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THE APPLICATION OF A TIME DELAY MODEL

TO CHEMICAL ENGINEERING OPERATIONS

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### SUMMARY

Methods are developed for describing flow and transport phenomena in chemical process equipment in terms of random time delays that are undergone by material or energy elements in passing through the process.

It is shown how these methods may be applied to typical chemical engineering processes including exchange processes in packed beds, distillation and multiple reactions in complex flow regimes.

A new mixing concept, dynamic dispersion, is defined which may be used to account, in a formal way, for the disparity that sometimes exists between the behaviour of a process in the steady state and predictions based on the axial dispersion concept.

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## 1. INTRODUCTION

The studies reported in this thesis grew out of a general dissatisfaction with the sort of analysis, based on diffusion theory, usually presented to describe mixing during flow through packed beds. Without going into too much detail, the diffusion theory suffers from mathematical complexity in any case but the simplest, one-dimensional diffusion in an infinite medium flowing at constant velocity, is attempted. This in itself does not mean that the theory is unsatisfactory, but there are other conceptual difficulties: principally the questions of whether true backflow occurs and the associated problem of whether the downstream boundary has any influence. In practice it does not seem that conditions at the system outlet have much influence on what occurs inside the system and that backflow is unimportant, if not non-existent, in a variety of cases (1, 2). When the diffusion theory is used in these circumstances, the result is that the degree of true backflow predicted is small, but it does seem that an alternative treatment of the initial value or marching type is preferable, and possibly more realistic.

More or less the same period that has seen the development of the various diffusion models (reviewed by Levenspiel and Bischoff (3)) has also seen the development of the several penetration theories (4, 5, 6) to explain the mechanism of transfer processes between phases. In these theories it is considered that the transport is due to the motion of 'packets' of fluid from the bulk of the fluid to the interface and back again; the theories differ in the details of the distribution of lifetimes at the interface. The present study started with an attempt to apply these same ideas to the problem of representing the residence time distribution. In many flow situations there is a so-called stagnant region in which the flow rate in the direction of the main flow is zero or very small, but through which

material may circulate by diffusion or transverse flow. The time delay idea was to characterize mixing in terms of plug flow upon which is superimposed random delays which represent the random exchange between the flowing and 'stagnant' regions. This led fairly quickly to the abstraction that there is always a minimum transit time and that mixing may be represented by a random delay process relative to this minimum (which may be zero).

The emphasis in the chapters that follow is to look at the process from the point of view of its residence time distribution. We start with a brief description of the more common models for mixing in chemical process equipment, most of which are in fact time delay models of one sort or another, followed by some of the general properties of distributions including a few new results. This leads naturally on to a number of developments made, during the course of the present studies, of other models. These developments were made at various times, but are collected together for convenience and so that they do not intrude into the more systematic treatment of one dimensional and multidimensional time delay models that follow. We shall see that the time delay strategy is able to treat several phenomena in a reasonable way and leads to a new concept of dispersion modelling, namely that the spreading of residence times is due to two effects one of which disappears in the steady state. At the present this idea remains speculative, but it must be remarked that most of the evidence for the usual diffusion treatment is not against the new idea. Finally, the lines of future development are suggested.

## 2. MODELS FOR RESIDENCE TIME DISTRIBUTIONS IN CHEMICAL ENGINEERING.

### 2.1 Introduction

In this chapter some of the principal ideas which have been used to construct models of the mixing processes which occur in chemical process equipment will be discussed. The purpose is not to give an exhaustive survey of the literature but to compare and contrast the main themes of the literature and to show how they relate to the time delay idea. Comprehensive critical surveys in this field have been published in recent years by Levenspiel and Bischoff (1), Klinkenberg (2) and Verloop, de Nie and Heertjes (3). Also of interest is the book by Shepherd (4) describing how techniques very similar to those employed in chemical engineering have been used in biological studies.

Chemical engineering models fall into two main groups: those in which a basic unit is repeated several times with series interconnection and those in which a variety of units are connected together in a more arbitrary way. The former are essentially one-dimensional and the latter multi-dimensional. A similar distinction exists for models expressed in terms of differential equations. One-dimensional models have been developed in a systematic way and each model applied in a variety of situations. Their complexity has rather precluded this for multi-dimensional models, which have been analysed case by case.

### 2.2 The well-mixed vessel

The natural definition of perfect mixing is that the composition is everywhere the same when examined at a scale that is small compared with the vessel dimensions but large compared with molecular dimensions. This definition is not wholly satisfactory from the point of view of molecular interactions, but is sufficient to establish the residence time distribution. A material balance for a vessel of volume  $V$  through

which fluid flows at volumetric rate  $Q$  is:

$$Qc_i - Qc_o = V \frac{dc_o}{dt} \quad (1)$$

where  $c_i$  and  $c_o$  are the outlet concentrations. The outlet concentration for impulsive forcing is

$$c_o = \frac{V}{Q} e^{-Qt/V} \quad (2)$$

that is the residence time distribution is

$$f(t) = \frac{1}{\tau} e^{-t/\tau} \quad (3)$$

where  $\tau$  is the mean time.

This leads to an immediate interpretation in terms of time delays: there is no minimum transit time and the delays have a (negative) exponential distribution. Probabilistically, all flow elements present in the vessel at a given instant have the same chance of leaving in the next small increment of time.

Many more elaborate models are constructed from well-mixed vessels connected together in an appropriate way; the simplest of these is the tanks-in-series model.

### 2.3 The tanks-in-series mixing model

When  $n$  well-mixed vessels of identical size are connected in series, Fig. 1, a set of  $n$  equations of the same as Eq.(1) is obtained. The response to an impulse, the residence time distribution, is

$$f(t) = \frac{t^{n-1} e^{-t/\tau}}{(n-1)! \tau^n} \quad (4)$$

where  $\tau$  is the time constant per vessel. This model is of considerable importance for several reasons: historically, it was first discussed in 1918 by Ham and Coe (5) (Levenspiel and Bischoff (1) give other early references); it is a good qualitative one-parameter representation of many processes; for flow in packed beds a priori

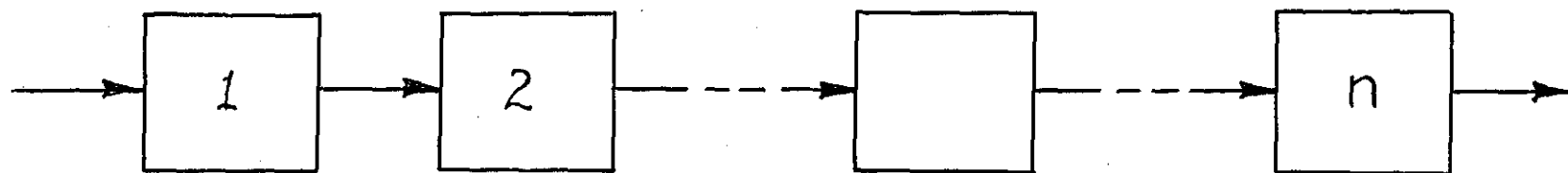


Fig. 1

The tanks-in-series mixing model

estimates of  $n$  based on particle dimensions give reasonable results (1). A drawback of the model is that  $n$  is apparently restricted to integral values of  $n$ , while a measured response might lie between those for adjacent  $n$ -values. It is in fact possible to generalize the model to remove this restriction quite easily. This is done in Sec. 5.2

The interpretation in terms of delays is again simple: each flow element undergoes  $n$  random delays and the residence time distribution is the distribution of the sum of  $n$  independent observations from an exponential distribution. In probability theory this is usually analysed via the characteristic function (Fourier transform) in a way that is analogous to the treatment using the Laplace transform that is familiar in chemical engineering.

#### 2.4 The tanks-in-series backflow model

Sometimes it is appropriate to consider that flow occurs between vessels in both directions, Fig. 2. This is the case with counter-current processes, e.g. fractionation, gas absorption, and on a microscale with diffusion. Several authors (6, 7, 8) have considered this case. The solutions of the model are not simple unless the number of vessels is small.

Probabilistically the essential feature that distinguishes the backflow model from the simple tanks-in-series model is that the number of delays is not also a random quantity. Retallick (6) has given a probabilistic treatment of this case.

#### 2.5 The diffusion model

The diffusion, or dispersion, model (9) is constructed by analogy with the treatment of molecular diffusion in a flowing medium. It is supposed that there is a diffusive flux counter to the concentration gradient superimposed on the bulk flow. For the one-dimensional case

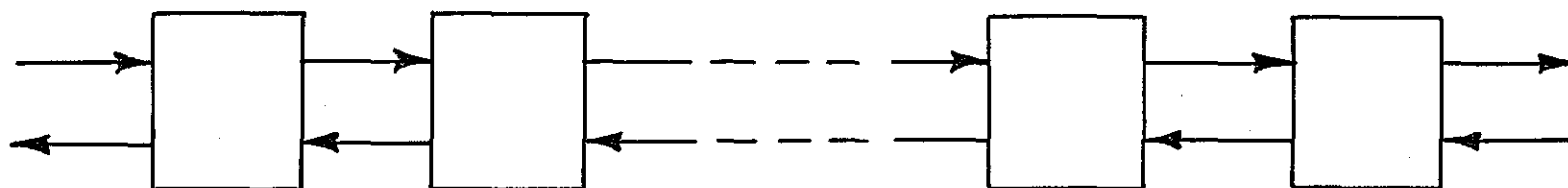


Fig. 2

The tanks-in-series-with-backflow mixing model

the flux of tracer at any section is:

$$\Phi = vc - D \frac{\partial c}{\partial x} \quad (5)$$

where  $c$  is the concentration at position  $x$  and time  $t$  in a stream moving at velocity  $v$ . The constant  $D$  is the diffusivity or dispersion constant. When this flux is incorporated into a material balance the diffusion equation for a moving medium:

$$D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x} = \frac{\partial c}{\partial t} \quad (6)$$

results.

Levenspiel and Bischoff (1) give solutions to Eq.(6) for several different sets of boundary conditions. It is sometimes stated that if diffusion is possible in the inlet or outlet, then the residence time distribution is affected. The effect is in fact more serious than this. Eq. (5) merely identifies the flux, not which tracer elements cross a given axial position, so that it is not possible to determine an expression for the residence time distribution in the usual sense.

The diffusion model is one of the most popular in chemical engineering and is widely employed in situations in which it is not clear why it should be employed. Klinkenberg's work (2) gives the impression that, whenever the residence time distribution fits a diffusion model response, it is both proper and desirable to use the model. This is only partly true. If it is only the dynamic response that is of interest, this approach is satisfactory. However, as so many mechanisms can be reduced to an 'equivalent' diffusion case, it follows that stimulus-response experiments cannot uniquely identify the mixing mechanism. The most sensitive technique for using response measurements to identify the mechanism is the use of the intensity function of Naor and Shinnar (10). This involves estimating the



instantaneous probability of a flow element leaving the system as a function of its age and requires precise measurements of the response. The relationship between the intensity function and directly measurable quantities is discussed in the next chapter.

The importance of the above observations on mechanism is that if some other phenomenon besides mixing occurs, the predicted system behaviour may well depend on how the mixing is represented. As a case in point, Bott and Azoory (11) have studied mixing in a wiped-film heat exchanger by the impulse response method and used the results to ascertain the extent to which the performance of the exchanger is affected by mixing. In a wiped-film exchanger much of the mixing is lateral in character and results in fluid elements taking a range of times in paths at a fixed axial position as is apparent from descriptions (12, 13) of the flow in transparent models where the flow can be seen. The one-dimensional diffusion treatment attributes all the spreading of residence times to axial mixing and results in a conservative estimate of the effect of mixing in this case. In fact Bott and Azoory conclude that for practical operating conditions axial mixing does not significantly degrade performance relative to the plug flow assumption, so there is no need to modify their conclusions. This may well not be the case for reactors. We return to this question in Chapter 8 where mixing is interpreted in terms of two effects, axial and dynamic dispersion.

Multidimensional dispersion models have been discussed by several workers whose results are summarized by Levenspiel and Bischoff (1). The main difficulty with these methods is their mathematical complexity.

The diffusion-type models are more naturally related to random shuffling than delays. The equations require boundary conditions to be imposed at the outlet as well as the inlet, which is an important difference between them and time-delay models.

## 2.6 The two layer (Anzelius) model

This model is another classic, dating from 1926 (14). The original application was regenerative heat transfer, but other processes, notably fixed bed mass transfer processes such as adsorption and ion exchange, and various forms of chromatography may be similarly described. The theory is available in several texts, e.g. Bird, Stewart and Lightfoot (15) and Bateman (16). The basic idea is that fluid flows in plug flow and interacts with a stagnant region in such a way that the rate of transfer between the flowing and stagnant regions is proportional to the concentration difference, Fig. 3.

As flow elements are only identified in terms of concentration, these assumptions are equivalent to assuming that each of the regions is locally well-mixed. Thus the residence time distribution is again the distribution of a random number of observations from an exponential distribution; there is also a dead time, or minimum possible transit time, because forward motion only takes place in the plug flow region. Analytical solutions of this model may be expressed in terms of Bessel functions (15, 16).

It is possible to generate several mechanisms that fit the above process description: it is possible that the 'stagnant' region is well mixed and that fluid flows through in such a way that there is little if any nett forward motion; the interaction may be characterized by a transfer coefficient as in heat transfer to a packing of high thermal conductivity; there may be transverse flow through pores of a variety of sizes to generate the exponential distribution.

## 2.7 The Deans-Levich Model

The Deans-Levich model is a discrete version of the Anzelius model and is illustrated in Fig. 4. It was proposed by Deans (17) to describe flow in packed beds and later discussed further by Levich, Markin and Chismadzhev (18) as a representation of dispersion in porous

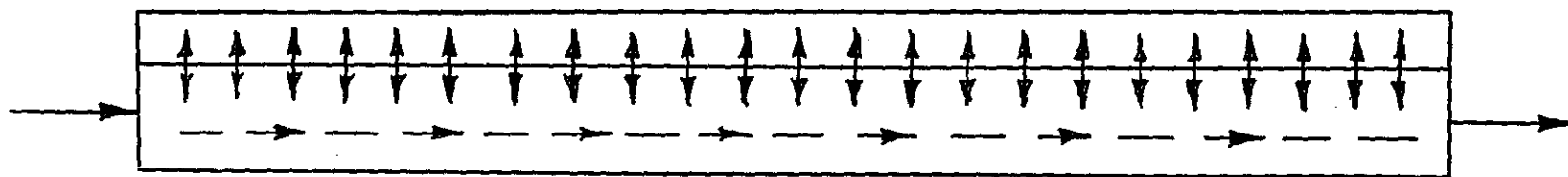


Fig. 3 The two-layer (Anzelius) mixing model

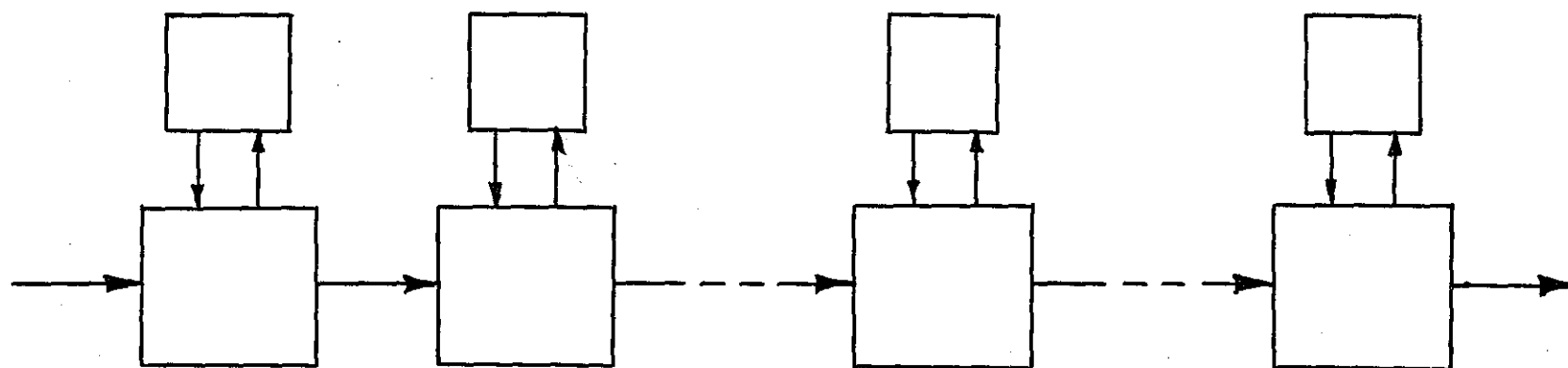


Fig. 4

The Deans-Levich mixing model

media. Deans gave the limiting (Anzelius) solution for an infinite number of stages while Levich and his co-workers obtained approximate solutions for a large number of stages. The analytical solution for this model is given later.

Probabilistically, the interpretation of this model in terms of delays is rather similar to that for the Anzelius model, except that only a finite number of delays is possible and that the dead time (minimum delay) is zero. Again it is possible for the exponential distribution to be generated in several ways.

## 2.8 The Cairns and Prausnitz (Einstein) model

Cairns and Prausnitz (19) have employed a model originally proposed by Einstein (20) to describe the motion of pebbles on the bed of a stream. It is considered that motion takes place in a series of random jumps and rest phases, the jumps being of negligibly short duration compared with the rest phases. This situation is equivalent to the Anzelius model with zero holdup in the flowing region.

## 2.9 Multidimensional models

Mathematically, the treatment of multidimensional models is difficult. As a result many models with special features designed to represent the details of specific processes have been proposed and treated case by case. Many examples are given in the reviews cited earlier. One of the objects in the present work was to generate a common method of treating multidimensional models in terms of time delays. Some success has been achieved in this and the methods are reported later.

### 3. RESIDENCE TIME DISTRIBUTIONS AND RELATED IDEAS.

#### 3.1 Density functions and distribution functions

The intuitive idea of distribution is adequate for most present purposes. It is unfortunate that two different usages have developed, in physics and probability theory, for describing distributions. Confusion can arise because the same word has different meanings in the two fields. The probability that a random variable  $X$  has a value  $x'$  in the range  $(x, x + dx)$  is denoted  $f(x) dx$ .  $f(x)$  is called the probability density function in probability theory and the distribution function in physics. Correspondingly the probability that  $x'$  is in  $(-\infty, x)$  is denoted  $F(x)$  and is called the distribution function (probability theory) or the cumulative distribution function (physics). In the present work the latter usage is adopted except that where the meaning is clear from the context the single word 'distribution' is used.

As the various possible values of  $x$  are mutually exclusive the additivity rule of probabilities implies that:

$$F(x) = \int_{-\infty}^x f(x) dx \quad (1)$$

whence 
$$f(x) = \frac{dF(x)}{dx} \quad (2)$$

When the distribution function is zero for part of the range of  $x$  it is convenient to take this into account in the limits of the integral. Residence times cannot be negative so that zero is then the appropriate lower limit.

Further obvious but useful properties are:

$$f(x) \geq 0 \quad (3)$$

$$\int_{-\infty}^{\infty} f(x) dx = F(\infty) = 1 \quad (4)$$

$$F(-\infty) = 0 \quad (5)$$

and the appropriate corresponding forms when the lower limit is not minus infinity.

Danckwerts (1) was the first to discuss residence time distributions in detail, and his notation for several concepts has become widely accepted. Several of the ideas that follow are due to Danckwerts, but his notation is not followed because it is in conflict with the type of notation usually used in probabilistic analyses. It is usual in probability theory to use lower case letters for density functions and the corresponding capital letters for distribution functions; Danckwerts uses capital letters for both. It is not wise to mix two conventions and, as the probability theory convention uses fewer letters, it is adopted here.

### 3.2 The residence time distribution

In general when material passes through a piece of process equipment, not all the material passes through in the same length of time. The very special case in which all elements of the material being processed take the same time to pass through rarely if ever occurs in practice. As this would occur if non-diffusing material passed through a straight conduit with a flat velocity profile, this situation is often called 'plug flow' and is a valuable concept because it frequently enables a limit to be put on the capabilities of process equipment.

The usual situation is that material passes through the equipment with a variety of residence times. This leads to the idea of a distribution of residence times: that is, the residence times are spread out and the spreading may be characterized by a density function, say  $f(t)$ . Intuitively this seems quite reasonable, but there are a number of situations in which the simple idea of residence time fails. For example: What is meant by 'residence time'

when it is possible for material, once having left a system, to reenter it? These and other conceptual difficulties can be avoided by specifying that the system under consideration is in a steady state flow regime and that material only enters and leaves the system by bulk flow, thus ensuring that residence is a once-only event. Inlets and outlets that obey this condition are called 'closed', Levenspiel (2), as opposed to 'open' boundaries at which diffusive effects prevent the unique determination of residence times. The distinction is comparable to that in thermodynamics in which diffusion across a system (control volume) boundary prevents an energy flux being split into heat and work interactions (3).

### 3.3 The impulse response

Imagine a quantity of tracer is introduced into the system entrance very quickly. It will emerge later from the system exit over a period of time. The results of this experiment clearly depend on the residence time distribution. If the flow situation is steady, repetition of the experiment will yield identical results. Steady injection of tracer may be regarded as indefinite repetition of the original experiment so that the result of the experiment when normalized to give proportions rather than concentrations is the residence time distribution. This conclusion is of considerable importance because the sudden injection of a quantity of tracer is easy to formalize mathematically. The Dirac delta function defined by:

$$\left. \begin{aligned} \delta(t-t') &= \infty, & t &= t' \\ &= 0, & t &\neq t' \\ \int_{-\infty}^{\infty} \delta(t-t') dt &= 1 \end{aligned} \right\} \quad (6)$$



is used to this end. The delta function has the advantage that it may be easily incorporated into the analysis of problems using integrals. Operational methods using integral transforms and separation of variables used to find Fourier series solutions are examples. These methods make use of the 'sifting' property:

$$\int_{-\infty}^{\infty} \delta(t-t') \varphi(t) dt = \varphi(t') \quad (7)$$

of the delta function.

The advantage of the impulse response as a characteristic of a process model is that it is usually simpler and more easily found mathematically than other responses, although the responses to step and sinusoidal forcing are frequently relatively simple. Responses to any other forcing functions may be determined from the impulse response by convolution, which numerically is a reliable procedure as it depends on integration. If one views the impulse in terms of its frequency content, this also suggests a central role for the impulse response because the response may be regarded as one which contains all frequencies in equal measure.

When the residence time distribution exists it is identical with the impulse response. However the impulse response exists independently of the idea of residence time.

### 3.4 The exit age distribution

It is sometimes convenient to think of a system in terms of the distribution of exit ages. This distribution is an attribute of the product at an instant in time and the experiment to measure it directly would involve coding a steady injection of tracer with its time of entry. The exit age distribution is identical with the residence time distribution, and the need to contrive experiments to measure the exit age distribution per se does not arise.

### 3.5 The internal age distribution

The distribution of ages within a piece of equipment is not the same as in the effluent. If a stream containing tracer at concentration  $c$  enters at a steady rate a proportion  $F^*(t)$  of the tracer that entered in  $(-t-dt, -t)$  will still be present at time zero. Thus the quantity with age less than  $t$ , i.e. that entered in  $(-t, 0)$ , is

$$cQ \int_0^t F^*(t') dt' \quad (8)$$

and the proportion is

$$\frac{\int_0^t F^*(t') dt'}{\int_0^\infty F^*(t') dt'} \quad (9)$$

The internal age distribution is obtained by differentiating this expression and is

$$h(t) = \frac{F^*(t)}{\int_0^\infty F^*(t) dt} = \frac{F^*(t)}{\bar{E}} \quad (10)$$

the value of the integral being given by Eqs. (17) and (19), below.

### 3.6 The intensity function

Sometimes, in search of a mechanism, one is led to consider the way in which the probability that an event occurs depends on the period of time in which it has not occurred: one's chances of dying this year depend on one's age. Thus in considering the residence time distribution for a stirred vessel it would be reasonable to attempt to relate the probability of a flow element leaving the vessel to, say, swirling. Age might enter the analysis in terms of the number of times the flow element has passed the outlet without leaving. Suppose that  $i(t)dt$  is the probability of a flow element of age  $t$  leaving the system in the time interval  $(t, t+dt)$ : that is,  $i(t)dt$  is

the conditional probability of leaving in  $(t, t+dt)$ , the condition being that the element is still present at time  $t$ . The multiplication rule for probabilities relates the unconditional probability to conditional probability as follows.

$$P(A) = P(A|B) \cdot P(B)$$

so that

$$f(t) dt = i(t) dt \cdot F^*(t) \quad (11)$$

or

$$i(t) = \frac{f(t)}{F^*(t)} = - \frac{d}{dt} \left[ \ln F^*(t) \right] \quad (12)$$

$i(t)$  is called the intensity or age-dependent risk function and has been advocated by Naor and Shinnar (4) and Heertjes (5) as a means for discriminating between residence time distributions.

### 3.7 The washout function

Suppose that a system is in the steady state, and continually fed with a stream containing tracer at a fixed concentration. At  $t = 0$  the tracer flow is stopped but conditions are otherwise maintained as before; some other material is substituted for tracer in the feed if necessary. The quantity of tracer present in the system at time  $t$  is given by the washout function  $g(t)$ . In principle  $g(t)$  contains the same sort of information as the functions that have been discussed previously. The properties of the washout function have not attracted much direct attention in the chemical engineering literature although the washout idea is clearly of importance in specifying acceptable levels of residual contamination after washing. An example that can be cited is the work of Tallmadge, Buffham and Barbolini (6, 7) on rinsing as practised in the metal finishing

industry. Washout functions and their properties have received more interest in biology in connection with perfusion and related techniques (8, 9).

The forcing function implied in the definition of  $g(t)$  is a negative step in the input of magnitude  $c$ , where  $c$  is the original steady feed concentration. A material balance:

Quantity remaining at  $t$

= quantity which will leave after  $t$

gives

$$g(t) = cQ \int_t^{\infty} F^*(t) dt \quad (13)$$

Differentiation shows how  $g(t)$  is related to more familiar functions:

$$\dot{g}(t) = -cQ F^*(t) \quad (14)$$

$$\ddot{g}(t) = cQ f(t) \quad (15)$$

and division of Eq (15) by Eq (14) gives

$$\frac{\ddot{g}(t)}{\dot{g}(t)} = \frac{d}{dt} \left[ \ln \dot{g}(t) \right] = -\frac{f(t)}{F^*(t)} \quad (16)$$

The washout function shares with the impulse response the property that its definition does not depend on the way boundary conditions are specified and so it remains defined in circumstances where the simple definition of residence time fails.

Extensions of the above ideas to systems with multiple independent inlets are possible.

### 3.8 The mean time

The mean time for a flow system with 'closed' boundaries is the ratio of the volume to the flow rate. This result has been discussed elsewhere (1) but the following demonstration of the result is very

simple and demonstrates its wide applicability. Equation (13) gives the steady state holdup of tracer as

$$g(0) = cQ \int_0^{\infty} F^*(t) dt \quad (17)$$

and integration by parts shows that

$$g(0) = cQ \left\{ \left[ F^* t \right]_0^{\infty} - \int_0^{\infty} t \frac{dF^*}{dt} dt \right\} \quad (18)$$

The product  $F^*t$  vanishes both when  $t = 0$  and when  $t \rightarrow \infty$ , so that, in view of Eq (2),

$$g(0) = cQ \int_0^{\infty} t f(t) dt = cQ \bar{t} \quad (19)$$

the integral in this equation being the mean time. For a system with one inlet, or several fed with tracer at rates such that their concentrations are the same, the steady state concentration must be the same as the feed concentration and  $g(0)$  is  $cV$ . Hence

$$\bar{t} = V/Q \quad (20)$$

#### 4. CHARACTERISTICS OF PROBABILITY DISTRIBUTIONS

##### 4.1 Moments

The moments of a probability distribution  $f(x)$  are defined by:

$$\mu_r' = \int_{-\infty}^{\infty} x^r f(x) dx, \quad r = 1, 2, 3, \dots \quad (1)$$

The zeroth moment is unity; the first moment or mean of  $x$  corresponds to the usual notion of the arithmetic average of  $x$ , so that  $\mu_1'$  may be interpreted as the average value of  $x$ . In addition to mean and average the term expectation, represented operationally  $E(\quad)$ , is also used. For values of  $r$  greater than unity the moments about the mean:

$$\mu_r = \int_{-\infty}^{\infty} (x - \mu_1')^r f(x) dx \quad (2)$$

are of rather more interest. These moments, called central moments, may be expressed in terms of the moments  $\mu_r'$  by multiplying out the  $(x - \mu_1')^r$  factor. E.g.

$$\begin{aligned} \mu_2 &= \int_{-\infty}^{\infty} (x^2 - 2\mu_1'x + \mu_1'^2) f(x) dx \\ &= \mu_2' - \mu_1'^2 \end{aligned} \quad (3)$$

The second central moment is called the variance, written  $\text{var}(x)$ , and is a measure of how spread out the  $f(x)$  curve is. The square root of the variance is the standard deviation,  $\sigma$ . Similarly the third central moment vanishes when  $f(x)$  is symmetrical about  $\mu_1'$ , as do all odd order central moments, and is a measure of the skewness of the curve.

Results corresponding to Eq(3) for the next few central moments are (1):

$$\mu_3 = \mu_3' - 3\mu_2'\mu_1' + 2\mu_1'^3 \quad (4)$$

$$\mu_4 = \mu_4' - 4\mu_3'\mu_1' + 6\mu_2'\mu_1'^2 - 3\mu_1'^4 \quad (5)$$

$$\mu_5 = \mu_5' - 5\mu_4'\mu_1' + 10\mu_3'\mu_1'^2 - 10\mu_2'\mu_1'^3 + 4\mu_1'^5 \quad (6)$$

When the variable is time it is usually the case that

$$f(t) = 0, \quad t < 0$$

so that the lower limit of the integrals may be taken as zero.

#### 4.2 Moment generating functions

A generating function is a function the coefficients of whose power series expansion give a desired set of parameters. In probability theory the integral

$$M(s) = \int_{-\infty}^{\infty} e^{st} f(t) dt$$

is frequently used as a moment generating function. However it is more convenient in the present context to use the related Laplace transform:

$$\bar{f}(s) = \int_0^{\infty} e^{-st} f(t) dt$$

since this is familiar and often known.

Expanding the exponential in the Laplace transform in a power series yields

$$\bar{f}(s) = \int_0^{\infty} \left( 1 - st + \frac{s^2 t^2}{2!} - \frac{s^3 t^3}{3!} + \dots \right) f(t) dt$$

$$= 1 - \mu_1' s + \mu_2' \frac{s^2}{2!} - \mu_3' \frac{s^3}{3!} + \dots \quad (7)$$

The coefficient of  $(-1)^r s^r / r!$  is the  $r$ th moment

Successive differentiation of Eq (7) shows that:

$$\left[ \frac{d^r \bar{f}(s)}{ds^r} \right]_{s=0} = (-1)^r \mu_r' , \quad (8)$$

a result that is also frequently useful. Corresponding rules based on the exponential Fourier transform, which uses  $e^{i\omega t}$  in place of  $e^{-st}$ , follow in the same way; the Fourier transform of a probability distribution is called a characteristic function (1). The logarithm of the characteristic function generates another set of coefficients,

the cumulants, which are closely related to the moments and which are often useful in calculating low order central moments.

#### 4.3 Cumulants

Instead of using

$$\ln \left\{ \int_{-\infty}^{\infty} e^{i\omega t} f(t) dt \right\}$$

as the cumulant generating function, it is again convenient for our purposes to use the Laplace transform. Expansion gives

$$\begin{aligned} \ln [\bar{f}(s)] &= \ln \left[ 1 - (\mu_1' s - \mu_2' \frac{s^2}{2!} + \mu_3' \frac{s^3}{3!} - \dots) \right] \\ &= - (\mu_1' s - \mu_2' \frac{s^2}{2!} + \mu_3' \frac{s^3}{3!} - \dots) \\ &\quad - \frac{1}{2} (\mu_1' s - \mu_2' \frac{s^2}{2!} + \dots)^2 \\ &\quad - \frac{1}{3} (\mu_1' s - \dots)^3 \\ &= -\mu_1' s + (\mu_2' - \mu_1'^2) \frac{s^2}{2!} \\ &\quad - (\mu_3' - 3\mu_2' \mu_1' + 2\mu_1'^3) \frac{s^3}{3!} + \dots \quad (9) \end{aligned}$$

The coefficients of  $(-1)^r s^r / r!$  in Eq (9) are the cumulants,  $\mathcal{K}_r$ , and comparison with Eqs (3) and (4) shows that:

$$\mathcal{K}_1 = \mu_1' \quad (10)$$

$$\mathcal{K}_2 = \mu_2 \quad (11)$$

$$\mathcal{K}_3 = \mu_3 \quad (12)$$

Beyond  $r = 3$  the method may still be used to find the moments, but the simple form breaks down (1).



#### 4.4 Probability moments

The moments of the probability rather than the time

$$\nu_r = \int_0^{\infty} f^r(t) dt \quad (13)$$

have certain attractions, but suffer from the drawback of being difficult to evaluate and manipulate. Levenspiel (2) has pointed out that  $\nu_2$  is a measure of the peakedness of the distribution and suggests it be called the 'emminence'. Engh (3) discusses blender performance in terms of this function.

#### 4.5 The probabilistic entropy

Shannon (4) defined the entropy for a discrete distribution as

$$S_D = -k \sum_i p_i \ln p_i \quad (14)$$

in his pioneering work on information theory. The entropy is a natural measure of the uncertainty of the outcome of an experiment with discrete outcomes (4, 5, 6). The uncertainty about the exact outcome of an experiment in which there is a continuous range of possible outcomes is infinite, which is reflected by the fact that  $S_D$  becomes infinite when the attempt is made to take the limit of Eq (14) to obtain the uncertainty for a continuous distribution.

The function

$$S_c = -k \int_0^{\infty} f(t) \ln f(t) dt \quad (15)$$

exists, however, and represents the relative uncertainty (4).  $S_c$  is a measure of the spread of  $f(t)$ , because the wider and flatter  $f(t)$  is, the more uncertain in relative terms is the result of a random observation.

Jaynes (7) has suggested a formalism for guarding against bias which is based on the entropy idea. This formalism is that the entropy should be maximized subject to constraints which express any known facts concerning averages and the like. When this is done one

obtains the 'maximally vague' (most spread out) distribution that fits the facts. Logically this is the best choice as a working hypothesis and is the 'minimally prejudiced' estimate of the distribution.

For a flow-mixing system that obeys the mean value theorem, Sec.3.8, and about which nothing else is known, Jaynes formalism gives

$$f(t) = \frac{Q}{V} e^{-Qt/V} \quad (16)$$

which is the residence time distribution for a perfect mixer. Thus the sense in which a perfect mixer is perfect from the residence time distribution point of view is that it induces the maximum possible spread in the residence time distribution. This result and one or two others is proved in Appendix I.

Although the entropy is an attractive measure of distribution spread, being fundamentally more suitable than the variance (see Appendix I), its major drawback is that it may be evaluated analytically for only a few very special cases. Moran (8) has recently remarked on how scarce applications of the entropy idea are in probability theory despite the appeal of the concept.

#### 4.6 Additivity of moments for independent events

Models of a serial nature are of frequent occurrence. Suppose that  $n$  random events with probability density functions  $f_i(t)$ ,  $i = 1, 2, 3, \dots, n$  occur in succession and call the density function for the composite event  $f(t)$ . This situation is familiar as  $n$  stirred vessels in series with residence time distributions  $f_i(t)$ . The Laplace transform of  $f(t)$  is

$$\bar{f}(s) = \prod_{i=1}^n \bar{f}_i(s) \quad (17)$$

because  $f(t)$  is the  $n$ -fold convolution of the  $f_1(t)$ . Taking logarithms:

$$\ln \bar{f}(s) = \sum_{i=1}^n \ln \bar{f}_i(s) \quad (18)$$

and expanding  $\ln \bar{f}(s)$  and  $\ln \bar{f}_i(s)$  as power series in  $s$ :

$$\begin{aligned} & -\mu_1' s + \mu_2 \frac{s^2}{2!} - \mu_3 \frac{s^3}{3!} + \dots \\ & = - \left( \sum_{i=1}^n \mu_{1,i}' \right) s + \left( \sum_{i=1}^n \mu_{2,i} \right) \frac{s^2}{2!} - \left( \sum_{i=1}^n \mu_{3,i} \right) \frac{s^3}{3!} + \dots \quad (19) \end{aligned}$$

which shows that the means, variances and skewnesses are additive.

#### 4.7 Miscellaneous distribution characteristics.

Many other characteristics may be defined that differ from distribution to distribution. Those described above are important in that they represent the distribution in terms of 'averages' assessed in a continuous way. Measures such as the median, the point which bisects the distribution; the quartiles, which divide the distribution into four equal areas; the location of the maximum probability; and the slope of the cumulative distribution function at the point at which it equals 0.5 are cruder measures which group the distribution into intervals and are consequently less discriminating. However these measures are usually easier to determine from experimental data; whether they are easily determined analytically depends on the mathematical form of the distribution considered.

## 5. SOME AD HOC DEVELOPMENTS OF TIME DELAY MODELS.

### 5.1 Introduction

In this chapter a number of developments and extensions of existing models of the time delay type are discussed. These include analytical solutions of hitherto unsolved problems, some new forms that were suggested by previous models and reinterpretations of previous models. The various topics discussed are arranged in a logical sequence rather than in the order in which they were developed. They arose during the course of the more general investigation and are collected together here for convenience.

### 5.2 A Generalized Tanks-in-Series Model

The transfer function for the tanks-in-series model is:

$$\bar{f}(s) = (\tau s + 1)^{-n} \quad (1)$$

in terms of actual time so that

$$f(t) = \frac{t^{n-1} e^{-t/\tau}}{(n-1)! \tau^n} \quad (2)$$

When this model is used to describe arbitrary mixing situations it is convenient to use normalized time units: i.e. a time scale such that the mean time is unity. The  $\sigma$ -domain and  $\theta$ -domain solutions are then

$$\bar{f}(\sigma) = \left( \frac{\sigma}{n} + 1 \right)^{-n} \quad (3)$$

$$f(\theta) = \frac{n^n \theta^{n-1} e^{-n\theta}}{(n-1)!} \quad (4)$$

For many situations this expression is a reasonably adequate one-parameter representation (1) especially for describing the responses

of columns when fairly high values of  $n$  are required. However, many workers, e.g. (2, 3), have found the model lacking in its ability to describe such phenomena as mixing in stirred vessels and fluidized beds. Often the physical response has characteristics intermediate between those for two low adjacent values of  $n$ , say 1 and 2 or 2 and 3. Since, in the situations in which the model is usually applied, the parameter  $n$  has no immediate physical significance, the suggestion arises: is it possible to retain the form of Eq.(4) with non-integral values of  $n$ ? The answer to this question is affirmative because it is not necessary to restrict  $n$  to integral values for Eq.(4) to have a valid inverse (4). If  $n$  is not integral the inverse is

$$f(\theta) = \frac{n^n \theta^{n-1} e^{-n\theta}}{\Gamma(n)}, \quad n > 0 \quad (5)$$

- a distribution known as the gamma distribution.

When  $n$  is integral the distribution takes the familiar form of an exponential decay if  $n$  is unity and a skewed bell-shaped curve that becomes less skew and more peaked for progressively higher values of  $n$ . This behaviour persists in the generalized form for  $n \geq 1$ , the curves for non-integral  $n$  lying between those for integral  $n$  in an intuitively satisfactory way. However, when  $0 > n > 1$  the curve takes a rather different form: it is infinite at  $\theta = 0$ , decays rapidly at first and finally decays more slowly than an exponential decay. These features are illustrated in Fig. 1.

The generalized tanks-in-series model then is an excellent example of the fact that the statement often made in the recent literature that plug flow and perfect mixing are extremes 'between' which all other mixing situations lie, is false. Early workers (5,6) did not make this mistake. Perfect mixing is an extreme in a very special sense - maximum spread of residence times - and can be regarded as being intermediate between perfect bypassing and plug flow,

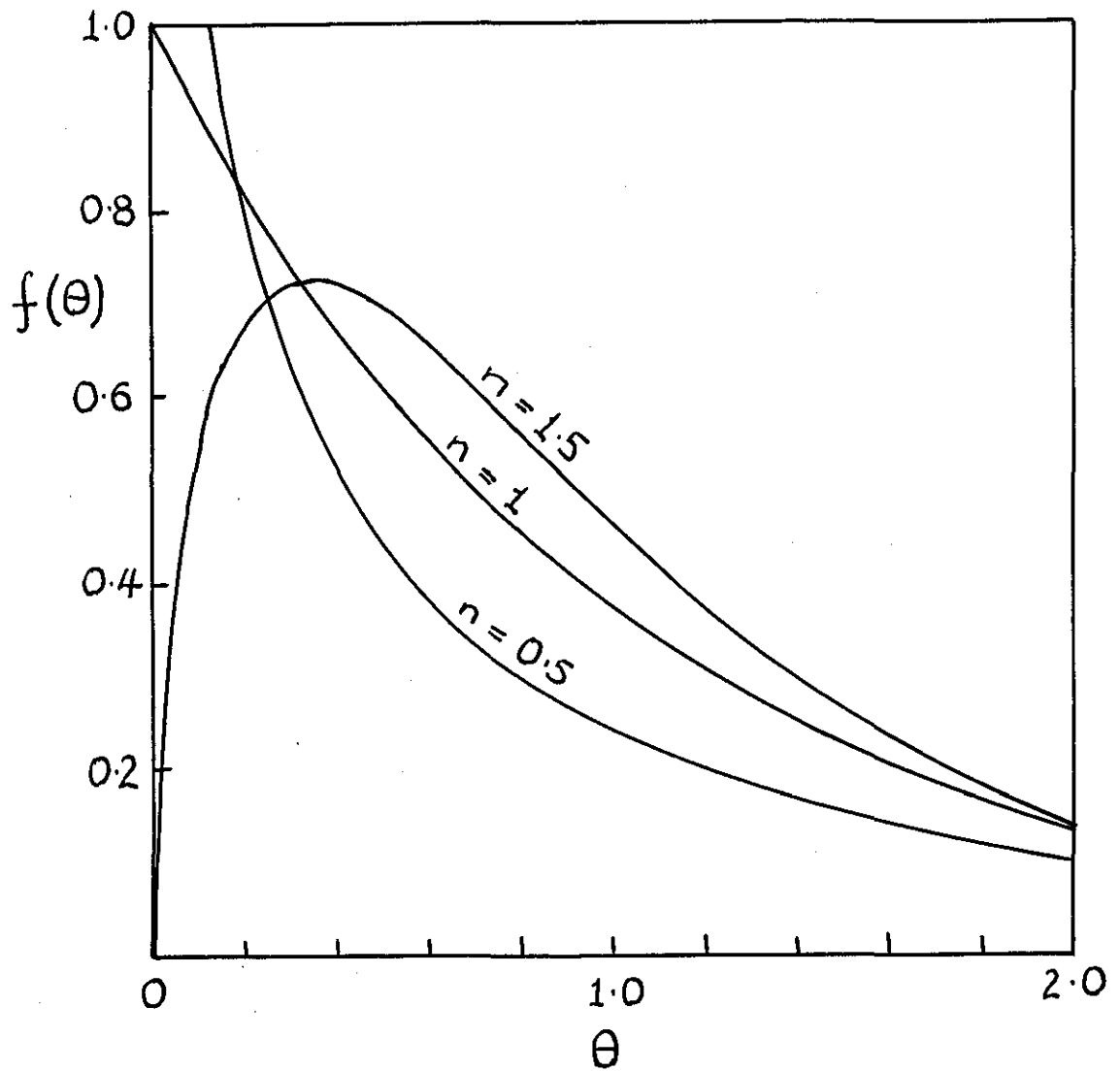


Fig.1 The gamma distribution, showing two types of deviation from perfect mixing.

both of which result in no spread of residence times. The natural measure for spread of residence times is the probabilistic entropy.

The moments of the generalized tanks-in-series model are most easily found by regarding the transfer function as a generating function (see 4.2) and are

$$\mu_r' = \frac{\Gamma(n+r)}{n^r \Gamma(n)} \quad (6)$$

from which it follows that the variance is

$$\text{var}(\theta) = n^{-1} \quad (7)$$

It is apparent from Fig. 1 that the model response possesses a maximum only when  $n > 1$ ; differentiation of Eq.5 shows that this occurs at

$$\hat{\theta} = 1 - \frac{1}{n} \quad (8)$$

Using the gamma distribution of residence times in a series replication model leads back to the same model. For if the prototype distribution transfer function is taken as

$$f_1(s) = (\tau s + 1)^{-m} \quad (9)$$

where  $m$  is not necessarily integral, and this is repeated  $n$  times in series, the result is

$$f_n(s) = (\tau s + 1)^{-mn} \quad (10)$$

which is identical in form to Eq (1).

These observations allow one an escape from the dilemma that occurs when the tanks-in-series model fits data but with a value of  $n$  that is in conflict with prior reasoning. If the prototype mixing processes are not perfect the number of stages identified experimentally will differ from the actual number.

Gibilaro (7) and Gibilaro, Kropholler and Spikins (8) have presented RTD data for a stirred vessel that show several interesting features including oscillations superimposed on an almost exponential decay, extremely high initial responses, and rapid rise followed by an almost exponential decay. The generalized tanks-in-series model is able to represent the latter two of these in a qualitative way as is shown in Figs. 2 and 3. The data are not fitted as well as they are by the more sophisticated, physically based models presented in the original references, but the fit is clearly a better representation than could be obtained from the tanks-in-series model conventionally interpreted.

### 5.3 A Two-Constant Generalized Tanks-in-Series Model

The success of the generalized tanks-in-series model in describing in a qualitative way a wide variety of mixing situations, ranging from stirred vessels showing bypass characteristics to packed columns, suggests that a similar model, based on comparable physical premises, but including another parameter could be very useful indeed. Suppose the unit cell is described by the transfer function

$$\bar{f}(s) = [(\tau_1 s + 1)(\tau_2 s + 1)]^{-1} \quad (11)$$

that is, the unit process is equivalent to two well-mixed regions of different volumes in series. When  $n$  such units are combined in series Fig. 4, the resultant transfer function is

$$\bar{f}(s) = [(\tau_1 s + 1)(\tau_2 s + 1)]^{-n} \quad (12)$$

or in normalized form

$$\bar{f}(\sigma) = \left[ \left( \frac{(1+\alpha)\sigma}{n} + 1 \right) \left( \frac{\alpha\sigma}{n} + 1 \right) \right]^{-n} \quad (13)$$



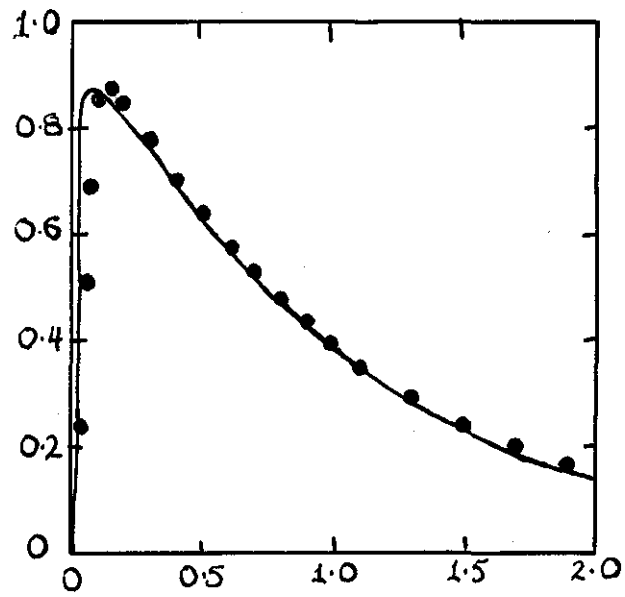


Fig. 2.

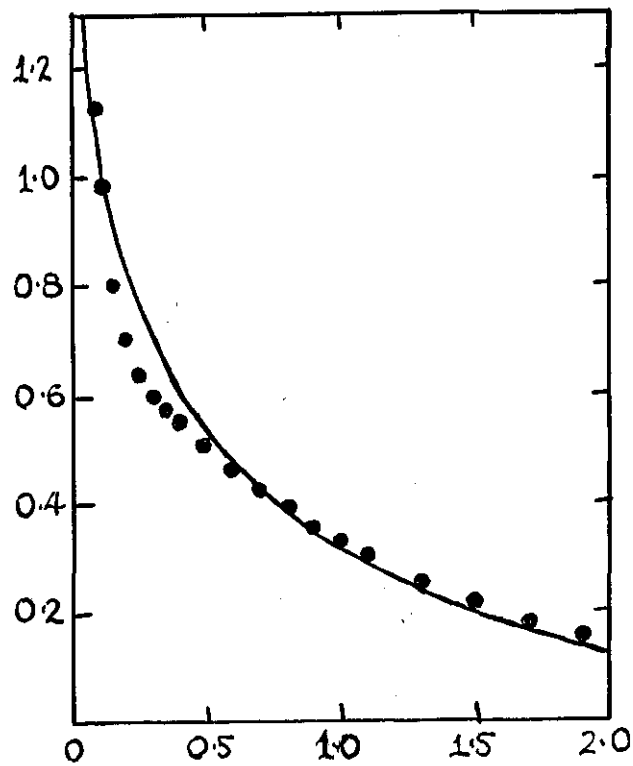


Fig. 3.

Figs. 2 and 3. The gamma distribution fitted to mixing tank residence time distributions.

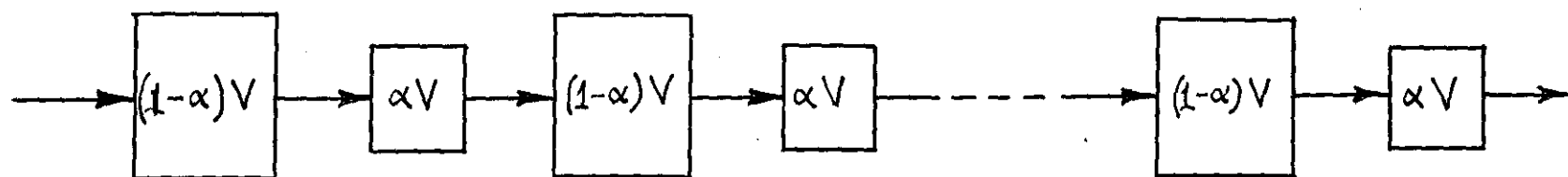


Fig 4

The two-constant tanks-in-series mixing model

where  $\alpha$  is in effect a volume ratio and is given by

$$\alpha = \tau_1 / (\tau_1 + \tau_2) \quad (14)$$

Had the unit process been taken as a combination of two gamma processes with the same index but different means, exactly the same form of normalized transfer function would have resulted.

Equation (13) reduces to the usual tanks-in-series model when  $\alpha = 1$  or 0 and is symmetrical about  $\alpha = \frac{1}{2}$ . Hence the range of  $\alpha$  can be conveniently taken as

$$1/2 \leq \alpha \leq 1 \quad (15)$$

When  $\alpha = \frac{1}{2}$  the model again reduces to tanks-in-series form but with twice as many tanks.

As with the tanks-in-series model, it is not necessary to restrict  $n$  to integral values in order to invert the transfer function. The inverse is (4):

$$f(\theta) = \frac{\sqrt{\pi} n^n}{\Gamma(n)} \left( \frac{\theta}{2\alpha-1} \right)^n \left[ \frac{\alpha(1-\alpha)\theta}{n(2\alpha-1)} \right]^{-1/2} e^{-n\theta/2\alpha(1-\alpha)} I_{n-\frac{1}{2}} \left\{ \frac{n(2\alpha-1)\theta}{2\alpha(1-\alpha)} \right\} \quad (16)$$

The moments of the response are most easily found by expanding Eq. (13) as a power series in  $\sigma$ . They are

$$\mu_0' = \mu_1' = 1 \quad (17)$$

$$\mu_2' = 1 + \frac{1 - 2\alpha(1-\alpha)}{n} \quad (18)$$

$$\mu_3' = 1 + \frac{1}{n} + \frac{2(n+1)}{n^2} [1 - 3\alpha(1-\alpha)] \quad (19)$$

The central moments could be established from the above results, but are more easily found from the cumulants:

$$\mu_2 = \frac{1 - 2\alpha(1-\alpha)}{n} \quad (20)$$

$$\mu_3 = \frac{2 [1 - 3\alpha(1-\alpha)]}{n^2} \quad (21)$$

If the moments are to be used directly in model simplification or to fit suitable data the simplest way to proceed is to eliminate  $\alpha(1-\alpha)$  between Eqs (20) and (21) to give the following quadratic for n:

$$\mu_3 n^2 - 3\mu_2 n + 1 = 0 \quad (22)$$

The value(s) of n thus found are then substituted into Eq.(20) to give a quadratic in  $\alpha$ . To be acceptable, values of n must be positive and  $\alpha$  may arbitrarily be restricted to  $0.5 < \alpha < 1$  remember.

This model may well be the basis for a good general-purpose simplified model for if a dead time is added the transfer function becomes

$$\bar{f}(s) = e^{-\tau_3 s} [(\tau_1 s + 1)(\tau_2 s + 1)]^{-n} \quad (23)$$

a form which includes the two:

$$\bar{f}(s) = e^{-\tau_3 s} (\tau_1 s + 1)^{-n} \quad (24)$$

and

$$\bar{f}(s) = e^{-\tau_3 s} (\tau_1 s + 1)(\tau_2 s + 1) \quad (25)$$

recently discussed for this purpose by Gibilaro and Lees (9). Also Myrén (10) has successfully used Eq.(24), fitted in the s-domain, to approximate transient thermal conduction.

#### 5.4 Infinite sequences of identical stirred tanks with backflow

The various cell models that have been previously discussed are capable of producing a wide variety of residence time distribution

shapes and can reflect the behaviour of many types of process equipment. There is, however, a significant aspect in which they are lacking: they cannot describe true backmixing. This feature can be introduced by incorporating flow in both directions between the cells, Fig.5. The characteristics of this model are very similar to those of the diffused plug flow model; indeed the equations that describe the model are the finite difference form of the diffusion model. As with the diffusion model, care is required in formulating the boundary conditions. End cells with a stream entering or leaving counter to the direction of the main flow correspond to the 'open' diffusion case while the absence of these flows corresponds to a 'closed' boundary condition. Considerable interest attaches to this model because not only can it be used to describe mixing in flow in packed beds and the like but the equations are analogous to those for counter-current stagewise processes.

The backflow model has received much attention in the literature (11, 12, 13, 14). The analytical solutions are cumbersome, but it will now be shown that the solutions for infinite sequences are simple and provide useful approximations. Unilateral (semi-infinite) and bilateral (infinite) sequences are considered.

Referring to Fig.5, a material balance over a typical stage yields:

$$q c_{n+1} - (Q + 2q) c_n + (Q + q) c_{n-1} = V \frac{dc_n}{dt} \quad (26)$$

where  $C_n$  is the concentration in the  $n$ th stage at time  $t$ ,  $Q$  is the through-flow rate,  $q$  is the backward flow-rate and  $V$  is the stage volume. A convenient dimensionless form of Eq.(26) is obtained by setting:

$$\alpha = q / (Q + q), \quad \tau = (Q + q)t / V, \quad y = c / c_0$$

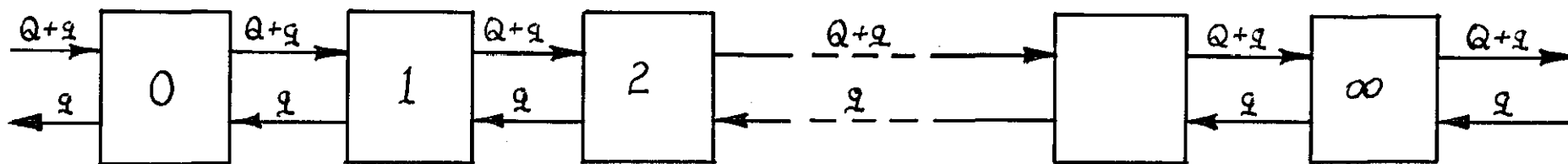


Fig. 5

The tanks-in-series-with-backflow model - infinite sequence

where  $C_0$  is a suitable constant with dimensions of concentration.

The result of making these substitutions is:

$$\alpha y_{n+1} - (1+\alpha) y_n + y_{n-1} = \frac{dy_n}{d\tau} \quad (27)$$

The response to impulsive forcing of the zeroth cell is most easily obtained by taking as initial conditions:

$$\begin{aligned} y_n(0) &= 0, \quad n \neq 0 \\ &= 1, \quad n = 0 \end{aligned} \quad (28)$$

which identifies  $C_0$  as the initial concentration in the zeroth tank.

The boundary conditions corresponding to the two types of infinite sequence discussed above are::

$$y_n(\tau) \rightarrow 0, \quad n \rightarrow \pm \infty \quad (29)$$

for the bilateral sequence and

$$\begin{aligned} y_n(\tau) &\rightarrow 0, \quad n \rightarrow \infty \\ y_{-1}(\tau) &= 0 \end{aligned} \quad (30)$$

for the unilateral sequence.

The Laplace transform of the model equation, Eq.(26), is

$$\alpha \bar{y}_{n+1} - (1+\alpha+s) \bar{y}_n + \bar{y}_{n-1} = y_n(0) \quad (31)$$

where, for the response to an impulse input of tracer to the zeroth stage,  $y_n(0)$  is given by Eq.(28). For a sequence that does not include the zeroth stage this may be written in finite difference form (15) as follows:

$$(\alpha E^2 - \sigma E + 1) \bar{y}_n = 0 \quad (32)$$

where  $\sigma = 1+\alpha+s$ . Substituting a trial solution:

$$\bar{y}_n = A \rho^n \quad (33)$$

shows that

$$\rho_{1,2} = \left[ \sigma \pm (\sigma^2 - 4\alpha)^{1/2} \right] / 2\alpha \quad (34)$$

and consequently that the general solution of Eq.(32) is

$$\bar{y}_n = A_1 \rho_1^n + A_2 \rho_2^n \quad (35)$$

When the 'constants'  $A_1$  and  $A_2$  are chosen so as to match the boundary condition at infinity and the special form of Eq (31) for  $n = 0$ , the results are:

$$\bar{y}_n(s) = \frac{1}{\sqrt{\sigma^2 - 4\alpha}} \left( \frac{\sigma - \sqrt{\sigma^2 - 4\alpha}}{2\alpha} \right)^n, \quad n \geq 0 \quad (36)$$

for the bilateral sequence, and:

$$\bar{y}_n(s) = \left( \frac{\sigma - \sqrt{\sigma^2 - 4\alpha}}{2\alpha} \right)^{n+1} \quad (37)$$

for the unilateral sequence.

The inverses of Eqs.(36) and (37) are (16):

$$y_n(\tau) = \alpha^{-n/2} e^{-(1+\alpha)\tau} I_n(2\sqrt{\alpha}\tau) \quad (38)$$

and

$$y_n(\tau) = (n+1) \alpha^{-(n+1)/2} \tau^{-1} e^{-(1+\alpha)\tau} I_{n+1}(2\sqrt{\alpha}\tau) \quad (39)$$

where  $I_n(\quad)$  is the  $n$ th order modified Bessel function of the first kind.

The Bessel function  $I_n(\quad)$  may be defined by:

$$I_n(z) = \frac{z^n}{2^n n!} \left[ 1 + \frac{z^2}{2(2n+2)} + \frac{z^4}{2 \cdot 4 \cdot (2n+2)(2n+4)} + \dots \right] \quad (40)$$

when  $n$  is integral; for large values of the argument the asymptotic series:

$$I_n(z) \sim \frac{e^z}{\sqrt{2\pi z}} \left[ 1 - \frac{4n^2-1}{8z} + \frac{(4n^2-1)(4n^2-9)}{2! (8z)^2} - \dots \right] \quad (41)$$

is useful. By retaining the leading term only of each series the following approximations are obtained.

Early response:

$$y_n(\tau) = \frac{e^{-(1+\alpha)\tau} \tau^n}{n!} \quad (42)$$



with  $\alpha\tau^2 \ll n + 1$  for a bilateral sequence and  $\alpha\tau^2 \ll n + 2$  for a unilateral sequence.

Late response or tail:

$$y_n(\tau) = \frac{e^{-(1-\sqrt{\alpha})^2 \tau}}{2 \alpha^{(n+1/2)/2} \sqrt{\pi \tau}} \quad (43)$$

with  $16\sqrt{\alpha}\tau \gg 4n^2 - 1$  for a bilateral sequence and

$$y_n(\tau) = \frac{(n+1) e^{-(1-\sqrt{\alpha})^2 \tau}}{2 \alpha^{(n+3/2)/2} \sqrt{\pi \tau^3}} \quad (44)$$

with  $16\sqrt{\alpha}\tau \gg 4(n+1)^2 - 1$  for a unilateral sequence.

The conditions of validity in the above expressions are given in full because they apply for all values of  $n$ ; for larger values of  $n$  they can be simplified. The inequalities represent the error in the calculated response; for example, if the ratio of the two sides is 100 : 1 the error is 1%.

In utilizing the stirred-tank-with-backflow model two different approaches may be employed, depending on the application. If the problem is couched in terms of real cells or equilibrium stages, the equations developed above are useful directly to obtain the response in terms of actual time. Alternatively the object might be to fit experimental data and treat  $n$  as an adjustable mixing index; normalized presentation is then more suitable. That is, new concentration and time variables,  $y^*$  and  $\tau^*$ , are defined such that

$$\int_0^\infty y^* d\tau^* = 1$$

and 
$$\int_0^\infty \tau^* y^* d\tau^* = 1$$

This is done by finding the zeroth and first moments of  $\bar{y}_n$  from  $\bar{y}_n$  and its derivative with respect to  $s$ . One obtains:

$$y_n^* = \left( n + \frac{1+\alpha}{1-\alpha} \right) y_n$$

and 
$$\tau^* = (1-\alpha)\tau / \left( n + \frac{1+\alpha}{1-\alpha} \right)$$

for a bilateral sequence, while:

$$y_n^* = \frac{n+1}{1-\alpha} y_n$$

and  $\tau^* = \frac{1-\alpha}{n+1} \tau$

for a unilateral sequence. In each case  $y_n^*(\tau^*)$  is the normalized response of tank n.

The analytical solutions presented above are exact; thus if the behaviour of an n-tank sequence (tanks 0 to n-1) that is part of an infinite sequence is to represent accurately the behaviour of a finite n-tank sequence it is only necessary to establish conditions in which the concentration history of the end tanks is matched. If n is relatively large, the exact nature of the boundary condition becomes unimportant, so the analytical solutions can be expected to provide good approximations. As a test the impulse responses of 3-, 6- and 12-tank sequences (n=2, 5 and 11) were calculated for  $\alpha = 0.5$  using the bilateral equations to compare Fig.6, with the residence time distributions for the corresponding 'closed-end' finite case calculated by Roemer and Durbin. The bilateral case was chosen for this comparison because the equations are simpler. For the lower values of n there is no useful similarity between the curves, but this is to be expected because the models are quite different. However for n = 11 (i.e. 12 tanks) the overall agreement is reasonable and the agreement between the early part of the curves is very good. For still higher values of n the agreement will be better.

The equations that describe stagewise separation processes are analogous to Eqs.(26), so that finite sequences with end tanks with backflow are also of interest (gas absorption). The unilateral approximation will predict the responses of all stages to composition disturbances in a feed (liquid or gas) stream to an absorber until the disturbance is noticeable at the other end of the column. For control

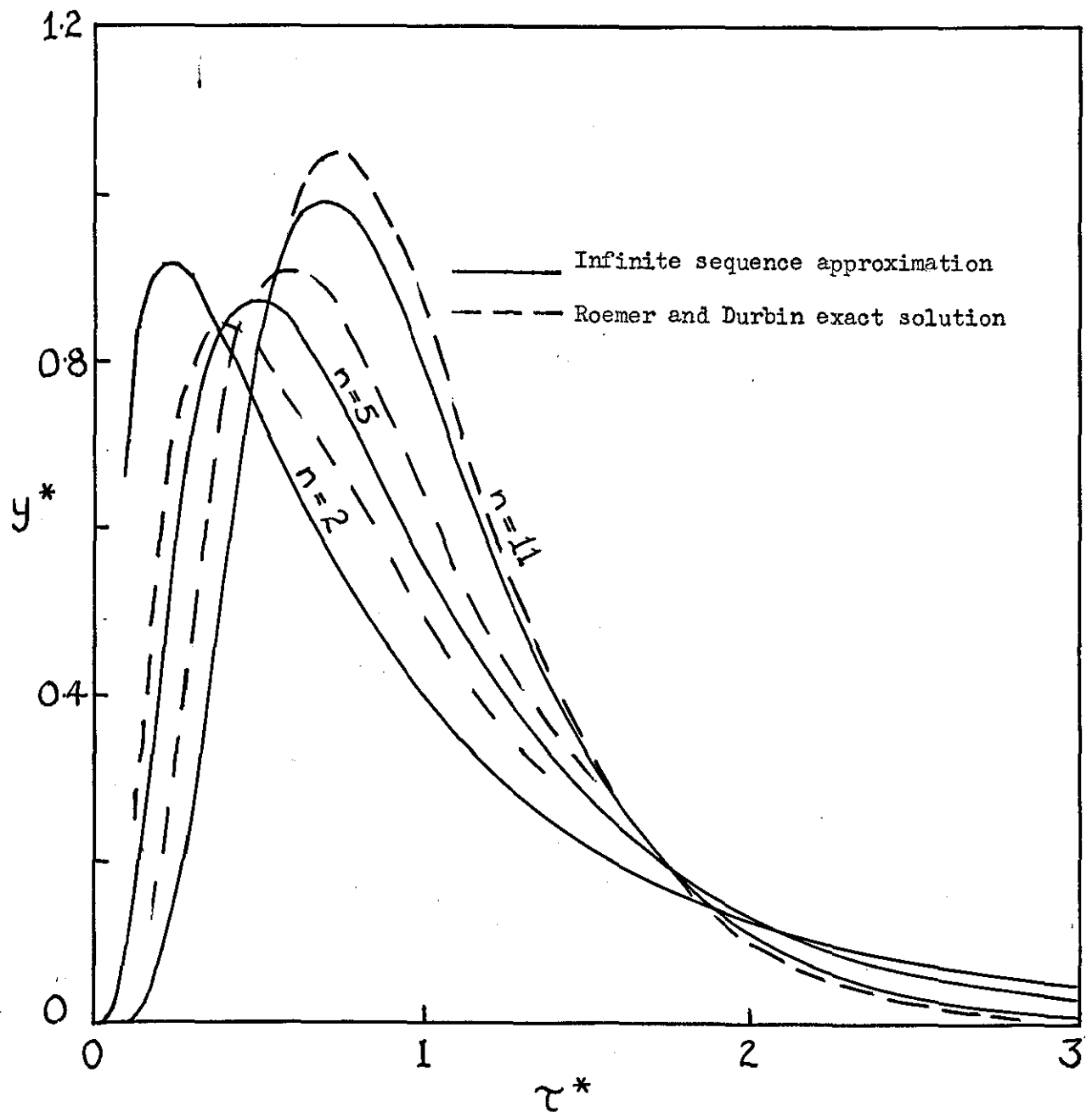


Fig. 6. Comparison of the bilaterally infinite backflow model with the calculations of Roemes and Durbin for the corresponding closed-end finite case. ( $\alpha = 0.5$ ).

purposes it is this early part of the response that is important. Similar reasoning applies to disturbances near the feed plate of a distillation column operating with a mixture of low relative volatility. In this case the equilibrium line is nearly straight and the liquid flow is almost the same above and below the feed plate so that the bilateral sequence equations may be applied. When the model is used in this way there is no need to be in any doubt about the validity of the approximation because the initial response of the remote plates may be calculated using the same expression, as is used for the response of the near plates.

### 5.5 The Deans-Levich model

This model has already been introduced in a qualitative way. It will now be discussed analytically. Levich et al (17) give the transfer function as:

$$\bar{f}_n(s) = \left[ \frac{\lambda(s+\sigma)}{s^2 + (\lambda + \nu + \sigma)s + \lambda\sigma} \right]^n \quad (45)$$

for  $n$  stages, where:

$$\lambda = \frac{q}{(1-\alpha)V} ; \quad \nu = \frac{p}{(1-\alpha)V} ; \quad \sigma = \frac{p}{\alpha V}$$

The notation is that used by Levich et al and is indicated in Fig. 7. Inversion of Eq.(45) yields the impulse response and the residence time distribution.

A convenient technique for inverting transforms of this type is the use of the Laurent series to determine the residues at the poles. The details of the method are given in texts on operational calculus, e.g. that of Churchill (4). The inverse transform is the sum of the coefficients of  $(s - s_i)^{-1}$  in the Laurent expansions of  $e^{st} \bar{f}_n(s)$  about the poles  $s = s_i$ ,  $i = 1, 2, 3, \dots$ , where the Laurent expansion is a series of the form:

$$\begin{aligned} & A_0 + A_1(s-s_i) + A_2(s-s_i)^2 + \dots \\ & + A_{-1}(s-s_i)^{-1} + A_{-2}(s-s_i)^{-2} + \dots \end{aligned} \quad (46)$$

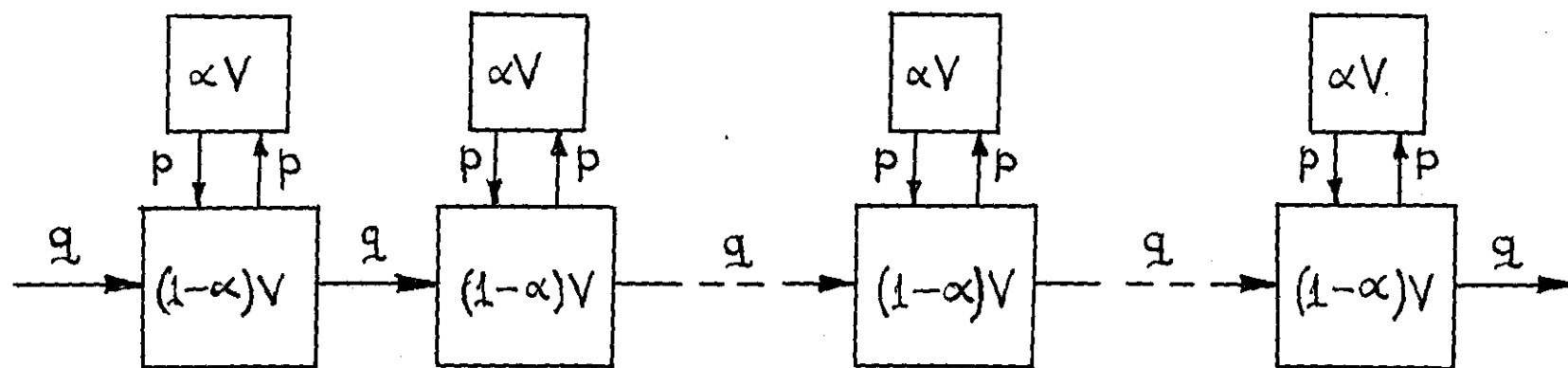


Fig. 7

The Deans-Levich mixing model

As  $e^{st}$  is an entire function, the poles of  $e^{st}\bar{f}_n(s)$  are identical with those of  $\bar{f}_n(s)$  and they occur at

$$s = \left[ -(\lambda + \nu + \gamma) \pm \sqrt{(\lambda + \nu + \gamma)^2 - 4\lambda\gamma} \right] / 2 \quad (47)$$

Since  $\lambda$ ,  $\nu$  and  $\gamma$  are real positive quantities, the poles are on the negative real axis and Eq.(45) may be rewritten:

$$\bar{f}_n(s) = \lambda^n \left[ \frac{s + \lambda}{(s + r_1)(s + r_2)} \right]^n \quad (48)$$

where both  $r_1$  and  $r_2$  are positive; i.e. the poles are at  $s = -r_1$  and  $s = -r_2$ .

Considering first the pole at  $s = -r_1$ ,  $e^{st}\bar{f}_n(s)$  may be written:

$$e^{st}\bar{f}_n(s) = \frac{\lambda^n e^{-r_1 t + (s+r_1)t} (\gamma - r_1)^n \left[ 1 + \frac{s+r_1}{r-r_1} \right]^n}{(s+r_1)^n (r_2-r_1)^n \left[ 1 + \frac{s+r_1}{r_2-r_1} \right]^n} \quad (49)$$

which form is suitable for expanding  $e^{st}\bar{f}_n(s)$  in powers of  $(s+r_1)$  by multiplying the following series:

$$e^{(s+r_1)t} = \sum_{j=0}^{\infty} \frac{(s+r_1)^j t^j}{j!} \quad (50)$$

$$\left[ 1 + \frac{s+r_1}{r-r_1} \right]^n = \sum_{k=0}^{k=n} \left( \frac{s+r_1}{r-r_1} \right)^k \frac{n!}{k!(n-k)!} \quad (51)$$

$$\left[ 1 + \frac{s+r_1}{r_2-r_1} \right]^{-n} = \sum_{l=0}^{\infty} (-1)^l \left( \frac{s+r_1}{r_2-r_1} \right)^l \frac{(n+l-1)!}{l!(n-1)!} \quad (52)$$

It follows that the coefficient of  $(s+r_1)^{-1}$  in the expansion of  $e^{st}\bar{f}_n(s)$  about the pole at  $s = -r_1$  is:

$$A_{-1} = \frac{e^{-r_1 t} (\gamma - r_1)^n \lambda^n}{(r_2 - r_1)^n} \sum \frac{(-1)^l n! (n+l-1)! (r_2 - r_1)^{-l} t^j}{j! k! l! (n-k)! (n-1)! (r - r_1)^k} \quad (53)$$

where the summation is taken over all triples  $(j, k, l)$  of which the individual members are non-negative and sum to  $n - 1$ . The summation is a power series in  $t$ ; call this series

$$g(t) = \sum_{j=0}^{n-1} B_{n,j} t^j, \quad (54)$$

then the  $B_{n,j}$  terms, obtained by factoring out  $t^j$  are:

$$B_{n,j} = \frac{n}{j!} \sum_{k+l=n-j-1} \frac{(-1)^l (n+l-1)!}{k! (n-k)! l! (r-r_1)^k (r_2-r_1)^l} \quad (55)$$

As in each term in this sum  $k + l$  has the value  $n-j-1$ ,  $l$  can be eliminated with the result:

$$B_{n,j} = \frac{n}{j!} \sum_{k=0}^{n-1-j} \frac{(-1)^{n-1-j-k} (2n-2-j-k)!}{k! (n-k)! (n-1-j-k)! (r-r_1)^k (r_2-r_1)^{n-1-j-k}} \quad (56)$$

Equations (53), (54) and (56) taken together give the contribution due to the pole at  $s = -r_1$ .

The contribution due to the pole at  $s = -r_2$  is similar and is easily found by interchanging  $r_1$  and  $r_2$  in these equations. Hence the final solution for the impulse response is:

$$\begin{aligned} f_n(t) = & K_1^n \left[ \sum_{j=0}^{n-1} B_{n,j} t^j \right] e^{-r_1 t} \\ & + K_2^n \left[ \sum_{j=0}^{n-1} C_{n,j} t^j \right] e^{-r_2 t} \end{aligned} \quad (57)$$

where  $K_1 = \lambda (r-r_1)/(r_2-r_1)$

$$K_2 = \lambda (r-r_2)/(r_1-r_2)$$

the  $B_{n,j}$  are given by Eq.(55) and the  $C_{n,j}$  are found from Eq.(55) by interchanging  $r_1$  and  $r_2$ . The constants  $r_1$  and  $r_2$  are, from Eq.47,

$$r_1, r_2 = \left[ (\lambda + \nu + \tau) \mp \sqrt{(\tau + \nu + \tau)^2 - 4\lambda\tau} \right] / 2 \quad (58)$$

Equation (57) is expressed in terms of actual time. When  $n$  is to be determined experimentally it is usually more convenient to use the data in normalized form. To express Eq.(57) in normalized form the time is measured in units equal to the mean time and  $f_n(t)$  is multiplied by the mean time to preserve the unit area property. The mean time is equal to the volume/flow-rate ratio for the system, i.e.  $nV/Q$

The moments of the Deans-Levich model will be established later when a unified treatment is given of this and several other models, see page 60.

#### 5.6 Alternative physical forms leading to the Deans-Levich model equations.

Fig. 8 shows the unit cell of the Deans-Levich model with all the extra flows that can have any physical significance added, except bypassing. Recycle in a process usually has the effect of substantially modifying the behaviour of the process. However in the present case recycle has only a quantitative effect, not a qualitative effect. Clearly recycle from either of the vessels to itself is irrelevant. The overall recycle loop shown in Fig. 8 is equivalent to the flows shown dotted in Fig.9; these flows present no new features and may be incorporated into flows already present in the system. Thus the model of Fig. 9 may be reduced to that of Fig. 10. It will now be shown that this augmented model is described by a transfer function of exactly the same form as the Deans-Levich model itself.



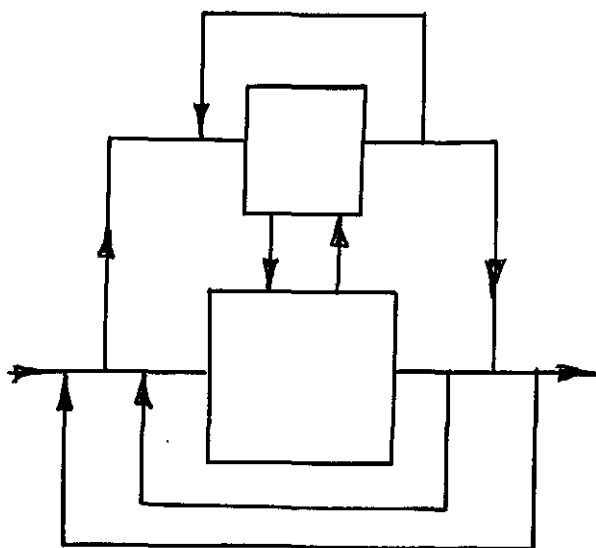


Fig. 8.

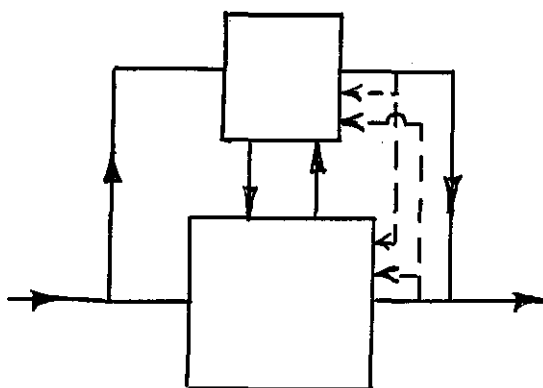


Fig. 9.

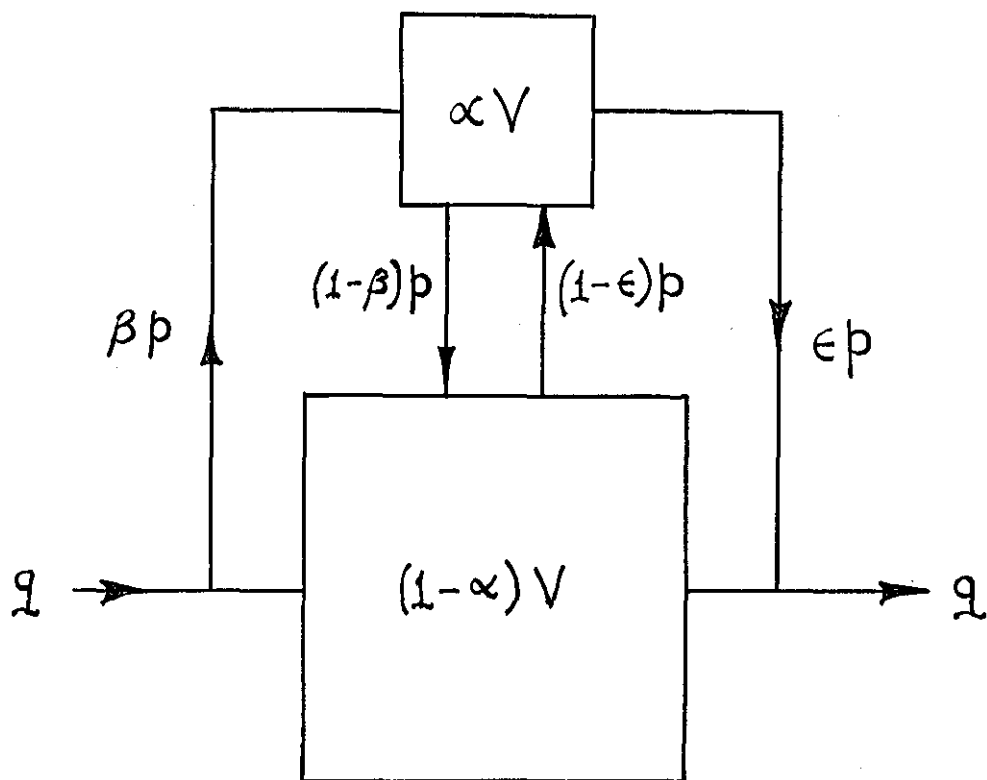


Fig. 10.

Figs. 8, 9 and 10. Generalized Deans-Levich unit cells.

Using the notation indicated in Fig. 10, a material balance in the 'main' region yields:

$$(q - \beta p) \bar{c}_{n-1} + (1 - \epsilon) p \bar{c}_n'' - [(1 - \beta) p + q - \epsilon p] \bar{c}_n' = (1 - \alpha) V s \bar{c}_n' \quad (59)$$

when transformed, and a balance on the 'stagnant' region gives:

$$\beta p \bar{c}_{n-1} + (1 - \beta) p \bar{c}_n' - p \bar{c}_n'' = \alpha V s \bar{c}_n'' \quad (60)$$

Now write these equations as:

$$A_1 + B_1 G''(s) = (C_1 + D_1 s) G_1'(s) \quad (61)$$

and

$$A_2 - (B_2 + E_2 s) G''(s) = C_2 G'(s) \quad (62)$$

where

$$A_1 = q - \beta p \quad ; \quad A_2 = \beta p$$

$$B_1 = (1 - \epsilon) p \quad ; \quad B_2 = p$$

$$C_1 = (1 - \beta) p + q - \epsilon p \quad ; \quad C_2 = (1 - \beta) p$$

$$D_1 = (1 - \alpha) V$$

$$E_2 = \alpha V$$

$$G'(s) = \frac{\bar{c}_n'}{\bar{c}_{n-1}} \quad ; \quad G''(s) = \frac{\bar{c}_n''}{\bar{c}_{n-1}}$$

All the constants A, B, C, D and E may be taken as positive because reversing the direction of the flows  $\beta p$  and  $\epsilon p$  simplifies the model. Equations (61) and (62) are readily solved for  $G'(s)$  and  $G''(s)$ :

$$G'(s) = \frac{A_2 B_2 - A_1 B_1}{D_1 E_2 s^2 + (B_2 D_1 + C_1 E_2) s + (B_2 C_1 - B_1 C_2)} \quad (63)$$

$$G''(s) = \frac{(A_1 C_2 + A_2 C_1) + A_2 D_1 s}{D_1 E_2 s^2 + (B_2 D_1 + C_1 E_2) s + (B_2 C_1 - B_1 C_2)} \quad (64)$$

A material balance at the point at which the streams leaving the two mixed regions come together gives:

$$\epsilon p \bar{c}_n'' + (q_1 - \epsilon p) \bar{c}_n' = q_1 \bar{c}_n \quad (65)$$

Or

$$(B_2 - B_1) G''(s) + (C_1 - C_2) G'(s) = q G(s) \quad (66)$$

where

$$G(s) = \bar{c}_n / \bar{c}_{n-1}$$

Thus

$$G(s) = \frac{a_1 s + a_0}{(b_2 s^2 + b_1 s + b_0) q} \quad (67)$$

where the a's and b's are implied by Equations (63), (64) and (66). For a model consisting of n replications of the cell illustrated in Fig. 10 connected in series the transfer function is

$$\bar{f}_n(s) = \left[ \frac{a_1 s + a_0}{(b_2 s^2 + b_1 s + b_0) q} \right]^n \quad (68)$$

which duplicates the form of Eq (45).

## 6. ONE-DIMENSIONAL TIME-DELAY MODELS

### 6.1 Introduction

Many chemical engineering situations are one-dimensional in the empirical sense that there is a predominant axial direction which is the average direction of flow; and that, after perhaps an entrance region in which the flow pattern is established, the flow pattern is independent of axial position in its essential features. Flow in pipes and packed beds falls into this category as does flow in coils and serpentine pipes which might not at first be thought of as one-dimensional.

The time delay description is designed to apply to the residence time distribution in any one-dimensional situation where there is a main flow region which communicates in some way with a side capacity. The model was first formulated to describe trickle flow in packed beds and this is probably as good an example as any to illustrate the reasoning that leads to the model.

In trickle flow in a packed bed the liquid is spread in an extended film over the surface of the packing. Relatively, the flow is rapid in the more nearly vertical portions of the film and less rapid in the more horizontal parts. At points of contact between packing pieces and on horizontal surfaces there are stagnant regions through which no bulk flow occurs, but which can communicate with the rest of the holdup by molecular diffusion. These observations lead to the suggestion that the spreading of residence times is due to:

- (i) random interchange between the stagnant\* and moving portions of the holdup;
- (ii) random transfer to portions of the holdup which are in slow near-horizontal motion;
- (iii) random merging and dividing of the more rapidly moving part of the holdup which has a distribution of velocities;
- and (iv) molecular diffusion.

\* The stagnant holdup referred to here is not the same as the static holdup, determined by draining experiments, which depends largely on surface tension.

Mechanisms, (i) and (ii) in this classification although physically different have much the same effect: material leaves the relatively rapidly moving part of the holdup and returns later at the same axial position. Mechanisms (ii) and (iii), the hydrodynamic mechanisms, differ only in degree physically, but have different effects; the former contributes to the spreading of residence times, whereas the latter makes the probabilities of flow elements entering into the other mechanisms more uniform and uncorrelated. Molecular diffusion as a means of axial transport is unimportant except in so far as it allows (i), the transverse diffusive mechanism, to take place. If this view of the mechanism of mixing in trickle flow is accepted, the major part of the spreading of residence times is due to random delays with respect to the rapidly moving part of the holdup. This is to be contrasted with the random axial shuffling that is postulated to account for the form of the diffusion-type models. A significant difference is that it has not been found necessary to suggest that some fluid elements may have negative velocities. This eliminates the difficulties with boundary conditions that occur with the diffusion models.

To sum up, the description that has been arrived at is:

The fluid may be considered in two parts, a relatively rapidly moving part and a relatively slowly moving part. Mixing is due to random interchange between these parts. No great error will be introduced by considering the rapidly moving part to be in plug flow.

## 6.2 Probabilistic treatment

By formulating the model in the way suggested above, the analysis has effectively been split into two parts: establishing the probability that  $n$  delays take place ( $n = 0, 1, 2, 3, \dots$ ); and determining the amount of spreading of the residence times that these delays cause.

### The stopping process

Let the probability that a flow element is delayed  $n$  times while travelling a distance  $x$  in the longitudinal direction be  $p_n(x)$ . If it is assumed that the conditional probability that a flow element is delayed in the ensuing element  $dx$  of length, is constant, say  $\alpha dx$ , then:

$$p_n(x+dx) = p_n(x) [1 - \alpha dx - O(dx)^2] + p_{n-1}(x) \cdot \alpha dx + O(dx)^2 \quad (1)$$

That is to say, the tracer may arrive at  $x + dx$  after being delayed  $n$  times: by stopping  $n$  times in  $(0, x)$  and not stopping in  $(x, x+dx)$ ; by stopping  $n-1$  times in  $(0, x)$  and once in  $(x, x+dx)$ ; and so on.

These compound events are mutually exclusive and their probabilities additive. The probabilities for the compound events themselves are obtained by multiplying the absolute probability of stopping  $n-j$  times in  $(0, x)$  by the conditional probability of stopping  $j$  times in  $(x, x+dx)$ . Taking the limit as  $dx \rightarrow 0$ , Eq.(1) becomes

$$\frac{dp_n}{dx} = \alpha (p_{n-1} - p_n) \quad , \quad n = 0, 1, 2, 3, \dots \quad (2)$$

A set of boundary conditions is needed before Eqs.(2) can be solved.

These are:

$$\begin{aligned} p_0(0) &= 1 \\ p_n(0) &= 0, \quad n = 1, 2, 3 \end{aligned} \quad (3)$$

because it is certain that a flow element will not stop in  $(0, 0)$ , which establishes  $p_0(0)$ ; and because it is impossible to stop in  $(0, 0)$ , which establishes the  $p_n(0)$ ,  $n \neq 0$ .

This set of equations and boundary conditions is of frequent occurrence in probability theory (1) and elsewhere. They are the same for example as those for the tanks-in-series mixing model with the first tank numbered '0'. The solutions are:

$$p_n(x) = \frac{(\alpha x)^n}{n!} e^{-\alpha x} \quad (4)$$

#### The restarting process

The simplest assumption that may be made is that all fluid elements in the stopped state have the same probability of restarting in next increment  $dt$  of time. One, but not the only, interpretation of this is that the 'stagnant' regions are well-mixed and all have the same time constant  $t_D$ . With the equal probability assumption, then, the delay time will be exponentially distributed and the sum of  $n$  delays will have the distribution:

$$f_n(t) = \frac{t^{n-1}}{(n-1)! t_D^n} e^{-t/t_D} \quad (5)$$

by analogy with the tanks-in-series mixing model.

#### The residence time distribution

The time a flow element takes to travel a distance  $x$  is the sum of the time the element has been delayed and the time it takes in flow. The flow time is the same regardless of the number of delays and in view of the plug flow assumption is constant for a given  $x$  and in fact is proportional to  $x$ . The probability that the total delay time is in  $(t, t+dt)$  is given by

$$g(t)dt = \sum_{n=0}^{\infty} p_n f_n(t) dt \quad (6)$$

where  $p_n f_n(t)dt$  is the probability that the delay time is in  $(t, t+dt)$  when  $n$  stops occur. Thus the final expression for the residence time distribution is

$$f(t) = 0, \quad t < t_0$$

$$f(t) = e^{-\alpha x} \left\{ \delta(t-t_0) + \frac{e^{-(t-t_0)/t_D}}{t-t_0} \sum_{n=1}^{\infty} \frac{[\alpha x (t-t_0)/t_D]^n}{n! (n-1)!} \right\} \quad (7)$$

where  $t_0$  is a dead time (the flow time).

The series in Eq(7) may be expressed in terms of a Bessel function (2) so that::

$$f(t) = 0, \quad t < t_0$$

$$f(t) = e^{-\alpha x} \left\{ \delta(t-t_0) + e^{-(t-t_0)/t_D} \sqrt{\frac{\alpha x}{t_D(t-t_0)}} I_1 \left( 2 \sqrt{\frac{\alpha x(t-t_0)}{t_D}} \right) \right\} \quad (8)$$

$$t \geq t_0$$

#### Gamma distributed delays

Any delay distribution for which the nth convolutions are known may be incorporated into the analysis at Eq(6). The gamma distribution is notable in that the convolutions of gamma distributions are themselves gamma distributions and also in the degree of flexibility that is obtained with a single parameter (Sec.52). When the gamma distribution of delay times is employed the result corresponding to Eq(7) is

$$f(t) = 0, \quad t < t_0$$

$$f(t) = e^{-\alpha x} \left\{ \delta(t-t_0) + e^{-(t-t_0)/t_D} \sum_{n=1}^{\infty} \left( \frac{m}{t_D} \right)^{nm} \frac{(\alpha x)^n (t-t_0)^{nm-1}}{n! \Gamma(nm)} \right\} \quad (9)$$

$$t \geq t_0$$

where  $t_D$  is again the mean of the delay time distribution and  $m$  is the gamma distribution parameter. Fig.1 shows the residence time distribution for several representative parameter values. Equation (9) is able to represent distributions that are rather more skew than the usual models for flow in packed beds. This flexibility is only achieved at the expense of extra parameters of course. Rathor has undertaken an extensive programme of experimental work on trickle flow in packed columns. He is studying the effect of several physical variables for a number of configurations some of which involve unusually high wall flow. The data are being fitted by a variety of



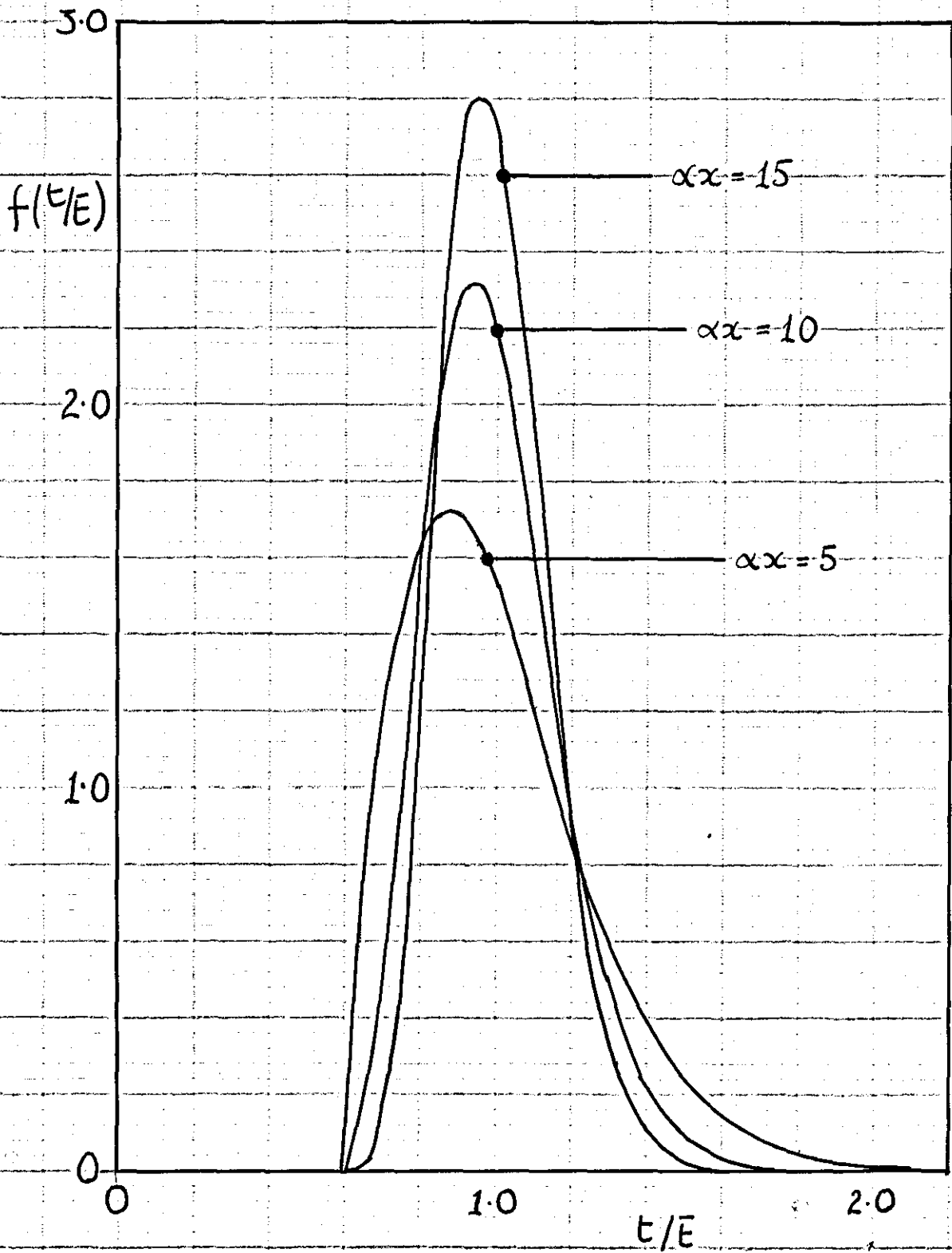


Fig.1(a)

Fig.1 Normalized residence time distributions for the time delay model with gamma-distributed delays.

(a)  $t_o/\bar{t} = 0.6$ ,  $m = -1$ ,  $\alpha x$  as shown.

(b)  $t_o/\bar{t} = 0.6$ ,  $\alpha x = 10$ ,  $m$  as shown.

(c)  $m = 1$ ,  $\alpha x = 10$ ,  $t_o/\bar{t}$  as shown.

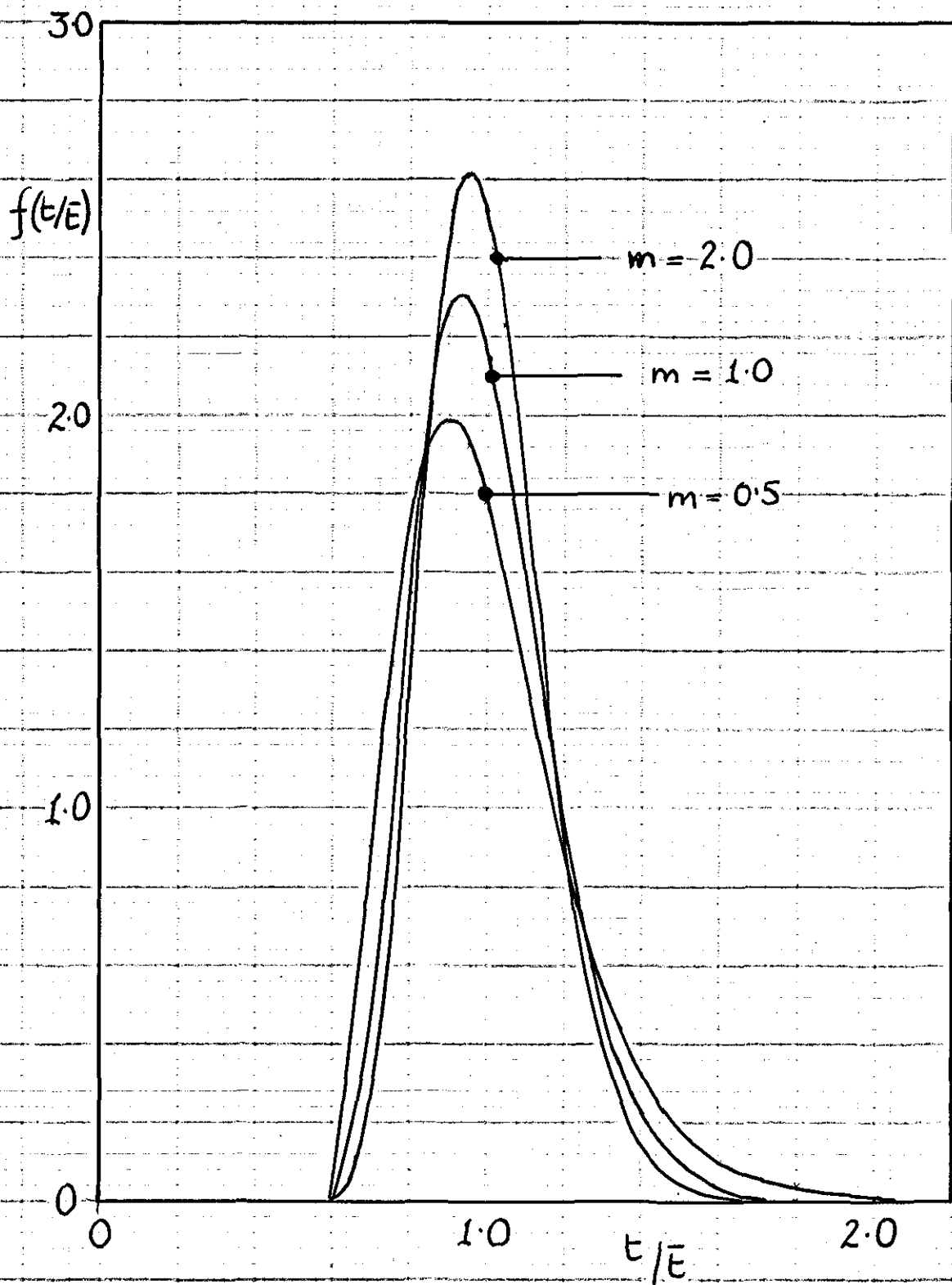


Fig. 1(b)

$\approx 1.0$   
 $0.5$   
 $1.0$   
 $2.0$   
 $\approx 0.6$

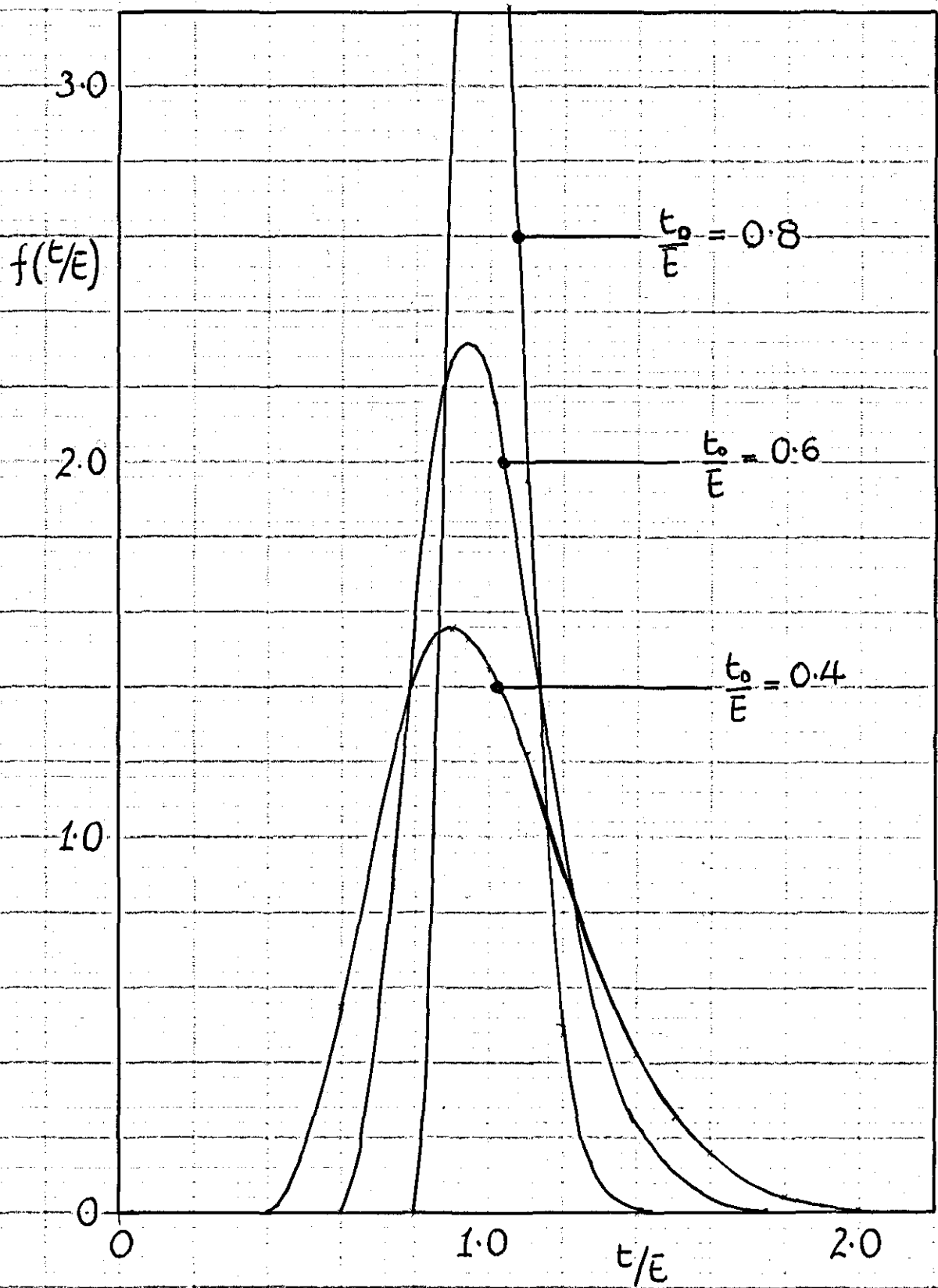


Fig. 1(c)

models in an attempt to assess which is best. Part of this work has been reported by Buffham, Gibilaro and Rathor (3) who show that the time delay model with exponentially distributed delay times fits the data well and consistently.

The parameter  $m$  may be interpreted as a measure of the degree of randomness of the delay process. When  $m$  is unity the delay process is completely random, that is all delayed elements have the same chance of moving on in the next time increment. As  $m$  is increased from unity the delay process becomes less random and the delay times more concentrated until when  $m \rightarrow \infty$  the delay times are not spread at all and the process is deterministic. When  $m$  is decreased from unity the delay process again becomes less random, short delays being favoured.

### 6.3 Unified treatment of several time-delay models from a cell model point of view

The Deans-Levich and the one-dimensional time-delay models represent the time-delay process in a similar but not identical fashion. It will now be shown how a unified treatment may be given that includes these and several other models as special cases. A cell model approach is adopted and it is found that the transfer functions and moments are established easily. This treatment is particularly interesting for the light it sheds on the interrelations between the various models.

#### The unified model and its transfer function

Fig. 2 illustrates a cell model which is identical to the Deans-Levich model except that the delay process is represented in an arbitrary fashion by the transfer function  $\bar{g}(s)$ .

A Laplace transformed material balance on a tracer component in the  $n$ th cell yields:

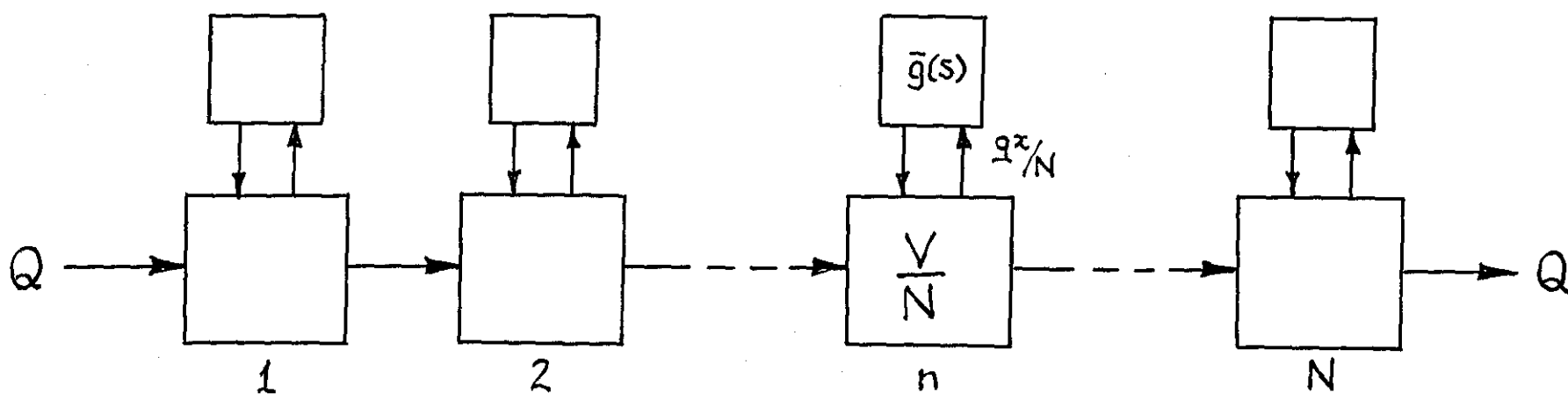


Fig. 2

Deans-Levich model - arbitrary delay process

$$\frac{\bar{c}_n(s)}{\bar{c}_{n-1}(s)} = \left\{ 1 + \frac{1}{N} \left[ t_0 s + \alpha x - \alpha x \bar{g}(s) \right] \right\}^{-1} \quad (10)$$

where  $t_0 = V/Q$  and  $\alpha = q/Q$ . The transfer function for the entire N-cell sequence is

$$\bar{f}_N(s) = \left\{ 1 + \frac{1}{N} \left[ t_0 s + \alpha x - \alpha x \bar{g}(s) \right] \right\}^{-N} \quad (11)$$

With the exponential distribution of delay times:

$$\bar{g}(s) = (t_0 s - 1)^{-1}, \quad (12)$$

the model reduces back to the Deans-Levich form immediately; however the model is generalized by using the gamma distribution of delay times:

$$\bar{g}(s) = \left( \frac{t_0 s}{m} + 1 \right)^{-m} \quad (13)$$

as before. The previous one-dimensional time delay model should result by taking the limit as  $N \rightarrow \infty$  of  $\bar{f}_N(s)$ . Now

$$\bar{f}(s) = \exp \left\{ -t_0 s - \alpha x + \alpha x \bar{g}(s) \right\} \quad (14)$$

because the model has been so constructed that the limiting process does not affect the parameters of the time delay distribution. Thus with  $\bar{g}(s)$  given by Eq(13) the inverse of Eq(14) should be identical to Eq(9). This will be confirmed later.

#### The moments of the impulse response

Equation (10) with  $\bar{g}(s)$  taking the gamma form, Eq(13) may be expressed:

$$\begin{aligned} \ln \bar{f}_N(s) = -N \left\{ \frac{1}{N} \left[ (t_0 + \alpha x t_0) s - \frac{\alpha x}{2!} \left( 1 + \frac{1}{m} \right) t_0^2 s^2 \right. \right. \\ \left. \left. + \frac{\alpha x}{3!} \left( 1 + \frac{1}{m} \right) \left( 1 + \frac{2}{m} \right) t_0^3 s^3 - \dots \right] \right. \\ \left. - \frac{1}{2N^2} \left[ (t_0 + \alpha x t_0) s - \frac{\alpha x}{2!} \left( 1 + \frac{1}{m} \right) t_0^2 s^2 + \dots \right]^2 \right. \\ \left. + \frac{1}{3N^2} \left[ (t_0 + \alpha x t_0) s - \dots \right]^3 - \dots \right\} \quad (15) \end{aligned}$$

by utilizing the series expansions for  $(1+a)^k$  and  $\ln(1+a)$  and carrying the expansions sufficiently far to generate terms up to  $s^3$ . The low order moments and cumulants are found by picking out the pertinent coefficients as described in Sec. 4.3, and are:

$$\mu_1' = t_0 + \alpha x t_D \quad (16)$$

$$\mu_2 = \alpha x \left(1 + \frac{1}{m}\right) t_D^2 + \frac{1}{N} (t_0 + \alpha x t_D)^2 \quad (17)$$

$$\begin{aligned} \mu_3 = & \alpha x \left(1 + \frac{1}{m}\right) \left(1 + \frac{2}{m}\right) t_D^3 \\ & + \frac{3}{N} \left(1 + \frac{1}{m}\right) \alpha x (t_0 + \alpha x t_D) t_D^2 \\ & + \frac{2}{N^2} (t_0 + \alpha x t_D)^3 \end{aligned} \quad (18)$$

The moments of the distributed version of the model are found by taking the limit as  $N \rightarrow \infty$ :

$$\mu_1' = t_0 + \alpha x t_D \quad (19)$$

$$\mu_2 = \alpha x \left(1 + \frac{1}{m}\right) t_D^2 \quad (20)$$

$$\mu_3 = \alpha x \left(1 + \frac{1}{m}\right) \left(1 + \frac{2}{m}\right) t_D^3 \quad (21)$$

Equations (17) and (20) indicate that both the variance and skewness of the impulse response increase indefinitely as  $m$  decreases to zero, irrespective of the value of  $N$ , provided it is fixed. The effect of changing  $N$  with  $m$  fixed is similar: decreasing  $N$  increases the skewness and variance. Also of significance is the skewness relative to the variance on a dimensionless basis. This only takes a simple form when  $N \rightarrow \infty$ : in this case

$$\frac{\mu_3}{\mu_2^{3/2}} = \frac{m+2}{[\alpha x m(m+1)]^{1/2}} \quad (22)$$

which increases as  $m$  decreases; the skewness increases more rapidly than the variance.

#### Additivity of variances

The form of Eq.(8) is interesting because it shows that the variance is made up of two additive parts: contributions due to the delay process and to the model being split into cells. The former is independent of the number of cells and the latter is independent of the delay distribution parameter and the same (cell mean-time squared divided by number of cells) as the variance of the tanks-in-series mixing model. So although the mixing mechanisms are not independent in the usual sense, their effects separate in the variance. This behaviour does not extend to the third central moment which is also additive for independent series mechanisms. The two contributions to the variance may be regarded as describing transverse and axial mixing.

#### Time-domain solutions

The inversion of a transfer function like Eq.(11) is a difficult task. The treatment for the Deans-Levich case, which is a simple form of Eq.(11), is complicated enough. Of most interest at present is to recover the time-domain form of the distributed model. This may be done by expanding Eq.(14) and inverting term-by-term:

$$\bar{f}(s) = e^{-t_0 s - \alpha x} \left\{ 1 + \alpha x \bar{g}(s) + \frac{[\alpha x \bar{g}(s)]^2}{2!} + \dots \right\} \quad (23)$$

and

$$f(t) = e^{-\alpha x} \sum_{n=0}^{\infty} \frac{(\alpha x)^n}{n!} g_n(t-t_0) \quad (24)$$

where  $g_n(t)$  is the inverse of  $[\bar{g}(s)]^n$ .



When the gamma distribution is used for  $\bar{g}(s)$ , Eq.(24) becomes:

$$f(t) = 0, \quad t < t_0$$

$$f(t) = e^{-\alpha x - m(t-t_0)/t_D} \sum_{n=0}^{\infty} \left(\frac{m}{t_D}\right)^{nm} \frac{(\alpha x)^n (t-t_0)^{nm-1}}{n! \Gamma(nm)}, \quad t \geq t_0 \quad (25)$$

by direct substitution of the inverse of  $[\bar{g}(s)]^n$ : i.e.

$$g_n(t) = \left(\frac{m}{t_D}\right)^{nm} \frac{t^{nm-1} e^{-mt/t_D}}{\Gamma(nm)} \quad (26)$$

The first term in the expansion of  $f(t)$  is an impulse of weight  $e^{-\alpha x}$  at  $t = t_0$  as is apparent from Eq.(23), so that Eqs.(25) and (9) are identical as it was supposed they would be.

#### Special cases

In the analysis presented above  $m$  may take any positive value. In particular  $m = 1$  represents an exponential distribution of delay times (a Markovian random delay process) and  $m \rightarrow \infty$  represents an impulse distribution of delay times (a deterministic delay process). These cases have been discussed previously. In the trivial case in which the side capacity is absent and  $N$  is finite the model reduces to the tanks-in-series model. It has previously been pointed out that the completely random distributed version of the model ( $N \rightarrow \infty$ ,  $m = 1$ ) is equivalent mathematically to the Anzelius regenerator model so that mixing by random lateral bulk flow and by interaction between a plug flow region and a static region via a transfer coefficient are indistinguishable by tracer experiments. When the delay process is random and the number of cells finite ( $N$  finite,  $m = 1$ ) we have the Deans-Levich model. Finally if the delay process is completely random and the transits between delays are extremely short ( $N \rightarrow \infty$ ,  $m = 1$ ,  $t_0 \rightarrow 0$ ) the Cairns and Prausnitz (Einstein) model results.

It is possible to match the dispersed plug flow model by matching moments for a variety of parameter values or by any other fitting

technique. However the dispersion model is not a special case of the present model, the most important difference being that no true backflow is incorporated in the time delay model.

#### 6.4 Formulation of time-delay models in terms of integro-differential equations

It will now be shown how some of the previous results may be established in an alternative way that is based fairly directly on physical reasoning and so is capable of extension in situations where sufficient information is available. The usual type of unsteady state material balance used in chemical engineering is applied to an element of 'bed'. When the mixing phenomenon is considered to be due to random lateral flow superimposed on forward plug flow, this balance may be written:

$$\begin{aligned} Qc + (q dx) \cdot c_R - Q \left[ c + \frac{\partial c}{\partial x} dx \right] - (q dx) c \\ = \frac{V}{x_0} \frac{\partial c}{\partial t} dx \end{aligned} \quad (27)$$

where  $Q$  is the forward flow rate and  $q$  is the transverse flow rate per unit length.

The return flow concentration  $c_R$  is established by considering the times at which the various flow elements of which the return flow consists, left the main flow. Material leaving the main stream at time  $\tau$  and arriving back at time  $t$  has been delayed for a time  $t - \tau$ . It follows that of the material arriving back at time  $t$  a proportion  $g(t - \tau)d\tau$  left the main stream in the time interval  $(\tau, \tau + d\tau)$ . The average concentration  $c_R$  of the returning material is obtained by summing the products of the concentrations  $c(\tau)$  and the proportions  $g(t - \tau)d\tau$ , it being assumed that all concentrations are zero for negative times:

$$c_R = \int_0^t c(\tau) g(t - \tau) d\tau \quad (28)$$

Inserting Eq.(28) into Eq.(27) and expressing the result in terms of  $\alpha$  and  $t_0$ , as before, gives

$$-\frac{\partial c}{\partial x} + \alpha \int_0^t c(\tau) g(t-\tau) d\tau - \alpha c = \frac{t_0}{x_0} \frac{\partial c}{\partial t} \quad (29)$$

The integral in this equation will be recognized as a convolution integral and the Laplace transform is:

$$-\frac{d\bar{c}}{dx} + \alpha \bar{c} \bar{g} - \alpha \bar{c} = \frac{t_0}{x_0} s \bar{c} \quad (30)$$

as the initial concentration is taken to be zero. For an impulse response

$$\bar{c}(0, s) = 1 \quad (31)$$

so that the solution of Eq.(30) for an impulse response (the transfer function) is

$$\bar{c} = \exp \left\{ -t_0 s - \alpha x + \alpha x \bar{g}(s) \right\} \quad (32)$$

which is identical to Eq.(14) as it clearly must be because the model is identical.

This way of developing the time delay model is rather appealing and suggests how axial dispersion due to differences in forward velocities can be incorporated into the analysis. Instead of material in the delay flow returning at the same axial position that it left the main stream, it can be returned at a range of downstream positions. That is to say, instead of the residence time distribution  $g(t)$  for the delay process, we consider a bivariate distribution  $g(x, t)$  such that  $g(x, t) dx dt$  is the probability that an element of flow material leaving the main stream at a given position returns at a time  $(t, t + dt)$  later at a distance  $(x, x + dx)$  downstream. With this redefinition of  $f$ , the analogue of Eq.(29) is

$$\begin{aligned}
 - \frac{\partial c}{\partial x} + \alpha \int_0^x \int_0^t c(x, \tau) g(x-x, t-\tau) d\tau dx - \alpha c \\
 = t_0 \frac{\partial c}{\partial t}
 \end{aligned}
 \tag{33}$$

It is not proposed to develop methods based on Eq.(33) in any great detail; they seem to be rather too complex to be justified by the current state of knowledge of mixing induced by complex flows. Nevertheless it is interesting to see in general terms how the idea might be worked out. Before doing this it should be noted that some of the quantities in Eq.(33) cannot be interpreted in exactly the same way as previously. Departures from the main flow are not necessarily delays, they may be 'advances'; the side flow now contributes to the forward flow which means that the flow terms must be expressed carefully; and, as a result,  $c$  is no longer the average concentration of material moving forward at  $x$ .

In the absence of any specific information about the form of  $f(x, t)$ , the most suitable way to proceed in general terms is to use the Laplace transform. Applied once the transformation leads to

$$- \frac{d\bar{c}}{dx} + \alpha \int_0^x \bar{c}(x, s) \bar{g}(x-x, s) dx - \alpha \bar{c} = t_0 s \bar{c}
 \tag{34}$$

and again

$$- [p\bar{c} - 1] + \alpha \bar{c} \bar{g} - \alpha \bar{c} = t_0 s \bar{c}
 \tag{35}$$

for the impulse response. Rearranging to obtain an expression explicit for  $\bar{c}$  we have

$$\bar{c}(p, s) = [p + t_0 s + \alpha - \alpha \bar{g}]^{-1}
 \tag{36}$$

which when inverted twice, first to recover  $x$  and then  $t$ , gives the time-domain solution.

## 7. TIME-DELAY MODELLING OF EXCHANGE PROCESSES IN PACKED BEDS.

### 7.1 Introduction

Recently Handley and Heggs (1) have presented experimental evidence to show that the two-layer (Anzelius) model is adequate to describe heat transfer in packed beds when the solid-phase transfer process is rapid, e.g. thermal conduction in a metal, and that the discrepancy that arises when the solid-phase transfer process is slow may be accounted for in terms of intraparticle conduction. Almost simultaneously Jeffreson (2) proposed a cell model that bears a striking resemblance to the Deans-Levich and  $\Gamma$ -distributed time delay cell models to describe the same phenomenon. The effects of intraparticle diffusion in spherical particles have been discussed by Rosen (3).

Jeffreson (2) developed his method in terms of frequency response analysis and suggested that time domain solutions be obtained numerically. Judging by the experimental results of Handley and Heggs (1) the time delay model possesses enough parameters to fit the transient response of packed beds to temperature upsets. In this chapter the time-delay model parameters are related to physical variables by considering the intraparticle conduction or diffusion process. First it is shown how the time-delay model and cell models of the Jeffreson type for heat and mass transfer may be written in terms of analogous equations. Next it is shown how the delay distribution parameter may be evaluated from the particle properties by considering the transient response of the particles and fitting by the method of moments. Finally the quality of the fit is assessed by considering the higher moments. Three different geometrical situations are investigated in this way in order to determine the influence of particle geometry. This leads to the proposal of a dimensionless group to characterize particle shape in terms of 'compactness'.

## 7.2 Models

### 7.2.1 The unified time-delay model

Referring back to Sec 6.3, the bed is considered to be composed of N cells in series each of which consists of a well-mixed region of volume V/N and a recycle flow whose dynamics may be represented by the transfer function:

$$F(s) = \left( \frac{t_D s}{m} + 1 \right)^{-m} \quad (1)$$

i.e. the gamma distribution. The material balance for the well-mixed portion of a typical cell is

$$C_{n-1} - C_n - \frac{q\alpha}{NQ} (C_n - C_{R,n}) = \frac{V}{NQ} \cdot \frac{dC_n}{dt} \quad (2)$$

### 7.2.2 Heat transfer and intraparticle conduction

Following Jeffreson's description (2) in which the packed bed is thought of as N well-mixed cells in contact with solid, a heat balance over the fluid in a typical cell yields:

$$T_{n-1} - T_n - \frac{h\alpha x}{NQ\rho_f C_f} (T_n - T'_{n,s}) = \frac{V}{NQ} \frac{dT_n}{dt} \quad (3)$$

Intraparticle conduction is represented by:

$$\alpha_T \nabla^2 T'_n = \frac{\partial T'_n}{\partial t} \quad (4)$$

and the interaction between the fluid and the packing by

$$\alpha_T (\text{grad } T'_n)_s = \frac{\alpha_T h}{\lambda} (T_n - T'_{n,s}) \quad (5)$$

Equation (5) is written in this unfamiliar way so that the pattern of Eqs (3), (4) and (5) will be repeated by Eqs. (9), (10) and (11) below.

### 7.2.3 Mass Transfer and intraparticle diffusion

Proceeding as above for the corresponding mass transfer case:

$$C_{n-1} - C_n - \frac{k\alpha x}{N\Omega} (C_n - K C'_{n,s}) = \frac{V}{N\Omega} \cdot \frac{dC_n}{dt} \quad (6)$$

represents the cell mass balance,

$$D \nabla^2 C'_n = \frac{\partial C'_n}{\partial t} \quad (7)$$

describes the intraparticle diffusion process, and the interaction equation is::

$$D (\text{grad } C'_n)_s = k (C_n - K C'_{n,s}) \quad (8)$$

In the above equations K is an equilibrium constant.

The change of variable  $C^* = KC$  puts the equations into the form:

$$C_{n-1} - C_n - \frac{k\alpha x}{N\Omega} (C_n - C^*_{n,s}) = \frac{V}{N\Omega} \frac{dC_n}{dt} \quad (9)$$

$$D \nabla^2 C_n^* = \frac{\partial C_n^*}{\partial t} \quad (10)$$

and

$$D (\text{grad } C_n^*)_s = K k (C_n - C^*_{n,s}) \quad (11)$$

### 7.2.4 General equations

Equations (2), (3) and (9) are of similar form. It is convenient to adopt:

$$u_{n-1} - u_n - \frac{\alpha x}{N} (u_n - u'_{n,s}) = \frac{t_0}{N} \frac{du_n}{dt} \quad (12)$$

to represent all these equations. The reason for explicitly preserving both x and N is that this retains x when N is made indefinitely large in an expression for the bed as a whole. The heat and mass

diffusion equations, Eqs.(4) and (10), and the interaction equations, Eqs.(5) and (11) are also similar and become in the new notation:

$$\mathfrak{D} \nabla^2 u_n' = \frac{\partial u_n'}{\partial t} \quad (13)$$

and

$$\mathfrak{D} (\text{grad } u_n')_s = \kappa (u_n - u_{n,s}') \quad (14)$$

The transfer function derived from Eq.(12) is:

$$G_1(s) = \left\{ 1 + \frac{1}{N} [t_0 s + \alpha x - \alpha x F(s)] \right\}^{-1} \quad (15)$$

where  $F(s)$  is the transfer function relating the particle surface potential  $u_{1,s}'$  to the fluid potential,  $u_1$ , while the transfer function for the bed as a whole is

$$G_N(s) = \left\{ 1 + \frac{1}{N} [t_0 s + \alpha x - \alpha x F(s)] \right\}^{-N} \quad (16)$$

When  $N$  is made infinitely large, Eq.(16) becomes

$$G(s) = \exp \left\{ -t_0 s - \alpha x + \alpha x F(s) \right\} \quad (17)$$

This result is of some practical importance because in the particular case where  $F(s)$  derives from the gamma distribution, i.e. is given by Eq.(1), Eq.(17) has the relatively simple inverse (9):

$$G(t) = e^{-\alpha x - m(t-t_0)/t_D} \sum_{j=0}^{\infty} \left( \frac{m}{t_D} \right)^{jm} \frac{(\alpha x)^j (t-t_0)^{jm-1}}{j! \Gamma(jm)}, \quad t \geq t_0$$

$$= 0, \quad t < t_0 \quad (18)$$

As the Anzelius treatment is successful for well-conducting packings and the discrepancies are of degree rather than kind when the packing conducts poorly (1) this generalization provides a useful tool to deal with intraparticle transport resistance.



### 7.3 Particle transfer functions and moments

7.3.1 The range of packing geometries used in chemical engineering operations is so wide and some of the shapes so bizarre that systematically evaluating the transfer functions would be a stupendous task. Jeffreson (2) has presented transfer functions based on eigenfunction expansions for the sphere and right circular cylinder. The transfer functions for plates with insulated edges, cylinders with insulated ends and spheres are found below in terms of transcendental functions. Each of these cases may be described using a single space variable if the temperature of the fluid surrounding it is uniform. Further, these shapes represent two extremes and an intermediate case and so illustrate the range of possible behaviour. The moments, found via the cumulants from the power series expansion of the logarithm of the transfer function, are used to fit the gamma distribution to the particle surface temperature impulse response and to assess the effects of geometry. The moments normalized with respect to the mean are also found.

In the stated geometries the diffusion equation takes the forms:

$$\partial \nabla^2 u' = \partial \frac{\partial^2 u'}{\partial y^2} = \frac{\partial u'}{\partial t} \quad (19)$$

(plate)

$$\partial \nabla^2 u' = \partial \left\{ \frac{\partial^2 u'}{\partial r^2} + \frac{1}{r} \frac{\partial u'}{\partial r} \right\} = \frac{\partial u'}{\partial t} \quad (20)$$

(cylinder)

$$\partial \nabla^2 u' = \partial \left\{ \frac{\partial^2 u'}{\partial r^2} + \frac{2}{r} \frac{\partial u'}{\partial r} \right\} = \frac{\partial u'}{\partial t} \quad (21)$$

(sphere)

In addition to the boundary condition, Eq.(14), the fact that the

gradient of the potential vanishes at the medial plane or axis or centre of the particles is used to solve these equations. It transpires that the normalized moments are simple functions of groups of the type  $(y_s K/D)$  or  $(r_s K/D)$ . As the ability of a bed to transfer heat or mass between phases depends largely on the interfacial area and as the capacity of the bed depends on the packing volume, it is useful to take as a characteristic packing dimension the ratio  $d$  of the packing volume to its area. Thus a group

$$Nu = dK/D$$

is defined: it is a modified Biot number.

### 7.3.2. The plate

The transform of Eq.(19)

$$D \frac{d^2 \bar{u}'}{dy^2} = s \bar{u}' \quad (22)$$

for zero initial concentration has a solution:

$$\bar{u}' = A(s) \cosh \sqrt{\frac{s}{D}} y \quad (23)$$

which has zero gradient at  $y = 0$  and so corresponds to a slab of thickness  $2y_s$ . Introducing Eq.(23) into (transformed) Eq.(14) and rearranging yields

$$\bar{u} = A(s) \left\{ \cosh \sqrt{\frac{s}{D}} y_s + \frac{\sqrt{sD}}{K} \sinh \sqrt{\frac{s}{D}} y_s \right\} \quad (24)$$

The transfer function is, from Eq (23) and (24)

$$F(s) = \frac{\bar{u}_s'}{\bar{u}} = \left\{ 1 + \frac{\sqrt{sD}}{K} \tanh \sqrt{\frac{s}{D}} y_s \right\}^{-1} \quad (25)$$

Expanding the hyperbolic tangent using the power series:

$$\tanh z = z - \frac{z^3}{3} + \frac{2}{15} z^5 - \dots$$

and substituting into Eq.(25) gives

$$F(s) = \left\{ 1 + \frac{1}{K} \left[ y_s s - \frac{1}{3} \frac{y_s^3}{\omega} s^2 + \frac{2}{15} \frac{y_s^5}{\omega^2} s^3 - \dots \right] \right\}^{-1} \quad (26)$$

When this expression is expanded yet again using

$$\ln(1+z) = z - \frac{1}{2} z^2 + \frac{1}{3} z^3 - \dots$$

the result is

$$\begin{aligned} \ln F(s) = & -\frac{y_s s}{K} + \left[ \frac{y_s^3}{3K\omega} + \frac{y_s^2}{2K^2} \right] s^2 \\ & - \left[ \frac{2}{15} \frac{y_s^5}{K\omega^2} + \frac{1}{3} \frac{y_s^4}{K^2\omega} + \frac{y_s^3}{3K^3} \right] + \dots \end{aligned} \quad (27)$$

as a power series in s.

Thus the moments, obtained from the cumulants as previously are:

$$\mu_1' = \frac{y_s}{K} = t_D \quad (28)$$

$$\mu_2 = \left[ \frac{2}{3} \frac{y_s^2 K}{\omega} + 1 \right] t_D^2 \quad (29)$$

and

$$\mu_3 = 2 \left[ \frac{2}{5} \frac{y_s^2 K^2}{\omega^2} + \frac{y_s K}{\omega} + 1 \right] t_D^3 \quad (30)$$

and the normalized moments expressed in terms of the modified Biot number are

$$\nu_2 = 1 + \frac{2}{3} Bi \quad (31)$$

$$\nu_3 = 2 \left[ 1 + Bi + \frac{2}{5} Bi^2 \right] \quad (32)$$

### 7.3.3 The cylinder

The transformed solution of Eq.(20) that has zero gradient at  $r = 0$  is

$$\bar{u}' = B(s) I_0 \left\{ \sqrt{\frac{s}{\mathfrak{D}}} r \right\} \quad (33)$$

Substituting this into the flux boundary condition, Eq.(14), gives

$$\bar{u} = B(s) \left\{ I_0 \left[ \sqrt{\frac{s}{\mathfrak{D}}} r_s \right] + \frac{\sqrt{s\mathfrak{D}}}{\kappa} I_1 \left[ \sqrt{\frac{s}{\mathfrak{D}}} r_s \right] \right\} \quad (34)$$

so that the transfer function is

$$F(s) = \left\{ 1 + \frac{\sqrt{s\mathfrak{D}}}{\kappa} I_1 \left[ \sqrt{\frac{s}{\mathfrak{D}}} r_s \right] / I_0 \left[ \sqrt{\frac{s}{\mathfrak{D}}} r_s \right] \right\}^{-1} \quad (35)$$

Performing the indicated division using the first few terms:

$$I_0(z) = 1 + \frac{1}{4} z^2 + \frac{1}{64} z^4 + \dots$$

$$I_1(z) = \frac{1}{2} z + \frac{1}{16} z^3 + \frac{1}{192} z^5 + \dots$$

of the series expansion of the Bessel functions leads to:

$$F(s) = \left\{ 1 + \frac{1}{\kappa} \left[ \frac{r_s s}{2} - \frac{1}{16} \frac{r_s^3 s^2}{\mathfrak{D}} + \frac{1}{96} \frac{r_s^5 s^3}{\mathfrak{D}} \right] \right\}^{-1} \quad (36)$$

and, the logarithm of the transfer function is:

$$\begin{aligned} \ln F(s) = & -\frac{r_s s}{2\kappa} + \left[ \frac{r_s^3}{16\kappa\mathfrak{D}} + \frac{r_s^2}{8\kappa^2} \right] s^2 \\ & - \left[ \frac{1}{96} \frac{r_s^5}{\kappa\mathfrak{D}^2} + \frac{1}{32} \frac{r_s^4}{\kappa^2\mathfrak{D}} + \frac{1}{24} \frac{r_s^3}{\kappa^3} \right] s^3 \dots \end{aligned} \quad (37)$$

as a power series in  $s$ .

The moments are

$$\mu_1' = \frac{r_s}{2\kappa} = t_D \quad (38)$$

$$\mu_2 = \left[ \frac{r_s \kappa}{2\mathfrak{D}} + 1 \right] t_D^2 \quad (39)$$

$$\mu_3 = 2 \left[ \frac{1}{4} \frac{r_s^2 \kappa^2}{\mathcal{D}^2} + \frac{3}{4} \frac{r_s \kappa}{\mathcal{D}} + 1 \right] t_D^3 \quad (40)$$

while the normalized moments are:

$$\mathcal{D}_2 = 1 + \text{Bi} \quad (41)$$

$$\mathcal{D}_3 = 2 \left[ 1 + \frac{3}{2} \text{Bi} + \text{Bi}^2 \right] \quad (42)$$

in terms of the Biot number.

#### 7.3.4. The Sphere

When the substitution  $v = ur$  is made, Eq.(21) becomes:

$$\mathcal{D} \frac{\partial^2 v}{\partial r^2} = \frac{\partial v}{\partial t} \quad (43)$$

and the zero gradient boundary condition becomes  $v = 0$  at  $r = 0$  so that the solution comparable to those found previously is

$$\bar{u}' = \frac{\bar{v}}{r} = \frac{C(s)}{r} \sinh \sqrt{\frac{s}{\mathcal{D}}} r \quad (44)$$

Proceeding as before, the transfer function:

$$F(s) = \left\{ 1 - \frac{\mathcal{D}}{r_s \kappa} + \frac{\sqrt{s \mathcal{D}}}{\kappa} \coth \sqrt{\frac{s}{\mathcal{D}}} r_s \right\} \quad (45)$$

is obtained.

The power series expansion of the hyperbolic cotangent is (14):

$$\coth z = \frac{1}{z} \left\{ 1 + \frac{z^2}{3} - \frac{z^4}{45} + \frac{2z^6}{945} - \dots \right\} \quad (46)$$

which when used in a comparable set of expansions to those used for the slab leads to:

$$F(s) = \left\{ 1 + \frac{1}{\kappa} \left[ \frac{r_s s}{3} - \frac{1}{45} \frac{r_s^3 s^2}{\mathcal{D}} + \frac{2}{945} \frac{r_s^5 s^3}{\mathcal{D}^2} - \dots \right] \right\}^{-1} \quad (47)$$

and

$$\ln F(s) = -\frac{r_s s}{3\kappa} + \left[ \frac{r_s^3}{45\kappa\vartheta} + \frac{r_s^2}{18\kappa^2} \right] s^2 - \left[ \frac{2}{945} \frac{r_s^5}{\kappa\vartheta^2} + \frac{1}{135} \frac{r_s^4}{\kappa^2\vartheta} + \frac{1}{81} \frac{r_s^3}{\kappa^3} \right] s^3 \quad (48)$$

Hence the moments are

$$\mu_1' = \frac{r_s}{3\kappa} = t_D \quad (49)$$

$$\mu_2 = \left[ \frac{2r_s\kappa}{5\vartheta} + 1 \right] t_D^2 \quad (50)$$

$$\mu_3 = 2 \left[ \frac{6}{35} \frac{r_s^2\kappa^2}{\vartheta^2} + \frac{3}{5} \frac{r_s\kappa}{\vartheta} + 1 \right] t_D^3 \quad (51)$$

and the normalized moments are::

$$\nu_2 = 1 + \frac{6}{5} Bi \quad (52)$$

$$\nu_3 = 2 \left[ 1 + \frac{9}{5} Bi + \frac{54}{35} Bi^2 \right] \quad (53)$$

#### 7.4 Fitting the gamma distribution to the particle dynamic response.

The gamma distribution has two parameters,  $t_D$  and  $m$ . It is of fundamental importance to fit the mean  $t_D$  because otherwise the conservation law (mass or heat) will be violated. This has been anticipated in the analyses above by using the symbol  $t_D$  for the mean time of the delay process in every case. Thus in the overall impulse response, Eq.(18) one sets

$$t_D = \frac{d}{\kappa} = \frac{\lambda d}{\alpha_r k} \quad \text{or} \quad \frac{d}{Kk} \quad (54)$$

The second parameter  $m$  may be fitted in a variety of ways of which the most convenient is to match variances. Gibilaro and Lees (4) have shown that moments-matching produces reasonable fits of functions roughly of the sort used here. Myrreen (5) gives an alternative method. The normalized central moments of the gamma distribution are:

$$\mu_2 = m^{-1} \quad (55)$$

$$\mu_3 = 2m^{-2} \quad (56)$$

so that the transient diffusion phenomenon is approximated by setting

$$\frac{1}{m} = 1 + \frac{2}{3} Bi \quad (57)$$

(plate)

$$\frac{1}{m} = 1 + Bi \quad (58)$$

(cylinder)

$$\frac{1}{m} = 1 + \frac{6}{5} Bi \quad (59)$$

(sphere)

in view of Eqs. (31), (41) and (52). Equations (57), (58) and (59) may be represented conveniently by

$$\frac{1}{m} = 1 + \beta Bi \quad (60)$$

in which  $\beta$  is a factor that depends on the packing geometry. An extreme range of packing configurations is covered by relatively small range - less than twofold - of  $\beta$ . For most packings, being less compact than the sphere, but not so extended as a plate, a value of  $\beta$  close to unity seems appropriate. Even for packed beds of spheres the particle-particle contacts make part of the surface area inaccessible to fluid and so effectively increase the volume to area ratio.

The method described above matches the mean and variance of the intraparticle diffusion process to those of the gamma distribution. The quality of the fit obtained can be judged by comparing the third central moments. From Eq.(56) the third moment of the fitted curve will be twice the square of the second moment. For the three geometries:

$$2 \nu_2^2 = 2 \left[ 1 + \frac{4}{3} Bi + \frac{4}{9} Bi^2 \right] \quad (61)$$

(plate)

$$2 \nu_2^2 = 2 \left[ 1 + 2 Bi + Bi^2 \right] \quad (62)$$

(cylinder)

$$2 \nu_2^2 = 2 \left[ 1 + \frac{12}{5} Bi + \frac{36}{25} Bi^2 \right] \quad (63)$$

(sphere)

These expressions are quite similar in form to Eqs. (32), (42) and (53) which indicates a reasonable fit, as the third moment is a severe test. As would be expected, the more rapid the intraparticle transfer process the better the fit, because the fitting method is exact for the exponential distribution obtained for the particle response when the diffusivity is infinite. ( $Bi = 0$ )

#### 7.5 Model response goodness-of-fit

The analyses above show that the gamma distribution fits the particle responses quite well. The overall responses for a model taking into account intraparticle diffusion and the corresponding time delay model, fitted as described, will match better because of their tendency towards being Gaussian. Again the third moment provides a sensitive test; the mean and second moment will automatically match exactly. As the time domain solution is available, Eq.(18), for the distributed time - delay model ( $N \rightarrow \infty$ ), it is the goodness-of-fit of



this case that will be discussed. The moments are determined from Eq.(17) via the cumulants. This is done by applying the binomial expansion to Eqs.(26), (36) and (47) and substituting the resulting series in  $s$  into:

$$\ln G(s) = -t_0 s - \alpha x + \alpha x F(s) \quad (64)$$

to obtain:

$$\ln G(s) = -(t_0 + \alpha x t_D) s + \alpha x t_D^2 \left[ 2 + \frac{2}{3} Bi \right] \frac{s^2}{2!} \quad (65)$$

$$- 6 \alpha x t_D^3 \left[ 1 + \frac{2}{3} Bi + \frac{2}{15} Bi^2 \right] \frac{s^3}{3!} \quad (66)$$

(plate)

$$\ln G(s) = -(t_0 + \alpha x t_D) s + \alpha x t_D^2 \left[ 2 + Bi \right] \frac{s^2}{2!} \quad (67)$$

$$- 6 \alpha x t_D^3 \left[ 1 + \frac{7}{6} Bi + \frac{1}{3} Bi^2 \right] \frac{s^3}{3!}$$

(cylinder)

$$\ln G(s) = -(t_0 + \alpha x t_D) s + \alpha x t_D^2 \left[ 2 + \frac{6}{5} Bi \right] \frac{s^2}{2!} \quad (68)$$

$$- 6 \alpha x t_D^3 \left[ 1 + \frac{6}{5} Bi + \frac{18}{35} Bi^2 \right] \frac{s^3}{3!}$$

(sphere)

In each case the coefficients of  $s^j/j!$  in the above equations are the first moment and the second and third central moments respectively of the model response.

The distributed unified time-delay model moments are: (69):

$$M_1' = t_0 + \alpha x t_D \quad (69)$$

$$M_2 = \alpha x \left(1 + \frac{1}{m}\right) t_D^2 \quad (70)$$

$$M_3 = \alpha x \left(1 + \frac{1}{m}\right) \left(1 + \frac{2}{m}\right) t_D^3 \quad (71)$$

Substituting into these expressions the fitted values of  $m$ , Eqs (57), (58) and (59), shows that the first and second moments are correct and that:

$$M_3 = 6\alpha x \left[1 + \frac{7}{9} Bi + \frac{4}{27} Bi^2\right] \quad (72)$$

(plate)

$$M_3 = 6\alpha x \left[1 + Bi + \frac{1}{3} Bi^2\right] \quad (73)$$

(cylinder)

$$M_3 = 6\alpha x \left[1 + \frac{7}{5} Bi + \frac{12}{25} Bi^2\right] \quad (74)$$

(sphere)

for the fitted model. The similarity of the dependence on  $Bi$  of these approximate third moments and the exact third moments, the coefficients of  $S^3/3!$ , in Eqs (66), (67) and (68) is striking.

## 7.6 Characterization of particle shape

The above analysis indicates that the volume to surface area ratio plays a significant role but does not completely characterise the packing elements. Another parameter  $\beta$  has already been suggested, but so far has only been related to thermal transients. However it does appear that this parameter depends on shape. The strategy of using the time delay model as an approximation would be improved if  $\beta$  could be predicted directly from the particle shape. Probably a single measure of particle shape will be adequate for this purpose as the dependency of the solution on  $\beta$  is relatively weak, the thermal properties already being accounted for in the Biot number.

The (volume) / (area)  $d$ , is more a measure of size than shape because a particle of any shape can have a specified value of  $d$ . As  $\beta$  is dimensionless it is appropriate to search for another quantity with the dimension of length to combine with  $d$  to form a dimensionless shape number. Particles differ in their compactness or the accessibility of their interiors in diffusive transport, so the shape number might reasonably be expected to be a measure of compactness if it is to be used as the basis of a method of predicting  $\beta$ . If a particle is compact it has a highly curved surface, which suggests the use of the surface curvature to define the second characteristic dimension. The areal average surface curvature is proposed for this purpose.

The radius of curvature of a plane curve at a point on the curve is

$$\rho = \lim_{d\sigma \rightarrow 0} \frac{d\sigma}{d\theta} \quad (75)$$

where  $d\theta$  is the angle included by normals drawn at the ends of an arc of length  $d\sigma$ . Clearly this meets the natural requirement of reducing to the radius for a circular arc. Local curvature is the reciprocal of radius of curvature. A plane may be drawn at many orientations and contain the normal to a surface, so a surface in general has many radii of normal curvature. The maximum and minimum normal curvatures occur in mutually perpendicular planes (6) and are called the principal normal curvatures  $1/\rho_1$  and  $1/\rho_2$ . The mean of these curvatures

$$\frac{1}{\rho_N} = \frac{1}{2} \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) \quad (76)$$

is at least an approximate measure of the mean normal curvature over all directions at a point on a surface. The curvature in a normal plane making an angle  $\phi$  with the plane of  $\rho_1$  is (6)

$$\frac{1}{\rho}(\phi) = \frac{\cos^2 \phi}{\rho_1} + \frac{\sin^2 \phi}{\rho_2} \quad (77)$$

and in the plane making an angle  $\phi$  with the plane of  $\rho_2$

$$\frac{1}{\rho} \left( \phi + \frac{\pi}{2} \right) = \frac{\sin^2 \phi}{\rho_1} + \frac{\cos^2 \phi}{\rho_2} \quad (78)$$

Thus the average of two curvatures in mutually perpendicular normal planes is always  $1/\rho_N$  by adding Eqs. (77) and (78), and it follows that Eq.(76) gives the normal curvature averaged over all directions. The areal average curvature then is defined by

$$\left\langle \frac{1}{\rho_N} \right\rangle = \frac{1}{2S} \iint_S \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) dS \quad (79)$$

and the shape factor is defined by

$$\gamma = 3d \left\langle \frac{1}{\rho_N} \right\rangle \quad (80)$$

where the factor 3 has been introduced to give  $\gamma$  the value unity for a sphere. It is interesting to note that the coefficients; 0,  $1/r$  and  $2/r$ ; of the second terms in the Laplacians in Eqs.(19), (20) and (21) have an immediate interpretation in terms of areal average curvatures, which also points to curvature as a characteristic of particle shape. The appropriateness of  $\gamma$  as a measure of compactness is seen in Table 1 where the different shapes are in a plausible order. In calculating the figures in this table, sharp edges are taken into account by considering the edge to be curved and taking the limit as the edge radius is reduced to zero. This procedure was suggested by Hilliard (7) and independently by Beresford (8). For convex particles the mean normal curvature is closely related (7) to the mean caliper diameter (the average distance over all orientations between parallel tangent planes)

$$d_c = \frac{S}{2\pi} \left\langle \frac{1}{\rho_N} \right\rangle \quad (81)$$

and to a variety of other averages including the mean perimeter and mean area of intersection of the particle by a plane (9) and the mean curvature averaged over all directions (10). Hilliard (7) gives a table of formulae for caliper diameter, surface area and volume that

Table 1 Compactness,  $\gamma$ , of some simple shapes.

Shape			
Infinite lamina, thickness $2a$	$a$	$0$	$0$
Infinite equilateral triangular prism face width $2a$ .	$\frac{\sqrt{3}a}{6}$	$\frac{\pi}{6a}$	$0.4535$
Infinite square prism, face width $2a$ .	$\frac{a}{2}$	$\frac{\pi}{8a}$	$0.5889$
Infinite regular hexagonal prism, face width $2a$	$\frac{\sqrt{3}a}{2}$	$\frac{\pi}{12a}$	$0.6802$
Infinite cylinder, radius $r$	$\frac{r}{2}$	$\frac{1}{2r}$	$0.7500$
Regular tetrahedron, edge $2a$ .	$\frac{\sqrt{6}a}{18}$	$\frac{\sqrt{3}(\pi - \sec^{-1}3)}{2a}$	$0.6759$
Cube, edge $2a$	$\frac{a}{3}$	$\frac{\pi}{4a}$	$0.7854$
Parallelepiped, edges, $2a$ ; $2a$ ; $4a$ .	$\frac{2a}{5}$	$\frac{\pi}{5a}$	$0.7540$
Parallelepiped, edges $2a$ ; $4a$ ; $4a$ .	$\frac{a}{2}$	$\frac{5\pi}{32a}$	$0.7363$
Sphere, radius $r$	$\frac{r}{3}$	$\frac{1}{r}$	$1.0000$
Cylinder with spherical caps, Cylinder length $2r$ , radius $r$ , cap radius $r$ .	$\frac{5r}{12}$	$\frac{3}{4r}$	$0.9375$

enables  $\bar{V}$  to be calculated for simple shapes and some more complex shapes such as spheroids and polyhedra. De.Hoff (10) describes a stereological counting method for determining the average surface curvature of particulate material from the tangents made with random lines. Techniques for determining  $\bar{d}$  for complex shapes in a similar way are better known and are based on the fact that the mean chord length,  $l$ , is given by (9, 11)

$$l = 4V_p / S = 4\bar{d} \quad (82)$$

The use of the parameter  $\bar{V}$  in predicting the effect of shape on transient diffusion and other phenomena is to be the subject of a future investigation. At present corresponding values of  $\beta$  and  $\bar{V}$  are known only for the three simple 'one-dimensional' geometries. However in view of the fairly weak dependence of the approximate time delay analysis on  $\beta$ , the curve in Fig. 1 is offered as an interim correlation.

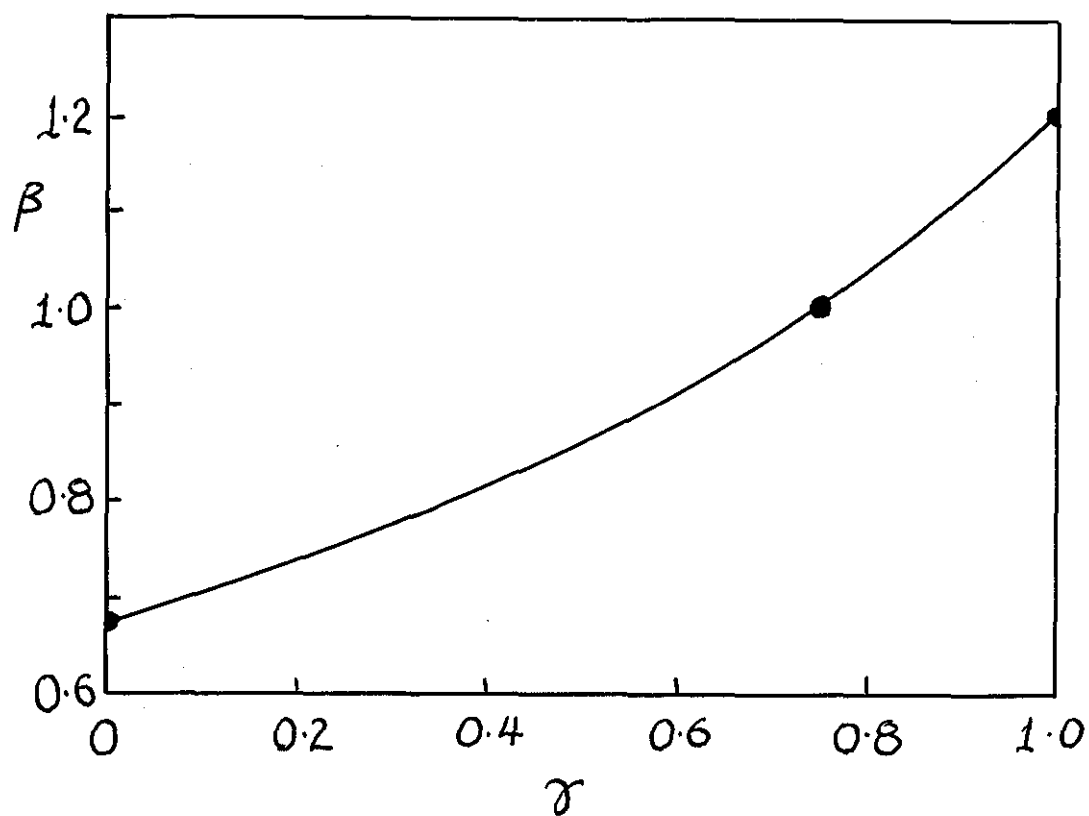


Fig. 1. Suggested relation between the transient diffusion shape factor  $\beta$  and the compactness  $\gamma$  .

## 8. DYNAMIC DISPERSION - A FORMAL APPROACH TO TRANSVERSE MIXING

### 8.1. The dynamic dispersion equation

In the preceding chapter methods have been developed which enable random transverse mixing to be treated in a variety of ways. A feature that these methods share is that the possibility of fluid being segregated into moving and stagnant regions is recognized directly. It will now be shown how similar results may be established in a formal way that is parallel in many respects to the usual formal one-dimensional treatment of the diffusion model.

If the diffusion idea were not so strongly entrenched one might, when presented with an impulse response for, say, flow in a packed bed, suggest that the flux depends on the time rate of change of the concentration gradient in a linear way:

$$\bar{\phi} = Vc + E \frac{\partial c}{\partial t} \quad (1)$$

The constant E may be called the 'dynamic dispersivity' because it represents the spreading of residence times as a dynamic phenomenon; it has the dimension of length. By incorporating Eq.(1) into a material balance we obtain:

$$E \frac{\partial^2 c}{\partial x \partial t} + V \frac{\partial c}{\partial x} + \frac{\partial c}{\partial t} = 0 \quad (2)$$

as the analogue of the one-dimensional diffusion equation for a flowing medium. This, the dynamic dispersion equation, has the ability to describe spreading of residence times as already mentioned, but needs only one boundary condition so that only inlet conditions need be specified.

### 8.2 Some solutions of the dynamic dispersion equation

Equation (2) is simplified if the dimensionless space and time variables:



$$\chi = x/E \quad \text{and} \quad \tau = Vt/E$$

are employed; it becomes:

$$\frac{\partial^2 c}{\partial \chi \partial \tau} + \frac{\partial c}{\partial \tau} + \frac{\partial c}{\partial \chi} = 0 \quad (3)$$

An impulse response solution can be found by incorporating an instantaneous plane source at  $\chi = 0$ ,  $\tau = 0$  into Eq.(3) and using transform methods. With the source added Eq.(3) becomes:

$$\frac{\partial^2 c}{\partial \chi \partial \tau} + \frac{\partial c}{\partial \tau} + \frac{\partial c}{\partial \chi} = \delta(\tau) \delta(\chi) \quad (4)$$

Applying the Laplace transform twice, first to eliminate  $\tau$  and introduce  $s$  and secondly to eliminate  $\chi$  and introduce  $p$ , yields:

$$\bar{c}(p, s) = \left[ (s+1) \left( p + \frac{s}{s+1} \right) \right]^{-1} \quad (5)$$

Recovering  $\chi$  by inverting with respect to  $p$  gives the transfer function:

$$\bar{c}(\chi, s) = \frac{1}{s+1} \exp \left\{ -\frac{s}{s+1} \chi \right\} \quad (6)$$

and a second inversion gives the impulse response or Green's function:

$$c = e^{-(\chi+\tau)} I_0(2\sqrt{\chi\tau}) \quad (7)$$

Alternatively the impulsive forcing can be described by the boundary condition:

$$\left[ c + \frac{\partial c}{\partial \tau} \right]_{\chi=0} = \delta(t) \quad (8)$$

This again yields Eq. (6) as the transfer function.

A slightly different type of forcing is to make an impulsive change in the concentration at  $\chi = 0$  instead of in the flux. The transfer function is then

$$\bar{c}(\chi, s) = \exp \left\{ -\frac{s}{s+1} \chi \right\} \quad (9)$$

and the corresponding response is

$$c = e^{-(\tau+\chi)} \left\{ \left( \frac{\chi}{\tau} \right)^{1/2} I_1(2\sqrt{\chi\tau}) + \delta(\tau) \right\} \quad (10)$$

Equations (7) and (10) are established using the transform pairs:

$$\frac{1}{s} e^{a/s} \longleftrightarrow I_0(2\sqrt{at}) \quad (11)$$

and

$$e^{a/s} - 1 \longleftrightarrow \left( \frac{a}{t} \right)^{1/2} I_1(2\sqrt{at}) \quad (12)$$

which are standard (1)

### 8.3 Extensions of the dynamic dispersion model

If it is imagined that mixing only takes place in a fraction  $\alpha$  of the length  $\chi$ , there will be a dead time of  $(1-\alpha)\chi$ . Thus replacing  $\chi$  by  $\alpha\chi$  in the transfer function and then multiplying by the transform of the dead time gives the partial plug flow versions of Eq. (6):

$$\bar{c} = \frac{1}{s+1} \exp \left\{ -\frac{\alpha s \chi}{s+1} - (1-\alpha)\chi s \right\} \quad (13)$$

and of Eq. (9):

$$\bar{c} = \exp \left\{ - \frac{\alpha s x}{s+1} - (1-\alpha) x s \right\} \quad (14)$$

The time-domain solutions are obtained by replacing  $x$  by  $\alpha x$  in Eqs. (7) and (10) and displacing  $\tau$  by  $(1-\alpha)x$ .

The equation

$$D \frac{\partial^2 c}{\partial x^2} - \frac{\partial^2 c}{\partial x \partial \tau} - \frac{\partial c}{\partial x} - \frac{\partial c}{\partial \tau} = 0 \quad (15)$$

takes into account both axial and dynamic dispersion. One more boundary condition is required to obtain a solution and so there are a great many possibilities as is the case with the diffusion equation. This model will not be explored further analytically except to note that while transfer functions can be obtained for the various cases without a great deal of difficulty, the inversion of the transfer functions is difficult.

#### 8.4 Discussion

From what has previously been said it is apparent that the formalism of introducing dynamic dispersion leads to tractable mathematics and impulse response expressions that appear quite reasonable. For conditions in which the relative amount of dispersion is small, i.e. long beds, small  $D$  and/or  $E$ , the dynamic and axial dispersion models are more or less equivalent in the residence time distributions they predict. This is because  $E \partial^2 c / \partial x \partial t$  and  $-D \partial^2 c / \partial x^2$  represent similar effects for impulse responses as most of the tracer is observed at position  $x$  at time  $\sim x/V$ . Thus if values of  $E$  and  $D$  are each determined for an impulse response for a long bed, they will be related by

$$EV \simeq D$$

(16)

Several of the expressions developed above for the residence time distribution are identical in form to those derived previously for random exchange models. Equation (7) is identical with the Einstein statistical model used by Cairns and Prausnitz (2). Equation (10) is equivalent to the random time-delay model with exponentially distributed time delays. Giddings (3) has derived forms equivalent to both Equations (7) and (10) in his theory of chromatography. Indeed Giddings' work makes clear the distinction between the two types of boundary condition. Equation (7) describes a situation in which the tracer is initially all present in the stationary phase (stagnant region) at the bed entrance, whilst Eq. (10) describes injection of tracer into the moving phase (flowing region) at the bed entrance.

This equivalence between the two dispersion models disappears when another phenomenon besides mixing occurs. For example, consider that the tracer is being consumed by a first order reaction; then:

$$D \frac{\partial^2 c}{\partial x^2} - V \frac{\partial c}{\partial x} - kc = \frac{\partial c}{\partial t} \quad (17)$$

and

$$E \frac{\partial^2 c}{\partial x \partial t} + V \frac{\partial c}{\partial x} + kc = - \frac{\partial c}{\partial t} \quad (18)$$

describe the combined effects of mixing and reaction in the two cases. The steady state forms of Eqs. (17) and (18) are quite different:

$$D \frac{d^2 c}{dx^2} - V \frac{dc}{dx} = kc \quad (19)$$

and

$$-V \frac{dc}{dx} = kc \quad (20)$$

although the residence time distributions are similar if the parameters obey Eq. (16).

A physical explanation of this is that  $D$  represents a mixing mechanism which always tends to even out the concentration whereas  $E$  does not and so has no effect on the steady state reaction rate, which is the same as in plug flow. Bischoff (4) has recently presented calculations of the exit concentration for steady state operation of a tubular reactor in which fully developed laminar flow exists, together with corresponding results for the one-dimensional axial dispersion equation based on the Taylor (5) expression for  $D$ . Table 1 presents these results, as conversions, together with the corresponding plug flow (pure dynamic dispersion) conversions. The exact conversions lie more or less midway between the conversions for the two models. Clearly the mixed axial and dynamic dispersion model Eq. (15), could represent both the residence time distribution and, combined with a reaction term, the conversion in a laminar flow reactor.

A final point to note is that the velocity must be in the positive direction of  $x$ . Equation (1) as it stands does not survive the simultaneous reversal of the signs of  $x$  and  $V$ . This may be corrected by replacing  $E$  by  $EV/|V|$ .

The concept of dynamic dispersion allows models in which the underlying mixing mechanism is transverse in nature to be constructed with the same facility as using the conventional dispersion model. Dynamic dispersion is not necessarily equivalent to axial diffusion but is best regarded as an additional mechanism that only makes itself felt in dynamic situations. Conversely if all the mixing mechanisms are characterised by a single diffusion constant determined from dynamic

TABLE 1

Conversion for first order reaction in  
laminar flow tubular reactor

$\beta$	$Z_L^*$	$R_1$	Conversion		
			Axial Dispersion	Exact	Dynamic Dispersion
0.25	0.2	0.1	0.093	0.094	0.095
	0.4	0.2	0.178	0.179	0.191
	0.6	0.3	0.255	0.256	0.259
	0.8	0.4	0.324	0.325	0.330
	1.0	0.5	0.388	0.388	0.394
2.5	0.2	1.0	0.583	0.595	0.632
	0.6	3.0	0.924	0.927	0.950
	1.0	5.0	0.9860	0.9865	0.9993
25	0.02	1.0	0.545	0.579	0.632
	0.05	2.5	0.792	0.856	0.918
	0.10	5.0	0.936	0.972	0.9993

$$\beta = \frac{kR^2}{4D_M}$$

$$Z_L^* = \frac{Pe}{24}$$

$$R_1 = \frac{kZ_L}{V}$$

experiments and predictions about other effects in the steady state are then made, they may be erroneous.

Dynamic dispersion is a powerful formalism for use in the 'building block' approach to model construction that complements the more usual axial dispersion idea.

## 9. NETWORK COMBING THEORY

### 9.1 Introduction

In this chapter methods are developed for solving models in which exponentially distributed time delays are considered to take place at arbitrarily arranged locations in space, with instantaneous transmission between locations, according to a probabilistic pattern. This can be regarded as a multidimensional extension of some of the previous methods. The time-delay strategy is again adopted and it will be seen that this leads to a theory of continuous-time Markov processes in a particularly simple way. Some applications of the method to familiar problems drawn from chemical engineering will be given. The cell model interpretation of the present scheme is a number of well-mixed stages with arbitrary steady flows between all the stages. For the time being it will be assumed that the time constants for all the vessels are the same and that the system has but one inlet and one outlet. These restrictions will be lifted later, as will the restriction of exponential mixing characteristics for the special case where each vessel has the same characteristics.

The arrangement of cells is referred to as a network. If a tracer particle endowed with the power of being able to tell when it passed from cell to cell in the network and a knowledge of chemical engineering were to pass through the network, it would report to an observer stationed at the outlet that it had passed through a sequence of so many well-mixed stages. It would of course give different assessments on different passes through the network, so the network is equivalent to a parallel arrangement of strings of vessels in series with appropriate flows through the strings and the volumes of the vessels in each path such as to make all the time constants equal. Thus an arbitrary network may be 'combed' to give a simpler parallel-series form whose dynamic response properties are identical to those



of the original network, Figs. 1 and 2. It is much easier to determine the residence time distribution and related properties for the combed network than for the original network. Clearly the first problem to be attacked is to assess the probability of passing through the system with  $n$  delays as this is the weighting factor for the  $n$ -vessel path in the combed network.

## 9.2 Network combing and the residence time distribution (equal time constants)

Taking the cell view for the moment, number of stages  $1, 2, 3, \dots, N$  starting with the cell the feed enters and ending with the cell the outflow leaves from; apart from these, no other restriction is necessary in the numbering; call the outlet itself  $N+1$ .

Let:

$V_i$  = volume of vessel  $i$

$Q_i$  = flow through vessel  $i$

$Q$  = flow through system

$q_{ij}$  = flow from vessel  $i$  to vessel  $j$

Then, the total flow through a given vessel is the sum of all the leaving flows:

$$Q_i = \sum_{j=1}^{N+1} q_{ij}, \quad \begin{aligned} q_{ii} &= 0 \\ q_{N+1, N+1} &= Q \\ q_{N+1, j} &= 0 \end{aligned} \quad (1)$$

As the time constants are presumed the same, the  $V_i$  and  $Q_i$  are related in pairs by

$$\tau = V_i / Q_i \quad (2)$$

The probability that when a move occurs it is from  $i$  to  $j$ , assuming the tracer to be in  $i$  already, is

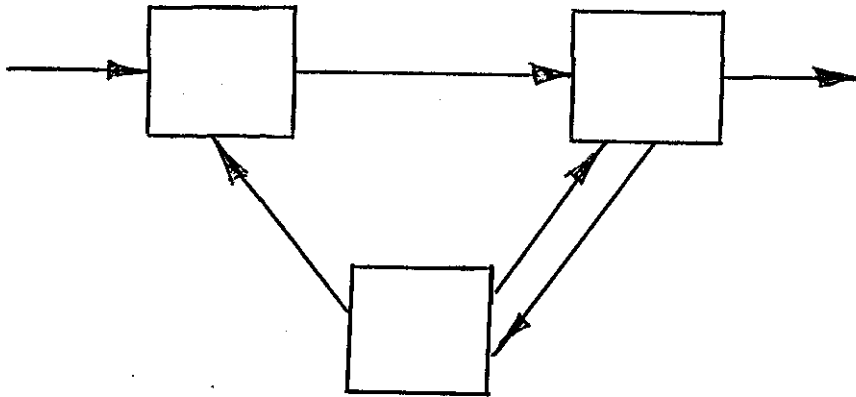


Fig. 1 A Network

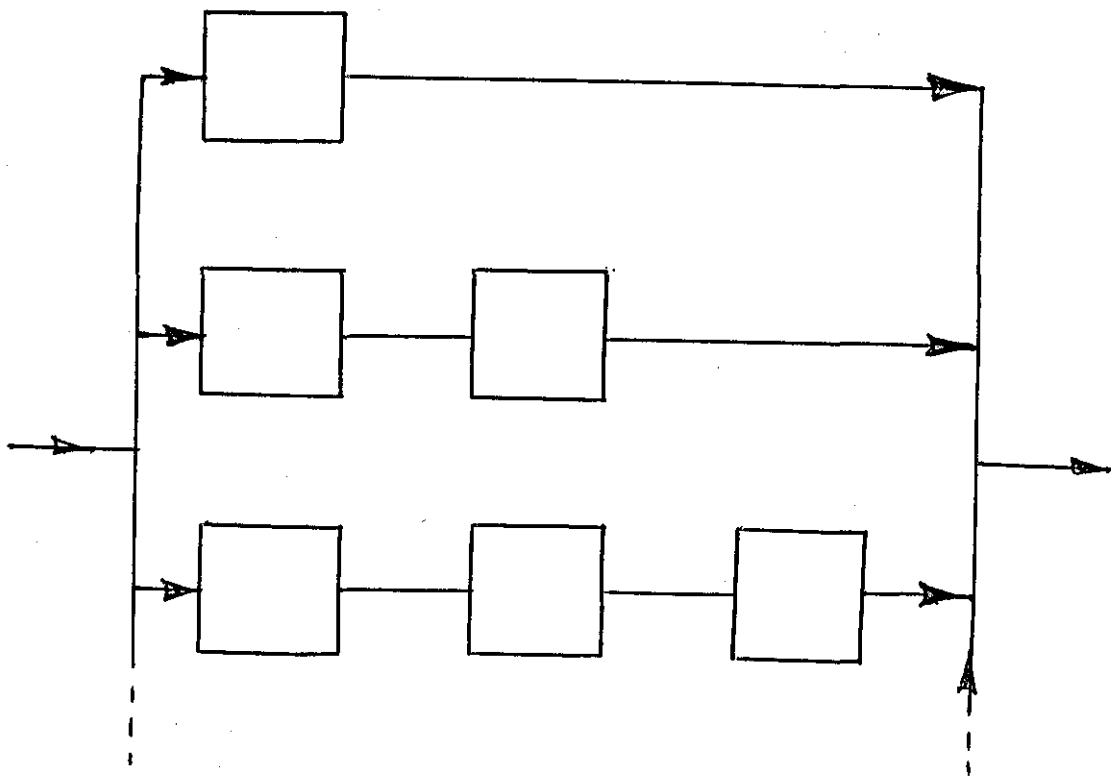


Fig. 2 The combed network

$$r_{ij} = q_{ij} / q_i \quad (3)$$

Now let the probability that a tracer element arrives in vessel  $i$  after the  $n$ th move on its journey through the network be  $s_i(n)$ , then the probability it reaches  $j$  after  $n+1$  moves is  $s_j(n+1)$ . In general it will be possible to reach vessel  $j$  from all the other vessels and  $s_j(n+1)$  is related to  $s_i(n)$  by

$$s_j(n+1) = \sum_{i=1}^N r_{ij} s_i(n) \quad (4)$$

which takes account of all possible moves. Equation (4) will be recognised as a vector-matrix product and can be written more briefly

$$\underline{s}(n+1) = \underline{s}(n) \cdot \underline{R} \quad (5)$$

where a single underscore indicates a vector and a double underscore a matrix,  $\underline{s}$  being the vector of elements  $s_i$  and  $\underline{R}$  being the matrix of elements  $r_{ij}$ . In the theory of Markov processes (1,2)  $\underline{s}$  is the state probability vector and  $\underline{R}$  is the transition matrix, or more specifically (2) the imbedded transition matrix. Successive application of Eq.(5) starting with  $\underline{s}(0)$  yields

$$\underline{s}(n) = \underline{s}(0) \cdot \underline{R}^n \quad (6)$$

As the tracer must initially be in the cell the feed enters, which we have chosen to number '1',

$$\underline{s}(0) = [1, 0, 0, \dots] \quad (7)$$

The final element,  $s_{N+1}$ , of  $\underline{s}$  gives the probability of the tracer having left the system after  $n$  moves have taken place, i.e.

$$s_{N+1}(n) = \sum_{n=1}^n p_n \quad (8)$$

where  $p_n$  is the probability of leaving the system in exactly  $n$  moves. Equation (8) shows that

$$p_n = S_{N+1}(n) - S_{N+1}(n-1) \quad (9)$$

so that the  $p_n$  may be determined from Eqs.(6) and (7).

Thus the flow  $Q^{(n)}$  in the  $n$ th strand of the combed network is

$$Q^{(n)} = p_n Q \quad (10)$$

and the residence time distribution for the  $n$ th strand is

$$f_n(t) = \frac{t^{n-1} e^{-t/\tau}}{(n-1)! \tau^n} \quad (11)$$

as each strand is  $n$  vessels in series, Sec 2.3.

The system residence time distribution is

$$f(t) = \sum_{n=1}^{\infty} \frac{t^{n-1} e^{-t/\tau}}{(n-1)! \tau^n} \cdot p_n \quad (12)$$

by summing the components due to the strands given above. In Eq.(12) the lower limit is  $n = 1$  because tracer must be delayed at least once in its passage through the system. A finite value of  $p_0$  corresponds to a portion of the inflow bypassing the system and is best accounted for separately.

### 9.3 Internal compositions

In addition to the residence time distribution, the internal compositions in the network are also of interest. It is not possible to determine the internal compositions in exactly the same way as the residence time distribution because of the difficulties involved in determining the residence time distribution at a point through which recycle, which must be considered in an arbitrary network, can occur.

An alternative way of looking at the transition process which is more useful in establishing the internal probabilities, is to consider

random delays occurring sequentially in time and to allocate these spatially by the transition process. When this view is adopted, one considers that delays are always taking place and their relevance is determined by the transition probabilities - delays occurring outside the system are irrelevant. The internal composition in a vessel of the network is directly related to the probability that a single tracer element is present in that vessel. Thus establishing the probability that the tracer is in a given vessel at time  $t$  solves the problem of finding the concentration-time history in all its essentials.

Looking at the system at time  $t$  the probability that  $n$  moves have occurred in  $(0, t)$  is

$$P_n(t) = \frac{1}{n!} \left( \frac{t}{\tau} \right)^n e^{-t/\tau}, \quad n = 0, 1, 2, \dots \quad (13)$$

In the ordinary tanks-in-series model this is the probability that the tracer has reached the  $(n+1)$ th tank. Now think of the network as being combed between vessel 1 and vessel  $i$ . In general,  $0, 1, 2, \dots$  delays can occur on a path between vessel 1 and vessel  $i$  and these can be represented by a combed network. The probability of being in vessel  $i$  after  $n$  transitions is  $s_i(n)$  so that the probability of being in vessel  $i$  at time  $t$  by a route involving  $n$  delays is  $s_i(n)P_n(t)$ . The total probability of being in vessel  $i$  at  $t$  is obtained by summing over all  $n$ :

$$S_i(t) = \sum_{n=0}^{\infty} s_i(n) P_n(t) \quad (14)$$

Substituting Eq.(13) into Eq.(14) and writing the result in the evident vector form :

$$\underline{S}(t) = \left\{ \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{t}{\tau} \right)^n \underline{S}(n) \right\} e^{-t/\tau} \quad (15)$$

which becomes:

$$\underline{S}(t) = \underline{S}(0) \left\{ \sum_{n=0}^{\infty} \frac{1}{n!} \left( \frac{t}{\tau} \right)^n \underline{R}^n \right\} e^{-t/\tau} \quad (16)$$

The usual definition of the exponential function can be carried over into matrix representations (3) so that Eq.(16) may be written:

$$\underline{S}(t) = \underline{S}(0) e^{\underline{R}t/\tau} e^{-t/\tau} \quad (17)$$

In Eqs.(16) and (17),  $\underline{S}(0)$  in derivation refers to  $n=0$ , but clearly the initial condition is the same whether expressed in terms of  $n$  or  $t$  so no confusion can result.

The compositions are found from Eq.(17) by writing the probabilities as

$$s_i(t) = \frac{V_i c_i(t)}{V_i c_i(0)}, \quad i = 1, 2, \dots, N \quad (18)$$

A corresponding form may be defined for the outlet state  $N+1$  by imagining an initially empty reservoir into which the system discharges:

$$s_{N+1}(t) = \frac{Q t c_{N+1}(t)}{V_i c_i(0)} \quad (19)$$

#### 9.4 Moments

The moments are useful response curve characteristics and also find use in model fitting techniques as has been previously discussed.

It is of some interest, then, that it is possible to establish quite simple expressions for the moments for network models. The  $r$ th moment vector of  $\underline{S}(t)$  is defined by:

$$\begin{aligned} \underline{M}_r &= [\mu_{r1}, \mu_{r2}, \dots, \mu_{rN}] \\ &= \int_0^{\infty} t^r \underline{S}(t) dt \end{aligned} \quad (20)$$

Substituting Eq.(16) into Eq.(20) and recognizing that:

$$\int_0^{\infty} \frac{1}{n!} \left( \frac{t}{\tau} \right)^n e^{-t/\tau} d\left( \frac{t}{\tau} \right) = 1, \quad (21)$$

leads to:

$$\underline{M}_r = \tau^{r+1} \underline{S}(0) \sum_{n=0}^{\infty} \frac{(n+r)!}{n!} \underline{R}^n \quad (22)$$

The zeroth moment occupies a special place in the theory because it gives the steady state corresponding to indefinite repetition of the original impulse input:

$$\underline{M}_0 = \tau \underline{S}(0) \sum_{n=0}^{\infty} \underline{R}^n \quad (23)$$

• which sums in the present case where  $\underline{R}$  is a stochastic matrix to give:

$$\underline{M}_0 = \tau \underline{S}(0) (\underline{I} - \underline{R})^{-1} \quad (24)$$

An alternative formulation of the moment vector is possible in terms of a recursion relation. Equation (22) may be written for the  $(r+1)$ th moments as:

$$\underline{M}_{r+1} = \tau^{r+2} \underline{S}(0) \left\{ \sum_{m=0}^{\infty} \frac{(m+r+1)!}{m!} \underline{R}^{m+1} + (r+1) \sum_{n=0}^{\infty} \frac{(n+r)!}{n!} \underline{R}^n \right\} \quad (25)$$

where  $m = n-1$ . Comparison of the two series in Eq.(25) with Eq.(22) shows that:

$$\underline{M}_{r+1} = \underline{M}_{r+1} \underline{R} + (r+1) \tau \underline{M}_r \quad (26)$$

which may be rearranged to:

$$\underline{M}_{r+1} = (r+1) \tau \underline{M}_r (\underline{I} - \underline{R})^{-1} \quad (27)$$

Repeated application of this recursion rule starting with  $\underline{M}_0$ , Eq.(24), yields the following alternative to Eq.(22):

$$\underline{M}_r = r! \tau^{r+1} \underline{S}(0) \left\{ (\underline{I} - \underline{R})^{-1} \right\}^{r+1} \quad (28)$$

Further, as  $(\underline{I}-\underline{R})^{-1}$  is the sum of the infinite matrix geometric series:

$$\underline{M}_r = r! \tau^{r+1} \underline{S}(0) \left\{ \sum_{n=0}^{\infty} \underline{R}^n \right\}^{r+1} \quad (29)$$

### 9.5 Non-equal time constants and network modification

The preceding analyses apply to the rather restricted case in which all the time constants are equal. Clearly network combining becomes a much more powerful technique when this restriction is removed. This is accomplished by replacing a network with arbitrary time constants by a modified network with the same state probability vector  $\underline{S}$ , but with a modified transition matrix  $\underline{R}^*$ . If a recycle loop with zero holdup is added to a well-stirred vessel, there is no observable effect because material is removed from the vessel and then remixed with material of the same composition. A material balance:

$$q_{ii} C_i - (Q_i + q_{ii}) C_i = V_i \frac{dc_i}{dt} \quad (30)$$

over a stage with recycle rate  $q_{ii}$  illustrates this; the term  $q_{ii} C_i$  cancels out. It will be recalled that the time constant  $\tau$  in the previous analysis is the ratio of a vessel volume to the flow rate through it. In the present case set

$$\tau_i = V_i / Q_i \quad (31)$$

the transition probabilities depend on the flows exactly as before. Now a set of arbitrary constants  $q_{ij}$  may be added into the flow matrix without affecting the system dynamics. By analogy with Eqs.(1), (2) and (3), pseudo-values of  $Q_i$ ,  $\tau_i$  and  $v_{ij}$ , which we write as  $Q_i^*$ ,  $\tau_i^*$  and  $v_{ij}^*$ , may be defined for the modified flow matrix:



$$Q_i^* = \sum_{j=1}^N q_{ij} \quad (32)$$

$$\tau_i^* = V_i / Q_i^* \quad (33)$$

and

$$r_{ij}^* = q_{ij} / Q_i^* \quad (34)$$

The effect this has on the time constants is particularly interesting; it enables  $\tau_i$  to be replaced by any value  $\tau_i^*$  that is smaller than the original value. This enables a set of  $\tau_i^*$  values to be chosen, by suitably specifying the  $q_{ii}$ , which are all equal. The simplest and best choice for this common value is the smallest value of  $\tau_i$ , say  $\tau_m$ . With this choice, the modified transition probabilities are given by:

$$r_{ij}^* = \frac{q_{ij}}{Q_i^*} = \frac{\tau_m q_{ij}}{V_i} \quad (35)$$

$$r_{ii}^* = \frac{Q_i^* - Q_i}{Q_i^*} = 1 - \frac{\tau_m}{\tau_i} \quad (36)$$

These operations have no effect on the state vector and all the equations for the equal time-constant case apply with the matrix  $\underline{R}$  replaced by the matrix  $\underline{R}^*$  of elements  $r_{ii}^*$  and  $r_{ij}^*$ .

## 9.6 More general initial conditions and multiple outlets

So far it has been assumed that only one stream enters the system. This assumption is not necessary and was introduced to simplify the description; the analysis applies for any initial condition. Indeed the probabilities  $s_i(t)$  may be interpreted as absolute quantities of mass

or energy or any other conserved entity, i.e. all that is required is that

$$\sum_{i=0}^{N+1} S_i(t) = \text{constant} \quad (37)$$

The  $s_i(0)$  may then be allocated according to the nature of the physical situation. Most situations in which there is more than one feed stream fall into one of two categories: manifolded systems in which a common stream is split between several vessels in a specified way; and independent-inlet systems in which in practice several inlets are independently manipulated. The former is best dealt with by allocating the initial probabilities in proportion to the inlet flows; and the latter by considering the responses to forcing the various inlets separately, as the responses so determined may then be combined in any desired proportion.

Multiple outlets may be dealt with in exactly the same way by defining more states  $N+2$ ,  $N+3$ , etc. However this increases the dimension of the matrix  $\underline{R}$  and so is to be avoided if possible.

## 9.7 Computation

Particularly in the case of the internal probabilities computation poses some problems. The direct use of Eq.(16) is unsatisfactory because for each time value considered many matrix multiplications are required. An alternative method is to make use of the fact that, as with ordinary exponentials, matrix exponentials converge in a few terms if the argument is small. Thus, from Eq.(16), we can write

$$\underline{S}(t+\Delta t) = \underline{S}(t) \left\{ \sum_{n=0}^k \frac{1}{n!} \left( \frac{\Delta t}{\tau} \right) \underline{R}^n \right\} e^{-\Delta t/\tau} \quad (38)$$

where  $k$  depends on the value of the finite time increment  $\Delta t$  which has

elapsed since  $t$ . This equation may be written

$$\underline{S}(t+\Delta t) = \underline{S}(t) \underline{\Pi}(\Delta t) \quad (39)$$

where

$$\underline{\Pi}(\Delta t) = e^{-\Delta t/\tau} \sum_{n=0}^k \frac{1}{n!} \left(\frac{\Delta t}{\tau}\right) \underline{R}^n \quad (40)$$

is a new transition matrix. (Compare the form of Eq.(39) with Eq.(5)).

As usual, if the series is converging rapidly the first term beyond the truncation point ( $n=k$ ) is a measure of error involved. A balance exists between the size of step  $\Delta t$  and the number of terms retained in the series. Equation (39) can be used as the basis for a computer routine to solve network problems, but may result in too small an increment size, or equivalently, too large a value of  $k$ . This defect may be overcome by making use of the fact that successive squaring generates high powers rapidly. Equation (39) is replaced by

$$\underline{S}(t + \ell \Delta t) = \underline{S}(t) \left[ \underline{\Pi}(\Delta t) \right]^\ell \quad (41)$$

where  $\ell$  is chosen to be a suitable power of two, so that the new transition matrix:

$$\underline{\Pi}'(\Delta t) = \left[ \underline{\Pi}(\Delta t) \right]^\ell \quad (42)$$

may be evaluated by squaring. The computing effort may also be reduced by increasing the time interval in the later stages of the calculation.

### 9.8 More general time delay distributions

The residence time distribution may be established when the transient mixing characteristics in all the vessels are the same. In practice it is necessary for the convolutions of the prototype distributions to be available. Several distributions with relatively

simple convolutions are given in Chapter 5 . The analysis is the same as on p.97 for exponential distributions and the residence time distribution is

$$f(t) = \sum_{n=1}^{\infty} p_n f_n(t) \quad (43)$$

where  $f_n(t)$  is the n-fold convolution of the prototype distribution and the  $p_n$  are found as before. It is tacitly assumed that the transition probabilities do not depend on residence time within the individual vessels. This assumption is not necessarily true for non-exponential distributions as it is a consequence of the perfect mixing assumption made in the previous analysis. In practice the truth or otherwise of this assumption depends on the exact nature of the interconnections.

# 10. APPLICATION OF NETWORK COMBINING TECHNIQUES TO CHEMICAL ENGINEERING PROBLEMS.

## 10.1 Introduction

The network combining theory presented in the previous chapter amounts to a theory for solving sets of first order differential equations of the following form:

$$\left. \begin{aligned} b_1 \frac{dy_1}{dt} &= -a_{11}y_1 + a_{12}y_2 + a_{13}y_3 + \dots + a_{1N}y_N \\ b_2 \frac{dy_2}{dt} &= a_{21}y_1 - a_{22}y_2 + a_{23}y_3 + \dots + a_{2N}y_N \\ &\dots\dots\dots \\ b_N \frac{dy_N}{dt} &= a_{N1}y_1 + a_{N2}y_2 + a_{N3}y_3 + \dots - a_Ny_N \end{aligned} \right\} \quad (1)$$

$$a_i = \sum_{j=1}^N a_{ij} \quad (2)$$

in which the a's and b's are either all positive or all negative. The  $b_i$  correspond to  $V_i$  in the previous chapter, the  $a_i$  to  $Q_i$ , the  $a_{ij}$  to  $q_{ji}$  and the  $y_i$  to  $c_i$ . Notice that the a subscripting which is conventional in this context is the transpose of the q and r subscripting which seemed natural before.

It is the relation, Eq.(2), between the co-efficients that confers special properties on the system of equations and permits the probabilistic interpretation or interpretation in terms of the flow of a conserved quantity. In this chapter the generality and power of the methods previously developed are illustrated by setting up equations describing several familiar problems in chemical engineering in network combining form. These examples are chosen as being somewhat less obvious applications than flow in networks of stirred vessels.

## 10.2 First-order chemical reaction in a flow system

Consider a reactor that can be adequately characterized as a flow network as far as flow is concerned, and suppose that the flows and volumes have been identified. If the temperature is constant a material balance on a reacting component yields, for a typical vessel:

$$V_i \frac{dc_i}{dt} = \sum_j q_{ji} c_j - Q_i c_i - K V_i c_i \quad (3)$$

where  $K$  is the reaction velocity constant. Thus if we set

$$Q_i' = Q_i + K V_i \quad (4)$$

and

$$q_{i,N+1}' = q_{i,N+1} + K V_i \quad (5)$$

the problem is cast into flow-mixing form and the methods already developed apply when  $Q_i$  and  $q_{i,N+1}$  are replaced by  $Q_i'$  and  $q_{i,N+1}'$ .

Apart from reactors per se a possible application of the above method is the application to tracer experiments with short-lived radio active tracers.

The extension to spatial dependence of the velocity constant, by virtue of temperature variation for example, follows immediately by replacing  $K$  by a set of constants  $K_i$ .

## 10.3 Arbitrary sets of first order reactions in a well-mixed reactor

A set of first-order homogenous reactions is specified by a matrix  $\underline{K}$  of velocity constants  $K_{ij}$ ;  $K_{ij}$  represents the conversion (flow) from one chemical species to another. All the species occupy the same volume so that:

$$\frac{dc_i}{dt} = \sum_j K_{ji} c_j - \left( \sum_j K_{ij} \right) c_i \quad (6)$$

where  $c_i$  is the molar concentration of the  $i$ th species. This problem is cast into the standard form by setting

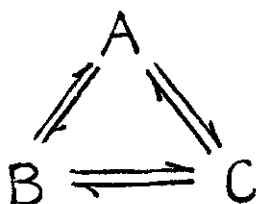
$$q_{ij} = k_{ij} \quad (7)$$

$$V_i = 1 \quad (8)$$

$$Q_i = \sum_j q_{ij} \quad (9)$$

$$\tau_i = 1 / Q_i \quad (10)$$

The initial state vector is set at the initial molar concentrations of the various species and the method gives the subsequent molar concentrations simultaneously. Fredrickson (1) has discussed the triangular reaction scheme ;



from a probabilistic point of view. Schemes such as this may be used to represent non-linear kinetics (1).

#### 10.4 Network reactors with complex linear kinetics

The results of the foregoing sections may be combined to give a treatment of a network reactor in which an arbitrarily complex system of first order reactions occurs. The problem is essentially one of notation, but, with care, this problem too can be cast into flow-mixing form. A balance on a typical vessel yields:

$$V_i \frac{dc_{ki}}{dt} = \sum_j q_{ji} c_{kj} - Q_i c_{ki} + V_i \sum_l K_{lk} - V_i K_k c_{ki} \quad (11)$$

where  $c_{ki}$  = molar concentration of component  $k$  in vessel  $i$ ,  
and  $K_{ki}$  = reaction velocity constant for conversion of component  $k$   
into component  $i$

with 
$$K_k = \sum_i K_{ki} \quad , \quad K_{kk} = 0$$

The state of the system can be thought of in terms of a matrix rather than a vector. However, many transitions between states are now prohibited: it is not possible to make simultaneous transitions between chemical and physical states; that is, the probability of a transition in which both subscripts,  $i$  and  $k$ , change is zero.

The concentration variables may be expressed in terms of a single subscript by using the pattern in Table 1. In effect the system is now defined in terms of quasi-vessels which, borrowing a term used by biologists (2), may be called 'compartments'. The compartment index  $\lambda$  is of the form:

$$\lambda = k + (i-1)M \quad (12)$$

where  $M$  is the number of components.

Table 1. Conversion of  $c_{ki}$  to single subscripting

Vessel Component	1	2	N	N+1
	Compartment			
1	1	M+1	(N-1)M+1	NM+1
2	2	M+2	(N-1)M+2	NM+2
3	3	M+3	(N-1)M+3	NM+3
M	M	2M	NM	(N+1)M

As an appropriate value of  $\lambda$  can be generated for each  $(k,i)$  pair it must be possible to express Eq.(11) as:



$$V_{\lambda} \frac{dc_{\lambda}}{dt} = \sum_{\mu} q'_{\mu\lambda} c_{\mu} - Q'_{\lambda} c_{\lambda} \quad (13)$$

where  $V_{\lambda}$  is the volume of compartment  $\lambda$

$q'_{\mu\lambda}$  represents physical or chemical flow from  $\mu$  to  $\lambda$

and  $Q'_{\lambda}$  accounts for all the removal mechanisms from compartment.

Examination of Eqs.(11) and (12) shows that:

$$V_{\lambda} = V_i, \quad k = 1, 2, 3, \dots, M \quad (14)$$

$$q'_{\mu\lambda} = q_{ji}, \quad \begin{matrix} \mu = k + (j-1)M \\ \lambda = k + (i-1)M \end{matrix} \quad (15a)$$

$$q'_{\mu\lambda} = V_{\lambda} K_{\ell k}, \quad \begin{matrix} \mu = k + (i-1)M \\ \lambda = k + (i-1)M \end{matrix} \quad (15b)$$

$$q'_{\mu\lambda} = 0; \quad \ell = k, i = j \quad (15c)$$

$$q'_{\mu\lambda} = 0; \quad \ell \neq k, i \neq j \quad (15d)$$

$$Q'_{\lambda} = Q_i + V_{\lambda} K_k \quad (16)$$

Calculating the compartmental volume and outflow vectors,  $[V_{\lambda}]$  and  $[Q'_{\lambda}]$  presents no problems, but calculating the flow matrix,  $[q'_{\lambda\mu}]$ , requires careful organization. The procedure is as follows: (i) set  $[q'_{\lambda\mu}] = \underline{0}$  so that Eqs. (15c) and (15d) are automatically accounted for; (ii) for each value of  $k$  in turn, examine  $[q_{ij}]$  term by term and enter the elements  $q_{ij}$  in the appropriate places in  $[q'_{\lambda\mu}]$  as specified by Eq.(15a); (iii) for each value of  $i$ , examine the  $[K_{kl}]$  matrix term by term, calculate the  $q'_{\lambda\mu}$ , Eqs. (14) and (15b), and enter the results at the appropriate places in  $[q'_{\lambda\mu}]$ .

It should be noted that the subscripts in Eqs.(15) are transposed; this is so that these quantities appear in these equations in exactly the same way as in the material balance equations.

When the compartmental volume and outflow vectors and the compartmental flow matrix have been calculated, the problem is in a form suitable for treatment using the methods developed in the previous chapter. If desired the  $\lambda$  indexing may be converted back to the (k,i) form and all the physical quantities may be recovered after the probabilistic calculations have been carried out.

Again spatial variation of the velocity constants is easily taken into account. The velocity constants might be written as  $[K_{kli}]$ ; i.e.  $K_{kli}$  is the constant for conversion of k into l in the ith vessel. If this variation is due to temperature the K's may be expressed:

$$K_{kli} = A_{kl} e^{-E_{kl}/RT_i} \quad (17)$$

presumably. In any case Eq.(15b) may still be employed.

#### 10.5 Binary distillation

Distillation is a non-linear process usually, because the curvature of the equilibrium line means that the coefficients in the material balance equations depend on composition. Two important cases exist in which simple linearized analysis is appropriate: distillation with low relative volatility and the dynamic response of a system in the steady state to small perturbations. A less important case where linearization is satisfactory is operation over a limited composition range. The response of a distillation column to perturbation, important in control theory, will now be considered in network combining terms. It will be assumed that the molar vapour and liquid flow rates and holdups are time independent and that the vapour and liquid streams leaving a given tray are in equilibrium. It will not be necessary to make any assumption concerning the tray-to-tray variation of the flows and holdups.

A material balance on a typical tray gives

$$V_i'' \frac{dy_i}{dt} + V_i' \frac{dx_i}{dt} = Q_{i-1}'' y_{i-1} + Q_{i+1}' x_{i+1} - Q_i'' y_i - Q_i' x_i \quad (18)$$

where

$V_i'$ ,  $V_i''$  = liquid, vapour molar holdup of tray i  
 $Q_i'$ ,  $Q_i''$  = liquid, vapour molar flow rates of streams leaving the trays indicated by the subscripts (counting upwards)  
 $x, y$  = mole fraction of a specified component in liquid, vapour.

Introducing the substitutions:

$$x = x_s + x_\tau, \quad y = y_s + y_\tau \quad (19)$$

which represent the steady state and transient parts of x and y, shows that the transient part satisfies Eq.(18). Now suppose that in the vicinity of  $(x_i, y_i)$

$$y = \alpha x + \beta \quad (20)$$

then clearly the transient parts are related by

$$y_i = \alpha_i x_i \quad (21)$$

Using this result to eliminate y from Eq.(18):

$$\begin{aligned} & (\alpha_i V_i'' + V_i') \frac{dx_i}{dt} \\ &= \alpha_{i-1} Q_{i-1}'' x_{i-1} + Q_{i+1}' x_{i+1} - (\alpha Q_i'' + Q_i') x_i \end{aligned} \quad (22)$$

which, remember, applies to deviations from the steady state. Equation (22) is of exactly the same form as the equation for a well-mixed stage

so that the results of the previous chapter apply. The time constants are given by:

$$\tau_i = \frac{\alpha_i V_i'' + V_i'}{\alpha_i q_i'' + q_i'} \quad (23)$$

and the transition probabilities by:

$$\begin{aligned} r_{ij} &= \alpha_i q_i'' / (\alpha_i q_i'' + q_i') \quad , \quad j = i+1 \\ r_{ij} &= q_i' / (\alpha_i q_i'' + q_i') \quad , \quad j = i-1 \end{aligned} \quad (24)$$

It is a feature of the method that it automatically takes into account such features as side streams and multiple feeds, and tray-to-tray variations of holdup and flows if these are composition independent. This case is of course a generalization of the tanks-in-series-with-backflow model which was discussed earlier.

#### 10.6 Solution of partial differential equations

Partial differential equations involving a complex spatial term and a single time derivative occur in most branches of engineering and physics. The finite difference approximating equations take the same form as the dynamic equations for a network of stirred vessels and so network combining methods apply directly to their solution. As an illustration consider transient diffusion or conduction in two space dimensions:

$$D \left( \frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} \right) = \frac{\partial c}{\partial t} \quad (25)$$

The set:

$$\frac{D}{h^2} (c_{i+1,j} + c_{i-1,j} + c_{i,j+1} + c_{i,j-1} - 4 c_{i,j}) = \frac{\partial c_{i,j}}{\partial t} \quad (26)$$

of differential difference equations, where the subscripts indicate mesh points and  $h$  the mesh size, is a representation of Eq.(25) that

is correct to third differences. A flow network with equal and opposite flows between all adjacent tanks would be described by a similar set of equations. So it follows immediately that the methods already developed apply after the double  $i,j$  subscripting has been replaced by a single subscripting scheme.

The method has not yet been explored as a means of solving partial differential equations, but appears to possess several important advantages. The numbering system that replaces the  $i,j$  system is completely arbitrary so that geometry is unimportant: three-dimensional and awkwardly shaped regions are treated easily. Perhaps a more significant advantage is that higher order finite difference approximations are again treated in exactly the same way. Finally it should be noted that the time variable is not finite differenced and a frequent cause of instability in numerical solutions is the finite differencing of the time variable.

## 11 FUTURE DEVELOPMENTS

### 11.1 One-dimensional time delay models

The one-dimensional time delay models developed in this work have great flexibility as far as the delay process is concerned, but are deficient in two respects. First, the mechanism for transfer into the delayed state is always completely random, and, secondly, the point of return is the same as the point of departure from the main stream. These considerations are not of crucial importance as long as the models are used to fit dynamic responses, but they do matter if an attempt is to be made to relate the delay process to more detailed mechanisms.

The treatment of the stopping process as being only partially random would probably best be treated in terms of an intensity function with respect to distance travelled. An approach that takes both the objections mentioned into account is the treatment in terms of integral equations (Sec. 6.3).

### 11.2 Particle characteristics and thermal transients

The particle shape factor suggested in Sec. 7.6 is of sufficient interest to warrant further study in a number of applications. A start has already been made on extending the work on thermal transients to more complex shapes to see whether the tentative correlation between  $\beta$  and  $\gamma$  suggested in Sec. 7.6 is valid. It is interesting that the definition of  $\gamma$  does not depend on the particle being discrete, or finite or convex. It follows that a value of  $\gamma$  exists for most geometrical shapes including the void spaces in porous media. Perhaps  $\gamma$  or other similarly-based parameters may be used for correlating flow of fluids in complex regions.

### 11.3 Dynamic dispersion

The dynamic dispersion idea, although speculative, clearly poses questions that need be answered. The argument that the conversion for a first order reaction depends only on the residence time distribution is frequently proved by showing that the transfer function and the conversion equations have identical mathematical form. However this depends on the model on which the transfer function is based having only first time derivatives. It is intended to attempt to devise direct experiments to test the dynamic dispersion idea.

### 11.4 Network combing

There are two directions in which it would be useful to extend the network combing method: to multicomponent situations and to systems involving nonlinear features. It is planned to work on both of these aspects, because success would lead to a method of immense value in chemical engineering design.

Another application which it is planned to investigate is polymerisation kinetics. The compartmental idea seems particularly appropriate to emulsion polymerisation.

## 12. PUBLISHED WORK

The following publications are based on the research reported in this thesis:

A generalization of the tanks-in-series mixing model.  
A.I Ch E Jl. 1968 14 805 (with L.G. Gibilaro)

The analytical solution of the Deans-Levich model for dispersion in porous media.  
Chem Engng Sci 1968 23 1399 (with L.G. Gibilaro)

Network combing of complex flowing mixing models  
Chem Engng Sci 1969 24 7 (with L.G. Gibilaro and H.W. Kropholler)

The impulse response of infinite sequences of stirred tanks with backflow.  
Ind Engng Chem Fundamentals, in press.

A probabilistic time-delay description of flow in packed beds.  
A I Ch E Jl in press. (with L.G. Gibilaro and M.N. Rathor).

Some developments and applications of the network combing technique in process dynamics.  
Chem Engng Sci, in press. (with H.W. Kropholler)

The washout curve residence time distribution and F-curve in tracer kinetics.  
Math. Biosciences, in press (with H.W. Kropholler)

On Petho's treatment of the residence time distribution in a flowing diffusing medium.  
Chem Engng Sci. in press.

The following manuscripts have been submitted for publication:

A unified time-delay model for dispersion in flowing media  
(with L.G. Gibilaro)

Intra-phase resistance to heat and mass transfer in packed beds and the time-delay model.

Speculations on a dynamic dispersive mechanism in chemical process equipment.



## NOMENCLATURE

As a variety of similar processes have been treated by different methods a single common system of nomenclature would be unwieldy. The spirit of the notation is the same throughout the thesis but the exact meanings of symbols differ from chapter to chapter. A list of the symbols in each chapter follows.

### Chapter 2

$c$	concentration
$c_i, c_o$	concentration of material entering, leaving a well-mixed vessel
$D$	diffusivity or dispersion constant
$f(t)$	residence time distribution
$n$	number of vessels
$Q$	flow-rate
$t$	time
$v$	velocity or volumetric flow-rate per unit cross-sectional area
$V$	volume
$x$	distance
$\Phi$	material flux
$\tau$	mean time

### Chapter 3

$c$	concentration
$f( )$	distribution (density) function, residence time distribution
$F( )$	(cumulative) distribution function, residence time cumulative distribution
$F^*( )$	$1 - F( )$
$g( )$	washout function

$h( )$	internal age distribution
$i( )$	intensity function
$Q$	flow-rate
$t, \bar{t}$	time, mean time
$V$	volume
$x$	unrestricted variable
$\varphi( )$	arbitrary function

#### Chapter 4

$f(t)$	residence time distribution
$f(x)$	distribution in general
$Q$	flow-rate
$r$	order of moment or cumulant
$s$	Laplace transform parameter
$S_c$	relative entropy, continuous distribution
$S_D$	entropy, discrete distribution
$t$	residence time
$V$	vessel volume
$x$	variable in general
$\chi_r$	rth cumulant
$\mu_r$	rth central moment
$\mu_r'$	rth moment about the origin
$\mathcal{D}_r$	rth probability moment

#### Chapter 5

$A_1, A_2$	arbitrary function of $s$ , Eq.(35)
$A_i$	Laurent series coefficients, Eq.(46)

$A_1, A_2, B_1, B_2, C_1, C_2, D_1, E_2$	extended Deans-Levich model parameters, defined following Eq.(62)
$a_0, a_1, b_0, b_1, b_2$	extended Deans-Levich model transfer function coefficients, Eq.(67)
$B_{n,j}$	Deans-Levich time-domain coefficient, Eq.(56).
$c_n$	concentration of stream leaving nth cell
$C_0$	constant with dimensions of concentration
$C'_n, C''_n$	Deans-Levich internal concentrations
$C_{n,j}$	Deans-Levich time-domain coefficients, Eq.(56) with $r_1, r_2$ interchanged
$E( )$	finite difference operator
$f(t)$	residence time distribution
$G(s)$	extended Deans-Levich transfer function
$G'(s), G''(s)$	transfer functions for extended Deans-Levich internal compositions
$i$	counting index, poles of Laplace transform.
$I_n( )$	nth order modified Bessel function of the first kind.
$j, k, l$	counting indices
$K_1, K_2$	constants, defined following Eq.(57)
$m$	gamma distribution parameter
$n$	counting index, model stages
$p, q$	flow-rates, Deans-Levich model
$q$	flow-rate in backflow model
$Q$	through-flow rate
$r$	order of moment
$s$	Laplace transform parameter
$t$	time
$V$	stage volume
$y$	$c/C_0$ , dimensionless concentration
$y^*$	normalized concentration, defined following Eq.(44)
$\alpha$	$\tau_1/(\tau_1 + \tau_2)$ volume ratio, two-constant generalized tanks-in-series model.

$\alpha$	$q/(q+Q)$ backflow ratio, backflow model
$\alpha$	volume ratio, Deans-Levich models
$\beta$	flow parameter, extended Deans-Levich model
$\tau$	$p/\alpha V$ , Deans-Levich model
$\Gamma( )$	gamma function
$\epsilon$	Flow parameter, extended Deans-Levich model
$\theta$	normalized time
$\lambda$	$q/(1-\alpha)V$ , Deans-Levich model
$\mu$	central moment
$\mu'$	moment
$\nu$	$p/(1-\alpha)V$ , Deans-Levich model
$\rho_1, \rho_2$	roots of finite difference subsidiary equation, backflow model
$\sigma$	Laplace transform parameter, normalized time basis
$\sigma$	$1+\alpha+S$ , backflow model
$\tau$	time-constant per vessel, tanks-in-series model.
$\tau$	$(Q+q)t/V$ backflow model dimensionless time
$\tau^*$	normalized time, backflow model
$\tau_1, \tau_2$	vessel time constants, two constant tanks-in-series model
$\tau_3$	dead time

## Chapter 6

$c$	concentration
$f(t)$	residence time distribution
$f_n(t)$	distribution of the sum of $n$ delay times
$f_N(t)$	residence time distribution for $N$ -cell model
$g(t)$	delay time distribution
$I_n(\ )$	$n$ th order modified Bessel function
$n$	number of delays
$N$	number of cells
$m$	gamma distribution parameter
$P_n$	probability of $n$ delays
$q$	transverse flow per unit length
$Q$	through-flow rate
$t$	time
$t_o$	dead time
$t_D$	mean delay time
$V$	volume
$x$	distance
$x_o$	length
$\alpha$	mean number of stops per unit length
$\delta(\ )$	Dirac delta function
$\Gamma(\ )$	gamma function
$\mu_r$	$r$ th central moment
$\mu_r'$	$r$ th moment

## Chapter 7

$a$	bed interfacial area per unit length
$A(s), B(s), C(s)$	undetermined functions of $s$ .
$B_i$	modified Biot number

$c$	concentration
$C_f, C_s$	fluid, solid specific heat
$d$	particle characteristic dimension,
$d_c$	particle mean caliper diameter
$D$	mass diffusivity
$\mathcal{D}$	diffusivity ( $D$ or $\alpha_T$ )
$F(s)$	particle transfer function or recycle transfer function.
$G(s)$	distributed model transfer function
$G_N(s)$	cell model transfer function ( $G_1(s)$ = transfer function for one cell)
$h$	heat transfer coefficient
$i, j$	counting indices
$I_0(\quad), I_1(\quad)$	zeroth, first order modified Bessel function of the first kind.
$k$	mass transfer coefficient
$K$	concentration ratio equilibrium constant.
$l$	mean sector length of particle
$m$	gamma distribution parameter
$M_1', M_2, M_3$	model impulse response mean and second and third central moments
$N$	number of cells
$q$	lateral flow rate per unit bed length
$Q$	throughput flow rate
$r$	radial coordinate of cylinder or sphere
$s$	Laplace transform parameter
$S$	particle surface area
$t$	time ( $t_0 = V/Q$ ; $t_D$ = mean delay time)
$T$	temperature
$u$	potential ( $T, c$ or $c^*$ )
$v$	$u_r$
$V$	bed void volume
$V_p$	particle volume
$x$	axial position, bed length

$y$	distance from medial plane of plate.
$z$	dummy variable in standard expansions
$\alpha$	$q/q, ha/Q\rho_f C_f$ or $ka/Q$
$\alpha_T$	thermal diffusivity
$\beta$	thermal shape factor
$\gamma$	geometrical shape factor
$\Gamma( )$	gamma function 11
$\kappa$	$Kk$ or $\alpha_T h/\lambda$
$\mu'_1, \mu_2, \mu_3$	particle impulse response first moment and second and third central moments ( $\mu'_1 = t_D$ )
$\nu_2, \nu_3$	particle impulse response second and third normalized central moments
$\rho_f, \rho_s$	fluid, solid density
$\rho_1, \rho_2, \rho_N$	radii of curvature
$\sigma$	curve length
Subscripts	
$i$	ith cell
$R$	recycle flow
$S$	solid surface
Superscripts	
$\bar{\phantom{x}}$ (overbar)	Laplace transformed variable
$\prime$ (prime)	solid phase

Chapter 8

C	Concentration
D	axial dispersion constant
$D_M$	molecular diffusivity
	D/VE
E	dynamic dispersion constant
$I_n( )$	nth order modified Bessel function of the first kind
k	first order reaction velocity constant
p	Laplace transform parameter (removes $\chi$ )
$P_e$	Peclet number ( $VZ_L/D_M$ )
R	tube radius
$R_1$	rate group ( $kZ_L/V$ )
S	Laplace transform parameter (removes $\tau$ )
t	time
V	velocity (or average velocity)
x	distance
$Z_L$	length of tubular reactor
$Z_L^+$	dimensionless reactor length ( $Pe/24$ )
$\alpha$	fraction of volume in which plug flow occurs
$\beta$	$kR^2/4D_M$
$\delta()$	Dirac delta function
$\tau$	dimensionless time ( $Vt/E$ )
$\Phi$	tracer flux
$\chi$	dimensionless distance ( $x/E$ )



Chapter 9

$c_i(t)$	concentration in $i$ th vessel at time $t$
$f(t)$	network residence time distribution
$f_n(t)$	residence time distribution for sequence of $n$ stages.
$i, j$	indices referring to vessels
$k$	summation limit
$l$	integer (power of 2)
$m$	$n + 1$
$\underline{M}_r$	vector of $r$ th moments
$n$	number of vessels on path through network
$N$	number of vessels in network
$P_n$	probability of traversing network by an $n$ -vessel path
$P_n(t)$	probability of $n$ vessel-to-vessel moves in time $t$
$q_{ij}$	vessel-to-vessel flow-rate
$Q$	nett flow-rate through network
$Q_i$	flow-rate through $i$ th vessel
$Q^{(m)}$	flow-rate in $n$ th strand of combed network
$r$	order of moment
$r_{ij}$	transition probability ( $i$ to $j$ )
$R$	transition matrix (of elements $r_{ij}$ )
$S_i$	state probability
$\underline{S}$	state probability vector
$t$	time
$V_i$	volume of $i$ th vessel
$\mu_{r,i}$	$r$ th moment of response of $i$ th vessel
$\Pi$	transition matrix, Eq(39).
$\tau_i$	$i$ th vessel time constant
$\tau_m$	$\min (\tau_i)$

## Chapter 10

The notation of Chapter 10 is basically the same as that in Chapter 9, but special notation used in the applications is explained where it is used.

#### 14. REFERENCES

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# APPENDIX I - SOME PROPERTIES OF THE ENTROPY OF RESIDENCE TIME DISTRIBUTIONS

The relative entropy of a continuous distribution defined over  $(0, \infty)$  is

$$S = - \int_0^{\infty} f(t) \ln f(t) dt \quad (1)$$

$S$  is a measure of the spread of a residence time distribution, that is to say it expresses the degree to which material entering the process at different times is mixed. In some circumstances this seems, subjectively at least, to be a criterion of mixing performance. This leads to the question: What is the nature of the residence time distribution that maximizes the spreading of residence times? In mathematical terms, the problem is to find the function  $f(t)$  that maximizes  $S$  subject to

$$\int_0^{\infty} f(t) dt = 1 \quad (2)$$

$$\int_0^{\infty} t f(t) dt = \frac{V}{Q} \quad (3)$$

The first of these conditions is necessary because  $f(t)$  is a distribution and the second is always true for systems with 'closed' boundaries, Sec. 3.8. Finding  $f(t)$  is a trivial exercise in variational calculus (1). The Euler-Lagrange equation is

$$\frac{\partial}{\partial f} (f \ln f + \mu_1 t f + \mu_2 f) = 0 \quad (4)$$

where  $\mu_1$  and  $\mu_2$  are undetermined parameters (Lagrangian multipliers).

The solution of Eq.(4) that satisfies Eqs.(2) and (3) is

$$f(t) = \frac{Q}{V} e^{-Qt/V} \quad (5)$$



so that the maximum spread mixer is the same as the mixer that is perfect in the usual sense.

The form of Eq.(1) is such that, for most of the theoretical residence time distributions that occur in chemical engineering, it is very difficult to find  $S$  analytically. An exception is the gamma distribution

$$f(t) = \frac{t^{n-1} e^{-t}}{\Gamma(n)} \quad (6)$$

Substituting Eq.(6) into Eq.(1)

$$\begin{aligned} S &= -\frac{1}{\Gamma(n)} \int_0^{\infty} t^{n-1} e^{-t} [(n-1) \ln t - t - \ln \Gamma(n)] dt \\ &= n + \ln \Gamma(n) - \frac{1}{\Gamma(n-1)} \int_0^{\infty} t^{n-1} e^{-t} \ln t dt \end{aligned} \quad (7)$$

The integral in Eq.(7) may be found in tables of Laplace transforms and is

$$\int_0^{\infty} t^{n-1} e^{-t} \ln t dt = \Gamma(n) \psi(n) \quad (8)$$

where  $\psi(n) = \frac{d(\ln \Gamma(n))}{dn}$

is the digamma function (2).

Thus

$$S = n + \ln \Gamma(n) - (n-1) \psi(n) \quad (9)$$

If the entropy is to be used as a distribution characteristic for fitting purposes it is useful to have the entropy based on normalized time units:

$$S = n + \ln \Gamma(n) - \ln n - (n-1) \psi(n) \quad (10)$$

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