PROGRESS TOWARDS THE *A PRIORI* DESIGN OF CHEMICAL REACTORS

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INTRODUCTION

Under certain fortunate circumstances it is possible to draw upon elementary laws of physical chemistry to design a reactor in an *a priori* sense such that reaction kinetics will receive sole emphasis. The Schwab reactor provides such an arrangement whereby a very small amount of finely divided catalyst is subjected to a uniform reaction environment in a rapidly flowing reactant stream. In a recent laboratory study[1] on the reactions of nitrogen atoms, compositional uniformity was assured in a flow-type reactor by conducting the experiment at low pressure so that the mean free path was substantially larger than the vessel size, thus providing the equivalent of a fully stirred vessel. On the other hand, in another laboratory flow-reactor study[2] also conducted at low pressure, experiments on the kinetics of graphite oxidation at high temperatures gave every evidence that mass diffusion substantially affected the over-all reaction responses to temperature and to the gaseous composition. Whether it be on the laboratory or industrial scale it is difficult to avoid the intrusion of physical phenomena on chemical rate processes, as systems are taken to the extremes of large reaction rates and dimensions. As a consequence of this situation the elements of chemical reactor systems have become the subject of separate study as a new, interesting branch of physical chemistry and engineering science which is still developing.

The combined effects of chemical kinetics and of physical processes, such as flow and the transport of mass and of heat in many kinds of reactor arrangements including the extremes of operational conditions, are suggested to be the proper subjects of study. Chemical reaction engineering, as it is sometimes called, will be recognized to have early roots in the classic studies of some fifty years ago. For example, in 1904, Nernst and Brunner[3], drawing on the results of the earlier dissolution experiments of Noyes and Whitney, suggested a theory for reactions at heterogeneous surfaces, the rate being limited by a stagnant film of liquid at the surface. Bodenstein and Wolgast[4], in 1908, conducted the homogeneous hydrogen–iodine reaction in a bulb-shaped flow-through reactor. In describing their results these authors introduced the idea of backmixing and also that of a differential reactor.

In the latter thirties, after an hiatus of almost three decades, the present quantitative period of reactor studies began with a rapid upsurge of interest. It was a time of great advance and stimulation in the synthetic chemical industry and in petroleum processing. The supporting engineering sciences of fluid mechanics, heat transfer and mass transfer were sufficiently well advanced to provide an initial supporting structure for the next step: the study of their coupling with reaction kinetics. It was a time, for example,

when the analogy which Chilton and Colburn draw between heat and mass transfer had the lustre of a new and intriguing idea. Two pioneering treatises on the interaction of chemical and physical phenomena, one by Damkohler[5] of Germany (1937), the other by Frank-Kamenetskii[6] of the U.S.S.R. (1947), are especially important landmarks in chemical reaction engineering. A small sampling of the names of other early contributors, namely, Denbigh of Great Britain, Boreskov of the U.S.S.R., Hougen of the United States, Kramers of Holland and Wicke of Germany, attests to the international character at the start of the then new branch of studies. This geographical spread of interest has continued and expanded to this day. In fairness it can be said that a world literature on chemical reactor elements has become established.

A question that seems worth asking at this time is: what progress, if any, has been made towards the physical design of chemical reactors from basic principles for realistic chemical systems?

The question is of obvious interest to the designer and developer of industrial reactors and processes. He is concerned with economically optimum conversion yields, with selectivity in the case of complex reactions and with the stability and controllability of the reactor. This question may also be of interest to the experimental kineticist who seeks chemical kinetic knowledge, preferably unencumbered by extraneous physical effects, but, in any case, with some hope of disentangling such effects should they intrude.

For present purposes the field of reactor studies may be divided into three parts. The first seems beyond immediate a priori design objectives because of incomplete theory, the second is in the domain of the moderately well understood, and the third is in the process of developing rapidly. Flames and other rapid reactions for which equilibrium distribution of energy may not necessarily be assumed may be considered in the first section. Systems in which turbulent fluid dynamic effects are important, again as in flames, and in jets or in fluidized beds also come into this section. Fortunately, many reactor arrangements, in the second section, may be considered ideal in the sense that local velocity, concentration and temperature gradients, if they exist, have a negligible effect on the course of chemical reaction. The ideal modes of conducting chemical experiments are the classic three, namely the batch reactor, the plug flow reactor which has a flat velocity profile, and the connected cascade of fully stirred tank reactors. These different modes of conducting reaction are well understood in principle and a wealth of literature on their employment for simple and complex reactions exists. For such ideal reactors, ample guidance is available for the a priori design of reactors and their optimization, the limiting circumstances frequently being the lack of knowledge of the detailed chemical kinetics.

I have chosen the packed bed reactor, a device which clearly falls in the third category as the specific subject of my paper. Its properties are actively being studied and, while many phenomena involved merit substantially more investigation, a workable mathematical model for purposes of realistic design is suggested to be evolving currently. Progress towards understanding the elements of packed bed technology has developed very rapidly in the last ten years or so through the efforts of many investigators.

Historically, the packed bed chemical reactor is one of the oldest arrangements for conducting gas–solid or liquid–solid chemical reactions on an industrial scale. Although newer processing techniques, such as the fluidized bed reactor are now also widely used, the packed bed reactor still continues to retain a secure position as the reactor of choice for the many synthetic chemical and petroleum processing reactions which do not involve extremes in thermal requirements or the need for a high rate of reprocessing of the solids. A packed bed is, simply, an assembly of uniformly sized particles, randomly arranged, which are held firmly in position as, for example, within a reactor tube or pipe. An intimate contact is achieved between the particles and the reactant fluid as the latter flows in a random manner between and around the particles, although when looked at as a whole, the space-average fluid motion along the tube is taken as unidirectional. Packed beds serve most commonly for catalytic reactions and for kiln or combustion reactions.

Let us look now (*Figure 1*) for purposes of discussion and analysis, at the sub-systems into which a packed bed assembly may be divided. In this discussion we shall assume that the bed consists of porous catalyst pellets. The reactant fluid is flowing from left to right, as indicated by the large arrows.
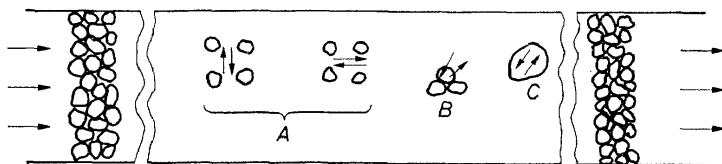

Figure 1. Major transport domains in packed bed reactors; *A*: *Inter*particle dispersions; *B*: *Inter*phase transport; *C*: *Intra*particle transport

As the reactant fluid flows in the external field between the particles, an effective time of contact is established between the ends of the reactor which, of course, depends upon the average flow rate and the length of the reactor. Dispersion effects *A* in the radial and the axial directions arise because of the complex flow patterns and the large spacial variations in the time-average velocity, which are caused by the presence of the particles. These dispersion-transport phenomena which carry heat and mass in the radial and axial directions contribute toward defining gross temperature and composition profiles between the tube centre and wall and between the ends of the reactor. For example, the location and magnitude of the hot spot for an exothermic reaction in a reactor which has walls controlled at a constant temperature depends upon coupled heat and mass balances which must include a proper consideration of these *inter*particle transport effects.

Each catalyst pellet *C* may be looked upon as a miniature reactor, within which a build-up of internal concentration and temperature gradients is potentially possible because of *intra*particle diffusion effects in the presence of distributed rates of reaction and heat evolution. The important problems of catalyst effectiveness and selectivity relate directly to the *intra*particle diffusion-reaction phenomena. In contrast to the time of contact in the external field, the effective time of contact for a reactant molecule within a

catalyst pellet does not depend upon flow but only on *intra*particle conditions and on the temperature and concentrations at the outer boundary.

Exterior and interior fields are obviously related by heat and mass flux boundary conditions afforded by the complex flows adjacent to the particle surfaces. The surface transfer resistances at this stage of packed bed reactor development ordinarily are averaged over the particle area and (regretfully, but necessarily) are expressed as film coefficients for heat and mass transfer.

The structure of a fixed bed catalytic reactor thus comprises[7] the *inter*particle, the *inter*phase and the *intra*particle domains: each in itself is a substantial field of study in relation to the nature and measurement of the pertinent transport mechanisms, their coupling with reaction rate formulations and the properties of the resulting solutions. Concept of the over-all reaction properties in various regimes of behaviour: hydrodynamic, chemical, mass diffusional and thermal for the different parts of the system currently are in process of study and development. Important criteria are being formulated for estimating the limits of regimes—the points of judgement that, for example, enable the laboratory experimentalist to be moderately certain that in no part of the system is the reaction restricted by diffusive processes: at the other extreme of conditions, the industrial designer is permitted to judge whether the reactor may be dangerously close to a point of thermal instability in any of its parts.

In what follows I shall first attempt to trace the development of a model for the behaviour of the external, *inter*particle field, a model which gives strong promise of providing a design unification in the numerical machine calculation of realistic reactor systems. I shall also indicate a few research areas in which rapid progress has been made recently, and others that appear to deserve attention.

EXTERNAL FIELD MODEL

The characterization of the dispersion of heat and of matter in a fluid that is streaming among particles is a subject of wide interest, not only in catalytic reactors but also in fine-pore flows, such as are encountered in underground reservoirs of oil and water. Restricting our attention here to the high flow conditions typical of reactors, let us first trace in outline the results of the very substantial experimental effort that serves as the basis for the construction of a model for dispersive behaviour. The subject divides itself naturally into (*i*) dispersion *lateral* to the flow direction, (*ii*) dispersion *parallel* to the flow direction and (*iii*) hydrodynamic limits of behaviour.

Let us first consider the various experimental arrangements (*Figure 2*) that have been employed in packed-bed dispersion studies. The point source tracer method has been used predominantly for the measurement of the radial or lateral components of transfer. A tracer material is released from a small tube, located axially near the entrance end of a bed of particles through which the main stream of fluid is coursing. For liquid studies, the tracer may, for example, be a dye or a conductive substance. In the case of gases, any convenient second gas which has the virtue of being detectable over several decades of concentration will suffice. Radial tracer dispersion profiles are then measured at different distances, or times of contact, along

the axial co-ordinate. Such profile data serve as the basis of subsequent analysis. The technique shown in the top right-hand part of the figure is that which was employed by Bakhurov and Boreskov, the earliest workers, who arranged for a planar contact to occur between tracer and main streams.
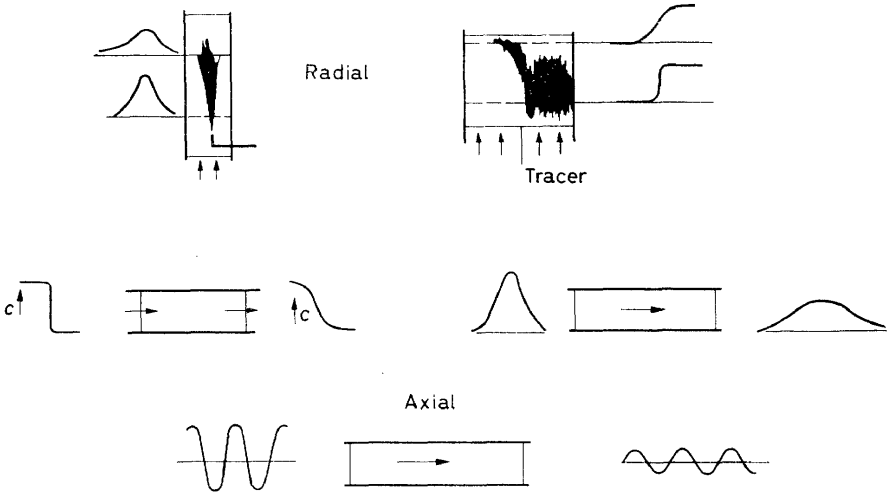

Figure 2. Graphical representation of various experimental arrangements for measuring radial and axial dispersion among particles

To measure purely *axial* dispersions it is clear that concentration gradients c must be established in the axial direction and such conditions have been arranged by various investigators in transient experiments. All three obvious methods indicated in the figure have now been employed, namely: the dispersion of a step-function tracer concentration, the attenuation of a tracer pulse and the damping and shift in phase of a sine-wave tracer concentration.

Radial Peclet group $\qquad\qquad$ Axial Peclet group

$$Pe_r = \frac{d_p u}{E_r} \qquad ; \qquad Pe_z = \frac{d_p u}{E_z}$$

$$\frac{\overline{X^2}}{2t} = E \qquad ; \qquad t = \frac{z}{u}$$

$$\overline{X^2}' = \frac{\overline{X^2}}{d_p^2} \qquad ; \qquad z' = \frac{z}{d_p}$$

$$\overline{X_r^2}' = \left(\frac{1}{Pe_r}\right)z' \qquad ; \qquad \overline{X_z^2}' = \left(\frac{1}{Pe_z}\right)z'$$

Figure 3. Dimensionless axial and radial dispersion groups as spreading constants

Data from transverse and axial dispersion experiments are analysed by means of the solutions of the pertinent differential equations with attendant boundary conditions. Two dimensionless groups (*Figure 3*) arise when the appropriate mathematical expressions are placed in dimensionless form and these groups serve to characterize the dispersion phenomena. They are the

radial and axial Peclet groups; the latter is called the Bodenstein number in Europe.

The groups are composed of the particle diameter, d_p, as the normalizing length term, the average linear velocity in the particle interstices, u, and the radial or axial dispersion constants, E_r and E_z, respectively. The dimensionless groups represent the ratios of the characteristic times for flow and for diffusion. It may be helpful to relate these groups to the well-known Einstein expression for diffusive dispersion in any randomly fluctuating field. Time here is defined as contact time, that is, distance/velocity. The mean-square dispersion spread $\overline{X^2}$ and the axial co-ordinate distance z are each normalized, as shown, by means of the particle diameter dimension. The Peclet dispersion groups finally are shown to be reciprocal proportionality constants in the Einstein equation, thereby relating the dimensionless mean square tracer displacement because of dispersion effects with dimensionless axial distance. It will be evident shortly that these relations hold only under restricted conditions of deep beds, such as were employed in the experimental determination of the values of the groups.
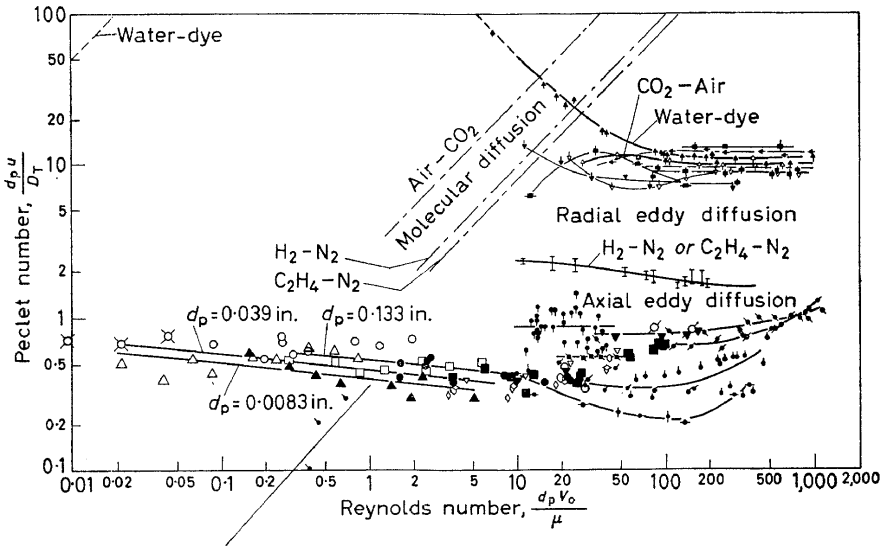

Figure 4. Compilation of data for axial and radial dispersion among particles, liquids and gases (Peclet group v. Reynolds number)

Let us now glance at the experimental results in which the Peclet numbers, for convenience, are related to a Reynolds number based upon particle diameter (*Figure 4*). The latter number is simply a dimensionless fluid velocity. The graph with its cloud of data points covers the results of the studies of many groups of investigators over the past dozen years and encompasses both radial and axial dispersion studies with air and with water as the primary fluids. The data are presented in double logarithmic form for convenience in compressing and representing the results. The upper band displays radial dispersion data from the work of Bakhurov and Boreskov[8], of Bernard[9], Latinen[10], Fahien and Smith[11], and of Plautz and Johnstone[12].

The next lower single curve presents the major set of data which exists for gas-phase axial dispersion, and is due to McHenry[13]. The lowest band of data points gives results for axial dispersion in liquids and derives from the work of Ebach and White[14], of Carberry and Bretton[15] and of Strang and Geankoplis[16].

The assembly of dispersion data, limited though it may be, displays an interesting interlocking series of hydrodynamic regions. These relations are set out in *Figure 5*; the data points have been removed. The diagonal lines represent the spread by *molecular diffusion* of the filaments of tracer substances, liquid and gaseous, as indicated.
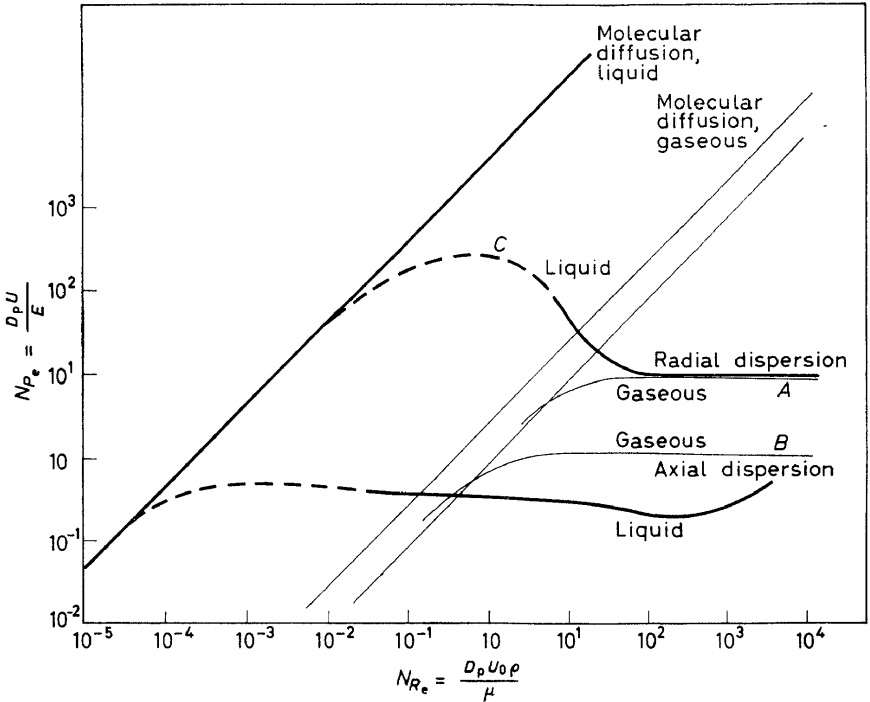

Figure 5. Axial and radial dispersion; interlocking hydrodynamic regions

We start our discussion of this figure with a description of the now accepted model of flow behaviour presumed to cause dispersion in packed beds. At high fluid velocities, a packed bed contains an interlocking series of thoroughly stirred regions, of the order of particle dimensions in size; the energy for mixing is derived from jet inpingement, expansion and contraction and the like within the interstices. Regions A and B describe radial and axial dispersions respectively and both are constant in the corresponding Peclet numbers. The Peclet number for *radial* dispersion is noted to be the same numerically for gases and liquids, but this is not the case for *axial* dispersion. Both regions A and B represent the model conditions in question and are the regions of particular importance in reactor technology.

We note that the fully developed *radial* dispersion region A is terminated at its lower end at a Reynolds number value of about 100 which is suggested to be an important fluid mechanical regime boundary. Below this boundary, as velocity is caused to decrease and as viscous flow is approached, dispersion by local eddy action gradually undergoes transition until finally it becomes mainly the result of ordinary molecular gaseous diffusion. Most industrial catalytic reactor conditions are located well above the critical Reynolds number in question, but small-scale laboratory experiments normally fall well below this value unless special provisions are taken to assure that they do not. In analogy to other fluid mechanical systems, as viscous flow conditions are approached, a Grasshoff type of local convective turnover effect may well be expected to develop because of density gradients that are induced either thermally or by local concentration gradients. From a design viewpoint they must be considered as extraneous effects and are to be avoided whenever possible.

Gaseous *axial* dispersion in curve B shows a more or less parallel transition behaviour toward the molecular processes just described. But what of the two liquid dispersion curves? These will be considered only briefly here with the statement that the rising radial liquid dispersion curve, C, has its origin in the persistence of *liquid* tracer filaments which are distributed about the packing-particles less and less randomly as the flow rate is decreased and viscous flow conditions are approached: ultimately a single tracer filament weaves back and forth among particles along the tube axis. The low value of the liquid phase axial dispersion curve at the bottom of the figure, when compared to its gaseous counterpart immediately above, is due in part to a Taylor axial diffusion mechanism which arises from a coupling of a velocity distribution with radial diffusive effects. The combination gives rise to an effective *axial* dispersion, the effect being greater, the smaller the molecular diffusivity, as was found to be the case experimentally.

We now come to an interesting question: Why do the magnitudes of the dispersive Peclet numbers, although constant, have different values in the fully developed mixing regimes? Why is the system anisotropic? The radial Peclet number is noted to have a numerical value of about twelve and that of the axial group, of about two. These values would appear to arise naturally from the properties of the cell mixing model and the ideas involved merit brief discussion.

The lateral dispersion effect is consistent with a random walk, a Galton quincunx description. As tracer material flows from one mixing cell level to the next in the tube, a succession of lateral displacements must occur because of the physical presence of the particles. The thorough mixing at each stage assures that the direction of travel of a tracer element shall be statistically independent of the direction of lateral motion in the previous cell. Through a straightforward elementary statistical development of the mean square displacement of tracer substance after passage through n layers of mixing cells, it may be shown that the lateral Peclet group should be constant (this was verified experimentally). It was also shown to depend in its absolute value on (*a*) the average scale or side-step distance in walking around a particle and on (*b*) the number of layers of mixing cells between source and measuring point. If we take the number of mixing cells in the

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axial direction to be of the order of the number of particles in that direction and the average scale of individual lateral displacements to be a fraction of the particle diameter, an estimate of the value of the lateral Peclet number is made which closely approximates the experimental value. Prausnitz[17], in a detailed study of concentration fluctuations in a tracer plume, rather than of the time-average values of which we have been speaking, was able to determine directly that the scale of lateral displacement mixing was one-quarter of a particle diameter. In short, an elementary random walk analysis serves to describe the observed lateral dispersion effects. Such description has been made by a number of investigators including Baron[18], Boreskov[8], Latinen[10] and Singer[19].

As we turn to the *axial* dispersion process, a key point, as suggested by Beek[7] is whether, in a sequence of interconnecting and thoroughly mixed stages, there is a significant amount of fluid backflow against the main stream. The state of the reactor in a local region will depend greatly on the presence or absence of such flows. For these to be effective it is necessary for the distance that should be traversed by backflow elements of fluid to be larger than the average size of the particle-associated mixing stages or permanent eddies. Such backflow streamers would of course mix with the fluid in stages directly upstream and thus would be the means for conveying a signal against the main stream. Such random backflow motions would provide the physical basis for a purely diffusive transport. If backflow is a predominant effect the form of the system may be closely approximated by a normal differential diffusion equation and characterized by a meaningful diffusion constant.

However, in the absence of backflow, and when the predominant dispersion effect is due to mixing in stages, reactor design should be accomplished by the solution of the difference equations which represent the discrete nature of the physical situation. Under the latter circumstances a diffusion constant in the local region of a well-stirred eddy must approach a value of zero and the designation of the diffusion equation to describe the state becomes meaningless. Although there have been no direct experiments devised, to date, to measure the extent of backmixing, the value of the axial Peclet number of *two* as determined by measurements in the limits of *deep* beds gives strong evidence that stage-wise mixing rather than backmixing is the predominant dispersion action. It will be recalled that the Peclet number is an inverse proportionality constant in the Einstein equation; it represents the spreading rate of a tracer pulse after a large number of mixing cells have been traversed if each cell is one particle diameter in depth. Aris and Amundson[20] analysed the axial dispersion property by tracing the changes in the probability density function with distance into the bed. This function, it will be recalled, is the probability that a molecule, introduced into the first mixer at the bed entrance at time, $T = 0$, will be located in the nth layer at time, T. As expected, a Poisson distribution represents conditions in the initial discrete stages at the bed entrance; with increasing bed depth and number of mixing stages a normal distribution is approached for which the diffusion equation becomes an appropriate description. A substantial approach toward this limit occurs in a depth of about twenty particles. The first authors to propose the cell mixing model, Kramers and Alberda[21]

analysed the same problem by making theoretical comparisons of the frequency response properties of the solutions of difference and of differential equations at various bed depths for a forcing sinusoidal tracer concentration input.

In order to summarize this point, we can state that within the specified high-velocity fluid mechanical regime a single model now exists which describes satisfactorily both lateral and axial dispersion effects in packed bed reactors. However, if the only advantage in the prescription of a difference equation formulation were to describe properly reaction behaviour in the regions of the bed entrance the accomplishments would be small at best. The significant gain is derived from a mathematical simplification which has a decisive advantage as we look forward to the detailed design of reactors for realistic chemical kinetics. As stated previously, if backmixing were important in contributing to axial dispersion, coupled non-linear differential equation heat and mass balances would be the appropriate system descriptions and the state within the reactor would depend on both the upstream and downstream boundary conditions. This state would lead to a mathematical situation that for a complete model is analytically intractable and numerically beyond present digital solution capacities in a practical sense. On the other hand, in the difference equation stirred-tank model, only conditions at the bed inlet need be satisfied and calculation may proceed down the bed in a so-called step by step marching technique.

REACTOR COMPUTATION

In a recent significant study[22], my colleague Lapidus and his collaborator, Deans, formulated a finite stage mathematical model for a fixed bed reactor in a form suitable for digital machine computations. The underlying basis of the work was the physical model of dispersion such as has been discussed here. The problem was reduced to two dimensions, because of radial symmetry, by the use of stirred volume elements which vary in size with radial distance, as shown in the wedge-shaped structure in *Figure 6*. The presence of two possible outlets from each perfectly stirred chamber produces a mixed average equivalent of particulate random walk and the axial dispersion mechanism also is retained. As an actual array of particles contains many more interconnecting passages than the computer model, this minimal mathematical formulation of the array was first tested by machine simulation of the axial and radial dispersion experiments which were published earlier. A very satisfactory agreement was secured between the results of the actual and simulated experiments. It is well known that the experimental radial Peclet number may vary because of such factors as particle shape and roughness: computer corrections may be made to match a set of actual bed properties. Transient phenomena and Taylor axial diffusion effects, such as occur most frequently in liquids, may also be readily included in the model.

When a chemical reaction rate is to be included in the formulation, one must deal in principle with mass balances that are non-linearly coupled with an energy balance. Depending upon the stoicheiometric relations, the number of mass balances may, under some circumstances, be selected so as to be

small in number. The virtue of the difference equation model is retained in a chemical reactor calculation, namely that the solution for the state of the exterior field retains its character as an initial value problem. At each geometric position in the bed, computational sub-routines may be called upon to supply a quantitative measure of the heat and mass flux rates issuing from the reactive particles into the external field of a given mixer element. Included, of course in these fluxes, would be the effects of all *intra*particle and *inter*phase rate processes.
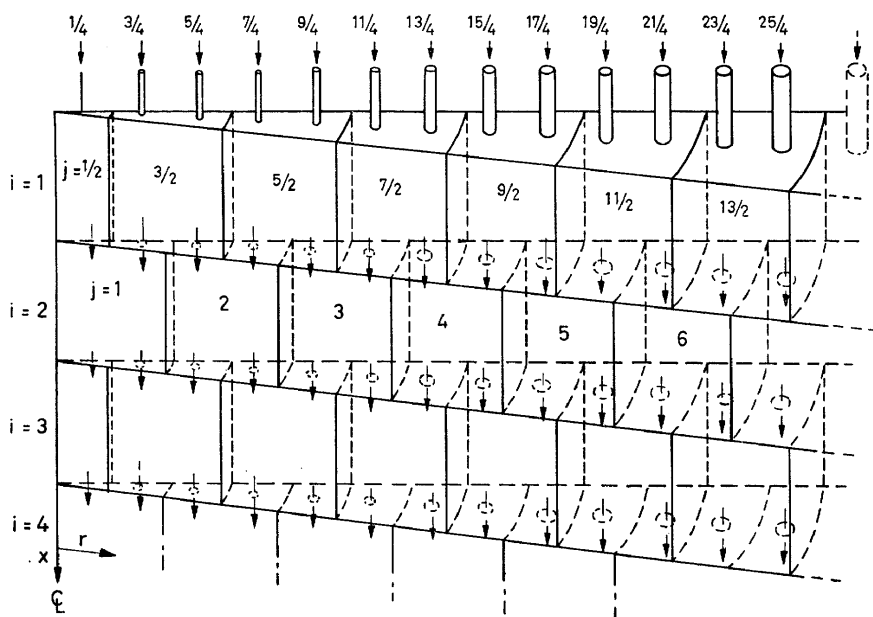

Figure 6. Finite stage basis for mathematical model of fixed bed reactor

As a test case Deans computed the temperature and concentration profiles on an IBM-704 computer for a first order reaction with an Arrhenius temperature function and with the inclusion of major physical effects such as radial and axial mixing, thermal coupling of heat and mass balances and heat transfer through the walls. A steady state solution for 360 stages in the axial direction required a machine time of only 35 seconds. Although the particle-to-tube ratio was only 10:1 in the illustrative example, there is no obvious computational upper limit to this ratio in steady state calculations except memory storage capacity. From these explorations it seems reasonable to conclude that even with moderately complex kinetics the computational means are now at hand for at least initial trials in the *a priori* steady-state design of packed bed reactors of industrial size and complexity.

It is often of interest to explore the transient responses of a reactor as, for example, in the starting of a reactor or in the assessment of reactor stability and controllability. In transient calculations the ordinary algebraic difference equations become ordinary non-linear difference-differential equations because of the inclusion of the derivatives of composition and temperature

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with time. The digital machine solutions for composition and temperature transients become more difficult than in the steady-state case with regard to matters of computational technique and substantially more time consuming. In fact it may take days to compute one complete dynamic response for an industrial size reactor.

Although the greatest initial interest in an *a priori* design is naturally centred on the steady-state properties of the reactor, it seems worth noting that in the next few years we may expect the computational time for transient analysis to be reduced drastically through an increasing availability of hybrid computers. These computers combine, in various ways, the most suitable features of an analogue computer with digital computers and memory storage capacity. Such combination computers will doubtlessly also increase the number of choices available among computing systems which are suitable for the steady-state design of reactors of any given complexity.

POTENTIALS AND LIMITATIONS

As soon as any new method of accomplishing objectives appears on the horizon, questions must be asked about its advantages compared to present procedures and especially about its limitations. Regarding advantages, since a computer model provides for the variables which change with reactor dimensions and capacity it is not difficult to envisage that its use as an adjunct to experimental work may well serve to decrease the number of costly developmental steps in the scale-up procedures between the laboratory and plant. One may anticipate also that simulation calculations will be used for the local optimization of reactor operation, reserving the pilot plant for verification of the model and of the optimum conditions. May I say at this point, however, that although the rôle of the pilot plant in the scale-up procedure may well change, a pilot plant serves many purposes and its demise is not being predicted, except perhaps in cases of kinetically very simple reactions. The ideas expressed here are not entirely new because simulation studies with analogue and with digital computers already are being pursued in the case of simple reactor types in which spacial distributions of the dependent variables are not significant, the so-called lumped parameter reactors of the second class that were mentioned earlier.

It will also be recognized that any computational scheme will be useful in a scientific or engineering sense only to the extent that the required physical and chemical constants are known accurately and to the extent which the model expresses the major mechanistic features which are important. Here, I shall comment on the availability of necessary information with regard to packed bed reactors.

CHEMICAL RATES

In reactor studies there is a paramount need to secure reliable and broadly valid chemical rate expressions. As part of the trend towards detailed reactor analysis, if not for other purposes, there is a trend towards an increase in the practice of starting a development with careful, well-planned laboratory rate studies and analyses. Increasingly statistical procedures are being brought to bear for the purpose of estimating values of the rate parameters,

of determining the precision of these parameters and, finally, of evaluating how adequately any derived theoretical mechanism model fits the data. It is suggested that another important part of a broad-based laboratory investigation is the provision of auxiliary means, other than precision of fit, for judging the self-consistency of a rate model. Several recent publications bear especially on these points. In a study of the water-gas shift reaction, Hulbert and Vasan[23] on the basis of an analysis of variance, concluded that the classic Temkin formulation did not apply to their catalyst, but on the other hand, two other possible models could not be distinguished within the precision of the data. Consequently, it was suggested that special experiments must be designed to elucidate mechanisms. Another paper, by Peterson[24], illustrates the advanced computational procedures of non-linear estimation as applied to the data of Ioffe and Sherman for the purpose of determining the kinetics and mechanism of naphthalene oxidation. The method was originally suggested by Box[25]. A final paper, by Sinfelt, Hurwitz and Shulman[26] provides a good illustration of the problems of developing self-consistent models. An identical over-all formulation for the catalytic methylcyclohexane dehydrogenation, consistent with the rate data, was secured by application of both the Langmuir-Hinshelwood catalysis formulation and a pseudo-steady state formulation. The latter formulation was given preference because of consistency with auxiliary information about the adsorptive properties of reactants and products.

Considering the transport properties in the various parts of packed bed reactors it is of interest to determine the adequacy of theories for reaction-diffusion coupling in the local *inter*particle, *inter*phase and *intra*particle regions. We are also concerned with the availability of the necessary transport constants. Finally, it is of interest to know if there are any criteria by which one can determine whether local variables in any part of the system may safely be excluded from the over-all formulation in an *a priori* design analysis. These subjects are extensive and only brief comments can be made about them here.

INTERPARTICLE FIELD

May I remind you that the solution of the exterior field problem with its mixing cell mechanism leads to the determination of point-by-point temperature and composition profiles. The results of a typical profile calculation in *Figure 7* illustrate a temperature maximum as encountered in an exothermic reaction. A substantial and quite satisfactory supporting literature exists for evaluating quantitatively the needed information about momentum losses for flow through a packing[27] and also for heat transfer through an assembly of particles; in the latter transport process consideration is given to the combined effects of flow, particle conductivity and radiation[28-31]. The properties in the centre of a large tube of particles are governed by the random statistical character of the bed. However, near the walls the surfaces serve to encourage an orderly arrangement of particles. In an interesting study by Roblee, Baird and Tierney[32] the average void fraction was found to be a function of the distance from the wall. A damped wave characteristic of the fraction void showed that random bed properties may not be assumed

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at least within two particle diameter distances from the wall. The effect of this transition between order and disorder on the boundary heat transfer characteristics is a difficult yet important subject that deserves to receive further research attention. I believe it can be said, however, that, with the exception just mentioned, design theory and estimates of the various transport constants needed for the calculation of the interparticle field are moderately well in hand. A similar statement also can be made about the limitations of the problem. Damkohler[5], at an early date, furnished a means of estimating conservatively the magnitude of the maximum temperature rise (or depression) in a reactor in the limit of small changes. Under such limiting conditions, temperature and heat release rates become parabolic functions of tube radius. In his development Damkohler assumed that the composition governing the reaction rate at the position of the maximum does not differ significantly from the inlet concentration, at least for the purpose in hand. The locus of the upper, stability limits, beyond which jacketed exothermic heat-exchanger reactors are no longer capable of permitting maxima to occur in axial temperature traverses, was presented recently by Barkelew[33].

INTERPHASE FIELD

We now turn to a brief view of the diffusion–reaction problem at particle surfaces in a packed bed. Because of the complicated flow patterns that exist in a bed, a simplified theory is used in which an effective hydrodynamic laminar film is presumed to provide the resistance to the diffusion of heat and of mass between the exterior field and the catalyst surface. The mass diffusion flux of each component through the film is balanced by the reaction flux at the surface. Reaction and diffusion rate steps occur in a series arrangement and the net result is a relationship of the form given in *Figure 8*, assuming a first order surface reaction for simplicity. The over-all rate, K, depends upon the film diffusion coefficient k_d and the reaction rate constant k_r in the reciprocal relationship shown. The reaction rate constant usually varies exponentially with temperature and is, of course, not dependent on fluid velocity. Mass transfer film coefficients, by contrast, have a small temperature dependence and a substantial dependence on average fluid velocity. The net result of these dependencies is the existence of chemically controlled and diffusion controlled regions of behaviour which are illustrated by the experimental data of Tu, Davis and Hottel[34] for the combustion of carbon. Such regimes are revealed when temperatures are changed over a wide range of values, or velocities are varied substantially at constant time of contact. There is ample evidence from the work of Wicke[35,36] on the reactions of carbon, and of Hurt[37] and Hulburt[23] on high-duty catalytic reactions, that the phenomenon of diffusive transfer at surfaces of packed beds can be important or controlling in gas-phase reactions even though such diffusion rates are normally very large.

An important contribution to reactor technology has been the experimental determination of generalized correlations for surface heat and mass transfer coefficients in beds of particles. The initial gas-phase studies of Gamson, Thodos, and Hougen[38] and liquid-phase studies of McCune[39] have been augmented by those of about ten other groups until, by now, a substantial
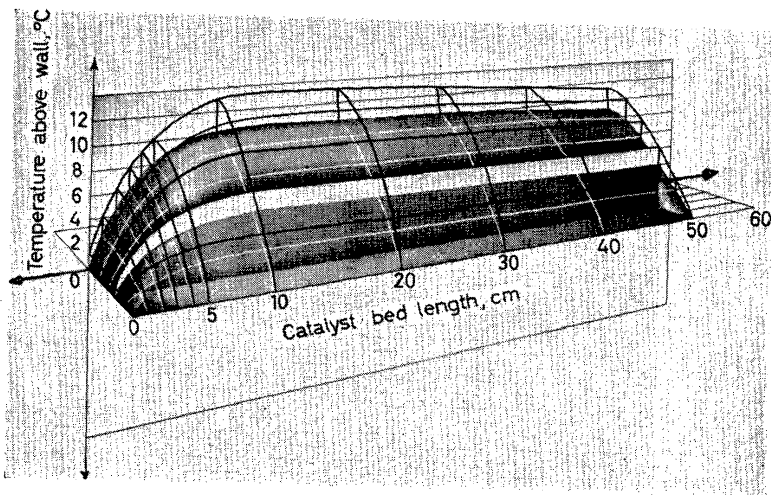
Figure 7. Computed temperature profile in fixed bed reactor showing gas and solids temperatures: exothermic reaction

design basis[40] is available for estimating average surface transport coefficients under a large variety of hydrodynamic circumstances. However, as pointed out by Beek, the mass transfer studies in question have been restricted to one directional diffusion of dilute components whereas diffusion during reaction conditions may well involve high concentrations of components and unbalanced diffusion fluxes. Such multi-component Strefan–Maxwell diffusion problems are complex at best, and estimates of diffusion flux interactions under turbulent flow and film transport conditions presently must be verified experimentally[41]. Much research remains to be done in film transport under high concentration multi-component conditions.
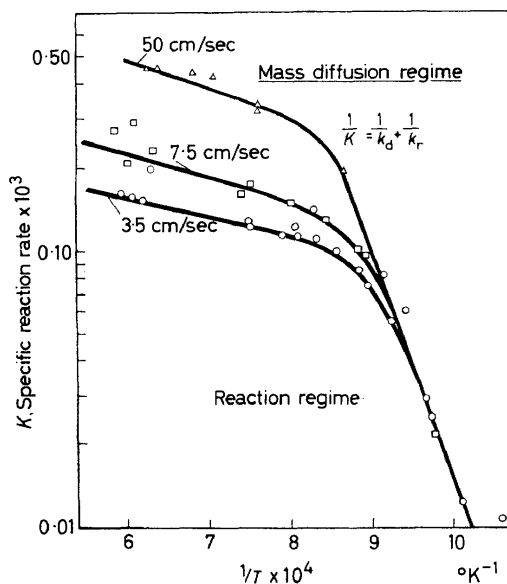

Figure 8. Reaction–diffusion at an interface showing transition between reaction regime and mass diffusion regime

The principles governing the limits of behaviour for interphase transport were developed some years ago and still retain their validity. The conditions for thermal instability with two steady states were first set forth by Frank-Kamenetskii[6] and those for the dominance of the chemical regime, by Hougen[42].

INTRAPARTICLE FIELD

The development of theory regarding transport and reaction within catalyst pellets is occurring more rapidly at present than at almost any time since the original isothermal theories of Thiele[43] and Zeldovich[44] were proposed in 1939. Present studies undertake to include the effects of thermal as well as of concentration gradients on the interior distribution of reaction rates and on the effectiveness of the interior surface for reaction.

In the isothermal theory which considers only mass transport and reaction, the diffusional resistance within the pores of a pellet serves to reduce the

concentration of reactant toward the centre of the pellet, thereby decreasing the average rate of reaction over the pellet, or its effectiveness, η. From dimensional arguments in *Figure 9*, let us develop the modulus on which the value of the effectiveness depends. Consider one pore into which a reactant is diffusing and reacting heterogeneously at the surface. The first equation is the Einstein equation in which the square of the mean diffusion distance is related to the local diffusion constant and time. Let us now consider the distance of penetration corresponding to the half-life of reaction, which is inversely proportional to the chemical rate constant. In doing so the defin-

ition of ϕ, the characteristic modulus, immediately becomes $\Phi = R\left(\dfrac{k}{D}\right)^{\frac{1}{2}}$.

The effectiveness factor, in turn, is the volume average rate of the diffusion-hindered reaction, compared to reaction in the same volume when the exterior concentration is completely accessible to all parts.

Integrations for different geometries and reaction kinetics lead to $(\eta - \phi)$ relations, which for simple kinetic systems are well recorded in the literature and which, when necessary, are computed numerically for complex kinetics. The contributions of interior mass diffusion to catalyst selectivity have been studied theoretically by Wheeler[45].

$$L^2 = 2Dt$$
$$t_{1/2} \sim \frac{1}{k}$$
$$L^2 \sim \frac{D}{k}$$

Modulus $\qquad \phi = L\left(\dfrac{D}{k}\right)^{1/2}$

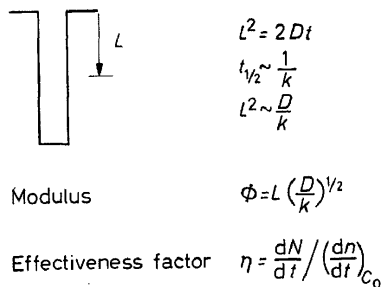Effectiveness factor $\qquad \eta = \dfrac{dN}{dt}\Big/\left(\dfrac{dn}{dt}\right)_{c_0}$

Figure 9. Definition of rate modulus and effectiveness factor for reaction and diffusion within a catalyst pellet

There is now ample evidence of the validity of the Thiele–Zeldovich model. For example, Wicke[36] and his co-workers who also pioneered in pore diffusion-reaction studies, were able to explain a wide scattering in the magnitude of the energy of activation in earlier work for the Bouduard reaction of $CO_2 + C$ by showing that such studies were, in fact, encompassed between the theoretical limits of a factor of two in the energy of activation. Apparently, earlier workers had inadvertently conducted experiments in a transition region between the natural limits of reaction predominance and diffusion predominance. A recent study on the combustion of carbon by Blyholder and Eyring[2] also yielded the predicted limits in the energy of activation. Changes in apparent order of reaction that are consistent with the theory were realized as well by these authors. Weisz and Prater[46] found that the isothermal Thiele–Zeldovitch theory provided a good model for the description of particle size and temperature effects in the cracking of cumene and also in the combustion of deposited carbon within silica-alumina catalysts. As a last example, Peters and Krabetz[47] accounted for deviations

from the Temkin–Pyzhev formulation for the synthesis of ammonia on an iron catalyst by analysis of interior pore diffusion effects.

Turning now to temperature effects, the maximum temperature rise which may be expected in a particle was first formulated by Damkohler[48] for a sphere, for any particle shape by Pshezhetskii and Rubenstein[49] and also for the general case by Prater[50] in an alternative formulation. The last-mentioned author showed that whereas the temperature rise during the combustion of carbon on a catalyst is very small, the temperature change is indeed significant in the dehydration of cyclohexane on a platinum-supported catalyst. A truism which had grown in the literature, namely, that a temperature change within a catalyst pellet is not likely to be important was thereby denied.

Within the past two years some half dozen independent solutions, analytical or numerical, have been brought forward for the combined heat and mass balances for reaction within a catalyst pellet. The initial presentation was by Schilson and Amundson[51] in 1959. Because of temperature enhancement of reaction rate it is shown that in the case of exothermic reactions effectiveness factors may rise to values substantially larger than unity and, in a given system, there may be a particle size which will correspond to a maximum of effectiveness.

A practical criterion for conditions which assure the substantial absence of diffusional effects in *intra*particle reactions, for all orders between zero and two, has been derived by Weisz[52] and has been shown to be valid in three experimental examples.

The particle interior is an interesting and complex system geometrically and catalytically, and also because of the number of alternative transport mechanisms that may exist. Perhaps this brief selection of recent investigations is indicative of recent research interests and directions. Mingle and Smith[53] made a theoretical analysis on the effect of the type of pore size distribution on catalyst effectiveness; Gilliland, Baddour and Russel[54] investigated transport mechanisms, particularly of the Volmer surface diffusion of large hydrocarbon molecules, and Sehr[55] compared three alternative methods of measuring the thermal conductivity of catalyst particles. The study of Tsu and Boudart[56] in our laboratory, on the recombination rates of hydrogen atoms on the surface of a giant single pore, is of special interest. The results suggest that surface diffusion transport may, at least in this instance, be part of the local act of heterogeneous chemical reaction.

CONCLUSION

I wish to suggest, in conclusion, that substantial progress has been made, in the case of packed bed reactors, toward the goal of being able to design such reactors from basic principles, rapidly and for realistic systems. The supporting physical and engineering sciences and the development of computational capabilities are sufficiently well advanced to encourage computational design explorations, at least in selected cases. A major problem, always, is to secure reliable chemical rate data and any widespread trend toward computational simulation may well serve to encourage the undertaking of basic laboratory chemical rate studies even more than at

present. A need for continuing research in certain engineering aspects of chemical reactors is indicated.

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