Extractive Reaction: Batch and Continuous-Flow Chemical Reaction Systems Dilute Case

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A reaction process occurring simultaneously with an extraction by an immiscible phase is referred to herein as *extractive reaction*.

Quantitative relations are developed which show how the rate of reaction, volumetric efficiency, and reactant conversion of a single-phase batch reaction can be enhanced by deliberately adding to the batch a second phase such as an immiscible solvent or an inert gas.

Analytical solutions are also obtained for continuous-flow extractive reactions of first order and of simple or complex stoichiometry occurring in single- or multistage stirred-tank reactors. The effect of recirculated or side streams is included.

Dilute systems and several types of reactions are considered. The equations are applicable, for instance, to liquid-liquid systems and solid-liquid or gas-liquid processes wherein reaction occurs in either the vapor or condensed phase.

The yield and rate of product formation for many reactions are affected, and often can be favorably increased, by the presence, or the deliberate, controlled addition to the reaction system, of an immiscible, extractive phase. Such operations, involving a simultaneous extraction and reaction process, will be herein referred to as *extractive reactions.*

The performance of such extractive reactions are compared herein to the yields and rate of the corresponding single-phase process. The developments are for batch and also for single- or multistage continuous-flow stirred-tank reactor installations operating on dilute, two-solvent, two-phase systems.

The term *extractive reaction* encompasses several unit operations, for example liquid-liquid extraction, gas absorption and desorption, leaching, distillation, and others wherein a reaction occurs simultaneously with the transfer processes. In the case of extractive reaction the emphasis is on affecting the conversion of a reaction process rather than on designing a unit to effect primarily an absorption, extraction, or separation operation. Related gas-absorption operations in which reactions occur in the gas or in the condensed phases simultaneously with mass transfer have in fact already received considerable attention in connection with the design of plate or packed columns.

Of course many commercially important chemical reactions normally take place in multiphase systems, for example sulfonation, nitration, alkylation, esterification, etc., and the ratio of the phases can be varied for optimum results. The reactants enter the system in two or more immiscible phases, and two phases are normally present during the reaction; however in addition one should consider that some reactions which are carried out in a single-phase system or are normally followed by a solvent extraction, distillation, or other separation operation may be improved by deliberately introducing a second extractive phase to affect the rate of a reaction and conversion to a desired product and/or simultaneously to achieve the separation of the products.

In the following development, mixing of the phases will always be considered as being high and so effective that they will be in physical equilibrium with each other at all times. With mass transfer essentially instantaneous, it is the chemical-reaction step which controls the over-all rate of the process. The agitation is also sufficient to ensure that at all times the concentrations in either phase are uniform throughout the reactor contents. The simplifications will be made that reaction takes

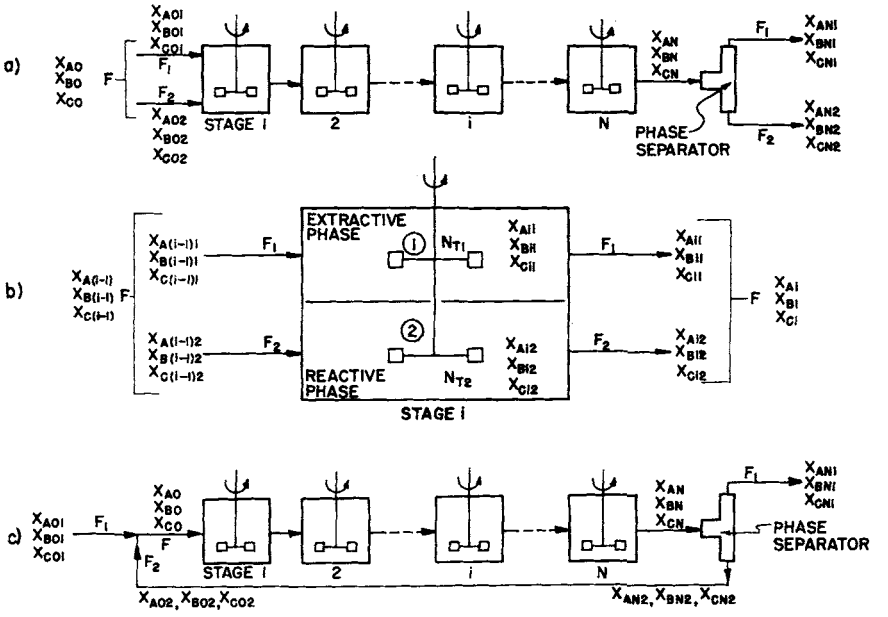

Fig. 1. Concurrent two-phase extractive-reaction systems, including separators and recirculation.

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place in one phase only and that the presence of solvent has no effect upon the rate constants and reaction mechanism. No reaction occurs in the inert, solvent phase or at the interphase. However the equations are easily modified to include reaction in both phases. Isothermal conditions are assumed. The phase equilibrium partition coefficients and solubilities are considered as being independent of concentrations. Such conditions may obtain closely if the reacting components are present in low concentrations. As an example, the reactants are in a dilute aqueous phase, and a second immiscible liquid, such as benzene, is added to affect an extractive reaction process; this constitutes a dilute, two-solvent, two-phase system, the two solvents being in this case water and benzene. In another example an inert gas is caused to flow through a dilute, reactive liquid phase so as to strip a product or feed a reactant. A solid reactant might be present in the liquid, when a three-phase extractive reaction process is involved.

For simplicity of text, ideal solutions are assumed, and so activity coefficients are not written into the equations. For specific cases this simplification can be modified as needed. Concentrated solutions, higher order reactions, and single-solvent, two-phase systems will be considered in a later paper. Numerical examples will also be given.

TWO-PHASE BATCH PROCESSES

First-Order Reversible Reactions

A first-order reversible reaction of kinetics $A \underset{k'}{\overset{k}{\rightleftharpoons}} B$ and of stoichiometry $aA = bB$ is occurring in a two-phase extractive reaction batch process. The rate of decrease of concentration of A, that is $-(1/V)(dn_A/dt)$, in a homogeneous irreversible reaction system is set equal to $k(n_A/V)$. However since the partition coefficients are defined in terms of mole fractions, it is deemed convenient in the following sections to express the rate equations in terms of mole fractions rather than concentrations.

The rate equation in a single-phase system is

$$-\frac{dn_A}{V} = \frac{k}{V} x_A n_T\, dt - \frac{k'}{V} x_B n_T\, dt \tag{1}$$

Since the two-phase reaction occurs in dilute concentrations, the phase volumes and the ratio of the total moles in the extractive layer to that of the reactive layer may be considered constant throughout the reaction process.

Equation (1) becomes

$$-dn_A = k\, x_A\, n_T\, dt - k'\, x_B\, n_T\, dt \tag{2}$$

and since in a two-phase system

$$n_A = n_{A_1} + n_{A_2} \tag{3}$$

then from (2) and (3)

$$dn_{A_1} + dn_{A_2} = k'\, x_{B_2}\, n_{T_2}\, dt - k\, x_{A_2}\, n_{T_2}\, dt \tag{4}$$

The partition coefficient of a component is given by the ratio of its mole fractions in the two phases; thus

$$\alpha_A = \frac{x_{A_1}}{x_{A_2}} = \frac{n_{A_1}\, n_{T_2}}{n_{A_2}\, n_{T_1}} = \frac{n_{A_1}}{n_{A_2} R}$$

Upon substitution (4) becomes

$$(\alpha_A R + 1) dn_{A_2} + \alpha_A\, n_{A_2}\, dR = k'\, x_{B_2}\, n_{T_2}\, dt - k\, x_{A_2}\, n_{T_2}\, dt \tag{5}$$

and since R is constant

$$(\alpha_A R + 1)\, dn_{A_2} = k'\, x_{B_2}\, n_{T_2}\, dt - k\, x_{A_2}\, n_{T_2}\, dt \tag{6}$$

From stoichiometry

$$x_{B_2} = \frac{\frac{b}{a} n_{A_0 T} + n_{B_0 T}}{n_{T_2}} - \frac{b}{a} x_{A_2}(\alpha_A R + 1)}{(\alpha_B R + 1)} \tag{7}$$

Combining (6) and (7) yields

$$-\frac{dx_{A_2}}{dt} = \frac{bk'\, x_{A_2}}{a(\alpha_B R + 1)} + \frac{k x_{A_2}}{\alpha_A R + 1} - \frac{k'[b n_{A_0 T} + a n_{B_0 T}]}{a n_{T_2}(\alpha_A R + 1)(\alpha_B R + 1)} \tag{8}$$

Equation (8) relates dx_{A_2}/dt, the change in mole fraction of component A within the reactive phase only, with time.

$$x_{A_2} = \frac{[bk'(\alpha_A R + 1) + ak(\alpha_B R + 1)]\, n_{T_2}\, x_{A_0 2} - k'(b n_{A_0 T} + a n_{B_0 T})(1 - e^{\sigma})}{[bk'(\alpha_A R + 1) + ak(\alpha_B R + 1)] n_{T_2} e^{\sigma}} \tag{10}$$

where

$$\sigma = \frac{[bk'(\alpha_A R + 1) + ak(\alpha_B R + 1)]}{a(\alpha_A R + 1)(\alpha_B R + 1)} t$$

Two-Phase Effect on Rate of Reaction, Time Ratio, Conversion Ratio, and Equilibrium Conversion

The development of expressions for the effect of an added phase on the rate of reaction, production per unit time, and equilibrium conversion of a single-phase system will now be illustrated for the above first-order reaction. Higher-order reactions can be treated in a similar manner.

When $R = 0$, (10) becomes

$$x_A = \frac{[bk' + ak]\, n_T x_{A_0} - k'(b n_{A_0} + a n_{B_0})(1 - e^{\nu})}{[bk' + ak]\, n_T e^{\nu}} \tag{11}$$

where

$$\nu = \left(\frac{b}{a} k' + k\right) t$$

Combination of (8), (9), (10), and (11) yields

$$-\frac{dx_{A_2}}{dt} = \frac{[bk'(\alpha_A R + 1) + ak(\alpha_B R + 1)]\, n_{T_2} x_{A_{02}} - k'(b n_{A_0 T} + a n_{B_0 T})}{a\, n_{T_2}(\alpha_A R + 1)(\alpha_B R + 1) e^{\sigma}} \tag{12}$$

and

$$-\frac{dx_A}{dt} = \frac{[bk' + ak] n_T x_{A_0} - k'(b n_{A_0} + a n_{B_0})}{a\, n_T\, e^{\nu}} \tag{13}$$

The instantaneous over-all influence of the added phase on the reaction rate is expressed by the ratio of the total reactant consumption rate in a two-phase process to that in a single-phase operation at equal reaction times; that is $E_r = \dfrac{dn_{AT}}{dn_A}$ when $t = t_{ER}$.

A time ratio is defined as the ratio t/t_{ER} of the times required for equal fractional molar conversions in a two-phase and in an alternate single-phase system when the initial total number of moles of component A charged to the systems are the same; that is

$$\frac{\Delta n_{AT}}{n_{A_0 T}} = \frac{\Delta n_A}{n_{A_0}} \text{ and } n_{A_0 T} = n_{A_0}$$

The effect of the added phase on the equilibrium conversion is indicated by the ratio of the fractional conversions at equilibrium and for equal total number of moles of reactants charged to the systems; that is

$$E_e = \frac{(n_{A_0 T} - n^*_{AT}) / n_{A_0 T}}{(n_{A_0} - n^*_A) / n_{A_0}} = \frac{(n_{A_0 T} - n^*_{AT})}{(n_{A_0} - n^*_A)} = \frac{\Delta n^*_{AT}}{\Delta n^*_A}$$

where $n_{A_0 T} = n_{A_0}$.

Reaction-Rate Ratio The single-phase reaction rate $-dx_A/dt$ is readily obtained from (8) by letting R be zero.

$$-\frac{dx_A}{dt} = \left(\frac{b}{a} k' + k\right) x_A - \frac{k'(b n_{A_0} + a n_{B_0})}{a n_T} \tag{9}$$

Also from (8) by integration

The ratio dx_{A2}/dx_A may be formed:

$$\frac{dx_{A2}}{dx_A} = \frac{e^{(\nu-\sigma)}\left[\frac{bk'}{\alpha_B R+1}+\frac{ak}{\alpha_A R+1}\right]x_{Ao2} - \frac{k'(bn_{AoT}+an_{BoT})}{n_{T2}(\alpha_A R+1)(\alpha_B R+1)}}{[bk'+ak]\ x_{Ao} - \frac{k'}{n_T}(bn_{Ao}+an_{Bo})} \quad (14)$$

An expression in terms of the total reactant consumption rate, dn_{AT}/dn_T, is obtained:

$$\frac{dx_{A2}}{dx_A} = \frac{dn_{AT}}{dn_A}\left[\frac{n_T}{n_{T2}(\alpha_A R+1)}\right] \quad (15)$$

Equations (14) and (15) give

$$E_r = \frac{dn_{AT}}{dn_A} = \frac{e^{(\nu-\sigma)}[bk'(\alpha_A R+1)+ak(\alpha_B R+1)]\,n_{T2}\,x_{Ao2} - k'(bn_{AoT}+an_{BoT})}{(\alpha_B R+1)[(bk'+ak)\,n_T\,x_{Ao} - k'(bn_{Ao}+an_{Bo})]} \quad (16)$$

Equation (16) describes the ratio of total reactant consumption rates for a first order reversible reaction as a function of time and the constants of the systems.

This relation can be advantageously applied for example to highly exothermic and autocatalytic reaction systems where the control of the rate of reaction for heat transfer or quality of product purposes is often of prime importance.

Time Ratio The integrated form of Equation (8) is

$$\frac{[bk'(\alpha_A R+1)+ak(\alpha_B R+1)]}{a(\alpha_A R+1)(\alpha_B R+1)}\,t_{EB} = \ln\left[\frac{[bk'(\alpha_A R+1)+ak(\alpha_B R+1)]\,n_{T2}\,x_{Ao2} - k'(bn_{AoT}+an_{BoT})}{[bk'(\alpha_A R+1)+ak(\alpha_B R+1)]\,n_{T2}\,x_{A2} - k'(bn_{AoT}+an_{BoT})}\right]$$

which when written for a single-phase system becomes

$$\left[\frac{bk'+ak}{a}\right]t = \ln\left[\frac{(bk'+ak)\,n_T\,x_{Ao} - k'(bn_{Ao}+an_{Bo})}{(bk'+ak)\,n_T\,x_A - k'(bn_{Ao}+an_{Bo})}\right]$$

If $\Delta n_{AT} = \Delta n_A$; that is, the moles of reactant converted in the extractive reaction and in the single-phase system are equal, then

$$n_{T2}x_{A2} = \frac{n_{AoT} - (n_{Ao}-n_A)}{(\alpha_A R+1)}$$

and molar balance requires

$$n_{T2}x_{Ao2} = n_{AoT}/(\alpha_A R+1)$$

From these relations a production time ratio t/t_{EB} is obtained:

$$\frac{t}{t_{EB}} = \frac{\frac{t\,[bk'(\alpha_A R+1)+ak(\alpha_B R+1)]}{a(\alpha_A R+1)(\alpha_B R+1)}}{akn_{AoT}\left(\frac{\alpha_B R+1}{\alpha_A R+1}\right) - ak'(n_{BoT})}$$

$$\ln\left[\frac{}{ak\left(\frac{\alpha_B R+1}{\alpha_A R+1}\right)[n_{AoT}-(n_{Ao}-n_A)] - k'[an_{BoT}+b(n_{Ao}-n_A)]}\right] \quad (17)$$

Equation (17) is the ratio of the times required to form equal moles of product for any initial concentrations or solvent ratios. If the ratio exceeds unity, the extractive reaction has the higher production per unit time.

When the initial total charges of component A are equal n_{AoT} is set equal to n_{Ao}, and (17) reduces to E_t, the ratio of times required to produce the same fractional conversion. E_t is a function of the molar phase ratio, the system properties, and the single-phase batch time.

Equilibrium Conversion Ratio. The value of the equilibrium constant, within the reactive phase of either a two- or a single-phase system, is a constant, and so

$$K_{eq} = k/k' = x^*_{B2}/x^*_{A2} = x^*_B/x^*_A = \frac{n^*_{B2}/n^*_{T2}}{n^*_{A2}/n^*_{T2}} = \frac{n^*_B/n^*_T}{n^*_A/n^*_T}$$

From a mass balance for a single-phase system

$$K_{eq.} = \frac{\frac{b}{a}(n_{Ao}-n^*_A)+n_{Bo}}{n^*_A} \quad (18)$$

From a mass balance for a two-phase system

$$K_{eq.} = \frac{(\alpha_A R+1)\left[\frac{b}{a}(n_{AoT}-(\alpha_A R+1)n^*_{A2})+n_{BoT}\right]}{n^*_{AT}(\alpha_B R+1)} \quad (19)$$

From (8), when $-dx_{A2}/dt = 0$

$$n^*_{A2} = \frac{k'[bn_{AoT}+an_{BoT}]}{bk'(\alpha_A R+1)+ak(\alpha_B R+1)} \quad (20)$$

Likewise from (8), when $dx_{A2}/dt = 0$ and also $R = 0$

$$n^*_A = \frac{k'[bn_{Ao}+an_{Bo}]}{bk'+ak} \quad (21)$$

By equating (18) and (19) there results

$$\frac{\Delta n^*_{AT}}{\Delta n^*_A} = \frac{b(\alpha_B R+1)\ n^*_{AT}\,(n_{AoT}-n^*_{AT})}{n^*_A(\alpha_A R+1)[b(n_{AoT}-n^*_{AT})+an_{BoT}]-[an_{Bo}\,n^*_{AT}(\alpha_B R+1)]} \quad (22)$$

If there is no initial component B present, n_{BoT} and n_{Bo} are zero, and with the substitution of Equations (20) and (21) Equation (22) reduces to

$$\frac{\Delta n^*_{AT}}{\Delta n^*_A} = \frac{n_{AoT}(\alpha_B R+1)\,(bk'+ak)}{n_{Ao}[bk'(\alpha_A R+1)+ak(\alpha_B R+1)]} \quad (23)$$

If $n_{AoT} = n_{Ao}$, then the equilibrium conversion ratio is obtained:

$$E_e = \frac{(\alpha_B R+1)(bk'+ak)}{bk'(\alpha_A R+1)+ak(\alpha_B R+1)} \quad (24)$$

This equation indicates an equilibrium-conversion advantage for the two-phase system when $\alpha_B > \alpha_A$.

TWO-PHASE CONTINUOUS STIRRED-TANK REACTOR SYSTEMS

The assumption of physical equilibrium between the phases in continuous extractive reaction processes can often best be achieved in continuous stirred-tank reactor (CSTR) systems, since it is in these installations that high levels of agitation can most readily be provided. In a CSTR chain the streams of the two phases can be arranged in several ways; hence the concurrent, crosscurrent, and countercurrent installations are of interest. Analytical solutions are illustrated herein for typical stoichiometrically simple as well as stoichiometrically complex first-order reaction systems.

Concurrent Arrangement

The kinetics and stoichiometry of the first-order reaction occurring in the system is taken as $A \xrightarrow{k} B \xrightarrow{k_1} C$. This is an example of a reaction which is kinetically and stoichiometrically complex (2).

In a concurrent arrangement the separation of the two phases need occur only at the end of the CSTR chain (Fig. 1*a*); however to facilitate the writing of the molar balances, an imagined separation of phases in stage i is schematized in Figure 1*b*.

$$F\,x_{A(i-1)} = F\,x_{Ai} + k\,n_{T2}\,x_{Ai2} \quad (25a)$$

$$F\,x_{B(i-1)} = F\,x_{Bi} + k_1\,n_{T2}\,x_{Bi2} - k\,n_{T2}\,x_{Ai2} \quad (25b)$$

$$F\,x_{C(i-1)} = F\,x_{Ci} - k_1\,n_{T2}\,x_{Bi2} \quad (25c)$$

with

$$F\,x_{Ai} = F_1\,x_{Ai1} + F_2\,x_{Ai2} \quad (26)$$

and identical relations for components B and C.

As in the batch case the two solvents are assumed completely immiscible or of partial miscibility not affected by the content of A, B, and C, which are present in low concentrations in either phase. Since the ratio of the phases within the reactors is not necessarily equal to the ratio of the flow rates,

$$\frac{F_1}{F_2} = \epsilon\,\frac{n_{T1}}{n_{T2}} = \epsilon R$$

where ϵ depends upon operating conditions and on the apparatus design, such for example as the position of baffles relative to the outlet tube (*1*). F_1, F_2, R, and ϵ can be assumed to remain constant along the reactor chain.

Then from (26)

$$x_{Ai2} = \frac{\epsilon R + 1}{\alpha_A\,\epsilon R + 1}\,x_{Ai} \quad (27)$$

Similar expressions are found for x_{Bi2} and x_{Ci2}.

Equations (25) become

$$x_{A(i-1)} = x_{Ai}\,(1 + A_1) \quad (28a)$$

$$x_{B(i-1)} = x_{Bi}\,(1 + A_2) - A_1\,x_{Ai} \quad (28b)$$

$$x_{C(i-1)} = x_{Ci} - A_2\,x_{Bi} \quad (28c)$$

where

$$A_1 = \frac{k\,n_{T2}}{F}\,\frac{\epsilon R + 1}{\alpha_A\,\epsilon R + 1} \text{ and}$$

$$A_2 = \frac{k_1\,n_{T2}}{F}\,\frac{\epsilon R + 1}{\alpha_B\,\epsilon R + 1}$$

From (28*a*) and (28*b*) a second-order difference equation is obtained:

$$x_{Bi}(1 + A_1)(1 + A_2) - x_{B(i-1)}(2 + A_1 + A_2) + x_{B(i-2)} = 0 \quad (29)$$

The roots of the characteristic equation are $\rho_1 = 1/1 + A_1$ and $\rho_2 = 1/1 + A_2$, and the general solution is, if $A_1 \neq A_2$:

$$x_{Bi} = G_1\,\rho_1^{\,i} + G_2\,\rho_2^{\,i} \quad (30)$$

By substituting (30) into (28*b*), one obtains

$$x_{Ai} = \frac{A_2 - A_1}{A_1}\,G_1\,\rho_1^{\,i} \quad (31)$$

and from (28*c*)

$$x_{Ci} = -\left[\frac{A_2}{A_1}\,G_1\,\rho_1^{\,i} + G_2\,\rho_2^{\,i}\right] + G_3 \quad (32)$$

The constants G_1, G_2, and G_3 are obtained from the boundary conditions, that is the feed compositions

$$x_{Ao} = \frac{F_1}{F}\,x_{Ao_1} + \frac{F_2}{F}\,x_{Ao_2}$$

with similar expressions for x_{Bo} and x_{Co}.

By equating these values of the feed to Equations (31), (30), and (32) when $i = 0$, one can obtain three equations in G_1, G_2, and G_3:

$$x_{Ao} = \frac{A_2 - A_1}{A_1}\,G_1,\quad x_{Bo} = G_1 + G_2,$$

$$x_{Co} = G_3 - \frac{A_2}{A_1}\,G_1 - G_2$$

The composition of the final product of the reactor chain, x_{AN}, x_{BN}, and x_{CN}, is given by Equations (31), (30), and (32), with $i = N$. In some cases the residence time of the reactive phase in the phase separator will need to be taken into account to get the actual values of x_{AN2}, x_{BN2} and x_{CN2}.

Recirculation of the reactive phase Recirculation of the reactive phase may result in better utilization of the reactants (Figure 1*c*). In this case $x_{Ao2} = x_{AN2}$, $x_{Bo2} = x_{BN2}$, and $x_{Co2} = x_{CN2}$. Equations (30), (31), and (32) remain the same; only the boundary conditions are changed so that

$$x_{Ao} = \frac{F_1}{F}\,x_{Ao1} + \frac{F_2}{F}\,x_{Ao2} = \frac{F_1}{F}\,x_{Ao1} + \frac{F_2}{F}\,x_{AN2}$$

Using the value of x_{AN2} given by Equation (31) one gets

$$x_{Ao} = \frac{\epsilon R\,x_{Ao1} + \dfrac{A_2 - A_1}{A_1}\,G_1\,\rho_1^{\,N}}{1 + \epsilon R} = \frac{A_2 - A_1}{A_1}\,G_1$$

and similarly

$$x_{Bo} = \frac{\epsilon R\,x_{Bo1} + G_1\,\rho_1^{\,N} + G_2\,\rho_2^{\,N}}{1 + \epsilon R} = G_1 + G_2$$

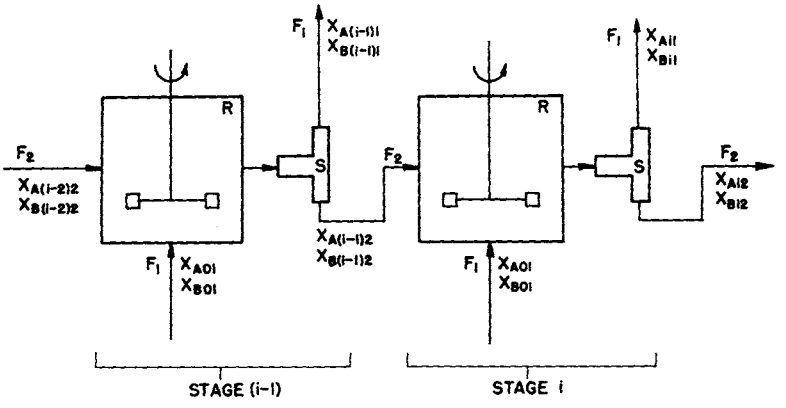
$$x_{Co} = \frac{\epsilon R\,x_{Co1} + G_3 - \dfrac{A_2}{A_1}\,G_1\rho_1^{\,N} - G_2\rho_2^{\,N}}{1 + \epsilon R} = G_3 - \frac{A_2}{A_1}\,G_1 - G_2$$

These equations allow the determination of G_1, G_2, and G_3 and the solution of the design problem.

Cross-current Arrangement

In this arrangement each reactor stage receives a stream of extractive phase, of the same composition for each stage, and also a stream of reactive phase coming from the phase separator of the preceding stage (Figure 2). If residence times in the phase separators are small compared with the holding times in the reactor stage, their effects may be neglected.

Crosscurrent operation may often be advantageous for reversible reactions; hence a first-order reversible reaction



R=REACTOR STAGE
S=PHASE SEPARATOR

Fig. 2. Countercurrent two-phase extractive-reaction system with separators.

will be considered. Its stoichiometry is expressed by $aA = bB$ and kinetics by $A \underset{k_1}{\overset{k}{\rightleftharpoons}} B$, so that

$$-\frac{dn_A}{dt} = a\,k\,n_A - a\,k_1\,n_B \text{ and}$$

$$\frac{dn_B}{dt} = b\,k\,n_A - b\,k_1\,n_B$$

The case selected is stoichiometrically simple. Since the concentrations of A and B are assumed small, F_1 and F_2 will be taken as constant, even if $a \neq b$.

Molar balances around the ith stage result in

$$x_{A(i-1)2} + \epsilon R\, x_{Ao_1} = x_{Ai_2}\left[1 + \epsilon R\alpha_A + k\,a\,\frac{n_{T_2}}{F_2}\right] - k_1\,a\,\frac{n_{T_2}}{F_2}\,x_{Bi_2} \qquad (33a)$$

$$x_{B(i-1)2} + \epsilon R\, x_{Bo_1} = x_{Bi_2}\left[1 + \epsilon R\alpha_B + k_1\,b\,\frac{n_{T_2}}{F_2}\right] - k\,b\,\frac{n_{T_2}}{F_2}\,x_{Ai_2} \qquad (33b)$$

For simplicity of presentation set $x_{Ao_1} = x_{Bo_1} = 0$; that is each stage receives an extractive stream of pure solvent.

By letting

$$1 + \epsilon R\,\alpha_A = A_1,\ 1 + \epsilon R\,\alpha_B = A_2,$$

$$k\,\frac{n_{T_2}}{F_2} = B_1 \text{ and } k_1\,\frac{n_{T_2}}{F_2} = B_2$$

Equations (33) become

$$x_{A(i-1)2} = (A_1 + a\,B_1)\,x_{Ai_2} - a\,B_2 x_{Bi_2} \qquad (34a)$$

$$x_{B(i-1)2} = (A_2 + b\,B_2)\,x_{Bi_2} - b\,B_1 x_{Ai_2} \qquad (34b)$$

By combining (34a) and (34b) one obtains the second order difference equation:

$$x_{Ai_2}[(A_2 + b\,B_2)(A_1 + a\,B_1) - a\,b\,B_1\,B_2] - x_{A(i-1)2}[A_1 + A_2 + a\,B_1 + b\,B_2] + x_{A(i-2)2} = 0 \qquad (35)$$

The roots of the corresponding characteristic equation are

$$\rho_1;\ \rho_2 = \frac{(A_1 + A_2 + aB_1 + bB_2) \pm \sqrt{(A_1 + aB_1 - A_2 - bB_2)^2 + 4ab\,B_1\,B_2}}{2[(A_1 + aB_1)(A_2 + bB_2) - a\,b\,B_1\,B_2]}$$

and the solution of (35) is

$$x_{Ai_2} = G_1\rho_1^{\,i} + G_2\rho_2^{\,i} \qquad (36)$$

From (44)

$$x_{Bi_2} = \frac{1}{a\,B_2}\left[G_1\left(A_1 + a\,B_1 - \frac{1}{\rho_1}\right)\rho_1^{\,i} + G_2\left(A_1 + a\,B_1 - \frac{1}{\rho_2}\right)\rho_2^{\,i}\right] \qquad (37)$$

The constants G_1 and G_2 are obtained by expressing the feed composition x_{Ao2} and x_{Bo2} by the means of Equations (36) and (37) when $i = 0$:

$$x_{Ao2} = G_1 + G_2$$

$$x_{Bo2} = \frac{1}{a\,B_2}\left[G_1\left(A_1 + a\,B_1 - \frac{1}{\rho_1}\right) + G_2\left(A_1 + a\,B_1 - \frac{1}{\rho_2}\right)\right]$$

As in the concurrent arrangement, the effect of reactive-phase recirculation can also be calculated.

Countercurrent Arrangement

Figure 3 schematizes the chain under consideration. Again residence times in the phase separators will be considered small. Since the equations for countercurrent arrangements quickly become elaborate, the simple case of a first-order reversible reaction $A \underset{k_1}{\overset{k}{\rightleftharpoons}} B$ is chosen here. However more complex first-order reactions can be similarly treated.

The molal balances for components A and B around the ith stage are

$$F_2\,x_{A(i+1)2} - (\alpha_A F_1 + F_2 + k\,n_{T_2})\,x_{Ai_2} + k_1\,n_{T_2}\,x_{Bi_2} + \alpha_A F_1\,x_{A(i-1)2} = 0 \qquad (38a)$$

$$F_2\,x_{B(i+1)2} - (\alpha_B F_1 + F_2 + k_1\,n_{T_2})\,x_{Bi_2} + k\;n_{T_2}\,x_{Ai_2} + \alpha_B F_1\,x_{B(i-1)2} = 0 \qquad (38b)$$

By letting

$$A_1 = \alpha_A\,\epsilon R + 1 + \frac{k\,n_{T_2}}{F_2},$$

$$B_1 = \frac{k_1\,n_{T_2}}{F_2},\ C_1 = \epsilon R\,\alpha_A$$

$$A_2 = \epsilon R\,\alpha_B + 1 + k_1\,\frac{n_{T_2}}{F_2},$$

$$B_2 = \frac{k\,n_{T_2}}{F_2}, \text{ and } C_2 = \epsilon R\,\alpha_B$$

Equations (38) become

$$x_{A(i+1)2} - A_1\,x_{Ai_2} + B_1\,x_{Bi_2} + C_1\,x_{A(i-1)2} = 0 \qquad (39a)$$

$$x_{B(i+1)2} - A_2\,x_{Bi_2} + B_2\,x_{Ai_2} + C_2\,x_{B(i-1)2} = 0 \qquad (39b)$$

From (39a) and (39b) the fourth order difference equation is found to be

$$x_{A(i+3)2} - (A_1 + A_2)\,x_{A(i+2)2} + (C_1 + C_2 + A_1A_2 - B_1B_2)\,x_{A(i+1)2} - (A_2C_1 + A_1C_2)\,x_{Ai_2} + C_1C_2\,x_{A(i-1)2} = 0 \qquad (40)$$

Since $A_1 = 1 + C_1 + B_2$ and $A_2 = 1 + C_2 + B_1$, the characteristic equation is

$$(\rho - 1)[\rho^3 - (1 + C_1 + C_2 + B_1 + B_2)\,\rho^2 + (C_1 + C_2 + C_1C_2 + B_2C_2 + B_1C_1)\,\rho - C_1C_2] = 0$$

whose roots are 1, ρ_1, ρ_2, and ρ_3. The general solution may then be written, if the roots all differ, as

$$x_{Ai_2} = G_o + G_1\rho_1^{\,i} + G_2\rho_2^{\,i} + G_3\rho_3^{\,i} \qquad (41)$$

and from (39)

$$x_{Bi_2} = \frac{-1}{B_1}[G_o(1 - A_1 + C_1) + G_1(\rho_1^{\,2} - A_1\rho_1 + C_1)\,\rho_1^{\,i-1} + G_2(\rho_2^{\,2} - A_1\rho_2 + C_1)\,\rho_2^{\,i-1} + G_3(\rho_3^{\,2} - A_1\rho_3 + C_1)\,\rho_3^{\,i-1}] \qquad (42)$$

The constants G_o, G_1, G_2, and G_3 are determined from the knowledge of the inlet streams compositions, x_{Ao_1}, x_{Bo_1}, $x_{A(N+1)2}$, and $x_{B(N+1)2}$. Similarly if $i = N + 1$, other inlet compositions $x_{A(N+1)2}$ and $x_{B(N+1)2}$ are given by Equations (41) and (42). The resulting set of four equations allows the determination of G_o, G_1, G_2, and G_3.

In the case of recirculation of the reactive phase from the separator of the first stage to the last-stage reactor, the boundary conditions are different. The composition of the fresh feed entering the system x_{Ao_2} and x_{Bo_2} is of course usually known, but $x_{A(N+1)2}$ and $x_{B(N+1)2}$ are unknown. These however are respectively equal to x_{A12} and x_{B12}, and so again a set of four equations leads to the values of the constants.

REMARKS

In a chemical reacting system the total number of components taking part in the reaction can be distinguished from the number of components playing a role in the kinetics. If there are S independent stoichiometric relations between the M components and S' independent stoichiometric relations between the M' components, in the general case $M \geqq M'$, $S \geqq S'$, and $S \geqq 1$. As an example consider the following set of reactions:

$$A + B \rightleftharpoons C + D$$
$$C + D \rightarrow E + F$$
$$A + E \rightarrow G + J$$

Here $M = 8$ and $M' = 5$ (A, B, C, D, E). The independent stoichiometric relations are

$$\Delta n_G = \Delta n_J$$
$$\Delta n_A + \Delta n_B + \Delta n_C + \Delta n_D + \Delta n_E$$

$$+ \Delta n_F + \Delta n_G + \Delta n_J = 0$$
$$\Delta n_G = \Delta n_D$$

then

$$S = 3 \text{ and } S' = 1$$

In addition to the S stoichiometric relations, kinetic analysis yields M rate equations, which, when combined with material balances over the reactor, form the basis of design calculations. The mathematical problem is one of solving these M differential or difference equations with the boundary conditions, usually given by the feed, product, or recycle compositions.

The number of equations to be solved simultaneously will be equal to the number of independent variables. In general (if phase-volume variations are neglected) this number is equal to the total number of components playing a role in the kinetics, minus the number of stoichiometric relations existing between these same components; that is $m = M' - S'$.

It is advantageous, as shown previously (2), to distinguish between kinetically simple reactions, that is where $m = 1$, and kinetically complex reactions, that is where $m > 1$. In the case of stoichiometrically simple reactions the use of the stoichiometric equation and of the initial conditions reduces the number of independent variables from M' to unity, and so in this case only one final equation has to be solved.

In a two-phase system, where physical equilibrium between the phases is assumed, the number of independent variables remains the same as in a single-phase system because additional relations, such as $a_1 = \alpha_A a_2$, give the composition of the phase when the composition of the other phase is known.

The available stoichiometric relations, however, can always be used to reduce the number of variables in conservative arrangements, that is where the total mass of reactants and products is the same in all portions of the system. Examples of conservative arrangements are batch, tubular, and single or multistage continuous stirred-tank reactors operating on single-phase reactions, and also batch and concurrent CSTR two-phase reaction systems. In such arrangements the boundary conditions may be given at any points of the system, without making impossible the use of the stoichiometric relations. In some cases, such as in a concurrent arrangement with recirculation, where boundary conditions are more complex, it can be more convenient for analytical purposes not to use the stoichiometric relations but rather to retain the original number of variables and to solve a larger number of simultaneous equations. Crosscurrent and countercurrent CSTR two-phase reaction arrangements are nonconservative; hence the S' stoichiometric relations cannot be used and $m = M'$. In a countercurrent arrangement the stoichiometric relations can be used only when the two necessary boundary conditions are given at the same end of the system.

If for any of the above listed nonconservative arrangements a stage-by-stage rather than an analytical solution is used, then, since a single stage is conservative, the stoichiometric relations can be applied.

The consequences of these remarks can be illustrated by considering first-order reaction systems. In such cases the simultaneous solution of the initial set of rate equations leads to one differential or difference equation, for example Equation (29) from (25), (35) from (33), and (40) from (38). In Table 1 the order p of the final equation to be solved is shown. It is seen how this order varies with the reactor type and arrangement used as well as with the reaction itself. The magnitude of p gives an idea of the complexity of the problem. It will be seen that for a countercurrent CSTR arrangement $p = 2M'$, because in the initial set the equations are of second order.

In a subsequent paper variations in volume will be considered. It will be seen that if the arrangement is conservative, $m = M - S$ and if nonconservative $m = M$.

TABLE 1. ORDER p OF THE DIFFERENTIAL (D) OR DIFFERENCE(Δ) EQUATION DESCRIBING HOMOGENEOUS AND TWO-PHASE PROCESSES WITH NEGLIGIBLE PHASE-VOLUME CHANGES

Reactor system	Reaction type: First order, stoichiometrically simple	Reaction type: First order, stoichiometrically complex
Single phase		
Batch or tubular	$D\,p = 1$	$D\,p = M' - S'$
Continuous stirred-tank reaction or	$\Delta\,p = 1$	$\Delta\,p = M' - S'$
Two-phase*		
Batch or tubular	$D\,p = 1$	$D\,p = M' - S'$
CSTR: Concurrent	$\Delta\,p = 1$	$\Delta\,p = M' - S'$
Concurrent with recirculation	$\Delta\,p = M'$	$\Delta\,p = M'$
Crosscurrent	$\Delta\,p = M'$	$\Delta\,p = M'$
Countercurrent	$\Delta\,p = 2M'$	$\Delta\,p = 2M'$

* When equilibrium is assumed between the phases.

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NOTATION

A, B, C, D, = components A, B, C, D
a, b, c, d = stoichiometric coefficients
E_e = equilibrium conversion ratio
E_r = rate ratio

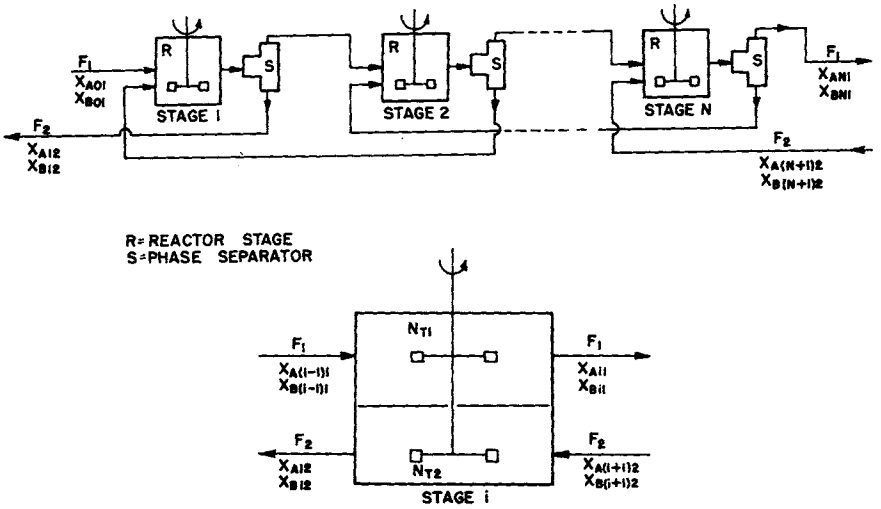

Fig. 3. Cross-current two-phase extractive-reaction system including separators.

F = molal flow rate of either or both phases, moles/min.
K = equilibrium constant
k, k_1, k_2 = reaction-rate constants
M = number of components taking part in the reaction
M' = number of components playing a role in the kinetics
m = number of independent variables
N = total number of stages in a chain
n = number of moles
N_{T1} = total number of moles in the extractive phase
n_{T2} = total number of moles in the reactive phase
p = order of differential or difference equation
R = ratio of the total number of moles in the extractive phase to the total number of moles in the reactive phase, n_{T1}/n_{T2}
S, S' = number of independent stoichiometric relations between the M or M' components
t = time
t_{ER} = time in an extractive reaction batch process
V = volume of the reactor
x_A = mole fraction of component A
x_{A1} = mole fraction of A in the extractive phase
$x_{A_{i1}}$ = mole fraction of A in the extractive phase of the ith reactor stage
α_A = partition coefficient of the component A, x_{A_1}/x_{A_2}
ϵ = factor relating the phase ratio in a reactor to the effluent flow rates, $F_1/F_2 = \epsilon R$

Subscripts

$A, B, C \ldots$ = components $A, B, C \ldots$
i = any stage in a reactor chain
o = initial conditions
T = total moles in either or both phases
1, 2 = extractive and reactive phase respectively

Superscripts

* = chemical equilibrium conditions

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Longitudinal Mixing in Fluidization

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Longitudinal mixing properties in liquid-solid fluidized beds were investigated by means of a salt-solution tracer technique. The electrical conductance breakthrough curves were measured with very small electrical conductivity probes for a step-function input of salt-solution tracer. Longitudinal eddy diffusivities were determined for 1.3- and 3.0-mm. lead spheres and 3.2-mm. glass spheres in 2- and 4-in.-diameter beds at a distance of 5 bed diam. from the injector and for various radial positions.

The longitudinal mixing properties are strongly affected by particle concentration; maximum mixing occurs at a fraction voids of 0.7. Longitudinal eddy diffusivity increases with particle density and with decreasing d_p/D ratio. Velocity profiles markedly influence the eddy-diffusivity profiles.

Fluidized systems have been of great interest in industry for the past decade or more and have come into prominence for use as chemical reactors. In most cases the yields of such reactors are highest when the radial mass transfer processes are maximized and the axial mass transfer processes minimized. The complicated hydrodynamic situation in fluidization defies theoretical analysis, except for very simplified and inexact approaches. Consequently there has been increased effort in the direction of definitive experimentation. A few radial-mixing studies have been conducted (*2, 10*), but data on longitudinal mixing in fluidized systems are rare. Gilliland, Mason, and Oliver (*9*) have presented a few data points for longitudinal diffusion in gas-solid fluidization, and these results yield longitudinal Peclet numbers (Ud_p/E) in the range of 0.0005 to 0.0015. Danckwerts *et al.* (*5*) investigated residence times in an industrial fluidized reactor, and their over-all Peclet number was of the order of 0.001.

The purpose of the present work was to determine and to investigate the important variables affecting the longitudinal mixing in liquid-solid fluidized systems. The mathematics of the model used here was originally presented by H. A. Einstein (*8*) in connection with the motion of pebbles in a water stream.

THEORY

The model applied to a packed bed assumes that the particles of packing material are stationary in space and that the fluid at the surface of the packing particles is stationary with respect to the main stream of fluid. If the assumption is made that the main fluid stream is moving rapidly with respect to the particles, then the model would be expected to be applicable to a fluidized bed. However if this assumption is only approximately valid, the mathematical results are still accurately applicable, owing to the central-limit theorem, provided that a large enough number of events is considered, that is, that the bed is of sufficient length.

The statistical model, which is discussed in detail elsewhere (*1, 11*), considers the motion of tracer corpuscles in the mainstream fluid. The corpuscles move according to a repeating pattern of a *motion phase* followed by a *rest phase*. A very small amount of time is required for the motion phase but the rest phase requires much longer. Thus the tracer corpuscles move, then rest, then move, etc. The rest phase may be thought of as taking place at the various stagnation points at each packing particle and in the eddies and the relatively stagnant points immediately downstream of the particles. The motion phase occurs during the rapid flow between particles.

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