

Interfacial Turbulence: Hydrodynamic Instability and the Marangoni Effect

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The origin of interfacial turbulence, spontaneous agitation of the interface between two unequilibrated liquids, has been explained in terms of classical flow, diffusion, and surface processes. The essence of the explanation is the long-known though much neglected Marangoni effect, wherein movement in an interface is caused by longitudinal variations of interfacial tension. It is proposed that interfacial turbulence is a manifestation of hydrodynamic instability, which is touched off by ever present, small, random fluctuations about the interface.

A simplified mathematical model has been analyzed in order to detail the mechanism of the "interfacial engine" which supplies the mechanical energy of interfacial turbulence. In its present form the analysis incorporates several drastic simplifications, though ways of removing some of these have been suggested. The groundwork has been laid for the more elaborate analyses that are needed for a decisive test of the theory.

The analysis shows how some systems may be stable with solute transfer in one direction yet unstable with transfer in the opposite direction, a striking result. It also suggests that interfacial turbulence is usually promoted by (1) solute transfer out of the phase of higher viscosity, (2) solute transfer out of the phase in which its diffusivity is lower, (3) large differences in kinematic viscosity and solute diffusivity between the two phases, (4) steep concentration gradients near the interface, (5) interfacial tension highly sensitive to solute concentration, (6) low viscosities and diffusivities in both phases, (7) absence of surface-active agents, and (8) interfaces of large extent.

That some of these effects have been observed in the laboratory lends credence to the theory.

Strange are the effects when unequilibrated liquids are brought into contact. If a solution of 10% methanol in toluene is placed quietly upon water, the water remains clear, but in the organic phase a turbid emulsion of water droplets appears. With a solution of 40% methanol in toluene the organic phase remains clear, while an emulsion appears in the water (19). Yet if pure toluene is placed upon water containing methanol, no spontaneous emulsification occurs. If pure toluene is placed upon an aqueous solution of butyric or valeric acid, there arises intense though localized stirring on the toluene side of the interface; but if under the same conditions the solute transferred is acetic or propionic acid, there is no stirring action at all (26). If diglycol laurate is placed upon water, streamers of the organic material very slowly extend downward into the water, bend round when they near the bottom of the container, and then slowly grow upward (19).

An extensive qualitative investigation by Wei (27) points up the widespread occurrence of these and similar effects. Having noticed localized stirring at the interface in certain liquid extraction experiments which gave unexpectedly high mass transfer coefficients, Wei went on to test systematically for spontaneous interfacial activity between many different liquids, some pure and others containing a solute. No activity is seen

when neither phase contains a solute. Sometimes there is activity when a single solute is extracted without chemical reaction. There is pronounced activity in almost every instance where the two phases contain reacting solutes. Wei distinguishes several general types of disturbance, which at times occur together: localized stirring with rippling and twitching of the interface; slow moving transparent streams leaving the interface, evidently differing slightly in composition or temperature from the bulk through which they move; slower moving opaque streams from the tips of which tiny droplets disengage, often forming an emulsion; and mistlike emulsions slowly forming about the interface. The intensity of the activity varies markedly from system to system. It is usually greater for solute transfer from organic to aqueous phase than for transfer in the opposite direction. It is also influenced by solute concentration and the presence of surface-active agents. The greatest intensity is observed when there is rapid and highly exothermic reaction between two solutes near the interface, especially in systems with low interfacial tension (23, 27).

In some cases the behavior is even more bizarre; for example, when a layer of wet isobutanol containing hydrochloric acid is gently placed upon water saturated with isobutanol and containing ammonia, not only is there rippling and twitching of the interface but also, after 30 sec. or so, a water drop forms in

the alcohol phase, grows, sags down into the interface, and then bursts through, acquiring in the process a thin covering film of isobutanol. The double drop is propelled several centimeters into the aqueous phase, whereupon it disintegrates, leaving a much smaller droplet of isobutanol that descends another 10 to 30 cm., reverses direction, rises to the interface, and finally merges with the upper phase. Meanwhile a new drop forms above the interface, and the sequence is repeated.

Although the experiments so far described all involve nearly flat interfaces, disturbances of the same sort occur at rounded interfaces. When a drop of liquid is formed at a capillary tip immersed in a second immiscible liquid and a solute is initially present in one or the other phase, the interface is, in many cases, disturbed by rippling, while the adjoining liquid is turbulently agitated (11, 14, 24). At times there are localized eruptions at the interface (24). If it is pendent, the entire drop often pulsates violently and erratically (5, 7, 11); unattached drops behave in the same way (11, 23, 24). As in Wei's experiments the occurrence and intensity of these effects depend on the solvents and solute employed, upon solute concentration, and sometimes upon the direction of solute transfer. Surface-active agents tend to reduce the violence of the upsets, sometimes suppressing them completely.

Convection develops spontaneously at gas-liquid interfaces too. The clean surface of an ether-water solution twitches continuously during evaporation of the ether. However, the Langmuirs (10) observed that certain insoluble surface films can arrest the motion, thereby greatly reducing the rate of evaporation.

All these phenomena, with the possible exception of some cases of spontaneous emulsification (4), involve gross fluid motions and therefore demand the concepts of hydrodynamics for their explanation. The situation is unusual, however, in that the source of energy for driving the flows surely is the difference in chemical potential between the two phases. In a closed system such a potential difference diminishes as thermodynamic equilibrium is approached; accordingly, it is found experimentally that as time passes after the phases are first brought together, the disturbances

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ultimately subside. Furthermore no disturbances are observed on contact of phases already nearly in equilibrium. It is as though an engine were actuated by concentration and temperature gradients, more precisely by a gradient of chemical potential in the neighborhood of the interface. Many investigators have suggested that the engine is the interface itself (7, 10, 14, 18, 19, 24), but no detailed theory of its action has been advanced, except one of limited scope recently proposed by Haydon (8). It is well known that longitudinal variations of surface tension not only cause movement in a liquid surface but also bring forces to bear on the underlying liquid, setting it in motion. This has been called the *Marangoni effect* (1), although it was first explained by James Thomson (25). There are several very familiar examples of surface-tension-driven flows: tears of strong wine (16, 25), camphor dance, and crystal climbing (1). It is therefore to be expected that a synthesis of the dynamics of an interface, hydrodynamics, and diffusional transport will be required for a quantitative understanding of the interfacial engine.

What is the practical significance of the various kinds of spontaneous interfacial agitation, which collectively have come to be called *interfacial turbulence*?* Rates of mass transfer tend to be abnormally high in those extraction systems in which interfacial turbulence occurs; this is evident from Lewis's continuing research with a variety of systems (12, 13). Transfer rates may be several times as great as predicted from measured single-phase rate coefficients and current theories which assume a stagnant interface, as Sherwood and Wei found with certain extraction systems involving simultaneous chemical reaction (27). Although reports of these effects have thus far come only from laboratory experiments under well-controlled conditions, interfacial turbulence must also occur in industrial practice, but when and to what extent are unsettled. Thus laboratory and pilot plant extraction studies cannot be interpreted and are of limited use in scale up unless the state of the interface is known or can be predicted.

INTERFACIAL TURBULENCE AND HYDRODYNAMIC STABILITY

What is the mechanism of interfacial turbulence? How can one recognize beforehand the situations in which it will arise? How can one predict its form and magnitude from first principles? Only when these queries have been answered will it be possible to attack the problem of great practical importance,

quantitative prediction of the effect of interfacial turbulence on the rate of mass transfer between phases.

The key to understanding interfacial turbulence is the answer to the question when is a given system unstable relative to small perturbations in the vicinity of the interface? This may be posed as a problem of hydrodynamic stability with diffusion and interfacial movement playing indispensable parts. The methods of conventional linearized stability theory (15, 22d) may then be applied to determine the conditions for the onset of instability and the nature of the dominant disturbance. Unless simplifications are made, the mathematical exposition becomes so overgrown that its connection with physical reality is obscured. To lay bare the path, attention is focused on a highly pruned model that is not strictly realizable. But if it displays the salient behavior of actual systems—and it does—the fruitfulness of the approach is established. Moreover the resultant simplified theory then provides the needed groundwork for handling more complete models.

The authors' approach parallels the analysis of the stability of thermally stratified layers of fluid, begun by Rayleigh, which has been successfully applied to the prediction of onset of convection in fluids heated from below (15b, 21).

Description of the Model

The configuration to be studied is two semi-infinite, quiescent fluid phases in contact along a plane interface. The phases are in thermal but not in chemical equilibrium. A single solute, present in such low concentration that fluid properties may be taken as constant, is transferring between the phases. In at least two other nonequilibrium situations interfacial turbulence may arise. These are transfer of heat between phases in chemical equilibrium and transfer of materials which can react chemically to release heat or surface-active products near the interface. The first of these is virtually the same as the case selected because of the formal similarities of mass and heat transport and of the composition and temperature dependencies of interfacial tension; the second is but a combination of the mass and heat transfer cases, with, to be sure, added complications.

In the undisturbed state of the authors' model there is steady transfer of solute. This requires that the concentration gradient be linear throughout each phase. Although such a state is not entirely realistic, states closely resembling it in the neighborhood of the interface do obtain after two unequilibrated phases are brought together and diffusion is allowed to proceed.

The stability of this system is studied relative to two-dimensional infinitesimal disturbances. It suffices to consider a single Fourier component corresponding to the roll cells shown in Figure 1, for any arbitrary infinitesimal disturbance can be repre-

sented by superposition of such components.

The relevant set of linear, homogeneous, partial differential equations contains time only through derivatives with respect to time. Hence the solutions contain an exponential time factor; that is, the disturbances either amplify or decay exponentially. Thus one is led to a characteristic-value problem with the growth-rate constant as the parameter, the solution of which gives the initial growth rate of a disturbance of given cell size (wave length). If the real part of the growth constant, the amplification factor, is negative for all values of cell size, the system is stable; if it is positive for some values of cell size, the system is unstable. The unstable disturbances do not continue indefinitely to grow exponentially in time, of course; they eventually reach some fully developed form of finite amplitude. The rigorous deduction of the resultant finite flow is such a formidable problem that approximate methods are in order. Of these the most promising is the method applied by Malkus and Veronis to the Rayleigh problem (17). They have shown how to relate the macroscopic flow to the solution of the corresponding linearized stability problem. In any case one may reasonably expect that the nature of the fully developed flow is closely connected with the properties of that infinitesimal disturbance which is dominant, that is for which the amplification factor has the greatest positive value.

One point deserves special emphasis. In this model interfacial turbulence may arise spontaneously from ever-present small fluctuations about the interface. Neither the large-scale convection currents postulated by Haydon (8) nor any other gross upset originating at a distance from the interface need necessarily be present in the system.

Qualitative Behavior of the Disturbed System

If solute is diffusing from phase A to phase B, the roll cell conveys liquid rich in solute from phase A and liquid lean in solute from phase B toward the interface at point 1 (Figure 1). In the case of a developing disturbance the rates of convection differ in the two phases, being higher in the phase of greater kinematic viscosity.* Consequently the net change in solute concentration at point 1 depends, in part, on the ratio of kinematic viscosities of the two phases. The net change also depends on the ratio of solute diffusivities in the two phases, because molecular diffusion alters the composition of each parcel of liquid as it is conveyed toward the interface, tending to restore the original linear concentration gradients but acting more strongly in the phase of higher diffusivity.

If viscosity is higher in phase A, for example, the convection current is stronger there. If in addition the diffusivity is lower in phase A, the flow-induced concentration upset there is less affected by diffusion than in phase B; hence the

*Both highly irregular and more or less ordered flows originating in the interface are included under the name.

*For an account of the effect of viscosity in accelerating flows, see Schlichting (22c).

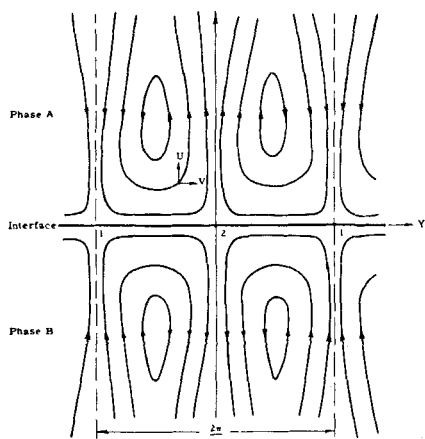


Fig. 1. Schematic diagram of flow disturbance showing circulation pattern of two-dimensional roll cells in cross section.

effect of the disturbance is greater on the side of phase A and the interfacial solute concentration is increased at 1. Because of symmetry and the necessary conservation of solute, the change in solute concentration is in the opposite direction at 2. Thus variations in concentration, hence also in interfacial tension, are induced along the interface. The interface is no longer in mechanical equilibrium and seeks a state of lower free energy through expansion of regions of low interfacial tension at the expense of adjacent regions of higher tension (the Marangoni effect). And because there can be no discontinuity in velocity at the interface, motion in it induces flows in the adjoining fluids.

Thus if interfacial tension increases with increasing solute concentration, the interface contracts at 1 and stretches at 2, and this motion opposes the original disturbance, causing it to be damped. If, on the other hand, interfacial tension decreases with increasing solute concentration, the motion of the interface is from 1 toward 2, which reinforces the original disturbance and causes it to be amplified.

Clearly if viscosity is lower and diffusivity is higher in phase A, or if the direction of solute transfer is reversed, the flow in the surface between 1 and 2 is reversed, producing just the converse of the effect described above. If the viscosity and diffusivity are both higher in the same phase, however, the direction of motion in the interface cannot be inferred except from the more detailed analysis which follows, for in this case convection and diffusion evidently are competing effects.

From these intuitive arguments one may anticipate that the stability of the disturbed system depends on the viscosity ratio, the diffusivity ratio, the direction of solute transfer, and the sign of the rate of change of interfacial tension with concentration. One sees that instability, when it occurs, is driven by

variations of surface tension; hence the phenomenon might be called *Marangoni instability*.

Synopsis of the Analysis

In dealing with an interface undergoing deformation, one should recognize that the interfacial tension under dynamic conditions differs from that exhibited under static conditions. In the following section the stability problem is formulated mathematically and its solution found. Because the coupling of flow and diffusion processes appears only in the interfacial shear-stress boundary condition on the flow and in the convective transport terms of the diffusion equation, it is possible to solve the hydrodynamic equations first. The diffusion equation describing the concentration disturbance is then solved, and finally the two solutions are combined by means of the interfacial shear-stress boundary condition to give the characteristic equation for the system.

Succeeding sections are devoted to the interpretation of the characteristic equation, which is complicated by the implicit nature of the equation and the necessity of handling both stationary and oscillatory instabilities, and to a discussion of the theoretical results. In this final section the consequences of the simplifying assumptions are reviewed, a program for generalizing the analysis is outlined, and some practical implications of the theory for the planning, reporting, and correlation of mass transfer experiments are given.

DYNAMIC INTERFACIAL TENSION

Long ago Plateau discovered experimentally, and Gibbs deduced rigorously, that in multicomponent systems extension of an interface produces an increase and contraction a decrease from the static interfacial tension, effects which resemble the action of a dilational viscosity operating in the surface (6). The magnitude of the change increases with rate of deformation and decreases with the rate at which equilibrium between the interface and the substrate phases is reestablished by transport of heat and material to or from the interface. This phenomenon is vital to this analysis because deformation of the interface results when an initial flow disturbance causes local variations in interfacial tension. This effect might be included in the analysis by computing the rates of change of temperature and concentration in and about a postulated separate surface phase. However, the required physical properties of the surface phase are unknown, and the computation is forbiddingly complex. Instead another approach, to be explained shortly, is used.

Another aspect of interfacial deformation must be considered. When an

interface is subjected to shear wholly in the plane of the interface, the surface molecules must be reoriented even when there is no change in area. The energy dissipated increases with the rate of shearing and is distinct from but analogous to the dissipation by ordinary viscosity in three-dimensional fluids. In many systems containing surface-active agents this surface shear viscosity is large and easily measured (9).

In classical fluid mechanics the substrate phases are treated as continuous media, and the phase interface is regarded as a mathematical surface subjected to a membrane tension. This approach is fruitful in physical problems where system dimensions and characteristic times are large compared with molecular dimensions and relaxation times, respectively. When these conditions obtain, the viscouslike interfacial effects described above are most conveniently incorporated into a hydrodynamic formulation by introducing two coefficients of surface viscosity. The stress, composition, and temperature of the substrate phases are assumed to follow the classical equations of motion and diffusion right up to a mathematical surface located in the phase interface. The two phases are assumed to be in thermal and chemical equilibrium at the interface. All departures of interfacial stress (tension) from that existing in a static system are attributed to surface viscosity regardless of their ultimate causes. The mathematical statement of this idealization of the interface is due to Boussinesq (3). By a procedure analogous to that used in deriving the Navier-Stokes equation it can be shown that any arbitrary surface deformation can be resolved into an isotropic dilation superimposed on a pure shear; likewise the stress in a surface can be resolved into an isotropic tension and a pure stress.* The dilational surface viscosity κ and the surface shear viscosity ϵ are defined as the ratios of the stress components to the corresponding components of the rate of deformation. These viscosities depend upon the temperature and composition of the substrate fluids and generally on the past history of

*Actually, surface deformation and stress are best represented as two-dimensional symmetric tensors.

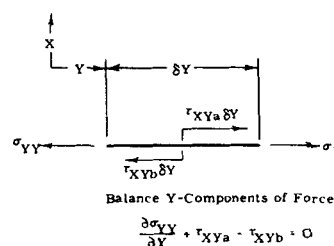


Fig. 2. Shear-stress boundary condition at the interface.

surface deformation. One can, however, consider only the simple case in which κ and ϵ are independent of the history of deformation. The corresponding idealization for three-dimensional fluids, which is actually the definition of a Newtonian fluid, proves to be entirely satisfactory for gases and many liquids. Nevertheless it is recognized that interfaces may exhibit any or all of the non-Newtonian effects that have been encountered in bulk fluids.

Thus in the first approximation the tension in the interface exceeds the static (equilibrium) interfacial tension by an amount κ times the rate of dilation (rate of area increase per unit original area per unit time), and the surface shear stress is ϵ times the rate of shearing in the interface.

MATHEMATICAL FORMULATION

Equations of Motion

For two-dimensional flow of an incompressible Newtonian fluid in the absence of body forces the Navier-Stokes equations reduce to (22b)

$$\frac{\partial U}{\partial t} + U \frac{\partial U}{\partial X} + V \frac{\partial U}{\partial Y} = -\frac{1}{\rho} \frac{\partial P}{\partial X} + \nu \left(\frac{\partial^2 U}{\partial X^2} + \frac{\partial^2 U}{\partial Y^2} \right) \quad (1)$$

$$\frac{\partial V}{\partial t} + U \frac{\partial V}{\partial X} + V \frac{\partial V}{\partial Y} = -\frac{1}{\rho} \frac{\partial P}{\partial Y} + \nu \left(\frac{\partial^2 V}{\partial X^2} + \frac{\partial^2 V}{\partial Y^2} \right) \quad (2)$$

The continuity equation is

$$\frac{\partial U}{\partial X} + \frac{\partial V}{\partial Y} = 0 \quad (3)$$

The development of flows of infinitesimal magnitude in an initially quiescent system is being investigated—that is, creeping flows; consequently the nonlinear terms of Equations (1) and (2) are of the second order of smallness and may be neglected in comparison with first-order terms. The pressure may be eliminated by cross differentiation and subtraction of Equation (1) from Equation (2):

$$\frac{\partial^2 V}{\partial t \partial X} - \frac{\partial^2 U}{\partial t \partial Y} = \nu \left(\frac{\partial^3 V}{\partial X^3} + \frac{\partial^3 V}{\partial X \partial Y^2} - \frac{\partial^3 U}{\partial X^2 \partial Y} - \frac{\partial^3 U}{\partial Y^3} \right) \quad (4)$$

It is convenient to introduce the stream function so that the continuity equation may be identically satisfied:

$$U = -\frac{\partial \psi}{\partial Y}, \quad V = \frac{\partial \psi}{\partial X}$$

A solution is sought for ψ of the form $\psi = \varphi(X)e^{i\alpha Y}e^{\beta t}$. With this form for

ψ one obtains from Equation (4) the Orr-Sommerfeld equation for a two-dimensional flow disturbance in an initially quiescent system:

$$\varphi'''' - 2\varphi'' + \varphi = \frac{\beta}{\alpha^2 \nu} (\varphi'' - \varphi) \quad (5)$$

The solution of this equation when $\beta \neq 0$ is

$$\varphi = \alpha_1 e^x + \alpha_2 e^{-x} + \alpha_3 e^{px} + \alpha_4 e^{-px} \quad (6)$$

where

$$p = \sqrt{1 + \frac{\beta}{\alpha^2 \nu}}$$

When $\beta = 0$, the solution is

$$\varphi = \alpha_5 e^x + \alpha_6 e^{-x} + \alpha_7 x e^x + \alpha_8 x e^{-x} \quad (6n)^*$$

where the arbitrary constants α_1 through α_8 are yet to be evaluated from the boundary conditions.

For simplicity it is supposed that the interfacial tension is sufficiently great so that the interface remains substantially planar. The eight boundary conditions required to specify φ (and thereby the velocities) in both phases are (i) to (iv) the disturbance remains finite at large distances from the interface; i.e. U_a and V_a are finite as $X \rightarrow \infty$ and likewise U_b and V_b as $X \rightarrow -\infty$; (v), (vi) the interface, which is the plane $X = 0$, is a streamline; that is $U_a(0, Y, t) = U_b(0, Y, t) = 0$; (vii) there is no slip at the interface; that is $V_a(0, Y, t) = V_b(0, Y, t)$; (viii) there is continuity of tangential stress at the interface. The essence of the analysis lies in (viii), which requires that

$$\tau_{XYb} - \tau_{XYa} = \frac{\partial \sigma_{YY}}{\partial Y} \quad \text{at } X = 0 \quad (7)$$

(Figure 2), where the shear stress on the upper side of the interface is given by (22a)

$$\tau_{XYa} = \mu_a \left(\frac{\partial U_a}{\partial Y} + \frac{\partial V_a}{\partial X} \right) \quad (8)$$

and similarly for the lower side. The interfacial tension in Equation (7) is the dynamic interfacial tension. In accordance with the formulation of Boussinesq (3), this tension depends upon the rate of deformation of the surface:

$$\sigma_{YY} = \sigma_0 + \kappa \left(\frac{\partial V}{\partial Y} + \frac{\partial W}{\partial Z} \right) + \epsilon \left(\frac{\partial V}{\partial Y} - \frac{\partial W}{\partial Z} \right) \quad \text{at } X=0 \quad (9)$$

It is assumed that the two phases are in thermodynamic equilibrium at all points of contact; hence σ_0 may be expressed in terms of the composition

*The letter n is used to identify formulas applying to the special case of $\beta = 0$ (neutrally stable stationary disturbance).

at $X = 0$ of either phase A or phase B. By hypothesis the concentration variations along the interface are small; hence with sufficient accuracy one can set

$$\frac{\partial \sigma_{YY}}{\partial Y} = \left(\frac{d\sigma_0}{dC_a} \right) \left(\frac{\partial C_a}{\partial Y} \right) + \mu_s \left(\frac{\partial^2 V}{\partial Y^2} \right) \quad \text{at } X = 0 \quad (10)$$

where $\mu_s = \kappa + \epsilon$ and the derivative $\partial W / \partial Z$ vanishes for the two-dimensional formulation.

Boundary conditions (i) to (vii) require that $\varphi_a(\infty) = \varphi_b(-\infty) = \varphi_a(0) = \varphi_b(0) = 0$ and $\varphi'_a(0) = \varphi'_b(0)$, whence

$$\varphi_a = \alpha_2 (e^{-x} - e^{-px}), \quad x \geq 0 \quad (11)$$

$$\varphi_b = -\alpha_2 \left(\frac{1-p_a}{1-p_b} \right) (e^x - e^{p_b x}), \quad x \leq 0 \quad (12)$$

or, in the case $\beta = 0$

$$\varphi_a = \alpha_8 x e^{-x}, \quad x \geq 0 \quad (11n)$$

$$\varphi_b = \alpha_8 x e^x, \quad x \leq 0 \quad (12n)$$

At this point one has solved the equations of motion for a roll-cell disturbance of wave length $\lambda = 2\pi/\alpha$ and small but unspecified (as reflected in the single remaining arbitrary constant) initial strength. The behavior with time of such disturbances is examined next, and to this end one considers the interfacial shear-stress boundary condition (viii), which with Equations (7) to (12) becomes

$$\zeta_a \left(\frac{\partial C_a}{\partial Y} \right)_{X=0} = \alpha_2 \mu_a \alpha^2 e^{i\alpha Y} e^{\beta t} (p_a - 1) \cdot \left[(1 + p_a) + \frac{\mu_b}{\mu_a} (1 + p_b) + \frac{\alpha \mu_s}{\mu_a} \right], \quad \beta \neq 0 \quad (13)$$

$$\zeta_a \left(\frac{\partial C_a}{\partial Y} \right)_{X=0} = 2\alpha_8 \mu_a \alpha^2 e^{i\alpha Y} \cdot \left(1 + \frac{\mu_b}{\mu_a} + \frac{\alpha_n \mu_s}{2\mu_a} \right), \quad \beta = 0 \quad (13n)$$

where $\zeta_a = d\sigma_0/dC_a$. These equations enable one to calculate the growth constant β for any given wave number α and assignment of system properties. First however one must determine the surface concentration gradient $(\partial C_a / \partial Y)_{X=0}$.

Diffusion Equations

For simplicity of illustration it is assumed that constant fluxes of solute have been established in the undisturbed system, at least within that region about the interface within which interfacial turbulence may arise. The undisturbed concentrations are taken as

$$C_a^0 = \mathcal{J}_a + \mathcal{L}_a X, \quad X \geq 0 \quad (14)$$

$$C_b^0 = g_b + \mathcal{L}_b X \quad X \leq 0 \quad (15) \quad \text{or}$$

These concentration distributions are perturbed by the flow disturbances already treated. The concentration disturbance is governed by the equation for diffusion in a constant-mass-density, binary, two-dimensional system

$$\frac{\partial C}{\partial t} + U \frac{\partial C}{\partial X} + V \frac{\partial C}{\partial Y} = \mathfrak{D} \left(\frac{\partial^2 C}{\partial X^2} + \frac{\partial^2 C}{\partial Y^2} \right) \quad (16)$$

where now

$$U = -i\alpha\varphi(X)e^{i\alpha Y}e^{\beta t} \quad (17)$$

$$V = \frac{d\varphi(X)}{dX} e^{i\alpha Y}e^{\beta t} \quad (18)$$

In the initial stages of growth of the disturbances the concentration perturbation is of the same order of smallness as the velocities. Therefore one sets

$$C = C^0(X) + G(X, Y, t) \quad (19)$$

inserts this expression in Equation (16), and neglects terms of the second order of smallness, thereby obtaining

$$\frac{\partial G}{\partial t} - \mathfrak{D} \left(\frac{\partial^2 G}{\partial X^2} + \frac{\partial^2 G}{\partial Y^2} \right) = -U \frac{dC^0}{dX} \quad (20)$$

A solution is sought for the concentration perturbation of the form $G = H(X)e^{i\alpha Y}e^{\beta t}$. With this form for G it follows from Equations (14), (15), (17), and (20) that $H(X)$ must satisfy

$$H'' - \left(1 + \frac{\beta}{\alpha^2 \mathfrak{D}} \right) H = -\frac{i\mathfrak{L}}{\alpha \mathfrak{D}} \varphi \quad (21)$$

The solution of this equation is

$$H_a(0) = \frac{l_b[I_b'(0) - q_b I_b(0)] - r^2 l_a[I_a'(0) + q_a I_a(0)]}{m_{ab} q_b + r^2 q_a} \quad (27)$$

$$H = \mathfrak{G}_9 e^{\alpha x} + \mathfrak{G}_{10} e^{-\alpha x} - lI \quad (22)$$

where

$$q = \sqrt{1 + \frac{\beta}{\alpha^2 \mathfrak{D}}}$$

$$l = i\mathfrak{L}/\alpha \mathfrak{D}$$

$$I = e^{\alpha x} \int e^{-2\alpha x} \int e^{\alpha x} \varphi(dx)^2$$

$$B = \frac{\left(\frac{q_b - 1}{q_b + p_b} - \frac{q_a - 1}{q_a + p_a} \right)}{\left(\frac{m_{ab}}{r^2} q_b + q_a \left[\frac{\mu_b}{\mu_a} (1 + p_b) + (1 + p_a) + \frac{\alpha \mu_s}{\mu_a} \right] \right)} \quad (29)$$

$$A = \frac{\left[\frac{r^2}{(q_b + 1)(q_b + p_b)} - \frac{1}{(q_a + 1)(q_a + p_a)} \right]}{d^2 \left(\frac{m_{ab}}{r^2} q_b + q_a \right) \left[\frac{\mu_b}{\mu_a} (1 + p_b) + (1 + p_a) + \frac{\alpha \mu_s}{\mu_a} \right]} \quad (30)$$

and

$$A_{Ns} = \frac{(r^2 - 1)}{8 d^2 \left(\frac{m_{ab}}{r^2} + 1 \right) \left(\frac{\mu_b}{\mu_a} + 1 + \frac{\alpha \mu_s}{2\mu_a} \right)}, \quad \beta = 0 \quad (30n)$$

where

$$B = \left(\frac{\mu_a}{\zeta_a \mathfrak{L}_a} \right) \beta \quad \text{and} \quad A = \left(\frac{\nu_a \mu_a}{\zeta_a \mathfrak{L}_a} \right) \alpha^2$$

are dimensionless forms of the growth constant and wave number, respectively. It is convenient to introduce additional dimensionless quantities:

$$\xi = \beta/\alpha^2 \mathfrak{D}_a = B/d^2 A$$

$$d = \sqrt{\mathfrak{D}_a/\nu_a}$$

$$e = \sqrt{\nu_a/\nu_b}$$

Then in Equations (29) and (30)

$$q_a = \sqrt{1 + \xi}, \quad q_b = \sqrt{1 + r^2 \xi}$$

$$p_a = \sqrt{1 + d^2 \xi}, \quad p_b = \sqrt{1 + d^2 e^2 \xi}$$

For a given system all the properties, d , e , r , m_{ab} , μ_b , μ_a , μ_s , ζ_a , \mathfrak{L}_a , and \mathfrak{D}_a , are assigned, and so Equation (29) determines the complex growth constant β (in B) for each wave number α (in A) of the disturbance. Unhappily this characteristic equation is implicit in the dependent variable B and besides contains four vexatious radicals.

INTERPRETATION OF THE CHARACTERISTIC EQUATION

The wave number of a disturbance is real and positive. The growth constant in $e^{\beta t}$ is complex:

$$\beta = \hat{\beta} \pm i\tilde{\beta}$$

Disturbances for which $\hat{\beta} < 0$ are damped; those for which $\hat{\beta} > 0$ are amplified and instability sets in.

Regimes of Instability

There exist two kinds of instability. The first is an oscillatory regime (sometimes named *overstability*), wherein the growing disturbance displays temporal periodicity with period $2\pi/\tilde{\beta}$ and a translatory motion with speed of propagation $\tilde{\beta}/\alpha$. The second is a stationary regime (often called *convective instability*) corresponding to $\tilde{\beta} = 0$, in which the disturbance grows in place without oscillation or translation. For each regime there may exist certain wave numbers for which $\hat{\beta} = 0$, an indication of marginal or neutral stability; that is the disturbance neither grows nor decays in time. Thus zeros of the function $\hat{\beta}(\alpha)$

Table 1 gives the particular integral I for the stream functions of Equations (11) and (12). The arbitrary constants \mathfrak{G}_9 and \mathfrak{G}_{10} (and \mathfrak{B}_9 and \mathfrak{B}_{10} for the second phase) are yet to be evaluated from the boundary conditions.

The boundary conditions required to specify H (and thereby the concentration) in both phases are

ix, x. The concentration disturbance vanishes at large distances from the interface; that is $C_a \rightarrow C_a^0$ as $X \rightarrow \infty$ and $C_b \rightarrow C_b^0$ as $X \rightarrow -\infty$

xi. The two phases are in thermodynamic equilibrium at the interface; that is $m_{ab}C_a(0, Y, t) = C_b(0, Y, t)$

xii. There is conservation of solute at the interface; that is, $\mathfrak{D}_a(\partial C_a/\partial X) = \mathfrak{D}_b(\partial C_b/\partial X)$ at $(0, Y, t)$. These conditions lead to the relations

$$m_{ab}g_a = g_b \quad (23)$$

$$r^2 \mathfrak{L}_a = \mathfrak{L}_b, \quad r^2 = \mathfrak{D}_a/\mathfrak{D}_b \quad (24)$$

for the undisturbed concentration distributions and

$$m_{ab}[\mathfrak{G}_{10} - l_a I_a(0)] = \mathfrak{B}_9 - l_b I_b(0) \quad (25)$$

$$r^2[\mathfrak{G}_{10} q_a + l_a I_a'(0)] = -\mathfrak{B}_9 q_b + l_b I_b'(0) \quad (26)$$

for the constants of the perturbed concentration distributions. From these expressions one finally obtains

from which the desired surface gradient follows immediately, since

$$\left(\frac{\partial C_a}{\partial Y} \right)_{X=0} = \left(\frac{\partial G_a}{\partial Y} \right)_{X=0} = H_a(0) i \alpha e^{i\alpha Y} e^{\beta t} \quad (28)$$

Characteristic Equation

Substituting Equations (27) and (28) in (13) gives

are of particular interest, since they demarcate stable and unstable wave numbers.

In some problems of hydrodynamic stability, for example the Rayleigh problem (15b, 21), it has been possible to prove the so-called "principle of exchange of stabilities," which states that $\beta < 0$ for all $\beta \neq 0$, whence all oscillatory disturbances decay and only the stationary regime of instability need be considered. However this principle does not apply to this model, as is shown below. The interpretation of Equation (29) is complicated by the existence of both regimes of instability; indeed in some cases they may set in simultaneously with one or the other dominating in time.

Functional Behavior

It is instructive to regard ξ temporarily as the independent variable in Equations (29) and (30) and to let μ_a be zero, since the equations are explicit from this point of view. The equations define two complex functions, $A = \hat{A} + i\tilde{A}$ and $B = \hat{B} + i\tilde{B}$, of the complex variable $\xi = \xi + i\tilde{\xi}$. In seeking conditions

$$\lim_{\xi \rightarrow \infty} B = \frac{(r^2 - e^2)}{(r + e)(r + de)(d + 1)\left(\frac{m_{ab}}{r} + 1\right)\left(\frac{\mu_b}{\mu_a}e + 1\right)}\xi^{-1} + 0(\xi^{-3/2}) \quad (32)$$

for instability one may restrict ξ and $\tilde{\xi}$ to nonnegative values; for if $\tilde{\xi} < 0$, then either $\beta < 0$ and the disturbance is damped or else $\alpha^2 < 0$, which is physically meaningless, and on physical grounds \hat{B} and \hat{A} are both even functions of ξ . The functions $A(\xi)$ and $B(\xi)$ are analytic on the quadrant $\xi \geq 0, \tilde{\xi} \geq 0$.

Because wave number must be real, only real values of A have physical meaning. Therefore one looks for parametric curves of $\hat{A} = 0$ in the quadrant of interest. One such curve is the real axis, inasmuch as $\hat{A}(\xi, 0)$ is identically zero. This curve corresponds to a stationary regime of instability, since $\tilde{B}(\xi, 0)$ is also identically zero.

Information about the stationary regime (and oscillatory regimes too) may be gained by an examination of the limiting behavior of $A(\xi)$ and $B(\xi)$.

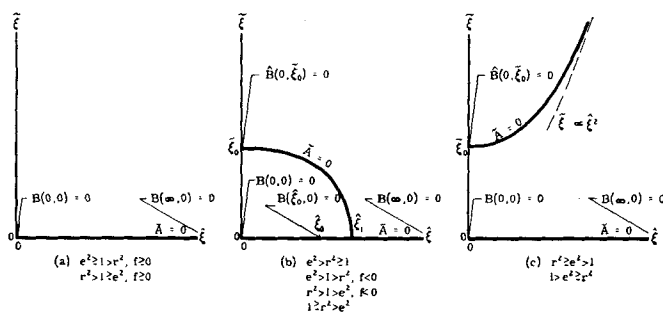


Fig. 3. The function \tilde{A} on the ξ plane.

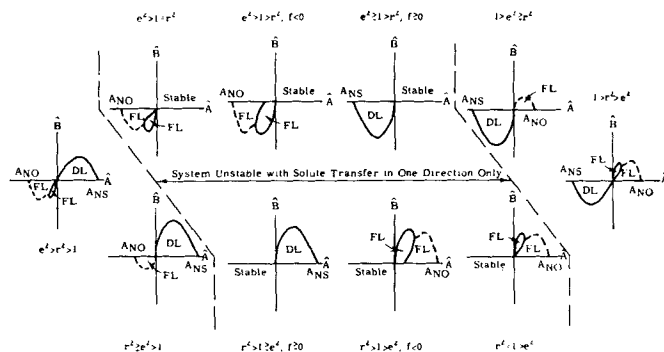


Fig. 4. Amplification factor vs. wave number (in dimensionless form). Solid curves denote stationary regimes; broken curves, oscillatory regimes. $e^2 \equiv v_a/v_b$; $r^2 \equiv D_a/D_b$; f given by Equation (34); $B \equiv (\mu_a/\xi_a \mathcal{L}_a)\beta$; $\hat{A} \equiv (v_a \mu_a/\xi_a \mathcal{L}_a)a^2$

Making use of the appropriate expansions in Equation (29), one finds, after some manipulation,

$$\lim_{\xi \rightarrow 0} B = \frac{(r^2 - 1)}{8\left(\frac{m_{ab}}{r^2} + 1\right)\left(\frac{\mu_b}{\mu_a} + 1 + \frac{\alpha\mu_s}{2\mu_a}\right)}\xi + 0(\xi^2) \quad (31)$$

where

$$f = \frac{r^2 + 1}{2} + \frac{m_{ab} + 1}{2\left(\frac{m_{ab}}{r^2} + 1\right)} + \frac{d^2\left(\frac{\mu_b}{\mu_a}e^2 + 1\right)}{4\left(\frac{\mu_b}{\mu_a} + 1 + \frac{\alpha_{NS}\mu_s}{2\mu_a}\right)} + \frac{d^2(r^2e^2 - 1)}{4(r^2 - 1)} \quad (34)$$

also, from Equation (30),

$$\lim_{\xi \rightarrow \infty} A = \frac{(r^2 - e^2)}{d^2(r + e)(r + de)(d + 1)\left(\frac{m_{ab}}{r} + 1\right)\left(\frac{\mu_b}{\mu_a}e + 1\right)}\xi^{-2} + \frac{(e^2 - 1)\left[\frac{\mu_b}{\mu_a}(r + de) + d + 1\right]}{d^3(e + 1)(r + de)(d + 1)\left(\frac{m_{ab}}{r} + 1\right)\left(\frac{\mu_b}{\mu_a}e + 1\right)^2}\xi^{-5/2} + 0(\xi^{-3}) \quad (35)$$

$$\lim_{\xi \rightarrow 0} A = \frac{(r^2 - 1)}{8d^2\left(\frac{m_{ab}}{r^2} + 1\right)\left(\frac{\mu_b}{\mu_a} + 1 + \frac{\alpha\mu_s}{2\mu_a}\right)}(1 - \xi f) + 0(\xi^2) = A_{NS}(1 - \xi f) + 0(\xi^2) \quad (33)$$

Thus two zeros of the characteristic function $B(A)$ are

$$B = 0 \text{ for } A = A_{NS} \quad [\xi = 0; \text{ cf. Equation (30n)}] \\ B = 0 \text{ for } A = 0 \quad (\xi \rightarrow \infty)$$

and these represent neutrally stable stationary disturbances of wave numbers $\alpha = \alpha_{NS}$ and $\alpha = 0$, respectively.

There may exist a third distinct zero of $B(\xi)$ by virtue of a zero of the numerator of Equation (29) for real ξ . It can be proved that there exists exactly one such additional zero, at $\xi = \xi_0$ where $0 < \xi_0 < \infty$, if, and only if, the quantities $(r^2 - 1)$ and $(r^2 - e^2)$ are of opposite signs.* If $B(\xi_0) = 0$, then $A(\xi_0) = 0$, and the point

$$B = 0 \text{ for } A = 0 \quad (\xi = \xi_0)$$

*See Appendix, which has been deposited as document No. 6048 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for \$1.25 for photoprints or 35-mm. microfilm.

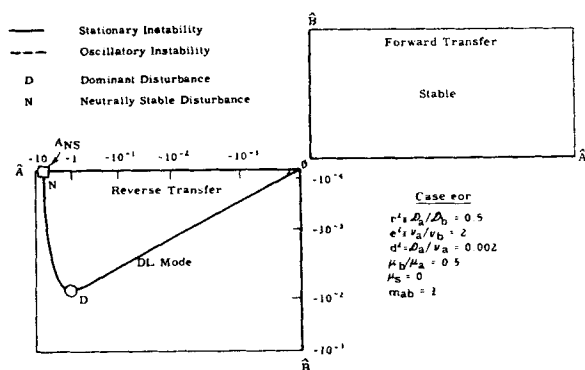


Fig. 5. Results of computation.

represents another neutrally stable stationary disturbance of wave number $\alpha = 0$. Whenever this is the case, the function $B(A)$ is evidently double valued on some interval of A which contains $A = 0$.

To establish the existence of oscillatory regimes, one looks for zeros of $\tilde{A}(0, \xi)$, which must lie on parametric curves of $\tilde{A} = 0$. Moreover these zeros are also zeros of $\tilde{B}(0, \xi)$ and therefore represent neutrally stable oscillatory disturbances (provided $\xi \neq 0$). The argument hinges on the limiting behavior of \tilde{A} , which is easily inferred from Equations (33) and (35) and is given in Table 2. There it is seen that in the limit $\xi = 0$, $\xi \rightarrow 0$, \tilde{A} has the same sign as $-(r^2 - 1)f$; in the limit $\xi = 0$, $\xi \rightarrow \infty$, it has the same sign as $(e^2 - 1)$. It follows immediately that if $(r^2 - 1)f$ and $(e^2 - 1)$ have the same sign, there exists an odd number of zeros of $\tilde{A}(0, \xi)$, and there is at least one wave number α_{NO} for which the system is neutrally stable relative to an oscillatory disturbance. On the other hand, if $(r^2 - 1)f$ and $(e^2 - 1)$ are of opposite signs an even number of zeros of $\tilde{A}(0, \xi)$ exist, and so it is at least possible that the system is stable relative to oscillatory disturbances.

The oscillatory and stationary regimes are connected if $\partial \tilde{A} / \partial \xi = \partial \tilde{A} / \partial \xi = 0$ at some point $(\xi, 0)$, that is if there is a saddle point on the real axis. At such a saddle point A has a local extremum, and the curve of $\tilde{A} = 0$ lying on the real axis and representing stationary instability is intersected perpendicularly by a second curve of $\tilde{A} = 0$ representing oscillatory instability. It can be shown that there is a saddle point on the real axis if $(r^2 - 1)$ and $(r^2 - e^2)$ are of opposite signs [note that this is the same criterion as applies to the existence of a third zero of $B(\xi)$] or if f is negative and $(r^2 - 1)$ and $(r^2 - e^2)$ have the same sign.*

Not every curve of oscillatory instability, however, intersects the real axis. For if $(e^2 - 1)$ and $(r^2 - e^2)$ have the same sign, there may be no saddle

point on the real axis, but there is a curve of $\tilde{A} = 0$ which approaches asymptotically a parabola, ξ proportional to ξ^2 , and terminates at the branch point, $\xi = \infty$. Furthermore, if $(e^2 - 1)$ and $(r^2 - e^2)$ are of opposite signs, there is no branch of $\tilde{A} = 0$ in the far reaches of the quadrant.*

It may be concluded from all this information that three possible pictures of $\tilde{A}(\xi, \xi) = 0$, contingent on the relative magnitudes of r^2 , e^2 , and unity and on the sign of f , are as shown schematically in Figure 3. In these three pictures, which encompass all possible combinations of the parameters, the heavy lines are loci of unstable disturbances. Although the possibility of additional curves of $\tilde{A} = 0$ intruding across the imaginary axis has not been ruled out entirely,* such curves would require the existence of more than one neutrally stable oscillatory disturbance, which seems unlikely on physical grounds. Furthermore, none have been found in the course of extensive numerical solutions of the characteristic equation.

Criteria for Instability

The physical behavior of the system for any given set of parameters may be inferred from the dependence, implicit in Figure 3, of amplification factor on real wave number. This dependence is clear in Figure 4, where the dimensionless amplification factor $\tilde{B} = \beta(\mu_a/\zeta_a \mathcal{L}_a)$ is plotted as a function of the dimensionless wave number $\tilde{A} = \alpha^2(\nu_a \mu_a / \zeta_a \mathcal{L}_a)$ for all of the loci of instability in Figure 3. Both \tilde{B} and \tilde{A} can be either positive or negative depending on the signs of \mathcal{L}_a (which defines the direction of transfer) and ζ_a (which gives the change of interfacial tension with concentration). Now for instability both β and α^2 are positive, and therefore \tilde{B} and \tilde{A} have the same sign; in other words, only the first and third quadrants of the plots in Figure 4 can contain instability curves. From the figure it may be seen that the location of such curves, in one or the other or both quadrants, depends on the viscosity and diffusivity ratios and the related param-

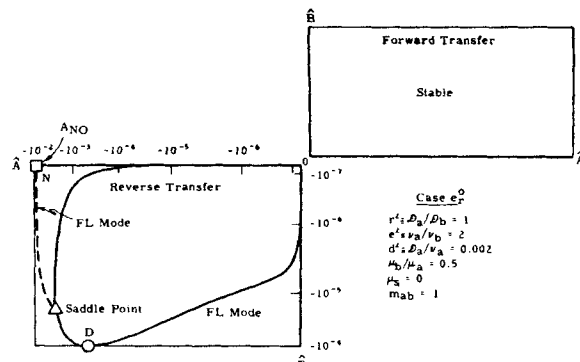


Fig. 6. Results of computation.

eter f . It is further seen that regardless of the parameter values there is at least one instability curve in every case. Once physical properties have been assigned, the sign of \tilde{A} depends solely on the direction of solute transfer (sign of \mathcal{L}_a). Thus one is led to a remarkable conclusion: the system studied here is always unstable relative to roll-cell disturbances—if not with solute transfer from phase A to phase B , then with transfer in the opposite direction. Moreover if kinematic viscosity and solute diffusivity are both lower in one phase (that is, $e^2 > 1$ and $r^2 > 1$ or $e^2 < 1$ and $r^2 < 1$ in Figure 4) the system is unstable with transfer in either direction. This result decides the point left unsettled in the preliminary description of the behavior of the disturbed system: how does the system behave when convection and diffusion are competing effects? Although these effects appear to be in competition, the system responds to the one promoting instability in a given situation. It should be remarked here that systems in which viscosity and diffusivity are both lower in the same phase are not often encountered.

Interfacial tension commonly decreases with increasing solute concentration in a two-phase system; that is, the concentration coefficient of interfacial tension ζ_a is usually negative. When this is the case, instability arises whenever solute is being transferred out of the phase in which kinematic viscosity is higher or out of the phase in which solute diffusivity is lower.

If the kinematic viscosities are equal ($e^2 = 1$), the onset of instability clearly is controlled by the restorative action of molecular diffusion. Conversely, if the diffusivities are equal ($r^2 = 1$), the flow effects are paramount. It is on this basis that the distinction is drawn in Figure 4 between diffusion-limited and flow-limited modes, labeled DL and FL , respectively.

It is evident from Figure 4 and the preceding investigation of functional behavior that even when instability occurs the system remains stable relative to all disturbances with wave number

*See footnote p. 519.

*See footnote p. 519.

TABLE 1. QUANTITIES APPEARING IN EQUATIONS (22) TO (28)

	$\phi(x)/\mu$	$I(x)/\mu$	$I(0)/\mu$	$I'(0)/\mu$	$H_0(0)/\mu$
$B \neq 0$					
Phase a $x \geq 0$	$e^{-x} - e^{-p_a x}$	$\left(\frac{e^{-x}}{q_a^2 - 1} - \frac{e^{-p_a x}}{q_a^2 - p_a^2}\right)$	$\frac{(p_a^2 - 1)}{(q_a^2 - 1)(q_a^2 - p_a^2)}$	$\frac{(1 - p_a)(q_a^2 - p_a)}{(q_a^2 - 1)(q_a^2 - p_a^2)}$	$\frac{d_a^2 \alpha (p_a - 1)}{\beta (\frac{p_a}{q_a} + q_a)} \left(\frac{q_a^{-1}}{q_a + p_a} - \frac{q_a^{-1}}{q_a + p_a} \right)$
Phase b $x \leq 0$	$-\left(\frac{1 - p_a}{1 - p_b}\right) (e^x - e^{p_b x})$	$\left(\frac{1 - p_a}{1 - p_b}\right) \left(\frac{e^x}{q_b^2 - 1} - \frac{e^{p_b x}}{q_b^2 - p_b^2} \right)$	$-\left(\frac{1 - p_a}{q_b^2 - 1}\right) \frac{(p_b^2 - 1)}{(q_b^2 - p_b^2)}$	$-\left(\frac{1 - p_a}{q_b^2 - 1}\right) \frac{(q_b^2 - p_b)}{(q_b^2 - p_b^2)}$	
$B = 0$					
Phase a $x \geq 0$	$x e^{-x}$	$-\frac{x(x+1)}{4} e^{-x}$	0	-1/4	$\frac{d_a^2 (1 - r^2)}{4 \alpha d_a (\frac{p_a}{r} + 1)}$
Phase b $x \leq 0$	$x e^{-x}$	$\frac{x(x-1)}{4} e^{-x}$	0	-1/4	

TABLE 2. LIMITING BEHAVIOR OF EQUATIONS (29) AND (30),
INHERENTLY POSITIVE CONSTANTS ARE OMITTED

$\hat{\xi}$	$\hat{\xi}$	\hat{A}	\hat{A}	\hat{B}
$\rightarrow 0$	$= 0$	$(r^2 - 1)$	0	$(r^2 - 1)\hat{\xi}$
$= 0$	$\rightarrow 0$	$(r^2 - 1)$	$-(r^2 - 1)r\hat{\xi}$	$(r^2 - 1)r\hat{\xi}^2$
$= 0$	$\rightarrow \infty$	$-(r^2 - e^2)\hat{\xi}^{-2}$	$(e^2 - 1)\hat{\xi}^{-5/2}$	$-(e^2 - 1)\hat{\xi}^{-3/2}$
$\rightarrow \infty$	$= 0$	$(r^2 - e^2)\hat{\xi}^{-2}$	0	$(r^2 - e^2)\hat{\xi}^{-1}$
$\hat{\xi} = \hat{\xi} \rightarrow \infty$		$-(e^2 - 1)\hat{\xi}^{-5/2}$	$-(r^2 - e^2)\hat{\xi}^{-2}$	$-(r^2 - e^2)\hat{\xi}^{-1}$

greater than some finite value, $\alpha_N(\alpha_{NS}$ or $\alpha_{NO})$. Furthermore, the unstable disturbances with very small wave numbers are amplified least rapidly; hence there is one wave number α_D , where $0 < \alpha_D < \alpha_N$, which is amplified most rapidly and ultimately dominates the system. Now wave length or cell size is inversely proportional to wave number; that is, $\lambda = 2\pi/\alpha$. Thus in small cells the motive force in the interface is more than offset by the viscous shear forces opposing motion, and the initial motion is damped. The contrary is true when cell size is larger than $\lambda_N = 2\pi/\alpha_N$, and the motion is amplified; the rate of amplification is vanishingly small in extremely large cells because of the inertia of the greater volume of fluid per cell.

Whereas the onset of instability is governed by the signs of the quantities $\nu_a - \nu_b$, $\mathcal{D}_a - \mathcal{D}_b$, ζ_a , and \mathcal{L}_a , the cell size and the rate of amplification of the dominant disturbance are also influenced by the magnitudes of these quantities and of the ordinary viscosities μ_a and μ_b , the surface viscosity μ_s , the Schmidt number d^{-2} , and the solute distribution coefficient m_{ab} as well. The qualitative effects may be summarized as follows: stronger variation of interfacial tension with concentration and steeper concentration gradients promote smaller cells and more rapid amplification, and so also do greater disparities of viscosity and diffusivity between phases. Higher diffusivities and viscosities in both phases lead to larger cells and slower amplification, and this tendency is more pronounced in the range of small cell sizes. The qualitative effects of d^2 and m_{ab} are not directly evident and hence must be found by calculation.

Results of Computation

That the authors' simplified model is subject to Marangoni instability is now established. Yet it may be that the wave lengths are so great, or the amplification rates so slow that the instability cannot manifest itself within the space and time available in the laboratory. Accordingly, values of α and β have been computed for four typical cases, selected to include all the regimes and modes of instability which are described above. The parameters which do not strongly affect the kind of instability, d , m_{ab} , μ_b/μ_a , and μ_s , were assigned the same values in all four cases. So also was the ratio of kinematic viscosities, at $e^2 = 2$. The cases were distinguished by four different values of the diffusivity ratio, $r^2 = 0.5, 1, 1.5$, and 4.

The results of the computations are shown in dimensionless form in Figures 5 through 8, where an unusual coordinate scale is employed for clarity of presentation.* Of greatest consequence are the points corresponding to neutrally stable and dominant disturbances; these are labeled N and D , respectively, in Figures 5 through 8 and are also given in Table 3.* Note that the dominant disturbance is of much smaller wave length (greater wave number) and is amplified far more rapidly in the diffusion-limited modes than in the flow-limited modes. Note also the curious contrast between the cases in Figures 6 and 7. In both when ever the direction of transfer is such as to make A negative (reverse direction of transfer), stationary and oscillatory disturbances set in simultaneously. A stationary disturbance prevails if the solute diffusivities are equal (Figure 6), whereas an oscillatory disturbance pre-

*The computations themselves are tabulated in the Appendix. See footnote on p. 519.

dominates if the diffusivity ratio is 1.5 (Figure 7).

To convert the calculated dimensionless quantities to the desired wave lengths and amplification factors, it is necessary to assign magnitudes to certain physical properties. Let $\mu_a = 10^{-2}$ g./cm.(sec.) and $\rho_a = 1$ g./cc. Then $\nu_a = 10^{-2}$ sq. cm./sec. and, because the Schmidt number $d^{-2} = 5 \times 10^2$, it follows that $\mathcal{D}_a = 2 \times 10^{-5}$ sq. cm./sec. Let the concentration coefficient of interfacial tension $\zeta_a = -10^2$ (g./sec.²)/ (g./cc.), a value typical of such systems as toluene-water with acetic acid as the consolute (28). Let the undisturbed concentration gradient $\mathcal{L}_a = 1$ (g./cc.)/cm., a value that obtains at the interface 0.4 sec. after a phase A containing 1% of solute is contacted with a phase B initially devoid of solute, if $m_{ab} = 1$ and $\mathcal{D}_b = 2 \times 10^{-5}$ sq. cm./sec. The magnitudes of λ and β are then as given in Table 4. It should be emphasized that Table 4 contains the results of sample calculations. By choosing other values for the physical properties, it is possible to obtain values of λ and β which differ from those shown by severalfold or even, in extreme cases, by a few orders of magnitude.

Neither the tabulated wave lengths nor amplification factors are so large as to refute the explanation of interfacial turbulence in terms of Marangoni instability. The flow-limited modes are characterized by dominant disturbances which have cells a few millimeters in breadth and which double in intensity every second or so. In marked contrast are the dominant disturbances of the diffusion-limited modes, which are of much smaller cell size and are amplified far more rapidly. The microscopic scale of the latter type of disturbance and the rapidity with which it develops suggest a possible explanation for the lack of visible convective motion in some instances of spontaneous emulsification (4, 19).

DISCUSSION

The conception of Marangoni instability has led to a credible explanation of interfacial turbulence. The analysis shows clearly how it is possible for some systems to be unstable with solute transfer in one direction yet stable with transfer in the opposite direction, and others to be unstable with either direction of transfer. The analysis also shows that instability may be contingent upon other parameters heretofore unsuspected. These are the direction in which interfacial tension changes with solute concentration and the signs of differences between the solute diffusivities and kinematic viscosities of the two phases. The theoretical results suggest several variables whose influence may account for observed contrasts in intensity of interfacial

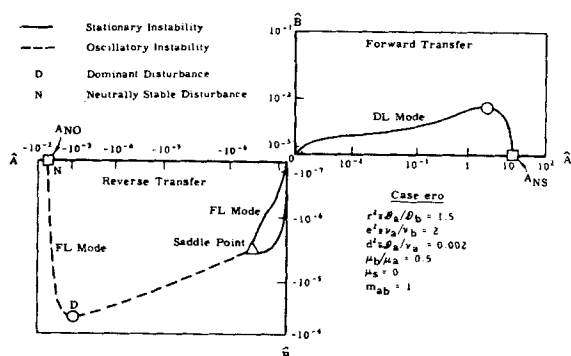


Fig. 7. Results of computation.

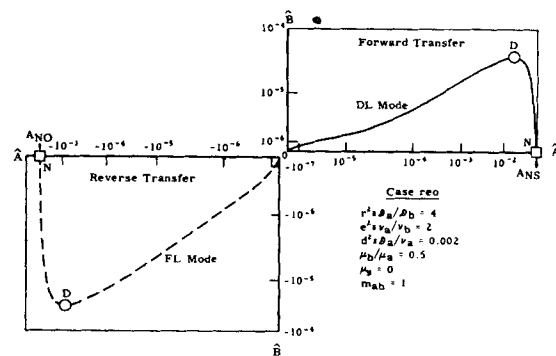


Fig. 8. Results of computation.

turbulence from one system to the next. The importance of two of these is already confirmed by experiment; they are the steepness of the concentration profile near the interface, which is related to the initial difference of solute concentrations, and the magnitude of the surface viscosity, which reflects the presence of highly surface-active agents.

The explanation is not completely convincing however. At present the analysis is based on a model too simplified to be reproduced in the laboratory; therefore direct, quantitative comparisons with experiment are impossible. Although many new experiments come to mind, the additional evidence that they will provide cannot be used for a decisive test of the theory until several of its deficiencies have been removed.

First one may ask to what extent temperature variations along the interface contribute to the Marangoni effect. Some investigators have speculated that interfacial agitation is caused by variations of interfacial tension occurring as a result of uneven release of heat of solution when solute passes through the interface (2, 14). This effect is easily incorporated in the authors' simplified treatment. The interfacial flux boundary condition on the diffusion equation is altered to include a heat-source term, and an appropriate undisturbed temperature profile is assumed. The interfacial shear-stress boundary condition on the flow equation is recast to account for the dependence of interfacial tension on temperature as well as on concentration. The resulting characteristic equation for $B(A)$ includes a term that represents the solution heat effect, a term involving the heat of transfer, the relative rates of change of interfacial tension with temperature and concentration, and the ratio of mass to thermal diffusivities. By inserting in this term the properties of one typical system, benzene-acetone-water, one finds the interfacial forces generated by temperature variations to be roughly a thousandfold less than those simultaneously generated by concentration variations. This comparison, though by no means settling the matter, suggests that it will be most profitable to con-

centrate on consequences of solute transfer in isothermal systems.

Other troublesome complications which are not included in the simplified theory but which are of importance in experiments are

1. The disturbances are not two dimensional.
2. The interface does not remain fixed in position; rather, it is free to twitch.
3. The system does not consist of two semi-infinite slabs; very often one phase is in the form of nearly spherical drops.
4. Solute transfer is not steady in the undisturbed state.
5. Not only is there transfer of solute, but the solvents themselves interdiffuse.
6. The diffusivities, rather than being constants, usually depend strongly on concentration.

Analyses that take the first four items into account are in progress and will be reported in detail later, but some remarks about them are apt here. A pattern of cylindrical convection cells oriented

normal to the interface, which simulates square or hexagonal cell patterns, leads to the same characteristic equation as given above for the two-dimensional, roll-cell pattern. The present proscription on motion of the interface normal to itself, which amounts to a tacit assumption of great interfacial tension, is easily removed by allowing the interface to be deformed by the normal fluid stresses. When this is done, an additional parameter that involves the magnitude of interfacial tension appears in the characteristic equation. It will probably be possible in this way to explain the more intense interfacial turbulence in systems of lower interfacial tension. The formulation of the stability problem for a spherical drop suspended in a second phase is straightforward. Solutions of stability problems in which the undisturbed system is not at steady state are hard to find. However, if the undisturbed diffusion changes the system much less rapidly than the nascent disturbances do, one can use the artifice of freezing

TABLE 4. TYPICAL MAGNITUDES

$$\zeta_a = -100 \frac{\text{dynes/cm}}{\text{gm/cm}^3}, \mu_a = .01 \frac{\text{gm}}{(\text{cm})(\text{sec})}, D_a = 2 \times 10^{-5} \frac{\text{cm}^2}{\text{sec}}, m_{ab} = 1, \frac{H_b}{T_a} = 2, \mu_s = 0$$

Case	eor	eor	ero	reo
ν_a/ν_b	2	2	2	2
D_a/D_b	0.5	1	1.5	4
Transfer from Phase B to Phase A, $\mathcal{L}_a = -1.0 (\text{gm/cm}^3)/\text{cm}$				
Mode	Stable	Stable	DL	DL
Neutrally stable wave length, λ_N , cm	-	-	.0018	.00063
Temporal period, $2\pi/\bar{\beta}_N$, sec	-	-	∞	∞
Speed of propagation, $\bar{\beta}_N/\alpha_N$, cm/sec	-	-	0	0
Dominant wave length, λ_D , cm	-	-	.0039	.0014
Amplification factor, $\bar{\beta}_D$, sec ⁻¹	-	-	64	350
Temporal period, $2\pi/\bar{\beta}_D$, sec	-	-	∞	∞
Speed of propagation, $\bar{\beta}_D/\alpha_D$, cm/sec	-	-	0	0
Transfer from Phase A to Phase B, $\mathcal{L}_a = +1.0 (\text{gm/cm}^3)/\text{cm}$				
Mode	DL	FL	FL	FL
Neutrally stable wave length, λ_N , cm	.0024	.070	.082	.086
Temporal period, $2\pi/\bar{\beta}_N$, sec	-	19	.77	.45
Speed of propagation, $\bar{\beta}_N/\alpha_N$, cm/sec	0	.0037	.11	.19
Dominant wave length, λ_D , cm	.0053	.27	.25	.20
Amplification factor, $\bar{\beta}_D$, sec ⁻¹	71	.99	.43	.32
Temporal period, $2\pi/\bar{\beta}_D$, sec	∞	∞	2.4	1.0
Speed of propagation, $\bar{\beta}_D/\alpha_D$, cm/sec	0	0	.10	.20

the concentration profile in its shape at any arbitrary instant and examining the stability of the system in that state. This scheme was recently applied to the Rayleigh problem by Morton (20).

The above list is ordered roughly in increasing mathematical difficulty. The ordering is also nearly that of increasing physical importance, the matter of variable diffusivities being greatest consequence for linking experiment with theory. But the fruitfulness of the simplified treatment justifies more elaborate analyses, for which the ground work is now laid.

Recommendations

Although the goal of a full understanding of interphase mass transfer is still a long way off, the following recommendations may hasten its attainment. Since interfacial turbulence unquestionably enhances the rate of mass transfer, experimenters studying extraction should, whenever possible, report direct observations of the phase interface with their extraction data. In any case the direction of transfer, concentration levels, and presence or absence of surface-active contamination should be noted. Viscosities, diffusivities, and the variation of interfacial tension with composition should be estimated or, preferably, measured. This information will be needed not only for the proper interpretation of simple laboratory experiments, but also for the rational scale up of bench and pilot plant extraction equipment.

Good empirical correlations of mass transfer rates in liquid-liquid extraction are lacking, partly because interfacial effects have been overlooked. (The same is true of flooding-point and capacity correlations.) More trustworthy correlations can be made by the conservative expedient of simply rejecting data known or suspected to be affected by interfacial turbulence. But sooner or later, in order to exploit fully the effect when it does occur, a correlation should be developed which accounts for those parameters that influence the onset and intensity of interfacial turbulence.

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NOTATION

A	$= (\nu_a \mu_a / \zeta_a \mathcal{L}_a) \alpha^2$, dimensionless wave number
α	$=$ constant of integration
B	$= (\mu_a / \zeta_a \mathcal{L}_a) \beta$, dimensionless growth constant
β	$=$ constant of integration
C	$=$ solute concentration $[ML^{-3}]$
d	$= \sqrt{D_a / \nu_a}$, dimensionless
\mathcal{D}	$=$ solute diffusivity $[L^2\theta^{-1}]$

e	$= \sqrt{\nu_a / \nu_b}$, dimensionless
f	$=$ function defined by Equation (34), dimensionless
G	$=$ concentration perturbation $[ML^{-3}]$
H	$=$ X part of the concentration perturbation $[ML^{-3}]$
i	$= \sqrt{-1}$
I	$=$ particular integral in Equation (22)
\mathcal{J}	$=$ undisturbed interfacial concentration $[ML^{-3}]$
l	$= (i/\alpha \mathcal{D}) \mathcal{L} [ML^{-3}\theta]$
\mathcal{L}	$=$ undisturbed concentration gradient $[ML^{-4}]$
m_{ab}	$= C_b/C_a$ at equilibrium, dimensionless
p	$= \sqrt{1 + (\beta/\alpha^2 \nu)}$, dimensionless
P	$=$ pressure $[ML^{-1}\theta^{-2}]$
q	$= \sqrt{1 + (\beta/\alpha^2 \mathcal{D})}$ dimensionless
r	$= \sqrt{D_a/D_b}$, dimensionless
t	$=$ time coordinate $[\theta]$
U, V, W	$=$ X, Y , and Z components of velocity $[L\theta^{-1}]$
X, Y, Z	$=$ spatial coordinates $[L]$

Greek Letters

α	$=$ wave number $[L^{-1}]$
β	$=$ growth constant $[\theta^{-1}]$
$\tilde{\beta}$	$=$ circular frequency
$\hat{\beta}$	$=$ amplification factor for the disturbance
ϵ	$=$ surface-shear viscosity $[M\theta^{-1}]$
ζ	$=$ concentration coefficient of interfacial tension $[L^2\theta^{-2}]$
κ	$=$ dilational surface viscosity $[M\theta^{-1}]$
λ	$=$ wave length $[L]$
μ	$=$ ordinary viscosity $[ML^{-1}\theta^{-1}]$
μ_s	$= \epsilon + \kappa$, composite surface viscosity $[M\theta^{-1}]$
ν	$=$ kinematic viscosity $[L^2\theta^{-1}]$
ξ	$= \beta/\alpha^2 D_a$, dimensionless
ρ	$=$ density $[ML^{-3}]$
σ_0	$=$ equilibrium interfacial tension $[M\theta^{-2}]$
σ_{YV}	$=$ Y component of the longitudinal surface stress $[M\theta^{-2}]$
τ_{YV}	$=$ Y component of the fluid shear stress $[ML^{-1}\theta^{-2}]$
φ	$=$ X part of the stream function $[L^2\theta^{-1}]$
ψ	$=$ stream function $[L^2\theta^{-1}]$

Subscripts

a	$=$ phase $A (X > 0)$
b	$=$ phase $B (X < 0)$
D	$=$ dominant unstable disturbance
N	$=$ neutrally stable disturbance
O	$=$ oscillatory disturbance
S	$=$ stationary disturbance

Superscripts

0	$=$ value in the undisturbed state
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\wedge	$=$ real part in a complex variable
\sim	$=$ imaginary part of a complex variable
primes	$=$ differentiation with respect to dimensionless quantity
x	$= \alpha X$

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