

- Diagrams of B. S. En Steels," 1 ed., Iron and Steel Institute, London, England (1949).
4. Campbell, J. B., *Materials and Methods*, 42, 98 (April, 1955).
 5. Damkohler, G., *Z. Electrochem.*, 42, 846 (1936).
 6. Forst, W., and P. A. Giguere, *J. Phys. Chem.*, 62, 340 (1958).
 7. Hartnett, J. P., and E. R. G. Eckert, "Heat Transfer and Fluid Mechanics Institute," Berkeley, California, Preprints, p. 54 (1958).
 8. Hirschfelder, J. O., C. F. Curtiss, and R. B. Bird, "Molecular Theory of Gases and Liquids," Wiley, New York (1954).
 9. Hoare, D. E., J. B. Protheroe, and A. D. Walsh, *Nature*, 182, 654 (1958).
 10. Lillie, H. R., Personal communication, Corning Glass Works, Corning, New York (November 2, 1959).
 11. Mickley, H. S., R. C. Ross, A. L. Squyers, and W. E. Stewart, *Natl. Advisory Comm. Aeronaut., Tech. Note No. 3208* (1954).
 12. Mickley, H. S., T. K. Sherwood, and C. E. Reed, "Applied Mathematics in Chemical Engineering," 2 ed., p. 298, McGraw-Hill, New York (1957).
 13. Ritter, H. L., and L. C. Drake, *Ind. Eng. Chem. Anal. Ed.*, 17, 782 (1945).
 14. Sane, J. O., S.M. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1959).
 15. Satterfield, C. N., and T. W. Stein, *Ind. Eng. Chem.*, 49, 1173 (1957).
 16. Schwart, G. L., and M. M. Kristal, "Corrosion of Chemical Apparatus," p. 82, translated from the Russian, Chapman and Hall, Ltd., London, England (1959).
 17. Stubbs, H. E., Sc.D. thesis, Univ. Mich., Ann Arbor, Michigan (1959).
 18. Tammaro, N. J., Personal communication, Corning Glass Works, Corning, New York (December 8, 1958).
 19. Tinkler, J. D., and A. B. Metzner, *Ind. Eng. Chem.*, 53, 663 (1961).
 20. Thiele, E. W., *ibid.*, 31, 916 (1939).
 21. Wechsler, A. E., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (January, 1961).
 22. Weger, E., and E. Effron, Paper presented at Annual Christmas Symposium of Industrial and Engineering Chemistry Division of American Chemical Society at Johns Hopkins Univ., Baltimore, Maryland (December 28, 1959).
 23. Weisz, P. B., and J. S. Hicks, *Chem. Eng. Sci.*, 17, 265 (1962).
 24. Wheeler, A., "Catalysis," P. H. Emmett, ed., Vol. 2, Chapt. 2, pp. 105-165, Reinhold, New York (1955).
 25. ———, "Advances in Catalysis," Vol. 3, pp 250-326, Academic Press, New York (1951).
 26. Yeung, R. S. C., Sc.D. thesis, Mass. Inst. Technol., Cambridge, Massachusetts (1961). See also Satterfield, C. N., and R. S. C. Yeung, *Ind. Eng. Chem. Fundamentals Quart.*, to be published.

Manuscript received October 13, 1961; revision received July 11, 1962; paper accepted July 17, 1962. Paper presented at A.I.Ch.E. Los Angeles meeting.

Dispersed Phase Mixing: I. Theory and Effects in Simple Reactors

R. L. CURL

Shell Development Company, Emeryville, California

When drops in a two-liquid phase chemical reactor are able to mix with one another by coalescences and redispersions, any spread of concentration among the drops tends to be averaged out. This phenomenon can affect average reaction rate and selectivity in non first-order reactions or mass transfer rate controlled reactions in the dispersed phase. It was found that for mass transfer rate controlled reactions, or the equivalent zero-order reaction, quite large dispersed phase mixing rates are required to bring conversions close to the level obtained with complete mixing.

A well-stirred flow reactor which contains two immiscible liquid phases generally can be treated as an ideal stage with respect to the residence time distribution and the concentration uniformity of the continuous phase. For the dispersed phase however the distribution of concentration among the drop population in the same vessel depends not only upon the residence time distributions and reaction or mass transfer conditions but also upon the number of coalescences and redispersions that occur during a nominal residence time. Therefore when a chemical reaction of other than first order occurs in the dispersed phase in such a reactor, mixing of that phase can have an important effect on the reactor size required for a given conversion or on the conversion and selectivity in a given reactor. The two extremes of no mixing and complete mixing of the dispersed phase have been considered by Rietema (5) for a single-stage reactor in which a zero-order reaction is proceeding in the dispersed phase. He calculated the ratio of residence times required for a given conversion for

these two cases and found for example that mixing can make a factor of 3 difference at 80% conversion.

More recently Madden and Damerrell (3) have described work in which they measured the rate of dispersed phase mixing in a 5½ in. diameter stirred vessel. The question naturally arises of whether under particular circumstances a certain measured rate of dispersed phase mixing represents a case closer to no mixing or to complete mixing. It would also be desirable to estimate the actual effect of mixing on the conversion or selectivity in a particular system. A mathematical model is presented here for the simultaneous effects of reaction, mass transfer, and dispersed phase mixing in a continuous flow stirred reactor. From this there are obtained the consequences in batch mixing, zero-order chemical reactions, and cases of mass transfer controlled reactions in the dispersed phase. The model used is a simplified one. For example it is assumed that all drops in the system are of equal size and have equal probability of coalescing, and that redispersion occurs immediately after a coalescence to form two equal drops.

It is possible to consider any number of combinations of direction of mass transfer, number and order of reaction, consecutive reactions, and series or other arrangements of stages. However the intent here is primarily to suggest a model for dispersed phase mixing which subsequently can be introduced into various reaction and reactor schemes. The examples and applications given here are both by way of example and to provide quantitative answers for a case of basic interest, the zero-order or mass transfer controlled reaction.

There is similarity between the phenomena associated with incomplete dispersed phase mixing and incomplete homogeneous mixing. In the terminology of Danckwerts (1) the latter is segregated flow and is the cause of changes in overall reaction rate for reactions of other than first order. In the homogeneous case the scale of segregation may have a number of definitions as there are no sharp boundaries between the clumps or streaks of different concentrations. In the present case the phase boundary permits a clearer concept of segregation or concentration distribution.

This idea of homogeneous but segregated flow has been extended by Zwietering (8) to continuous flow sys-

R. L. Curl is with Technische Hogeschool Te Eindhoven, Eindhoven, Holland.

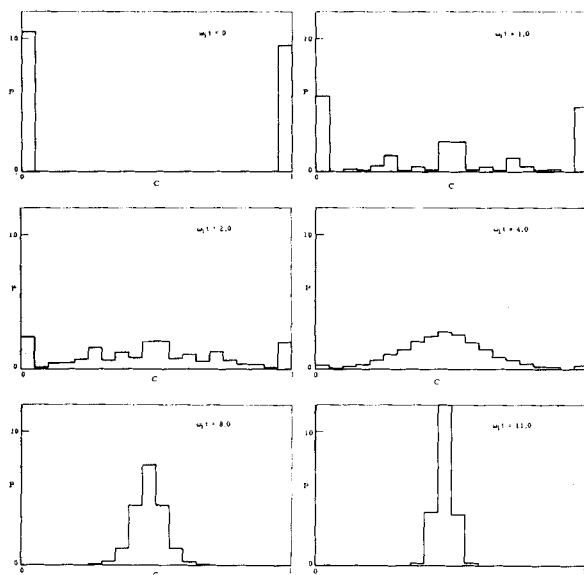


Fig. 1. Evolution of the concentration distribution frequency function as mixing proceeds.

tems with arbitrary residence time distributions in order to calculate the conversions with a chemical reaction of arbitrary order for the extremes of minimum segregation and complete segregation.

In the present work on dispersed phase segregation a well-mixed (continuous phase) single-stage reactor is the basis of all calculations. The solution of the problem of dispersed phase mixing in a reactor system with an arbitrary residence time distribution would provide a generalization to arbitrary degrees of mixing of Zwietering's conclusions, to the extent that the dispersed phase mixing model is applicable to homogeneous mixing. This aspect of the problem is here left to the future.

DISPERSED PHASE MIXING

The mechanism of dispersed phase mixing adopted in this report follows. All drops in the system are assumed to be the same size. Coalescences take place at random between two drops having a solute concentration of c_1 and c_2 , respectively, and redispersion occurs immediately to produce two equal drops of the same concentration $\frac{1}{2}(c_1 + c_2)$. The collision rate is u , and the total number of drops in the system is U . The contribution of this mechanism to changes in the frequency function f.f. (probability density distribution) of drop concentration will now be considered.

The total number of ways in which collision may occur between two of the U drops is the number of ways $\binom{U}{2}$ in which the U drops may be taken two at a time. Given two mutually exclusive sets of drops (G_1) and (G_2)

with G_1 and G_2 drops, respectively, the number of ways that a member of (G_1) can coalesce with a member of (G_2) is equal to

$$\binom{G_1 + G_2}{2} - \binom{G_1}{2} - \binom{G_2}{2} \quad (1)$$

and hence the rate of all successful collisions which involve only a member of (G_1) plus a member of (G_2) is equal to this divided by $\binom{U}{2}$, times u , or

$$\frac{2G_1G_2}{U(U-1)} u \quad (2)$$

Since each collision yields two drops of the new concentration, the rate of creation of such average drops is close to

$$\frac{4G_1G_2}{U^2} u \quad (3)$$

if U is very large.

One now divides the maximum concentration range into N intervals of concentration Δc wide and defines as $p(n)\Delta c$ the fraction of the drops with concentration within the n th concentration interval $(n - 1/2 \pm 1/2)\Delta c$. [$p(n)$] is the discontinuous frequency function of the concentration distribution and is equal to G_n/v . It will be assumed to be zero outside of the range $1 \leq n \leq N$. Then the rate of creation of new drops in the concentration interval $(n - 1/2 \pm 1/2)\Delta c$, owing to all collisions between drops in all symmetrically located concentration intervals is from Equation (3)

$$4u \sum_{i=1}^n p(n+i) p(n-i) (\Delta c)^2 \quad (4)$$

Drops also are produced in the specified interval by collision between drops in certain asymmetrically located concentration intervals. Each such collision yields two new drops, but it will be assumed that only half the successful collisions produce drops in the desired interval. Therefore the contribution to the rate of formation of drops from asymmetric concentration intervals is

$$2u \sum_{i=0}^n [p(n+i) p(n-i-1) + p(n+i+1) p(n-i)] (\Delta c)^2 \quad (5)$$

Equation (4) excludes collision of drops within the interval itself. Equation (5) includes the contribution due to collision of drops in the central interval with those in the two adjacent intervals.

Drops in the interval are also lost by collision with drops of other concentrations at the rate

$$2up(n)[1 - p(n)\Delta c]\Delta c \quad (6)$$

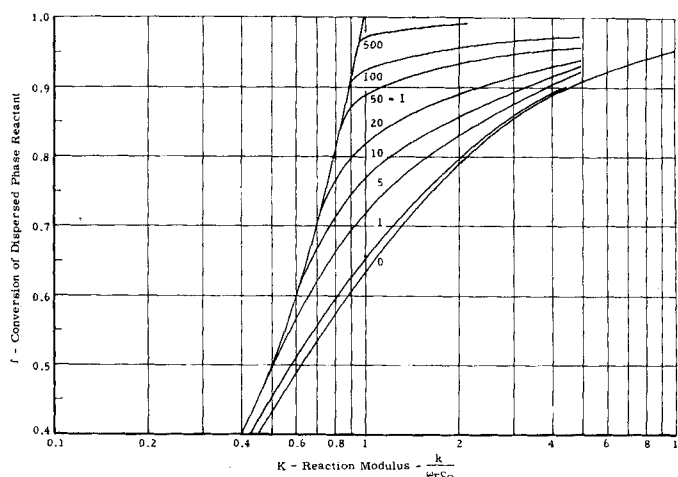


Fig. 2. Effect of dispersed phase mixing on the conversion for a zero-order reaction in the drops in a single-stage, two-phase, stirred reactor.

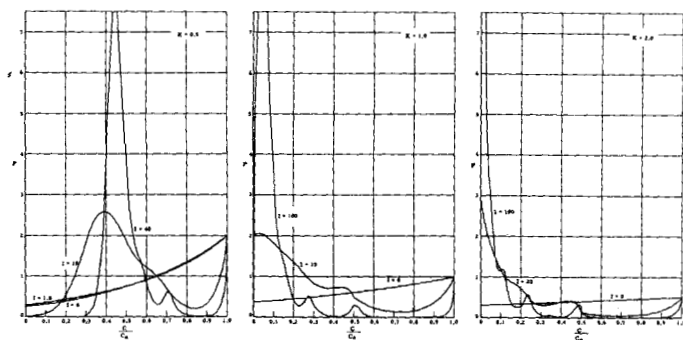


Fig. 3. Frequency function of dimensionless concentration for a zero-order reaction in the dispersed phase.

which includes the collisions with the adjacent intervals which return drops to the central interval. With no other sources of drops of concentration $(n - 1/2 \pm 1/2)\Delta c$, the rate of change of $Up(n)\Delta c$, the total number of drops in the interval, may be written as the sum of Equations (4), (5), and (6), which after they are rearranged and divided by $U\Delta c$ become

$$\frac{\partial p(n)}{\partial t} = \omega_i \left\{ \sum_{i=0}^n [p(n+i) + p(n+i+1)] [p(n-i) + p(n-i-1)] \Delta c - p(n) \right\} \quad (7)$$

where $\omega_i = 2u/U$ is the number of dispersed phase volumes involved in coalescences per unit time. This is defined as the rate of dispersed phase mixing. If p is continuous, the limit $\Delta c \rightarrow 0$ may be taken readily to give

$$\frac{\partial p}{\partial t} + p = 4 \int_0^\infty p(c + \alpha)p(c - \alpha)d\alpha \quad (8)$$

This equation represents the transient spreading by coalescences and redispersals of a solute among the drops of a stirred batch emulsion in accordance with the suggested mechanism. Whether the sum or integral form is preferred depends on the application. As no analytical solution is known, the former was used for machine computations. Although the integral form was derived by taking the limit $\Delta c \rightarrow 0$ for p continuous, certain manipulations may be made with a more general p , which may include any number of discontinuities in p or in its distribution function.

TRANSIENT SOLUTE SPREADING

Equation (7) was solved on a digital computer for twenty concentration intervals and with the time step $\omega_i \Delta t = 0.2$. With initial conditions of $p(1)\Delta c = 10/19$ and $p(20)\Delta c = 9/19$ the distribution evolved as shown in Figure 1.

It is characteristic that an emulsion which originally is very nonuniform in concentration becomes at $\omega_i t \approx 2.0$ relatively uniform in that most concentrations are represented among the drops. The approach to a final mixed condition proceeds quite slowly with a considerable spread of concentration remaining even at $\omega_i t = 11$, when the total volume of dispersed phase which

has entered into coalescences is eleven times the dispersed phase volume.

The concentration f.r.f. which evolves in accordance with this mechanism does not approach a normal distribution. If Equation (8) is multiplied through by $(c - \bar{c})^r$, where $\bar{c}$ is the average concentration, and the equation is then integrated formally over the range of concentrations, an expression may be obtained for the transient in the r th moment of the distribution about the mean, namely

$$\frac{\partial \mu_r}{\partial t} + \mu_r = \frac{1}{2^r} \int_0^\infty \int_0^\infty [(\beta - \bar{c}) + (\gamma - \bar{c})]^r p(\beta)p(\gamma)d\beta d\gamma \quad (9)$$

from which one may obtain the results shown in Table 1.

As expected the average remains constant and the variance drops to

zero. On the other hand the skewness remains constant and the peakedness increases without limit. For a normal distribution $a_3 = 0$ and $a_4 = 3$.

The behavior shown in Figure 1 is similar to that found experimentally for the mixing of solids by Weidenbaum and Bonilla (6) who show the results of tumbling mixing of sand and salt in equivalent coordinates. They used a normal distribution to represent the theoretical limit in their mixing process. While this may be appropriate when a limiting distribution exists, in the present case the limit is an impulse at the average concentration.

The equation for the variance given in Table 1 has been suggested for solids mixing (with experimental evidence) by Oyama and Ayaki (4) based on a linear random-walk model. Lacey (2) arrives at a similar expression from a linear diffusion model of solids mixing. The analogy between the dispersed phase mixing case and solids mixing appears to reside in part in the analogy between the discrete drop in one case and the fixed sampling volume used in the latter. The subject of solids mixing has been reviewed by Weidenbaum (7).

CHEMICAL REACTION OCCURRING IN THE DISPERSED PHASE

The consumption by reaction of a chemical species in the dispersed phase also transfers drops to different concentrations and hence affects the f.r.f. of drop concentration. If one assumes that in each drop, owing to chemical reaction of order s

$$\frac{dc}{dt} = -kc^s \quad (10)$$

then $Up(n+1)\Delta c$ drops enter the interval $(n - 1/2 \pm 1/2)\Delta c$ in the time interval $\Delta t = (c + \Delta c)^{-s} \Delta c/k$, while $Up(n)\Delta c$ drops leave the interval in $\Delta t = c^{-s} \Delta c/k$. The net rate of addition of drops to $(n - 1/2 \pm 1/2)\Delta c$ is therefore

$$Uk \frac{(c + \Delta c)^s p(n+1)\Delta c - c^s p(n)\Delta c}{\Delta c} \quad (11)$$

TABLE 1. PROPERTIES OF CONCENTRATION DISTRIBUTION DURING TRANSIENT MIXING

Area of distribution	$\mu_0 = 1$
Mean	$\mu_1 = 0 \quad [m_1(t) = m_1(0)]$
	$-\frac{\omega_i t}{2}$
Variance (central)	$\mu_2(t) = \mu_2(0) e^{-\frac{\omega_i t}{2}}$
Skewness	$a_3(t) = \frac{\mu_3(t)}{\mu_2^{3/2}(t)} = a_3(0)$
Peakedness	$a_4(t) = \frac{\mu_4(t)}{\mu_2^2(t)} = \left[\left(3 + \frac{\mu_4(0)}{\mu_2^2(0)} \right) e^{\frac{\omega_i t}{8}} - 3 \right]$

If the reaction system is a well-stirred single-stage reactor with volume V and flow rate Q , and the fraction dispersed phase in the feed is ϕ_1 , then the addition of drops to the distribution in the reactor at any time makes a contribution of $U(\phi_1 Q / \phi_2 V) p_s(n) \Delta c$, while the effluent removes drops at the rate $U(\phi_1 Q / \phi_2 V) p(n) \Delta c$. Combining these two terms with Equations (4) to (6) and (11), taking the limit $\Delta c \rightarrow 0$, and dividing through by $U \Delta c \phi_1 Q / \phi_2 V$, one obtains the equation for a single-stage reactor with a reaction of order s proceeding in the drop phase:

$$\frac{\partial p}{\omega_r \partial t} = p_o - p + I \left[4 \int_0^c p^* p^* d\alpha - p \right] + c_o K \frac{\partial c^* p}{\partial c} \quad (12)$$

where the residence frequency $\omega_r = \phi_1 Q / \phi_2 V$; $I = (\omega_t / \omega_r)$, and $K = k / \omega_r c_o$. An abbreviation has been used for the argument of the integral.

ZERO-ORDER REACTION IN THE DISPERSED PHASE

Equation (12), in the difference forms of Equations (4) to (6) and (11), has been solved numerically to obtain the steady state solutions for

cases between the extremes solved by Rietema for a single-feed concentration $[p_o(c) = \delta(c_o - c)]$ and a zero-order reaction in the drops ($s = 0$). The equations must be handled carefully because of the possible existence of delta function solutions. Since this occurs when $s < 1$, appropriate steps were taken to handle the singularity at $c = 0$ which represents the fraction of the drops in which the reactant has been entirely consumed. Equation (12) was solved on a digital computer

by allowing the transient to evolve to the steady state for different number of Δc intervals (25, 50, and 100) and extrapolating the calculated values for conversion and g to $\Delta c = 0$. The calculation was considered to have reached steady state when all the values of $\Delta p / \omega_r \Delta t$ and $\Delta g / \omega_r \Delta t$ became less than 5×10^{-4} . The results are given in Figure 2 as the fraction of the reactant in the feed which is converted (f) for a given K . The two limiting curves for $I = 0$ and $I = \infty$ are Rietema's solutions. The conversion is defined as

$$f = 1 - \int_0^c \frac{c}{c_o} p dc \quad (13)$$

Figure 2 shows that the drop interaction rate has a pronounced effect on conversion. At 90% conversion for example the vessel volume, or residence time, for no mixing ($I = 0$) is $4.7/0.9 = 5.2$ times that for complete mixing ($I = \infty$). A mixing rate corresponding to fifty volumes of dispersed phase interacting in one average residence time ($I = 50$) still requires about 30% larger reactor volume than for complete mixing.

Several of the concentration distributions resulting from combinations of I and K are shown in Figure 3.

Rietema (5) proposed the zero-order problem as an approximation to a purely mass transfer rate controlled reaction. As he pointed out, a real reaction would decrease in rate near zero concentration. The approximation assumes it does not. A more serious difficulty arises however in connection with the fact that after the drop phase reactant is consumed, the continuous phase reactant would actually continue to transfer into these depleted drops. Then when these drops coalesced with some containing the other reactant, further reaction (conversion) would occur. Therefore dispersed phase mix-

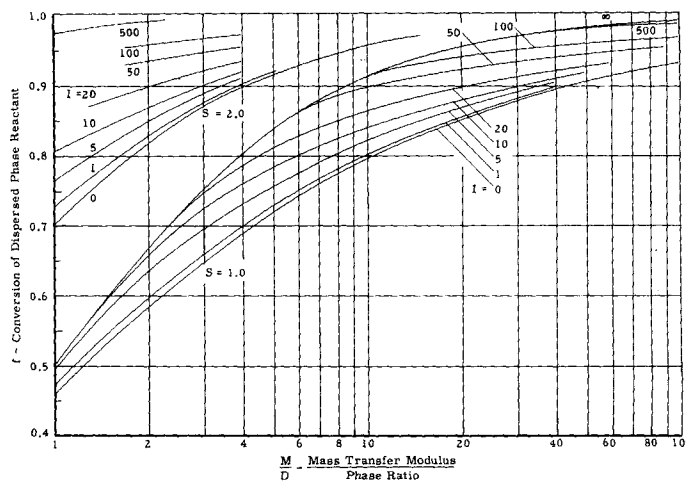


Fig. 5. Effect of dispersed phase mixing on the conversion for a mass transfer controlled reaction in the drops in a single-stage, two-phase, stirred reactor for two different values of the stoichiometric ratio S .

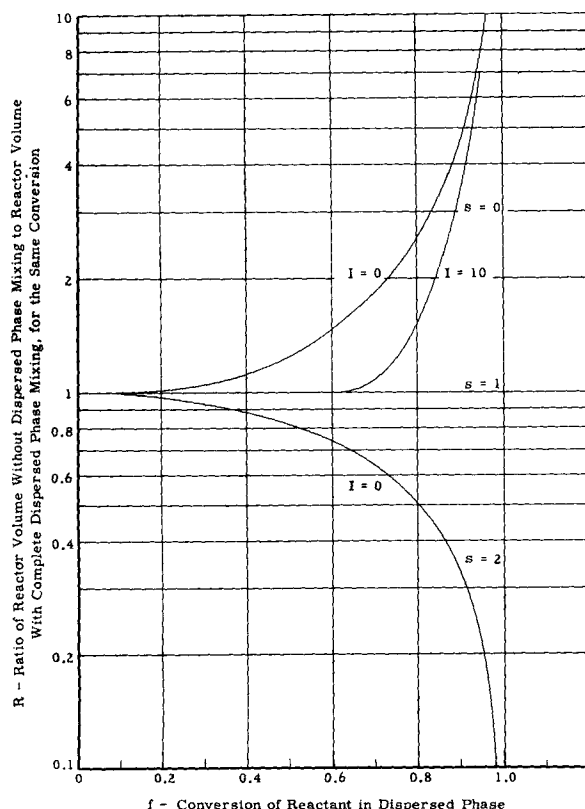


Fig. 4. Effect of dispersed phase mixing on conversion with zero-, first-, or second-order reactions in the dispersed phase.

ing can contribute another mechanism of apparent mass transfer to reacting drops. The above results can be readily transformed to represent a mass transfer rate controlled reaction but only under the condition that the transferring species cannot build up in the depleted drops. This is analogous to the fact that in the case of no dispersed phase mixing the concentration distribution of the continuous phase reactant in the drops does not influence conversion except by changing the available concentration driving force for transfer.

SECOND-ORDER REACTION IN THE DISPERSED PHASE

Equation (12) may be used to calculate conversion when a second-order

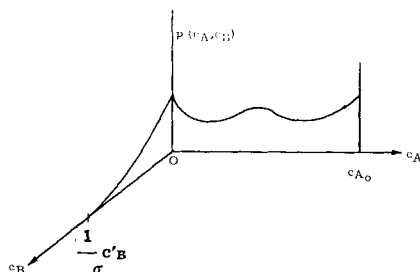


Fig. 6. Frequency function of c_A and c_B when they are mutually exclusive.

reaction is occurring in the drop phase by setting s equal to 2.0. A detailed study of this case has not yet been made, but the limiting solutions ($I = 0$, $I = \infty$) are interesting as they provide a comparison with low-order reactions.

With $I = 0$ and $s = 2$ in Equation (12), the steady state equation becomes

$$\delta(c_0 - c) - p + c_0 K \frac{dc^2 p}{dc} = 0 \quad (14)$$

which is readily solved to give

$$p = \frac{e}{Kc_0 c^2} - \frac{1}{Kc_0 c} \quad (15)$$

from which may be obtained, by multiplication by c , integration and use of Equation (13)

$$f = 1 - \gamma \int_0^x \frac{e^{-\lambda}}{\lambda} d\lambda \quad (16)$$

where

$$\gamma = \frac{1}{Kc_0^2}$$

With $I = \infty$ and $s = 2$, a material balance on the reacting component gives

$$c = c_0(1 - Kc^2) \quad (17)$$

or

$$f = 1 - \frac{\gamma}{2} \left[\sqrt{1 + \frac{4}{\gamma}} - 1 \right] \quad (18)$$

To compare the reactor volume required in the case of a completely mixed drop phase with that required when no mixing occurs, at the same conversion, set

$$R = \frac{V_{I=0}}{V_{I=\infty}} = \frac{\gamma_{I=0}}{\gamma_{I=\infty}} \quad (19)$$

and since from Equations (17) and (19)

$$\gamma_{I=0} = \frac{(1-f)^2}{Rf} \quad (20)$$

Equation (16) becomes

$$\frac{1-f}{Rf} e^{\frac{(1-f)^2}{Rf}} \int_0^{\frac{(1-f)^2}{Rf}} \frac{e^{-\lambda}}{\lambda} d\lambda = 1 \quad (21)$$

which gives R implicitly in terms of f . This relation is shown in Figure 4 along with the equivalent result for a zero-order reaction found by Rietema (5), and the zero-order reactor result when $I = 10$ (compared with complete dispersed phase mixing) obtained in the present study.

In general dispersed phase mixing increases the conversion for a zero-order reaction in the dispersed phase while it decreases the conversion for a second- or higher-order reaction in the dispersed phase. Therefore whether it is desirable to encourage or discourage dispersed phase mixing by some means depends on the relative order of the important reactions.

MASS TRANSFER CONTROLLED REACTION—INSOLUBLE REACTANT

A reaction which is completely mass transfer rate controlled may be described by the above model of a zero-order reaction in the dispersed phase. Assume that a reactant (B) is transferring from the continuous phase, where it has concentration c_B' , into the dispersed phase where it reacts instantaneously with component (A), and also that (B) is not otherwise soluble in the dispersed phase. [An example would be Madden's (3) system with iodine in the continuous hydrocarbon phase transferring into the aqueous dispersed phase containing sodium thiosulfate.]

Then mass balances on the reactants give

$$(c_{A0} - c_A)\phi_1 Q = (c_{B0}' - c_B')(1 - \phi_1)Q = c_B' k_m a \phi_2 V (1 - g) \quad (22)$$

where $k_m a$ is the specific mass transfer coefficient and $\bar{c}_A$ the average concentration of (A) in the drops. In a zero-order reaction

$$(c_{A0} - \bar{c}_A)\phi_1 Q = f c_{A0} \phi_1 Q = kV\phi_2(1 - g) \quad (23)$$

so there is obtained

$$M = \frac{DK}{S - f} \quad (24)$$

where

$$M = \frac{k_m a}{\omega_r}, \quad D = \frac{1 - \phi_1}{\phi_1}, \quad S = \frac{(1 - \phi_1)c_{B0}'}{\phi_1 c_{A0}}$$

For particular S and D Equation (24) transforms the results of the zero-order reaction calculation by Equation (12) to the equivalent mass transfer limited case. Figure 2 is replotted in Figure 5 as f vs. M/D for $S = 1.0$ and 2.0 .

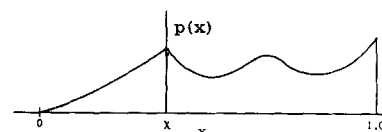


Fig. 7. Transformed distribution of Figure 6.

MASS TRANSFER CONTROLLED REACTION—SOLUBLE REACTANT

If the reactant (B) is soluble in the drop phase and therefore continues to transfer into a drop even after the total consumption of (A), a drop which acquires some concentration of (B) might coalesce with a drop containing (A), leading to the loss in the new drops of whichever reactant was not in excess. The solubility of (B) in the drops will therefore lead to a higher conversion of (A). The development of this case is of interest both because it is more nearly the real case and because it illustrates how one particular joint probability distribution of two concentrations may be handled.

Because of the assumption that the reaction is very fast, no drop can contain both reactants, and therefore the joint concentration frequency function takes the form shown in Figure 6 with values only on the concentration coordinate axes and zero elsewhere. Now since the coalescence of drops of concentration c_B and c_A produces two new

drops of concentration $\frac{1}{2}(c_A + c_B)$,

depending on whether (A) or (B) is in excess, c_B may be looked upon as a negative concentration with respect to c_A , and hence averages may be taken as in the original derivation. The maximum possible drop concentration of (A) is c_{A0} in the entering drops. The maximum possible drop concentration of (B) is c_B'/σ , where c_B' is the continuous phase concentration of (B) and σ is the partition coefficient (the

equilibrium value of c_B'/c_B). With the changes of variable

$$c_A = \frac{c_B'}{\sigma} \left[\left(1 + \frac{\sigma c_{A0}}{c_B'} \right) x - 1 \right] \quad (25a)$$

and

$$\frac{c_B'}{c_B' + \sigma c_{A0}} = \chi \quad (25b)$$

plus an appreciation of the fact that c_B may be considered as $[-c_A]$ in the dispersed phase mixing model, the distribution in Figure 6 may be unfolded and transformed to that in Figure 7. Only the reaction term in Equation (12) need be modified to apply it to this new case. The modification must distinguish between the zero-order nature of the transfer of reactant when $\chi \leq x \leq 1$, and the first-order behavior when $0 \leq x \leq \chi$:

$$\chi \leq x \leq 1$$

$$\frac{dc_A}{dt} = -k_m a c_B' \quad (26)$$

or, with change of variables

$$\frac{dx}{dt} = -k_m a \sigma \chi \quad (27)$$

$$\chi = \frac{(1 + M\sigma)S - M\sigma f}{(1 + M\sigma)S - M\sigma F + [D\sigma + M\sigma(1 + D\sigma)]} \quad (35)$$

The last term in Equation (12) then becomes

$$\frac{k_m a \sigma \chi}{\omega_r} \frac{\partial p}{\partial x} \quad (28)$$

$$0 \leq x \leq \chi$$

$$\frac{d[-c_A]}{dt} = \frac{dc_B}{dt} = k_m a (c_B' - \sigma c_B) \quad (29)$$

or, with change of variables

$$\frac{dx}{dt} = -k_m a \sigma \chi \frac{x}{\chi} \quad (30)$$

The last term in Equation (12) then becomes

$$\frac{k_m a \sigma \chi}{\omega_r} \frac{\partial \frac{x}{\chi} p}{\partial x} \quad (31)$$

With these substitutions Equation (12) takes the form

$$\frac{\partial p}{\omega_r \partial t} = p_0 - p + I \left[4 \int_0^x p^* p^* d\alpha - p \right] + M\sigma \chi \frac{\partial h p}{\partial x} \quad (32)$$

where h is x/χ , $0 \leq x \leq \chi$, and 1 in $\chi \leq x \leq 1$. The steady state form of Equation (32) must be solved simultaneously with an expression for χ

which may be obtained from the material balance expressions for the steady state

$$\phi_1 (c_{A0} - \bar{c}_A) = (1 - \phi_1) (c_{B0}' - \bar{c}_B') - \phi_1 \bar{c}_B \quad (33)$$

and

$$Q(1 - \phi_1) (c_{B0}' - \bar{c}_B') = k_m a V \phi_2 (c_B' - \sigma \bar{c}_B) \quad (34)$$

where $\bar{c}_A$ or $\bar{c}_B$ are the average concentrations of (A) or (B) over the whole drop phase. The expression for χ defined by (25b) becomes

In these variables the conversion of reactant (A) is given by

$$f = 1 - \int_x^1 \left(\frac{x - \chi}{1 - \chi} \right) p dx \quad (36)$$

Equations (32) and (35) have been solved numerically with a computer by the transient technique used for Equation (12). The equations were combined by calculating at each time step

TABLE 2. CALCULATED CONVERSIONS IN A TWO-PHASE, SINGLE-STAGE, MASS TRANSFER CONTROLLED REACTION (SOLUBLE REACTANT) WITH DISPERSED PHASE MIXING

$M\sigma$	I	$D\sigma = 1.0$ $S = 1.0$		χ
		f	f'	
0.5	0	0.317	0.328	0.400
	10.0	0.334	0.334	0.339
	∞	0.333	0.333	0.400
1.0	0	0.443	0.489	0.341
	0	0.444	0.490	0.340*
	10.0	0.500	0.500	0.333
2.0	0	0.544	0.618	0.275
	1.0	0.581	0.633	0.268
	100.0	0.673	0.673	0.248
	∞	0.667	0.667	0.250

* Computed from Equations (35), (41), and (42).

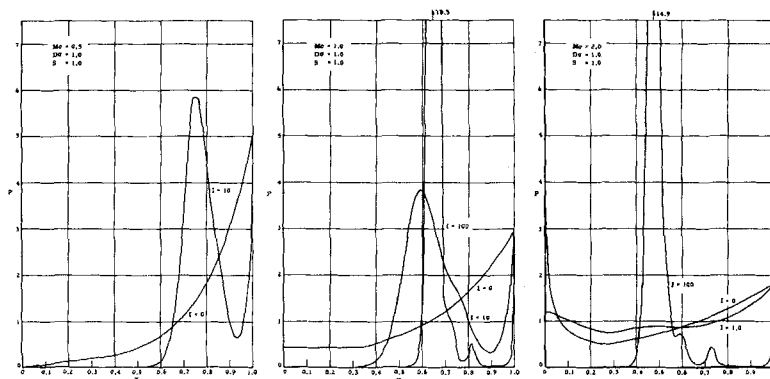


Fig. 8. Frequency function of dimensionless concentration for a mass transfer controlled reaction with a soluble diffusing reactant.

values of χ and f consistent with (35) and (36) and using that χ for the next time interval. This method does not yield the correct transient solution, since Equation (35) is only correct in the steady state. The numerical method was arranged so that instability did not result from the shifting values of χ computed at each step.

The numerical method converged too slowly for it to be practical to explore a wide range of values of M , D , S , σ , and I . Those that were run are listed in Table 2, and the distributions $p(x)$ are given in Figure 8.

Rietema (5) showed that the zero-order reaction has as its limiting conversion, for no and complete dispersed phase mixing (in the nomenclature of the present work)

$$I = 0: \quad f = K(1 - e^{-\frac{1}{K}}) \quad (37)$$

and

$$I = \infty \quad f = K, 0 \leq K \leq 1 \quad (38)$$

$$f = 1, 1 \leq K$$

When the reactant is soluble in the dispersed phase and the reaction is mass transfer controlled, Equation (32) may be solved analytically to give the result that the conversion with complete dispersed phase mixing and soluble product is the same as in the mass transfer analogy to Rietema's solutions, while the conversion with no dispersed phase mixing and soluble reactant is given by the simultaneous equations

$$f = \theta (1 - e^{-\frac{1}{\theta}}) \quad (39)$$

and

$$\theta = M\sigma \frac{(1 + M\sigma)S - M\sigma f}{D\sigma + M\sigma(1 + D\sigma)} \quad (40)$$

These were used to calculate the results given for $I = 0$ in Table 2. The distribution of concentration for this case is readily calculated by integrating Equation (32) set equal to zero with $I = 0$. There is obtained

$$-\frac{1}{M\sigma} \left(\frac{1 - \chi}{\chi} \right) \quad \frac{1}{M\sigma} - 1$$

$$p = \frac{e}{M\sigma\chi} \left(\frac{x}{\chi} \right) \quad 0 \leq x \leq \chi \quad (41)$$

$$p = \frac{e}{M\sigma\chi} \quad \chi \leq x \leq 1 \quad (42)$$

This distribution is plotted in Figure 8 for $I = 0$.

The conversion may be defined in two ways when a soluble reactant is transferring to the drop phase. The actual fraction of the reactant (A) left in the drop phase as the dispersion leaves the reactor has been called f . However if after leaving the reactor the dispersed phase is settled out, that (B) which was in drops would also react and consume (A). The resultant higher conversion is designated f' in Table 2. It is computed from $f' = f + \bar{x}_B$, where $\bar{x}_B$ is the portion of the distribution with $x < \chi$, averaged over the whole range.

One distribution was computed for $I = 0$ with $M\sigma = 1.0$. The results are given in Table 2 for both the exact and the numerical computation. The differences are negligible, indicating that the computation had progressed to nearly the steady state. The concentration distributions were almost identical.

DISCUSSION

In a zero-order or mass transfer controlled reaction in the dispersed phase of a single-stage reactor quite large dispersed phase mixing frequencies, relative to the residence frequency, must be obtained to approach correspondence to complete mixing in the dispersed phase. This may be thought of as the possibility of early exiting from the reactor of some nearly unconverted drops. While at 80% conversion mixing of the dispersed phase may reduce the reaction volume required by nearly a factor of 3, this requires a value of ω_i as much as fifty times ω_r . Madden (3) found values of ω_i as high as 30 min.⁻¹ in a water dispersed system (toluene continuous). Hence residence times in this system in excess of about 2 min. are required to approach complete mixing from the standpoint of the chemical conversion. Studies reported in Part II of this paper (9) found similar values for the rate of dispersed phase mixing but at significantly higher specific power inputs than used by Madden.

The term in Equation (12) for dispersed phase mixing may be introduced into equations for a variety of other systems to find its effect on conversion or selectivity. While dispersed phase mixing does not affect the conversion in a reaction system of only first-order reactions, it does strongly influence the variance of concentration

in the drop phase and hence any events which may depend on the variance, such as the rate of production of some by-product by a higher-order reaction. If the by-product reaction is important even when present to only a small extent, the results given in Figures 3 and 8 may be used to calculate the effect of dispersed phase mixing on the degree of by-product formation if one assumes that the distribution is only negligibly affected by the additional reactions.

The model used here does not include effects due to a distribution of drop sizes, uneven breakup of drops, or a distribution of probabilities of coalescence with drop size or concentration. While a more complex analysis may eventually be called for, it was thought desirable at this time to devote effort to determining the qualitative effects to be expected on the basis of a simple model. At such time as either this model is shown inadequate for particular computations or experiments demonstrate departures from its prediction, the more complicated interactions will have to be considered. While the derivations have been on the basis of a single concentration in the dispersed phase feed to the reactors, the results are readily generalized to a distribution of concentration in the feed such as would be the case if stages were cascaded.

ACKNOWLEDGMENT

The author wishes to thank Mrs. Doris Lidke and Miss Jane Merritt for writing the programs for a Datatron and an IBM-7090 computer, respectively, on which the calculations reported here were performed.

NOTATION

a_s	= skewness of frequency function
a_i	= peakedness of frequency function
$c, (c')$	= concentration in drop (continuous) phase
$c_o, (c'_o)$	= feed concentration in drop (continuous) phase
$\bar{c}, (\bar{c}')$	= average concentration in drop (continuous) phase
D	= feed phase ratio, $\frac{(1-\phi_1)}{\phi_1}$
f	= fraction of dispersed phase reactant converted in reactor
f'	= fraction of dispersed phase reactant converted in mixed reactor effluent
g	= fraction of drop phase with identically zero concentration
G	= sets of drops
h	= function of x/χ
i	= integer summation index
I	= dispersed phase mixing modulus ω_i/ω_r
k	= reaction rate constant
k_{ma}	= mass transfer coefficient per unit volume of dispersed phase

K	= reaction modulus, $(k)/(\omega_r c_o)$
m_r	= r^{th} moment of fr.f.
M	= mass transfer modulus, $(k_{ma})/(\omega_r)$
n	= drop concentration interval index
N	= intervals of drop concentration in range
$p, p(c), p(n)$	= frequency function (fr.f.) of drop concentration
p_o	= feed fr.f. of drop concentration
p^+, p^-	= abbreviations for $p(c + \alpha)$, $p(c - \alpha)$
Q	= total volume flow rate to reactor
r	= moment designation
s	= order of reaction
S	= stoichiometric ratio, $\frac{(1-\phi_1)c_{Bo'}}{\phi_1 c_{Ao}}$
t	= time
u	= drop collision rate
U	= number of drops in vessel
V	= reactor volume
x	= dimensionless concentration variable

Greek Letters

$\alpha, \beta, \lambda, \theta$	= dummy variables
$\delta(x - x_i)$	= delta function at $x = x_i$
Δc	= concentration increment
μ_r	= r^{th} central moment of fr.f.
γ	= partition coefficient, c'/c at equilibrium
ϕ_1	= dispersed phase fraction in flows
ϕ_2	= dispersed phase fraction in reactor vessel
χ	= transformed zero concentration
ω_i	= dispersed phase mixing frequency, $2u/U$
ω_r	= residence frequency, $(Q\phi_1)/(V\phi_2)$

Subscripts

A, B = reactants (A) and (B)

LITERATURE CITED

1. Danckwerts, P. V., *Chem. Eng. Sci.*, **8**, 1/2, p. 93 (1958).
2. Lacey, P. M., *J. Appl. Chem. London*, **4**, p. 257 (1954).
3. Madden, A. J., and G. L. Damerell, *A.I.Ch.E. Journal*, **8**, No. 2, p. 233 (May, 1962).
4. Oyama, V., and K. Ayaki, *Kagaku Kikai*, **20**, No. 4, p. 6 (1956).
5. Rietema, K., *Chem. Eng. Sci.*, **8**, 1/2, p. 103 (1958).
6. Weidenbaum, S. S., and C. F. Bonilla, *Chem. Eng. Progr.*, **51**, p. 27-J (1955).
7. Weidenbaum, S. S., "Mixing of Solids," E. Drew, ed., *Advances in Chemical Engineering Part II*, p. 209, Academic Press, New York (1958).
8. Zwietering, T. N., *Chem. Eng. Sci.*, **11**, No. 1, pp. 1-15 (1959).
9. Miller, R. S., J. L. Ralph, R. L. Curl, and G. D. Towell, *A.I.Ch.E. Journal*, **9**, No. 2, p. 196 (1963).

Manuscript received January 2, 1962; revision received May 23, 1962; paper accepted May 23, 1962. Paper presented at A.I.Ch.E. Los Angeles meeting.