FLOW and TRANSFER at FLUID INTERFACES*
Part I - Lessons from Research

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Chemical engineers cannot escape dealing with mass and heat transfer across fluid interface that are in more or less chaotic motion, chaos that goes under the name of turbulence. There is little need to emphasize in this magazine why a thorough understanding of flow and transfer at fluid interfaces is an important research goal—and ultimately a standard tool in the kit of practicing engineers.

Put broadly, the problem I wish to discuss is that of transfer in chaotic or turbulent flow systems, particularly those in which turbulence is generated at some distance from the interface but comes to bombard it, so to speak. Underlying this broad problem there is an important basic question: What are the effects of convective movements on otherwise diffusive transport, particularly in the neighborhood of fluid interfaces?

Fluid interfaces are mobile and can move and deform in ways that solid boundaries cannot. It is important to bear this in mind, because solid boundaries are so much simpler and better studied that they are the underpinning for most of one's intuition in this area. I think it instructive to look at the ways in which the chemical engineering profession has tried to model flow and transfer at fluid interfaces in the past. For simplicity, let us disregard such complications as the transfer resistance of the second phase, diffusion-induced convection, inhomogeneous properties, interfacial-tension gradients, chemical reaction effects, and so on. We can then identify four or five stages in the development of transfer models.

STAGE ONE: NO FLUID MECHANICS

The earliest working model can be traced back to Newton's empirical law of cooling, in essence a one-parameter representation of convective diffusion near a solid surface. The same tactic emerged between 1895 and 1905 in the idea of a diffusion layer or stagnant film adjacent to a soluble solid in contact with stirred solvent. The principals were all chemists, the Americans Noyes and Whitney, Russian Shchukarev, and German Nernst. In 1912 Irving Langmuir, having completed his PhD with Nernst and quit Stevens Institute of Technology to join General Electric, reported on his studies of heat transfer from lamp filaments. Citing the high viscosity and high thermal conductivity of gases at filament temperatures of 2200°K and higher, Langmuir stated that the loss of heat by free convection—and even forced convection—takes place exactly as if there were a film of stationary gas around the filament, through which the heat is carried entirely by conduction. This idea of a conduction or diffusion film was picked up by W. K. Lewis and his chemical engineering colleagues at MIT, who elaborated it into the familiar "two-film theory" of transfer across *fluid* interfaces. But in doing so they obscured the hot and hypothetical character of Langmuir's stationary film: Lewis and Whitman (1924) actually wrote of surface layers of liquid "practically free of mixing by convection," which could be interpreted as merely laminar flow, probably rectilinear flow, possibly plug flow and effectively stagnant films. Successive editions of the standard textbook by Walker, Lewis, and McAdams appear to have spread the stagnant-film picture along with the series-resistance concept. Chemical engineers focussed on measurement and correlation of "film thicknesses" or "transfer coefficients."

The physical picture from this first stage consists of separate diffusion resistances characterized by lumped parameters as in elementary electrical circuits. It requires only simple algebra, although an ordinary differential equation is in the background. Rather than fixed potential or fixed flux at phase boundaries it in effect rests on the next simplest boundary condition, a linear relation between flux and potential involving only a single empirical parameter to describe whatever combination of convection and diffusion exists. There is no evidence of familiarity with relevant concepts from classical inviscid hydrodynamics, much less from the viscous flow theory that was available in the first decades of the century.

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What are the effects of convective movement on otherwise diffusive transport, particularly in the neighborhood of fluid interfaces?

STAGE TWO: RECTILINEAR FLOW IDEAS

Higbie in his 1934 thesis and well-known 1935 paper recognized that when gas and liquid are brought together there must first of all be penetration of the liquid by the dissolving gas, and that this sort of thing happens repeatedly in bubbler absorbers and packed towers, any bit of interface between gas and liquid having a limited life or time of exposure. Much the same idea had been put forward independently by the Dutch physiologists Dirken and Mook in 1930, who were concerned with gas exchange with blood yet judged it worthwhile to study basic aspects of absorption. Like Higbie they attempted to demonstrate their idea experimentally. Higbie knew and understood the physical chemical literature on diffusion. On the fluid mechanical side he had some appreciation of turbulent flow, for example in Miyagi's experiments; but he adopted the Lewis-and-Whitman picture of a film of liquid at the interface and regarded it as being in streamline flow, by which he evidently meant rectilinear, plug-like motion. Vyazovov in 1940 and Pigford independently in 1941 applied "penetration theory" to absorption into falling liquid films in rectilinear flow with semi-parabolic velocity profiles—taking a convective diffusion effect into explicit account for the first time. Such endeavors were familiar from the heat transfer literature, however, for example in Leveque's 1928 analysis which was featured in T. B. Drew's wonderfully prescient paper a few years later in the Transactions of the AIChE. Mass transfer into rectilinear flows is still an active topic, as evidenced by researches by Kramers and Kreyger (1956), Beek and Bakker (1967), Byers and King (1967), and one of my coworkers, Majoch.

Historically in the second stage the model consisted of highly idealized flow parallel to the fluid interface, flow that somehow is regularly interrupted after an ill-defined exposure time, and can then be re-established. Analysis of transfer involved a comparatively simple partial differential equation more familiar in the theory of heat conduction, where many relevant problems had already been solved. By the mid-40's the powerful Laplace transform technique was an effective tool in the hands of a few chemical engineers. Fluid mechanical concepts were not, but Prandtl's boundary layer notions were being applied elsewhere to heat transfer between solids and fluids.

STAGE THREE: TURBULENT DISTRIBUTION FUNCTIONS

This stage might have opened with chemical engineering notice of the 1932 Royal Society paper by Fage and Townend reporting microscope observations of suspended particles in "semi-turbulent" motion 0.001 inch from a *solid* wall, well within a "laminar" or viscous sublayer thirty times thicker. Or of the summary and discussion of those observations in Goldstein's "Modern Developments in Fluid Dynamics," the beacon work that appeared in 1938. Or of the 1949 paper by Kishinevskii and Pamfilov, in which hypotheses of laminar sublayers and films near fluid interfaces in well-agitated systems were rejected in favor of a picture of turbulence *continuously* renewing interface and transferring solute by convection alone. The investigators from Kishinev employed very fuzzy algebra and integral calculus and did not hit upon the convincing arguments for their heretical contention that the mass transfer coefficient could be independent of molecular diffusivity; worse still at that time, they wrote in Russian. Two years later and independently, Danckwerts too rejected the by then conventional misconception of a "stagnant" film; he held it likely that "turbulence" can extend to a fluid interface, erasing all resemblance to laminar boundary layer flow there; and he set about showing that working formulas derived from the stagnant-film hypothesis can be derived equally well from more palatable hypotheses. In his well-known surface renewal theory Danckwerts related the rate of absorption by penetration in Higbie's model, to an empirical parameter s characterizing the rate and reflecting the statistics of surface renewal—on grounds that an undefined "scale of turbulence" is so much greater than the "depth of penetration" that "relative motion of liquid at different levels close beneath the surface may be disregarded" (as I shall bring out later, this presumption can be quite inaccurate). The basic contribution was the application of statistical ideas to the picture of surface renewal, or replacement, as a stochastic process

powered by an underlying turbulent field. Subsequently Danckwerts, Hanratty, Davidson, Perlmutter, King, Koppel and others have put forward various distribution functions of surface age, exposure time, or residence time. Andrew, Dobbins, Toor and Marchello, and Harriott have proposed modifications in Higbie's original penetration model, one reason being to bridge the gap between the old film formulas and the surface-renewal formulas for the dependence of mass transfer coefficient on molecular diffusivity. The same reason has led still others to offer rankly empirical correlating formulas that warrant no further comment.

The dominant physical picture in the third stage is of locally intermittent yet grossly steady "surface renewal" by distinct "eddies" the arrivals of which follow various statistics that are supposed to represent the essence of turbulence. There is evidence here of growing awareness of fluid mechanics and of considerable mastery of the mathematics of age and residence-time distributions, the latter a topic that became increasingly fashionable in chemical engineering analysis during the fifties.

STAGE TWO *bis* : CURVILINEAR FLOW WORK

Simultaneously with the preceding stage there emerged, from analyses of simple laboratory absorbers designed for basic studies, a lot of information on the effect of curvilinear laminar convection on diffusion. This information can be used to construct significant generalizations of Higbie's original penetration model (as I shall discuss later). First came a rather crude analysis by Lynn, Straatemeier, and Kramers in 1955 of absorption into the nonuniform film flow over the surface of a sphere. Davidson and Cullen then treated the same problem more satisfyingly with the convective diffusion equation. In the same period I tackled end effects in wetted-wall columns and laminar liquid jets, and a year or two later the papers by Scriven and Pigford appeared, emphasizing the strong effect of the velocity component *normal* to an accelerating interface and presenting accurate general formulas for situations in which the scale of relative tangential motion is much greater than the "depth of penetration." The same results were independently rederived by Angelo, Lightfoot, and Howard in 1966 and presented with emphasis on the surface dilatation, divergence, or "stretch" that accompanies convective motion normal to the interface. Models of flow and transfer in boundary layers at fluid interfaces in nearly rectilinear flows have been treated by Potter (1957), Beek and Bakker (1961), and notably Goren (1966). Others have studied the simultaneous diffusion and convection around a growing bubble. The most significant curvilinear flow work (in my estimation, and for reasons to be discussed) is my former co-worker W. C. Chan's exact solutions of the problem of transient convective diffusion in irrotational stagnation flow, which formed part of his 1964 thesis. Very recently Majoch, exploiting a 1967 observation by Romanians Ruckenstein and Berbente, has added a solution for a case of rotational stagnation flow as well.

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These developments reflect increasing mastery of the relevant fluid mechanics, expanding experience with the convective diffusion equation, and growing proficiency in the similarity and approximate methods for solving it.

STAGE FOUR: TURBULENCE CONCEPTS AND MODEL FLOWS

Levich, as described in the translation of the second edition of his "Physicochemical Hydrodynamics," was the first to apply Prandtl's mixing length scheme of dimensional analysis—for that is all it is—to absorption at a fluid interface buffeted by eddies generated at depth. His attempt spawned others by Ruckenstein and by C. J. King, the latter placing the greatest reliance on the controversial notion of a turbulent eddy diffusivity, the origins and justifications of which lie in the rather different process of turbulent transfer across mean streamlines that are nearly rectilinear, as in duct, boundary-layer, and jet flows. More fundamental turbulence theory is in short supply, and what is available has been classified by the authority Townsend into wall turbulence, free turbulence, and convective turbulence. Conspicuous in its absence is a corpus of what I would call interfacial turbulence had not that term been pre-empted; "free boundary turbulence" must do. Free boundary turbulence is convective chaos only

partially constrained by the presence of an interface that allows great freedom of tangential movement, and restricted though appreciable freedom of normal movement.—and which is capable dramatic conversions of larger scale into smaller scale motions.

Danckwerts remarked in his 1951 surface-renewal paper that "A complete development of the subject would require further discussion of the relation of s [the renewal rate, or reciprocal of mean exposure time] to the hydrodynamics and geometry of the system." Only very recently have the first tentative steps been taken in this direction, for example by Shulman and Mellish in observing flow patterns in packed towers (1967), Fortescue and Pearson using turbulent channel flows (1967), and Ting and Davies with turbulent liquid jets (1967). Efforts are also afoot to relate to turbulence parameters not only the constants in distribution functions, but also their functional forms and the local flow-and-transfer models—Chan's microflow elements—which are regarded as being distributed. In still unpublished work my former associates Spriggs and Grgurich and I have toyed with a fascinating experimental model of a turbulent "eddy" (of which more later). Two years ago Boyd, Muenz, and Marchello reported experiments on the effect of simple progressive surface wave motion on gas absorption; unhappily any effect was overridden by extraneous large-scale convective motion. The same complication intervened in the more recent investigation of absorption into standing surface waves by Mani and Goren (as it had in a cruder attempt under my supervision in 1964, and as it probably did in the experiments of Bretsznajder and Pasiuk in Poland a couple years earlier). Attempts at analyzing the effects of surface waves on transfer in seemingly accessible special cases have been made by Chan (1964), Bentwich (1966), E. E. O'Brien, (1967), and my Brazilian associate Vieira.

In this current stage of development turbulence concepts and model flows have not yet been united. Attackers on both fronts are, or ought to be, armed with the same increasing mastery of fluid mechanics that I pointed out earlier. Unfortunately the basic fluid mechanical information that is really needed is simply not available, and one should ask whether chemical engineers are to continue messing around with what little is available, or are they to go after some needed "engineering science" themselves?

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STAGE FIVE: PENDING DEVELOPMENTS

For reasons some of which should become clearer as I proceed, I believe the major areas of research on flow and transfer at fluid interfaces in the near future will be—or should be!—the following: 1. Observations of turbulent interfaces by high-speed, high-magnification photography and, later on, measurements of correlation and intermittency factors within the fluids. 2. Theory of convective diffusion fields, particularly velocity fields which admit useful exact solutions or typify periodic and almost periodic motions. 3. Comparative studies of the sensitivity of final working formulas to the details of both model microflow elements and the distribution functions they might follow. 4: Theory of free-boundary turbulence, transversely isotropic and unidirectionally inhomogeneous.

Actually I set out above not to prognosticate, but to examine the ways in which chemical engineers have thought about transfer between fluid phases. It is obvious that the successive stages in their thinking have depended directly on the current levels of physical *and* mathematical sophistication. The sophistication must be possessed both by the innovator, who has to express original physical insight in mathematical language if it is to support engineering calculations, *and* by the user, who must grasp that language and should understand the underlying physical insight. We can see failures on both counts in the histories of the (stagnant!) film, penetration, and renewal theories, which have frequently been less than perfectly understood—even among chemical engineering textbook writers.

Though I haven't emphasized the fact in the foregoing review, I should point out that there is a lasting value of *simplicity* in a concept, a model, or a theory. The simplicity of something that has served us well in the past is a strong driving force for rationalizing it anew after we have become aware of its considerable limitations and

perhaps temporarily rejected it in the light of newly won sophistication. An obvious example can be seen in the multitude of interpretations the mass transfer coefficient has earned since its filmy start. On the other hand, there is real danger in too easy or too attractive a model. The formalism of the film theory apparently was so elementary as to have deceived students and mature engineers alike into investigating basic mechanisms no farther during a couple of decades of Middle Ages. And a different example: Fascination with distribution functions and the like seems to have been so great as to obscure the distinction between the statistics obeyed by model elements and the working of an individual element, and to inhibit inquiry into the latter during a decade or more of the Modern Age.

POSTSCRIPT

This seems an appropriate juncture, before returning to flow and transfer, to express my opinion that as engineers learn new science, however esoteric, and acquire mathematical skill, however abstract, their tradition and habit of practicality will produce engineering applications. The applications may come directly in invention, design, and operation or less directly—and often more profoundly—in concepts and patterns of thought that pass into what we call "physical intuition" and "engineering judgment."

Yesterday's dimly viewed science and incomprehensible mathematics are today's engineering research areas and tomorrow's engineering practice—and undergraduate course contents. Of course the undergraduate student must learn what engineering is about, and he should see in his professors a broad selection of engineering experience and outlook. But he should also have the opportunity of acquiring a truly liberal education, and this requires continually up-to-date scientific and technological competence within the engineering faculty. Maintaining this kind of competence takes research and substantial numbers of professors of the sort called engineering scientists—or, pejoratively, pseudoscientists. In my experience it is greatly aided by the presence of true scientists on the engineering faculty. True or false, these are persons whose participation signals the decline and fall of real engineering to a certain type of mind. Yet, how much might earlier competence in the areas of fluid mechanics and applied mathematics I mentioned have benefitted my present subject and chemical engineering in general! Suppose the young metallurgical engineer with a PhD in physical chemistry, Irving Langmuir, had joined the engineers and entrepreneurs at a leading university instead of the chemistry professors at Stevens! Why weren't there other young Langmuirs, more Drews and Higbies, researchers who scouted in the literature of physiology and Soviet applied science, critics to point out that not all films are 2300 degrees hot and stagnant? . . .

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