Continuous-flow Stirred Tank Reactors: Solid-liquid Systems

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The theory and design of continuous stirred tank reactors are extended to the complex but industrially important field of continuous-heterogeneous-reaction systems. The present investigation is concerned with the elementary process occurring when solid particles and a liquid flow into and from a single reactor or a chain of these reactors. The equations are developed for dissolution processes, and the theoretical size distributions and specific areas are confirmed experimentally. Performance is also related to operating conditions and reactor design.

Continuous stirred tank reactors (*CSTR*) have important industrial as well as laboratory possibilities which need to be exploited. The theory however has not been extended to the continuous processing of solid-liquid systems. In many cases the high agitation levels required preclude the use of tubular installations for these systems.

The present investigation extends the previously reported work of this laboratory on homogeneous systems (*1, 6, 4*) to solid-liquid systems. As a basis for similar studies on heterogeneous reactions a simple solid-liquid dissolution system has been chosen for this study. This has an important experimental advantage over liquid- and gas-liquid systems in that the interphase contact area is definite and readily measurable. This paper is concerned with the theory and experimental investigation of the dissolution process occurring in continuous stirred tank reactors.

In a continuous solid-liquid reaction system the solid particles can remain unchanged in size during the reactions, as, for example, in catalytic reactions, ion exchange, or leaching; increase in size, as in polymerization and crystallization; or decrease in size, as in dissolution or other similar reaction processes.

With continuous flow of liquid through a stirred tank reactor, three methods of solid operation can be used: an *open solid-flow system,* where solid particles enter and leave the reactor continuously; a *choked solid-flow system,* where solid particles enter continuously but are physically prevented from leaving the reactor; and an *enclosed solid-flow system,* where the solid is placed initially in the reactor but no solid particles enter or leave after that time.

ELEMENTARY THEORY

The essentials of the reactor systems to be considered are shown diagrammatically in Figure 1. The unit reactor consists of an agitated vessel into which flow a liquid and an essentially continuous stream of solid particles. The location and design of inlets and outlets and the method of agitation and transport in the assembly of reactors depend on the particular effects desired and the preferred over-all design. The liquid, and in some operations the solid, products also flow out continuously from the unit reactors. For greater volumetric efficiency and high conversion several reactors may be placed in series in vertical-tower or horizontal arrangements. The solid and liquid flows can be concurrent or countercurrent if separators are interposed.

The bases of the development are that steady state prevails, there are many small solid particles in the feed and in the reactor, and agitation is sufficient to make the liquid concentration essentially uniform around each particle and equal to the concentration in the effluent. Usually these are common, practical conditions for operation. They may be attained even in a basket type of design which retains the agitated solid and through which the solution flows rapidly.

While the solid-liquid ratio in an open solid-flow reactor may differ from that in the effluent, and the solid may or may not be uniformly distributed within the reactor volume, the approximation will be made in the following discussion that every solid particle has an equal probability of leaving the reactor. That is, there is no size selection and the holding

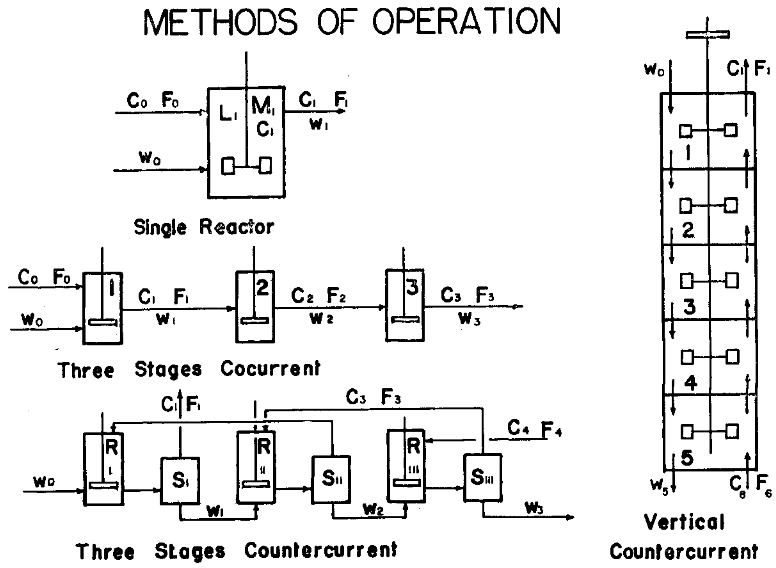

Fig. 1. Continuous-flow stirred-tank-reactor systems for two-phase operations.

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time for the solid is assumed independent of particle size. For this condition it is necessary that the solid agitation level be sufficient to circulate even the largest particles rapidly to the outlet. This approximation must of course be examined or verified experimentally for each installation.

In a choked solid or enclosed solid-flow system the situation is simpler. It is not essential that the solid be circulated to the outlet or throughout the reactor; it is necessary only that each solid particle be exposed to the same reaction conditions and that liquid mixing be uniform.

The basic equations governing these methods of operation will now be developed and experimental evidence presented which supports the bases and conclusions of the theoretical development.

Open Solid-flow System

Figure 1 shows a single continuous-flow stirred tank reactor operating with feed and effluent streams containing solid particles and liquid. For the present, all the feed particles are assumed to be identical in size.

In the steady state, and with the same completely uniform dispersion of solid in the reactor and in the effluent stream, the mass rate of withdrawal of solid particles, $-(dM_1/dt)$, is equal to the mass of particles in the reactor M_1, multiplied by the ratio of the liquid effluent rate F_1 to the liquid mass in the reactor L_1.

$$-\left(\frac{dM_1}{dt}\right) = M_1 \frac{F_1}{L_1} = w_1 \qquad (1)$$

In the steady state the rate w_1 is independent of time.

Equation (1) holds only if the mass ratio of solid to liquid in the effluent is equal to that in the reactor. However, when these ratios are not equal, as is often the case in such systems, a modifying factor is required. The modifying factor, α, is defined as the solid-to-liquid mass ratio in the effluent divided by the solid-to-liquid mass ratio in the reactor

$$\alpha_1 = \frac{w_1/F_1}{M_1/L_1} = \frac{L_1/F_1}{M_1/w_1} \qquad (2)$$

Two holding times are distinguishable, namely, a liquid holding time, θ_{L_1}, defined as the ratio L_1/F_1, and a solid holding time, θ_{s_1}, defined as the ratio M_1/w_1. By the definitions of the holding times,

$$\alpha_1 = \frac{\theta_{L_1}}{\theta_{s_1}} \qquad (3)$$

Rewriting Equation (1) to take account of nonuniform dispersion of the solid in the reactor and in the effluent stream and inserting Equation (3) results in

$$-\left(\frac{dM_1}{dt}\right) = \alpha_1 M_1 \frac{F_1}{L_1} = w_1$$

or

$$-\frac{dM_1}{M_1} = \alpha_1 \frac{dt}{\theta_{L_1}} = \frac{dt}{\theta_{s_1}} \qquad (4)$$

If only the set of solid particles which are present in the reactor at an arbitrary zero time is considered, the integral of Equation (4) will give the mass fraction of this particular set of solid particles still remaining in the reactor at any future time t.

$$\frac{M_{1_t}}{M_{1_0}} = y_t = e^{-t/\theta_{s_1}} \qquad (5)$$

The subscripts 0 and t refer to the abovementioned arbitrary time interval but, since steady state prevails, these equations also hold for any and all time intervals. Thus, y_t is the mass fraction of the solid contents of the reactor which have a residence time of t or longer. This mass fraction is equivalent to the number fraction under the ideal purging conditions assumed, as M_1 and w_1 have the same size distributions. Also

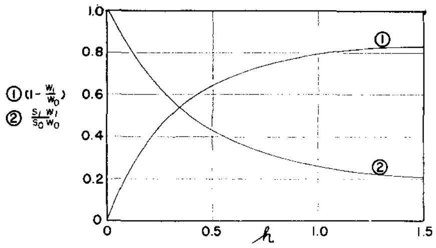

Fig. 2. Computation aid for reactor design, Equations (13*a*) and (15*a*).

$$d(1 - y_t) = \frac{1}{\theta_{s_1}} e^{-t/\theta_{s_1}}\, dt \qquad (6)$$

represents the fraction of the particles which have a residence time between t and $t + dt$.

The application of Equation (6) to a reaction process wherein the solid mass is changing will be considered next. While the operation may be steady state, and so the sizes of the particles in the effluent remain constant with time, the masses of the individual particles in the reactor change during their passage through the reactor. In general the rate equation governing the process is

$$-\frac{dm}{dt} = f(m, a, C) \qquad (7)$$

where m and a are the mass and surface area of the solid at time t in a liquid concentration C. The surface area of a particle may be related empirically to the particle mass, so that in the steady state where the liquid concentration is a constant, Equation (7) reduces to $-dm/dt = f'(m)$ and integrates to

$$m/m_0 = g(t) \qquad (8)$$

where m_0 is the initial mass of a particle.

The product of m/m_0 and $d(1 - y_t)$ equals the fraction of the feed which leaves the reactor at time t, i.e., the ratio of the differential solid effluent rate, dw_1, to the solid feed rate, w_0.

$$\frac{dw_1}{w_0} = \frac{1}{\theta_{s_1}} g(t) e^{-t/\theta_{s_1}}\, dt$$

With T the time at which the particle disappears by reaction or simple dissolution as calculated by Equation (8), then, because the lifetime T is the longest time any particle can remain in the reactor, the total solid effluent rate w_1 is

$$\frac{w_1}{w_0} = \frac{1}{\theta_{s_1}} \int_0^T g(t) e^{-t/\theta_{s_1}}\, dt \qquad (9)$$

Although Equations (7), (8), and (9) are written in terms of mass changes, similar equations can also be written in terms of other characteristics which change during the process, such as specific surface, size distribution, activity of catalysts, or saturation of adsorbents.

These equations will be applied in this work to a dissolution process, and the validity of the final equations will be verified experimentally. It is assumed that the rate of mass transfer for dissolution of the solid is expressed by the equation

$$-\frac{dm}{dt} = ka\Delta \qquad (10)$$

with

$$\Delta = (C_s\rho_s - C\rho)$$

where a solid of mass m at time t is being dissolved in a liquid of concentration $C\rho$ (mass per unit volume). The term $C_s\rho_s$ is the saturation concentration, and k is an experimentally determined coefficient dependent on the level of agitation, temperature, and the usual rate-determining properties of the liquid and solid (*8*). An equation of the form of (10) can describe the rate of certain heterogeneous reactions with rates proportional to the surface of the solid and to some function of the reactant concentrations; hence the subsequent development can also be applied to these chemical reaction processes.

For a particle which retains its original shape, the surface area remains proportional to the ⅔ power of its mass.

$$-\frac{dm}{dt} = kbm^{2/3}\Delta \qquad (10a)$$

where b is an area proportionality factor. Integration gives

$$\frac{m}{m_0} = \left(1 - \frac{t}{T}\right)^3 = g(t) \qquad (11)$$

where

$$T = \frac{3}{kbm_0^{-1/3}\Delta} = \frac{3}{ks_0\Delta} \qquad (12)$$

s_0 being the initial specific surface of the particle. Substituting in Equation (9) for integration yields

$$\frac{w_1}{w_0} = \frac{1}{\theta_{s_1}} \int_0^T \left(1 - \frac{t}{T}\right)^3 e^{-t/\theta_{s_1}}\, dt \qquad (13)$$

If

$$h_1 = \frac{\theta_{s_1}}{T} = \left(\frac{k_1 s_0 \Delta_1 L_1}{3\alpha_1 F_1}\right)$$

integration gives

$$1 - \frac{w_1}{w_0} = 3h_1[1 - 2h_1 + 2h_1^2(1 - e^{-1/h_1})] \qquad (13a)$$

Equation (13*a*) relates analytically the effluent solid rate, w_1, in terms of the liquid-concentration difference, Δ_1, solid-feed rate, w_0, solid holding time, θ_{s_1}, and initial specific surface, s_0. It can be used to calculate the mass transfer coefficient k_1 from experimental data, or, if k and α can be estimated, the equation can be used to predict the performance of a proposed reaction unit.

The specific surface of the solid in the reactor or the effluent can also be calculated by an equation similar to (9). By a previous assumption, $a/a_0 = (m/m_0)^{2/3}$, and from Equation (11)

$$\frac{a}{a_0} = \left(1 - \frac{t}{T}\right)^2 \qquad (14)$$

Proceeding in the same manner as in deriving Equation (13) gives the ratio of the total surface leaving to that entering as

$$\frac{\text{leaving surface}}{\text{entering surface}} = \frac{s_1 w_1}{s_0 w_0} = \frac{1}{\theta_{s_1}} \int_0^T \left(1 - \frac{t}{T}\right)^2 e^{-t/\theta_{s_1}}\, dt \qquad (15)$$

Integration gives

$$\frac{s_1 w_1}{s_0 w_0} = 1 - 2h_1 + 2h_1^2(1 - e^{-1/h_1}) \qquad (15a)$$

The equation relates the outgoing total surface $s_1 w_1$ to the operating variables and to the rate coefficient k_1.

From a plot of Equation (13*a*), Figure 2, a value of h_1 is obtained from the value of w_1/w_0. Then from a plot of Equation (15*a*), also on Figure 2, this value of h_1 may be used to obtain s_1/s_0. Thus the specific surface of the solid in the reactor and in the effluent is obtained when only the ratio of the solid flow rates w_1/w_0 and the initial specific surface s_0 are known. This value of h_1 can also be used to obtain the rate coefficient k_1 from the operating data by means of the expression

$$k_1 = \frac{3h_1 w_1}{s_0 \Delta_1 M_1} \qquad (16)$$

From Equations (13*a*) and (15*a*)

$$\frac{s_1 w_1}{s_0 w_0} = \frac{1 - \dfrac{w_1}{w_0}}{3h_1} = \frac{w_0 - w_1}{w_0 K_1 \theta_{s_1}}$$

Then by substitution from Equation (12)

$$k_1 = \frac{w_0 - w_1}{s_1 \Delta_1 M_1} \qquad (17)$$

Equation (17) expresses the solid-flow rates in terms of internal reactor conditions. It also follows directly from a material balance if the same coefficient k_1 is assumed to hold when applied to the over-all reactor conditions.

$$w_0 - w_1 = C_1 F_1 - C_0 F_0 = k_1 A_1 \Delta_1 = k_1 s_1 M_1 \Delta_1 \qquad (17a)$$

The use of Equation (16) involves the assumption that the size distributions of the effluent w_1 and the reactor contents M_1 are the same and that the transfer coefficient k_1 is independent of particle size. Experimentally this will be checked by comparing calculated and measured specific surfaces of the effluent solid.

To arrive at the size distribution of the effluent solid if no change in particle shape during dissolution is again assumed, the linear dimensions of a particle will be represented by $(x/x_0) = (m/m_0)^{1/3}$ where x is the selected linear dimension of the particle. Combining with Equation (11) results in the relation between particle size and reaction time

$$\frac{x}{x_0} = \left(1 - \frac{t}{T}\right) \qquad (18)$$

where x_0 is the size of the feed particle. By use of Equation (6) and (18), the differential size distribution in the reactor and effluent is expressed by

$$Y(x) = \frac{100 w_0}{h_1 w_1} \frac{x^3}{x_0^4} \cdot \exp\left\{-\left(\frac{x_0 - x}{h_1 x_0}\right)\right\} \qquad (19)$$

where $Y(x)\, dx$ is the weight percentage of the particles which have a size between x and $x + dx$. Equation (19) is applied in the experimental section.

Choked Solid-flow System

Liquid flows into and out of the stirred reactor and a stream of solid particles enters continuously, but the particles are prevented from leaving the reactor, for example, by a screen. The effluent solid rate w_1 being zero for this method of operation, a material balance for the solid gives

$$C_1 = \frac{C_0 F_0 + w_0}{F_0 + w_0} \qquad (20)$$

That is, the outgoing liquid concentration C_1 is independent of internal reactor conditions. However, since the effluent liquid concentration C_1 must be less than the saturation concentration C_s, the ratio w_0/F_0 is limited as follows:

$$\frac{w_0}{F_0} < \frac{C_s - C_0}{1 - C_0} \qquad (21)$$

If this relation is not satisfied, the solid accumulates in the reactor and steady state cannot be attained.

As no particles escape before complete dissolution, the total solid mass in the reactor is

$$M_1 = \int_0^T m \frac{w_0}{m_0}\, dt$$

and substituting from Equation (11) gives

$$\frac{M_1}{w_0} = \int_0^T \left(1 - \frac{t}{T}\right)^3 dt \qquad (22)$$

which reduces to

$$\frac{M_1}{w_0} = \frac{T}{4} \qquad (22a)$$

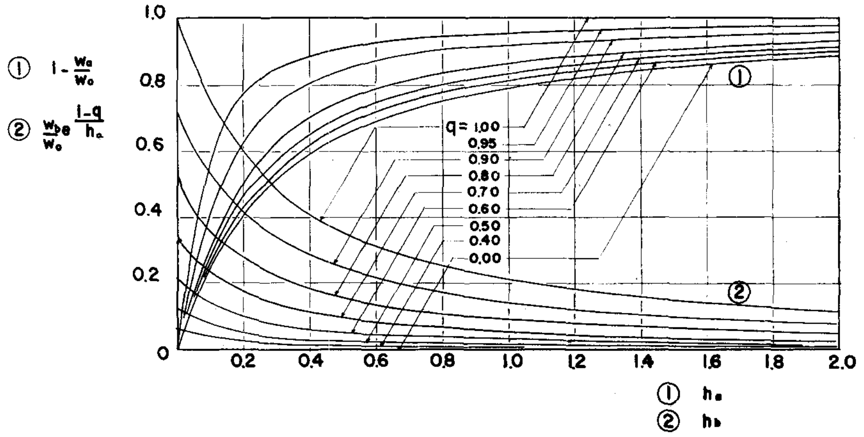

Fig. 3. Computation aid for reactor design, two-group theory, solid-flow-rate equations (33) and (34).

The ratio of the solid surface in the reactor s_1M_1 to the surface in the solid feed s_0w_0 is

$$\frac{s_1M_1}{s_0w_0} = \int_0^T \left(1 - \frac{t}{T}\right)^2 dt \qquad (23)$$

$$\frac{s_1M_1}{s_0w_0} = \frac{T}{3} \qquad (23a)$$

Combining (22*a*) and (23*a*) yields

$$\frac{s_1}{s_0} = \frac{4}{3} \qquad (24)$$

Thus in the steady state the ratio of the specific surface of the solid in a choked reactor to that of the feed is a constant, provided that the particles retain their shape throughout dissolution and dissolve under the same concentration gradient. Experimentally, relation (24) was checked by stopping all the feed and effluent streams and letting the holdup mass M_1 dissolve to a value M_1' corresponding to saturation. From a mass balance on the solid

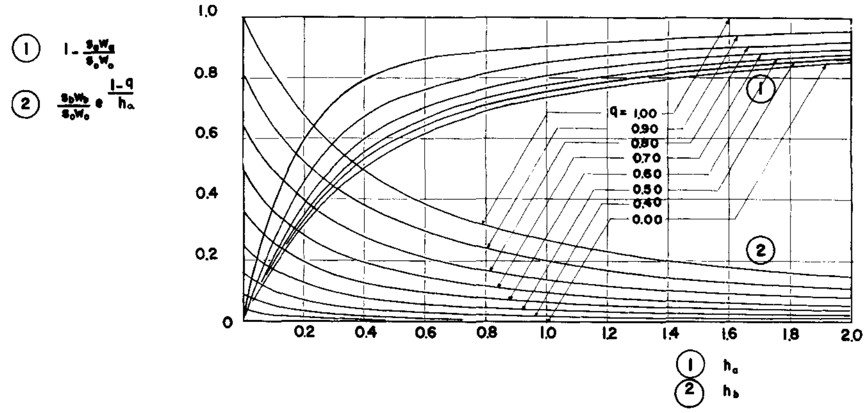

Fig. 4. Computation aid for reactor design, two-group theory, Surface-area equations (35) and (36).

$$M_1 - M_1' = L_1 \frac{C_s - C_1}{1 - C_s} \qquad (25)$$

and the initial specific surface s_1 is related to the final measured value s_1', by

$$\frac{s_1}{s_1'} = \left(\frac{M_1'}{M_1}\right)^{1/4} \qquad (26)$$

The batch dissolution up to saturation requires theoretically an infinite time which, along a fictitious dissolution path with constant concentration difference Δ_1, is equivalent to a finite time t_s, independent of initial particle size. Thus the final mass m' of a particle which arrived in the reactor at time t before flow was stopped is

$$\frac{m'}{m_0} = \left(1 - \frac{t + t_s}{T}\right)^3$$

Then

$$\frac{M_1'}{M_1} = \frac{4}{T}\int_0^{T-t_s} \left(1 - \frac{t + t_s}{T}\right)^3 dt = \left(1 - \frac{t_s}{T}\right)^4$$

$$\frac{s_1'M_1'}{s_1M_1} = \frac{3}{T}\int_0^{T-t_s} \left(1 - \frac{t + t_s}{T}\right)^2 dt = \left(1 - \frac{t_s}{T}\right)^3$$

and relation (26) results.

Choked solid operation is a limiting case of an open solid-flow process for low solid-discharge rates. This occurs when the holding time θ_s is large compared with the dissolution time T, under which conditions the parameter h becomes large. Limiting expressions which may be used as approximations are, when h is large,

$$\frac{w_1}{w_0} \cong \frac{1}{4h_1}, \qquad \frac{M_1}{w_0} \cong \frac{T}{4}\left(1 - \frac{1}{5h_1}\right),$$

$$\frac{s_1w_1}{s_0w_0} \cong \frac{1}{3h_1}$$

For nearly insoluble material and low holding times, h is small and the following approximations hold:

$$\frac{w_1}{w_0} \cong 1 - 3h_1,$$

$$\frac{M_1}{w_0} \cong \theta_s(1 - 3h_1),$$

$$\frac{s_1w_1}{s_0w_0} \cong 1 - 2h_1$$

Two modifications of choked design which can be expected in practice are the basket type and the partially choked reactor. In a basket-type reactor the larger solid particles are retained by a screened container in a limited portion of the vessel. In a partially choked reactor a screen is placed at the outlet of the reactor but its openings are so large that particles of an appreciable size escape into the outlet tube.

Under the reactor conditions uniformly sized particles of lifetime T are fed to the reactor and held exposed to optimum liquid circulation by the screen basket. After a residence time T_B in the basket which brings their dimensions to the screen hole dimension, d_B, the particles escape through the screen openings and then undergo normal purging from the remaining reactor volume.

$$T - T_B = \frac{3}{k_Bbp\Delta} d_B = \lambda d_B \qquad (27)$$

where p is the shape factor in the relation $x = pm^{1/3}$. By equations similar to (22) and (23) the holdup mass and the specific surface ratio in the basket are found to be

$$\frac{M_B}{w_0} = \frac{T}{4}\left[1 - \left(1 - \frac{T_B}{T}\right)^4\right]$$

$$\frac{s_B}{s_0} = \frac{4}{3}\,\frac{\left[1 - \left(1 - \frac{T_B}{T}\right)^3\right]}{\left[1 - \left(1 - \frac{T_B}{T}\right)^4\right]}$$

The solid effluent rate w_B from the basket is

$$w_B = w_0\left(1 - \frac{T_B}{T}\right)^3$$

These equations may be applied to a partially choked reactor if the particles escape immediately after reaching size d_B.

The equations for open solid flow hold in the main body of the reactor outside the basket, with an appropriate holding time θ_s and a particle life T_R.

$$T_R = \frac{k_B}{k_R}(T - T_B)$$

The dissolution coefficients in the reactor and the basket, k_R and k_B, may be slightly different owing to different flow conditions. The total mass transfer in the reactor is

$$w_0 - w_1 = (k_Bs_BM_B + k_Rs_RM_R)\Delta$$

where

$$\frac{s_RM_R}{s_0w_0} = \theta_s\left(1 - \frac{T_B}{T}\right)^2[1 - 2h_R + 2h_R^2(1 - e^{-1/h_R})]$$

and

$$\frac{w_1}{w_0} = \left(1 - \frac{T_B}{T}\right)^3\{1 - 3h_R[1 - 2h_R + 2h_R^2(1 - e^{-1/h_R})]\}$$

with

$$h_R = \frac{\theta_s}{T_R}$$

Enclosed Solid-flow System

An approach to steady state operation is possible with this method if the solid is essentially unchanged during the reaction. For mass transfer

$$C_1F_1 - C_0F_0 = k_1s_0M_0(C_s\rho_s - C_1\rho_1) \qquad (28)$$

If the density change of the liquid in the reaction is small and if the factor D is the fractional approach to equilibrium of the effluent liquid, there results

$$D = \frac{C_1 - C_0}{C_s - C_0} = \frac{1}{1 + \dfrac{F_0}{k_1s_0M_0\rho_s}} \qquad (29)$$

Batch System

Agitated reactors, of course, may also be operated by the batch method for both solid and liquid. The following equation, which may be used for calculating mass transfer coefficients for this method of operation, is derived from Equation (10a).

$$\int_{C_0}^{C} \frac{dC}{(1-C)^2\left(1+\frac{L_0}{M_0}\frac{C_0-C}{1-C}\right)^{2/3}(C_s\rho_s - C\rho)} = \frac{ks_0M_0t}{L_0(1-C_0)} \qquad (30)$$

In the experimental section coefficients for nonflow or batch experiments obtained by Equation (30) will be compared with the coefficients for flow experiments.

EXTENSIONS OF THE THEORY

Two-group Theory

Experimental evidence shows that if the agitation is insufficient, the coefficient α and therefore θ_s depend upon the size of the solid particles. The preceding elementary theory can still be applied within limits under these conditions by using an average value of θ_s. However a more detailed treatment may be useful where effects of size are important.

When feed particles of uniform size x and mean residence time θ_a reach a size x', their mean residence time becomes θ_b. If T and T' represent the lifetimes corresponding to sizes x and x' under the reactor conditions, the residence time distribution is then described by

$$y = e^{-t/\theta_a} \qquad t < T - T' \qquad (31)$$

$$y = \exp\left\{-(T-T')\left(\frac{1}{\theta_a}-\frac{1}{\theta_b}\right)\right\}e^{-t/\theta_b}$$
$$T - T' < t < T \qquad (32)$$

where the holding times are defined as

$$\theta_a = \frac{M_a}{w_a}, \qquad \theta_b = \frac{M_b}{w_b}$$

a and b referring to the fractions of the holdup mass and the effluent solid, which consist of particles having a size respectively larger and smaller than x'. Then, as in Equation (13),

$$\frac{w_a}{w_0} = \int_0^{T-T'}\left(1-\frac{t}{T}\right)^3\frac{1}{\theta_a}e^{-t/\theta_a}\,dt$$

$$\frac{w_b}{w_0} = \int_{T-T'}^{T}\left(1-\frac{t}{T}\right)^3\frac{1}{\theta_b}$$
$$\cdot\exp\left\{-(T-T')\left(\frac{1}{\theta_a}-\frac{1}{\theta_b}\right)\right\}e^{-t/\theta_b}\,dt$$

Integration yields

$$\frac{w_a}{w_0} = 1 - 3h_a + 6h_a^2 - 6h_a^3$$
$$- e^{-(1-q)/h_a}[q^3 - 3h_aq^2$$
$$+ 6h_a^2q - 6h_a^3] \qquad (33)$$

$$\frac{w_b}{w_0} = e^{-(1-q)/h_a}[q^3 - 3h_bq^2 + 6h_b^2q$$
$$- 6h_b^3(1 - e^{-q/h_b})] \qquad (34)$$

where

$$h_a = \frac{\theta_a}{T}, \quad h_b = \frac{\theta_b}{T}, \quad q = \frac{T'}{T} = \frac{x'}{x}$$

Experimental evidence for the use of two different holding times could be obtained by screening the effluent at a reasonable value of q and comparing the values of θ_a and θ_b given by Equations (33) and (34). For convenience plots of $1 - (w_a/w_0)$ and $(w_b/w_0)\ e^{(1-q)/h_a}$ vs. h_a and h_b for different values of q are shown on Figure 3.

Having determined the θ_a and θ_b which best describe the purging process, one obtains the surface area in the reactor from

$$s_1M_1 = \theta_a(s_aw_a) + \theta_b(s_bw_b)$$

with

$$M_1 = \theta_aw_a + \theta_bw_b$$

and

$$\frac{s_aw_a}{s_0w_0} = \int_0^{T-T'}\left(1-\frac{t}{T}\right)^2\frac{1}{\theta_a}e^{-t/\theta_a}\,dt$$

$$\frac{s_bw_b}{s_0w_0} = \int_{T-T'}^{T}\left(1-\frac{t}{T}\right)^2\frac{1}{\theta_b}$$
$$\cdot\exp\left\{-(T-T')\left(\frac{1}{\theta_a}-\frac{1}{\theta_b}\right)\right\}e^{-t/\theta_b}\,dt$$

Integration gives

$$\frac{s_aw_a}{s_0w_0} = 1 - 2h_a + 2h_a^2$$
$$- e^{-(1-q)/h_a}(q^2 - 2h_aq + 2h_a^2) \qquad (35)$$

$$\frac{s_bw_b}{s_0w_0} = e^{-(1-q)/h_a}[q^2 - 2h_bq$$
$$+ 2h_b^2(1 - e^{-q/h_b})] \qquad (36)$$

Plots of these expressions are shown in Figure 4.

This treatment can be extended to several size groups or to a continuous model if sufficient experimental data are available.

Equations for Nonuniform Feeds

In the preceding derivations the particles in the entering stream were uniform in size. The size distribution within the reactor and in the effluent stream has been expressed for this condition by Equation (19). In practice the feed to a reactor may be nonuniform in size. In any event the effluent from a unit in a chain of reactors will have a size distribution which must be taken into account to predict the performance of succeeding reactors. It is therefore desirable for sequential reactor design to solve the general problem of nonuniform feeds.

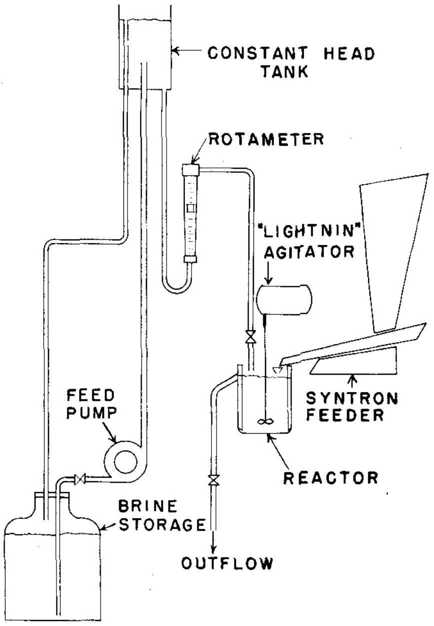

Fig. 5. Experimental arrangement for continuous operation.

If $Y_0(x)$ represents the differential size distribution of the solid feed, $Y_0(x)$ is related to $P_0(x)$, the cumulative weight percentage passing the screen of size x, by

$$P_0(x) = 100\int_{x_a}^{x} Y_0(\xi)\,d\xi \qquad (37)$$

where x_0 is the smallest size of particle present in the feed.

Equation (12) can be written in the form

$$T = \lambda x_0 \qquad (38)$$

where $\lambda = 3/kbp\Delta$ and p is the shape factor, $p = xm^{-1/3}$. The function $X_0(T)$ representing the weight fraction of the feed particles which have dissolution times between T and $T + dT$ is then

$$X_0(T) = \frac{1}{\lambda}Y_0\left(\frac{T}{\lambda}\right)$$

This lifetime distribution, $X_0(T)$, has been introduced here instead of the usual particle-size distribution, $Y_0(x)$, for consistency with the preceding derivations.

For an open-solid-flow reactor Equation (13) becomes

$$\frac{w_1}{w_0} = \int_{T_a}^{T_b} X_0(T)\left[\int_0^T\left(1-\frac{t}{T}\right)^3\right.$$
$$\left.\cdot\frac{1}{\theta_s}e^{-t/\theta_s}\,dt\right]dT$$

where T_a and T_b correspond to the smallest and largest particle sizes in the feed. Substituting from Equation (13a) yields

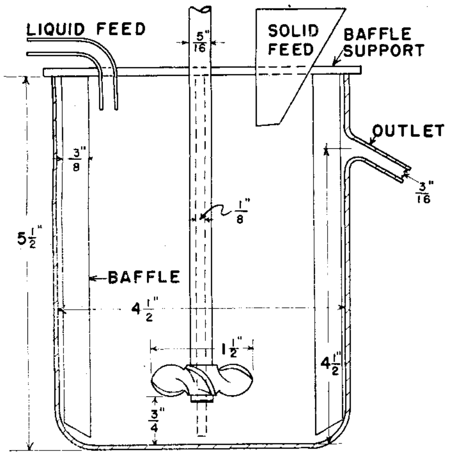

Fig. 6. Detail of experimental reactor.

$$\frac{w_1}{w_0} = \int_{T_a}^{T_b} X_0(T)\left[1 - 3\,\frac{\theta_s}{T} + 6\,\frac{\theta_s^{\,2}}{T^2} - 6\,\frac{\theta_s^{\,3}}{T^3} + 6\,\frac{\theta_s^{\,3}}{T^3}\,e^{-T/\theta_s}\right] dT \qquad (39)$$

And for specific surfaces from (15)

$$\frac{s_1 w_1}{s_0 w_0} = \frac{\displaystyle\int_{T_a}^{T_b} X_0(T)\left[\int_0^T \frac{1}{\theta_s}\left(1 - \frac{t}{T}\right)^2 e^{-t/\theta_s}\,dt\right]\frac{dT}{T}}{\displaystyle\int_{T_a}^{T_b} X_0(T)\,\frac{dT}{T}}$$

or

$$\frac{s_1 w_1}{s_0 w_0} = \frac{\displaystyle\int_{T_a}^{T_b} X_0(T)\left[1 - 2\,\frac{\theta_s}{T} + 2\,\frac{\theta_s^{\,2}}{T^2} - 2\,\frac{\theta_s^{\,2}}{T^2}\,e^{-T/\theta_s}\right]\frac{dT}{T}}{\displaystyle\int_{T_a}^{T_b} X_0(T)\,\frac{dT}{T}} \qquad (40)$$

For the choked solid case the same method gives the following expressions:

$$M_1 = \frac{w_0}{4}\int_{T_a}^{T_b} T X_0(T)\,dT \qquad (41)$$

$$\frac{s_1 M_1}{s_0 w_0} = \frac{1}{3\displaystyle\int_{T_a}^{T_b} X_0(T)\,\frac{dT}{T}} \qquad (42)$$

The size distribution of the solid effluent from a reactor receiving a feed of distribution $X_0(T)$ is obtained by integrating

$$X_0(T)\,\frac{1}{\theta_{s_1}}\left(1 - \frac{t}{T}\right)^3 e^{-t/\theta_{s_1}}\,dt\,dT$$

at constant effluent lifetime T_1, with $T_1 = T - t$, over the range of T:

$$X_1(T_1) = \frac{w_0}{w_1}\int_\Omega X_0(T)\,\frac{1}{\theta_{s_1}} \cdot \left(\frac{T_1}{T}\right)^3 \exp\left\{-\frac{T - T_1}{\theta_{s_1}}\right\} dT \qquad (43)$$

where the range of integration Ω is

from T_a to T_b for $0 < T_1 < T_a$

from T_1 to T_b for $T_a < T_1 < T_b$

Formal integration of Equation (43) can be made for the cases of a Gaudin or a log-probability distribution in the feed. Graphical or approximate procedures can of course also be used.

Multiple Reactors

The problem of sequential reactor design is now completely solved in theory. An example is the design of a series of reactors to dissolve a given amount of solid per unit time. If the size distribution of the initial solid is given, Equation (39) gives θ_{s_1}, the solid holding time in the first reactor, and Equation (40) gives the total surface area in the first reactor. The concentration difference is calculated from Equation (17*a*), which also gives the required liquid flow rate. The reactor volume can then be calculated from experimental values of α. The size distribution $X_1(T_1)$ of the feed to the second reactor is given by Equation (43). The solid holding time in the second reactor θ_{s_2} is obtained by the substitution of $X_1(T_1)$ in Equation (39), the subscript designations being increased by 1. This procedure is repeated for all the reactors in the chain. Concurrent, countercurrent, or mixed operation can be calculated by this step-by-step procedure.

EXPERIMENTAL

The experimental part of this study is divided into mixing and mass transfer sections. In the mixing section the effect of physical variables on the continuous mixing of sand and water was examined. These experiments provided needed insight into the mixing process and aided in the planning of the mass transfer experiments.

The mass transfer (dissolution) experiments were carried out to verify the previously derived equations relating mass transfer coefficient, surface area, and size distribution. For this purpose a relatively simple system—sodium chloride and concentrated brine—was chosen. The use of the brine instead of water was required to provide sufficient effluent solid for surface and size determinations even though its use may have decreased the accuracy of the mass transfer coefficients to a small extent. Although most of the runs were made by use of the open solid-flow method of operation, choked solid flow and batch were also investigated briefly.

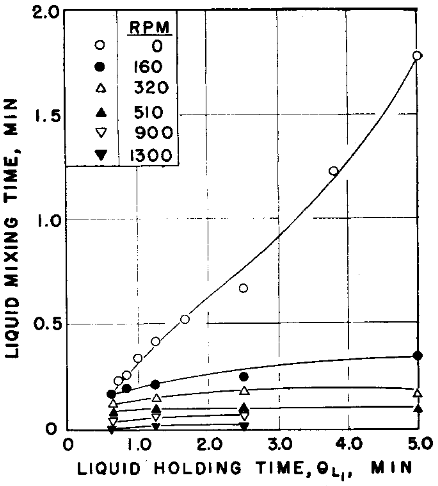

Fig. 7. Liquid mixing time for a dye injected into the feed stream of the reactor.

A vibratory feeder, Syntron Company model FM-0-10, produced a substantially continuous stream of solid particles from a hopper, with rate variations to the reactor of about 5% and very little particle breakage. The solid particles dropped into the open top reactor through a small funnel located above the liquid surface (Figures 5 and 6). The metered liquid entered the reactor through the feed tube also located slightly above the surface of the liquid.

The glass, flat-bottomed, 1.3-liter reactor (Figure 6) had four 3/8- by 1/8-in. brass baffles spaced 90 deg. apart along its inside periphery. Agitation was supplied by a commercial stainless steel 45-deg. pitch three-bladed, marine-type propeller 1½ in. in diam., which rotated so as to force the solution downward.

The air-permeability apparatus used to determine the solid specific surface has been previously described in detail (*3*). For the batch experiments a rapid sampling device was used which consisted of a vacuum manifold with six constricted glass sample tubes of about 5-ml. capacity dipping into the liquid and connected to the vacuum through stopcocks (*10*). Small wads of glass wool were placed in the tubes to prevent the solid from entering the samples. When a stopcock was rotated, a liquid sample was quickly obtained.

A commercially available salt, Morton's Bakers' *A*, consisting of uniform cubic crystals of sodium chloride, was used. After being screened into three fractions, 20/30, 30/40, and 40/50 U. S. mesh sizes, the salt was dried at 150°F. to facilitate free flow. An 87% saturated brine was used as the liquid feed.

Open Solid-flow System

The average duration of a run after establishment of steady flow conditions was about 20 min. During this time at least six 250- to 500-ml. samples were obtained by directing the effluent into a Büchner funnel to separate the solid rapidly from the liquid. The solid from the steady state samples (normally four of the six) was combined and used in the screen analyses and surface measurements. Runs made at a liquid feed rate of 500 g./min. or less did not reach steady state but continued to build up solid throughout the run.

At the end of a run the feeds and outflow were stopped and the reactor contents agitated for several hours. The mass of solid in the reactor at steady state could be calculated from the final conditions by the increase in concentration plus the mass of solid remaining.

The densities of the liquid samples were measured by pycnometer, and their salt content was determined by evaporation. The solid samples were dried and screened in 3-in.-diam. screens and their specific surface was determined by the air-permeability method.

Choked Solid-flow System

The procedure for this type of operation was the same as for the open-solid method except that a 270-mesh Tyler screen was placed just inside the reactor outlet to restrict the solid outflow.

Batch System

The initial solid was dropped into the reactor with the impeller rotating. Samples were then taken at 10-sec. intervals by momentarily opening each stopcock in turn. The samples were again analyzed for salt content by evaporation.

MIXING IN SOLID-LIQUID FLOW SYSTEMS

Two agitation levels prevail in a continuous-flow stirred tank reactor, one pertaining to the solid phase, the other to the liquid. Contributions to these levels come from the impellers and also from the kinetic energy of the inlet streams (*4*). In the case of ideal mixing in a multiphase *CSTR* the distribution of residence times for each phase is expressed by an equation of the form $y = e^{-t/\theta}$. Under such conditions *CSTR* operation can be described by the elementary theory. If agitation and outlet conditions are so favorable that θ_s is entirely independent of particle size, θ_s is also equal to θ_L, i.e., $\alpha = 1.0$. Since this is not usually attained, θ_s, as used in the elementary theory, is a mean solid holding time and is usually different from θ_L. The use of a mean θ_s seems justified in view of the good agreement of the experimental and calculated size-distribution curves for the effluent solid.

In the experiments reported, the whole reactor volume (Figure 6) was accessible to the particles. Except where otherwise indicated in the mixing experiments, the feeds were water and sand, where the sand had a density of 2.65 g./cc. and a size distribution of 33% between 30 and 40 mesh, 66% between 40 and 50 mesh, and 1% less than 50 mesh.

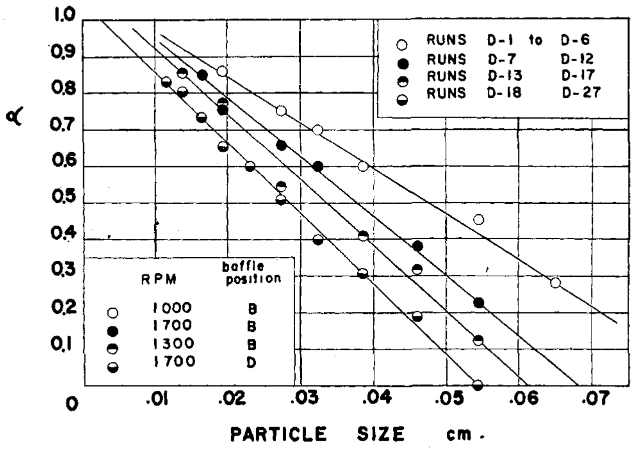

Fig. 8. Effect of particle size on holding time ratio.

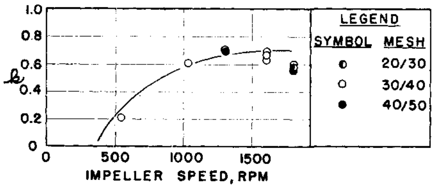

Fig. 9. Batch system, mass transfer coefficients.

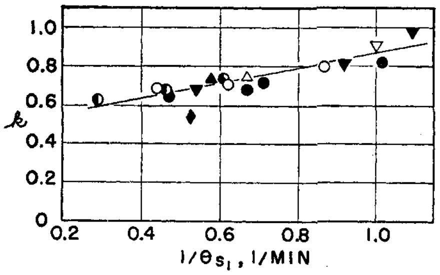

Fig. 10. Open solid-flow system. Mass transfer coefficients. Equation (16) vs. reciprocal holding time.

Liquid- and Solid-mixing Times

The liquid-mixing time was determined by an experimental method previously reported (*4*), wherein a small amount of dye solution was injected into the liquid feed and the time for uniform mixing observed. At impeller speeds above 900 rev./min. this liquid-mixing time was found to be a small fraction of the liquid holding time, except when the rate of liquid feed was high (Figure 7). The assumption of a uniform liquid concentration throughout the reactor is, therefore, closely approached when applied to the liquid phase in solid-liquid mixing.

The time for solid mixing was also found to be short (Table 1*). The time recorded was the interval between the start of the impeller in the reactor at rest containing 50 g. of sand, and the time when the mean solid-flow pattern was no longer seen to change; for example, at 810, 1,400, and 1,800 rev./min. the time interval is only 3.0, 1.2, and 0.7 sec. respectively.

The instantaneous solid-flow pattern fluctuates continually in a continuous-flow solid-liquid reactor. Clouds of particles swirl in a pulsating manner about the reactor and into the outlet tube. These particle clouds are usually less than 1 in. in diameter and recur roughly once or twice a second at impeller speeds of 1,000 rev./min. and higher. Effluent samples, therefore, must be taken for a time which is long in terms of the frequency of the pulsations. Similar fluctuations of concentration have been observed in the effluent of a *CSTR* with a homogeneous chemical reaction (*4*).

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*The tables and remaining figures are on file as document 5325 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

Holding-time Ratio

For design purposes the solids content at steady state in a *CSTR* unit usually must be known, since it determines the total area of contact between the phases in the reactor. An extensive investigation would be required to obtain a generalized quantitative correlation of the solids content with the numerous design and operating variables. Shown here in a general way are the effects of a few of the more important variables.

The holding-time ratio α is defined by Equation (2) as the ratio of solid to liquid in the effluent divided by this ratio in the reactor. Not only is α a measure of the uniformity of solid mixing, but it is indicative of the sampling process occurring at the outlet. In the mixing experiments α at steady state was found to vary widely with the impeller position, baffle position, particle size, impeller speed, and solid- and liquid-flow rate. These variations, illustrated by Figures 8 to 13 and Tables 2 and 4,* indicate trends to be expected by the designer.

Although the location of the outlet nozzle would be an important variable in a study of the kind, a simple top outlet only was used. This location prevents clogging or settling which might be expected to occur with other outlet locations. For a top outlet an α approaching unity indicates good mixing and usually corresponds to desirable operating conditions. Accordingly, the variables of baffle position and impeller location were set at the maxima obtained in the runs.

The effect of particle size on α is illustrated in Figure 8 by use of closely sieved fractions of crushed sand. Increasing the impeller speed increases the rate of circulation, decreases the thickness of the clear area near the surface, and increases α.

Low values of α, and hence operating conditions less than optimum, are encountered for sand at low solid-flow rates or high liquid-flow rates. In the mass transfer experiments, however, at high liquid-flow rates little change in α is observed when the liquid-flow rate is varied. Limiting operating conditions occur at very high solid-flow rates or low liquid-flow rates when the reactor overloads with solid. These overloaded flooding conditions occurred when the mass of solid salt in the 1,300-cc. reactor was above about 150 g. Although the speed of the impeller was maintained, there was little solid turnover. The solid collected in the reactor bottom and continued to increase indefinitely.

MASS TRANSFER RESULTS

Open Solid-flow System

Rate coefficients. The mass transfer coefficient k of each run (Tables 3 and 4*) was calculated by Equation (16) and corrected to 25°C. For purposes of comparison the coefficients were also calculated by Equation (17), and the very good agreement (2.5% deviation) of the sets verifies the equivalence of the two equations.

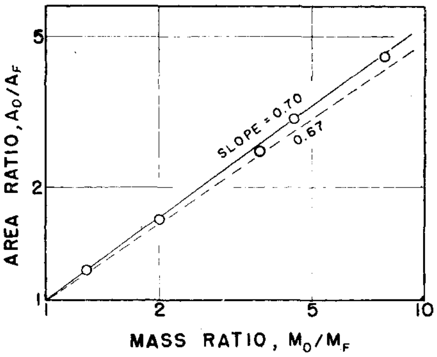

Fig. 11. Batch experiment, comparison of calculated and measured variation of surface area with mass in dissolution.

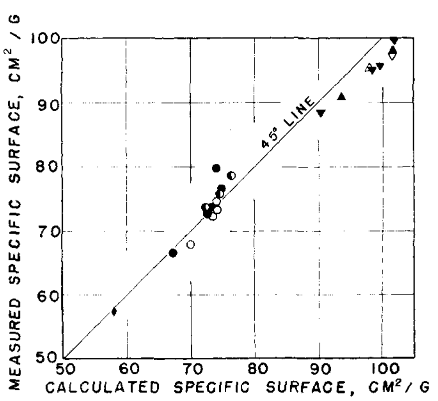

Fig. 12. Open solid-flow system, comparison of calculated and measured specific surface of outlet solid.

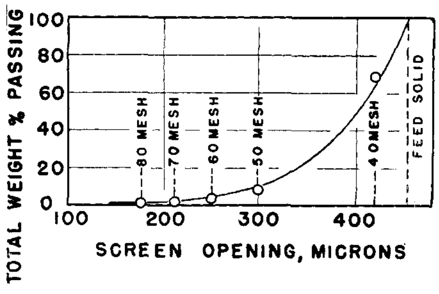

Fig. 13. Comparison of calculated curve and experimental size measurements of outlet solid, run C-3.

All the coefficients were in the range from 0.6 to 1.0 g./(min.)(sq. cm.)(g./cc.), but contrary to expectations no discernible correlation with impeller speed was obtained. (All runs were made at 1,000 rev./min. or above.) The average of the coefficients of the runs at each impeller speed (1,000, 1,300, 1,600, and 1,800 rev./min.) varied only between 0.70 and 0.78. An error of about 15% could be expected in the k values because the expressions involve the differences of nearly equal quantities. The small particle sizes probably explain the lack of correlation of k with impeller speed. Because of the rapid circulation of the particles in the reactor, the relative velocity between the liquid and the particles is much less sensitive to impeller speed than is the case with large particles.

The batch results (Table 5* and Figure 9) also show an insensitivity of k to impeller speed at speeds above 1,000 rev./min. The batch coefficients agree well with the open-solid-flow coefficients and show no appreciable effect of particle size. This is in accord with the results of other investigators working with larger sized particles (*2*, *5*, *9*, *10*). The average within variation for the batch runs was about 5%.

The quantity $1/\theta_s$ is a measure of the rate of solid turnover in the reactor and as such should represent a contribution to the reactor mixing conditions. A plot of $1/\theta_s$ vs. k (Figure 10) shows the small but definite effect of this factor.

Although all runs were at a nominal steady state (shown by concentration vs. time plots), random fluctuations in feed rates and especially in mixing pattern resulted in minor discrepancies in the material balances calculated by Equation (17*a*). The average of the discrepancies for all runs was 2.5%.

Particle-surface Area. The equations developed depend on the assumption that the surface area of the particles varies as the ⅔ power of the mass. However, rounding off of the particles and fragmentation are possible, and so an experimental verification of this assumption is desirable. Brine of known concentration containing varying amounts of 30/40 mesh salt was saturated by agitation in a beaker. The residual solid was dried and its specific surface determined by air permeability. The results when plotted on logarithmic coordinates (Figure 11) show a variation in area as the 0.70 power of the mass, which is close to the assumed 0.67.

In the continuous-flow mass transfer

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*See footnote on page 503.

*See footnote on page 503.

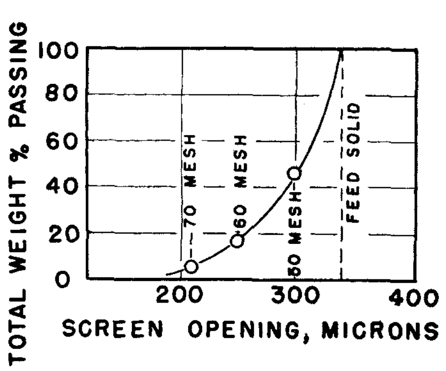

Fig. 14. Comparison of calculated curve and experimental size measurements of outlet solid. Run C-14.

experiments, the specific surface of the effluent solid from the reactor was calculated by use of Equation (15*a*) in conjunction with a plot of Equation (13*a*). These calculated areas are compared in Table 6* and Figure 12 to the specific surface measured by air permeability. There is good agreement (2.5%), confirming Equation (15*a*), which permits the calculation of the surface of the outgoing solid when only the feed and effluent rates and the feed specific surface are known.

Size Distribution. A basic assumption in the derivation of the equations of the elementary theory is that there is no size selection at the outlet. This assumption was confirmed by use of the sand-water system and also by the results described below.

The size distributions of the effluent solid of the runs were calculated by Equation (19). When these calculated distributions were compared with the measured distributions, surprisingly good agreement was obtained in view of the inherent errors in screening. The results for some typical runs are shown in Table 7* and Figures 13 and 14. The size of the feed was calculated by the relation $x_0 = 6/s_0\rho$.

Choked Solid-flow System

Several runs were performed with this method of operation (Tables 8 and 9*) in order to test the validity of the eqlations developed. The rate coefficients were calculated by the relation $k = w_0/s_1\Delta_1 M_1$ and Equation (24). All coefficients were in the range from 0.97 to 1.14, and there is again no apparent effect of impeller speed.

The average coefficient for this method of operation is 1.08, which is appreciably higher than the average coefficients of the other methods. A troublesome problem in the choked solid runs was the rapid build-up of solid particles on the outlet screen. A significant portion of the reactor solid was held on the screen in spite of frequent scraping with a spatula. It is believed that a major cause of the higher coefficients obtained in these runs is the very rapid dissolution of the particles on the screen resulting from the high liquid velocities through the miniature packed bed. Another contributing factor, although quite minor, was fines passing through the screen and subsequently dissolving in the sample flasks.

The values of C calculated by Equation (20) checked the measured values very closely, with an average deviation of only 0.0011 g./g.

The specific surface of the reactor solid was calculated by Equation (26) by use of the measured surface of the residual solid remaining after saturation of the solution. The ratio of the steady state specific surface to that of the feed solid is predicted by Equation (24) to be 4/3. The measured ratios were in good agreement, being 1.27, 1.26, 1.33, and 1.31 for the four runs having residual solid.

ACKNOWLEDGMENT

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NOTATION

a = effective surface area of a single solid particle, sq. cm.

A = effective surface area of total reactor solid, sq. cm.

b = area proportionality constant = $m^{-2/3}a$, cm^{2}g.$^{-2/3}$

C = liquid concentration, g. solute/solution

d_B = basket screen hole dimension, cm.

D = degree of reaction

F = liquid flow rate, g./min.

h = ratio of solid holding time to particle lifetime = θ_s/T

k = mass transfer coefficient, g./(min.)(sq. cm.)(g./cc.)

L = liquid holdup in reactor, g.

M = solid holdup in reactor, g.

m = mass of a single solid particle, g.

p = shape factor = $m^{-1/3}x$, cm. g.$^{-1/3}$

q = parameter in two-group theory ($q = T'/T$)

s = specific surface of solid, sq. cm./g.

t = time, min.

T = time of complete dissolution (lifetime) of a solid particle, min.

w = solid flow rate, g./min.

x = selected dimension of particle, cm.

y_t = fraction of reactor contents having a residence time of t or longer

α = holding time ratio, θ_L/θ_s

Δ = concentration difference = $(C_s\rho_s - C\rho)$, g./cc.

λ = lifetime to size proportionality constant, min./cm.

ρ = density of solution, g./cc.

θ_L = liquid holding time, L/F, min.

θ_s = solid holding time, W/w, min.

ξ = integration variable

Subscripts

0 = feed to first reactor or to zero time or to feed

1 = the contents and effluent of the first vessel

a, b = size groups separated by size x' (lifetime T') in two-group theory; or smallest and largest size of feed particles

B = basket-type reactor

R = reaction space outside of basket

s = saturation

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*See footnote on page 503.