actual values for various values of $\frac{\beta}{\alpha}$, $\frac{k}{\alpha}$.

The results of the above comparisons clearly show at once that the Beta distribution approximation is far better than the Gamma approximation, at least for first order kinetics. All the assumed distributional forms give perfect answers at ideal mixing ($\beta = \infty$) but only the two Beta approximations (6.31 and 6.35) match perfectly at the other extreme - complete segregation ($\beta = 0$). This is true because, at $\beta = 0$, the distribution $p(y)$ for first order reactions at steady state is given by

$$p(y) = \frac{\alpha}{k} (1-y)^{\left(\frac{\alpha}{k} - 1\right)} \quad (7.9)$$

which is actually a Beta distribution of the type (6.31) or (6.35) with parameters $a = 1$, $b = \alpha/k$, $\psi_3 = 0$.

In comparing the two-parameter distributions to the corresponding three parameter forms, there is no question that, in all cases, the three parameter forms are at least as good as the corresponding two parameter forms. It is also noticed, that as β/α decreases, the Gamma distribution approximations (6.9 and 6.14) grow worse steadily. This can possibly be due to the physical unreality of having an unbounded concentration, a shortcoming which was mentioned earlier as the reason the Beta distribution forms would be expected to yield better results than the Gamma approximations. It is further noted, that if interest lies in the low range of β/α , then the moment closing technique utilizing the Beta approximation forms gives excellent results, whereas the expansion method of Chapter V fails to yield any results at all.

However, the latter technique is tailor made for the range of large β/α which in practical cases, is the area of predominant interest.

A few typical results for fourth moments are shown in Table 1. It is immediately noticeable that the three parameter Beta distribution is the best approximation of the four shown. If the two parameter approximations for the Beta and Gamma distributions are compared, it appears that, in some cases, the Gamma distribution gives better results. However, for these two approximation forms, the two parameter Beta approximation always gives values of μ_3 , the third moment, closer to the actual values than does the two parameter Gamma approximation.

These results are shown perhaps more clearly in Figures 1 and 2. In Figure 1, both actual values of the third moment and values given by the two parameter distribution approximations are plotted vs. reaction rate constant k/α for $\beta/\alpha = 0, 10, \infty$. At $\frac{\beta}{\alpha} = 0$, the solid curve is for the actual values as well as for the two parameter Beta distribution. At $\frac{\beta}{\alpha} = 10$, the Beta distribution values disagree only very slightly with the actual values in the middle of the range of $\frac{k}{\alpha}$. At $\beta/\alpha = \infty$, all the curves coincide. This shows clearly that the Beta distribution is better able to approximate the real distribution for first order kinetics. Further proof is given in Figure 2, where fourth moments are plotted for the various distributions. Not shown is the three parameter Beta distribution, since these values all lie so close to the actual values that, on this figure, the lines would be coincidental for the two. The three parameter Gamma approximation is seen to be always better than the two parameter Gamma approxi-

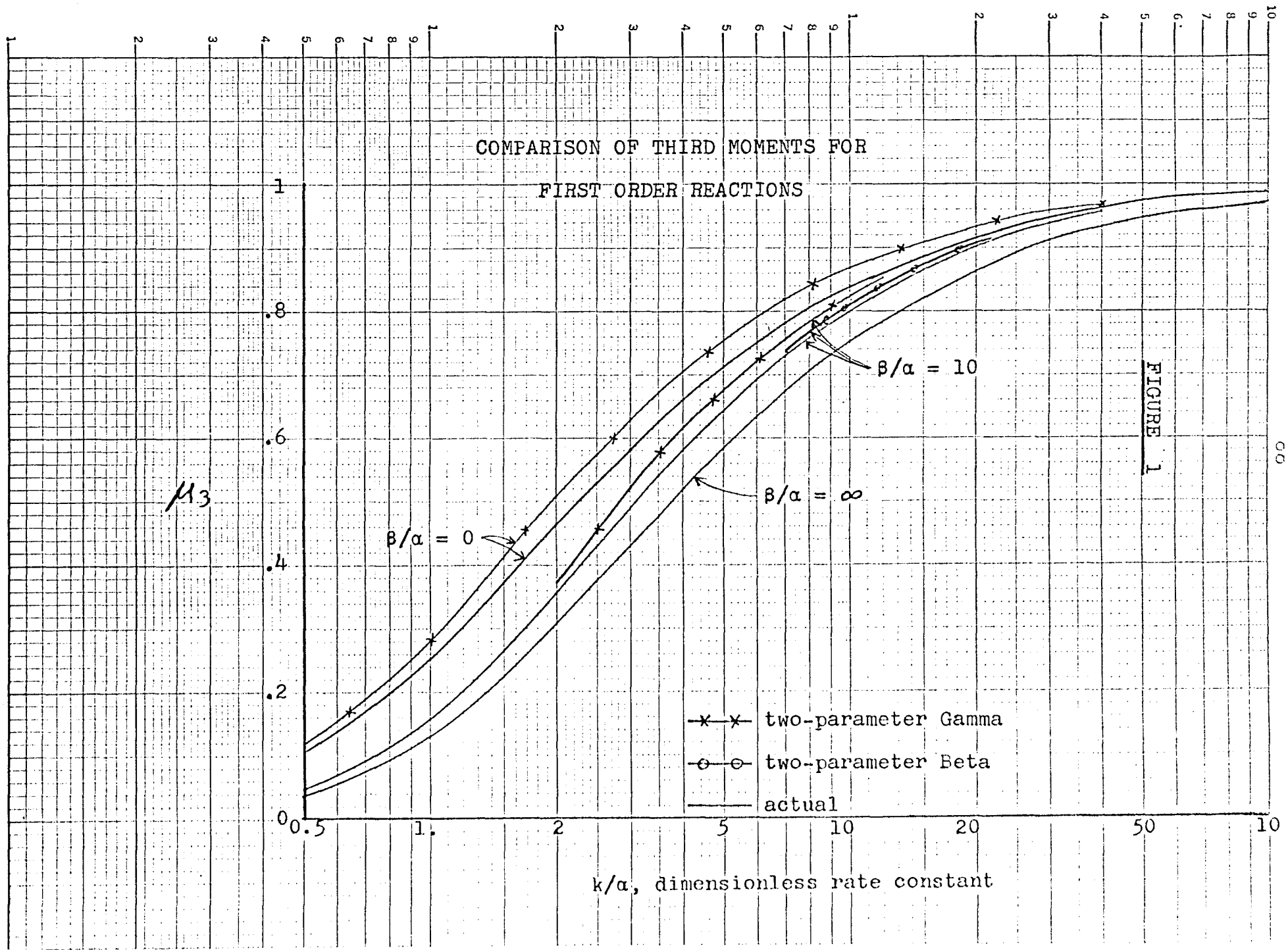
TABLE 1

VALUES OF THE FOURTH MOMENT FOR FIRST ORDER REACTIONS--
 ACTUAL VALUES AS COMPARED TO THOSE
 PREDICTED BY MOMENT CLOSING METHODS

$\frac{k}{\alpha}$	$\frac{\beta}{\alpha}$	μ	A	B	C	D
1	100	.0649	.0662	.0646	.0658	.0645
5	100	.4994	.5073	.4980	.5058	.4968
10	100	.7053	.7141	.7043	.7135	.7019
20	100	.8456	.8527	.8453	.8542	.8422
10	50	.7212	.7331	.7206	.7355	.7154
10	10	.7724	.7829	.7730	.8069	.7581
10	1	.8110	.8129	.8112	.8614	.7899
10	0	.8174	.8174	.8174	.8705	.7951

Code

A : μ_4 from 2-par. Beta approx. (6.31)
 B : μ_4 from 3-par. Beta approx. (6.35)
 C : μ_4 from 2-par. Gamma approx. (6.9)
 D : μ_4 from 3-par. Gamma approx. (6.14)



COMPARISON OF FOURTH MOMENTS FOR FIRST ORDER REACTIONS

μ_4

$\beta/\alpha = 0$

$\beta/\alpha = 10$

$\beta/\alpha = \infty$

- x-x- two-parameter Gamma
- - - three-parameter Gamma
- o-o- two-parameter Beta
- actual

k/α , dimensionless rate constant

FIGURE 2

mation, although not always better than the two parameter Beta distribution. Once again, at $\beta/\alpha = 0$, the Beta distribution values coincide with the actual values, and at $\beta/\alpha = \infty$, all the values fall on the same curve.

The graphs clearly indicate that the Beta distribution more closely approximates the actual distribution for the present case. The distribution-free results using the methods of Chapter V are better (in fact they are exact) where the series converges, and are especially useful for large values of β/α . The remaining examples in this chapter will reinforce this belief.

VII.3 Second Order Reactions

Since for first order reactions the methods of Chapters V and VI are not required, other investigators [22,36,39] using Curl's mixing model have focused their attention on second order reactions. For this case, again with y as fractional conversion, the kinetics are given by

$$R(y) = \frac{k}{\alpha} c_0 (1-y)^2 \quad (7.10)$$

where c_0 is the concentration of reagent in the feed stream. Substitution of (7.10) into (7.2), at steady state, gives

$$\begin{aligned} \mu_1 &= \frac{kc_0}{\alpha} (1-2\mu_1+\mu_2) \\ \mu_2 + \frac{\beta}{\alpha} (\mu_2-\mu_1)^2 &= \frac{2kc_0}{\alpha} (\mu_1-2\mu_2+\mu_3) \\ \mu_3 + \frac{3}{2} \frac{\beta}{\alpha} (\mu_3-\mu_1\mu_2) &= \frac{3kc_0}{\alpha} (\mu_2-2\mu_3+\mu_4) \\ \mu_4 + \frac{\beta}{4\alpha} (7\mu_4-4\mu_1\mu_3-3\mu_2^2) &= \frac{4kc_0}{\alpha} (\mu_3-2\mu_4+\mu_5) \end{aligned} \quad (7.11)$$

where the feed has been taken to be product-free.

It is apparent that the set of equations (7.11) is not closed. The first equation involves μ_1 and μ_2 , and each additional equation introduces another unknown moment, so that there is always one more unknown than equations available. These equations are readily solvable by direct methods, however, at the extremes of mixing--i.e.-- $\beta/\alpha = \infty$ and $\beta/\alpha = 0$. For the perfectly mixed case, equation (3.29) leads to

$$\mu_n = (\mu_1)^n \quad (7.12)$$

which, with (7.10), gives

$$\mu_1 = \frac{1 + 2\frac{kc_0}{\alpha} - \sqrt{1 + 4\frac{kc_0}{\alpha}}}{2\frac{kc_0}{\alpha}} \quad (7.13)$$

for the mean fractional conversion. For the completely segregated case $\left[\frac{\beta}{\alpha} = 0\right]$, the mean conversion is given by

$$\mu = \int_0^{\infty} C_B(t) f(t) dt \quad (7.14)$$

where $C_B(t)$ is the mean conversion at time t for second order reactions carried out in a batch reactor, and $f(t)$ is the residence time distribution (3.20). The time t in (7.14) is the same dimensionless time of equation (7.1), so that (3.20) becomes

$$f(t) = e^{-t} \quad ; \quad t > 0 \quad (7.15)$$

and with

$$C_B(t) = \frac{\frac{kc_0 t}{\alpha}}{1 + \frac{kc_0 t}{\alpha}} \quad (7.16)$$

equation (7.14) gives

$$\mu = \int_0^{\infty} \frac{\frac{kc_0 t}{\alpha}}{1 + \frac{kc_0 t}{\alpha}} e^{-t} dt \quad (7.17)$$

With the change of variable

$$\xi = e^{-t} \quad (7.18)$$

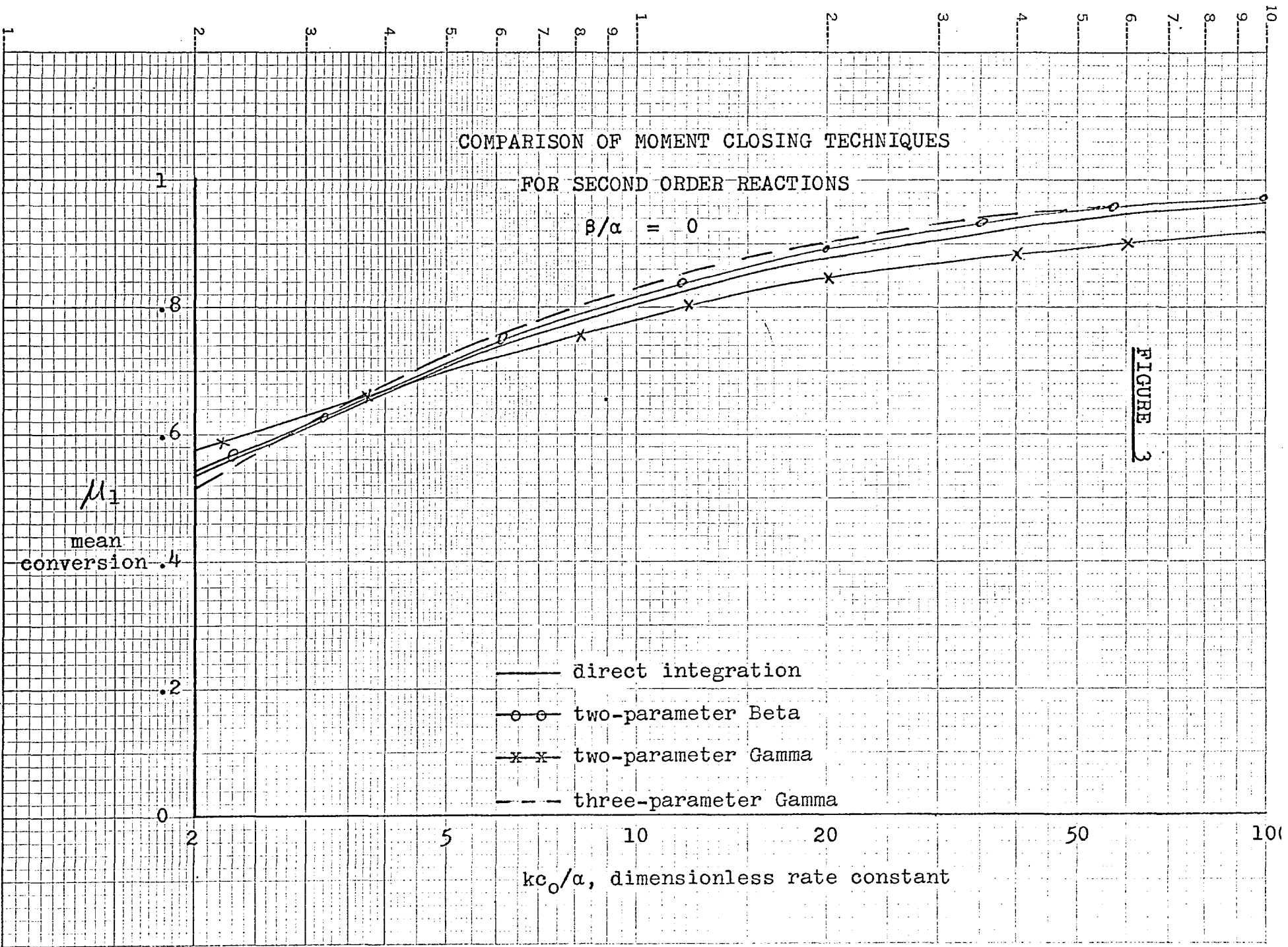
(7.17) becomes

$$\mu = \int_0^1 \frac{\ln(1/\xi)}{\frac{\alpha}{kc_0} + \ln(1/\xi)} d\xi \quad (7.19)$$

which can be numerically integrated using such standard techniques as the trapezoid rule or Simpson's rule.

For the case of ideal mixing, the solutions of Chapters V and VI agree exactly with (7.13). This is not true, however, for the completely segregated case, $\beta/\alpha = 0$. At this extreme, the methods of Chapter V no longer apply, but the moment closing methods of Chapter VI can be compared to the result of directly evaluating (7.19). This comparison is shown in Figure 3. It is quickly noticed from this figure that, of the curves shown, the 2 parameter Beta distribution gives the results closest to the direct integration results. The 3-parameter Beta distribution results are not shown, because to the precision of this figure, these results would virtually coincide with the results of the direct evaluation. So that, for $\beta/\alpha = 0$, the results obtained using the Beta distribution as an approximation to the actual distribution are far better than those obtained using the Gamma distribution. The methods of Chapter VI show that this is also true for small values of β/α , but as β/α increases, the results become less distinguishable.

For intermediate degrees of mixing, the set of equations (7.11) can be attacked by the methods of Chapters V and VI, and the results obtained by these methods may be compared to the results of other investigators. Spielman and Levenspiel [39] used a Monte Carlo approach of numerically simulating the physical situation as depicted by the mathematical mixing model. Shain [36] used an unsteady state computational procedure with an extrapolation modification. Hulburt and Akiyama [22] used the moment closing technique with the two parameter Gamma dis-



tribution form (6.9) as an approximation to $p(y)$. That the methods all agree very well can be seen by looking at Figure 4, where conversion is plotted as a function of k/α , with parameter β/α for the Beta distribution moment closer. The results of the other investigators are not distinguished since, to the accuracy of reading the published graphs, the results are in agreement. The expansion method, for $\beta/\alpha = 50, 200, 500$, gives results which coincide with those of the moment closing technique shown. For $\beta/\alpha = 5$, the results of the expansion method do not seem numerically to converge in the range of kc_0/α shown. These expansion results are shown in Table 2. The range of convergence of these expansions as one would estimate it numerically from the leading terms, is approximately given by

$$\beta > 3kc_0 + \alpha \quad (7.20)$$

so that for large kc_0/α , large values of β/α are required.

As mentioned in Chapter VI, the moment closing methods contain inherent checks on their reliability. These checks consist of comparing higher moments as given by the distribution with those obtained from the equations (7.11). It was found in all cases for the Beta distribution that the agreement is very good. For the Gamma distributions, the agreement is poor for low values of β/α but increasingly better as β/α increases.

Based on the results given here for second order reactions, the following conclusions can be drawn:

- 1) If interest centers around high values of β/α , then the expansion method of Chapter V, the easiest method to apply, is the preferred

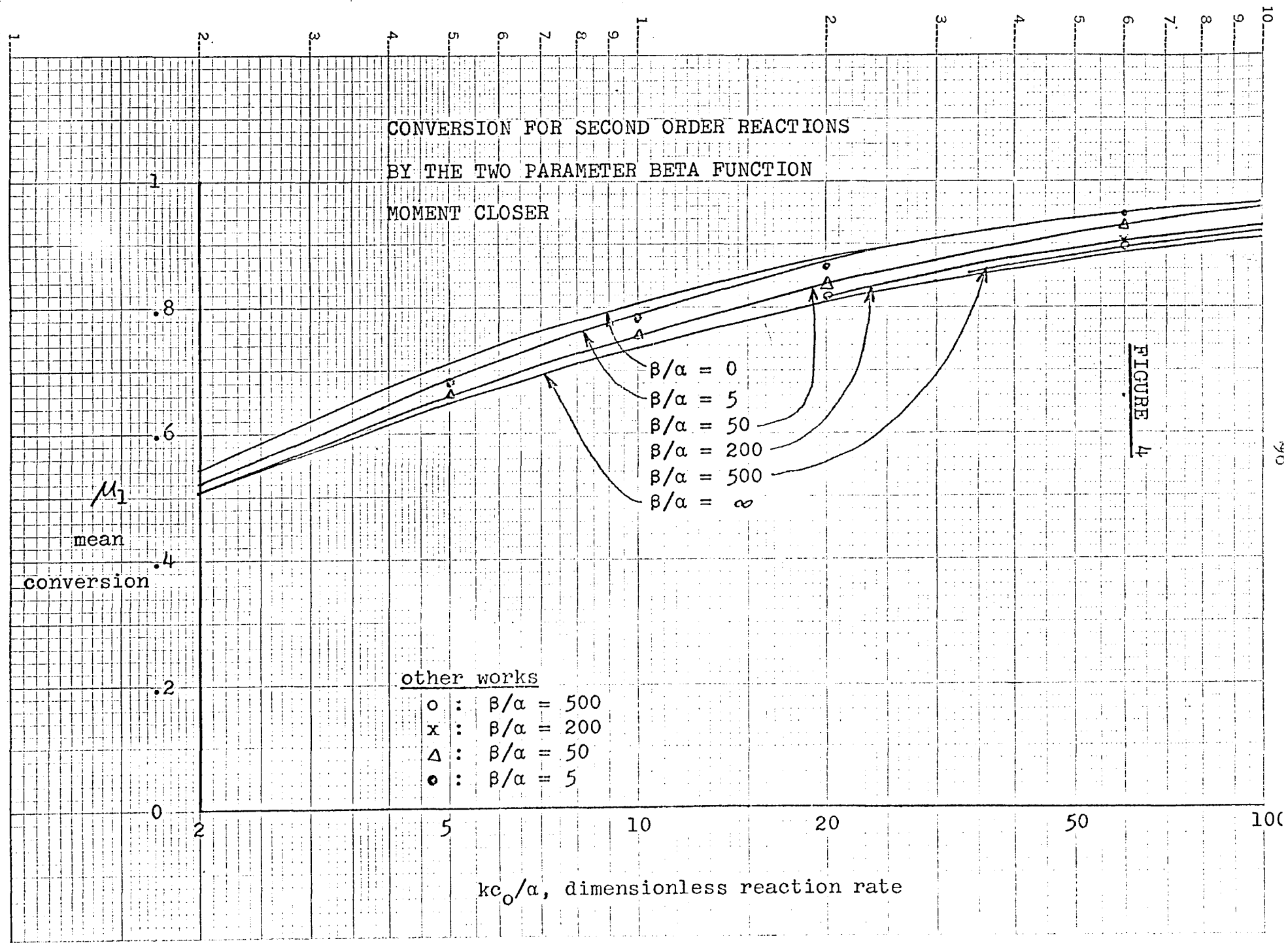


FIGURE 4

TABLE 2

SOLUTION FOR SECOND ORDER REACTIONS (7.10)
BY THE EXPANSION METHOD

$$\frac{kc_0}{\alpha} = 2$$

$$\mu_1 = 0.500 + \frac{0.167}{(\beta/\alpha)} - \frac{0.926}{(\beta/\alpha)^2} + \frac{6.00}{(\beta/\alpha)^3} \dots$$

$$\frac{kc_0}{\alpha} = 10$$

$$\mu_1 = 0.730 + \frac{0.832}{(\beta/\alpha)} - \frac{14.94}{(\beta/\alpha)^2} + \frac{338}{(\beta/\alpha)^3} \dots$$

$$\frac{kc_0}{\alpha} = 100$$

$$\mu_1 = 0.905 + \frac{4.09}{(\beta/\alpha)} - \frac{532}{(\beta/\alpha)^2} + \frac{94,700}{(\beta/\alpha)^3} \dots$$

method of solution. This method has the added feature of being distribution free.

- 2) If the whole range $0 < \beta/\alpha < \infty$ is of interest, then the moment closing technique using the two parameter Beta distribution is best. It is much easier to use than the three-parameter form, and more accurate than the Gamma approximations.

In the following chapters, the expansion method will be used to obtain all the results, with the two-parameter Beta distribution moment closer used to spot-check the results.

VII.4 A Third Example

In the previous two sections, first and second order reactions were considered. In this section, an artificial kinetic system is examined, suggested by the types of kinetics to be studied in Chapter IX. For this case,

$$R(y) = \frac{kc_0}{\alpha} y(1-y) \quad (7.21)$$

where y may be thought of as fractional conversion and c_0 as feed concentration. For this system, with $y = 0$ in the feed stream, there can be no reaction until there is mixing, and even then, the system must be ignited. In the steady state analysis, the system is considered to be in the ignited state, and any material fed to the reactor must mix before it can undergo chemical reaction. Substitution of (7.21) into (7.2) at steady state gives

$$\begin{aligned} \mu_1 &= \frac{kc_0}{\alpha} (\mu_1 - \mu_2) \\ \mu_2 + \frac{\beta}{\alpha} (\mu_2 - \mu_1)^2 &= \frac{2kc_0}{\alpha} (\mu_2 - \mu_3) \\ \mu_3 + \frac{3\beta}{2\alpha} (\mu_3 - \mu_1 \mu_2) &= \frac{3kc_0}{\alpha} (\mu_3 - \mu_4) \\ \mu_4 + \frac{\beta}{4\alpha} (7\mu_4 - 4\mu_1 \mu_3 - 3\mu_2^2) &= \frac{4kc_0}{\alpha} (\mu_4 - \mu_5) \end{aligned} \quad (7.22)$$

For the perfectly mixed case, (7.12) combined with (7.22) gives

$$\mu_1 = \frac{\frac{kc_0}{\alpha} - 1}{kc_0/\alpha} \quad (7.23)$$

for $kc_0 = \alpha$, and

$$\mu_1 = 0 \quad (7.24)$$

otherwise. The methods of Chapters V and VI will always be in agreement with the actual values at this extreme of mixing. At the other extreme, however, the expansion method no longer applies, and the moment closing methods based on the Gamma distribution approximation have, in some cases, extraneous or erroneous nonzero solutions at $\beta/\alpha = 0$. This is not true, however, for the Beta distribution moment closer. For the two parameter Beta approximation, at $\beta/\alpha = 0$, there is a clear contradiction if one tries to solve the set of equations without allowing for $\mu_1 = 0$. For the three parameter Beta approximation, this is not so clear since the equations are much more unwieldy, but no nonzero solutions for μ_1 were found in the range 0, 1 using this technique.

For intermediate values of β/α , the moment closing methods agree well with the results of the expansion method in the range where both apply. This range is approximately given by (7.20). For lower values of β/α , the Beta distributions give slightly better results, based on the inherent checks on the third and fourth moments. For very low values of β/α , the Gamma distribution results are completely unreliable.

In Figure 5, mean conversion is shown as a function of reaction rate constant for various values of mixing intensity. As kc_0/α decreases, the effect of lowering β/α is more pronounced, but for all kc_0/α , there can be no reaction without mixing, as shown by the line for $\beta/\alpha = 0$. In Figure 6, the variance is also shown, as determined by the expansion method

MEAN CONVERSION FOR $R(y) = \frac{kc_0}{\alpha} y (1-y)$
 BY THE TWO PARAMETER BETA FUNCTION MOMENT
 CLOSING TECHNIQUE

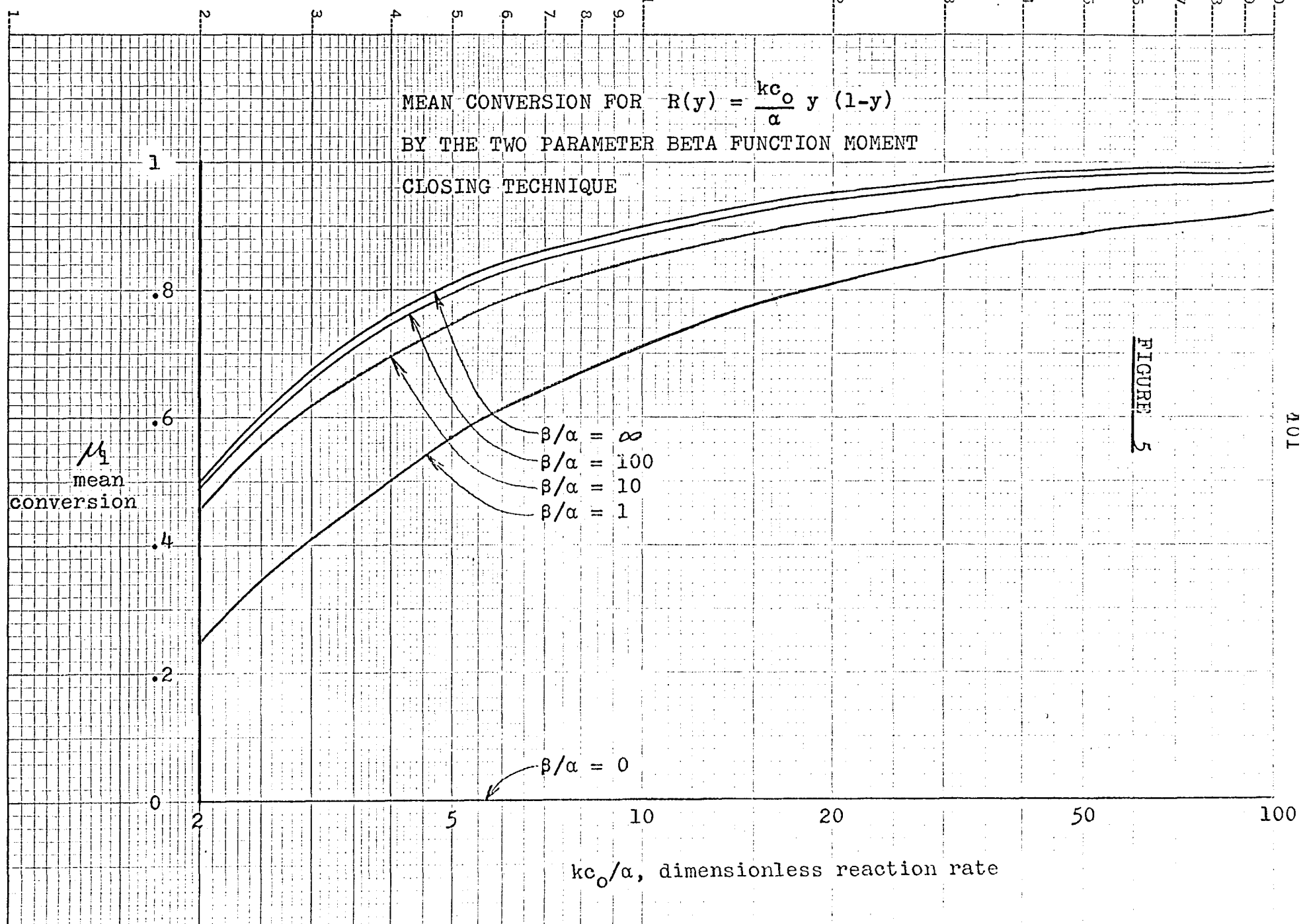
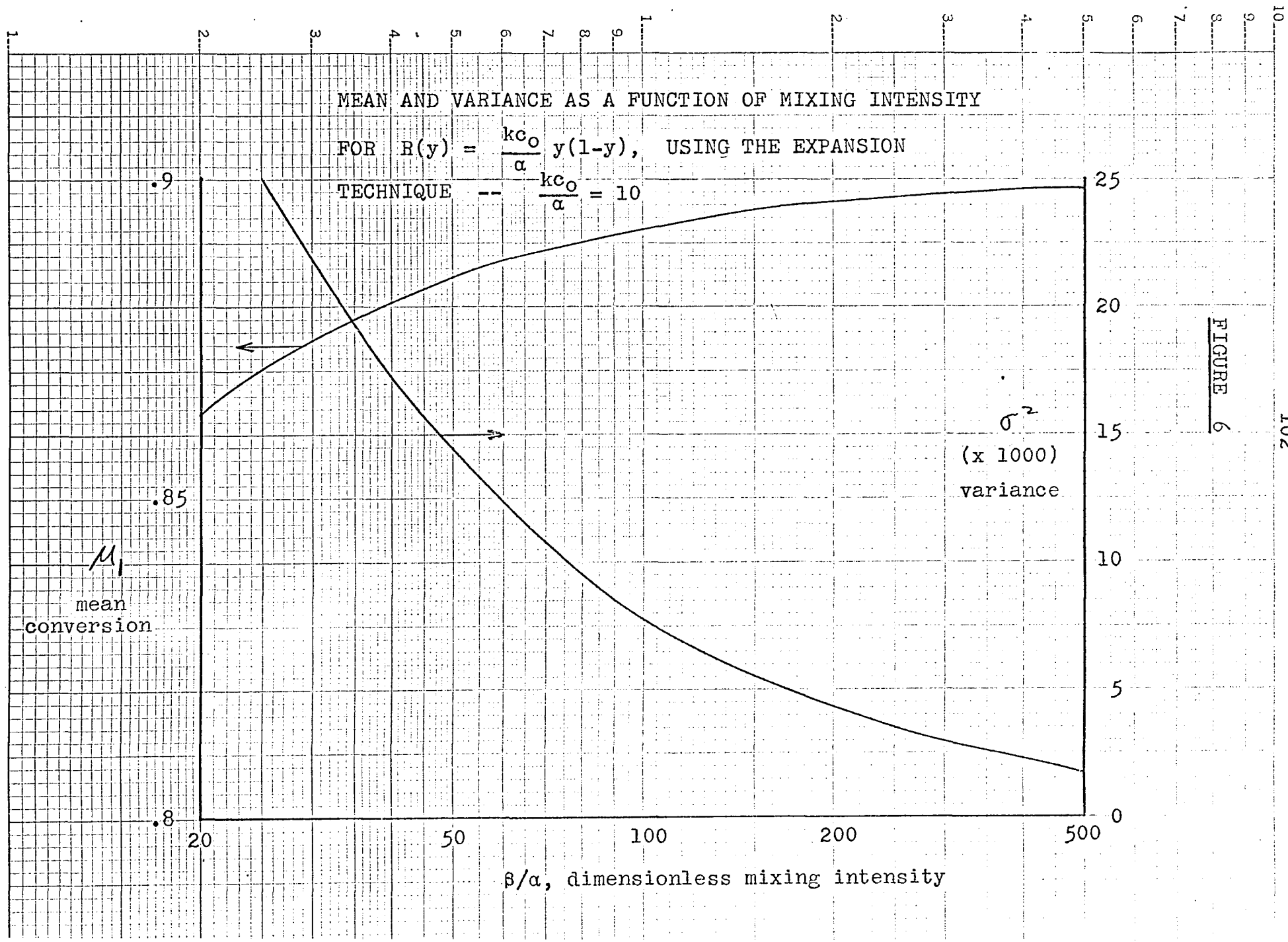


FIGURE 5

FIGURE 6



for $kc_0/\alpha = 10$. For this reaction system, the variance is zero at both extremes of mixing, so that it is obvious that it reaches a maximum at some finite mixing intensity. Indeed, one can find bounds on σ^2 , since

$$0 \leq \mu_2 \leq \mu_1 \leq 1$$

and

$$\sigma^2 = \mu_2 - \mu_1^2$$

so that

$$\sigma^2 \leq \mu_1(1-\mu_1) \quad (7.25)$$

The results of this section reinforce the conclusions drawn at the end of the previous section. The body of results to follow will be obtained using the expansion method, except where specifically stated otherwise. No further results will be obtained using the Gamma distribution or the 3 parameter Beta distribution.

CHAPTER VIII

APPLICATION TO VARIOUS REACTION SYSTEMS

VIII.1 The Question of Scale-Up

In the preceding chapters, methods were developed to predict the effect of mixing on homogeneous chemical reactions. This work can now be summarized into a design and scale-up procedure for stirred tank reactors. The method as described is limited to reactants which are completely miscible, but it can be extended to certain heterogeneous reaction systems.

In the design of stirred tank reactors (either continuous or batch), two types of problems generally arise. The first is the design of such a reactor to carry out a specific reaction whose overall kinetics is known. The problem of present concern is to scale-up such a reactor on the basis of small-scale laboratory experiments. For single simple one path reactions, the only concern is that the conversion is not adversely affected, and this can be assured by the use of safety factors. The more complex and challenging case is when product quality might be affected by the scale-up, and in this case there is no way of compensating for the lack of precise knowledge by the use of a larger reactor volume. This can be especially critical in systems involving nucleation such as crystallization and certain polymerization processes, where the nucleation might be very sensitive to relatively small deviations in local concentrations.

The problem of scaling up a homogeneous reaction is therefore basically to evaluate the effect of mixing on the reaction. The overall mixing time is really the important criterion, and as was shown in Chapter II, it is impractical to try to hold this constant during scale-up. Although, as compared to other continuous reactors, the design of stirred tank reactors leaves much greater freedom, as the mixing time may be adjusted independently of the residence time and reactor scale, the mixing time is only subject to limited control.

If the kinetics of all possible undesired side reactions is at least approximately known, then the methods of Chapters V and VI can be used to estimate the minimum value of β/α necessary to guarantee the specifications. In some cases, there may be a maximum value of β/α -- that is, mixing may have a detrimental effect. Thus for example, in the homogeneous second order reaction of section VII.3, a degree of segregation different from zero improves conversion.

It is not practical, however, to control the mixing so that it is incomplete, while maintaining good agitation heat transfer. If no agitation is necessary, a plug flow reactor should be used. If mixing is necessary, then a cascade of stirred tanks may be the answer. In the cases of present interest, mixing is necessary to promote contact between species or to minimize by-product formation.

If it becomes impractical to obtain a sufficiently high value of β/α in a very large reactor, several smaller reactors connected in parallel might provide simpler and cheaper solution. Also, as was mentioned in Chapter II, agitator design

and location of feed pipes plays an important role. Although there is insufficient data in this area, it appears evident that the use of multiple agitators and multiple feed injections can considerably increase β/α without increasing the power requirements.

VIII.2 General First Order Kinetics

Before discussing some interesting examples of complex kinetics, it will be shown that for all systems of first order reactions, any measure of mean conversion is independent of the micro-mixing. Consider the system of first order reactions where the i^{th} concentration component y_i behaves in batch according to

$$\frac{dy_i}{dt} = \sum_{j=1}^s a_{ij} y_j \quad ; \quad i = 1, 2, \dots, s \quad (8.1)$$

Equation (3.15) gives

$$\begin{aligned} \frac{\partial p(\underline{y}, t)}{\partial t} + \sum_{i=1}^s \sum_{j=1}^s a_{ij} \frac{\partial}{\partial y_i} \{ y_j p(\underline{y}, t) \} \\ = \alpha p^*(\underline{y}, t) - (\alpha + 2\beta) p(\underline{y}, t) \\ + 2\beta \int \int p(\underline{y}', t) p(\underline{y}'', t) \delta \left(\frac{\underline{y}' + \underline{y}''}{2} - \underline{y} \right) d\underline{y}' d\underline{y}'' \end{aligned} \quad (8.2)$$

Multiplying by y_n and integrating gives

$$\begin{aligned} \frac{d\mu_{1;n}}{dt} - \sum_{j=1}^s a_{nj} \mu_{1;j} = \alpha (\mu_{1;n}^* - \mu_{1;n}) \\ ; \quad n = 1, 2, \dots, s \end{aligned} \quad (8.3)$$

where $\mu_{1;i}$ is the i^{th} mean of p as in equation (5.34). The set of equations (8.3) constitutes s differential equations in the s unknowns $\mu_{1;1}$ through $\mu_{1;s}$; and with suitable initial conditions, can be solved for these time-varying quantities, independent of the value of β . This concludes the proof.

As an example, consider the consecutive first order reaction scheme



and denote the mole fractions of A and B by y_1 and y_2 respectively. Then the batch reaction rate equations are

$$\begin{aligned} \frac{dy_1}{dt} &= -k_1 y_1 \\ \frac{dy_2}{dt} &= k_1 y_1 - k_2 y_2 \end{aligned} \quad (8.5)$$

and with the feed being pure A (mole fraction of one), equation (8.3) becomes

$$\begin{aligned} \frac{d\mu_{1;1}}{dt} + k_1 \mu_{1;1} &= \alpha(1 - \mu_{1;1}) \\ \frac{d\mu_{1;2}}{dt} - k_1 \mu_{1;1} + k_2 \mu_{1;2} &= -\alpha \mu_{1;2} \end{aligned} \quad (8.6)$$

If the reactor initially contains inert material, so that the initial conditions are

$$\mu_{1;1}(0) = \mu_{1;2}(0) = 0$$

(8.6) can be solved to give

$$\begin{aligned} \mu_{1;1} &= \frac{\alpha}{k_1 + \alpha} \left(1 - e^{-(k_1 + \alpha)t} \right) \\ \mu_{1;2} &= \frac{\alpha k_1}{(\alpha + k_1)(\alpha + k_2)} \left(1 - e^{-(\alpha + k_2)t} \right) \\ &+ \begin{cases} \frac{\alpha k_1}{\alpha + k_1} t e^{-(\alpha + k_1)t} & ; k_1 = k_2 \\ \frac{\alpha k_1}{\alpha + k_1} \cdot \frac{e^{-(\alpha + k_1)t} - e^{-(\alpha + k_2)t}}{k_1 - k_2} & ; k_1 \neq k_2 \end{cases} \end{aligned} \quad (8.7)$$

and denoting the concentration of C by y_3 gives

$$\mu_{1;3} = 1 - \mu_{1;1} - \mu_{1;2} \quad (8.8)$$

These are of course just the familiar results for an ideally stirred tank reactor.

VIII.3 The Use of the Expansion Method

In Chapter V, a method was outlined for solving the non-linear integro-differential equation (3.5) which results from application of Curl's mathematical mixing model to quite general reaction systems. The present section is given over to the steady state solution of an example for a common reaction system where reagents A and B react to form products as follows



Raw materials A and B can be fed either separately or as one premixed feed.

Denoting the concentrations (mole fractions) of A and B by y_1 and y_2 respectively, the reaction rates are given by

$$\begin{aligned} \frac{dy_1}{dt} &= - \frac{kc_0}{\alpha} y_1 y_2 \\ \frac{dy_2}{dt} &= - \frac{kc_0}{\alpha} y_1 y_2 \end{aligned} \quad (8.10)$$

where c_0 is the total concentration of reagents A and B in the feed, and the α appears since time is taken as dimensionless time, measured in multiples of $1/\alpha$. Equation (5.22) gives $p^{(0)}$ as

$$p^{(0)}(y_1, y_2) = \delta(y_1 - \mu_{10}^{(0)}) \delta(y_2 - \mu_{01}^{(0)}) \quad (8.11)$$

where the mean values μ_{01} and μ_{10} are determined by the overall material balances (5.40)

$$\left. \begin{aligned} \mu_{10}^{(0)} + \frac{kc_0}{\alpha} \mu_{01}^{(0)} \mu_{10}^{(0)} &= \mu_{10}^* \\ \mu_{01}^{(0)} + \frac{kc_0}{\alpha} \mu_{10}^{(0)} \mu_{01}^{(0)} &= \mu_{01}^* \end{aligned} \right\} \quad (8.12)$$

which gives

$$\mu_{10}^{(0)} = \frac{- \left\{ 1 + \frac{kc_0}{\alpha} (\mu_{01}^* - \mu_{10}^*) \right\} + \sqrt{4 \mu_{10}^* \frac{kc_0}{\alpha} + \left\{ 1 + \frac{kc_0}{\alpha} (\mu_{01}^* - \mu_{10}^*) \right\}^2}}{2 \frac{kc_0}{\alpha}}$$

$$\mu_{01}^{(0)} = \mu_{10}^{(0)} + \mu_{01}^* - \mu_{10}^* \quad (8.13)$$

With $p^{(0)}$ in hand, the moments of $p^{(1)}$ are found by coupling (5.46) with the material balances (5.48). The latter become for this case

$$\left. \begin{aligned} \mu_{10}^{(1)} + \frac{k}{\alpha} \mu_{11}^{(1)} &= 0 \\ \mu_{01}^{(1)} + \frac{k}{\alpha} \mu_{11}^{(1)} &= 0 \end{aligned} \right\} \quad (8.14)$$

which together with (5.46) for $m_1 = m_2 = 1$

$$\begin{aligned} \mu_{11}^{(1)} - \frac{1}{2} \left[\mu_{01}^{(0)} \mu_{10}^{(1)} + \mu_{10}^{(0)} \mu_{01}^{(1)} + \mu_{11}^{(1)} \right] \\ = \mu_{11}^* - \mu_{01}^{(0)} \mu_{10}^{(0)} - \frac{kc_0}{\alpha} \mu_{10}^{(0)} \mu_{01}^{(0)} \left[\mu_{01}^{(0)} + \mu_{10}^{(0)} \right] \end{aligned} \quad (8.15)$$

can be solved for the moments of $p^{(1)}$ as

$$\mu_{11}^{(0)} = \frac{2 \{ \mu_{11}^{(0)} - \mu_{10}^{(0)} \mu_{01}^{(0)} - \frac{kc_0}{\alpha} \mu_{10}^{(0)} \mu_{01}^{(0)} [\mu_{01}^{(0)} + \mu_{10}^{(0)}] \}}{1 + \frac{kc_0}{\alpha} [\mu_{01}^{(0)} + \mu_{10}^{(0)}]}$$

$$\mu_{01}^{(1)} = \mu_{10}^{(1)} = - \frac{kc_0}{\alpha} \mu_{11}^{(0)}$$

(8.16)

Higher moments of $p^{(1)}$ may be evaluated by taking (5.46) for m_1, m_2 running up from zero as long as for any desired m_1, m_2 , for all previous pairs n_1, n_2 such that $n_1 \leq m_1, n_2 \leq m_2, n_1 + n_2 \leq m_1 + m_2$, the moments $\mu_{n_1 n_2}^{(0)}$ have already been evaluated.

The higher $p^{(j)}$ are handled in the same way, and are not shown here. However, equations (8.13) and (8.16) will be evaluated for some simple cases.

Case 1

The first case to be examined is that of separate feed lines for reagents A and B. For this case, the feed distribution is given by (see 4.23)

$$p^*(y_1, y_2) = \phi \delta(y_1 - y_1^0) \delta(y_2)$$

$$+ (1 - \phi) \delta(y_1) \delta(y_2 - y_2^0)$$

(8.17)

where ϕ is that fraction of the total feed represented by the feed containing reagent A. The relevant moments are then

$$\left. \begin{aligned} \mu_{10}^* &= y_1^0 \phi \\ \mu_{01}^* &= y_2^0 (1-\phi) \\ \mu_{11}^* &= 0 \end{aligned} \right\} \quad (8.18)$$

Taking $y_1^0 = y_2^0 = 1$, $\frac{kc}{\alpha} = 4$ and $\phi = \frac{1}{2}$ and using (8.13), the moments on $p^{(0)}$ are found to be

$$\mu_{10}^{(0)} = \mu_{01}^{(0)} = .25 \quad (8.19)$$

so that (8.16) gives

$$\begin{aligned} \mu_{11}^{(1)} &= -\frac{1}{8} \\ \mu_{01}^{(1)} &= \mu_{10}^{(1)} = \frac{1}{2} \end{aligned} \quad (8.20)$$

Assembling the moments as in (5.50) up to terms linear in $\frac{1}{\lambda}$ gives

$$\mu_{01} = \mu_{10} = \frac{1}{4} + \frac{1}{2\lambda} + \dots \quad (8.21)$$

Premixed feed, as will be seen below, has different behavior.

Case 2

The second case is that of premixed feeds for which

$$p^*(y_1, y_2) = \delta(y_1 - y_1^0) \delta(y_2 - y_2^0) \quad (8.22)$$

and the relevant moments of p^* are

$$\left. \begin{aligned} \mu_{01}^* &= y_2^0 \\ \mu_{10}^* &= y_1^0 \\ \mu_{11}^* &= y_1^0 y_2^0 \end{aligned} \right\} \quad (8.23)$$

For $y_1^0 = y_2^0 = \frac{1}{2}$ and $\frac{kc_0}{\alpha} = 4$, equation (8.13) gives the same results as indicated in (8.19). Equation (8.16) then gives

$$\left. \begin{aligned} \mu_{11}^{(1)} &= \frac{1}{24} \\ \mu_{01}^{(1)} &= \mu_{10}^{(1)} = -\frac{1}{6} \end{aligned} \right\} \quad (8.24)$$

Assembling the moments as in (5.50) up to linear terms now gives

$$\mu_{01} = \mu_{10} = \frac{1}{4} - \frac{1}{6\lambda} + \dots \quad (8.25)$$

so that, up to first order terms, mixing hurts the reaction. This result could have been predicted qualitatively since for premixed stoichiometric feeds, the reaction system (8.9) is equivalent to a simple second order reaction system. Thus (8.25) would have been obtained for the solution to the reaction system



with $c_0 = \frac{1}{2}$ and $\frac{kc_0}{\alpha} = 2$

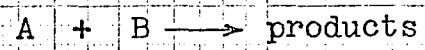
VIII.4 Bimolecular Reactions

In the previous section, the use of the expansion method was illustrated for the case of bimolecular reactions where reagents A and B react to form products according to (8.9). This section is given over to an illustration of some typical results for the case of A and B fed separately, with the feed distribution p^* given as in (8.17). The results are all obtained by the expansion method illustrated earlier with two separate feeds of pure A and pure B.

In Figure 7, the effect of mixing is clearly shown. Without mixing, no reaction can occur, as shown by the line for $\beta/\alpha = 0$. As β/α increases, the fractional conversion increases up to a limiting value for perfect mixing. The results shown in Figure 7 are in direct contrast to the results obtained by Spielman and Levenspiel [39] using a Monte Carlo approach. Their results are suspect since they do not agree with the known perfect-mixing behavior.

To compare the results shown in Figure 4 to those of Figure 7, one must multiply the dimensionless reaction rate constant of Figure 4 by two. This is true since mixing the two separate feeds for bimolecular reactions stoichiometrically is equivalent to halving the initial concentration for second order reactions when the mixing is ideal, thereby halving the effective value of $\frac{kc}{\alpha}$. Comparing these figures in this way clearly shows the different role mixing plays in the two cases. Increased mixing increases conversion for the bimolecular case with separate feeds, whereas increased mixing reduces conversion for the simple second order kinetics.

THE EFFECT OF MIXING INTENSITY ON BIMOLECULAR REACTIONS -- STOICHIOMETRIC FEED



fractional conversion

- $\beta/\alpha = \infty$
- $\beta/\alpha = 50$
- $\beta/\alpha = 25$
- $\beta/\alpha = 10$
- $\beta/\alpha = 2.5$

$\beta/\alpha = 0$

kc_0/α , dimensionless reaction rate constant

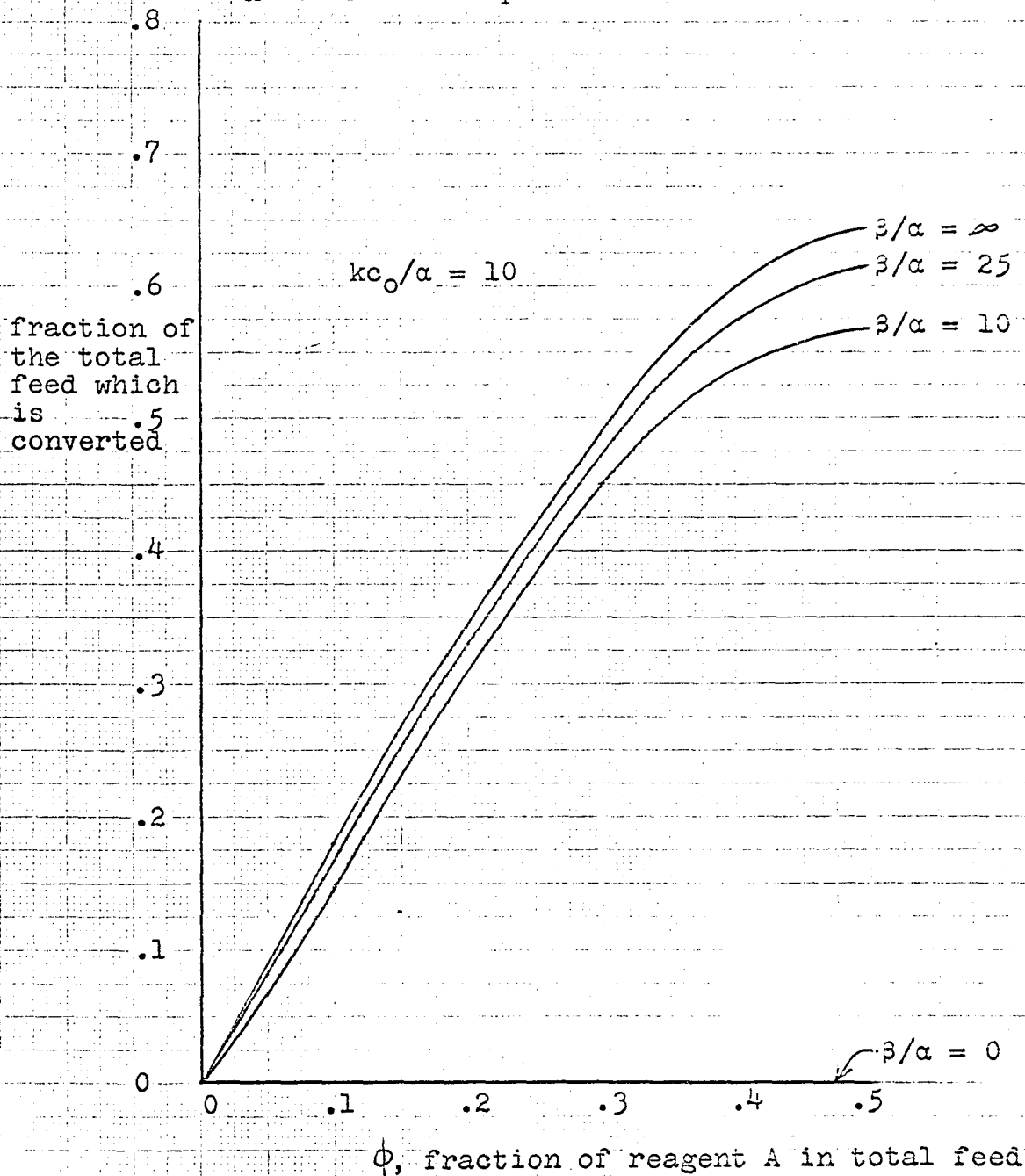
FIGURE 2

The effect of mixing becomes really pronounced for the bimolecular case as departures from ideal mixing become large.

In Figure 8, the effect of using an excess of either reagent is illustrated. This might be desirable if one of the reagents is very expensive and the other is cheap and easy to separate from the product. Figure 8 might then be useful in design or scale-up or in an economic optimization.

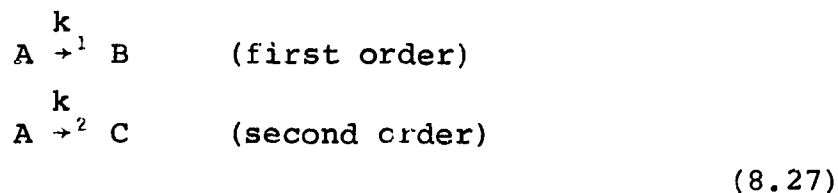
FIGURE 8

THE EFFECT OF MIXING INTENSITY ON BIMOLECULAR
REACTIONS -- NONSTOICHIOMETRIC FEED



VIII.5 Parallel Reactions

Consider the reaction system



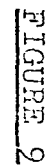
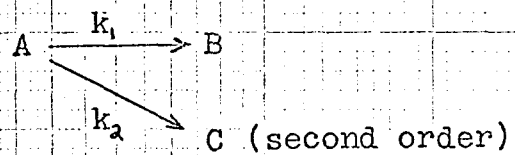
where B is the desired product. The reaction kinetics are described by the batch rate expressions

$$\begin{aligned} \frac{dy_1}{dt} &= -k_1 y_1 - k_2 c_0 y_1^2 \\ \frac{dy_2}{dt} &= k_1 y_1 \end{aligned} \quad (8.28)$$

the concentrations of A and B having been expressed as mole fractions y_1 and y_2 respectively. For this kinetic system, intense mixing favors the reaction of lower order and therefore failure to mix well enough will adversely affect product quality.

If the side product is not separated, and the conversion is high, the reduction of β/α due to scale-up might have a serious effect. Safety factors are no longer applicable, since just increasing the residence time without altering the intensity of agitation will not prevent the side reaction from occurring in the concentrated region near the inlet.

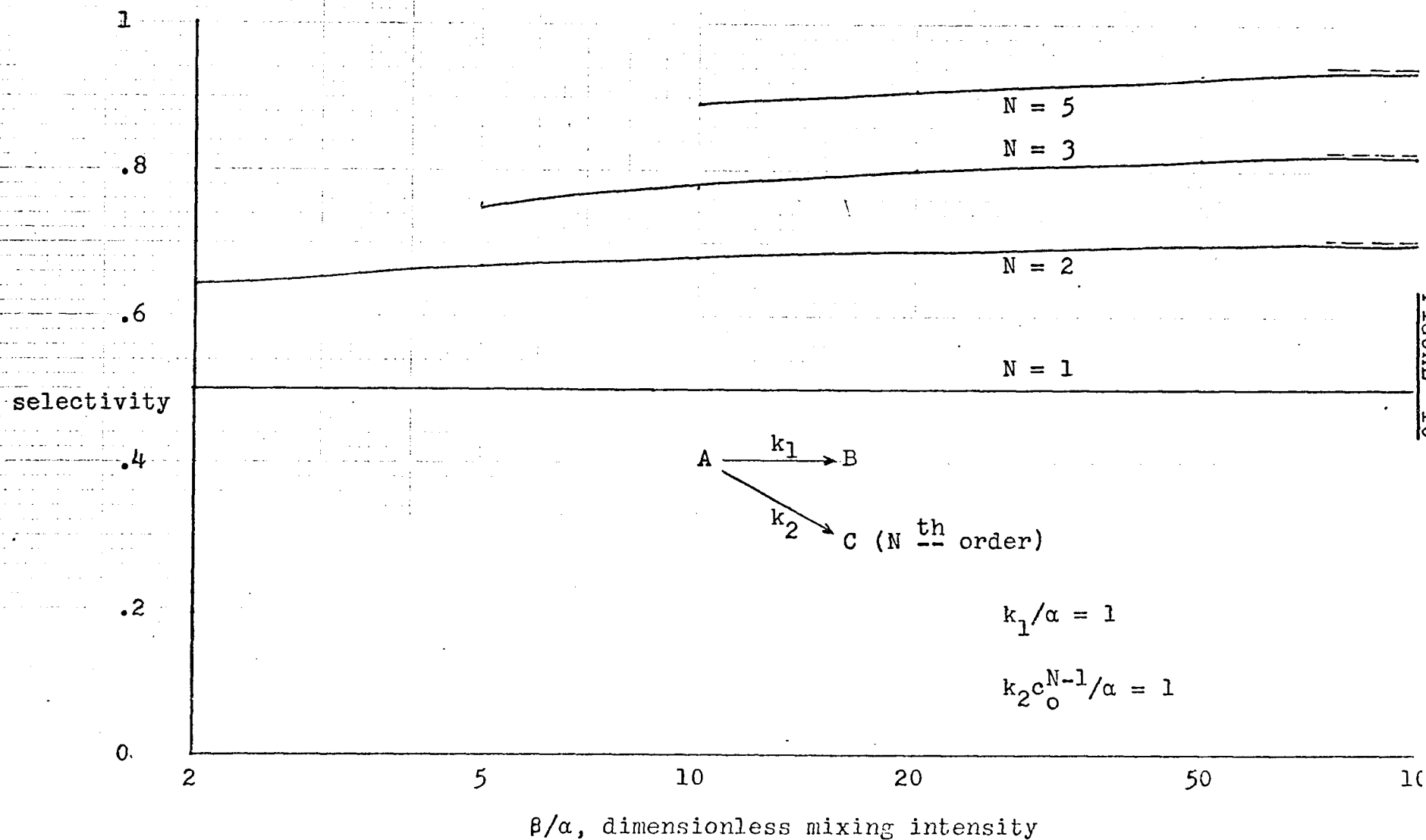
Some idea of the magnitudes involved can be obtained by looking at Figure 9 where the selectivity, defined as the ratio of amount of product formed to the amount of raw material used, is plotted as a function of mixing intensity as evaluated by the 2-parameter Beta distribution moment closing



technique of Chapter VI. Comparison of the results using the expansion method shows that the two are in excellent agreement in the range where both apply. Also shown in Figure 9 are some values obtained by Shain [36] which can be seen to agree fairly well.

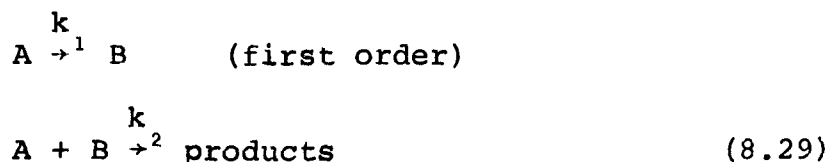
If the undesirable reaction is N^{th} order, it can be observed that, for $N = 1$, mixing plays no role. As can be seen from Figure 10, the greater is N , the more sensitive is the system to departures from ideal mixing, as is expected. It is evident that, for the reaction system (8.27), great care should be used in any scale-up study. With the aid of the methods outlined in Chapters V and VI, and the scale-up equation (2.39), estimates can be made of reactor performance and the need for alternative action shown when necessary.

EFFECT OF THE ORDER OF THE SIDE REACTION ON SELECTIVITY FOR PARALLEL REACTIONS



VIII.6 Consecutive Reactions

Another interesting case is the consecutive reaction scheme



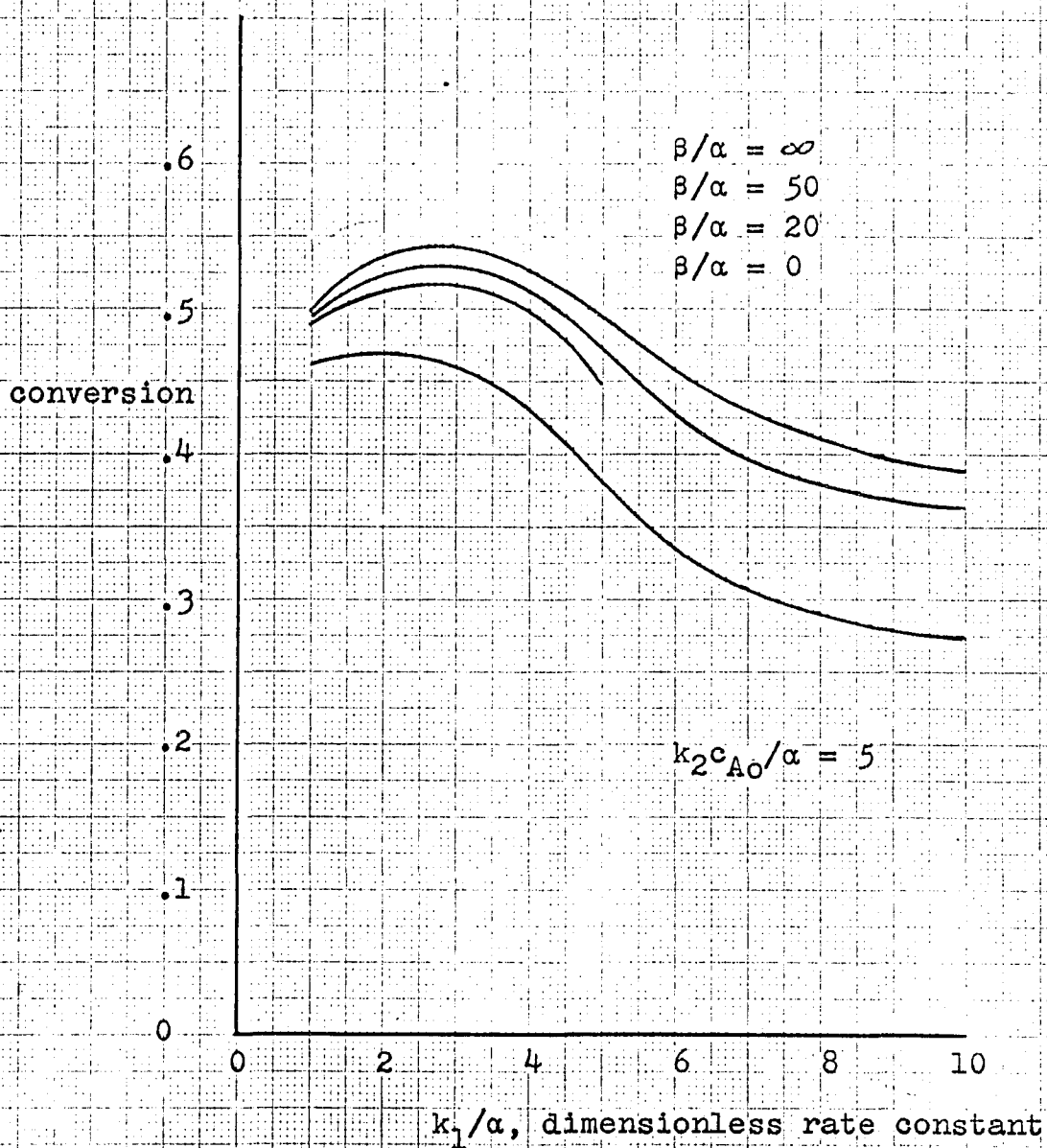
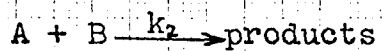
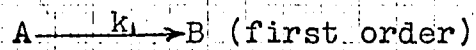
where reagent A must first react to form some intermediate B before further reacting with B to form products. It can be seen from Figure 11 that departures from ideal mixing cause reductions in conversion. It can be further seen from Figure 11 that increasing k_1 does not necessarily increase conversion. In fact, for given values of $k_2 c_{A_0}/\alpha$ and β/α , there is an optimum value of k_1/α . This strange fact is easily explained, however. If the initiation reaction is slow, the controlling factor for the second step will be the amount of intermediate B present in the reactor. If the initiation is rapid, the second reaction will be controlled by the amount of unreacted reagent A remaining. In the latter case, the outlet stream will contain large amounts of intermediate B.

Unlike the parallel reactions of the previous section, the reduced conversion on scale-up for the consecutive reactions (8.29) can be easily handled by the use of safety factors. An increased residence time increases the effective reaction rates for both reactions equally so that there is no danger of producing excessively large amounts of intermediate B by overdesigning.

If the initiation step is N^{th} order, $N > 1$, then the mix-

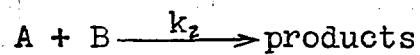
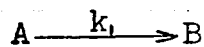
FIGURE 11

CONVERSION FOR CONSECUTIVE REACTIONS AS
A FUNCTION OF REACTION RATE CONSTANT



ing effect depends on the kinetics. A typical case is shown in Figure 12. No further problems are introduced by this complication.

CONVERSION FOR CONSECUTIVE REACTIONS AS A FUNCTION OF MIXING INTENSITY



$$k_1 c_{A_0}^{N-1} / \alpha = k_2 c_{A_0} / \alpha = 5$$

conversion

.6

.5

.4

20

50

100

200

500

1000

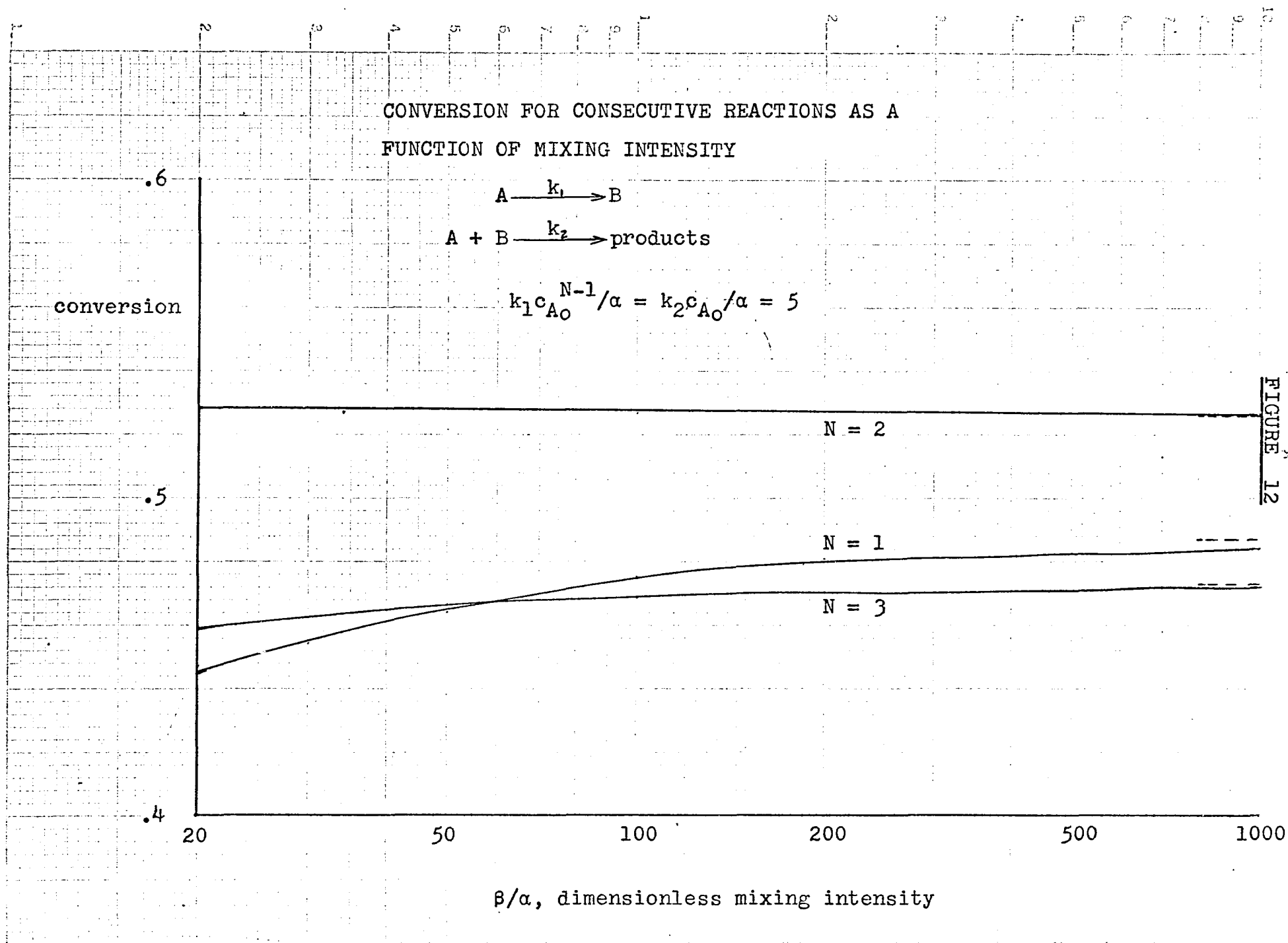
β/α , dimensionless mixing intensity

$N = 2$

$N = 1$

$N = 3$

FIGURE 12



VIII.7 A Complex Scheme of Parallel Kinetics

The last kinetic scheme to be considered in this chapter is the complex parallel case

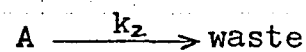
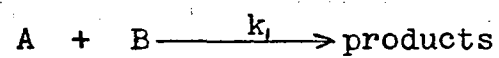


where reagents A and B are fed separately into the reactor. In this case, selectivity is defined as that fraction of the total reagents used which ends up as product.

It is easily seen for this case that an excess of B is desirable but in cases where B is expensive and/or difficult to separate from the product, this is not always practicable. An economic balance may be needed in this case. Also, it is obvious that premixing of the feeds would help, and indeed, the best solution may well be to use a plug-flow or batch reactor with premixed feed. In any case, complex kinetics such as (8.30) should be investigated thoroughly to determine the best type of reactor and operating conditions.

The reaction system (8.30) is seen to consist of a bimolecular reaction of the type discussed in sections VIII.3,4, together with a first order decomposition of one of the reagents. Figure 13 shows the effect of mixing on selectivity when the effective rate constants for the two reactions are equal. Although the yield is increased by increasing the residence time, the selectivity is decreased. Figure 14 shows the effect of using an excess of either reagent. It is to be noted that the conversion for these cases is more sensitive than is selectivity to departures from ideal mixing.

SELECTIVITY FOR COMPLEX PARALLEL KINETICS AS A
FUNCTION OF MIXING INTENSITY -- STOICHIOMETRIC FEEDS



selectivity

$$k_1 c_{A0} / \alpha = k_2 / \alpha = 1$$

$$= 5$$

$$= 10$$

FIGURE 13

β/α , dimensionless mixing intensity

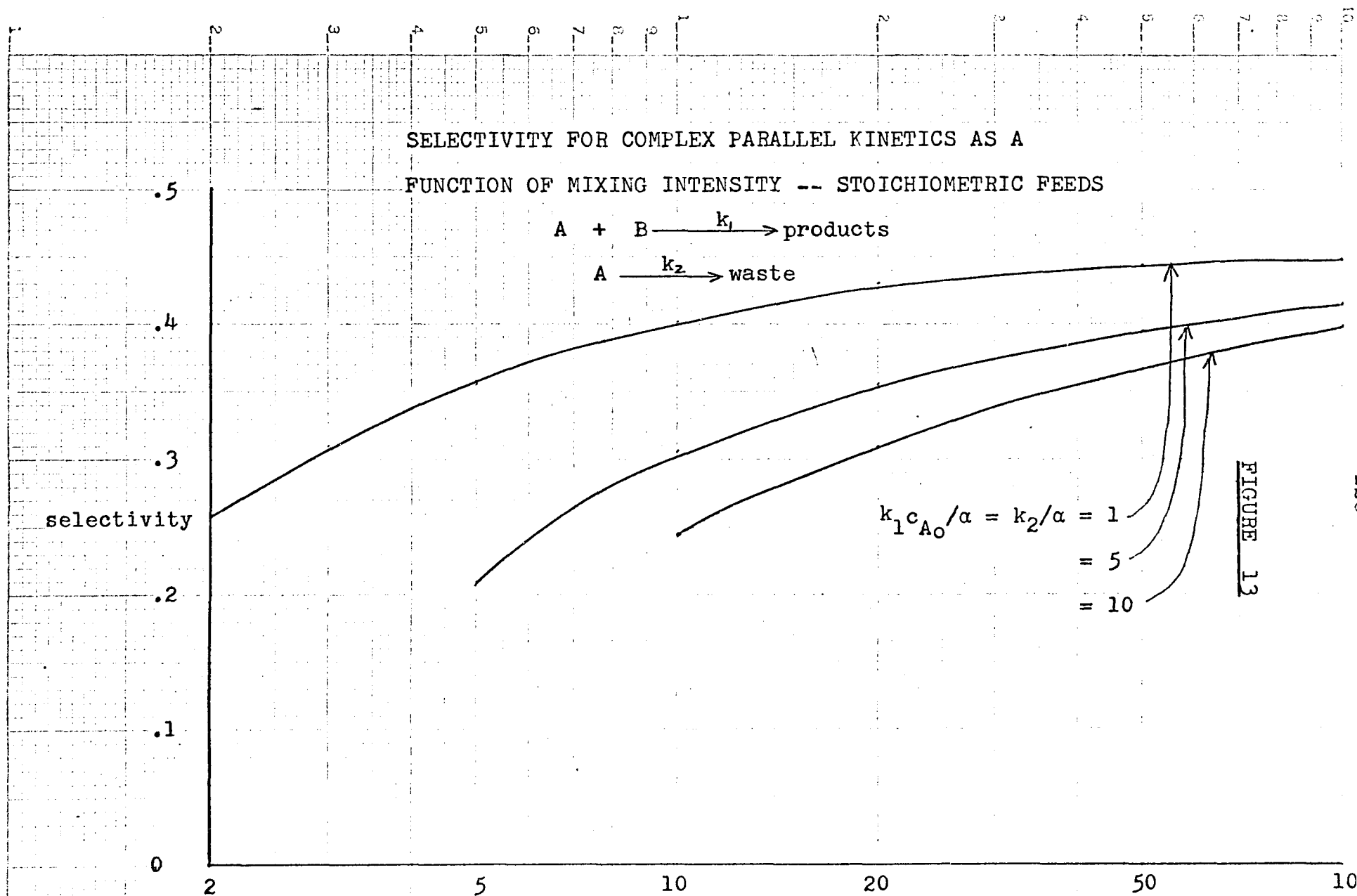
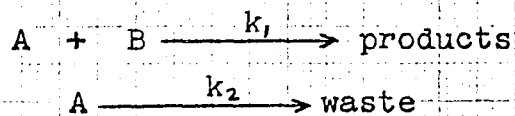
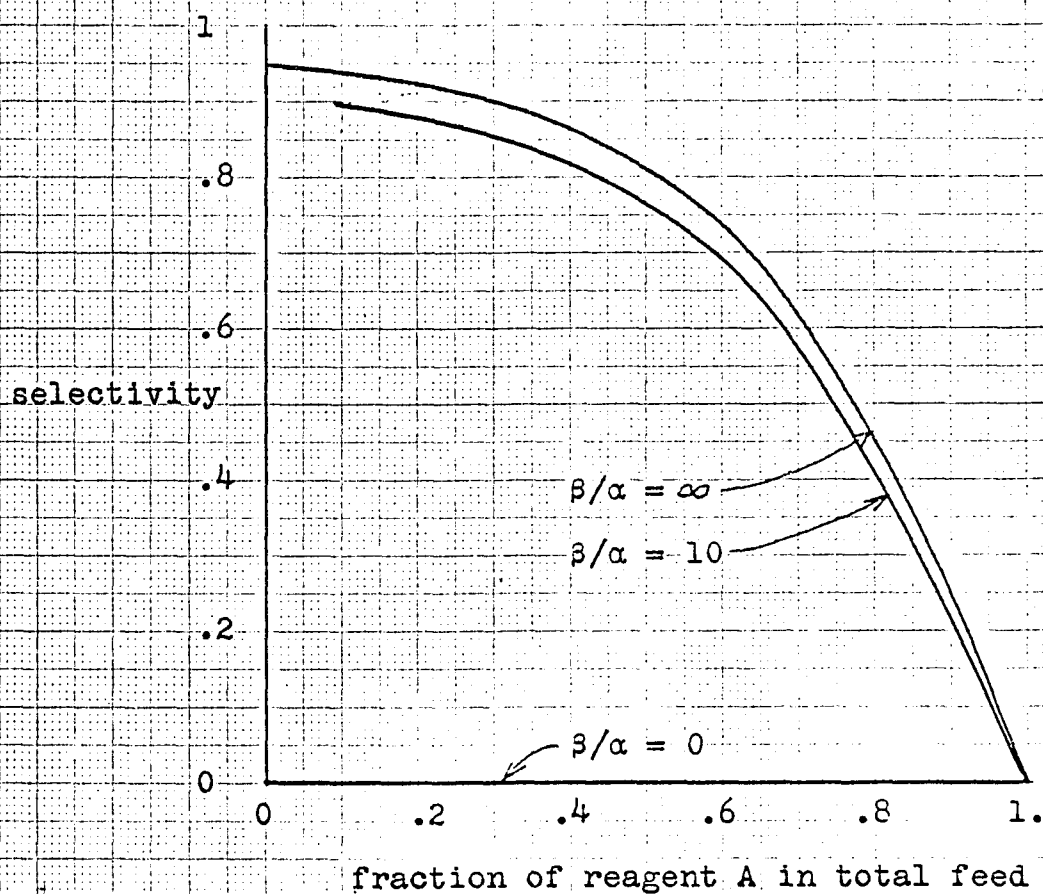


FIGURE 14

SELECTIVITY FOR COMPLEX PARALLEL KINETICS
WITH NONSTOICHIOMETRIC FEEDS



$$k_1 c_0 / \alpha = 10, \quad k_2 / \alpha = 1$$



CHAPTER IX

APPLICATION TO ADIABATIC SYSTEMS

IX.1 Introduction

In autothermic processes, the temperature level at which the reaction proceeds is maintained by the heat of reaction alone. Such reactions were shown by van Heerden [43,44] to have three steady state solutions, one of which is unstable. One of the stable solutions corresponds to an unignited state with very little conversion, and the other to an ignited state with nearly complete conversion. An example of this type of reactor is the gas combustor of section II.4.

To operate an autothermic reaction system at the stable ignited state requires that heat is fed back along the reaction path. This could be accomplished, for example, in a plug flow reactor where the entering reactant mixture is preheated by heat exchange with the outlet products. In the case of jet combustors, the evolved heat is fed back by mixing of the products and reactants in the combustion chamber.

An example of the latter type is the spherical combustor used in the kinetic experiments of Longwell [27] to study fast reactions, where ideal mixing is assumed. In contrast to the considerable body of experimental investigations existing on the mixing performance of mechanical agitators, there is little data on the quantitative aspects of mixing in

gas reactors of the Longwell type. It has been shown [35] that considerable recirculation exists. That is, on the macro-scale, the mixing is close to ideal. In addition to circulation of the fluid introduced by the jets, good overall mixing requires the dissipation of local concentration fluctuations by turbulence. That is, it is necessary that the jets have sufficient energy so that their penetration length into the reactor is very large as compared to the reactor diameter, so that the turbulent energy is not dissipated near the entrance of the jet.

Admittedly, turbulent combustion is a very complex process and cannot be given a completely analytical description. However, in a well-designed reactor, mixing intensities are very high and the mixing time is short as compared to the residence time. In such well-agitated reactors, the turbulent motion on a small scale becomes quite uniform and locally isotropic, so that the analysis of Chapter II applies, leading up to (2.42)

$$\beta/\alpha = \frac{1}{4} \left(\frac{L^2}{S} \right)^{2/3} \quad (9.1)$$

which relates the mixing intensity β/α to the jet design parameter L^2/S .

Use can now be made of the stochastic mixing model introduced in Chapter III which allows one to simulate the basic features of the real turbulent mixing process. By the methods outlined in Chapters V and VI, it is then possible to compute both the steady and the dynamic behavior of complex

adiabatic reaction systems, and for small deviations from complete mixing, the results of such computation should predict quite well how far the performance of the actual combustor deviates from an ideal one. Reasonable estimates of the mixing intensity required to achieve conditions close to ideal mixing are then obtained.

In the preceding chapters, it was shown that, for isothermal reactions, the mixing intensity necessary to approach ideal mixing strongly depends on the kinetics of the reaction. Applying the same method to combustion reactors allows one to make some quantitative estimates of the effect of incomplete mixing on mixed combustors. In this chapter, calculations are presented for adiabatic reaction systems showing the shift in the effective reaction rate curve, and especially the reduction in blowout limit, with decreasing mixing intensity. From such calculations, it is possible to predict how high a mixing intensity is needed to approximate perfect mixing, and how this level depends on the reaction kinetics.

IX.2 The Reaction Rate

The mixing equation for Curl's mathematical model as derived in Chapter III is

$$\begin{aligned} \frac{1}{\alpha} \frac{\partial p}{\partial t}(c, t) + \frac{1}{\alpha} \frac{\partial}{\partial c} \{r(c)p(c, t)\} = \{p^*(c, t) - p(c, t)\} \\ + \frac{2\beta}{\alpha} \left\{ \int \int p(c', t)p(c'', t) \delta\left(\frac{c'+c''}{2} - c\right) dc' dc'' - p(c, t) \right\} \end{aligned} \quad (9.2)$$

where $p^*(c, t)$ is the concentration distribution for the feed, $1/\alpha$ the nominal residence time of material in the tank, and $2\beta/\alpha$ the dimensionless mixing intensity. The reaction rate $r(c)$ describes the kinetics for an adiabatic reaction carried out in a batch reactor. This can be evaluated by making material and energy balances.

A material balance in a batch reactor states simply

$$\frac{dc}{dt} = -kc^n \quad (9.3)$$

for n^{th} order reactions, where n is commonly 1 or 2. If the dependence of the rate constant k on temperature is taken as an Arrhenius relation, this becomes

$$\frac{dc}{dt} = -A_0 e^{-E/RT} c^n \quad (9.4)$$

where A_0 is of the nature of a frequency factor. A simple heat balance then gives

$$\frac{dT}{dt} = -\left[\frac{-\Delta H}{\rho c_p}\right] A_0 e^{-E/RT} c^n \quad (9.5)$$

where ρ is the density of the reacting mixture, c_p its heat capacity, and $-\Delta H$ the heat given off per mole of reactant consumed. If the initial temperature is T_0 , and T_f is defined as the temperature reached at complete conversion

$$T_f = T_0 + \frac{-\Delta H C_0}{\rho c_p} \quad (9.6)$$

then it is easily seen from (9.4) and (9.5) that the function

$$T - (T_f - T_0) \frac{C}{C_0} \quad (9.7)$$

is invariant in time. It then follows that temperature can be related to concentration in an adiabatic batch reactor as

$$\frac{T - T_0}{T_f - T_0} = \frac{C_0 - C}{C_0} \quad (9.8)$$

where the right hand side of (9.8) is just the conversion y . Combining (9.4) and (9.8) and expressing concentration in terms of conversion then gives

$$\begin{aligned} \frac{dy}{dt} &= A_0 C_0^{n-1} e^{-\left[\frac{E/RT_0}{1 + \frac{T_f - T_0}{T_0} y} \right]} (1-y)^n \\ &= r(y) \end{aligned} \quad (9.9)$$

The rate expression (9.9) is analytically rather intractable, and for exothermic reactions, where E/RT_0 may be of the order of 20 to 80, and $\frac{T_f - T_0}{T_0}$ of the order of 2 to 6 (van Heerden [44] gives values of 27 and 2 for adiabatic

oxidation of naphthalene), Spalding [38] has suggested that it may usefully be approximated in the form

$$r(y) = k(y+\zeta)^m(1-y)^n \quad (9.10)$$

The parameter ζ might be taken equal to zero

$$r(y) = ky^m(1-y)^n \quad (9.11)$$

if one were not especially interested in capturing the low conversion behavior. A comparison between (9.9) and (9.11) in a representative situation is shown in Figure 15.

With any of the forms (3.7), (3.8), the rate expression $r(y)$ may be written

$$r(y) = kR(y) \quad (9.12)$$

where, provided m and n are whole numbers, R is a polynomial in y . The equation (9.2) may then be written

$$\begin{aligned} \frac{1}{\alpha} \frac{\partial p(y,t)}{\partial t} + \frac{k}{\alpha} \frac{\partial}{\partial y} \{R(y)p(y,t)\} &= \delta(y) - p(y,t) \\ &+ \frac{2\beta}{\alpha} \left\{ \int \int p(y',t) p(y'',t) \delta\left(\frac{y'+y''}{2} - y\right) dy' dy'' \right. \\ &\quad \left. - p(y,t) \right\} \end{aligned} \quad (9.13)$$

where $\delta(y)$ represents a feed of unconverted material. With t scaled on $1/\alpha$, the behavior of the system for any given form of $R(y)$ is seen to be controlled by the dimensionless mixing intensity β/α and the dimensionless flow rate α/k . The polynomial character of $R(y)$ greatly simplifies the solution of (9.13) and the methods of Chapters V and VI are applicable. The results discussed in the next section are all for the

APPROXIMATE RATE EXPRESSIONS

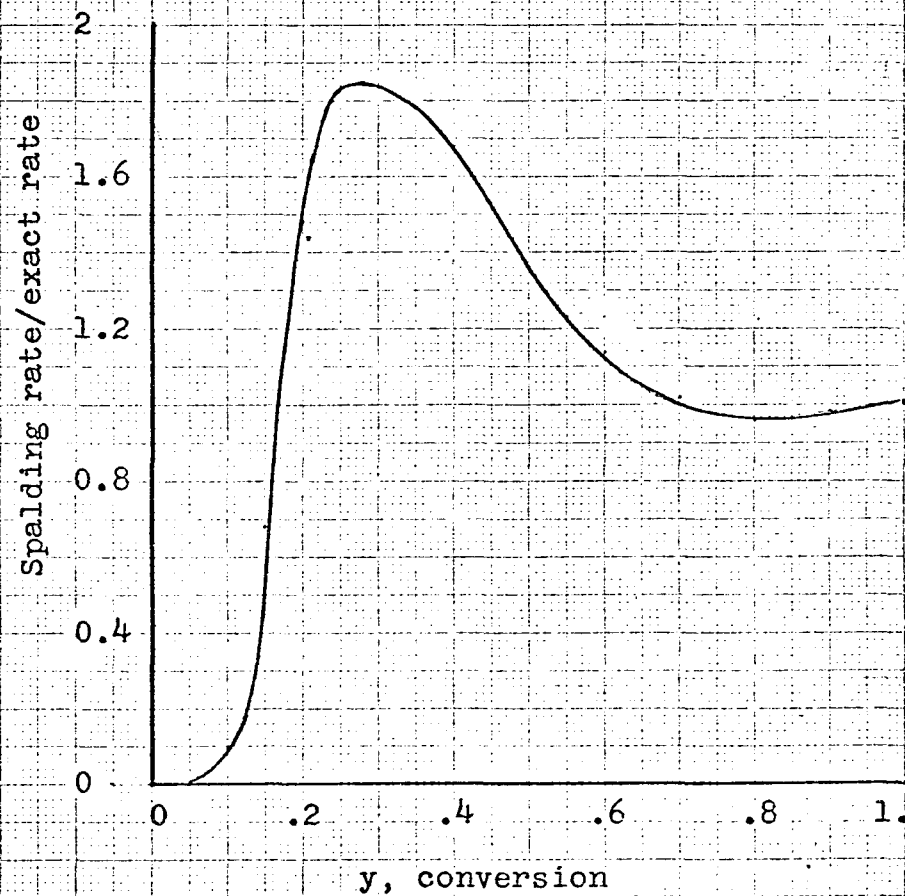
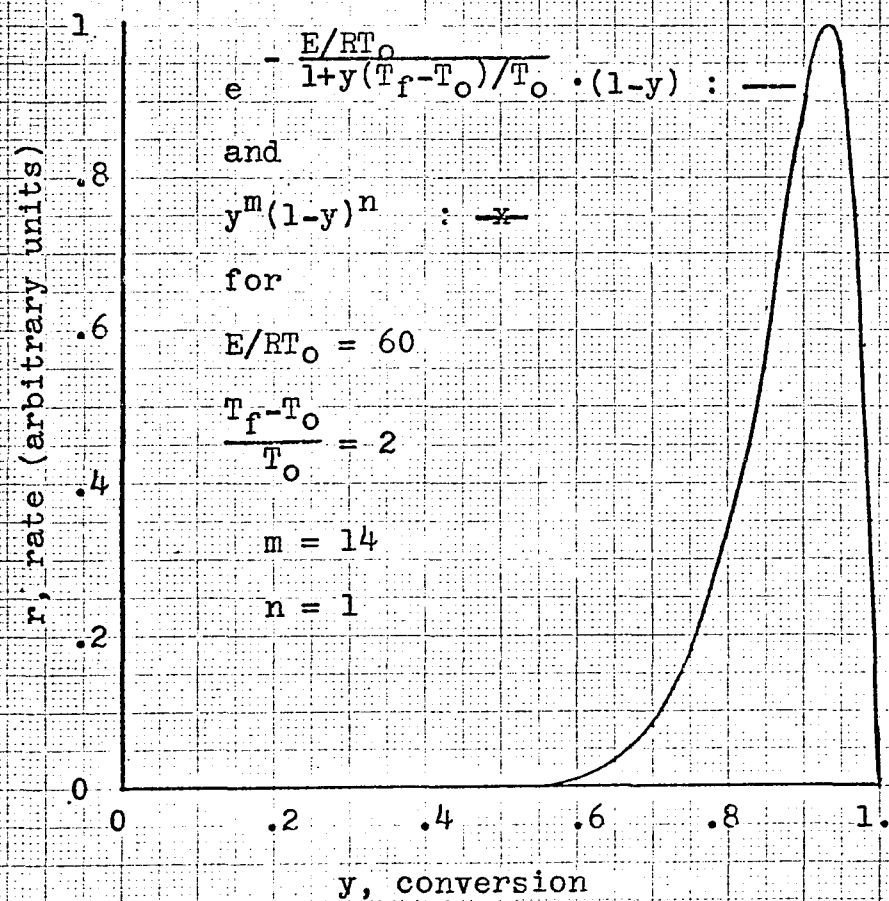


FIGURE 15

kinetic form (9.11) and are obtained by the expansion methods of Chapter V.

For ideal mixing ($\beta/\alpha = \infty$), the steady state solution is found to be

$$R(\mu) = \frac{\alpha}{k}\mu \quad (9.14)$$

where μ is the mean conversion. This equation can be solved for μ by plotting both the left and right hand sides versus μ on the same coordinates. The intersection points give the solutions. For sufficiently low values of α/k , three steady states are obtained, the intermediate one being unstable and the lowest representing, to this kinetic approximation, no conversion. As α/k is increased, eventually a point is reached where the only solution is the unconverted unignited state, and this point is called blowout. Physically, blowout results when heat is carried out of the reactor by the products faster than it can be produced, for all temperatures above the unignited stable condition. This can be corrected for exothermic adiabatic processes by reducing the flow rate and thereby lowering the rate of heat removal. In practice, it is hard to carry out a reaction adiabatically at low-flow rates and as the flow rate is lowered, the heat loss becomes greater. For this reason, many exothermic processes cannot be carried out adiabatically and, even for those processes where adiabatic operation is possible, too low a flow rate will cause excessive heat losses and the reaction will be quenched.

IX.3 Results and Conclusions

For any given form of reaction rate, it is possible once and for all to compute the effect of imperfect mixing, and exhibit it in a generalized form by plotting the conversion as a function of the mixing intensity β/α , for different levels of the throughput α/k . Here the mixing intensity β is normalized on the reciprocal mean residence time α , and α itself which measures the throughput, is normalized on the kinetic parameter k , which serves as a time constant for the reaction. The results are all based on the Spalding approximation for exothermic reaction rates according to which the reaction rate under adiabatic conditions can be expressed as a function of conversion y as in (9.11).

Figures 16 through 22 show how the effective reaction rate curve, taken in the dimensionless form $r(y)/k$, is shifted under the influence of the mixing intensity β/α . These curves are obtained by calculating the average conversions according to the method of Chapter V, and plotting them along lines whose slope is the corresponding α/k . Three steady states are obtained for each operating condition, the intermediate one being unstable just as for complete mixing, and the lowest representing, to this kinetic approximation, no conversion. For each β/α , the resulting curve then has the same character as $r(y)/k$ for ideal mixing (infinite β), in that its intersections with lines of slope α/k give the average steady conversions. One can see that for high values of β/α , the curve approaches the curve for infinite mixing. The value of β/α for which the mix-

FIGURE 16

THE EFFECT OF MIXING INTENSITY ON
APPARENT REACTION RATE

$$r(y) = k y^3 (1-y)$$

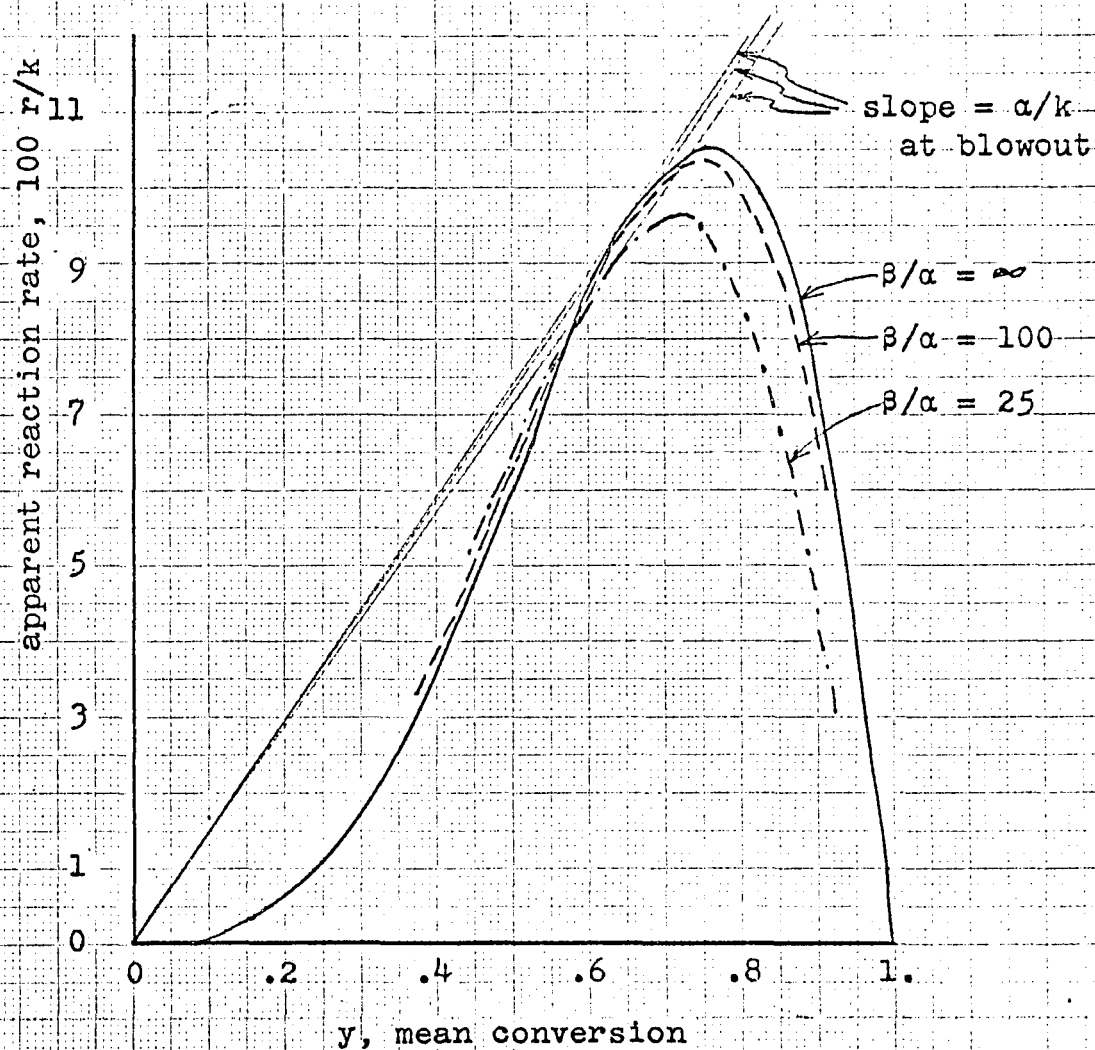


FIGURE 17

THE EFFECT OF MIXING INTENSITY
ON APPARENT REACTION RATE

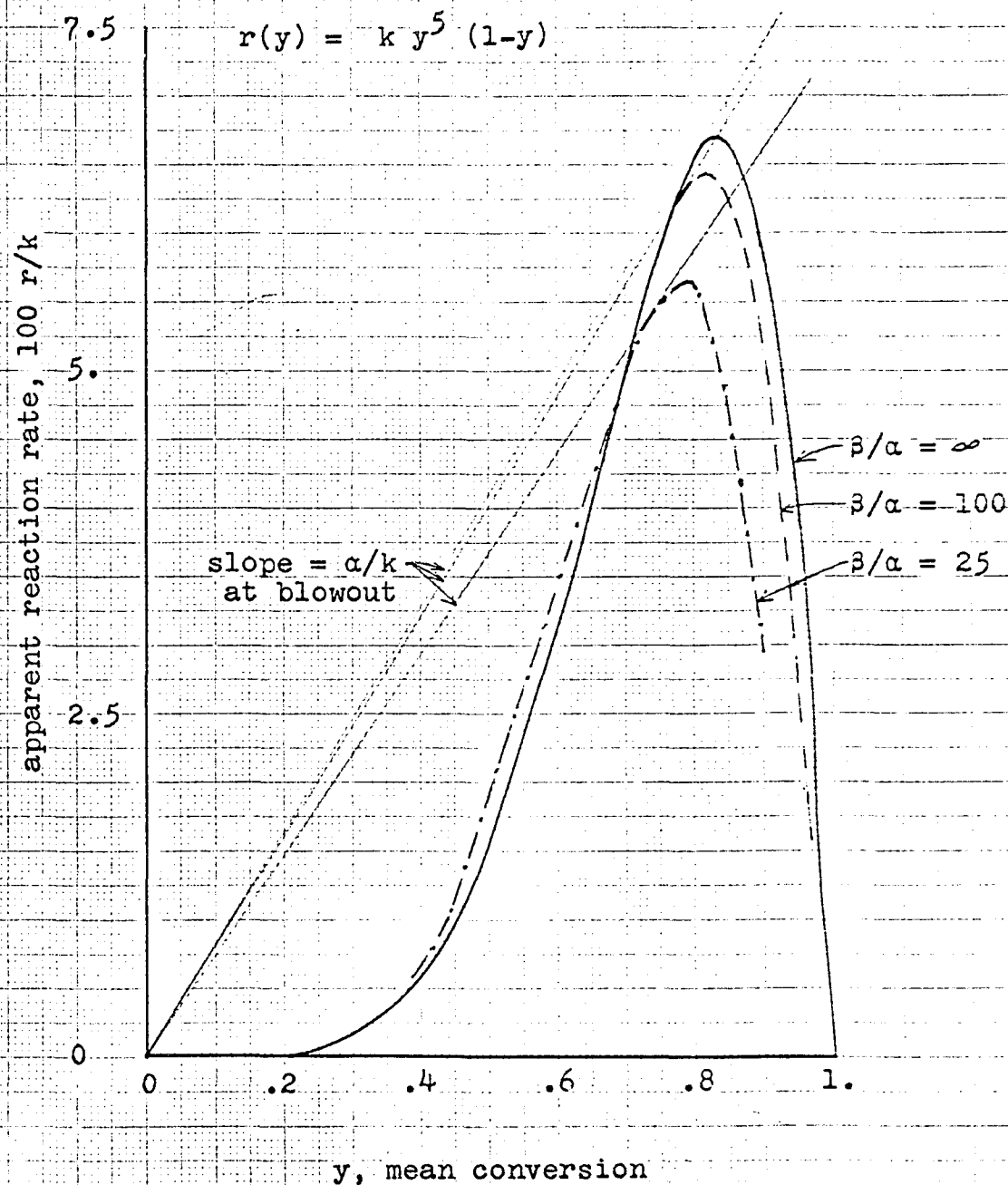


FIGURE 18

THE EFFECT OF MIXING INTENSITY
ON APPARENT REACTION RATE

$$r(y) = k y^{10}(1-y)$$

apparent reaction rate, $100 r/k$

3

2

1

0

0

.2

.4

.6

.8

1.

y , mean conversion

$\beta/\alpha = \infty$

$\beta/\alpha = 100$

$\beta/\alpha = 25$

slope = α/k
at blowout

FIGURE 19

THE EFFECT OF MIXING INTENSITY
ON APPARENT REACTION RATE

$$r(y) = k y^{1.5}(1-y)$$

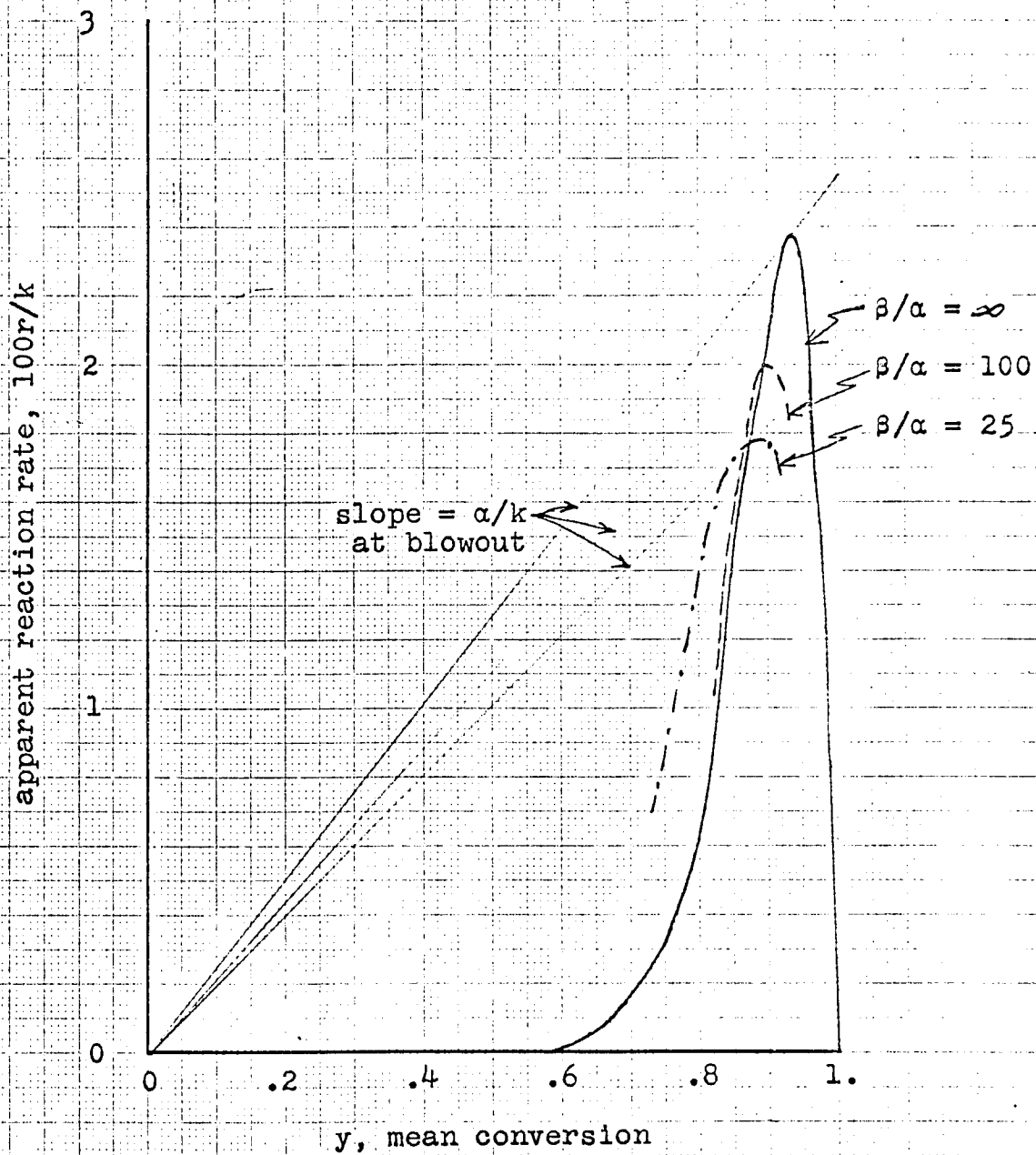


FIGURE 20

THE EFFECT OF MIXING INTENSITY
ON APPARENT REACTION RATE

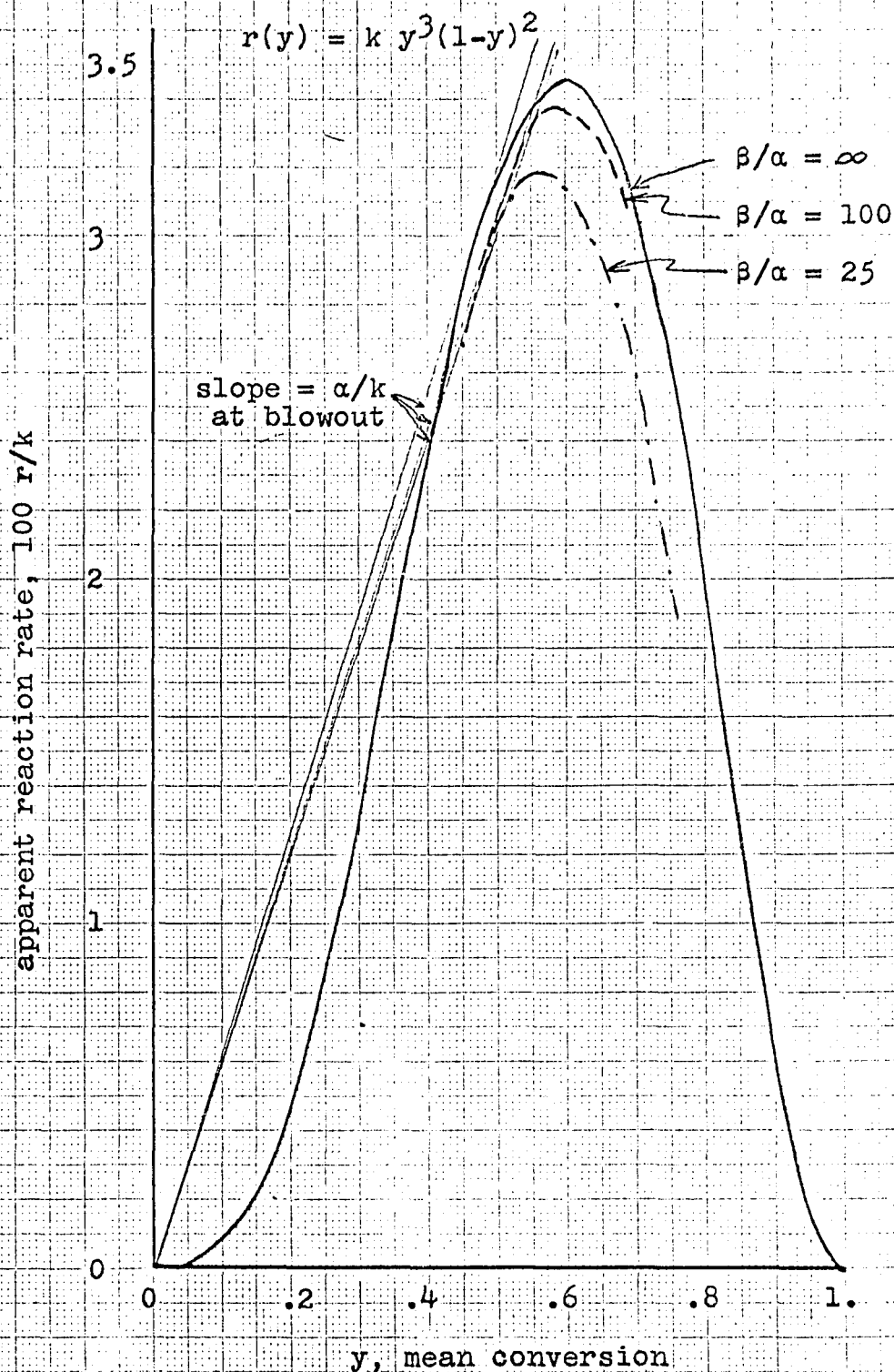


FIGURE 21

THE EFFECT OF MIXING INTENSITY
ON APPARENT REACTION RATE

$$r(y) = k y^5 (1-y)^2$$

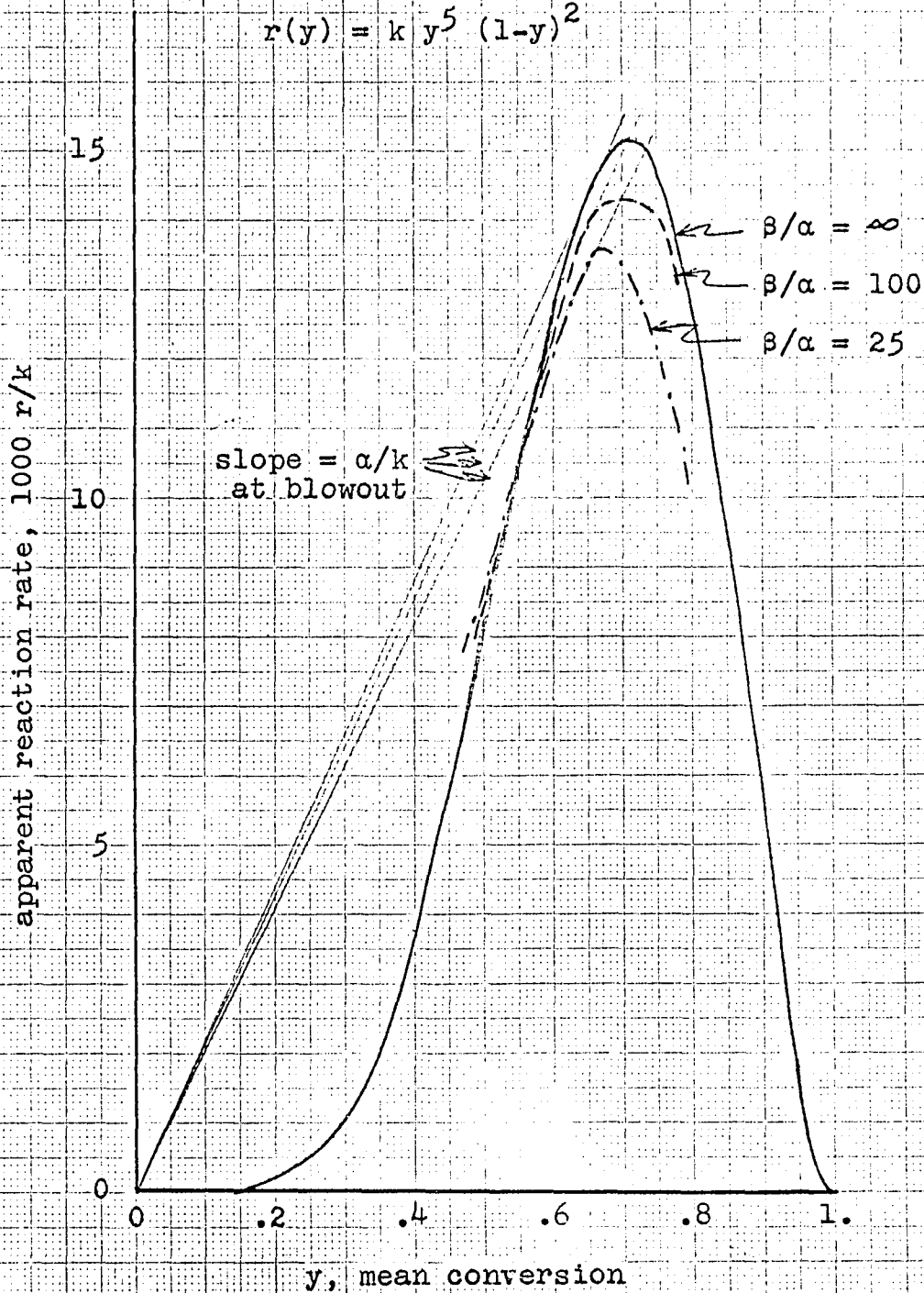


FIGURE 22

THE EFFECT OF MIXING INTENSITY
ON APPARENT REACTION RATE

$$r(y) = k y^{10} (1-y)^2$$

apparent reaction rate, 1000 r/k

4

3

2

1

0

0

.2

.4

.6

.8

1.

y , mean conversion

 $\beta/\alpha = \infty$ $\beta/\alpha = 100$ $\beta/\alpha = 25$

slope = α/k
at blowout

ing becomes for practical purposes ideal increases with increasing m and n . The averaged reaction rate is also much more sensitive to mixing for high values of α . This means that near the critical flow rate at which the reaction extinguishes, the system is most sensitive to mixing, which is in good agreement with the experimental evidence.

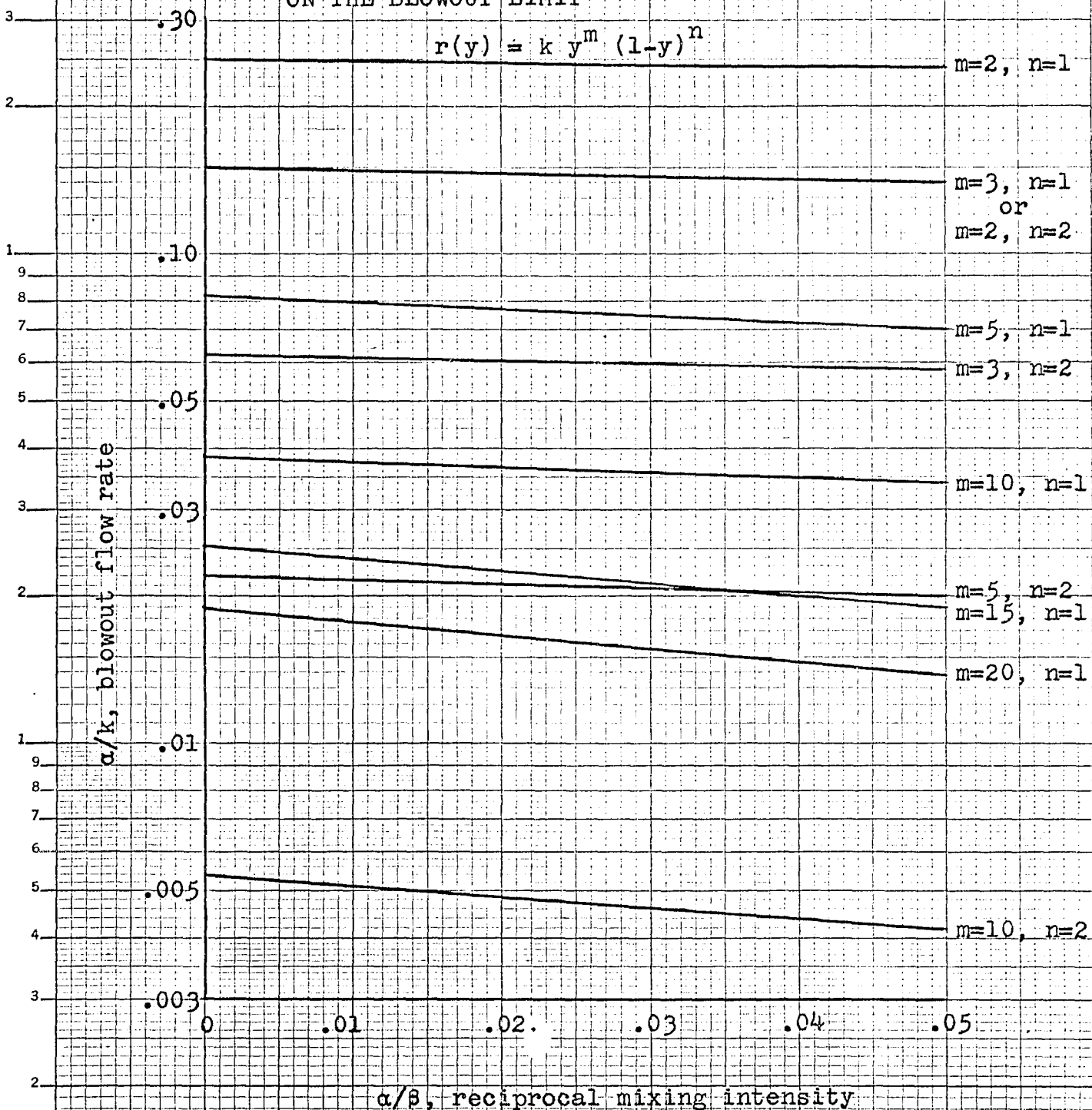
In Figure 23 the critical value of α/k at blowout is plotted as a function of β/α for different values of m and n . For a fixed n , these curves show that the larger m is, that is, the steeper the dependence of reaction rate on conversion, the stronger is the effect of β/α . However, for $\beta/\alpha > 25$, the mistake made is relatively small, and in the most sensitive case ($m = 20$, $n = 1$) does not exceed 25%. Nevertheless, the dependence of the blowout limit on the reaction kinetics does indicate that attempts to correlate it with parameters of injector design, such as the pressure drop, should be viewed with some caution. Further, the fact that the reactor is insensitive to mixing for a specific reaction at one mixing rate does not guarantee the same independence for other reactions at this mixing rate. The results of Figures 16 through 23 should however provide soon good guidelines in this direction.

In Figure 24, the variance of the conversion is shown as a function of β/α . Only the stable steady state points are considered. The standard deviation, normalized on the mean conversion, is essentially independent of the kinetic parameters and the flow rate over the whole working range; examples of departure from this standard form for very low values of α/k are

FIGURE 23

THE EFFECT OF MIXING INTENSITY
ON THE BLOWOUT LIMIT

$$r(y) = k y^m (1-y)^n$$



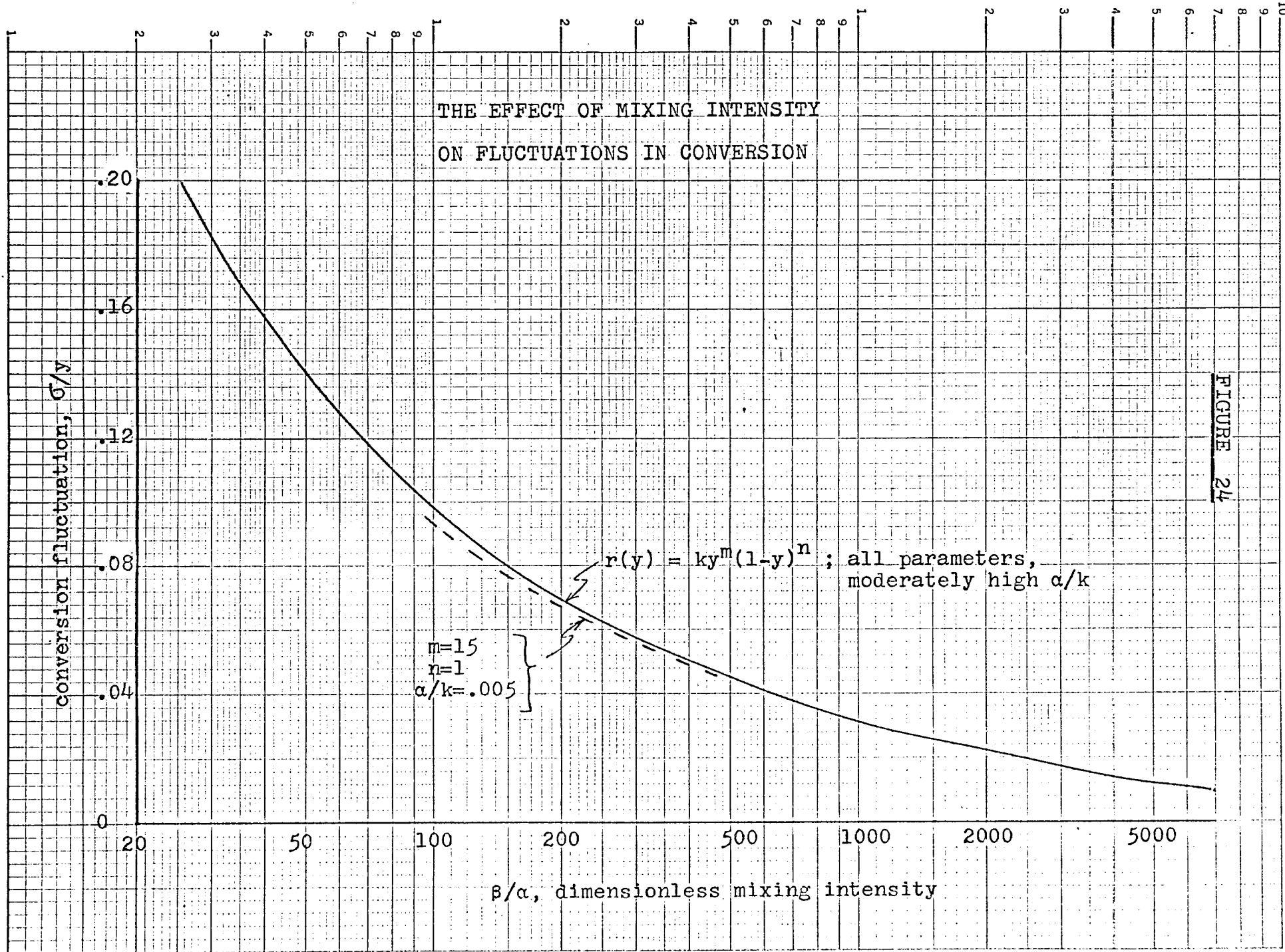


FIGURE 24

shown for representative values of m and n . It is also noted that for high but realizeable values of β/α , the variance becomes so small that the original assumption made that the reactor is mixed really applies. For lower values of β/α the variance starts to increase rapidly. If the variance becomes very large, the mixing model of Chapter III really does not apply because then the reaction becomes localized and flame fronts may start to exist. The model has the interesting feature that it predicts a change from mixed combustion to highly localized combustion at lower mixing rates.

There are two general conclusions that can be drawn from the above results. One is that quite high mixing intensities or pressure drops are needed for exothermic reactions to approach conditions of ideal mixing. But with a well-designed reactor, such mixing rates are still feasible. Further research on the mixing patterns in such reactors would be very worthwhile. A second general conclusion was pointed out in section II.4. That is, since according to (2.42) keeping β/α constant at different reactor sizes requires keeping L^2/S constant, and since according to (2.41) keeping α constant requires keeping Sv/L^3 constant, it follows that in scaling up in such a way as to keep the same α and β , v/L must also be kept the same. The pressure drop needed to achieve the desired level of β/α will then increase with reactor size and accordingly as small a reactor as will not give excessive heat losses or too low a Reynolds number should be used.

CHAPTER X

APPLICATION TO POLYMERIZATION SYSTEMS

X.1 Introduction

In the preceding chapter, the coalescence model was used to investigate the effect of mixing on the performance of mixed combustors. In the present chapter, the method is extended to an example of really complex kinetics. A typical polymerization system is considered, in which nucleation (in this case, initiation) is expected to play an important role. Such a system is homogeneous radical polymerization.

In studying the performance of polymerization systems, one is commonly interested in the monomer conversion and the polymer size distribution. This latter quantity, however, can be obtained for relatively few polymerization processes [18,20,26,48,49]. In size distribution studies of complex polymerization systems, a stationary state is usually assumed [49]. In most cases, knowledge of the breadth of the size distribution in addition to the mean polymer size is sufficient, and the former is usually characterized by the dispersion index, defined as the ratio of weight average to number average molecular size. This quantity is readily obtained from the first few moments of the size distribution.

Denbigh [16,17] first recognized that mixing plays an important role in polymerization and accordingly he compared

the performance of a batch reactor to that of an ideal mixer. He concluded that two opposing factors influence the molecular size distribution in such cases--the residence time distribution and the concentration history. Which factor predominates is dependent upon whether the mean lifetime of growing polymer is short or long compared to the duration of reaction. For the homogeneous radical polymerization to be investigated in this chapter, the ratio of mean polymer lifetime to mean residence time is given by

$$\frac{\alpha \bar{X}_n}{k_p \bar{M}}$$

where α is the inverse mean residence time, $\bar{X}_n$ is the number average molecular weight of polymer, k_p is the polymerization rate constant and $\bar{M}$ is the mean concentration of monomer. If this quantity is small, Denbigh predicts a lower dispersion index for continuous than for batch operation, and if it is large, the opposite should be true.

Tadmor and Biesenberger [6,41] strengthen Denbigh's argument by considering also a completely segregated stirred tank reactor ($\beta = 0$ in the coalescence model). Their results show that this type of reactor always yields a greater dispersion index than either the batch reactor or the ideal mixer.

The plan of the present chapter is to investigate the effect of deviations from ideal mixing on the performance of a stirred reactor in which a homogeneous radical polymerization is being carried out. Initiator and monomer streams are fed either separately or premixed with initiation being first

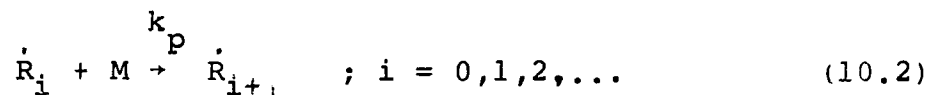
order in initiator concentration and termination occurring by combination of two growing radicals. The objectives of this are to demonstrate the use of the mixing model in a really complex situation, to investigate how various factors influence the magnitude of the effect caused by departures from ideal mixing, and also to investigate further the remarks made by Denbigh.

X.2 The System Equations

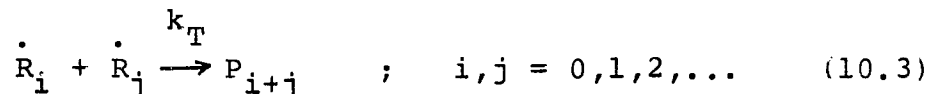
The polymerization system to be studied consists of an initiation step, followed by chain propagation and ended by a termination step. In the initiation step, initiator I decomposes into the primary radical $\dot{R}_O$:



The propagation step consists of monomer M reacting with radical $\dot{R}_i$ containing i monomer units, to form a radical having i + 1 monomer units.



The rate constant for this step, k_p , is assumed to be independent of the number of monomer units in the reacting radical. This is known as the principle of equal reactivity. Finally, termination consists of the combination of two radicals to form polymer



The batch kinetic expressions for this system have been set down by Saidel and Katz [34] who used the continuous version of the kinetic equations as have Amundson and coworkers [48,49]. Saidel's results will be quoted here.

The system equations are given by

$$\frac{dI}{dt} = -k_I I$$

$$\frac{dM}{dt} = -k_p M \int f(z, t) dz$$

$$\begin{aligned} \frac{\partial f(x, t)}{\partial t} + k_p M \frac{\partial f(x, t)}{\partial x} = & 2k_I I \delta(x) \\ & - k_T f(x, t) \int f(z, t) dz \end{aligned}$$

$$\frac{\partial g(x, t)}{\partial t} = \frac{1}{2} k_T \int_{z \leq x} f(x-z, t) f(z, t) dz$$

(10.4)

where x is polymer size reckoned in monomer units, $f(x, t)dx$ represents the concentration of radicals having size in the range $(x, x+dx)$ in the system at time t , $g(x, t)dx$ is a similar quantity for terminated polymers, and z is a dummy integration variable. The constants k_I , k_p and k_T are the rate constants for initiation, propagation and termination, respectively, and I and M stand for the concentrations of initiator and monomer respectively.

Defining the moments for the radical and polymer size distributions as

$$\left. \begin{aligned} \lambda_i &= \int x^i f(x, t) dx \\ \gamma_i &= \int x^i g(x, t) dx \end{aligned} \right\} \quad (10.5)$$

equations (10.4) become

$$\frac{dI}{dt} = -k_I I$$

$$\frac{d\lambda_0}{dt} = 2k_I I - k_T \lambda_0^2$$

$$\frac{dM}{dt} = -k_p M \lambda_0$$

$$\frac{d\lambda_i}{dt} = k_p M i \lambda_{i-1} - k_T \lambda_0 \lambda_i \quad ; \quad i = 1, 2, \dots$$

$$\frac{d\gamma_i}{dt} = \frac{k_T}{2} \sum_{j=0}^i \binom{i}{j} \lambda_j \lambda_{i-j} ; i=0, 1, 2, \dots$$

(10.6)

Equations (10.6) are the batch "kinetic" equations for the homogeneous radical polymerization system. The leading moments λ_0 and γ_0 denote the concentration of radicals and terminated polymer respectively. The moments λ_i and γ_i denote the total amount of monomer per reactor volume associated with the radicals and terminated polymer respectively. The number average degree of polymerization $\bar{X}_n$ and the weight average degree of polymerization $\bar{X}_w$ are related to the moments as

$$\bar{X}_{nr} = \lambda_1 / \lambda_0$$

$$\bar{X}_{wr} = \lambda_2 / \lambda_1$$

(10.7)

for the growing radicals,

$$\bar{X}_{np} = \gamma_1 / \gamma_0$$

$$\bar{X}_{wp} = \gamma_2 / \gamma_1$$

(10.8)

for the terminated polymer, and

$$\bar{X}_n = (\lambda_1 + \gamma_1) / (\lambda_0 + \gamma_0)$$

$$\bar{X}_w = (\lambda_2 + \gamma_2) / (\lambda_1 + \gamma_1)$$

(10.9)

for the combined growing and terminated polymer. With any of the definitions (10.7), (10.8) or (10.9), the dispersion index is given by the ratio of weight average to number average degree of polymerization. Thus

$$D_r = \bar{X}_{wr} / \bar{X}_{nr}$$

$$D_p = \bar{X}_{wp} / \bar{X}_{np}$$

$$D = \bar{X}_w / \bar{X}_n$$

(10.10)

In order then to carry sufficient knowledge to evaluate the effect of mixing on the degree of polymerization and the dispersion index D or D_p , a total of eight "reaction" equations must be kept. The eight batch rate equations necessary are for I , M , λ_0 , λ_1 , λ_2 , γ_0 , γ_1 , γ_2 , and these are all contained in the set (10.6). The right hand sides of these equations being all polynomial expressions, the expansion machinery of Chapter V may now be employed to generate a few of the terms in the series for conversion, degree of polymerization, and dispersion index.

X.3 Results

The first results to be obtained from the expansion machinery of Chapter V are values of the eight variables for the perfectly mixed case. These results will be used to set up some new nomenclature for the body of results to follow.

First, let y_I be defined by

$$y_I = \frac{1}{\frac{k_I}{\alpha} + 1} \quad (10.11)$$

The parameter y_I is just the fraction of initiator which does not react to form primary radicals under conditions of ideal mixing, and y_I replaces k_I as an independent variable. The parameter α is, of course, just the inverse mean residence time.

Similarly, k_T is replaced by a new parameter y

$$y = \frac{\sqrt{1 + 8 \frac{k_T}{\alpha} I_0 (1 - y_I)} - 1}{2} \quad (10.12)$$

with $\alpha y / k_T$ representing the total concentration of radicals in the reactor when mixing is ideal. Here I_0 is the concentration of initiator in the feed.

The third rate constant, k_p , is replaced by y_m

$$y_m = \frac{1}{1 + \left(\frac{k_p}{k_T} \right) y} \quad (10.13)$$

the fraction of monomer unconverted under ideal mixing conditions.

With the above nomenclature in hand, the results obtained from the expansion method can now be set down. These

results are obtained by very lengthy laborious algebraic calculations which are not reproduced here. The results follow.

The fraction of monomer remaining unconverted is given by

$$\frac{M}{M_0} = y_m + \frac{f_m}{\lambda} + \frac{g_m}{\lambda^2} + o\left(\frac{1}{\lambda^2}\right) \quad (10.14)$$

where λ is just the dimensionless mixing intensity $2\beta/\alpha$. Here, M_0 is the concentration of monomer in the feed. The first correction, f_m , is given by

$$f_m = 2(1-y_m) \left[1 - \frac{(1+y)}{(1+2y)} y_m \right] \quad (10.15)$$

and the second correction, g_m , by

$$\begin{aligned} g_m = & \frac{4(1+y)(1-y_m)}{y_I} \left\{ \frac{1}{1+2y} y_m - e_1 \right\} \\ & + \frac{4}{3y_m} + \frac{4(2y-5)(1+y)}{3(1+2y)} \\ & + \frac{4(11+49y+61y^2+17y^3)}{3(1+2y)^3} y_m \\ & - \frac{4(16+76y+116y^2+67y^3+16y^4)}{3(1+2y)^3} y_m^2 \\ & + \frac{(1+y)(14+25y)}{3(1+2y)^2} y_m^3 \\ & + \frac{4(2y-5)(1+y)}{3(1+2y)} y_m^4 \end{aligned} \quad (10.16)$$

where e_1 is a parameter which depends on the type of feed used.
For premixed monomer and initiator,

$$e_1 = 1 \quad ; \quad \text{premixed feed} \quad (10.17)$$

and for separate feed lines

$$e_1 = 0 \quad ; \quad \text{separate feeds} \quad (10.18)$$

Similar results are obtained for the degree of polymerization. The parameter M_0 , the concentration of monomer in the feed, is here replaced by the dimensionless group.

$$\frac{k_p M_0}{\alpha}$$

and one finds, using the expansion method outlined in Chapter V,

$$\bar{X}_{np} = \frac{k_p M_0}{\alpha} \cdot \frac{2y_m}{(1+y)} \left[1 + \frac{f_x}{\lambda} + \frac{g_x}{\lambda^2} + o\left(\frac{1}{\lambda^2}\right) \right] \quad (10.19)$$

where the first correction, f_x , is given by

$$f_x = \frac{2(1+y)}{(1+2y)} y_m - 2 \quad (10.20)$$

and the second correction, g_x , by

$$\begin{aligned}
g_x = & \frac{4}{y_I} \{ 1 - \frac{1+y}{1+2y} y_m + (1+y) e_1 \} \\
& + \frac{4(2y-5)(1+y)}{3(1+2y)} y_m^3 \\
& + \frac{4(8+14y+17y^2+4y^3)}{3(1+2y)^2} y_m^2 \\
& - \frac{4(8y^4+5y^3+19y^2+20y+5)}{3(1+2y)^3} y_m \\
& + \frac{4(4+4y-3y^2-2y^3)}{3(1+y)(1+2y)} \\
& - \frac{8}{3y_m}
\end{aligned} \tag{10.21}$$

where e_1 is the same feed-dependent parameter as given in (10.17), (10.18).

In the same way, the expansion for the dispersion index is found to be

$$D_p = 1.5 + \frac{f_D}{\lambda} + \frac{g_D}{\lambda^2} + o\left(\frac{1}{\lambda^2}\right) \tag{10.22}$$

where

$$f_D \equiv 0 \tag{10.23}$$

and the second correction is

$$\begin{aligned}
g_D = & - \frac{4(1+y)}{y_I y_m} e_1 \\
& + \frac{4(16+19y+2y^2)}{3(1+2y)} y_m^2 \\
& - \frac{4(30+42y+10y^2)}{3(1+2y)} y_m
\end{aligned} \tag{continued}$$

$$\begin{aligned}
& + \frac{4(20+53y+40y^2+6y^3)}{3(1+y)(1+2y)} \\
& + \frac{4(2y^2-11y-9)}{3(1+2y)y_m} \\
& + \frac{4}{3} \{2+(1+y)e_2\} \cdot \frac{1}{y_m^2}
\end{aligned} \tag{10.24}$$

where e_1 and e_2 are feed dependent parameters, with e_1 as given in (10.17), (10.18) and e_2 by

$$e_2 = \begin{cases} 1 & ; \text{premixed feed} \\ \frac{1}{1-\phi} & ; \text{separate feeds} \end{cases} \tag{10.25}$$

where ϕ is, for separate feeds of initiator and monomer, the volume fraction of the total feed represented by the initiator stream.

A few words, perhaps, are in order about the meaning of I_0 and M_0 . For premixed feeds, there is no difficulty -- I_0 and M_0 represent the initiator and monomer concentrations respectively, in the feed. For separate feeds, however, they are used a little differently. For separate feed lines of initiator and monomer, I_0 and M_0 represent the concentrations of initiator and monomer in the total feed, as if the two feeds were actually premixed. This definition is artificial, but it has the advantage that it allows the results to be written in a compact way for both feed systems at once.

Equation (10.22) gives the dispersion index for terminated polymer only. The difference between this index and those for radicals only and total polymer can be indicated

by considering their values for an ideally mixed reactor. Equation (10.22) gives that, for ideal mixing, D_p is 1.5. Under the same conditions,

$$D_r = 2$$

$$D = \frac{2(1+\frac{3}{2}y)(1+\frac{1}{2}y)}{(1+y)^2} \quad (10.26)$$

so that it is easily seen that the bounds on D for ideal mixing are the values of D_p and D_r , that is, for ideal mixing,

$$1.5 \leq D \leq 2 \quad (10.27)$$

Up to this point, nothing has been said about the convergence of the series (10.14), (10.19) or (10.22). With expressions as complex as these, very little can be said analytically, but it seems that in the worst case, if

$$\lambda > \frac{4(1+y)}{y_I y_m^2} \quad (10.28)$$

each of these series should exhibit a numerical convergence. This condition could be made a little less stringent if only premixed feeds are considered, but (10.28) should cover any situation.

X.4 Discussion

A discussion of the results naturally begins with a consideration of the system behavior under some limiting conditions. Perhaps the most interesting limiting case to examine is that of very high conversion. The easiest way to look at behavior in this region is to consider what happens as the conversion for perfect mixing nears completion--that is, as y_m approaches zero. For this case, for equation (10.14) one finds

$$\left. \begin{array}{l} f_m \rightarrow 2 \\ g_m \sim \frac{4}{3y_m} \end{array} \right\} \text{ as } y_m \downarrow 0 \quad (10.29)$$

so that the conversion is increasingly more sensitive to mixing as the ideal conversion nears completion. Similarly, for (10.19) one finds

$$\left. \begin{array}{l} f_x \rightarrow -2 \\ g_x \sim -\frac{8}{3y_m} \end{array} \right\} \text{ as } y_m \downarrow 0 \quad (10.30)$$

so that the number average molecular weight becomes more sensitive to departures from ideal mixing as y_m approaches zero. Finally, for (10.22) one finds

$$g_D \sim \frac{4}{3y_m^2} \{2 + (1+y)e_2\} \text{ as } y_m \downarrow 0 \quad (10.31)$$

so that, as y_m decreases to zero, the dispersion index becomes

more sensitive to mixing also. In other words, as ideal mixing conversion nears completion, conversion and degree of polymerization decrease more sharply, and the dispersion index, which measures the breadth of the polymer size distribution, increases more sharply with departures from ideal mixing. This behavior agrees with what one expects in such circumstances.

Another interesting case is that of low conversion. A convenient way of examining behavior in this region is to allow only a very short mean residence time. For this case, one finds

$$\begin{aligned}
 f_m &\sim -4 \frac{k_I^2 k_p k_T}{\alpha^4} \\
 g_m &\sim \frac{8k_I k_p}{\alpha^2} (1 - e_1) - \frac{1072}{3} \frac{k_I k_T}{\alpha^2} I_0 \\
 f_x &\sim -2 \left(1 + \frac{k_p}{k_T}\right) I_0 \frac{k_I k_T}{\alpha^2} \\
 g_x &\rightarrow 4 \text{ (premixed feed)} \\
 &\sim \frac{40}{3} \left(\frac{k_p}{k_T} - 1\right) I_0 \frac{k_I k_T}{\alpha^2} \text{ (separate feeds)} \\
 g_D &\rightarrow -4 \text{ (premixed feed)} \\
 &\rightarrow \frac{4\phi}{3(1-\phi)} \text{ (separate feeds)}
 \end{aligned}$$

as $\alpha \uparrow \infty$

(10.32)

From (10.32), it can be seen that for very small residence times, the system is fairly insensitive to departures from ideal mixing, as expected. Not much more can be determined from (10.32) probably since behavior at this end would perhaps better be explored by taking expansions around $\beta/\alpha = 0$.

Since equations (10.19) and (10.22) are written for terminated polymer only, it would be of little interest to explore behavior near $k_T = 0$. However, it might be profitable to look at the other extreme--that is, to examine the behavior when the termination rate is very high. For this case, one finds

$$f_m \rightarrow 0$$

$$g_m \rightarrow \frac{-32k_p I_0}{\alpha} (1-y_I) \left(\frac{2}{3} + \frac{e_1}{y_I} \right) - \frac{8}{3}$$

$$f_x \rightarrow 0$$

$$g_x \rightarrow \frac{4}{y_I} \sqrt{8 \frac{k_T}{\alpha} I_0 (1-y_I)} \quad (\text{premixed feed})$$

$$\rightarrow \frac{2}{y_I} - \frac{11}{6} - \frac{128k_p I_0}{3\alpha} (1-y_I) \quad (\text{separate feeds})$$

$$g_D \rightarrow 4 \left(\frac{1}{3} - \frac{1}{y_I} \right) \sqrt{8 \frac{k_T}{\alpha} I_0 (1-y_I)} \quad (\text{premixed feed})$$

$$\rightarrow \frac{4}{3(1-\phi)} \sqrt{8 \frac{k_T}{\alpha} I_0 (1-y_I)} \quad (\text{separate feeds})$$

as $k_T \uparrow \infty$

(10.33)

Equations (10.33) show that although there is no conversion of monomer at perfect mixing, this condition changes slowly as the mixing intensity is decreased. The degree of polymerization, which goes to zero in the limit of ideal mixing, begins to show some positive change for premixed feed in the second correction, but not for the case of separate feeds. The dispersion index, which is 1.5 for the perfectly mixed case, shows a negative change in the second correction for premixed feed, and a positive change for separate feeds. While the mechanism for the behavior mentioned above is unclear, it seems apparent that as k_T becomes large, there is more chance for radical growth if the feed is premixed than if there are separate feed lines for monomer and initiator.

In the above analysis of limiting cases, frequent mention was made of the differences in system behavior for premixed versus separate feeds. In general, one may notice several things from the equations in section X.3. First, it can be seen that the monomer conversion is not affected by the type of feed used, at least up to second order correction terms. Second, both g_m and g_D are always larger for separate feeds than they are for premixed feeds. This leads to the conclusion that premixing of monomer and initiator always results in a narrower distribution of higher molecular weight polymer.

Another difference between the two types of feed systems is that using separate feeds introduces a new variable into the analysis. This variable, ϕ , is the volume fraction of the total feed represented by the initiator-bearing stream.

It can be shown that monomer conversion and number average molecular weight do not depend on ϕ . The dispersion index, however, does depend on ϕ and this dependence becomes manifest as soon as second correction terms are considered. From equation (10.24) one finds that the ϕ -dependence is shown in the term

$$\frac{4}{3y_m^2} (1+y) \frac{1}{1-\phi} \quad (10.34)$$

so that as ϕ increases, g_D increases, and hence the dispersion index increases for nonideal mixing. This is not what is expected and it may be argued that (10.34) appears in such a manner since only terminated polymer is being considered. However, it can be shown that for D , the dispersion index for growing radical and terminated polymer combined, the second correction term depends on ϕ through the expression

$$\frac{4}{3y_m^2} (2+y) \frac{1}{1-\phi} \quad (10.35)$$

which is larger than (10.34).

A more likely explanation of the above result is that expansions around $\beta = \infty$ predict the behavior in the region near ideal mixing. For large departures from ideal mixing, the dependence of the dispersion index on ϕ may be quite different from what is portrayed in (10.34), (10.35).

In section X.3 no mention is made of how the parameters e_1 and e_2 arise. They are, in fact second moments on the feed

distribution with

$$e_1 = \frac{\iint p^*(I, M) I M dI dM}{M_O I_O} \quad (10.36)$$

and

$$e_2 = \frac{\iint p^*(I, M) M^2 dI dM}{(M_O)^2} \quad (10.37)$$

The values of e_1 and e_2 given in (10.17), (10.18), and (10.25) can be quickly verified using the distribution

$$p^*(I, M) = \delta(I - I_O) \delta(M - M_O) \quad (10.38)$$

for premixed feed, and

$$\begin{aligned} p^*(I, M) = & \phi \delta\left(I - \frac{I_O}{\phi}\right) \delta(M) \\ & + (1 - \phi) \delta(I) \delta\left(M - \frac{M_O}{1 - \phi}\right) \end{aligned} \quad (10.39)$$

for separate feeds.

The difference in behavior exhibited by the system for the premixed feed as opposed to separate feeds is perhaps most clearly indicated in one of the limiting cases previously described. When the mean residence time approaches zero (see 10.32), g_D , which is, in fact, the first non-zero correction to the dispersion index D_p , is negative for premixed feed and positive for separate feeds. By investigating several numerical examples, it can be shown that this is not only true in the

limit as $\alpha \rightarrow \infty$, but holds for small mean residence times in general.

That negative values of g_D should be encountered is understandable since, for a batch process, the limiting value of the dispersion index at time zero, which is also the initial value of the instantaneous dispersion index, is given by

$$D_p = \frac{56}{45} \quad ; \quad \text{batch, } t \rightarrow 0 \quad (10.40)$$

Since D_p for ideal mixing is always 1.5 regardless of the mean residence time, it follows that departures from ideal mixing could decrease D_p if the mean residence time is small. That this is in fact true only for the case of premixed feed is not very surprising. When the initiator and monomer are fed separately, departures from ideal mixing cause the occurrence of regions where initiator and monomer are still unmixed, thereby increasing the dispersion index. For premixed feed, however, even without mixing (e.g. - $\beta = 0$) reaction between initiator and monomer proceeds, and this effect is indeed manifest in the second correction as can be noted from (10.15), (10.16) or (10.20), (10.21) where the e_1 -term in the second correction to conversion and degree of polymerization, respectively, acts to negate the effect of the first correction.

In the polymerization scheme used by Denbigh [16,17] and Tadmor and Biesenberger [6,41], there is no initiator, so in fact there is no question as to what type of feed is used. The initial reaction of monomer to form radical is zero order, and all further reactions are second order combinations as in

the system discussed in this chapter. The two systems become very similar when the present system is modified to zero order initiation with a premixed feed. The modification to zero order initiation is made simply by setting y_I equal to 1 in the equations in this and the previous section. For this modified system, the correction to the dispersion index, g_D , is negative for small values of $\frac{1}{\alpha}$, and positive for large values of $\frac{1}{\alpha}$. This fact is completely in accord then with Denbigh's statement regarding the ratio of mean polymer lifetime to mean residence time, and hence the results obtained here may be regarded as a mathematical expression of the more instinctive arguments of Denbigh and others.

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Nomenclature

A	: empirical parameter
A, B, C	: chemical symbols for reaction equations
A_0	: frequency factor
a	: free parameter in Gamma distribution
a, b	: free parameters in Beta distribution
a_{ij}	: j th component of reaction rate for y_i
B	: boundary or surface of region R
$B(a, b)$	: Beta function
$B^{(a, b)}(y)$	: Beta distribution weighting function
c	: concentration
c'	: concentration fluctuation
c', c''	: dummy concentration variables
$\underline{c}$	: vector of concentrations
c_0	: feed concentration
$c_B(t)$	: conversion in a batch reactor after time t
c_i	: concentration of the i th component
c_p	: heat capacity
D	: dispersion index
D_p	: dispersion index for terminated polymer only
D_r	: dispersion index for growing radicals only
$\mathcal{D}$	: molecular diffusivity
dS	: differential surface area
E	: activation energy
e_1, e_2	: feed dependent quantities for polymerization system

F	: functional dependence of β
$f(t)$	: residence time distribution
$f_1, \dots, f_n$	: implicit equation functions
f_D	: first correction in expansion for the dispersion index
f_m	: first correction in expansion for the monomer conversion
f_x	: first correction in expansion for the number average molecular weight
fc_n	: functional dependence of β in natural units
$G_n^{(a,b)}(y)$	: Jacobi polynomials
$g(\theta)$	: age distribution
g_D	: second correction term in expansion for the dispersion index
g_m	: second correction term in expansion for the monomer conversion
g_x	: second correction term in expansion for the number average molecular weight
grad	: gradient
$H_n(a,b)$	: normalization of Jacobi polynomials
$-\Delta H$	: heat of reaction
I	: initiator; initiator concentration
I_0	: initiator concentration in the feed
J	: degree of segregation
K	: collision intensity parameter
k	: reaction rate constant
k_i	: rate constant for the i th reaction
k_I	: initiation rate constant
k_P	: polymerization rate constant
k_T	: termination rate constant
L	: characteristic linear dimension of the mixing system

$L_n^{(\gamma)}(z)$	: Laguerre polynomials
l_d	: Taylor (dissipation) microscale
l_m	: microscale for turbulent mixing
M	: monomer; concentration of monomer
M	: degree of polynomial rate expression
$\bar{M}$	: average concentration of monomer
M_0	: concentration of monomer in the feed
m, n	: parameters in Spalding approximation to adiabatic reaction rate
N	: agitator speed
N, n	: reaction order
n	: number of parameters in proposed distribution approximation
P_i	: terminated polymer molecule having i monomer units
$p(c, t)$	: concentration distribution at time t
$p^*(c, t)$	: concentration distribution for the feed at time t
$p^*(I, M)$	: feed distribution in polymerization system
$p(y_1, y_2)$	: steady state concentration distribution
$p^{(j)}(y, t)$	: j th term in expansion of $p(y, t)$
Q	: total number of particles in the reactor
$q(c, t)$	: particle number distribution
R	: universal gas constant
$R(y)$	: dimensionless reaction rate
$R_{\mathcal{A}}(y)$	: dimensionless reaction rate for $y_{\mathcal{A}}$
$\dot{R}_i$	: growing free radical having i monomer units
Re	: Reynolds number
R	: region of space
r	: batch reaction rate
r_i	: batch reaction rate for c_i

S	: cross-sectional area of inlet jets
s	: number of independent concentration variables
T	: absolute temperature
T_o	: initial temperature
T_f	: temperature at complete conversion
t	: time; dimensionless time
u	: root mean square velocity fluctuation
u_j	: velocity in direction x_j
u_v	: velocity normal to the boundary B
V	: volume of region
v	: inlet velocity
w	: particle inflow-outflow rate
$w^{(\gamma)}_{Iz}$	: Gamma distribution weighting function
$\bar{X}_n$	: number average molecular weight
$\bar{X}_{np}$	: number average molecular weight for terminated polymer only
$\bar{X}_{nr}$	: number average molecular weight for growing radicals only
$\bar{X}_w$	: weight average molecular weight
$\bar{X}_{wp}$	: weight average molecular weight for terminated polymer only
$\bar{X}_{wr}$	: weight average molecular weight for growing radicals only
x	: polymer size reckoned in monomer units
$\underline{x}$	: position vector
x_j	: coordinate direction
X_v	: outward normal to boundary B
y	: dimensionless concentration variable, such as fractional conversion
y', y''	: dummy dimensionless concentration variables

$\underline{y}$: dimensionless concentration vector

y_i : dimensionless concentration of the i th component

y_I : fraction of initiator unreacted for ideal mixing

y_m : fraction of monomer unreacted for ideal mixing

z : $=\gamma y/a$ for Gamma distribution and Laguerre polynomials

z : a dummy integration variable

Greek Letters

α	: inverse mean residence time
β	: mixing intensity parameter
γ	: free parameter in Gamma distribution
$\bar{\gamma}$	: $= \int \bar{\gamma}^2 \psi(\bar{\gamma}) d\bar{\gamma}$
ϵ	: power input per unit mass of working fluid
ζ	: parameter in Spalding approximation to adiabatic reaction rate
η	: empirical efficiency factor
θ	: age of a subparticle
$\bar{\theta}$	: mean age of a particle
λ	: $= 2\beta/\alpha$, dimensionless mixing intensity
μ	: mean concentration
μ	: viscosity
μ^*	: mean feed concentration
μ_j	: jth moment of $p(c, t)$
μ_j^*	: jth moment of $p^*(c, t)$
$\mu_{1;s}$	: mean value of y_s in the reactor
$\mu_{1;s}^*$	: mean value of y_s in the feed
$\mu_{m_1 m_2 \dots m_s}$	: multidimensional moment of $p = \int y_1^{m_1} y_2^{m_2} \dots y_s^{m_s} p(\underline{y}, t) d\underline{y}$
$\mu_{m_1 m_2 \dots m_s}^*$	: multidimensional moment of $p^* = \int y_1^{m_1} y_2^{m_2} \dots y_s^{m_s} p^*(\underline{y}, t) d\underline{y}$
$\mu_m^{(j)}(t)$	: jth term in expansion of $\mu_m(t)$
ν	: molecular kinematic viscosity

ξ	: $= e^{-t}$, integration variable
ρ	: density
σ^2	: variance
$*\sigma^2$	: variance in feed
σ_j^2	: jth term in the expansion of
τ_m	: mixing time
ϕ	: fraction of the total feed represented by the tracerless stream
ϕ	: fraction of the total feed represented by the initiator stream in polymerization study
ϕ_n	: constants in expansion of $p(y)$ in Laguerre polynomials
$\psi(\bar{\theta}, t)$	: distribution of mean ages among the particles
ψ_n	: constants in expansion of $p(y)$ in Jacobi polynomials

VITA

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"The Effect of Imperfect Mixing on Stirred
Combustion Reactors," Twelfth International Symposium
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"Scale-up Criteria for Stirred Tank Reactors,"
A. I. Ch. E. Journal, 15, November, 1969

In October, 1968, John was married to the former Lucille Ann Voltaggio, and in September, 1969, he was appointed Assistant Professor of Chemical Engineering at Lafayette College in Easton, Pennsylvania where he is now employed.