

Dispersed phase mixing effects on second moments in dominantly first-order, backmix reactors

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Abstract—An idealized model for dispersed phase mixing is used to find the relative rates of $A+A$, $B+B$ and $A+B$ reactions when the reaction $A \rightleftharpoons B$ is dominant, first order and reversible. A large possible effect of mixing on the $A+A$ reaction is demonstrated, while the effect on $B+B$ on $A+B$ is never greater than a factor of two.

The results are applicable to estimating the effect of mixing on second order by-product reactions which are important when present to a small extent. In addition, this represents the first analytical solution to the mixing-reaction equation.

THE DIRECTION and magnitude of the effect of dispersed phase mixing on the conversion in systems with reaction within the dispersed phase has now been calculated for zero and second order reactions (CURL [1]; SPIELMAN and LEVENSPIEL [2]), using an idealized mixing model. These and related works on segregation in chemical reactors are reviewed by RIETEMA [3].

The idealized mixing model assumes that all drops are the same size, that coalescence occurs at random, and that after coalescence the newly formed drop is completely mixed and breaks immediately into two drops of the same size. While admittedly unrealistic, this simple model is all we have until something is learned of the details of the coalescence and breaking processes in reactors. In the meantime the idealized model has probably provided semi-quantitative answers to several questions about the performance of dispersed phase reactors.

The Monte Carlo calculation procedure of Spielman and Levenspiel is admirably suited for computationally modelling more complex systems. Therefore there exists a relatively simple calculation procedure for obtaining numerical answers to as many more mixing-reaction systems as we can imagine.

Nevertheless there still remain reasons for being interested in possible analytical solutions of the equations describing the system. These may not only clarify the interaction of the parameters in the mixing-reaction models but also provide a more direct or simpler calculation of numerical results.

The general mixing-reaction equation (CURL [1]) is:

$$\frac{\partial p}{\omega_r \partial t} = p_0 - p + J \left[2 \int_0^\infty p(2c - \alpha)p(\alpha) d\alpha - p \right] + K \frac{\partial c^n p}{\partial c} \quad (1)$$

for the probability density distribution, $p(c, t)$ of drop concentration. This has no known analytical solution. The difficulty associated with solving it is illustrated by converting it to the r th (integer) moments (m_r) of p , giving

$$\frac{\partial m_r}{\omega_r \partial t} = m_{r(0)} - m_r + J \left[\frac{1}{2^r} \sum_{k=0}^r \binom{r}{k} m_{r-k} m_k - m_r \right] - K r m_{r+n-1} \quad (2)$$

(If $r+n-1=0$, m_0 must exclude the area under any singularity at the origin and need not equal 1.0.) For $n \neq 1$ there is no finite (closed) set of simultaneous equations allowing the calculation of the individual m_r . Either equations for always higher moments, or endless fractional moments, are required. HULBERT and KATZ [4] point out the possibility of closing or truncating the infinite set of equations by approximating the distribution p with a series of special functions. This has not yet been attempted for this mixing-reaction model. Here the interest is in elucidating an analytical solution to Eq. (2). In particular, we see that we may obtain all the moments if $n=1$, although this is the one case where dispersed phase mixing does not affect the

reactant conversion (RIETEMA [3]). However, there is a practical situation in which we are interested in the higher moments of the distribution of concentration in the mixing-first order reaction situation. That this also yields analytical results is a benefit in further contemplation of related problems.

Consider a reversible first order chemical reaction $A \rightleftharpoons B$ taking place in the drops in a dispersed phase, backmix reactor. The mean concentration of A, $\overline{C_A}$, will depend only upon the dispersed phase residence time and the kinetic rate constants. However, let us worry about the possibility of the second order reactions $A + A$, $B + B$ or $A + B$ going to some product which is undesirable in even trace quantities. The average rates of these reactions depend on the quantities $\overline{C_A^2}$, $\overline{C_B^2}$ and $\overline{C_A C_B}$ in the reactor, but these in turn depend on the rate of dispersed phase mixing. Hence, if we neglect the contribution of these reactions to the mass-balance in the reactor, we have a readily solvable problem, and can obtain analytical expressions for the extent to which dispersed phase mixing affects the relative rate of these possible by-product reactions.

For simplicity consider that only A is fed in the dispersed phase, at concentration C_{A0} . Stoichiometry requires that, due to reaction alone, the concentrations of A and B are related by

$$C_B = C_{A0} - C_A \quad (3)$$

Now, dispersed phase mixing, with the simple model of CURL [1], produces drops having the average concentrations of the species in the mixing drops. Hence the drops resulting from mixing must also have C_A and C_B as given by Eq. (3). This is shown in Fig. 1, where it is apparent that mixing of two

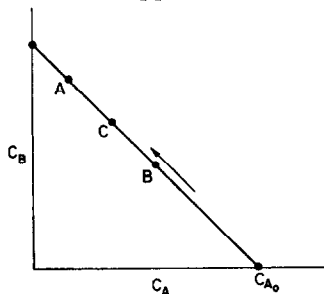


FIG. 1. The locus of all possible drop concentrations in the present system. The coalescence of a drop from Pt A with one from Pt B simply produces two at Pt C. The arrow indicates the direction of drop "motion" due to reaction.

drops from different locations on the line produces a concentration pair lying on the line. Therefore, even though we might have thought that the problem would have to be developed in terms of the joint probability density distribution $p(C_A, C_B)$, the dependence between C_A and C_B reduces the problem to one dimension. It is convenient to non-dimensionalize concentration by setting $y = C_A/C_{A0}$. In the one dimensional reaction (or "phase") space of y , the reaction velocity is, using first order kinetics and Eq. (3),

$$\frac{dy}{dt} = k_2 - (k_1 + k_2)y \quad (4)$$

The conservation equation, analogous to Eq. (1) is, in the steady state:

$$p_0 - p + I \left[2 \int_0^\infty p(2y - \alpha)p(\alpha)d\alpha - p \right] - \frac{\partial}{\partial y} (k_2 - (k_1 + k_2)y)p = 0 \quad (5)$$

(The reaction term is conveniently obtained from the conservation, or "Liouville" equation, such as shown by HULBURT and KATZ [4]). The reaction moduli K_1 and K_2 , equal to k_1/ω_r and k_2/ω_r , are for the forward and reverse reaction respectively.

The associated moment equation is:

$$m_{r_0} - m_r - I \left[\frac{1}{2^r} \sum_{k=0}^r \binom{r}{k} m_{r-k} m_k - m_r \right] - r[(K_1 + K_2)m_r - K_2 m_{r-1}] = 0 \quad (6)$$

We immediately obtain (since $m_0 = 1$ and m_{r_0} has been assumed to equal 1.0):

$$m_1 = \frac{1 + K_2}{1 + K_1 + K_2} \quad (7)$$

$$m_2 = \frac{1 + 2K_2 + m_1^2(I/2)}{1 + 2(K_1 + K_2) + (I/2)} \quad (8)$$

We seek the means $\overline{C_A^2}$, $\overline{C_B^2}$ and $\overline{C_A C_B}$. In dimensionless form, using a joint moment notation, these are, respectively:

$$m_{20} = \overline{y^2} = m_2 \quad (9)$$

$$m_{02} = \overline{(1-y)^2} = 1 - 2m_1 + m_2 \quad (10)$$

$$m_{11} = \overline{y(1-y)} = m_1 - m_2 \quad (11)$$

while

$$m_{10} = \bar{y} = m_1 \quad (12)$$

$$m_{01} = 1 - \bar{y} = 1 - m_1 \quad (13)$$

With $I \rightarrow \infty$, the well mixed dispersed phase situation, the concentrations are uniform throughout and we would have

$$m_{20} = m_{10}^2 \quad (14)$$

$$m_{02} = m_{01}^2 \quad (15)$$

$$m_{11} = m_{10}m_{01} \quad (16)$$

The relative rates of the trace second order reactions, with respect to the well mixed case, are then

$$\gamma_{20} = \frac{\overline{C_A^2}}{\overline{C_A}^2} = \frac{m_{20}}{m_{10}^2} \quad (17)$$

$$\gamma_{02} = \frac{\overline{C_B^2}}{\overline{C_B}^2} = \frac{m_{02}}{m_{01}^2} \quad (18)$$

$$\gamma_{11} = \frac{\overline{C_A C_B}}{\overline{C_A} \overline{C_B}} = \frac{m_{11}}{m_{10} m_{01}} \quad (19)$$

In place of the reaction moduli, the following variables are chosen to represent the reaction conditions:

1. Possible equilibrium conversion (from 7 and 13, $K_{1,2} \rightarrow \infty$)

$$E = m_{01e} = \frac{K_1}{K_1 + K_2} \quad (20)$$

2. Fractional approach to equilibrium (from 7, 13 and 20)

$$A = \frac{m_{01}}{m_{01e}} = \frac{K_1 + K_2}{1 + K_1 + K_2} \quad (21)$$

The conversion itself is simply $m_{01} = AE$ (and $m_{10} = 1 - AE$). With some algebraic manipulation of Eqs. (7)–(21), we obtain the relations for the effect of dispersed phase mixing:

$$\gamma_{20} = \frac{1 - A + 2A(1-E)(1-AE) + (1-A)(1-AE)^2(I/2)}{(1-AE)^2[1+A+(1-A)(I/2)]} \quad (22)$$

$$\gamma_{02} = \frac{2 + (1-A)(I/2)}{2A + (1-A)[1 + (I/2)]} \quad (23)$$

$$\gamma_{11} = \frac{A(1-E) + (1-AE)[1 + (1-A)(I/2)]}{(1-AE)[1+A+(1-A)(I/2)]} \quad (24)$$

Interestingly enough the mixing parameter for these associated second order reactions appears as $I/2$, a definition preferred by SPIELMAN and LEVEN-SPIEL [2], as in the Monte Carlo procedure it represents the number of coalescences occurring in the reactor during the mean time between drop entries. However, $I/2$ would not be the form if we wanted higher moment relations. The parameter I is preferred here as it represents the volume fraction of the dispersed phase entering into coalescences per dispersed phase residence time.

Equations (22)–(24) are shown in Figs. 2–4. Equation (7) for γ_{02} does not depend on E . We see

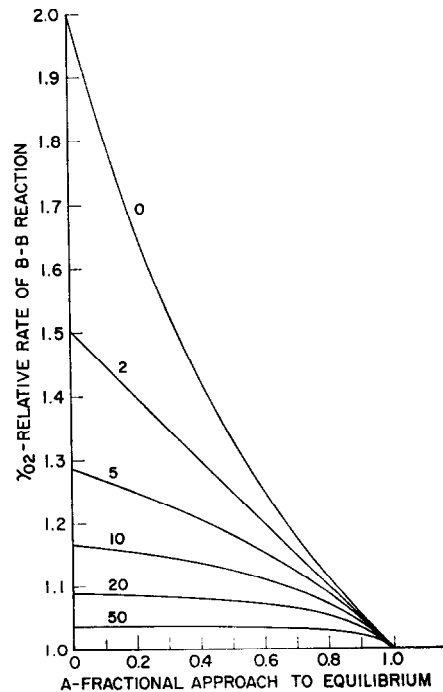


FIG. 2. Rate of reaction B+B relative to rate at $I = \infty$ vs. fractional approach to equilibrium.

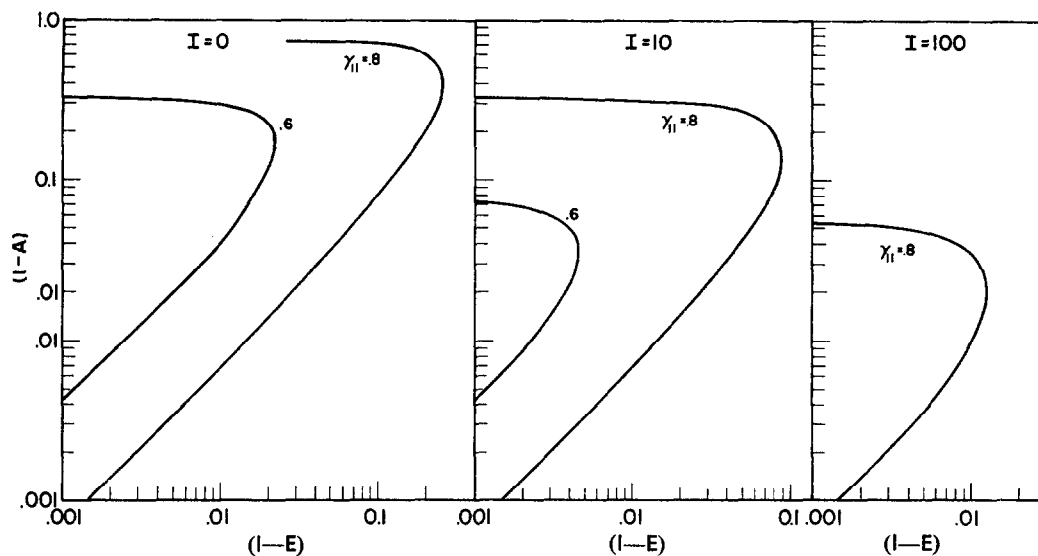


FIG. 3. Rate of reaction $A+B$ relative to rate at $I=\infty$. Contours are for constant γ_{11} . Values at high conversion are included by plotting parametrically vs. $1-A$ and $1-E$.

that dispersed phase mixing can produce a two-fold difference in the relative rate of the second order reaction $B+B$, increasing I decreasing the importance of this reaction (the "usual" direction for the effect of mixing in a second order reaction). This dependence is also found for the reaction $A+A$, although here γ_{20} may become very large at high conversions (similar to the irreversible second order reaction results of SPIELMAN and LEVENSPIEL [2]). However the relative rate of reaction $A+B$ is *increased* by dispersed phase mixing, as shown by γ_{11} increasing, within the limits of 0.5 to 1.0, with increasing I . This is qualitatively similar to an $A+B$ reaction ($A+B$ separated in the feed) analyzed by SPIELMAN and LEVENSPIEL [7].

As might be expected γ_{20}^{-1} , with $E=1.0$, becomes asymptotic to the "performance ratio" of Spielman and Levenspiel for a second order reaction, at low conversions. Incidentally, with $I=0$, the present γ_{20} is nearly identical to the "performance ratio" for a reactor with an irreversible zero-order reaction. There may be an intuitive argument for this, but it is not known to the author.

We see that it would be advisable to increase dispersed phase mixing if the reactions $A+A$ or $B+B$ are the undesired side reactions, although the

effect on the latter is small; while we would wish to maintain a segregated dispersed phase if $A+B$ were the undesired reaction. We also see that in all cases extremely large mixing rates are necessary to approach the "completely mixed" situation, especially at high conversions.

To what extent a particular rate can be obtained depends on the fluid phases, reactor geometry and mixing rate, as shown by MILLER *et al.* [5], MADDEN and DAMERELL [6], and GROOTHUIS and ZUIDERWEG [7].

NOTATION

A	fractional approach to equilibrium, C_B/C_{Be}
C	concentration of reactant in drop
\bar{C}	mean concentration of reactant over all drops
E	equilibrium conversion for first order reaction
I	dispersed phase mixing modulus, ω_i/ω_r
k	reaction rate constant, time^{-1}
K	reaction modulus, k/ω_r
m_r	r th moment of $p(y)$, y^r
$m_{rr'}$	r, r' joint moment, $y^r(1-y)^{r'}$
n	order of reaction
p	probability density distribution of c, y or other variates
r	order of moment
t	time
y	dimensionless concentration, C_A/C_{A0}
α	dummy variable

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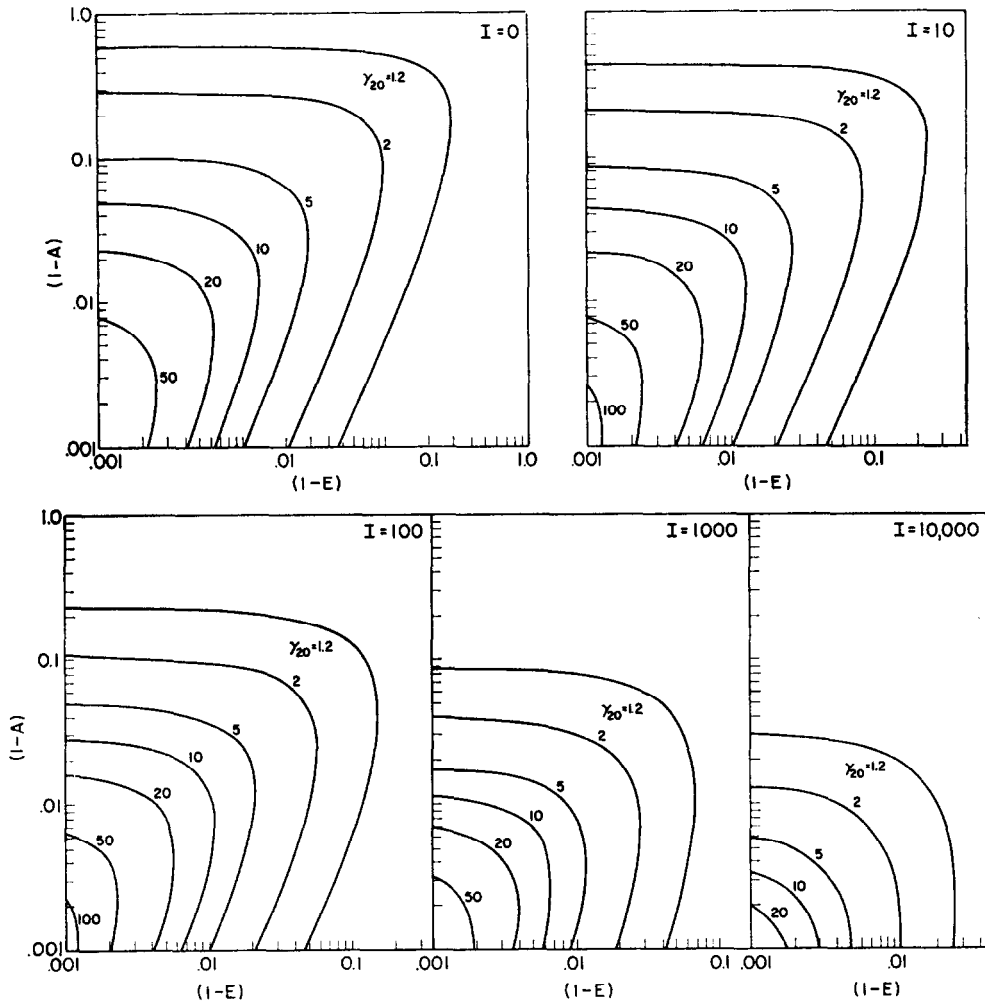


FIG. 4. Rate of reaction A+B relative to rate at $I = \infty$. Contours are for constant γ_{20} .

γ_{rr} : higher order reaction rates relative to complete mixing,

$$\frac{m_{rr'}}{\bar{y}^r (1-\bar{y})^{r'}}$$

ω_r : residence frequency for dispersed phase, time^{-1}

ω_i : dispersed phase mixing rate, time^{-1}

Subscripts

- 1, 2 forward and reverse reaction, respectively
- A, B refers to reactants A and B
- e equilibrium condition
- (O) feed condition

Operation

- (—) mean value.

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Résumé—L'auteur a employé un modèle idéalisé pour étudier les effets du degré de mélange sur la vitesse relative des réactions simultanées du type $A+A$, $B+B$, et $A+B$, dans le cas où la réaction $A\rightleftharpoons B$, du supposée du premier ordre et réversible, est la plus rapide. L'on démontre ainsi la possibilité d'un effet de mélange prononcé sur la vitesse de la Reaction $A+A$, tandis que l'effet sur les réactions $B+B$ et $A+B$ peut s'exprimer par un facteur qui n'est jamais plus grand que deux.

Les résultats de cet étude pourraient s'employer pour estimer l'effet du degré de mélange sur les réactions du deuxième ordre des sous-produits, dont des traces ont un effet important. En outre, ils représentent la première solution analytique des équations de mélange-reaction.

Zusammenfassung—Ein idealisiertes Modell für das Mischen disperser Phasen dient zur Auffindung der Relativgeschwindigkeiten der Reaktionen $A+A$, $B+B$ und $A+B$, wenn die Reaktion $A\rightleftharpoons B$ vorherrschend, erster Ordnung und umkehrbar ist. Ein möglichst grosser Mischeffekt auf die Reaktion $A+A$ wird dargestellt, während der Effekt auf $B+B$ oder $A+B$ nie grösser als ein Faktor zwei ist.

Die Ergebnisse sind zur Abschätzung des Mischeffekts auf Nebenproduktreaktionen zweiter Ordnung anwendbar, welche zu einem geringen Mass vorhanden-bedeutend sind. Darüberhinaus stellt die erste analytische Lösung der Mischreaktionsgleichung dar.