Recent developments have been the expansion of the interdepartmental ocean technology program to include the Medical School and Applied Electrophysics Department, the estabishment of a curricular group by Professor Warren S. Wooster, Chairman of the Scripps Graduate Department, to design the curriculum and initiate new courses which may be appropriate, and the selection of the University of California at San Diego for a Sea Grant College program.

SUMMARY

Greater efforts are needed in the development of applied marine science if the United States is to take full advantage of the potentially valuable resources of the oceans. Education will play a vital role in establishing the technological base, and the federal government has moved to assist the development of ocean engineering, especially through the Sea Grant College Act. The University of California at San Diego is developing a PhD program in Applied Marine Sciences in response to the awakening national awareness of the need to harvest the wealth as well as the knowedge of the sea.

ACKNOWLEDGMENT

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1968 Award Lecture

FLOW and TRANSFER at FLUID INTERFACES*

Part III - Convective Diffusion

L. E. SCRIVEN
University of Minnesota
Minneapolis, Minn.

LET US CONSIDER steady, two-dimensional cases of the three classes of basic flow represented in Figures 2 and 6. These are parallel flow, in which surface dilation is absent; nearly parallel flow, in which there is mild surface dilation of "rejuvenation"; and irrotational stagnation flow, in which there is strong surface dilation and concomitantly the effect of convection normal to the interface completely overshadows that of convection parallel to the interface. The appropriately specialized versions of the convective diffusion equation are tabluated in Figure 11. Note that in the first two categories diffusion parallel to the interface can be neglected in comparison with convection in that direction. The boundary conditions in every case are a uniform and constant equilibrium concentration at the fluid interface and an unchanging concentration at great depths.

The leading convective diffusion solution for parallel flow is that of Leveque (1928), rederived by Elser (1949) and Kramers and Kreyger (1956); approximate solutions for some other instances of parallel flow have been computed by Beek and Bakker (1967) and Byers and King (1967). Perhaps the most useful exact solution will be that obtained recently by my coworker Majoch and described in Figure 12; although the

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Parallel Flow $$0 + v_z(x)\frac{\partial c}{\partial z} = \mathcal{D}\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2}\right] \quad \left(\frac{\partial^2 c}{\partial z^2} \to 0\right)$$

Nearly Parallel Flow $$v_x(x,z)\frac{\partial c}{\partial x} + v_z(z)\frac{\partial c}{\partial z} = \mathcal{D}\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2}\right] \quad \left(\frac{\partial^2 c}{\partial z^2} \to 0\right)$$

$$v_x = -\int(\partial v_z/\partial z)\,dx$$

Stagnation Flow $$\frac{\partial c}{\partial t} + v_x(x)\frac{\partial c}{\partial x} + v_z(z)\frac{\partial c}{\partial z} = \mathcal{D}\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2}\right]$$

$$v_x = ax \quad , \quad v_z = -az$$

Fig. 11.—Convection Diffusion Equations.

Leveque solution is the special case n = 1(i.e., $v_z = ax$) the range n>1 corresponds to vanishing shear stress at the interface and is more relevant to flow and transfer at free surfaces. The solution conveys the very important lesson that convection and diffusion are not additive processes

$$ax^n\frac{\partial c}{\partial z} = \mathcal{D}\frac{\partial^2 c}{\partial x^2}, \qquad c(x,0) = c(\infty,z) = c_o, \qquad c(0,z) = c_e$$

Similarity transformation $\eta = xf(z)$:

$$-(n+2)\eta^{n+1}\frac{dc}{d\eta} = \frac{d^2c}{d\eta^2} \quad \text{provided} \quad f^{n+1}\frac{df}{dz} = \frac{(n+2)\mathcal{D}}{a}$$

$$\frac{c - c_o}{c_e - c_o} = \frac{n+2}{\Gamma(1/n+2)}\int_0^{\eta}\exp(-y^{n+2})dy \quad \text{if} \quad f(z) = \left[\frac{(n+2)^2\mathcal{D}z}{a}\right]^{\frac{1}{n+2}}$$

Fig. 12.—Steady Transfer—Parallel Flow. (Majoch & Scriven 1968).

(with the trivial, inconsequential exception of rigid-body motion parallel to a concentration gradient). Convection affects diffusion by tilting and sharpening or dulling concentration gradients, and it can do this even when flow is perpendicular to the overall concentration difference. This fundamental feature of the convective diffusion process was scarcely known in the era of Lewis and Whitman and Higbie, nor has it gotten enough attention from those following in Danckwerts' steps. Whether relative motion of liquid at different depths close beneath an interface may safely be neglected depends very much on the nature of that motion.

The most informative convective diffusion solution for nearly parallel flow is, in my opinion, one I published with R. L. Pigford in 1959 as part of a study of flow and transfer in laminar liquid jets. It was rediscovered in a somewhat different context by Angelo, Lightfoot, and Howard (1966). It rests on an approximation valid insofar as the streamwise varying tangential component of velocity is substantially independent of depth within the zone penetrated by convective diffusion (Figure 13); equivalently, it

By continuity $$v_x = -\int_0^x(\partial v_x/\partial z)dx \simeq -x\frac{dv_s}{dz}$$

Hence $$-x\left(\frac{dv_s}{dx}\right)\frac{\partial c}{\partial x} + v_s(z)\frac{\partial c}{\partial z} \simeq \mathcal{D}\frac{\partial^2 c}{\partial x^2}$$

Approximate solutions by the "integral method" led to the similarity transformation $\eta = xf(z)$ and exact solution.

Fig. 13.—Steady Transfer—Nearly Parallel Flow (1).

holds in the zone where flow is so dominated by boundary conditions that the normal component of velocity is proportional to distance from the interface (as we saw at the outset). The solution, interestingly derivable in different ways, again illustrates the merging of convection and

$$-2\eta\frac{dc}{d\eta} = \frac{d^2c}{d\eta^2} \quad \text{provided} \quad \frac{v_s}{f^3}\frac{df}{dz} - \frac{1}{f^2}\frac{dv_s}{dz} = -2\mathcal{D}$$

$$\frac{c - c_o}{c_e - c_o} = \operatorname{erfc}\eta \quad \text{provided} \quad f(z) = \frac{v_s(z)}{\sqrt{B + 4\mathcal{D}\int_0^z v_s(\zeta)d\zeta}}$$

$$\eta = xf(z), \qquad B \text{ from b.c. @ } z = 0$$

Fig. 14.—Steady Transfer—Nearly Parallel Flow (2). (Scriven & Pigford 1956, 1959).

diffusion into a single process (Figure 14). The corresponding flux formula (not shown) confirms that a velocity component toward the interface, hence $dv_s/dx>0$, enhances interphase transfer even though the velocity component vanishes *at* the interface; conversely a normal component away from the interface, hence $dv_s/dz>0$, reduces the rate of interphase transfer —though not in the same proportion, generally. These phenomena stand out in the next class of flow.

Because velocity normal to the interface has the greatest effect on interphase transfer, it is logical to seek the class of flows that most fully typifies normal motion and still leaves the convective diffusion equation tractable. Chan selected two-dimensional and axisymmetric, irrotational stagnation flows, which nearly fulfill the Navier-Stokes equation, do satisfy the kinematic and tangential traction boundary conditions at free surfaces, and epitomize the fact that relative normal velocity near free interfaces increases linearly with depth (v_z=-az; cf. Figure 11). The history of convective diffusion solutions is interesting. By separation of variables and series

$$\frac{\partial c}{\partial t} + a(t)x\frac{\partial c}{\partial x} - a(t)z\frac{\partial c}{\partial z} = \mathcal{D}\left[\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial z^2}\right] \quad \text{and i.c. + b.c.'s}$$

Invariant under $x \longrightarrow x' = x - A\exp[\int_0^t a(t)dt]$

Therefore $c(x + dA, z, t) = c(x, z, t)$ and $\partial c/\partial x = 0$

$$\frac{\partial c}{\partial t} - a(t)z\frac{\partial c}{\partial z} = \mathcal{D}\frac{\partial^2 c}{\partial z^2}$$

Fig. 15.—Unsteady Transfer—Unsteady Irrotational Stagnation Flow (1).

expansions Chan in 1963 obtained a formal solution of great generality and little practicality, except that he very shrewdly identified the particular series for flux at the interface in the case of main interest (1964). Simultaneously a co-worker, B. A. Finlayson, obtained close approximations by weighted-residual methods. Within a a month my former colleague, C. V. Sternling, pointed out privately that a transformation of variables leads to a closed-form solution in the case of main interest. Within another month Chan (1964) justified this solution by a symmetry argument (Figure 15) and rederived it by the similarity transformation technique to which nearly parallel flow had yielded earlier. More recently we have identified Sternling's variables as material coordinates and a curiously warped time (Figure 16). From the Daliesque point of view these variables provide, the convective diffusion process appears as though it were pure diffusion (unsteady diffusion equation in Figure 16), which is remarkable — and a subject of current investigation.

Material coordinates: $\xi = x\exp(-\int_0^t a(t)dt)$, $\zeta = z\exp(\int_0^t a(t)dt)$

Warped time: $\tau = \int_0^t \exp[2\int_0^{t'} a(t'')dt'']dt'$

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial \zeta^2}, \quad c(\zeta, 0) = c(\infty, \tau) = c_o, \quad c(0, \tau) = c_3$$

$$\frac{c - c_o}{c_e - c_o} = \text{erfc}\left[\frac{\zeta}{\sqrt{4\mathcal{D}\tau}}\right] = \text{erfc}\left[\frac{z}{\sqrt{\frac{2\mathcal{D}}{a}[1 - \exp(-2at)]}}\right] \quad \text{steady flow}$$

Fig. 16.—Unsteady Transfer—Unsteady Irrotational Stagnation Flow (2).

The convective diffusion solution for steady, irrotational stagnation flows yields the formula for flux at the interface shown in Figure 17 and graphed in Figures 18 and 19. Study reveals that so long as the exposure time is no longer than it takes fluid particles to move 20% closer to or farther from the interface, the simpler formula for penetration solely by diffusion is a fair approximation; one also finds that there is no

Stagnation-flow model: $j = (c_e - c_o)\sqrt{\frac{\mathcal{D}}{\pi t}} \cdot \sqrt{\frac{2at}{1 - e^{-2at}}}$

Penetration model: $j_* = (c_e - c_o)\sqrt{\frac{\mathcal{D}}{\pi t}}$

$$\frac{k}{k_*} = \frac{j}{j_*} = \sqrt{\frac{2at}{1 - e^{-2at}}}$$

Fig. 17.—Instantaneous Mass Flux.

natural length scale with which to compare a purely diffusive penetration depth $\sqrt{\mathcal{D}t}$. At longer exposure times, flow toward the interface ($a>0$) steepens the concentration gradient at the interface appreciably and therefore the formula indicates increased transfer rates; conversely, transfer rates and concentration gradients are reduced by flow away from the interface

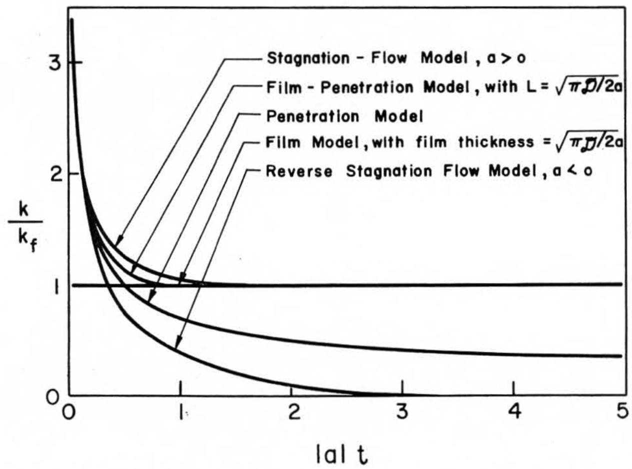

Fig. 18.—Instantaneous Transfer Coefficients vs. Time (Dimensionless Forms).

($a<0$, "reverse stagnation flow"). At very long exposure times, the flux in stagnation flow asymptotically approaches a *constant* value, which is also characteristic of film models of flow and transfer (Figure 18). On the other hand the flux in reverse stagnation flow asymptotically approaches zero, as does the flux in the penetration model; but the former diminishes so rapidly with time that the total amount transferred approaches a finite asymptote, whereas the total transferred increases without bond in the penetration model (Figure 19). Normal convection away from the interface eventually brings the concentration at all finite depths to the interfacial value, effectively saturating the liquid and leaving its equivalent to a "stagnant pocket" of the sort suggested by Perlmutter (1961).

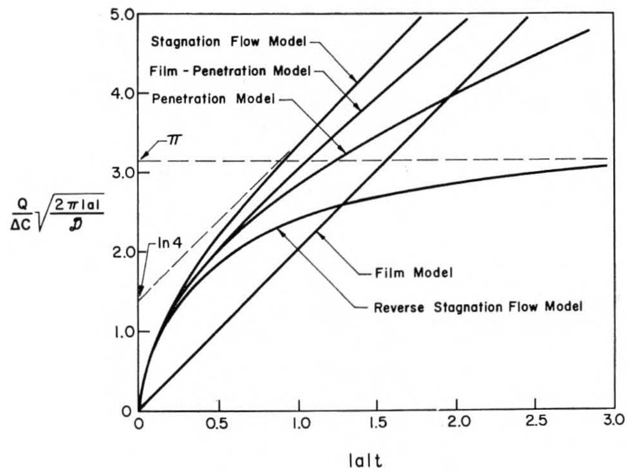

Fig. 19.—Total Transfer vs. Time of Exposure (Dimensionless Forms).

THE SIMPLE STAGNATION FLOW model accounts for the greatest effect convection can have on diffusion in transfer at fluid interfaces. In its functional behavior it spans the film model, the penetration model, and even an undeveloped stagnant-pocket model. Populations of stagnation flows of different flow strengths ($a>0$, $a=0$, $a<0$) can match the transfer performance of the various and sundry combinations, elaborations, and populations of less realistic microflow elements that we reviewed earlier. The stagnation flow model is the first to build convection right into the basic transfer process in the microflow element, and the result is a "master equation" that clarifies why each of the earlier models yields a functional form of mass transfer coefficient that may be useful in one or another range of practical circumstances.

Furthermore, the convective diffusion solutions for *unsteady* stagnation flows might permit more accurate modeling of turbulent action, in that they can account for development periods of microflow elements, i.e., the interruptive events need not be taken as instantaneous. What's more, populations of stagnation flows can be mixed with populations of other types of microflow elements to give even more versatile correlating formulas for transfer rates. I do not believe, though, that these are directions in which to push research, although comparative studies of the sensitivity of final working formulas to microflow elements and distribution functions probably would be widely instructive. Before turning to what I think is needed more, I should comment on one feature by which certain models can be differentiated.

This distinguishing feature is the way in

$$k \propto \mathcal{D}^n$$

Fictitious film	$n = 1$	Film-penetration	$1/2 \leq n \leq 1$
Penetration models	$n = 1/2$	Subsurface sweep (Beek & Bakker)	$1/2 \leq n \leq 2/3$
Surface rejuvenation Stagnation flows	$n = 1/2$	Subsurface sweep (Majoch)	$1/2 \leq n \leq 1$

Fig. 20.—Diffusivity Dependence of Mass Transfer Coefficient.

which mass transfer coefficient depends on the coefficient of molecular diffusion. The models we have been considering are contrasted in Figure 20; in all of them the mass transfer coefficient varies as the diffusivity raised to a power of from one-half to one, which is the range encompassing most experimental results. Yet there are a few data in the literature which indicate a weaker dependence on diffusivity, even no dependence at all. To account for such data several correlating formulas have been put forward: see Figure 21. Kishinevski's arguments are unconvincing but I suspect the data and his formula can be rationalized in terms of *time-averaged* convective flux by chaotic motions back and forth across the *mean* position of the fluid interface — a subject of further investigation. King has explored possibilities inherent in an empirical "eddy diffusivity" for scalar transport in free boundary turbulence, and has noted that were eddy diffusivity to increase linearly with distance from the interface (measured in a frame of reference moving with the interface, presumably), the average transfer coefficient would be proportional to the square-root of molecular diffusivity in the first instant of exposure and would become progressively less dependent as exposure time increased. But as Majoch recently pointed out at Minnesota, such an eddy diffusivity corresponds to a mean normal component of relative velocity everywhere including *at* the interface (cf. Figure 21), and while this would amount to a convective mechanism quite independent of molecular diffusivity, it does violate the elementary kinematic boundary condition of

Kishinevskii (1949, 1954): $j = \text{"}v_n c\text{"} = \overline{v_n c}, \quad \therefore n = 0$

Davies (1963): $j = \text{"}v_n \Delta c\text{"} + \Delta c\sqrt{\mathcal{D}/\pi t}, \quad \therefore 0 \leq n \leq 1/2$

King (1966): $\frac{\partial \bar{c}}{\partial t} = \frac{\partial}{\partial z}\left[(\mathcal{D} + \text{"}\epsilon\text{"})\frac{\partial \bar{c}}{\partial z}\right], \epsilon = az \Longrightarrow 0 \leq n \leq 1/2$

But $\epsilon = az \Longrightarrow \frac{\partial \bar{c}}{\partial t} - \underset{\sim\sim}{a\frac{\partial \bar{c}}{\partial z}} = (\mathcal{D} + az)\frac{\partial^2 \bar{c}}{\partial z^2}, \quad \therefore 0 \leq n \leq 1/2$

N.B. $\epsilon = az^2 \Longrightarrow \frac{\partial \bar{c}}{\partial t} - \underset{\sim\sim}{2az\frac{\partial \bar{c}}{\partial z}} = (\mathcal{D} + az^2)\frac{\partial^2 \bar{c}}{\partial z^2}, \quad \therefore n = 1/2$

Fig. 21.—Correlating Formulas for Weak Diffusivity Dependence.

. . . a "vorton" arriving at glancing incidence at a fluid interface is "scattered" . . . the toroidal eddy arrives . . . pushes along the surface briefly as it tips forward and then, parting company from the "ripplons" it has raised, it descends somewhat less energetically back into the bulk phase.

hydrodynamics. The lesson here is that such crude concepts as eddy diffusivity are poor substitutes nowadays for experimental and theoretical fluid mechanics together with the instantaneous and time-average convective diffusion equations. Nevertheless it does happen that an eddy diffusivity that increased as the *square* of distance from the interface would come very close to producing the same concentration field and mass transfer coefficient as a certain stagnation flow (Figure 21). And a *negative* eddy diffusivity that decreased in the same way would nearly match the corresponding reverse stagnation flow in its effect!

IN OUR ONGOING PROGRAM at Minnesota for understanding flow and transfer at fluid interfaces the question of greatest current interest is how periodic motions, such as accompany progressive and standing surface waves, affect diffusion. While we have some partial answers the state of the results is still such that they are more easily sketched in lecture than in writing. They and the further questions they raise do not point toward an eventually comprehensive theory of convective diffusion fields.

Vortex rings are the simplest experimental models of the "eddies" that according to surface renewal, surface replacement, or surface rejuvenation notions are responsible for interrupting quiescent interludes of diffusion at interfaces. In a preliminary to observing turbulent interfaces carefully, we have watched the encounters of dye-marked vortex rings with water-air and water-benzene interfaces. That this is edifying is plain from the motion-picture record, but it is difficult to summarize all of the wonderful things one sees. It will have to suffice here to report that under certain circumstances a "vorton" arriving at glancing incidence at a fluid interface is "scattered"; in other words the toroidal eddy arrives from the bulk phase, pushes along the surface briefly as it tips forward and then, parting company from the "ripplons" it has raised, it descends somewhat less energetically back into the bulk phase. Vortons arriving at rigid surfaces are invariably annihilated, incidentally—another contrast between the boundary conditions at rigid walls and fluid interfaces.

Beyond these sorts of studies, what I think is needed is research on the mechanics of fluid interfaces under turbulent bombardment, research designed to shed light on such matters as when populations of microflow elements are appropriate and how to relate the parameters of the elements and of their distribution functions to fundamental parameters of the turbulence — which is to say, to parameters in a turbulence theory that is not yet well in hand.

Not everyone would agree. In closing let me call your attention to the viewpoint of someone in closer touch with the practical problem past and present. P. V. Danckwerts evidently never returned to the hydrodynamic issues that he acknowledged but left unexplored in his well-known 1951 paper. At the Twentieth Congress on Theoretical and Applied Chemistry in Moscow fourteen years later, according to the twice-translated version in the first issue of *Theoretical Foundations of Chemical Engineering,* he said,

> "The problem of the absorption of gases, from the industrial aspect, has an essentially practical character and our approach to it must be pragmatic. This does not mean the negation of the role which the scientific understanding of the phenomenon plays but it must be understood that the contemporary state of applied sciences at times makes us overemphasize the value of analytical methods and that, in the case of too great expenditures of time in clarifying the mechanism of processes, the substance of the practical problem may fall from view."

ChE news

OPPORTUNITIES FOR DISADVANTAGED YOUTH AT BERKELEY

The Chemical Engineering Department of the University of California at Berkeley has obtained funds to support a limited number of minority-group students in both its undergraduate and graduate programs. At the graduate level a student without formal training in chemical engi-