A Review of

THE DEVELOPMENT OF MASS TRANSFER THEORY

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Mass transfer has always been a central theme in chemical engineering. We have developed a special competence in the design of separation processes from batch distillation to diffusion plants for enriching uranium—235—and have had little competition from other branches in this area. Perhaps chemical engineering would not have been developed as it has if mechanical engineers had studied physical chemistry.

The basic tools available to the engineer in the design of a separation scheme are three: the laws of conservation of mass, energy, and the elements; data and theory pertaining to phase equilibria; and knowledge of rates of transport from one phase to another. The usual plan is to accomplish a preferential enrichment of a desired species in a second phase, followed by inexpensive mechanical separation of the gases, liquids, or solids. It is my intention to talk about the third tool of the design engineer—knowledge of mass transfer between phases—with a critical review of the research over the years which has led to the present state of this art.

This is not only the twentieth anniversary of the department at Houston but the fiftieth anniversary of the publication of "Principles of Chemical Engineering" by Walker, Lewis, and McAdams in 1923. That book was a milestone, for it established chemical engineering as a separate and unique branch of engineering, and stimulated the proliferation of chemical engineering departments in many universities. Its focus on the quantitative treatment of the unit operations was challenging and exciting, and the "unit operations" concept served the profession well for some twenty years.

The name "chemical engineering" had been coined by Davis in England some fifty years earlier, and there was at least one curriculum labeled "chemical engineering" by 1888. The early four-year curricula generally consisted of two years of mechanical engineering and two years of chemistry. By 1923 the new approach had much to start with. Physical chemistry was well developed; multiple effect evaporation and rectification had been invented in Europe; and the ideas of reflux and countercurrent staging had been recognized and analyzed.

The concept of staged operations appears to be unique to chemical engineering. Several years ago a well-known mechanical engineer told me that he had visited Oak Ridge and had been astounded by the plant's capacity to produce uranium 235. I told him that I had understood the productive capacity to be an extremely well-guarded secret, and asked how he had learned what it was. He answered that it was simple—he had seen the sizes and estimated the r. p. m. of the circulating gas compressors. I asked him if he had ever heard of reflux. His reply was "No, what is reflux?"

There were not many chemical engineers in the twenties and early thirties, but much was accomplished in the development of the unit operations. McCabe and Thiele, working within a few feet of each other at M. I. T., independently conceived their graphical representation of Sorel's algebraic analysis of binary rectification. The now-familiar friction factor graph was imported from England and publicized in this country by chemical engineers. The simpler staged operations were analyzed, and the McCabe-Thiele diagram adapted for gas absorption, solvent extraction, and leaching. The humidity chart had been invented by Grosvenor in 1908 and was published

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in Volume 1 of the Transactions of the American Institute of Chemical Engineers, greatly simplifying analyses of drying and air conditioning.

EARLY PERIOD

IN THIS PERIOD OF some twenty years prior to World War II the emphasis was on the collection and correlation of data intended to be of direct use by the practicing design engineer. Industry had few such data and published little, so schools felt a responsibility to fill the need. This urge to be immediately helpful to industry has largely disappeared today; research in schools is now along more scientific and theoretical lines, hopefully of value to industry a generation hence. Our rapport with industry has suffered.

Research on mass transfer between phases was strong in the twenties and thirties, even as it is today. Then, as now, the research was mostly by academics. The film model had been invented by Nernst in 1904, and by others around the turn of the century. This was elaborated by Whitman and Lewis [20, 37] through the concept of additivity of resistances of two phases in contact. Murphree [22] defined a useful plate or stage efficiency, which was shown to be related to rate coefficients. The main variables affecting plate efficiency—contactor design, fluid properties and the nature of the phase equilibria—were elucidated in numerous thesis investigations by graduate students. But the most remarkable thing about this period was the obsession with studies of packed towers. Most of the experimental work was carried out in 2- and 3-in. columns, much too small to provide useful design data for the industrial process engineer. Data were obtained on flooding, holdup, and pressure drop as well as mass transfer rates, and correlations based on dimensionless groups were developed, without much reference to any valid theory. The profession seemed to have a one-track mind, and the AIChE was referred to as "Packed Tower Institute." Important as packed towers were, and continue to be, it appeared that academic investigators had lost their sense of perspective, neglecting other problems of similar relevance and importance.

Let me turn now to a review of the developments of the theory of mass transfer processes, with a few critical comments as to which of these seem now to be of importance, and which do not. Even in the twenties we were in moderately good shape as to how to deal with diffusion within a single phase. Physical chemists had provided us with an understanding of diffusion in gases, and by 1934 we had semi-empirical correlations of diffusion coefficients in binary gas systems. The classical kinetic theory has since been developed to allow for interactions between unlike molecules, and the modern kinetic theory is adequate for most engineering purposes. There still is no adequate theory of the liquid state, however, and we must rely on inadequate empirical correlations of diffusion coefficients in liquids. Chemical engineers have been major contributors to the development of the useful correlations now available.

THE MAIN THRUST of the theoretical studies has been quite logically on mass transfer between phases, since the understanding of the factors which determine the rate of transfer is the basic objective.

If the flow past the interface is laminar, analysis is often possible by combining the transport relations with equations describing the flow field. This has been done successfully for laminar flow in tubes, rotating disks, falling liquid films on inclined or vertical surfaces, over spheres, and creeping flow around spheres. The theoretical analyses for such cases are sometimes better than the experimental data.

> Perhaps ChE is emerging from an era of empiricism . . . we have much concern with complex physical phenomena, and we have not yet arrived at the point where all can be left to the computer.

In industrial practice, however, the flow past the mass-transfer interface is usually turbulent, and attempts at theoretical analysis have been frustrated by the lack of an adequate understanding of turbulence—especially of turbulence near a phase boundary. What progress has been made is due as much to chemical engineers as to specialists in fluid mechanics. The early approach was to develop empirical correlations relating dimensionless groups, such as the mass-transfer Nusselt number, and the Reynold and Schmidt numbers. This was hardly a theoretical approach in any real sense, but has served a useful purpose over a period of many years.

One theoretical approach which has fascinated so many workers is the development of the so-called "analogies" between mass, momentum, and heat transfer. If these could be successful, they would provide a way to use the accumulated body of knowledge regarding turbulent flow of fluids for the prediction of mass and heat transfer coefficients. The first of these was the Reynolds analogy, which stated that the Stanton number for heat transfer should be equal to one-half the Fanning friction factor. This came close to fitting experimental data on heat transfer in tubes with gases in turbulent flow, but not for water or oils. It made no allowance for the different molecular properties of the fluids.

Attempts to clarify the situation focussed on transfer from a turbulent fluid to a solid surface, as in the case of fully-developed turbulent flow in a round tube. Consideration of transfer between two fluids, as from gas to liquid, or between two immiscible liquids, came later. It was well established that in pipe flow there is no slip at the wall, so it seemed logical that turbulent mixing could play no part in the transport mechanism as the distance from the wall approached the mathematical limit of zero. In this limit the mass transfer flux should be proportional to the flux power of the molecular diffusion coefficient, D. The main turbulent stream is so well mixed that solute is transported radially at fluxes much greater than can possibly be explained by molecular diffusion. In the two limits of the wall and the main flow the radial flux is proportional to D^1 and D^0, respectively. It is not surprising that most of our mass transfer correlations show the mass transfer coefficient to be proportional to D^n, where n is between zero and unity.

The spectrum of motion from eddies to molecules is suggested by this little verse—authorship unknown:

Big size whirls have little whirls
That feed on their velocity
And little whirls have lesser whirls
And so on to viscosity.

It seems logical to assume that molecular and eddy diffusion take place in parallel, and that the flux toward the wall can be expressed by a version of Fick's law in which the "total diffusivity" is the sum of the molecular diffusion coefficient, D, and the eddy diffusion coefficient, E. The first is a property of a binary mixture, but the eddy coefficient E depends on the nature of the flow and the distance from the wall.

By the late twenties the early "stagnant film" model was realized to be a gross oversimplification. Whitman, who is often mistakenly quoted as having applied it rigorously, noted in 1922 that a sharp boundary was assumed between the stagnant film and the turbulent core, but that "actually no such sharp demarcation exists." Whitman and Lewis did not advocate the film model; their papers developed a way to add the resistances of two fluid phases in contact.

ANALOGIES

SINCE MASS TRANSFER at a phase boundary depends on the varying eddy diffusivity it is evident that any theory of the overall process will necessarily require a theory of the variation of E with the flow conditions and the distance from the wall. The first attempt to allow for the large variation of E with distance in the vicinity of the wall was made in 1932 by a well-known chemical engineer, the late E. V. Murphree [22]. Murphree assumed the total diffusivity to vary as the cube of the distance from the wall, y, up to some limit y_1, beyond which the parabolic velocity defficiency law determined the nature of the flow in the bulk or turbulent core. This semi-empirical approach correlated data on heat transfer in pipes over a limited range of Prandtl numbers, which the Reynolds analogy had failed to do.

1939 saw the publication of Von Karman's elegant analysis [34] of the possibilities of developing a unified theory of mass, heat, and mo-

Professor Sherwood joined the Berkeley faculty in 1970, after spending most of his professional life at M.I.T. After five years with the O.S.R.D. during the war, he was Dean of Engineering at M.I.T. from 1948-1954. Many of his publications have dealt with various aspects of mass transfer, and "Mass Transfer" is the title of a new book now in press, written jointly with R. L. Pigford and C. R. Wilke. He is the recipient of the Walker, Founder's, and Lewis awards of the AIChE, the Murphree award of the A.C.S., and the Presidential Medal for Merit.

mentum transport from a turbulent stream to a solid wall; this had been a fascinating idea since Reynolds' time. Eddies appear to transport mass, heat, or momentum by similar if not identical processes, so it seemed logical that E could be equated, or related to, the eddy viscosity. The similarity of the three processes is suggested by comparing the Reynolds modification of the Navier-Stokes equations for turbulent flow in the x-direction:

Momentum:

$$\bar{U}_x \frac{\partial \bar{U}_x}{\partial x} + \bar{U}_y \frac{\partial \bar{U}_x}{\partial y} + \bar{U}_z \frac{\partial \bar{U}_x}{\partial z} = \frac{1}{\rho}\left[\frac{\partial}{\partial x}\left(\mu \frac{\partial \bar{U}_x}{\partial x} - \rho\, \overline{u_x u_x}\right) + \frac{\partial}{\partial y}\left(\mu \frac{\partial \bar{U}_x}{\partial y} - \rho\, \overline{u_x u_y}\right) + \frac{\partial}{\partial z}\left(\mu \frac{\partial \bar{U}_x}{\partial z} - \rho\, \overline{u_x u_z}\right)\right] - \frac{g_c}{\rho}\frac{\partial \bar{P}}{\partial x} \quad (1)$$

Heat:

$$\bar{U}_x \frac{\partial \bar{T}}{\partial x} + \bar{U}_y \frac{\partial \bar{T}}{\partial y} + \bar{U}_z \frac{\partial \bar{T}}{\partial z} = \frac{1}{\rho C_p}\left[\frac{\partial}{\partial x}\left(k \frac{\partial \bar{T}}{\partial x} - \rho C_p \overline{u_x t}\right) + \frac{\partial}{\partial y}\left(k \frac{\partial \bar{T}}{\partial y} - \rho C_p \overline{u_y t}\right) + \frac{\partial}{\partial z}\left(k \frac{\partial \bar{T}}{\partial z} - \rho C_p \overline{u_z t}\right)\right] \quad (2)$$

Mass:

$$\bar{U}_x \frac{\partial \bar{Y}_A}{\partial x} + \bar{U}_y \frac{\partial \bar{Y}_A}{\partial y} + \bar{U}_z \frac{\partial \bar{Y}_A}{\partial z} = \frac{\partial}{\partial x}\left(D \frac{\partial \bar{Y}_A}{\partial x} - \overline{u_x Y_A'}\right) + \frac{\partial}{\partial y}\left(D \frac{\partial \bar{Y}_A}{\partial y} - \overline{u_y Y_A'}\right) + \frac{\partial}{\partial z}\left(D \frac{\partial \bar{Y}_A}{\partial z} - \overline{u_z Y_A'}\right) \quad (3)$$

It is noted that the similarity is not complete: momentum is a vector but temperature and mole fractions are scalars. The first equation has an extra term involving pressure gradient. Furthermore, as Beddingfield and Drew [1] have shown, the equation for mass transfer is valid as written only for low concentrations of the species being transferred if diffusion velocities are to be related to a plane of no net molal transport in order to gain the advantage that D in binary gas systems is then independent of concentration.

A remarkable general correlation of velocity profiles for turbulent flow in pipes had been developed by workers in fluid mechanics, from which the eddy viscosity could be obtained. Velocity profiles for both gases and liquids over a wide range of Reynolds numbers were represented by a single curve of u^+ vs. y^+, where u^+ is a dimensionless local velocity, and y^+ the dimensionless distance from the wall. The eddy viscosity is obtained from the slope of this curve. Von Karman wrote simple equations for three segments of the $u^+ \sim y^+$ function, and differentiated these to obtain the eddy viscosity as a function of y^+. He then assumed the eddy diffusion coefficient to be equal to the eddy viscosity, and integrated the heat flux equation from wall to bulk fluid. The result was an equation relating the Stanton number for heat transfer to the friction factor and the Prandtl number, which agreed quite well with data on heat transfer data for gases and various liquids. The corresponding equation for mass transfer is easily obtained and has the same form.

Von Karman's publication precipitated a minor avalanche of variations of the analogy idea, and these are still coming out (33, 35, 36). Von Karman's analysis can be understood by noting the basic equations employed, here written for mass transfer:

$$\tau g_c = -(\nu + E_v)\frac{d(\bar{U}\rho)}{dy} = \frac{1}{2} f \rho \bar{U}_{Av}^2 \frac{r}{r_w} \quad (4)$$

$$u^+ = f(y^+) \quad (5)$$

$$u^+ \equiv \frac{\bar{U}}{\bar{U}_{Av}}\sqrt{\frac{2}{f}}\,;\; y^+ \equiv \frac{(r_o - r)\bar{U}_{Av}}{\nu}\sqrt{\frac{f}{2}}$$

$$E_v/\nu = \frac{r}{r_w}\frac{dy^+}{du^+} - 1 \cong E_D/\nu \quad (6)$$

$$J_A = k_c(C_{Av} - C_w) = -(D + E_D)\frac{dc}{dy} \quad (7)$$

$$\frac{1}{St} = \frac{\bar{U}_{Av}}{k_c} = \frac{2}{f} + \sqrt{\frac{2}{f}}\, f(Sc) \quad (8)$$

The function of the Schmidt number stems from the assumed relation between u^+ and y^+; the variation of St with the Reynolds number appears in the friction factor.

Various simplifying assumptions are involved in arriving at the last equation by the derivation outlined. Most of these are reasonable, though it is now known that E_D and E_v may differ substantially. In fact Von Karman's analysis, and later modifications of it, represent heat transfer data for turbulent flow in pipes quite well. Most of the heat transfer data involved Prandtl numbers in the range of about 0.5 to 35. The theory failed, however for heat transfer to liquid metals, which have very small Prandtl numbers. Of more importance in chemical engineering, the analysis failed seriously for high Schmidt numbers. In the liquid systems of interest to chemical engineers the Schmidt numbers range from several hundred to several thousand. Much research has been directed towards improving this situation by modifying the analogy approach.

In liquid systems with high Schmidt numbers the concentration boundary layer is exceedingly thin, that is, almost all of the concentration drop occurs within a few microns of the wall, generally at y^+ from zero to perhaps 2. There are essentially no data on the velocity profiles in this region; it is too close to the wall for measurements by Pitot tubes. Furthermore, since in this region u^+ and y^+ are very nearly equal, the precision in getting E_v by Eq. 6 is very poor. It appears now that it may be some years before we have a quantative understanding of this region very near the wall; current research using optical techniques indicates that the flow patterns there are quite complicated.

In this dilemma, numerous analysts have simply assumed the needed function. Anyone can develop a new "analogy" by doing this. It doesn't matter whether one assumes a new $u^+ \backsim y^+$ relation, or E_v as a function of y^+, or, more directly, E_D as a function of y or y^+. By trial and error one can find a basic function which will lead to an integrated final equation fitting the data over a wide range of Prandtl and Schmidt numbers.

IT SEEMS TO ME that there have been more "analogies" developed in this way than we have any need for. Most involve too much of an aspect of assuming the answer to be called theoretical accomplishments. What we seem to need is new and better techniques for studying the wall region. Nedderman [23] and Fowles [29] have employed optical methods to record direction and speed of particles flowing very near the wall. Interferometric and laser techniques may work, and Kline's photographs [18] of dye streaks and tiny bubbles are fascinating. Already the idea of a laminar sublayer has been made obsolete—by observation, not by theory.

Now let me go back to 1934 and comment on the remarkably simple and useful Chilton- Colburn analogy, which may be expressed in the form

$$\frac{k_c}{U_{Av}} Sc^{2/3} = \frac{h}{C_p \rho U_{Av}} Pr^{2/3} = \frac{f}{2} \qquad (9)$$

I suspect that this was based on (a) the observation that the simple Reynolds analogy held for heat transfer when Pr was near unity, (b) the fact that $Pr^{2/3}$ had been shown theoretically to apply to transport through a laminar boundary layer, (c) the apparent validity of the simple empirical function 1.0 $Pr^{2/3}$ to represent heat transfer data over a limited range of Pr, and (d) an intuitive guess that because of the similarity of the mechanisms of heat and mass transfer k_c should vary with Sc in the same way that h does with Pr. In any case it has been found to agree surprisingly well with a large amount of subsequent data. The first equality seems to be general for turbulent flow; and second when there is only "skin friction" with no form drag. It is interesting that the proper choice of constants in Murphree's analysis will make it agree with Chilton and Colburn [5].

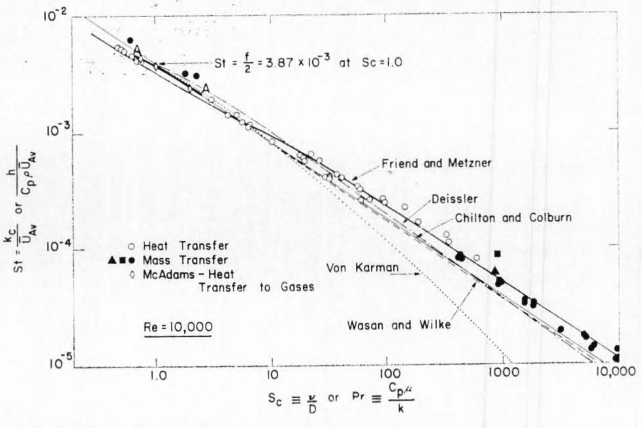

FIG. 1 Plot of Sc vs Pr for Re=10,000.

Let me summarize this review of the analogies by showing how several of them compare with data on heat and mass transfer for fully developed turbulent flow in a tube. Figure 1 is a graph of St vs. Sc or Pr for Re=10,000, with lines representing five of the better-known analogies. The open circles represent data on heat transfer to gases, water, oils, molten salt, organic liquids, and aqueous solutions of sugars. These were collected from the extensive literature by Friend and Metzner [11]. The solid points at large Sc represent the excellent data of Myerink and Friedlander [21] and of Harriott and Hamilton [14] on the dissolution of tubes of slightly soluble solid organic acids. The solid points at $0.6 < Sc < 2.5$ are Gilliland's data [12] for vaporization of liquids into air in a wetted-wall column. McAdam's correlation for heat transfer to gasses is shown as line A-A.

At Sc=1, all of the lines shown pass near $St = \frac{1}{2}f = 3.87 \times 10^3$, which the Reynolds analogy requires. Friend and Metzner's line passes through the data ponts, as is perhaps to be expected, since their analogy is based on the data points represented by the open circles. The recent analogy developed by Notter and Sleicher [24], based on carefully selected heat transfer data, agrees closely with Friend and Metzner. The Von Karman line, based on the general correlation of velocity profiles, does poorly. This is because Von Karman took the eddy diffusivity to be zero from the wall to $y^+ = 5$; it is now clear that a very small amount of eddy diffusion at low values of y^+ can be quite important at large Sc. The most remarkable thing about this comparison is the fact that the Chilton-Colburn analogy does as well as it does; their equation was proposed at a time when there were no data on heat transfer above a Pr of about 20, and no data on mass transfer at Sc greater than 2.6. It is also notable that this graph represents an enormous range of flow conditions and of physical properties of the fluids.

I have discussed these analogies at some length because they constitute a major effort to develop a theory of mass transfer between phases in the important turbulent regime. There are also the "models," of which the first was the "stagnant film" model. It implies that the transport rate should be proportional to the first power of the molecular diffusion coefficient, which is not true, but it can still be successfully employed for a variety of purposes. It gives reliable predictions of the **ratio** of the mass transfer flux with simultaneous chemical reaction to that attained without chemical reaction under similar conditions. It does equally well in predicting the effect of convective fluxes in the direction of diffusion on the rates of mass or heat transfer.

INTERPHASE MASS TRANSFER

NUMEROUS MODELS OF the conditions at a phase boundary have been proposed to provide a basis for a theory of interphase mass transfer. The three best known are the stagnant film model, the penetration theory, and the turbulent boundary layer model. The allowance for the variation of eddy diffusivity with distance from the wall, as in the analogies, is the basis of the turbulent boundary layer model.

The penetration model pictures small fluid elements contacting the phase boundary for brief periods during which transient diffusion occurs, and then being replaced by fresh fluid from the bulk. This was suggested by Higbie in 1935 [16] as applicable to bubbles moving in a liquid, and to gas-liquid contacting in packed towers, where freshly mixed liquid is supplied to successive packing elements. It lead to the conclusion that the transport flux should be proportional to the square root of the molecular diffusion coefficient. This has been found to be approximately true in a wide variety of flow systems, including the absorption of sparingly soluble gases in packed towers.

An important extension of the penetration theory was proposed by Professor Danckwerts in 1951 [7]. Whereas Higbie had taken the exposure time to be the same for all of the repeated contacts of the fluid with the interface, Danckwerts employed a wide spectrum of contact times and averaged the varying degrees of penetration. Like the Higbie model, this concept leads to the conclusion that the transport flux should be proportional to the square root of D. It is not generally believed that fluid eddies reach a fixed interface, such as the wall of a tube, but there is increasing evidence that this may be so. The model makes particularly good sense when applied to conditions at the interface between a gas and a stirred liquid. Watching the surface of a swift but deep river, or of a well-stirred liquid in a laboratory vessel, it is not hard to discern fluid elements which come up from below and then appear to move back down after brief periods of contact with the air at the surface.

As applied in the simplest cases, these four models lead to the following equations for the mass transfer coefficient k_c:

$$\text{Film:}\quad k_c = \frac{D}{y_0} \tag{10}$$

$$\text{Penetration:}\quad k_c = 2\sqrt{\frac{D}{\pi t}} \tag{11}$$

$$\text{Surface-Renewal:}\quad k_c = \sqrt{Ds} \tag{12}$$

Turbulent Boundary Layer:

$$k_c = \frac{U_{Av}}{\frac{2}{f} + \sqrt{\frac{2}{f}}\, f(Sc)} \tag{13}$$

The first three, to be useful, require knowledge of the effective film thickness, y_0, the contact time, t, or the fractional rate of surface renewal, s. The last requires that $f_2(Sc)$ be specified, which could be done if the variation of eddy diffusivity through the boundary layer were known. Little is known about y_o, t, s, or $f_2(Sc)$, so as theories all four models are incomplete.

It is interesting that the models described perhaps owe their origin to Osborne Reynolds [27] who wrote in 1874 that the heat flux to a wall "is proportional to the internal diffusion of the fluid at and near the surface," and states that the heat flux depends on two things: **"1. the natural internal diffusion of the fluid when at rest, and 2. the eddies caused by the visible motion which mixes the fluid up and continually brings fresh particles into contact with the surface.** The first of these causes is independent of the velocity of the fluid. . . The second cause, the effect of the eddies, arises entirely from the motion of the fluid. . ."

SIMULTANEOUS CHEMICAL REACTION

IT IS NOT POSSIBLE for me to cover much of the development of the various theories used in practice by chemical engineers, even in the restricted area of mass transfer, but let me comment on two other important theoretical developments. The first is mass transfer with simultaneous chemical reaction, the subject of numerous papers in our journals. This started in 1929 by Hatta [15], who employed the film model to develop a theory of gas absorption followed by reaction in the liquid, as in the absorption of CO_2 by alkaline solutions. Following Hatta there has been a proliferation of theoretical analyses of all kinds of cases thought to be of practical importance, and useful generalizations, notably by Hoftyzer and Van Krevelen [17] and by Brian [3, 4]. Hatta's use of the film model was suspect, but Danckwerts and Kennedy [8] have shown that the penetration model gives essentially the same results in many instances.

These theories do not predict rates of mass transfer, but generally lead to equations expressing the enhancement of the rate by the simultaneous reaction, that is, the ratio of the rate with chemical reaction to that for physical absorption. Professor Danckwerts' recent book [9] summarizes the whole subject, with special reference to the absorption of acid gases by alkaline solutions, so important in the manufacture of hydrogen and of synthetic natural gas.

It might seem that some of the cases analyzed will never find practical application, but one cannot predict. When I recently had occasion to analyze the process of SO_2 absorption by a suspension of limestone particles in a stack gas scrubber I was surprised and pleased to find this case analyzed in a published paper (26). However, it may be that we are running into the law of diminishing returns in pursuing these anlyses, and that more experimental studies are in order. There is nothing like a surprising new fact to stimulate the development of better concepts and theories.

It is not generally believed that fluid eddies reach a fixed interface, such as the wall of a tube, but there is increasing evidence that this may be so.

Another area in which we have made great progress is that of diffusion and reaction in porous catalysts. This subject is of great practical importance because of the enormous success of catalytic processes in the chemical and petroleum industries. The pioneering papers of the U. S. chemical engineer Thiele [32], and the Russian Zeldowitsch [38] in 1939, started a flurry of experimental and theoretical studies. We have now learned a lot about bulk and Knudsen diffusion in pores of simple geometry, and are beginning to tackle the much more difficult problem of surface diffusion. All kinds of cases have been analyzed, assuming both power-law and Langmuir-Hinshelwood kinetics, heat effects, and various geometrics of the catalyst particle. The decrease in the effectiveness factor with increase in particle size is understood at least qualitatively, although I find highly successful catalyst research people in industry who use the theory so little that they think a low effectiveness factor indicates a relatively inactive catalyst.

Apart from the present mystery regarding surface diffusion, the stumbling blocks to better development of the theory would appear to be inadequate understanding of the mechanism of surface catalysis, and the difficulty of describing the complex structure of a porous solid by one or two numbers.

Many industrial processes involve the absorption of reacting gases by a liquid containing suspended particles of a catalyst. This operation was described quantitatively in 1932 by three chemists [6], who showed the merit of plotting the reciprocal of the rate vs. the reciprocal of the catalyst loading in the slurry. The intercept, corresponding to infinite catalyst loading, is a measure of the mass transfer resistance to the absorption of the gas. The situation has been generally understood by chemical engineers for 40 years, but there are still some chemists who attempt to analyze such processes by power-law or other kinetics when the controlling factor is actually the rate of gas absorption.

THE MARANGONI EFFECT

FINALLY, LET ME COMMENT briefly on the phenomenon of interfacial turbulence, or the Marangoni effect. Spontaneous emulsification of two liquids has been known for many years, but the important role of interfacial turbulence on mass transfer at an interface was brought forcibly to the attention of chemical engineers by Lewis and Pratt in 1953 [19], and by Jim Wei [28] in the course of his doctorate research in 1957. As mass transfer takes place, the solute concentration, and consequently, the interfacial tension vary from spot to spot over the surface. This causes spreading and contraction of the surface elements, which "is so rapid that the momentum of the spreading liquid is sufficient to break the center of the point source and expose subjacent liquid drawn from below the surface (10)." The result is surface renewal, usually with development of ripples, and an increase in the rate of mass transfer. The effect depends on the direction of the mass transfer flux, and the phenomenon obviously introduces new and difficult problems in attempts at theoretical analyses of mass transfer between two fluid phases.

Research directed to an understanding of the role of interfacial turbulence on mass transfer has proliferated in the last twenty years. This is proper, since the effect can be quite large, and requires major adjustment of the simple two-film picture. Excellent pictures of the phenomenon have been published by Dr. H. Sawistowski of Imperial College, London, and by others. The first important theoretical attacks appear to be those of Pearson [25] and of Sternling and Scriven [30]; Brian's recent introduction of the Gibbs layer adsorption extends the theory and is evidently a major contribution [2]. But the theory of this phenomenon, of real practical importance, is still in its infancy. Its development to the point of practical application in design presents a challenge to chemical engineers inclined towards theoretical studies. Do not tackle it without a thorough background in physical and colloid chemistry.

Chemical engineers can be proud of the development of the profession since Walker, Lewis, and McAdams in 1923. The chemical and petroleum industries have prospered, with the help of U.S.-trained chemical engineers. Plants have been built and operated successfully, usually at a profit. But our contributions to the theory of mass transfer between phases have not been remarkable, at least within the definition of a theory as being valid for quantitative *a priori* predictions useful in design. A major difficulty is that we desire theories applicable in turbulent flow, and not much basically new has been learned about turbulence in the last 40 years.

However, chemical engineers have developed a unique skill in using the *form* of a theory. A modest theory is better than no theory at all. Even the simple equation $q = UA\Delta t$ for heat transfer enables us to eliminate two variables and concentrate our attention on the manner in which the heat transfer coefficient varies with the geometry and the fluid flow. There are many examples of this. The Van Laar equations for binary vapor-liquid equilibria were rejected by scientists because the theory did not work in the prediction of the constants. But chemical engineers found the *form* of the theory to be remarkably good—two data points are enough to provide the Van Laar constants, and make it possible to predict complete y-x diagrams for complex binaries, including azeotropes.

> It may be that we are running into the law of diminishing returns . . . and that more experimental studies are in order. There is nothing like a surprising new fact to stimulate the development of better concepts and theories.

Similarly, the models of the mechanism of mass transfer between phases provide the form if not the substance of a theory, and make it possible to develop correlations of experimental data on a rational and useful basis.

It is too much to expect that in fifty years we would have developed a fundamental and quantitative theory which would enable us to predict rates of mass transfer in turbulent flow. That is a goal for the future, probably requiring more progress in understanding turbulence. Such a theory would be a feat comparable to the development of the kinetic theory of gases, and these are not frequent.

THEORETICAL ACCOMPLISHMENTS

THERE HAVE, OF COURSE, been a number of theoretical accomplishments about which chemical engineers can be proud. The wet-bulb thermometer is a fascinating example. This device was not understood until about 100 years ago, when Maxwell, using what amounted to our film theory, explained the dynamic equilibrium established when the rate of heat transfer from air to wet wick just equalled the latent heat of vaporization of the water evaporating at the wet-bulb temperature. About 1910 it was noticed by Willis Carrier that the wet-bulb temperature coincided with the calculated temperature of adiabatic saturation. Why should this be? It was some years later that W. K. Lewis and J. H. Arnold explained this. The ratio of the heat transfer coefficient, air to wet-bulb, to the mass transfer coefficient determining vaporization, depends on the molecular properties of air and water, and these just happen to have values such that the equations for the wet-bulb depression and for adiabatic saturation become quantitatively identical. Carrier's observations for water wet-bulbs were explained, but were shown to be based on a remarkable natural coincidence, and not general for other gases and liquids.

These studies established the ratio of heat and mass transfer coefficients for air and water vapor. This led to Merkel's ingenious analysis of cooling tower operation and the engineering design method used today. It is remarkable that a theoretical analysis of the wet-bulb thermometer provided the basis for a simple and practical design procedure for cooling towers. Merkels' method also applies in the design of dehumidifiers.

I am sure that G. I. Taylor does not think of himself as a chemical engineer, but we need people like him in chemical engineering. In 1954 he developed a theory of longitudinal dispersion in open pipes, based on a generalized correlation of velocity profiles in turbulent flow [31]. Figure 2 indicates how well the theory works. The points and dotted curve show the dispersion of a radioactive tracer pulse after flowing 43 miles in an oil pipe-line in hilly country [13]. The solid curve is predicted by the Taylor theory. The agreement seems only fair, but is really quite remarkable in view of the fact that the tracer took 85,000 seconds to travel the 43 miles to the test station. The predicted dispersion coefficient was 594 $cm^2/sec.$; the value required to fit the data is about twice that. The Taylor theory did not allow for pumps and elbows in the line.

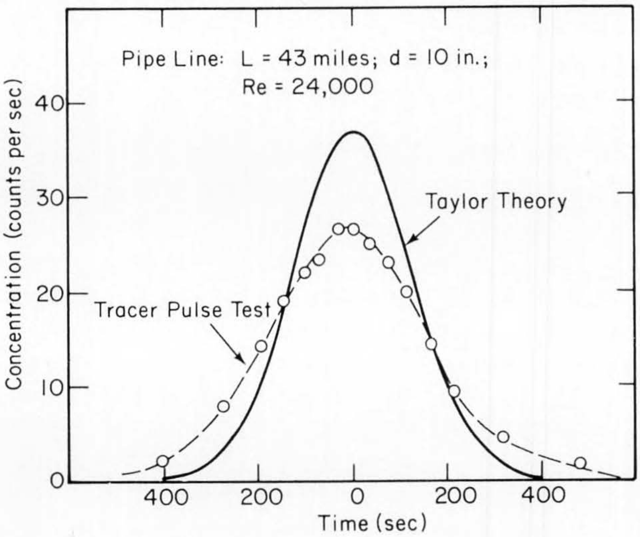

FIG. 2. Comparison between theory and experiment.

FUTURE NEEDS

WE HAVE COME A LONG WAY in fifty years, but we have much yet to do. It would seem that new complications, such as interfacial turbulence, are appearing more frequently than theory advances. In my judgment the major goal is a basic theory of the mechanism of mass transfer between phases in turbulent flow. To attain this we shall need a better understanding of flow conditions at a phase boundary. I believe chemical engineers are as likely to provide this as specialists in fluid mechanics, but it seems that it may be some years before we have it.

Of perhaps equal importance is a theory of mass transfer with simultaneous chemical reaction at a catalyst surface. The mass transfer elements of such theory are in fair shape, but surface catalysis is still an empirical art. Realizing this, chemical engineers are joining chemists in a growing program of research on catalysis. Many chemical engineering departments now have strong programs of basic research on catalysis. Perhaps the reason for this trend is the realization that the chemical reactor is the heart of the industrial chemical process, and that the unit operations are often peripheral.

Perhaps chemical engineering is emerging from an era of empiricism. Electrical engineers need only the

physical properties of their components; from there on design is a job for the computer. We have much more concern with complex physical phenomena, and we have not yet arrived at the point where all can be left to the computer. In a way I hope we never will, for chemical engineering is so much more fun when we don't know very much.

Pending the ultimate development of theory, we continue to do well. Very large plants are designed, on the basis of empiricism or half-formed theory, and operate. There are no more failures than encountered by bridge designers, who have a complete theory of stresses in a structure. Some of our industrial processes even make money, and provide our profession not only with a livelihood but satisfying careers for chemical engineers. □

SYMBOLS AND NOMENCLATURE

C = concentration, g moles/cm^3
C_p = heat capacity, g cal/(g mole) (°K)
D = molecular diffusion coefficient, cm^2/sec.
E = eddy diffusion coefficient, cm^2/sec.
E_D = eddy diffusion coefficient for mass transfer, cm^2/sec.
E_v = eddy viscosity, cm^2/sec.
f = Fanning friction factor
g_c = conversion factor (=32.2 in English system of units)
J_A = molal diffusion flux of A in absence of superposed convection, g moles/(sec)(cm^2).
k = thermal conductivity, g cal/(sec) (cm^2) (°K/cm)
k_c = mass transfer coefficient, cm/sec.
P = pressure, g/cm^2
Pr = Prandtl number, $= C_p\mu/k$
r = radial distance from axis of tube, cm.
r_w = tube radius, cm.
s = fractional rate of surface renewal, sec^{-1}.
Sc = Schmidt number, $= \mu/\rho D = \mu/D$
St = Stanton number $= k_c/U_{AV}$
t = fluctuating temperature, °K
T = time-mean temperature, °K
u = fluctuating velocity, cm/sec.
u^+ = dimensionless velocity, defined by Equation 5
U_{AV} = time-mean average velocity, cm/sec.
U_x = time-mean velocity at a point, in x-direction, cm/sec.
x, y, x = coordinates, cm.
y = distance in direction of diffusion, cm.
y_o = film thickness, cm.
y^+ = dimensionless distance from wall, defined by Equation 5
Y_A = time-mean mole fraction
Y' = fluctuating mole fraction
μ = viscosity, g/(sec) (cm).
v = kinematic viscosity, $= \mu/\rho$, cm^2/sec.
ρ = density, g/cm^3.

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