

## REVIEW ARTICLE NUMBER 37

# ENDS AND BEGINNINGS IN THE MATHEMATICAL MODELLING OF CHEMICAL ENGINEERING SYSTEMS

RUTHERFORD ARIS

Department of Chemical Engineering and Materials Science, University of Minnesota,  
Minneapolis MN 55455, U.S.A.

**Abstract**—The mathematical model is considered as an imitator of a natural phenomenon or an artificial construction. Its structure and expression are discussed with special reference to the establishment of boundary conditions and the importance of rendering the variables and parameters dimensionless. This is illustrated by the simpler models of chemical reactors and the mutual relationship of these is considered.

### CONTENTS

1. INTRODUCTION .....	2507
2. THE MODEL AS IMITATOR .....	2508
3. THE NATURE OF <i>IMITATIO</i> IN MATHEMATICAL MODELS .....	2508
4. THE STRUCTURE OF MODELS .....	2508
5. HYPOTHESES OF UNIFORMITY .....	2509
6. DIMENSIONLESS VARIABLES AND PARAMETERS .....	2510
7. SOME GENERAL PRINCIPLES FOR MAKING THE CHOICES OF DIMENSIONLESS QUANTITIES .....	2511
8. ALTERNATIVE FORMS OF EQUATIONS .....	2511
9. HOMOTOPIES OF MODELS .....	2512
10. THE INVERSE PROBLEM .....	2514
11. READING OTHER PEOPLE'S MODELS .....	2515
12. POLISHING .....	2516
NOTATION .....	2517
REFERENCES .....	2517
APPENDIX .....	2517

### 1. INTRODUCTION

It is always dangerous to claim a first reference to any philosophical puzzlement, but the oldest reference to the enigmatic circularity of ends and beginnings that I know of is by Guillaume de Machaut, the French poet and composer of the 14th century. He has a very characteristically convoluted rondeau, a sort of musical Möbius strip, which reads:

Ma fin est mon commencement  
et mon commencement ma fin  
et teneure vraitment

Ma fin est mon commencement

mes tiers chans trois fois seulement  
se retrograde et ainsi fin.

Ma fin est mon commencement  
et mon commencement ma fin.<sup>†</sup>

<sup>†</sup>My end is my beginning/and my beginning is my end/and this holds truly//My end is my beginning/my third song but thrice/turns back on itself and thus it ends.//My end is my beginning/and my beginning is my end. Guillaume de Machaut (ca 1300-1377) cultivated a wide variety of forms and styles in poetic and musical composition. He served John of Luxemburg as secretary and almoner and travelled with him before settling down in Rheims sometimes before 1340. Here he created a number of works dedicated to various patrons, including Jean, Duke of Berry, the famous bibliophile. He died in April 1377 and was buried in the cathedral at Rheims where he had served as canon.

Since I shall touch on the enlightening parallelism between mathematical modelling and other poetic arts, I venture to begin with this reference, which sees the end both as contained in the beginning and as a fresh beginning in itself and the beginning both as motivated by the end and as the start of a path leading to the end. Eliot in *Four Quartets* (*Little Gidding*, V, 214–216) puts it very plainly:

What we call the beginning is often the end  
And to make an end is to make a beginning.  
The end is where we start from.

## 2. THE MODEL AS IMITATOR

If we adopt the basically Aristotelian position that poetry is a form of imitation or *mimesis*, it is easy to accept mathematical modelling as a poetic activity, for, in doing it, we are engaged in a form of imitating nature in mathematical terms. There is the obvious first step of representing physical quantities as mathematical variables or parameters, but, beyond this, we need to incorporate physical laws and the constitution of the materials in question. This is done in the faith that the processes of mathematics "imitate", in some sense, the processes of nature and do so in a way that frees them from the accidents of particularity that cling to any experimental investigation. "From what we have said", writes Aristotle,<sup>1</sup> "it will be seen that the poet's function is to describe, not the thing that has happened, but a kind of thing that might happen, i.e. what is possible as being probable or necessary". The distinction that Aristotle makes between the poet and historian, namely that the latter "describes the thing that has been"<sup>2</sup> whereas the former "describes the kind of thing that might be" might serve as the distinction between *simulation* and *modelling*. In the former there is a definite attempt to reproduce the detail of reality, as seen through the eyes of the observations that have been made and may yet continue to be made. The model is thus "something more philosophic and of graver import" than the simulation "since its statements are of the nature rather of universals" than "singulars".<sup>3</sup> Notice that this has already introduced a final, or teleological, element into the approach to modelling, for it is clear that the purpose of a model has to be considered in its formulation.

## 3. THE NATURE OF IMITATIO IN MATHEMATICAL MODELS

For mathematical models some degree of imitation is of the essence, though it can be quite tenuous at times. There is not, so far as I know, any set of chemicals, A, B and C, that indulges in the reactions  $A \rightarrow B$ ,  $A + 2B \rightarrow 3B$ ,  $B \rightarrow C$ . Yet this model of Gray

and Scott, suggested, no doubt, by their deep knowledge of combustion kinetics, is an extraordinarily useful one. Less cluttered than the Brusselator, which has the same core, it isolates the essential autocatalytic and presents it in its simplest form. It is adaptable to realistic reactor models and not cumbered with "pool hypotheses". It is the analogue of, and attractively less "stiff" than, the classic case of the non-isothermal exothermic first-order reaction, for B plays the role of heat. Heat is a "product" of the exothermic reaction whose rate it enhances by raising the temperature. It is thus autocatalytic. Similarly, the model reaction in which A and B are adsorbed but need two adjacent vacant sites to combine as an instantly desorbed product C,  $A + S = A^*$ ,  $B + S = B^*$ ,  $A^* + B^* + 2S \rightarrow C + 4S$ , does not correspond to any known reaction, but has proved to be a useful system: it is isothermal, thus avoiding Arrhenius temperature dependencies; the vacant sites play the autocatalytic role and this model enjoys a certain symmetry that the other systems lack.

Simplified models sometimes also have a more subtle validity. It may be shown, for example, that certain types of behaviour are characteristic of certain classes of reaction, e.g. those with monotonic kinetics [i.e. if  $c$  is the concentration of a key reactant, the rate of reaction is  $r(c)$ , where  $dr/dc \geq 0$ ]. If this be true, it is quite legitimate to take as a typical example the simplest case, often the linear one,  $r(c) = kc$ . It is extraordinary how robust certain features of some models are. The map  $x_{n+1} = f(x_n, \lambda)$  from  $[0, 1]$  into  $[0, 1]$  shows the period-doubling route to chaos for virtually any unimodal function  $f$  which depends on  $\lambda$  in a "tunable" fashion.<sup>4</sup>

## 4. THE STRUCTURE OF MODELS

A model rests on certain physical laws, usually conservation principles. Thus, most equations are balances of some entity which is created or destroyed in the process being modelled. These laws are quite general. For example, let  $F$  be the net flux of some entity (such as mass or enthalpy) into a uniform region,  $G$  the total rate of generation of the same entity in the same region and  $H$  the total amount of it contained therein. Then

$$dH/dt = F + G. \quad (1)$$

This is a general balance relationship and is used to acknowledge some law of nature. The relations of  $F$ ,  $G$  and  $H$  to one another, or, equivalently, to some common variable, define the constitution of the particular system within which we are working and are known as constitutive relations.

If the entity is a particular chemical species present in the region in uniform concentration,  $c$ , and  $V$  the

<sup>1</sup>Aristotle, *Poetics* 1451a, 36.

<sup>2</sup>*Ibid.* 1451b, 5.

<sup>3</sup>*Ibid.* 1451b, 7.

<sup>4</sup>An early exposition of this system, which has not been bettered by later work, is contained in R. M. May's "Simple mathematical models with very complicated dynamics". *Nature* 261, 459 (1976).

volume of the system, then  $H = Vc$ . If the system is a stirred tank reactor with constant flow rate,  $q$ , both in and out, and it is perfectly mixed, so that the concentration of the effluent is  $c$ , then  $F = q(c_f - c)$ . If the reaction rate can be expressed as a function of the reactant concentration  $c$ , the rate of generation per unit volume is  $-r(c)$ , then  $G = -Vr(c)$ . Substituting, we have

$$V(\dot{dc}/dt) = q(c_f - c) - Vr(c). \quad (2)$$

Here  $F$ ,  $G$  and  $H$  are related to  $c$  by their constitutive relations, which define the nature of the flux and the kinetics of the reaction.

Notice how the purpose of the model affects its validity. Had the purpose been to study the mixing, as Professor Villermaux has so penetratingly done, this model would be completely unsuitable since it has assumed from the first that the mixing is perfect and the concentration a single variable. The curious misnomer "lumped parameter system" has been applied to the class of models governed by ordinary differential equations, as opposed to a "distributed parameter system", usually governed by partial differential equations with spatial independent variables. Both names make nonsense of the word parameter, which is a number that stands *by the side of* ( $\pi\acute{\alpha}\rho\alpha$ ) the problem and is not patient of being either lumped or distributed. The terms "lumped system" and "distributed system" are acceptable.

When the variables describing the state of the system are functions of spatial independent variables, we must apply the balance to an arbitrary volume. Moreover, the measure of flux becomes a vector,  $\mathbf{f}$ , such that  $\mathbf{f} \cdot \mathbf{n}$  is the flux per unit area through a surface element with normal  $\mathbf{n}$ , and generation and quantity have to be specified per unit volume as  $g$  and  $h$ . Then eq. (1) translates into

$$(\partial/\partial t) \iiint h \, dV = - \iint \mathbf{f} \cdot \mathbf{n} \, dS + \iiint g \, dV \quad (3)$$

where  $\mathbf{n}$  is the outward normal to the surface  $\partial\Omega$  surrounding an arbitrary volume  $\Omega$ . The use of Green's theorem and the recognition that, if the variables are continuous, the integrand of  $\iiint [\partial h/\partial t + \text{div } \mathbf{f} - g] \, dV$  must be zero almost everywhere leads to the partial differential equation

$$\partial h/\partial t = - \text{div } \mathbf{f} + g. \quad (4)$$

This might be applied to the plug flow, tubular reactor with dispersion. Here, there is one space variable,  $z$ , the distance from the inlet, and, if  $c$  is the concentration of the reactant as before,  $h = c$ ,  $r(c)$  was defined per unit volume, so  $g = r(c)$ .  $\mathbf{f}$  has only one component directed along the tube and composed of two parts, the convective  $vc$  and the dispersive  $-D(\partial c/\partial z)$ . Thus,

$$(\partial c/\partial t) + v(\partial c/\partial z) = D(\partial^2 c/\partial z^2) - r(c). \quad (5)$$

In addition to the specification of the initial distribution  $c(z, 0)$ , and in contrast to the lumped system whose equation already contains an inlet term, the distributed system also needs the boundary conditions at the inlet and the exit. For the tubular reactor, these are the much-debated Danckwerts boundary conditions,<sup>†</sup> which will be given here without comment, namely

$$vc_f = vc - D(\partial c/\partial z) \quad \text{at } z = 0$$

$$\partial c/\partial z = 0 \quad \text{at } z = L. \quad (6)$$

The doyen of mathematical modellers, N. R. Amundson,<sup>‡</sup> used to say that "all boundary conditions arise from nature".<sup>§</sup> He meant, I believe, that one's artefactual imagination goes into the model in a way that is removed from nature, whereas the boundary conditions express the physical inputs and outputs that derive from the natural context. Of course, the boundary conditions must be of the type that is mathematically appropriate to the equations. Thus, in the above example it has been assumed that the dispersion can be represented by a Fickian term  $-D(\partial c/\partial z)$ , which gives rise to a second-order derivative. Whether or not this is an adequate description of the hydrodynamic dispersion that obtains with a packed bed, or the Taylorian convective dispersion that is associated with a flow profile, is a question for the critics of the model. Once this commitment is made, the model is a second-order differential equation and, so, requires two boundary conditions. These express the fact that you want all that you put in to get in and all that gets out stays out. Their scandal is that they imply a discontinuity of concentration at the inlet but none at the outlet. Incidentally, Langmuir and Damköhler used the correct boundary conditions rather earlier than Danckwerts, but the attribution, now less commonly made explicit than heretofore, is not unjust, as it was not until Danckwerts' introduction that they were in general currency.

## 5. HYPOTHESES OF UNIFORMITY

In the Danckwerts Lecture for 1990, I dealt in some detail with the problem of systems that are, in part, uniform, either for good physical reasons or on account of some simplifying hypothesis. It is essential to take the balance over the *whole* of the uniform region and not to use a control volume which is a "slice" of both the lumped and the distributed parts. I will not

<sup>†</sup>For a fuller account of these than will be given here see the 5th Danckwerts lecture "Manners makyth modellers" given on 16 October 1990 and published in *Chem. Engng Sci.* **46**, 1535 (1991) and *Trans. Instn. Chem. Engrs* **69**, A165 (1991).

<sup>‡</sup>A selection of his papers was published under the title *The Mathematical Understanding of Chemical Engineering Systems* (Edited by A. Varma and R. Aris). Pergamon (1980).

<sup>§</sup>"Omnes conditiones circumferenciales ex natura oriuntur" or "παντα τα εφορια φυσα γιγνεται".

go into this question in detail again.<sup>7</sup> One explanation seems to lie in the nature of the boundary conditions in the two cases. For a distributed part of the system, the boundary conditions are strictly local, but in the lumped part, some features, that are in the boundary conditions in the distributed part, enter as terms in the equations. This is a rather vague statement and a better reason has been given by Astarita,<sup>1</sup> who has done a perturbation analysis of the simple system in which the uniform part is the limit of a distributed part as the dispersal becomes infinite. He shows that the balance over the *whole* of the lumped part is the correct zero-order expansion of the slice balance (appropriate enough so long as the dispersal is finite), whereas a slice into the lumped region is not.

#### 6. DIMENSIONLESS VARIABLES AND PARAMETERS

Foresight of the end plays a role in the next step of modelling, which is to render the equations dimensionless. I will not dilate here upon the analogy that I believe exists between poetic imagery and the proper appreciation of dimensionlessness,<sup>8</sup> but I cannot resist putting one passage to you. In the last canto of the *Paradiso*, Dante is reflecting on the immensity of his vision of *la luce eterna* (1.83) and he needs a parameter, a measure of the depth of the ultimate vision, in which he saw all things *legato con amore in un volume*, only to have it instantly buried within him in the deep oblivion of *tà ἄρρητα ῥήματα ἃ οὐκ ἐξὸν ἐντηρώμαρ λαλήσαι!*<sup>11</sup>

Un punto solo m'è maggior letargo  
che venticinque secoli alla 'mpresa,  
che fè Nettuno ammirar l'ombra d'Argo.<sup>9</sup>

We have here a ratio of two characteristic times, the prototypical dimensionless parameter. But it would be silly to think that the *value* of the ratio (it is  $10^{10}$  if a *punto* lasts 7.9 s) is at issue. As poetry, it is the richness of the poetic imagery that we treasure. We see the shadow of the Argo slipping over Neptune and his submarine court and feel his moment of apprehensive wonder at this new invention which was to give men control over his kingdom. This is a virtue of literature

that the abstraction of mathematics can only remotely follow. We have our own mythology and it is pleasant and harmless enough to be aware of, or even consciously to recall, the human associations of our craft. To be able to remember, for instance, the pioneering insight of Damköhler whenever we set up a reactor equation, and to wonder how he would have viewed current developments had his life been extended to a normal span. But this recollection and imaginative projection is not an integral part of our analysis as it is of the literary scholar's, and the engineering analyst, qua analyst, can be a great success even though he hold Henry Ford's opinion of history.<sup>\*\*</sup>

But we must return to eq. (2). Each term in it has the dimensions of moles per unit time. There is one characteristic concentration,  $c_f$ , so that it is natural to put  $u = c/c_f$ . But there are two characteristic times in the system:  $\theta = V/q$ , the residence time, and  $c_f/r(c_f)$ , the reaction time. If the intention is to examine the effect of varying the residence time  $\theta$ , it should not be used to render the time dimensionless; if the aim is to vary the kinetics then the time  $\theta$  should be so used. The two cases are:

$$P(u) = r(c_f u)/r(c_f) \quad (7)$$

$$t' = r(c_f)t/c_f \quad \tau = t/\theta \quad (8)$$

giving the equations

$$du/dt' = (1 - u)/Da - P(u)$$

and

$$du/d\tau = 1 - u - DaP(u) \quad (9)$$

and the Damköhler number is

$$Da = r(c_f)V/qc_f. \quad (10)$$

[Since this lecture was given, V. Balakotaiah has shown me a rather better way of seeing how the characteristic times interact. We have  $\theta$  as the characteristic time of residence and (say)  $\rho = c_f/r(c_f)$  as the characteristic time of reaction. Then dedimensionalizing everything except time,

$$du/dt = (1 - u)/\theta - P(u)/\rho.$$

The time can now be made dimensionless either by  $\theta$  or by  $\rho$  and the Damköhler number emerges as the ratio  $\theta/\rho$ . The advantage of Balakotaiah's formulation is that the limiting cases, in which one of the three quantities,  $t$ ,  $\theta$ ,  $\rho$ , is much smaller or much larger than the others, become very easy to formulate. The approach can be used to advantage in what follows, where Balakotaiah would recognize a third characteristic time, the dispersion time  $L^2/D$ . I will not pursue this method farther, as he will be publishing on this topic in the near future.]

Similarly, for the finite tubular reactor with dispersion,  $L/v$  plays the role of  $V/q = \theta$  and is one characteristic time, the other again being the reaction time,

<sup>7</sup>The topic is dealt with in *Chem. Engng Sci.* **46**, 1537–1538 (1991) and in *Trans. Instn. Chem. Engrs* **69**, 168–170 (1991). See, in particular, fn. 15.

<sup>8</sup>Published in *Chem. Engng Sci.* **48**, 823 (1993).

<sup>9</sup>See also my *Ut Simulacrum Poesis. New Literary History* **20**, 323 (1988–1989).

<sup>11</sup>"... unspeakable things which it is not lawful that a man should utter", St. Paul in II Cor. 12, 4.

<sup>12</sup>In Sayer's translation: One moment brings me deeper lethargy/Than 25 centuries brought the quest that dazed/ Neptune when Argo's shadow crossed the sea. I confess I owe the recollection of this passage, not to any great knowledge of the Divine Comedy, but to an exposition of the last canto by P. M. J. McNair, lately Serena Professor of Italian at the University of Birmingham, in a *lectura Dantis* that he gave when in the Faculty of Italian at Cambridge University on 25 October 1971. He must not, of course, be held responsible for my flights of fancy.

<sup>\*\*</sup>"History is bunk." Said under oath during his libel suit against the *Chicago Tribune*. July 1919.

$\rho = c_f/r(c_f)$ . Then the two versions are:

$$\partial u/\partial \tau' + (1/Da)(\partial u/\partial \zeta) = (1/DaPe)(\partial^2 u/\partial \zeta^2) - P(u) \quad (11)$$

$$\partial u/\partial \tau + \partial u/\partial \zeta = (1/Pe)(\partial^2 u/\partial \zeta^2) - DaP(u)$$

where

$$Da = r(c_f)L/vc_f, \quad \zeta = z/L \quad (12)$$

$$Pe = vL/D, \quad \phi^2 = DaPe.$$

This uses  $L$  as the characteristic length and the boundary conditions in both cases are

$$-(1/Pe)(\partial u/\partial \zeta) + u = 1 \quad \text{at } \zeta = 0 \quad (13)$$

$$(1/Pe)(\partial u/\partial \zeta) = 0 \quad \text{at } \zeta = 1.$$

If  $L$  is to be varied, in particular if it is to be allowed to go to infinity, it is not suitable to use as the characteristic length. There is, however, another length, namely the square root of  $Dc_f/r(c_f)$ . In this case

$$\partial u/\partial \tau + v(\partial u/\partial \eta) = (\partial^2 u/\partial \eta^2) - P(u) \quad (14)$$

where

$$\tau = r(c_f)t/c_f, \quad \eta = z[r(c_f)/Dc_f]^{1/2} \quad (15)$$

$$H = L[r(c_f)/Dc_f]^{1/2}, \quad v = v[c_f/Dr(c_f)]^{1/2}.$$

Notice that  $L$  now occurs only in  $H$  and, so, may be varied freely. The boundary conditions are

$$(1/v)(\partial u/\partial \eta) + u = 1 \quad \text{at } \eta = 0 \quad (16)$$

$$\partial u/\partial \eta = 0 \quad \text{at } \eta = H.$$

There is yet another way of making distance dimensionless, for  $vc_f/r(c_f)$  is also a characteristic length. Thus,

$$\tau = r(c_f)t/c_f, \quad \xi = zr(c_f)/vc_f \quad (17)$$

$$\Xi = Lr(c_f)/vc_f, \quad \Delta = Dr(c_f)/v^2c_f$$

giving the equation

$$\partial u/\partial \tau + \partial u/\partial \xi = \Delta(\partial^2 u/\partial \xi^2) - P(u) \quad (18)$$

with the boundary conditions

$$-\Delta(\partial u/\partial \xi) + u = 1 \quad \text{at } x = 0 \quad (19)$$

$$\partial u/\partial \xi = 0 \quad \text{at } \xi = \Xi.$$

In all cases there are two parameters,  $Da$  and  $Pe$  in the first,  $v$  and  $H$  in the second and  $\Delta$  and  $\Xi$  in the third, and, if only one appears in the equations, the other pops up in the boundary conditions.

## 7. SOME GENERAL PRINCIPLES FOR MAKING THE CHOICES OF DIMENSIONLESS QUANTITIES

Experience in working with dimensionless parameters suggests the following principles.

(a) If a study of the effect of varying a certain quantity is to be done, make sure that this quantity appears in none of the variables and in one and only one dimensionless parameter.

(b) Let the dimensionless dependent variables be

approximately in the range zero to one and let the dimensionless parameters bear the burden of showing the relative magnitudes of the several terms.

(c) Unless a physical dimension is going to be varied, let the independent dimensionless variables range over fixed finite intervals [often conveniently (0, 1),  $(-\pi, \pi)$  or such].

The choice among several alternatives is governed by the first of these considerations. Thus, if we are varying the dispersion coefficient  $D$ , the first mode is best. In particular, we note that, as  $D \rightarrow \infty$ , the tubular reactor goes over into the stirred tank. For if  $Pe = 0$  in eq. (11),  $\partial^2 u/\partial \zeta^2 = 0$ ,  $\partial u/\partial \zeta$  is constant, and this constant must be zero by the boundary condition at  $\zeta = 1$ . It follows that  $u$  is constant and a function of  $\tau$  only. Then integration of the second form of eq. (11) from 0 to 1 gives

$$\partial u/\partial \tau = (1/Pe)[(\partial u/\partial \zeta)_1 - (\partial u/\partial \zeta)_0] - DaP(u)$$

and, using the conditions (13), gives eqs (9), the equation for the stirred tank.<sup>7</sup>

The second of the three modes comes into its own if  $L$  or  $v$  is the quantity to be varied, since  $v$  appears only in  $v$ , and  $L$  only in  $H$ . In particular, if  $L \rightarrow \infty$ ,  $H$  does also and the second boundary condition is equivalent to requiring  $u$  to be finite as  $\eta \rightarrow \infty$ . If  $v = 0$ , the first spatial derivative disappears from the equation which becomes the equation for diffusion and reaction in a porous catalyst. Actually, the equations are more often couched in terms of the first of eqs (11). As  $v \rightarrow 0$ ,  $Pe \rightarrow 0$ ,  $Da \rightarrow \infty$ , but their product is the square of the Thiele modulus, commonly written as  $\phi^2$ , giving

$$\partial u/\partial \tau = \partial^2 u/\partial \zeta^2 - \phi^2 P(u) \quad (20)$$

(note that  $\phi = H$ ). The boundary conditions do not go over into those commonly used for the porous slab. This seems to be because, in the limiting case of no flow, the physical situation is radically different and, since "all boundary conditions arise from nature", they must be reformulated to reflect this properly.

Questions of catalyst dilution can best be answered within the framework of the third mode of dedimensionalization. For, if the catalyst in a bed is diluted to a fraction of its activity  $1/R$ ,  $r(c_f)$  becomes  $r(c_f)/R$  and  $L$  becomes  $LR$ . Thus,  $\Xi$  is unaltered and  $\Delta$  is diminished by a factor of  $R$ . This is the known phenomenon of the amelioration of longitudinal dispersion by catalyst dilution.<sup>2</sup>

## 8. ALTERNATIVE FORMS OF EQUATIONS

Sometimes, it pays to look at sets of first-order equations rather than a single higher-order equation.

<sup>7</sup>This limiting case is the mathematical argument in favor of Danckwerts' boundary conditions. The physical argument is that an internal minimum of the concentration of a disappearing reactant is implausible.

<sup>2</sup>See Ho, T. C. and White, B. S., 1991, Mitigation of backmixing via catalyst dilution. *Chem. Engng Sci.* **46**, 1861; Aris, R., 1992, Comments on mitigation of backmixing via catalyst dilution. *Chem. Engng Sci.* **47**, 507.

For example, the steady-state form of eqs (11) is

$$(1/Pe)(d^2u/d\zeta^2) - (du/d\zeta) - DaP(u) = 0 \quad (21)$$

with boundary conditions

$$\begin{aligned} -(1/Pe)(du/d\zeta) + u &= 1 \quad \text{at } \zeta = 0 \\ du/d\zeta &= 0 \quad \text{at } \zeta = 1. \end{aligned} \quad (22)$$

If  $w = (1/Pe)(du/d\zeta)$ , we have

$$\begin{aligned} (du/d\zeta) &= Pe w \\ (dw/d\zeta) &= DaP(u) + Pe w. \end{aligned} \quad (23)$$

The solutions to these equations can be represented by curves in the  $u$ - $w$  plane that satisfy

$$dw/du = 1 + DaP(u)/Pe w = 1 + \Delta P(u)/w \quad (24)$$

and which pass from  $u - w = 1$  to  $w = 0$  in the fourth quadrant. For a given pair of parameters,  $Da$  and  $Pe$ , there is a unique trajectory passing from the diagonal, where  $\zeta$  is taken as zero, to the  $u$ -axis, where it reaches the value 1. But it would be a mistake to seek this trajectory by trial and error, changing the starting point  $(u_0, u_0 - 1)$  until the  $u$ -axis is reached along the trajectory at exactly  $\zeta = 1$ , for all such trajectories are solutions for the given ratio  $\Delta$  and some  $Pe$ . What that value of  $Pe$  is can be calculated from either of the integrals

$$Pe = \int_{u_1}^{u_0} \frac{du}{-w} = \int_0^{u_0-1} \frac{dw}{w + \Delta P(u)} \quad (25)$$

This is equivalent to using  $\zeta/\Delta = vz/D$  as the dimensionless length variable, which is well suited to studying the effect of varying length.

In fact, we see [Fig. 1(A) is drawn for  $\Delta = 1$  and a second-order reaction  $P(u) = u^2$ ] that the trajectories must start on the part of the diagonal to the right of  $u_0$ , the starting point of the trajectory that goes to the origin and for which  $Pe$  is infinite. The origin is a critical point of eq. (23) with Jacobian

$$\begin{bmatrix} 0 & Pe \\ DaP'(0) & Pe \end{bmatrix}$$

and hence eigenvalues

$$\frac{Pe}{2} \pm \sqrt{\left(\frac{Pe}{2}\right)^2 + Pe Da P'(0)}$$

and eigenvectors

$$\left[ \frac{1}{(1/2) \pm \sqrt{(1/4) + \Delta P'(0)}} \right]$$

The origin is thus a saddlepoint and the incoming eigen-trajectory the path corresponding to a reactor of infinite length and given Damköhler/Peclet ratio,  $\Delta$ . Figure 1(B) shows some of these trajectories for various  $\Delta$ .

Sometimes, it may help to see the equations beyond the bounds of physical reality. Figure 1(C) shows the phase plane for  $P(u) = u^2$  for all values of  $u$  and  $w$ .

There is a sympathy here, in this playing around with different formulations of a model, with the poet's

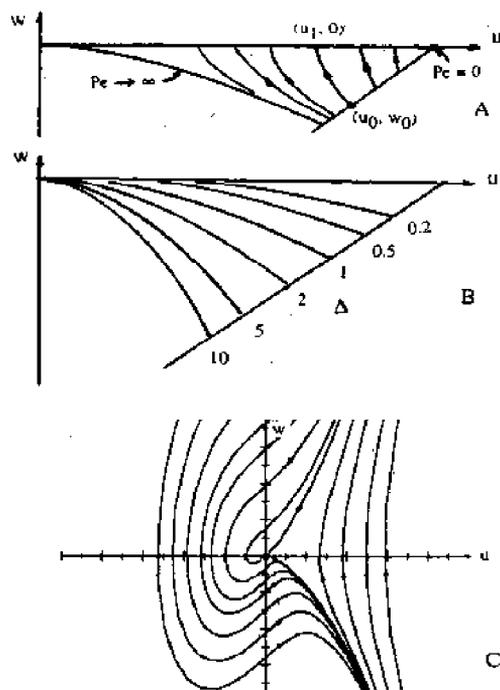


Fig. 1. (A) Trajectories of  $\mathcal{F}$  in the  $u$ - $w$  plane for various  $Pe$ ,  $\Delta = 1$ . (B) Trajectories of  $\mathcal{F}$  in the  $u$ - $w$  plane for various  $\Delta$ ,  $Pe = \infty$ . (C) Trajectories of  $\mathcal{F}$  in the whole  $u$ - $w$  plane for  $\Delta = 1$ .

perpetual struggle with words. As Eliot has it (*East Coker*, 172):

So here I am, in the middle way, having had  
twenty years—  
Twenty years largely wasted, the years of *l'entre  
deux guerres*  
Trying to learn to use words, and every attempt  
Is a wholly new start, and a different kind of  
failure  
Because one has only learned to get the better of  
words  
For the thing one no longer has to say, or the  
way in which  
One is no longer disposed to say it. And so each  
venture  
Is a new beginning, a raid on the inarticulate . . .

## 9. HOMOTOPIES OF MODELS

If  $D \rightarrow 0$  in the dispersion model, we reach one of the simplest models used in chemical reaction engineering, the plug flow tubular reactor, or PFTR. In the steady state, it satisfies the equations

$$du/dx = -P(u), \quad u(0) = 1. \quad (26)$$

This can be solved implicitly by quadrature

$$\zeta = \int_{u(\zeta)}^1 \frac{dv}{P(v)} \quad (27)$$

The other limit has been treated above and yields the equation of the stirred tank, or CSTR. Let us denote the system of equations (26) for the plug flow reactor by  $\mathcal{P}$ , and the stirred-tank equations (9) by  $\mathcal{Q}$ , and those for the tubular reactor with dispersion by  $\mathcal{F}$ .

Now  $\mathcal{F}$  forms a homotopic family between  $\mathcal{P}$  and  $\mathcal{Q}$ . If we set<sup>†</sup>  $\gamma = 2/(Pe + 2)$ ,  $\gamma \rightarrow 0$  corresponds to  $\mathcal{F} \rightarrow \mathcal{P}$  and  $\gamma \rightarrow 1$  to  $\mathcal{F} \rightarrow \mathcal{Q}$ . The solution to the linear case is the only one that can be written down in closed form. It is obviously a combination of exponentials of  $\mu\xi$  and  $-\nu\xi$ , where  $\xi = z/L$  and

$$\mu = (1 - \gamma)\{[1 + 2Da\gamma/(1 - \gamma)]^{1/2} + 1\}/\gamma \quad (28)$$

$$\nu = (1 - \gamma)\{[1 + 2Da\gamma/(1 - \gamma)]^{1/2} - 1\}/\gamma. \quad (29)$$

In fact, setting  $\xi = 1$  and

$$\sigma = [1 + Da\gamma/(1 - \gamma)]/[1 + 2Da\gamma/(1 - \gamma)]^{1/2} \quad (30)$$

we have

$$u(Da, \gamma) = 2/\{(\sigma + 1)e^\nu - (\sigma - 1)e^{-\mu}\}. \quad (31)$$

Note that as  $\gamma \rightarrow 0$ ,  $\mu \rightarrow \infty$ ,  $\nu \rightarrow Da$  and  $\sigma \rightarrow 1$ , so that  $w \rightarrow \exp(-Da)$ , whereas, when  $\gamma \rightarrow 1$ ,  $\mu, \nu \rightarrow [2Da(1 - \gamma)/\gamma]^{1/2}$ ,  $\sigma \rightarrow [Da\gamma/2(1 - \gamma)]^{-1/2}$  and  $u \rightarrow 1/(1 + Da)$ .

There are other ways of devising homotopic families. The stirred tank may be broken down into  $N$  stirred tanks each of  $(1/N)$ th the size of the original. Then

$$u_{n-1} - u_n - (Da/N)P(u_n) = 0, \quad u_0 = 1 \quad (32)$$

is a set of equations for the concentration of reactant in the several tanks. As  $N \rightarrow \infty$ ,  $N(u_n - u_{n-1}) \rightarrow u'(\xi)$  and we obtain the equations of  $\mathcal{P}$ . Clearly, when  $N = 1$ , we have the system  $\mathcal{Q}$ . Thus,  $\beta = 1/N$  is a normalized parameter that takes the homotopic system  $\mathcal{S}$  of the CSTR sequence from  $\mathcal{P}$  at  $\beta = 0$  to  $\mathcal{Q}$  at  $\beta = 1$ . The case of linear kinetics gives

$$u_N = u(Da, \beta) = (1 + \beta Da)^{(-1/\beta)}. \quad (33)$$

The full asymptotic expansion of  $(1 + \beta Da)^{-1/\beta}$  as  $\beta \rightarrow 0$  is not obvious, but may be obtained by expanding  $\exp[x - N \ln(1 + x/N)]$ , which is valid for  $N > x$ . It gives

$$(1 + x/N)^{-N} \sim e^{-x} + (x^2/2N)e^{-x} + [a(x)/N^2]e^{-x} + O(N^{-3})$$

and

$$a(x) = \frac{x^3}{24}(3x - 8).$$

This gives an asymptotic formula for the model  $\mathcal{S}$  as

<sup>†</sup>V. Balakotaiah has pointed out to me that a better form for  $\gamma$  would be  $\Gamma = (2/Pe) - (2/Pe^2)[1 - \exp(-Pe)]$ , which has the same limits and is the variance of the residence-time distribution, as are  $\alpha$  and  $\beta$  for the other two families. We shall see later how perceptive this remark is, but the formula for  $\Gamma$  cannot be inverted so that  $Pe$  or  $\gamma$  must serve in a parametric representation.

$\beta \rightarrow 0$  in the linear case. The other limiting case,  $\beta \rightarrow 1$ , is trivial.

A third way of getting from  $\mathcal{P}$  to  $\mathcal{Q}$  is by a PFTR with a recycle stream. If the ratio of the volumetric flow rate of the recycle stream to the volumetric flow rate of the feed is  $\lambda$ , the Damköhler number for the reactor is  $Da/(1 + \lambda) = Da(1 - \alpha)$  if

$$\alpha = \lambda/(1 + \lambda). \quad (34)$$

Thus, if  $u$  is the exit value of  $c/c_f$  and  $U$  the inlet value,

$$U = 1 - \alpha + \alpha u \quad (35)$$

and

$$Da(1 - \alpha) = \int_u^U \frac{dx}{\rho(x)}. \quad (36)$$

Clearly, when  $\alpha = 0$ ,  $U = 1$  and eq. (31) is the same as eq. (27), i.e.  $\mathcal{R} \rightarrow \mathcal{P}$ . As  $\alpha \rightarrow 1$ ,  $U \rightarrow u$ , since  $U - u = (1 - \alpha)(1 - u)$  and, dividing through by  $(1 - \alpha)$ , we have  $Da = (1 - u)/P(u)$ , which is the same as eqs (9). Thus,  $\mathcal{R} = \mathcal{Q}$ .

In particular, for a first-order reaction,  $P(x) = x$  and

$$\ln(U/u) = \ln[\alpha + (1 - \alpha)/u] = Da(1 - \alpha)$$

or

$$u(Da, \alpha) = (1 - \alpha) \exp[-(1 - \alpha)Da]/\{1 - \alpha \times \exp[-(1 - \alpha)Da]\}. \quad (37)$$

Again the limiting cases give  $u(Da, 0) = \exp(-Da)$  and  $u(Da, 1) = 1/(1 + Da)$ , as we should expect.

The scope of the homotopy can be seen from several figures drawn for first-order kinetics. Figure 2 shows a comparison of the three homotopes at  $\alpha = \beta = \gamma = 0.5$ . In this semi-log plot, the exponential  $\exp(-Da)$  of  $\mathcal{P}$  is a straight line. Figures 3-5 show that the homotopic parameters spread the curves out nicely between the exponential,  $\mathcal{P}$ , and hyperbolic,  $\mathcal{Q}$ , limits. In these figures,  $\alpha$ ,  $\beta$  and  $\gamma$  are the parameters for  $\mathcal{R}$ ,  $\mathcal{S}$  and  $\mathcal{F}$ , respectively.

It is clear that all three families give rather similar monotone curves and that it may be hard to distinguish them. One device is to use the difference between the  $1/(1 + Da)$  of the model  $\mathcal{Q}$  and the

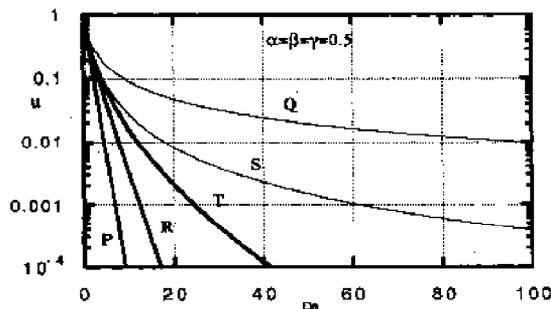
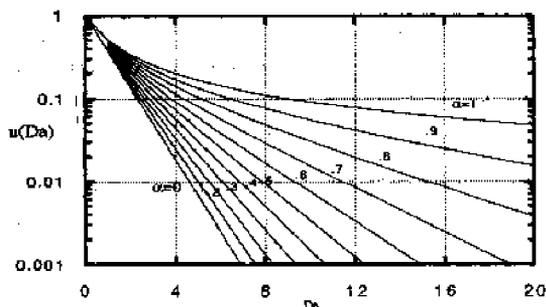
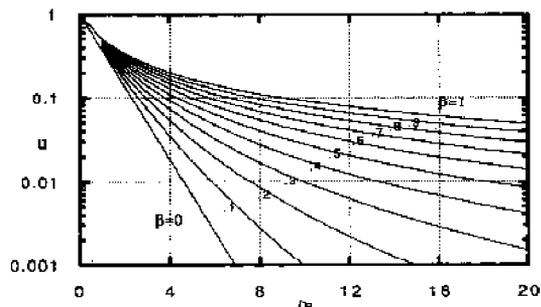
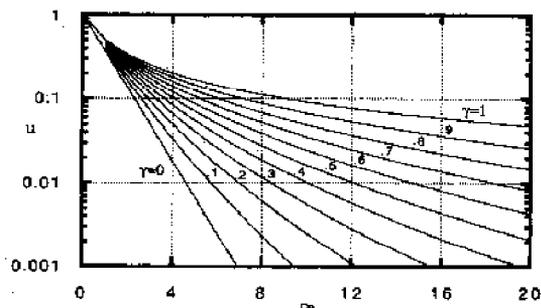


Fig. 2. The  $u-Da$  relationship for the homotopic families.

Fig. 3. Performance of  $\mathcal{R}$  for  $\alpha = 0 (0.1) 1$ .Fig. 4. Performance of  $\mathcal{S}$  for  $\beta = 0 (0.1) 1$ .Fig. 5. Performance of  $\mathcal{F}$  for  $\gamma = 0 (0.1) 1$ .

$\exp(-Da)$  of  $\mathcal{P}$  as the scale at a given  $Da$ , writing

$$U(Da, \alpha) = [u(Da, \alpha) - \exp(-Da)] / [1/(1+Da) - \exp(-Da)] \quad (38)$$

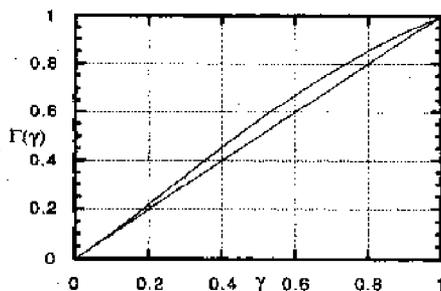
with similar expressions when the parameter is  $\beta$  or  $\gamma$ . With a certain amount of algebraic labour, the asymptotic behaviour as  $Da \rightarrow 0$  can be obtained. Thus, in the linear cases, we have

$$U(Da, \alpha) \sim \alpha + \alpha(1-\alpha)Da/3 + \dots,$$

$$U(Da, \beta) \sim \beta + 2\beta(1-\beta)Da/3 + \dots$$

$$U(Da, \gamma) \sim \Gamma(\gamma) = [\gamma/(1-\gamma)] \{1 - (1/2) \times [\gamma/(1-\gamma) \{1 - \exp[-2(1-\gamma)/\gamma]\}]\}. \quad (39)$$

Figure 5 shows that this function does not differ

Fig. 6. The function  $\Gamma(\gamma)$ .

greatly from  $\gamma$  over the whole interval. It is, of course, the variance which Balakotaiah suggested (v. sup. fn. 26), and suggests a fourth general principle for the choice of dimensionless parameters to be added to those above; namely, whenever possible choose parameters that have a deeper meaning.

#### 10. THE INVERSE PROBLEM

The steady-state performance of a chemical reactor is still of fundamental importance to chemical reactor analysis, even though the exciting advances are being made in the understanding of dynamics of reacting systems. The direct problem, that of calculating the performance of a reactor when the model and kinetics are provided, is largely solved, thanks to the power of the computing engines of our day. The inverse problem, even in quite elementary situations, can, however, still present considerable difficulties and we are far from a comprehensive answer. For example, if we confine ourselves to monotonic reaction kinetics and know the performance of the reactor through determination of the exit concentration as a function of the Damköhler number,  $u = f(Da)$ . This will clearly depend on the nature of the mixing in the reactor, which, at this level of sophistication, we associate with a choice of model for the reactor. If we have a partially mixed reactor and model it as a CSTR, we would infer the wrong kinetic expression. To take an extreme example, a first-order reaction in the stirred tank would, by eq. (9), give

$$f(Da) = 1/(1+Da).$$

If this performance were mistakenly thought to be that of a monotonic reaction in a PFTR with no dispersion, it would be thought to satisfy eq. (11) and so correspond to a kinetic expression  $P(u)$  obtained by eliminating  $Da$  between  $P(u) = -f'(Da)$  and  $u = f(Da)$ , i.e.  $P(u) = u^2$ . A first-order reaction appears to be second-order if the nature of the reactor is ignored. Similarly, a first-order reaction in a PFTR gives  $f(Da) = \exp(-Da)$ , and, by eqs (9), this performance on the part of a CSTR would imply kinetics  $P(u) = (1-u)/[\ln(1/u)]$ . Figure 7 shows the difference this makes.

The two extremes of the homotopic family  $\mathcal{P}$ , the PFTR, and  $\mathcal{Q}$ , the CSTR, yield easily to the inverse problem, for, given  $f(Da)$ ,  $P(u)$  is obtained by elimin-

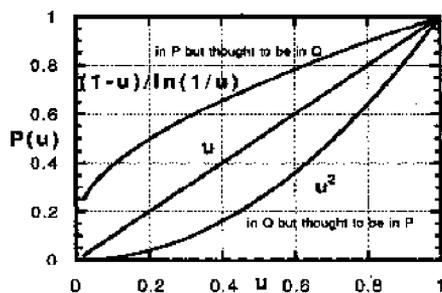


Fig. 7. Apparent kinetics when  $\mathcal{P}$  and  $\mathcal{Q}$  are confused.

ating  $Da$  between

$$\mathcal{P}: u = f(Da), P(u) = -f'(Da) \quad (40)$$

$$\mathcal{Q}: u = f(Da), P(u) = [1 - f(Da)]/Da. \quad (41)$$

Alternatively, we can use  $Da$  as a parameter along the  $u$ - $P(u)$  curve. The data are assumed to be normalized so that  $f(1) = 1$ ; hence,  $Da = 0$  corresponds to  $(u, P) = (1, 1)$  and  $Da = \infty$  to  $(u, P) = (0, 0)$ .

But if the two extremes are easy, the intermediate members of the homotopy are very refractory when it comes to finding an algorithm for the inverse problem. True, there is always the possibility of fitting, by least-squared deviation, an appropriate  $P(u)$  curve, but this is not a satisfying answer except under the exigencies of practice. Consider only the configuration of two CSTRs in sequence;

$$1 - u_1 - (Da/2)P(u_1) = 0 \quad (42)$$

$$u_1 - u_2 - (Da/2)P(u_2).$$

The data give  $u_2 = f(Da)$  and say nothing about  $u_1$ . The equations can, however, be solved in the form

$$u_1 = u_2 + (Da/2)P(u_2) \quad (43)$$

$$P(u_1) = (2/Da)[1 - u_2 - (Da/2)P(u_2)]. \quad (44)$$

Were the kinetic law known, it would have been represented by a monotonic curve from  $(0, 0)$  to  $(1, 1)$  and, starting from  $[u_2, P(u_2)]$ , the point  $[u_1, P(u_1)]$  could be found from eqs (43) and (44) and would be on the same kinetic curve. The value of  $Da$  used in these equations would be given by the inverse function,  $F$ , of  $f$ , i.e.  $Da = F(u_2) = F[f(Da)]$ . Since the kinetic law is not known, the best we can hope for is an intelligent guess; but, from this starting point, these equations provide a map that can be used repeatedly and would, had the starting point been exact, give a sequence of points converging on  $(1, 1)$ . If this critical point is a saddle, we have a practical trial-and-error method that starts with a guessed value for  $P(u)$  and finds the separatrix by iterating until the trajectory hesitates long enough in the neighbourhood of  $(1, 1)$  before diverging to left or right. However, it is limited to the case of two stirred tanks, for an extension to three would give only three equations for the four unknown intermediate values of  $u$  and  $P(u)$ .

## 11. READING OTHER PEOPLE'S MODELS

The simplest models provide the foundations for more complex models which have to be constructed to answer more complicated problems. Thus, the equations given so far are for the isothermal tubular reactor (sometimes paradoxically known as an "empty" tubular reactor). A momentum balance is required if the assumption of plug flow is discarded and an enthalpy balance is needed to obtain an equation for the temperature. With a packed bed, a further set of equations is needed for the distribution of concentration and temperature within the particles, though Carberry has shown that the pellets may often be taken as isothermal.<sup>1</sup> I will not go into the detail of setting up such a set of equations, for this has been covered in masterly fashion in a paper that deserves to be better known than it is.<sup>2</sup> Rather will I start from a model in the literature and try to show how to read it. It is entirely justifiable, in writing a paper, to suppress some of the tedium of the research and start with a developed model taking it for granted that the reader can fill in the missing stages at will. There is an analogy here with literary criticism, or rather, with what used to be called the "lower" criticism—the establishment of the text. This has a faintly old-fashioned ring in days when a student can become indignant at having his paper on the line "To thy high requiem become a god" rejected, "just because" he had misread his fancy, "god", for Keats' "sod"! The so-called higher criticism is concerned with the interpretation of the text, and this presumes the lower, in that it needs a valid text to work from. There is a tendency on the part of some modern critics to place less emphasis on the author than common sense would allow and I have tried to give one common reader's conclusions after venturing into the stormy seas of contemporary criticism elsewhere.<sup>3</sup> We are fortunate in the engineering sciences to have a precise language, impoverished of overtones it may be (see remarks above), but it is not generally obnoxious to the popular -isms, interpretive fashions or political corrections of the day. It makes our congresses more sober affairs than the risibilities of MLA meetings, but, paradoxically, frees us to take ourselves rather less seriously than do our literary brethren.

As a brief example of how one begins to read another's model, let me refer to a paper of Balakotaiyah and Luss<sup>4</sup> which uses the two-phase model of the catalytic bed. Thus, we read at the top of

<sup>1</sup>Carberry, J. J., 1967, Alcuni aspetti ingegneristici riguardanti la reazione catalitica. *Quad. Ing. Chim. Ital.* 3, 73.

<sup>2</sup>Amundson, N. R., 1970, Mathematical models of fixed bed reactors. *Berichte der Bunsen-Gesellschaft für physikalische Chemie* 74, 90; Also to be found in *The Mathematical Understanding of Chemical Engineering Systems* (Edited by A. Varma and R. Aris), pp. 101-109. Pergamon, London (1980).

<sup>3</sup>Aris, R., An essay on contemporary criticism. *New Literary History* (to appear).

<sup>4</sup>Balakotaiyah, V. and Luss, D., 1991, Explicit runaway criterion for catalytic reactors with transport limitations. *A.I.Ch.E. J.* 37, 17808.

page 1781: "Assuming plug flow and negligible axial dispersion, the dimensionless energy balance for a first-order reaction has the form:

$$d\theta/d\xi = \Delta \exp(\theta_s)\eta - St(\theta - \theta_c), \quad \theta(0) = 0''.$$

We should—and can, in a paper as well written as this is—be able instantly to recognize (and subsequently confirm from the definitions that follow and the Notation at the end of the paper) the three dimensionless temperatures; the first,  $\theta$ , is the temperature of the reaction stream (since it is a function of  $\xi$  and since it is the driving force in the wall cooling term—which is identified by the Stanton number), the second,  $\theta_c$ , the wall temperature (because of its occurrence in the wall cooling term) and the third,  $\theta_s$ , the catalyst pellet temperature (because it is in the reaction term). We note also that the positive exponential is being used and check back to see if this assumption is made explicit in the previous paragraph, which we may not have read thoroughly in our haste to get to the equations. It is, for we read: "We assume that the temperature rise at ignition is small enough so that the Arrhenius temperature dependence can be replaced by the positive exponential approximation." Our eyes catch the next sentence: "We also neglect the reactant consumption in the fluid phase (but account for diffusional limitations within the catalyst". So  $\eta$ , which one might otherwise have thought to be the dimensionless concentration of a first-order reactant, is an effectiveness factor. This is confirmed by a glance downwards to eq. (6), where the familiar form of the effectiveness of an isothermal sphere is to be seen, followed by the definitions of the Biot number and Thiele modulus. Why is the Thiele modulus a function of  $\theta_s$ ? Of course! through the rate constant under the square root, which is why there is an exponential of  $0.5\theta_s$ —the result of the positive exponential approximation.

A glance at their definitions (using their equation numbers),

$$\begin{aligned} \theta &= (E/RT_f)(T - T_f/T_f) \\ \theta_c &= (E/RT_f)(T_c - T_f/T_f) \end{aligned} \quad (2)$$

$$St = 4UL/d_1 u_0 \rho_f c_{pf}, \quad \xi = s/L$$

$\Delta = [k(T_f)L/u_0] \cdot [(-\Delta H)C_f/\rho_f c_{pf} T_f] \cdot [E/RT_f]''$  confirms these first impressions and reveals the formidable dimensionless group  $\Delta$ . This appears to be the product of a Damköhler, a Prater and an Arrhenius number; the latter two appear in the parameter  $B$  in Luss and Balakotaiah's definition (5).

Next, we are given the relation between the "solid and fluid temperatures . . .

$$\theta_s = \theta + B Da_{ph} \eta \exp(\theta_s) \quad (3)$$

where  $Da_{ph}$  is the particle heat Damköhler number defined by:

$$Da_{ph} = [\rho_f c_{pf} k(T_f)/h] \cdot [V_p/S_p] \quad (4)''.$$

This must derive from a heat balance on the particle,

which, though isothermal, is a source of heat through the exothermic reaction within which it just balances the loss of heat to the fluid. The "particle heat Damköhler number" is unfamiliar—is it a new one? Certainly it is a Damköhler number, in the sense that it is the ratio of a reaction rate to a transport rate, but it does not correspond to any of the four numbers in Damköhler's classic paper.<sup>1</sup> It can be written as  $[k(T_f)L/u_0]/[S_p Lh/V_p u_0 \rho_f c_{pf}]$ , where the first term is the Damköhler number already in use,  $\Delta/B$ , and the second is constructed like a reciprocal Stanton number, but with the particle heat transfer coefficient,  $h$ , in place of the wall transfer coefficient,  $U$ . We are not surprised to see it later in a ratio with the Stanton number.

Since it is my purpose here to illustrate how one reads a model that one meets for the first time in someone else's work, I have set down my reaction to the introduction to this paper. Once one has grasped the basic model one can go on to the higher criticism of it. Such is not my purpose here.

## 12. POLISHING

In a 1976 paper I attempted to give some maxims for mathematical modelling. Since the last was "These maxims will self-destruct. Make your own!" I would be inconsistent were I to repeat them here.<sup>2</sup> On review, they stand up quite well and most have been exercised in this essay. I will allude to but one and that the first, so that my end may be my beginning—or, at least, yesteryear's beginning. "Cast the problem in as elegant a form as possible."

The role of aesthetics in the pursuit of truth has long been a question of vital interest to scientists.<sup>3</sup> I am not pretending that the mathematical models with which the engineer deals have the same significance as the general theory of relativity although, in these days of the resurgence of popular culture, such pretensions might be encouraged in certain quarters. But mathematical models by their very name may be expected to share the elegance that is one of the chief criteria of good mathematics. Its hallmarks are economy and aptness. The passage from Eliot that I began with continues:<sup>4</sup>

And every phrase  
And sentence that is right (where every word is at  
home,  
Taking its place to support the others,  
The word neither diffident nor ostentatious,

<sup>1</sup>Damköhler, G., 1936, Einfüße der Strömung, Diffusion und des Wärmeüberganges auf die Leistung von Reaktionsöfen. *Z. Elektrochem.* 42, 846.

<sup>2</sup>How to get the most out of an equation without really trying. *Chem. Engrng Educ.* 10, 114 (1976) to be reprinted as an appendix to Dover's forthcoming reprint of my *Mathematical Modelling Techniques*. Pitman, London (1978).

<sup>3</sup>See, for instance, Chandrasekhar, S., 1987, *Truth and Beauty: Aesthetics and Motivations in Science*. University of Chicago Press, Chicago.

<sup>4</sup>T. S. Eliot, *Four Quartets*. Little Gidding, V, 216–226.

An easy commerce of the old and the new,  
The common word exact without vulgarity,  
The formal word precise but not pedantic,  
The complete consort dancing together)  
Every phrase and every sentence is an end and  
a beginning,  
Every poem an epitaph.

## Dare I add?

Every choice and every equation is an end and  
a beginning,  
Every model an epitaph.

## NOTATION

A, B, C	chemical species
A*, B*	adsorbed chemical species
a(x)	coefficient in the asymptotic expansion of eq. (33)
Da	Damköhler number
f, F	flux vector, net flux
g, G	generation per unit volume, total generation
h, H	content per unit volume, content (e.g. mass, enthalpy)
L	length of tubular reactor
N	number of stages in $\mathcal{S}$
$\mathcal{P}$	PFTR with no dispersion
Pe	Peclet number
P(u)	dimensionless reaction rate
$\mathcal{Q}$	CSTR
q	volumetric flow rate
$\mathcal{R}$	recycle reactor
r(c)	reaction rate
$\mathcal{S}$	sequence of CSTRs
$\mathcal{F}$	PFTR with dispersion
U(Da, .)	concentration as a fraction of the difference between $\mathcal{P}$ and $\mathcal{Q}$
u	dimensionless concentration
V	volume of reactor
w	(1/Pe)(du/dz)
z	distance from inlet in PFTR

## Greek letters

$\alpha, \beta, \gamma$	homotopy parameters
$\Gamma$	alternative parameter to $\gamma$
$\Delta$	Da/Pe
$\zeta, \eta, \xi$	forms of dimensionless length
$\mu, \nu$	exponents in the solution of $\mathcal{F}$ for linear kinetics
$\omega$	D/VL, dispersion or reciprocal Peclet number
$\sigma$	constant in the solution of $\mathcal{F}$ for linear kinetics [eq. (30)]
$\tau, \tau'$	dimensionless time

## REFERENCES

- Amundson, N. R. and Luss, D., 1968, Qualitative and quantitative observations on the tubular reactor. *Can. J. Chem. Engng* **41**, 424.  
Amundson, N. R. and Aris, R., 1957, Some remarks on

- longitudinal mixing or diffusion in fixed beds. *A.I.Ch.E. J.* **3**, 280.  
Aris, R., 1969, *Elementary Chemical Reactor Analysis*. Prentice-Hall Englewood Cliffs, NJ; reprinted by Butterworths, Boston (1989).  
Bodenstein, M. and Wolgast, K., 1908, Reaktionsgeschwindigkeit in strömenden Gasen. *Z. phys. Chem.* **61**, 422.  
Damköhler, G., 1937, Einflüsse der Strömung, Diffusion und Wärmeüberganges auf die Leistung von Reaktionsöfen. II. Die isotherme, raumbeständige, homogene Reaktion erster Ordnung. *Z. Elektrochem.* **43**, 1.  
Danckwerts, P. V., 1953, Continuous flow systems, distribution of residence times. *Chem. Engng Sci.* **2**, 1.  
Förster, Th. and Geib, K. H., 1934, Die theoretische Behandlung chemischer Reaktionen in strömenden Systemen. *Ann. Phys.* **20**, 250.  
Gunn, D. J. and Vortmeyer, D., 1990, Equivalence between the dispersion and cell models in chemical reactors. *A.I.Ch.E. J.* **36**, 1449.  
Langmuir, I., 1908, The velocity of reactions in gases moving through heated vessels and the effect of convection and diffusion. *J. Am. Ceram. Soc.* **30**, 55.  
Lapidus, L. and Deans, H. A., 1960, A computational model for predicting and correlating the behavior of fixed-bed reactors. *A.I.Ch.E. J.* **6**, 656, 663.  
Levenspiel, O., 1972, *Chemical Reaction Engineering*, 2nd Edition. Wiley, New York.  
McHenry, K. W. and Wilhelm, R., 1957, Axial mixing of binary gas mixtures flowing in a random bed of spheres. *A.I.Ch.E. J.* **3**, 83.

## APPENDIX

It might be appropriate to draw attention to some of the early work on the one-phase tubular reactor model, even if only by way of an appendix which makes no pretence to comprehensiveness. The solution of  $\mathcal{F}$  was obtained by Irving Langmuir in 1908, though this paper does not seem to have had much currency, for Förster and Geib in 1934 (quoted by Damköhler in 1937) refer to the 1908 paper by Bodenstein and Wolgast that provoked Langmuir's, but not to Langmuir's solution, obtained by linearization. The boundary conditions (Danckwerts, 1953), over which much ink was spilled in the 1950s, were obtained by Langmuir in 1908 and he deals with the limiting cases of "mixing nearly complete" and "only slight mixing". Langmuir appears to have been the first to have considered the homotopy  $\mathcal{P} \rightarrow \mathcal{F} \rightarrow \mathcal{Q}$  and the homotopy parameters,  $\alpha, \beta, \gamma$ , that we have been using might suitably be called Langmuir numbers, save that this was a minor work of a scientist best known for many other achievements. Förster and Geib, anticipating, though not explicitly, the idea of a residence-time distribution, used a curiously round-about method of obtaining the steady-state solution, first determining the residence-time distribution and then integrating the exponential over all times. They credit Bodenstein and Wolgast (1908) with recognizing that there are different reaction times and with giving  $\mathcal{Q}$  as the limiting case of  $\mathcal{F}$ . This anticipates Danckwerts' (1953) treatment of the residence time distribution by nearly 20 years, though, of course with nothing like Danckwerts' generality, since it deals only with the case of longitudinal dispersion in a tube. The analogy between  $\mathcal{P}$  and  $\mathcal{F}$  is, of course, standard text book fare (Levenspiel, 1972; Aris, 1989). Amundson and Aris (1957) showed how it fitted with the observation that the Peclet number (based on the particle diameter) in a packed bed has a value near 2, as Wilhelm and McHenry (1957) had found in an elegant series of experiments. Lapidus and Deans (1960) exploited it for more detailed models of the packed bed. More recently, Gunn and Vortmeyer (1990) have introduced a reaction-independent transformation that shows how the  $\mathcal{P}, \mathcal{F}$  equivalence holds for systems of first-order reactions. Their parameter  $p$  is my  $\gamma$  and is interpreted as the probability of axial displacement.