COMMUNICATIONS TO THE EDITOR

Location of the Reaction Zone in Liquid-Liquid Systems

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In heterogeneous reaction systems yield and selectivity may differ greatly, depending on the phases in which the desired reaction and the side reactions occur. This is true of certain important systems in which the reactants are brought together by two immiscible liquids in either of which the desired reaction can proceed. The relative rates of formation of product and by-products may differ appreciably in the two liquids; hence yield and selectivity may be improved by so adjusting the operating variables as to force reaction to occur in that phase where the desired reaction is favored. The problem is identification of the pertinent variables and prediction of their effects.

The following analysis of an idealized model has proved useful in providing insight into the behavior of liquid-liquid systems in which chemical reaction occurs close to the interface at a rate rapid compared with the rates of diffusion of the reactants. It is a generalization of the theory of unsteady state absorption with rapid second-order, irreversible reaction worked out by Sherwood and Pigford (*3*) and Danckwerts (*1*).

Let two stagnant, semi-infinite phases be brought into contact along a planar interface, phase 1 containing a uniform, dilute concentration of reactant A and phase 2 containing a uniform, dilute concentration of reactant B (Figure 1*a*). Suppose that an infinitely fast, irreversible reaction

$$A + \nu B \rightarrow \text{products}$$

can occur in either phase. Because the reaction between A and B is instantaneous the two cannot coexist at any point in the system. Thus reaction is restricted to a vanishingly thin zone which parallels the interface and in general moves away from the interface into one or the other phase as the indigenous reactant is consumed.

Assume for the moment that the reaction front moves into phase 2 (Figure 1*b*). The set of equations governing diffusion of the two reactants within the three regions into which the system may be divided is

$$\frac{\partial C_{A1}}{\partial t} = D_{A1}\frac{\partial^2 C_{A1}}{\partial x^2},\ x < 0 \qquad (1)$$

$$\frac{\partial C_{A2}}{\partial t} = D_{A2}\frac{\partial^2 C_{A2}}{\partial x^2},\ 0 < x < x' \qquad (2)$$

$$\frac{\partial C_{B2}}{\partial t} = D_{B2}\frac{\partial^2 C_{B2}}{\partial x^2},\ x' < x \qquad (3)$$

$$C_{A1}(-x,0) = C^\circ_{A1} = C_{A1}(-\infty,t) \qquad (4, 5)$$

$$C_{B2}(x,0) = C^\circ_{B2} = C_{B2}(\infty,t) \qquad (6, 7)$$

$$C_{A1}(0,t) = m\, C_{A2}(0,t) \qquad (8)$$

$$C_{A2}(x,0) = C_{A2}(x',t) = C_{B2}(x',t) = 0 \qquad (9, 10, 11)$$

$$D_{A1}\frac{\partial C_{A1}}{\partial x} = D_{A2}\frac{\partial C_{A2}}{\partial x},\ x = 0 \qquad (12)$$

$$-\nu D_{A2}\frac{\partial C_{A2}}{\partial x} = D_{B2}\frac{\partial C_{B2}}{\partial x},\ x = x' \qquad (13)$$

Sherwood and Pigford (*3*) have shown that the motion of the reaction front is governed by

$$\frac{dx'}{dt} = -\frac{\dfrac{\partial C_{A2}}{\partial t}}{\dfrac{\partial C_{A2}}{\partial x}} = -\frac{\dfrac{\partial C_{B2}}{\partial t}}{\dfrac{\partial C_{B2}}{\partial x}},\ x = x' \qquad (14)$$

On dimensional grounds regard concentrations as functions of the single independent variable $\eta \equiv x/2\sqrt{D_{A2}t}$. Then

$$\frac{dx'}{dt} = \frac{\left(\dfrac{\partial C_{A2}}{\partial \eta}\right)\left(\dfrac{\partial \eta}{\partial t}\right)}{\left(\dfrac{\partial C_{A2}}{\partial \eta}\right)\left(\dfrac{\partial \eta}{\partial x}\right)} = \frac{x'}{2t} \qquad (15)$$

and integration gives for the reaction-front coordinate

$$x' = 2\sqrt{\alpha t} \qquad (16)$$

when the integration constant is taken as $2\sqrt{\alpha}$ (positive root).

The solution of this set of equations is

$$\frac{C_{A1}}{C^\circ_{A1}} = 1 - \frac{\gamma\,\text{erfc}(-\gamma\eta)}{m\,\text{erf}(\lambda) + \gamma},\ x < 0 \qquad (17)$$

$$\frac{C_{A2}}{C^\circ_{A1}} = \frac{\text{erfc}\ (\eta) - \text{erfc}\ (\lambda)}{m\,\text{erf}\ (\lambda) + \gamma},\quad 0 < x < 2\sqrt{\alpha t} \qquad (18)$$

$$\frac{C_{B2}}{C^\circ_{B2}} = 1 - \frac{\text{erfc}\ (\omega\eta)}{\text{erfc}\ (\omega\lambda)} \qquad (19)$$

The rate of consumption of A at the reaction front is

$$S_A = -\,D_{A2}\frac{\partial C_{A2}}{\partial x},\ x = 2\sqrt{\alpha t}$$

$$= \frac{C^\circ_{A1}\exp\ (-\lambda^2)}{m\,\text{erf}\ (\lambda) + \gamma}\sqrt{\frac{D_{A2}}{\pi t}} \qquad (20)$$

The instantaneous mass transfer rate of A across the interface is

$$N_A = -\,D_{A2}\frac{\partial C_{A2}}{\partial x},\ x = 0$$

$$= \frac{C^\circ_{A1}}{m\,\text{erf}\ (\lambda) + \gamma}\sqrt{\frac{D_{A2}}{\pi t}} \qquad (21)$$

which is exactly half the corresponding average mass transfer rate up to a total contact time t.

The value of the pivotal constant α (α is presently disguised as $\lambda \equiv \sqrt{\alpha/D_{A2}}$) is not yet determined. It is evaluated from the boundary condition at the reaction front, Equation (13), which can now be rewritten in the awkwardly transcendental form

$$\frac{\exp(-\lambda^2)\ \exp(\lambda^2\omega^2)\ \text{erfc}(\lambda\omega)}{1 + (m/\gamma)\ \text{erf}(\lambda)} = \frac{\gamma C_{B2}}{\nu\omega C^\circ_{A1}} = R,\ \text{say} \qquad (22)$$

In the limiting case of no diffusional resistance in phase 1 this reduces to a result obtained for a single phase by Danckwerts and by Sherwood and Pigford, provided the distribution and stoichiometric coefficients are put equal to unity.[*]

Assume that on the contrary the reaction front moves into phase 1 (Figure 1*c*). The derivation is easily repeated. The new solution is simply the

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[*] By a typographical error r appears in place of $\sqrt{r}$ in the denominator of the first term of Equation (415) of (*3*), with which Equation (22) is to be compared.

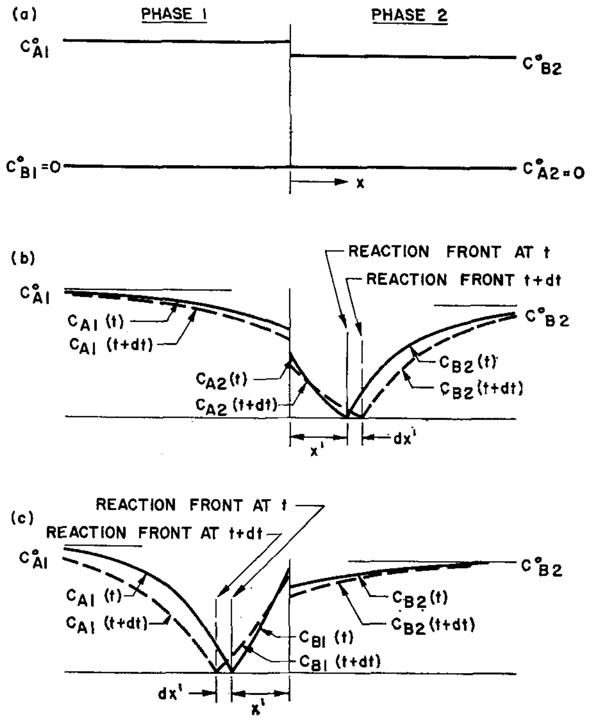

Fig. 1. Concentration profiles for infinitely fast irreversible second-order reaction.

old one with all roles interchanged. Now however $x' = -2\sqrt{\alpha t}$, and the constant α (in the new disguise $\Lambda \equiv \sqrt{\alpha/D_{B1}}$) is evaluated from

$$\frac{\exp(-\Lambda^2)\exp(\Lambda^2\Omega^2)\operatorname{erfc}(\Lambda\Omega)}{1+(M/\Gamma)\operatorname{erf}(\Lambda)} = \frac{\nu\Gamma C^\circ_{A1}}{\Omega C^\circ_{B2}} = 1/R \qquad (23)$$

Inspection of Equations (22) and (23) reveals a simple criterion for the direction of motion of the reaction front away from its initial location in the interface. Because all of the parameters are real, nonnegative quantities it follows from the nature of the exponential and error functions that the left-hand sides of both equations can never exceed unity, regardless of the magnitude of α. Furthermore the two equations are equivalent in the limit $\alpha = 0$ ($\lambda = \Lambda = 0$, whence $R = 1$). Therefore

$R < 1$, front moves into phase 2
$R = 1$, front remains at interface
$R > 1$, front moves into phase 1

$$R \equiv \frac{C^\circ_{B2}}{\nu C^\circ_{A1}}\sqrt{\frac{D_{B2}}{D_{A1}}} \qquad (24)$$

is accordingly a measure of the relative rates of diffusion of the two reactants toward the reaction front, that is a measure of the availability of reactants for reaction in phase 1 over their availability for reaction in phase 2. This criterion confirms the expectation that when reaction-rate constants are sufficiently high, reaction will proceed in that phase in which the indigenous reactant is more dilute and more slowly diffusing. Reaction can be forced to occur in phase 1, for example, by raising the concentration level of B in phase 2 or by lowering that of A in phase 1, or even by altering the viscosities and thereby the diffusivities.

In the foregoing derivation infinitely fast reaction is assumed. In the second approximation noninfinite reaction rate has two consequences: a broadening of the reaction front into a zone of finite width within which most of the reaction takes place, and some effect on the velocity at which the zone moves. The broadening can be estimated. If a finite zone is assumed with boundaries the positions of which vary as the square root of time, and if the reactant concentrations within the zone are represented by parabolic equations in the reduced variable η (a boundary-layer type of approximation), then it is found that the total rate of reaction within the zone is given by

$$k_2\int_{x'}^{x'+d} C_{A2}\,C_{B2}\,dx = \frac{30\,D_{A2}\,D_{B2}}{k_2\,d} \qquad (25)$$

Equating this to the rate of consumption given by Equation (20) one obtains an estimate of the reaction zone thickness for fast reaction in phase 2:

$$d \simeq \frac{30\,D_{B2}\exp(\lambda^2)\,[m\operatorname{erf}(\lambda)+\gamma]}{k_2\,\lambda\,C^\circ_{A1}} \qquad (26)$$

An analogous formula applies if the zone moves into phase 1.

If the rate constants for the two phases differ enough, the consequence of finite rate may be temporary or even permanent overthrow of the availability ratio criterion. The possibility can be crudely demonstrated. When the two phases are brought together, diffusion is initially very rapid, overshadowing reaction. If it is assumed that diffusion proceeds without reaction for some arbitrary starting period, the concentration distributions at the end of that period are easily obtained. From these follow the respective total rates of reaction in each phase at the instant reaction suddenly begins. Thus if the ratio

$$\frac{k_1\int_{-\infty}^{0} C_{A1}\,C_{B1}\,dx}{k_2\int_{-0}^{\infty} C_{A2}\,C_{B2}\,dx} = \frac{k_1\left(m+\sqrt{\dfrac{D_{A2}}{D_{B1}}+\dfrac{D_{A2}}{D_{A1}}}-\sqrt{\dfrac{D_{A2}}{D_{B1}}}\right)}{k_2\left(M\sqrt{\dfrac{D_{A2}}{D_{B1}}}+\sqrt{1+\dfrac{D_{A2}}{D_{B2}}}-1\right)} \qquad (27)$$

is greater than unity, more reaction takes place in phase 1 and conversely. Hence there may be a strong tendency for the reaction zone, if anything of the sort exists, to move into that phase for which the rate constant is larger. If the ratio of rate constants is sensitive to temperature, reaction can be encouraged in phase 1 for example by properly selecting the operating temperature.

Because in practice one or both phases are more or less vigorously agitated it is instructive to consider the availability ratio criterion in the light of Danckwert's surface renewal theory (2). Turbulent or laminar convection repeatedly brings fresh fluid from the interior of each phase to the interface, where it is transitorily exposed to the opposite phase. During each exposure diffusion and reaction are supposed to proceed in much the same manner as in the idealized model analyzed above. Consequently reaction should be promoted in phase 1 by contriving to supply reactant A at low concentration in the interior of phase 1, by maintaining a raised concentration level of B in the bulk of phase 2, or by arranging agitation so that surface renewal is relatively more rapid from the side of phase 2. When, as is often the case, one liquid is dispersed in another, the same conclusions can be drawn even though the surface renewal theory may not be well suited to the interior of drops whose volume and circulation are small. Furthermore transfer of reactant from the dispersed phase is enhanced by subdividing drops into smaller droplets. Thus finer dispersion should tend to keep the reaction zone in the continuous phase, the same effect as increased diffusivity in the dispersed phase, according to the availability ratio criterion.

NOTATION

C_{ij} = concentration of the i-th reactant in the j-th phase $[ML^{-3}]$
d = reaction zone thickness $[L]$
D_{ij} = diffusivity of the i-th reactant in the j-th phase $[L^2T^{-1}]$
k_j = reaction rate constant in the j-th phase $[M^{-1}L^3T^{-1}]$
m = equilibrium distribution ratio for A, C_{A1}/C_{A2}
M = equilibrium distribution ratio for B, C_{B2}/C_{B1}
N_i = transfer rate of the i-th reactant across the interface $[ML^{-2}T^{-1}]$
R = availability ratio, $\frac{C^\circ_{B2}}{\nu C^\circ_{A1}}\sqrt{\frac{D_{B2}}{D_{A1}}}$
S_i = consumption rate of the i-th reactant at the reaction front $[ML^{-2}T^{-1}]$
t = time coordinate $[T]$
x = position coordinate $[L]$
x' = position coordinate of the reaction zone $[L]$

Greek Letters

α = proportionality constant $[L^2T^{-1}]$
γ = $\sqrt{D_{A2}/D_{A1}}$
Γ = $\sqrt{D_{B1}/D_{B2}}$
η = $x/2\sqrt{D_{A2}t}$
λ = $\sqrt{\alpha/D_{A2}}$
Λ = $\sqrt{\alpha/D_{B1}}$
ν = stoichiometric coefficient
ω = $\sqrt{D_{A2}/D_{B2}}$
Ω = $\sqrt{D_{B1}/D_{A1}}$

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Finite-Difference Transforms for Application to Stage by Stage Processes

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The stage by stage operations of chemical engineering may be calculated by iterative means, or handled by graphical manipulations. The former is tedious; the latter is often useful but leads to somewhat uncertain results when many-stage processes are treated. An analytical method for solving stage by stage problems would have obvious advantages. Such a method has been devised for linear systems (*3, 4, 5*); the method involves finite-difference transforms that are analogous to the Laplace transform. The basis of this method was developed originally in the electrical engineering field for application to control problems. The transform was called the *z-Transform,* corresponding to the $\sigma(p)$ function defined below. There are also alternate transform techniques (*1, 2, 7, 8*) which are more powerful for some applications.

Let y_n denote a function of stage number n. Define the finite-difference transform as follows:

$$F(y_n) = \gamma(p) = \frac{p-1}{p}\left(y_0 + \frac{y_1}{p} + \frac{y_2}{p^2} + \dots\right)$$

$$= \frac{p-1}{p} \cdot \sigma(p)$$

or

$$\gamma(p) = \frac{p-1}{p} \sum_{n=0}^{\infty} \frac{y_n}{p^n}$$

$$= \frac{p-1}{p} \cdot \sigma(p)$$

where

$$p = \text{a parameter}$$

$$\sigma(p) = y_0 + \frac{y_1}{p} + \frac{y_2}{p^2} + \dots.$$

The transform of $y_n = 1$ is 1:

$$F(1) = \gamma(p) = \frac{p-1}{p}\left(1 + \frac{1}{p} + \frac{1}{p^2} + \dots\right)$$

$$= \frac{p-1}{p} \cdot \frac{1}{1-\frac{1}{p}} = 1$$

The transform of $y_n = n$ is $1/(p-1)$.

$$F(n) = \gamma(p) = \frac{p-1}{p}\left(0 + \frac{1}{p} + \frac{2}{p^2} + \dots\right)$$

$$= -(p-1)\frac{\partial}{\partial p}\left(1 + \frac{1}{p} + \frac{1}{p^2} + \dots\right)$$

$$= -(p-1)\frac{\partial}{\partial p}(p/p-1)$$

$$= \frac{p-1}{(p-1)^2} = \frac{1}{p-1}$$

If the transform of y_n is $\gamma(p)$, the transform of y_{n+1} is

$$F(y_{n+1}) = \frac{p-1}{p}\left(y_1 + \frac{y_2}{p} + \frac{y_3}{p^2} + \dots\right)$$

$$= p\left(F(y_n) - \frac{p-1}{p}y_0\right)$$

$$= p\,\gamma(p) - (p-1)y_0$$

The transform of $\Delta y = y_{n+1} - y_n$ is $F(y_{n+1}) - F(y_n) = (p-1)(\gamma(p) - y_0)$. The transform of $n\,y_n$ is found by noting that