A Course in

TRANSPORT PHENOMENA IN MULTICOMPONENT, MULTIPHASE, REACTING SYSTEMS

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MOST OF THE SYSTEMS that are of interest to chemical engineers involve two or more phases, several chemical components, and a strong coupling between heat, mass and momentum transport. A cursory examination of the classical reactor design and mass transfer operations encountered in ChE suggests that the course title listed above would encompass a major segment of all ChE processes. A quick survey of the currently available texts designed for the training of graduate students in ChE reveals the need for a rigorous treatment of multicomponent, multiphase systems.

With the exception of the excellent text by Slattery (1972), the method of volume averaging as a rational route to the transport equations for multiphase systems is generally ignored. Although the method is little more than a decade old [Whitaker (1967), Slattery (1967)], we are rapidly approaching the point where the formalism is sufficiently well understood so that it is suitable for incorporation into our graduate courses. Under the circumstances, we believe that the general knowledge now available under the heading of "transport phenomena" is ready to be extended to include a rational treatment of multiphase systems.

One of the major strengths of the graduate program in ChE at U.C. Davis is a series of core courses available to the graduate students in fluid mechanics, heat transfer, mass transfer and chemical reactor design. These courses are taught at a level consistent with texts by Aris (1962), Whitaker (1968, 1977a), Bird, Stewart and Lightfoot (1960) and Smith (1970). These courses provide a sound introduction to the laws of continuum physics for single component systems and deal with a variety of multiphase systems via simplified models. To supplement and consolidate this material, a course was instituted that would concentrate on a rigorous development of the multicomponent transport equations, boundary conditions at phase interfaces, and volume-averaged transport equations for multiphase reacting systems. The lecture notes represent the origins of a graduate level text in chemical reactor design.

Reactor design texts uniformly assume a level of sophistication below that of Bird, Stewart and Lightfoot (1960) and have paid no heed to the method of volume averaging given by Slattery (1972). While these developments are perhaps recent by engineering time scales, the subject of fluid mechanics is ancient by comparison (Truesdell, 1968) and its incorporation into our studies of reactor design is long overdue.

Reactor design is the one area that is purely the province of the ChE, and it is the most appropriate vehicle for describing the intricacies of the coupling of momentum, heat and mass transport for multicomponent multiphase systems. It is not unusual to find reactor design texts (Smith, 1970; Carberry, 1976; Aris, 1969) that do not mention the governing differential equations for conservation of a given species, or the momentum and thermal energy equation for multicomponent systems, even though these equations govern all transport processes in chemical reactors. The development of appropriate governing differential equations (via volume averaging) for transport in multiphase systems (chemical reactors) is not included. This is probably the major failure of such texts. The normal procedure is to assume in an ad-hoc fashion that the form of the transport equations and fluxes in multiphase systems are the

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same as those for a homogeneous fluid but with appropriate empirical parameters. The dependence of these parameters on the structure of the porous media and the physical properties of the components and the chemical reaction rate is left unexplored.

A good example of this approach is the governing equation usually proposed to describe diffusion and chemical reaction within a catalyst pellet. The catalyst pellet is treated as a homogeneous medium, and diffusion in such pellets is assumed to be governed by means of flux expression analogous to Fick's Law of Diffusion with an effective intraparticle diffusivity. However, using volume-averaging techniques, it is possible to obtain differential equations for diffusion in a porous media and a mathematical description of the dependence of the intraparticle diffusivity on system parameters. One advantage of such an approach is that it allows for a more thorough investigation of the assumptions normally made regarding the magnitude of terms in the governing differential equation. Furthermore, an accurate mathematical description of transport parameters in multiphase systems allows for the development of a more rational experimental program aimed at unraveling the magnitude of different contributions to the transport parameters. Finally, this type of analysis provides the student with a more rigorous framework to carry on further studies and helps to place in perspective within the student's mind the interrelations between transport processes in a homogeneous fluid and in a porous media.

In the paragraphs that follow, we outline the content of this course and the way in which the material is presented. We feel this provides a more rational approach to the training of graduate students in chemical engineering.

AXIOMS FOR SPECIES BODIES

THE FIRST THIRD OF the course is always devoted to the essential theoretical elements of transport in multiphase systems. The presentation is based on the continuum point of view, thus the laws of physics for multicomponent systems are the first order of business. Here we follow the approach of Truesdell and Toupin (1960) and introduce the concept of a *species body*. The kinematics, ie., time derivatives of point functions and volume integrals, of species bodies are carried over from previous studies of single component systems. The general balance equation for single component systems

$$\frac{D}{Dt}\int_{V_m(t)} \psi dV = \int_{A_m(t)} \omega dA + \int_{V_m(t)} \sigma dV \qquad (1)$$

is easily extended to the species body and the axioms for mass are stated as

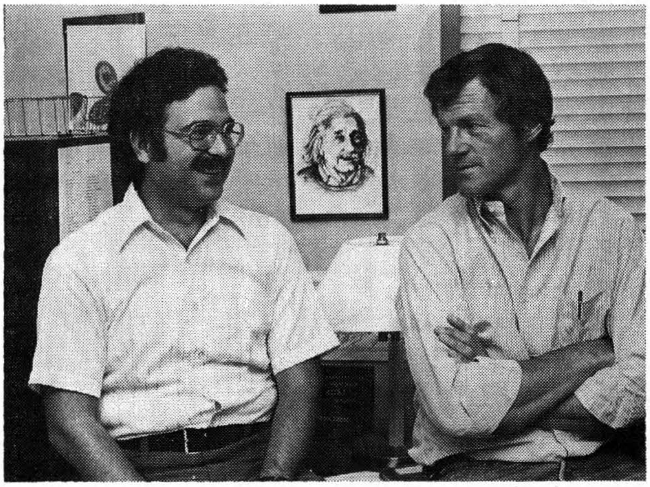
I. The mass postulate for the A^{th} species

$$\frac{D}{Dt}\int_{V_A(t)} \rho_A dV = \int_{V_A(t)} r_A dV \qquad (2)$$

II. Conservation of total mass owing to chemical reaction

$$\sum_{A=1}^{A=N} r_A = 0 \qquad (3)$$

Equation 2 quickly leads us to the species contin-



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uity equation in terms of the species density and mass average velocity,

$$\frac{\partial \rho_A}{\partial t} + \nabla \cdot (\rho_A \mathbf{v}) = -\nabla \cdot \mathbf{j}_A + r_A \tag{4}$$

or in terms of the concentration and the molar average velocity

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}^*) = -\nabla \cdot \mathbf{J}_A + R_A \tag{5}$$

The latter form is, of course, preferred by chemical engineers because kinetic constitutive equations and phase equalibrium relations are most conveniently stated in terms of molar quantities.

The presence of the mass average velocity in Eq. 4 and the molar average velocity in Eq. 5 naturally raises questions about the determination of these velocities by means of the laws of mechanics. At this point the revised linear and angular momentum postulates are introduced and the derived species equations are summed to obtain

$$\rho \frac{D\mathbf{v}}{Dt} = \rho \mathbf{b} + \nabla \cdot \underline{\underline{\mathbf{T}}} \tag{6}$$

$$\underline{\underline{\mathbf{T}}} = \underline{\underline{\mathbf{T}}}^t \tag{7}$$

Here the stress tensor consists of the sum of partial stresses and species diffusive stresses. It is consistent with the kinetic theory of dilute gases to represent $\underline{\underline{\mathbf{T}}}$ in terms of the rate of strain tensor; however, the idea of equipresence (Truesdell and Noll, 1965) is envoked in order to keep the door open for more general constitutive equations.

The pattern of analysis is now established and the revised energy axioms are presented for a species body. The development is restricted to what Bataille and Kestin (1977) refer to as "strongly interacting mixtures", and the thermal energy equation for the mixture is obtained by summing the individual species equations leading to

$$\rho \frac{De}{Dt} = -\nabla \cdot \mathbf{q} - \nabla \cdot \sum_{A=1}^{A=N} h_A \mathbf{j}_A - p \nabla \cdot \mathbf{v} +$$

$$\nabla \mathbf{v} : \underline{\underline{\tau}} + \Phi + \left\{ \begin{matrix} \text{diffusive terms of} \\ \text{negligible importance} \end{matrix} \right\} \tag{8}$$

where e is the internal energy of the mixture defined in the usual manner. The result is also presented in terms of the enthalpy for later use in constructing boundary conditions at phase interfaces, and in terms of the temperature. The latter form is, of course, useful for solving energy transport problems and gives rise to the source term owing to chemical reaction. The diffusive terms in Eq. 8 consist of the diffusive kinetic energy, diffusive rates of working, etc., and order of magnitude analysis (Whitaker, 1977) can be used to establish that these terms are negligible for practical cases.

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BOUNDARY CONDITIONS AT PHASE INTERFACES

WITH THE TRANSPORT equations for multicomponent systems at our disposal, we are naturally led to consider the matter of boundary conditions at phase interfaces. Following a route similar to that proposed by Slattery (1972), we develop a general surface transport equation. In integral form this transport equation is represented as

$$\frac{D}{Dt} \int_{A_{\alpha\beta}(t)} \Psi dA + \int_{C} \Omega ds - \int_{A_{\alpha\beta}(t)} \Sigma dA =$$

$$\int_{A_{\alpha\beta}(t)} [\psi^\alpha (\mathbf{v}^\alpha - \mathbf{w}) - \psi^\beta (\mathbf{v}^\beta - \mathbf{w})] \cdot \underline{\xi}_{\alpha\beta} dA + \int_{A_{\alpha\beta}(t)} (\omega^\alpha - \omega^\beta) dA \tag{9}$$

Here the upper case Greek letters denote the intrinsic surface quantities associated with the lower case Greek letters in Eq. 1, the area $A_{\alpha\beta}(t)$ represents a material surface element, $\underline{\xi}_{\alpha\beta}$ represents the unit normal vector pointing from the α-phase into the β-phase, and w represents the velocity of the interface.

At this point in the course, special forms of Eq. 9 are considered, i.e., the surface element $A_{\alpha\beta}(t)$ is fixed in space, or the surface is flat, or all the terms on the left hand side are zero. These severe restrictions are necessary because the rigorous analysis leading to the surface transport equation (Aris, 1962), makes use of the surface divergence theorem and a general understanding of differential geometry (McConnell, 1957). The subject is of considerable interest to chemical engineers (Rosner, 1976; Berg, 1970), but, as yet, a simple route to the desired result has not yet been found. Both Professor Rosner at Yale and Professor Slattery at Northwestern are preparing monographs on this subject, and their works will certainly help us with the treatment of this aspect of multiphase transport phenomena.

We avoid the vector form of Eq. 9 altogether, and consider only special cases associated with heat and mass transfer along with chemical reaction at the interface. While the attack here is obviously something less than what we would desire, it does allow us to point out just how it is that we go about constructing boundary conditions at phase interfaces, ie., we make specific statements about the left hand side of Eq. 9 based on experimental observations. For example, if we use the *species form* of Eq. 9 associated with the mass postulate given by Eq. 2 and make the statements

ψ_A = constant (surface concentration is constant)
$\Omega_A = 0$ (follows from Eq. 2)
$\Sigma_A = 0$ (there is no surface reaction)
$\overset{(A)}{A}_{\alpha\beta}(t) = \overset{(A)}{A}_{\alpha\beta}$ (the Ath species surface element is fixed in space)

we find that Eq. 9 leads us to *continuity of mass flux* expressed as

$$\overset{\alpha}{\rho}_A(\overset{\alpha}{\mathbf{v}}_A-\mathbf{w})\cdot\underline{\xi_{\alpha\beta}} = \overset{\beta}{\rho}_A(\overset{\beta}{\mathbf{v}}_A-\mathbf{w})\cdot\underline{\xi_{\alpha\beta}} \qquad (10)$$

This approach forces one to specifically identify the characteristics of the surface en route to Eq. 10, as opposed to specifying continuity of mass flux with either vague or non-existent references to the properties of the surfaces.

THE VOLUME AVERAGING THEOREM

With the multicomponent transport equations and multiphase boundary conditions at our disposal, we can proceed to the study of transport phenomena in multiphase systems. Our prime mathematical tool here is the spatial averaging theorem [Slattery, 1967; Whitaker, 1967; Gray and Lee, 1977; Bachmat, 1972] which can be stated as

$$<\nabla\psi_\alpha> = \nabla<\psi_\alpha> + \frac{1}{V}\int_{A_{\alpha\beta}(t)} \psi_\alpha \mathbf{n}_{\alpha\beta}\,dA \qquad (11)$$

for a two phase system. Here the angular brackets are used to denote the volume average which is given by

$$<\psi_\alpha> = \frac{1}{V}\int_V \psi_\alpha dV = \frac{1}{V}\int_{V_\alpha(t)} \psi_\alpha dV \qquad (12)$$

where V represents the averaging volume

$$V = V_\alpha(t) + V_\beta(t) \qquad (13)$$

The second of Eqs. 12 is obtained because ψ_α is zero in the β-phase.

AREAS OF APPLICATION

Armed with the governing differential equations, a scheme for constructing boundary conditions and the volume averaging theorem, we are ready to explore a variety of phenomena. The choice here depends on the students and instructor. On the Davis campus there is a large Water Science and Engineering group, and students from that discipline are interested in the theoretical underpinnings of d'Arcy's law (Gray and O'Neill, 1976), dispersion in porous media (Whitaker, 1967), and multiphase flow in porous media (Slattery, 1970). Chemical engineering students show an interest in these subjects provided one mentions oil reservoir calculations, tertiary oil recovery processes and the moderate Reynolds number flows that occur in packed bed reactors. Recent studies of trickle bed reactors (Herskowitz, Carbonell and Smith, 1978) indicate the importance of the hydrodynamics of two-phase flow in packed bed reactors and this subject can be attacked in a rational manner using the method of volume averaging, although the contact line phenomena escapes our understanding at the moment. The hydraulics of distillation trays and the mechanics of sediment transport are other subjects that can be profitably analyzed using the volume averaging method.

For chemical engineering students, the problems of heat and mass transfer in porous media hold the most interest. In particular, the unravelling of previous ad hoc developments of transport processes in catalyst pellets has considerable appeal and represents a challenging theoretical problem. If one avoids the problem of Knudsen and transition region diffusion and restricts one-

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self to linear adsorption isotherms and linear, irreversible kinetics, one can volume average Eq. 5 to obtain

$$\epsilon_\alpha \left(1 + \frac{K a_v}{\epsilon_\alpha} \right) \frac{\partial \langle c_A \rangle^\alpha}{\partial t} + \nabla \cdot [\langle c_A \rangle^\alpha \langle \mathbf{v}^* \rangle] + \nabla \cdot \langle \tilde{c}_A \tilde{\mathbf{v}}^* \rangle = \nabla \cdot \left\{ \epsilon_\alpha D_A \nabla \langle c_A \rangle^\alpha - \frac{D_A}{V} \int_{A_{\alpha\beta}} \tilde{c}_A \mathbf{n}_{\alpha\beta} \, dA \right\} - a_v k K \langle c_A \rangle^\alpha \tag{14}$$

Here we are confronted with two unknown parameters $\tilde{c}_A \tilde{\mathbf{v}}^*$ and $\tilde{c}_A$ for which we need constitutive equations. The route to be followed here has been hinted at in prior publications (Whitaker, 1967, 1971, 1977b) but never fully exploited. Essentially, it represents the closure problem of turbulence (Launder, 1976) and requires that the transport equations for $\tilde{c}_A$ and $\tilde{c}_A \tilde{\mathbf{v}}^*$ be derived. In the study of turbulence the closure is obtained by proposing constitutive equations for the higher order correlations in the Reynolds stress transport equations; however, this is impossible for the $\tilde{c}_A$ and $\tilde{c}_A \tilde{\mathbf{v}}^*$ transport equations because the geometric details of the porous media are unknown. Nevertheless, the transport equations for $\tilde{c}_A$ and $\tilde{c}_A \tilde{\mathbf{v}}^*$ can be used as a guide for the direct construction of constitutive equations required in Eq. 14. This type of approach leads to a transport equation for $\langle c_A \rangle^\alpha$ of the form

$$\epsilon_\alpha \left(1 + \frac{K a_v}{\epsilon_\alpha} \right) \frac{\partial \langle c_A \rangle^\alpha}{\partial t} + (\langle \mathbf{v} \rangle + \mathbf{A}) \cdot \nabla \langle c_A \rangle^\alpha = \nabla \cdot \left\{ \underline{\underline{\underline{\underline{\mathbf{D}}}}} \vdots \langle \mathbf{v} \rangle \langle \mathbf{v} \rangle \nabla \langle c_A \rangle^\alpha + \underline{\underline{\underline{\underline{\mathbf{K}}}}} \vdots \langle \mathbf{v} \rangle \langle \mathbf{v} \rangle \nabla \langle c_A \rangle^\alpha (a_v k K \langle c_A \rangle^\alpha) \right\} + \nabla \cdot \left\{ \epsilon_\alpha D_A \nabla \langle c_A \rangle^\alpha - \epsilon_\alpha D_A \underline{\underline{\mathbf{B}}} \cdot \nabla \langle c_A \rangle^\alpha \right\} - a_v k K \langle c_A \rangle^\alpha \tag{15}$$

Here the vector **A** and the second order tensor $\underline{\underline{\mathbf{B}}}$ are functions of the reaction rate parameter $a_v k K$ thus suggesting that the effective diffusivity may depend on the reaction rate and that the portion of the dispersive term which appears in the convective transport term also depends on $a_v k K$.

Equation 15 can be simplified for a variety of special cases and compared to transport equations in current use. Use of this method allows us to clearly identify the origin of dispersion coefficients and effective diffusivities and to say something about the dependence of these quantities on system parameters. It is important to notice that all the terms in Eq. 14 are precisely defined and thus susceptible to determination by the solution of boundary value problems for model porous media. Here we are thinking in terms of the work of Snyder and Stewart (1966), Sorensen and Stewart (1974), Payatakes et al, 1973, and forthcoming works by Brenner (1978) on both flow and mass transfer in spatially periodic porous media.

Other topics of interest in the reactor design area that can be handled using the volume-averaging approach include:

1. An analysis of flow distributions and flow instabilities in chemical reactors, in particular, trickle bed and fluidized bed reactors.
2. Determination of effective thermal conductivities for catalyst pellets and chemical reactors.
3. Determination of dispersion coefficients for chemical reactors. These topics and many others can be handled at the discretion of the instructor.

What we find most attractive about the approach followed in this course is that it provides the student with a rigorous framework with which to carry on further studies, and puts in perspective the interrelation between transport processes in a single phase and the analogous processes in multiphase systems.

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BOOK REVIEW: Thermodynamics

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features made the book a treat to review. On the other hand, the book has an unevenness about its presentation, in its continuity and its definition of some concepts. These shortcomings would make its use as an undergraduate text quite difficult; at the graduate level, a competent teacher would be required to aid the student in "reading between the lines" and filling in what this reviewer feels are gaps in the unified presentation of thermodynamics. There are very few problems to solve in the text except for the later chapters. The price of this book will probably discourage widespread course adoption as well.

In all fairness, however, the book is constructed from the viewpoint of an eminent thermodynamicist and, in that context, will satisfy the scientist or engineer who has had some experience or is presently working in the area of applied thermodynamics. Such an individual would find this book an enlightening refresher course on the fundamentals, with a broad enough selection of applications (presented in the form of examples) to satisfy most readers' particular interests. Those seriously interested in thermodynamics per se or the instruction of thermodynamics owe themselves more than a casual perusal of this book.

Chapter 3 on pure phases is a strong chapter particularly in its discussion of equations-of-state. Unfortunately, such an area is constantly undergoing change, and current workers will find the content somewhat outdated, a risk that every writer in this area runs. This chapter is preceded by thoughtful and challenging chapters on physics and the two laws of thermodynamics. This reviewer was impressed by Chapters 5-7 on phase equilibria and solutions; the author employs a kind of "case method" in the sense of using examples prior to the complete statement of what concept he has in mind demonstrating. The examples are quite interesting and often probe deeper into certain well-known thermodynamic phenomena than one is accustomed in a text (e.g., the inflection in the vapor pressure curve of a pure substance; the discussion of azeotropy; vapor-liquid criticality, although this topic is preceded by only a shallow attempt at explaining phase stability). Chapter 8 on electrolytes and Chapter 10 on work modes other than those of compression or expansion (entitled "various phenomena") are unique in comparison with existing texts and quite well done. Chapter 9 on chemical reactions is basically a collection of examples of the author's choosing.

This reviewer, although finding more than an occasional "gem" of insight in this book, had the feeling that the text was for the most part composed of material which significantly predates its publication date. The author appears influenced by the text of Lewis and Randall. The book lacks the "freshness" one finds in, e.g., the book by Modell and Reid, who are more successful in unifying the field of thermodynamics. Despite the shortcomings mentioned above, Redlich's book can reward the diligent reader with a sound perspective of thermodynamics and its practice. □