A Course in

HEAT AND MASS TRANSFER

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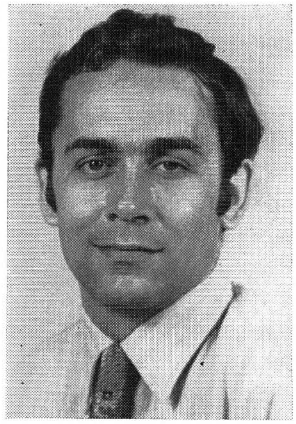
THIS COURSE HAS traditionally been taken by first year graduate students in Chemical Engineering, whether or not they intend to terminate at the Master's level or continue towards the doctorate. It is offered in the spring semester and is preceded in the fall semester by a fluid mechanics course, although students starting in the spring semester reverse the order with little apparent trauma.

The prime object of the course is to make a step change in the student's perception of and approach to the subject. Undergraduates are comfortable at a more or less elementary level of approach to heat and mass transfer. What is meant by comfortable is that they can define and solve transport problems which fit into this framework with a sense of security and, depending upon their undergraduate preparation, they have some kind of a feeling that there are other ways of approaching the same problems. They are rarely secure with these other approaches, however.

There are two dangers which arise in attempting to effect too rapid a change in a student's viewpoint. At one extreme he may not develop enough of a grasp of the more sophisticated viewpoint to feel secure with it. In his later work this student will fall back on the approach he is secure with (his undergraduate approach) and he will attempt to force problems he faces into this narrower framework. This student may make a fine engineer under some circumstances, but he has probably wasted much of his time in the course. At the other extreme the student decides all situations must be treated with the powerful new tools he has mastered. This student practices overkill at all opportunities and makes a mediocre engineer. Thus a student must not just understand the new approaches introduced in the course, he must also understand when and when not to use them. Although the course content is primarily engineering science, both words need to be taken seriously.

Herbert L. Toor was born June 22, 1927. He received his B.S. from Drexel Institute of Technology; his M.S. and Ph.D. from Northwestern University. He has been employed as Research Chemist, Monsanto Chemicals, Limited 1952-1953. He is presently Professor of Chemical Engineering (1961-) and Head of the Department of Chemical Engineering (1965-). He is the author of numerous papers on diffusion and a recipient of the Alan Colburn award of the AIChE. (Left)

Duane Condiff received his Ph.D. in Chemical Engineering from the University of Minnesota in 1965. Following this he spent one year doing post doctoral research in Theoretical Chemistry at the University of Wisconsin, and has been teaching Chemical Engineering at Carnegie-Mellon University for four years. His major research is conducted in the field of non-equilibrium statistical mechanics with emphasis upon applications to the molecular and particulate theories of transport.

It seems that the best way for a student to both learn new material and to get it in perspective is to solve lots of problems, and that is just what he does in the course. A mixture of various kinds of problems is used; exercises to help learn new material, frequently out of BSL, problems which require skillful application of the advanced material, problems which can and should be solved by elementary methods. The course meets four hours a week and slightly less than half that time is taken up with discussing problem solutions.

We find BSL to be most useful and although not used as a textbook (there is no real textbook for the course) students are expected to read and understand almost all the material in that book.

A few general rules. The student should not get bogged down in mathematics, a good physical feel for a situation is crucial; intuition, quick approximations and a feel for magnitudes and dominant effects need encouragement.

For pedagogical purposes it seems to be desirable to cover heat and mass transfer mostly sequentially, and since a good deal (but not all) of the heat transfer material can be carried over to mass transfer, somewhere between one half and two thirds of the first part of the semester is devoted to heat transfer. However, straightforward mass transfer analogies are noted as they arise throughout the first part of the course.

HEAT TRANSFER

The course starts out with a map of the field, a sketch of the various levels of analysis available and a categorization of the levels of analysis needed to handle various types of problems and to answer various types of questions. Review problems of the McAdams type are assigned here and macroscopic balances are briefly reviewed.

Differential balances are discussed from a general viewpoint and special and important examples in heat and mass transfer are obtained rapidly, leaving close examination of assumptions and approximations for later. This leads naturally into the constitutive equations of Fourier and Fick which are examined from various viewpoints. The extension to the general linear system is apparent at this stage but is not pursued until the later part of the course.

One dimensional conduction and convection problems are assigned and discussed during this period and while the student is gaining experience and a feel for the subject, a rather rigorous derivation of the energy equation is presented both for pure components and mixtures with concentration gradients.

A nice way to introduce unsteady conduction is through source solutions and reflection methods which depend heavily on physical concepts, but later emphasis is placed on similarity solutions and Sturm-Liouville methods. Ideas of relaxation times, penetration times and distances, the relationship between Nusselt numbers and temperature profiles are emphasized and then extended from non-flow to flow situations. Dimensional analysis of complex differential equations is stressed emphasizing the viewpoint that in most situations an engineer neither needs nor is able to obtain complete solutions to the energy equation, but that the equation still remains a powerful tool. The general definition of a Nusselt Number is used to attempt to drive students away from the use of the "film coefficient" terminology, not always with complete success.

Examples of misbehaved Nusselt Numbers, multiphase systems, frictional heat generation, particularly in boundary layers are used to emphasize the limitations of the normal ideas of heat transfer coefficients.

Energy and mass transport in turbulent fluids present their normal difficulties in a course of this type. The best we can do with the available time as far as the modern ideas go, is to sketch some of the basic concepts of statistical turbulence, the state of the art and the relationship of the fine scale to the course scale. The main emphasis is placed on the time averaged equations and eddy diffusivities. The similar mathematical structure of the time averaged equations to the equations used earlier in describing non-turbulent systems is used to show the underlying unity in gradient transport systems. The history of analogies is considered and their relationships to the boundary value viewpoint is stressed. Film and penetration ideas are also discussed briefly at this stage and various engineering applications are treated.

The subjects of radiation and heat transfer with phase changes are treated primarily with problem assignments, mainly because of time constraints.

MASS TRANSFER

The relationship between mass and heat transfer is somewhat like the relationship between the English and American languages; if you know one subject you can get by in the other, but confusion and embarassment are a consequence of not recognizing the difference between the two.

The general reference velocity is treated as a linear combination of component velocities and the more common reference velocities are then shown to be useful special cases.

The constitutive equation in the simple binary system is first obtained as the linear relationship between the flux and concentration gradient which must go to zero when the system is at a uniform concentration, and the consequences of using different concentration measures or thermodynamic functions are considered.

The choice of the usual binary diffusivity is shown to be a consequence of its symmetry $D_{12} = D_{21}$ and the inverted form of the diffusion equation, the Stefan-Maxwell form, is used to bring out the essential arbitrariness in the usual formulations.

After considering the relationship between diffusion and random walk processes, Brownian motion, the Stokes-Einstein equation, and the prediction of binary diffusion coefficients, irreversible thermodynamics is used as a convenient way to obtain general forms of the constitutive equations both for heat and mass transfer, and various kinds of coupled systems are considered.

At this point a comparison of the dimensionless energy equation with the dimensionless convective-diffusion equation is carried out to isolate those passive systems (stagnant, laminar, turbulent) in which the solutions to the two equations are the same.

The remainder of the course then concentrates on those mass transfer problems which have no heat transfer analogues or in which the heat transfer analogue has not been considered earlier. Diffusion induced flows, mass transfer with chemical reactions and with phase changes, and multicomponent mass transfer are typically treated. The utility of hydrodynamic models in making engineering estimates of the effect on mass transfer of phenomena such as chemical reactions or convection at a boundary is stressed and then interfacial effects and interphase mass transfer are treated.

The specific material covered in a course of this type is probably less important than the attitude the student carries away; one would like to have him take away the viewpoint that there are powerful tools available, but that they cannot be used blindly, that skill, judgment and common sense are still necessary tools of the engineer.

For the last two years the in-class teaching of graduate heat and mass transfer at C-MU has been handled by D.C. In this endeavor concerted efforts are constantly being made to capture some of the flavor, to uphold the standards, and to take advantage of (and hopefully build upon) the techniques and philosophy of the course as previously taught by Professor Toor. In addition to this tradition, the instructor has had the benefits of material from two excellent series of courses in heat and mass transfer taught in the sixties at the University of Minnesota by Professor W. Ranz and by Professor A. G. Fredrickson. In the latter case, the courses were taken by Dr. Clarence Miller of C-MU, to whom we are grateful for making available to us his extremely fine set of notes.

Underlying the structure of our current course is a continued stress of theoretical fundamentals and a liberal dosage of assigned practice problems. The student has to learn how to apply the existing methods, but he also has to and wants to understand why they work; and he must be able to judge whether an approach to a particular problem is applicable or inapplicable, or unnecessarily elaborate, or not sufficiently exact for the purposes at hand. For the development of this type of judgment there is, of course, no substitute for the experience of problem solving; but without the added guidance of a thorough understanding of fundamentals, the development of such judgment would surely be severely retarded.

The nucleus of assigned reading for the course continues to be the material of parts II and III of BSL, which the student studies concurrently, or reviews in detail as the case may be. At present most of the students enrolling in the course have had a thorough exposure to dyadics and tensors in the "fluids" course taught the previous semester by Professor Brenner, and this background is utilized to advantage in establishing the compact forms of the general macroscopic equations of transport.

However, this is worked up to gradually. The course begins with the qualitative discussion of physical mechanisms of bulk phase transport from the macroscopic, microscopic, and what we have come to call the "micro-macroscopic" points of view. In the macroscopic view, the distinction is drawn between convective, radiative, and diffusive types of transport with emphasis upon the need for constitutive relations in the latter instance. Here the difference between definition and a physical law is discussed, and followed up by a description of the role of thermodynamic limitations. Then a review of the scaler and invariant formulations of the basic transport laws of Fourier, Fick, and Newton is provided with some attention given to the physical notion of an anisotropic medium.

In the microscopic picture, discussion is lim-

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ited for this course to a qualitative description of the origins of kinetic and collisional transfer contributions to the fluxes, their relative importance in gases, liquids, and solids, the philosophical inadequacies and "ball park" relevancies of the mean free path theory of constitutive relations, and the important role of rigorous non equilibrium statistical mechanics in this connection. When time permits at this stage of the introduction, the understanding of the microscopic picture is augmented by a lecture surveying the several angles to the theory of Brownian motion.

For the micromacroscopic mechanisms, i.e., for random and difficult to detail motions of small but macroscopic fluid elements, a common thread is woven through the ideas of turbulent eddy diffusivities, dispersion in flow through porous media, etc. The analogy of these physical mechanisms to gas kinetic fluxes is also brought out. These points are illustrated by means of several examples. The first is an estimate on the level of a mean free path approach, of the radial dispersion coefficient for mixing in the flow of fluid through a bed packed randomly with spherical pellets. A second example discussed is a detailed mean free path type "ball park" estimate of the effective transverse thermal conducitivity due to the mixing in the wakes of small gas bubbles rising steadily through a liquid.

The student's coverage of shell balance problems (BSL Chapter 9) affords an occasion to discuss the basis of flat (temperature) profile models. This too is done within the context of examples. One of these is the model of a cylindrical infrared heat filter with heat radiation passing longitudinally while being partially absorbed according to Lambert's Law. In a first pass at the problem the sides are taken to be perfectly insulated, a flat transverse temperature profile is assumed, and with the use of external heat transfer coefficients at the ends, the equation for one dimensional heat conduction with source is obtained by a shell balance and solved. In a second pass we allow for heat loss at the sides with a finite external resistance, but still employ a flat temperature profile model. In a third pass, the partial differential equation for steady state two dimensional conduction with source is obtained by a shell balance, and the complete boundary value problem is identified. The problem is rendered dimensionless and three independent dimensionless parameters are identified along with the dimensionless variables. Without solving the boundary value problem, the solution is shown to be equivalent to the flat temperature profile models of the first two passes when appropriately selected dimensionless parameters approach zero. This is done in the second instance by means of a regular perturbation analysis which is employed to derive the flat profile model directly. In another example, a similar perturbation analysis of a more exact problem is used to derive the flat profile model which is outlined in §9.7 of BSL for conduction in a rectangular cooling fin.

In all of such analyses, the mathematical methods per se are relegated to positions of somewhat lesser significance in favor of the lessons to be gleaned from the results of the derivations. Thus, the value of studying the problem in non dimensional form is emphasized along with the importance of recognizing apriori the dimensionless criteria for the approximate validity of flat temperature profile models. In this same vein, the assigned problems are oriented towards using such models with an intuitive recognition of the criteria for their validity.

For purposes of contrast, the general to specific approach is employed in part for treating the problem of forced convection heat transfer to a fluid engaging in turbulent or laminar flow through a conduit. Thus, the equation of change for cup mixing temperature is utilized to explain physically why the asymptotic problem with *constant wall heat flux* is unique in its simplicity. Then for this boundary condition the expression for the asymptotic internal heat transfer coefficient for pipe flow in terms of multiple integrals involving velocity profile and position dependent diffusivities is derived. Using this, the result for laminar flow of a Newtonian fluid (BSL, §9.8) as well as those for plug flow and for flow of an Ellis-model fluid are recovered as special cases by straightforward integrations. Extensions to treat the effect of compressibility and/or viscous dissipation have been used in examinations.

Proceeding to the general macroscopic transport equations, a vector tensor derivation is given for the general generic form of such equations.

(Continued on page 195)

Chapter 10: **Sterilization of Air**

1. sterilization by heat due to adiabatic compression
2. use of packed bed
3. theory of Gaden and Humphrey
4. Friedlander's analysis
5. mechanisms of particles removal from air
6. Pelect number
7. correlation of experimental data

references: Chapter 3 in "Biochemical and Biological Engineering Science" vol. 1 by N. Blakebrough

Chapter 11: **Sterilization of Liquid**

1. chemical methods
2. cationic detergent, ethylene and propylene oxide
3. chlorination in water treatment
4. phenol number
5. sterilization and pasteurization by heat
6. logrithmic death equation
7. Q-10 theory
8. temperature profile and its integration
9. Z-value and F-value
10. continuous sterilization process and equipment
11. inactivation by heat.

reference: Chapter 13 in "Biochemical Engineering" by F. C. Webb (Van Nostrand 1964)
Chapter 8 in "Biochemical Engineering" by S. Aiba, A. E. Humphrey, and N. F. Millis

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HEAT & MASS TRANSFER: Toor & Condiff

Toor & Condiff (Continued from page 191)

This form is specialized to obtain the general mass, momentum, and energy balances wherein conservation of mass, Newton's law of mechanics, and the first law of thermodynamics are each identified as a condition on the respective source terms. The assumption of local equilibrium is then introduced and employed to obtain the entropy balance, with identification of the positive definiteness of the source term as the second law of thermodynamics. Then follows a short survey of the highlights of irreversible thermodynamics using polyadics as a means of providing (i) a compact description of the linear laws of transport for an anisotropic medium, and (ii) a demonstration of Curie's theorem as a mathematical consequence of the assumption of isotropic transport coefficient tensors. It is hopefully made "crystal clear" that a violation of Onsager reciprocal relations is not excluded by any of the macroscopic principles.

With the closed and simplified versions of transport equations derived, methods of getting approximate and exact solutions for special heat transfer and analogous mass transfer problems are examined, though somewhat briefly. The sequence of study starts with the solution of problems categorized as (i) constant wall temperature penetration (BSL 10.R. 9.P, ex. 11.1-1, plug flow past a flat plate, etc.) all treated together by a similarity argument, (ii) constant wall heat flux penetration (BSL ex. 11.2-2, 9.R, etc.) also solved simultaneously by a similarity argument, and (iii) penetration in combination with external wall resistance. For case (iii) the similarity arguments are shown to break down and so the Laplace transform method is introduced, applied here, and pursued a bit further. Next the separation solutions are developed generally in conjunction with a concise survey of the Sturm-Liouville eigenvalue problem. This permits in particular a look at the general solution forms for forced convection heat transfer to fluid flowing in a conduit with boundary conditions of *constant wall temperature* or of transfer in series with an *external resistance* (e.g., the insulated pipe). The relationship of the lead eigenvalue to the asymptotic internal transfer coefficient is established at this point.

The separations solutions, and their special suitability for long time results provides a natural lead into the concept of relaxation time, which in turn is expanded into the ideas of multiple time scale analysis and their use in the justification of quasi steady state (qss) approximations. An example is the estimate of the time required to freeze a can of beer (for simplicity the beer is taken to be water) which is made using a one dimensional qss approximation. This approximation is then shown by a simple comparison of time scales to be necessarily invalid at the initial and final stages of the freezing process. Another example is the qss estimate of the time and distance of fall of an evaporating spherical raindrop with Stokes law drag, heat transfer correlations, and an analogy assumption for heat and mass transfer.

Problems emphasize the use of qss approximations with intuitive understanding of when they would not be accurate. Additional attention is given to problems with transfer across moving boundaries, especially boundaries where phase changes or fast reactions occur. There is a lecture devoted to the convective diffusion towards a rotating disc, and in this discussion the essential boundary-layer like character of the exact solution is brought out. This points the way to a development of boundary layer equations by simplified asymptotic arguments, with the Von

Karman - Pohlhausen integral approximations considered within the broader framework of the method of moments. Condensations problems and the film models are then considered with their limitations discussed. In particular, the Nusselt theory is developed as the simplest conceivable approximation from within the framework of the method of moments.

In treating turbulent transport we aim more for perspective than for completeness. The approach is to first initiate the student by developing one of the penetration models, and then to distribute for reading, copies of the 1968 award lecture of Professor L. E. Scriven, as published in *Chemical Engineering Education.* Discussion is then focused upon the time averaged equations, emphasizing that the literature on turbulence is often concerned with a deeper understanding of the position dependent turbulent diffusivities which we use. Introduced is an idealized concept which we call the "intense turbulence limit." This physical limit concept allows us to tie together several loose ends. Considering the tendencies of relaxation times towards zero at the limit, and the effective quasi steady state behavior of the boundary transition regions, it is argued on grounds more physical than mathematical that at the limit, (i) the asymptotic internal heat transfer coefficients are totally independent of boundary conditions, and (ii) the asymptotic transfer coefficients are reached instantly, i.e., the entrance region approaches zero in size. The tie-in to reality is then made by noting that often in turbulent flow one is operating near the ideal limit, flow of liquid metals being an exception, and that consequently in the use of empiracle correlations for design purposes one is seldom concerned about sensitivity of transfer coefficients to boundary conditions. From this we proceed to a review of design calculations, overall balances, and from thence to radiation, all by way of solving problems. Engineering problems of the quick number or quick conclusion variety are interspersed for balance.

In the time remaining a systematic treatment of mass transfer is attempted with emphasis upon problems without heat transfer analogies ("active" as opposed to "passive" transport). The problems include combined heat and mass transfer situations and are quite often built upon assignments prepared by H.L.T. Solutions are later distributed for all assigned problems. Discussion commences with diffusion kinematics based upon species *velocities* and in terms of these, definitions of arbitrary and the three principal types of convective (reference) velocities, fluxes of species or their energies, entropies, etc., and the arbitrary break up of these fluxes into diffusive and convective contributions. Diffusion laws for concentration diffusion are brought out in terms of relative species velocities, $\mathbf{v}_i - \mathbf{v}_j$, by means of the component momentum balances. The general Einstein connection between the binary friction and diffusion coefficients then permits conversion, in the binary case, to the doubly invariant forms of Ficks law for arbitrary reference velocity, from which all other forms follow. In the multicomponent case, the reduction of the component momentum balances to the ideal gas Stefan-Maxwell form is then described in similar fashion, and followed by the concentration diffusion laws with respect to the useful volume average reference velocity. Pressure diffusion, thermal diffusion, and diffusion due to externally applied fields are brought in by means of the irreversible thermodynamics for multicomponent systems. Obtained in particular are the general isotropic linear laws for heat and mass transfer in terms of both Onsager and Curtiss-Hirschfelder multicomponent diffusion coefficients, with the theoretical superiority of the mass average reference velocity indicated. (Wherever the going becomes difficult or notation heavy, notes are written out for distribution.) The tie-in to Ficks law for binary systems is then immediately made.

There is emphasis on mass transfer coefficients; there are problems discussed or assigned on film theory, flame models, the corrections for normal mass flow at boundaries, charge transport, a detailed treatment of density gradient centrifugation, etc. Up to now, time has expired before overall balances for multicomponent or active systems could be treated systematically.

Finally, it should be evident that the course is, of necessity, partly survey in nature, and that many of the topics treated, or not treated, warrant a great deal more time. Those students with little prior experience are usually left with a feeling that they have more to learn, but have acquired some facility with and an overview of some of the more advanced methods and ideas, a proper perspective for terminal and continuing students alike.