Mass Transfer to Particles: Part I.
Suspended in Agitated Tanks

PETER HARRIOTT

American Cyanamid Company, Stamford, Connecticut

Mass transfer coefficients were measured for particles suspended in agitated, baffled tanks. The coefficients for a given particle size and a given fluid vary with the 0.10 to 0.15 power of the power dissipated per unit volume. The coefficients, which cover a one hundred fold range, are about 1.5 to 8 times those predicted from the correlations for fixed particles if the terminal velocity is used to calculate the particle Reynolds number. The measured effects of particle diameter, diffusivity, viscosity, and density difference cannot be described by a simple exponential equation or by previous empirical correlations. The effects of these variables can be explained by using a slip-velocity theory combined with a modified penetration theory.

Studies of the rate of mass transfer to suspended particles are pertinent to many processes. For example in crystallization there is always a drop in solute concentration from the bulk of the solution to the face of a growing crystal. In some cases the crystal growth rate is limited by the rate of diffusion to the surface, but even when diffusion is not controlling, the mass transfer resistance should be used to calculate the actual surface concentration for any fundamental study of the crystallization mechanism. Similarly in reactions with suspended solid catalysts the diffusion of reactants to the catalyst surface influences and may limit the over-all reaction rate. Data for transfer to suspended solids are also valuable for studies of mass transfer between agitated fluid phases, since very small drops or bubbles usually act as rigid spheres. Even for large drops traces of surface-active impurities may inhibit drop circulation and reduce the external transfer coefficients almost to those for rigid spheres (*5*).

Only a few of the forty or more studies of transfer to particles in stirred tanks will be discussed here; some deal mainly with large pellets which are not completely suspended, and many are restricted to unbaffled or partially baffled vessels of a particular shape. Several recent studies in fully baffled tanks with standard turbine impellers should have given consistent results, but the scatter of the data and the large differences in effects reported by different workers make the published correlations very uncertain. For example the reported effect of stirrer speed on the transfer coefficient has ranged from N^0 (*2*, *17*) to $N^{0.9}$ (*1*, *13*), and the reported effects of fluid properties cover almost as wide a range of exponents (*1*). There are also theoretical objections to the present empirical correlations; the use of separate equations for heat and mass transfer (*10*, *15*) is not justified, and the use of the stirrer diameter instead of the particle diameter in both the Sherwood and Reynolds numbers indicates that the correlations have no fundamental significance and cannot be extrapolated.

The aims of this study were to develop a more reliable correlation for suspended particles based on a wider range of variables and more accurate measuring techniques and also to explain the measured effects with existing or new theories of mass transfer. The mass transfer study also seemed a promising way of learning more about turbulence in stirred tanks. Most of the experimental work was done in open baffled tanks with turbine impellers, but a few tests were made in unbaffled tanks. About half of the data were obtained by following the neutralization of ion exchange beads under conditions where the internal resistance was negligible. Since the beads were almost perfect spheres and attrition and agglomeration were negligible, the area for mass transfer was known much more accurately than for tests with dissolving solids. Runs were also made with small spheres of organic acids and with boric acid, lead sulfate, and zinc. In all tests the change in solution concentration was followed by continuously recording either the pH or the conductivity of the solution. The tests covered a fivefold range of tank and turbine sizes, a tenfold range of stirrer speeds, a one thousandfold range of particle sizes and density differences, and a fortyfold range of viscosities and diffusivities.

SLIP-VELOCITY THEORIES

The slip-velocity theories are based on the correlations for steady state transfer to particles fixed in space, with the average slip velocity used to calculate the Reynolds number. When natural convection effects are absent and when the Reynolds number exceeds 1, the transfer rate for single spheres is given by the semitheoretical equation (*22*)

$$N_{Sh} = 2 + 0.6\,(N_{Re})^{0.5}\,(N_{Sc})^{0.33} \qquad (1)$$

For low Reynolds numbers the boundary-layer calculations of Friedlander (*3*) are probably more accurate. Three approaches for obtaining a characteristic slip velocity are discussed here. The simplest method uses the terminal velocity, with the understanding that this gives only the minimum values of the coefficient. For small particles the average slip velocity can be predicted if the turbulence parameters are known. For large particles no corresponding theory is available, and only approximate limits for the effective slip velocity can be predicted.

If the terminal velocity is used to calculate the Reynolds number, Equation (1) should give the minimum value to be expected for the transfer coefficient for suspended particles. For a given system the ratio of the actual coefficient to the minimum coefficient would presumably depend on the stirrer speed or the power input, and the effects of particle size, diffusivity, and similar variables on k_c would be predicted from their effects on k_c^*. Figure 1 is a plot of the minimum coefficients for transfer to spheres falling in water. The graph indicates why so many workers have found no effect of particle size. In the range from 100 to 1,000 μ the terminal velocity is approximately proportional to the diameter, and since the square root of the Reynolds number is also proportional to the diameter, the transfer coefficient is nearly constant. For very large particles v_t depends on $D_p^{0.5}$, and the transfer coefficient varies with $D_p^{-0.25}$. However particles larger than a few millimeters would rarely be completely suspended. For very small particles both k_c and k_c^* must increase with decreasing diameter, since the Sherwood number would never be less than 2, the value for diffusion in an infinite stagnant medium.

For viscous liquids the curves in Figure 1 are shifted down and to the right, which means that the coefficient should vary inversely with particle size up to larger sizes than in the case of water. The true effect of viscosity

---

Peter Harriott is with Cornell University, Ithaca, New York.

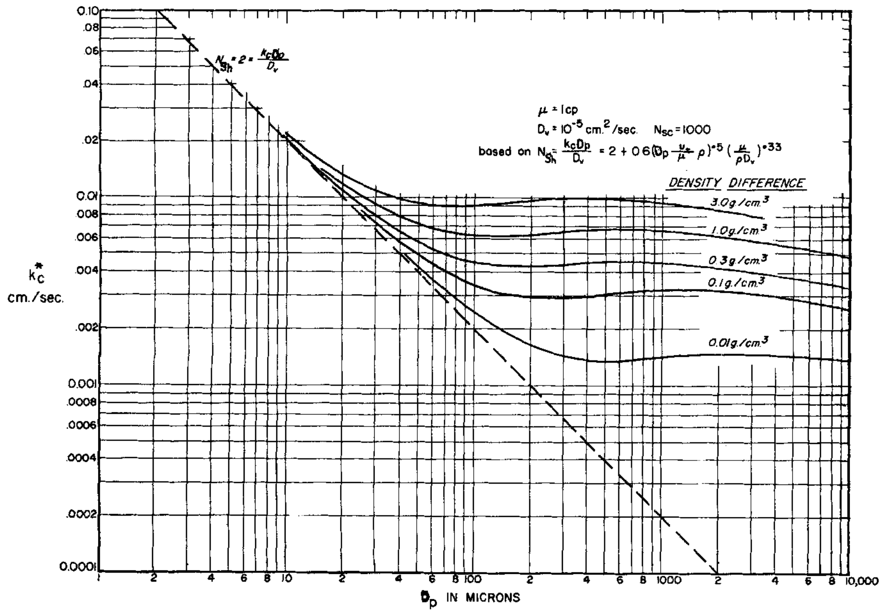

Fig. 1. Mass transfer coefficients for particles falling in water.

alone is much smaller than the effect of the resultant change in diffusivity, which usually varies inversely with viscosity. Based on Equation (1) k_c^* and thus k_c might be expected to vary with $(D_v^{0.7})/(\mu^{0.3})$ for large particles and with $(D_v^{1.0})/(\mu)^0$ for small particles. The coefficient k_c^* depends on the 0.3 to 0.4 power of the density difference for large heavy particles, and the exponent decreases to zero as the Sherwood number approaches 2.0.

If the general flow pattern and the turbulent velocity fluctuations in a stirred tank could be completely described, it would be possible to calculate the average slip velocity for use in Equation (1) or an equivalent correlation. The equations of motion for a small particle in a turbulent fluid were reviewed by Hinze (*9*), and Friedlander (*4*) used similar equations to calculate the effect of velocity fluctuations on transfer to particles carried along in an air stream. Although not enough is known about turbulence in stirred tanks to justify extensive calculations, the equation presented by Hinze can be used to predict the effects of system properties at a given turbulence level:

$$\overline{v_p^2} = \left(\frac{aTf_L + b^2}{aTf_L + 1}\right)\overline{v_f^2} \qquad (2)$$

$$\text{where } a = \frac{36\mu}{(2\rho_p + \rho_f)Dp^2}$$

$$b = \frac{3\rho_f}{2\rho_p + \rho_f}$$

f_L = Lagrangian integral time scale

If the average slip velocity is defined as

$$v_s = \sqrt{\overline{v_f^2}} - \sqrt{\overline{v_p^2}} \qquad (3)$$

the maximum velocity (corresponding to $aTf_L << 1$) would be

$$\max v_s = (1 - b)\sqrt{\overline{v_f^2}} \qquad (4)$$

For the resin particles used in the experimental study $\rho_p = 1.24$, and the maximum slip velocity would be 14% of the fluctuating fluid velocity. (The corresponding treatment in Friedlander's article neglects the apparent mass effect which is negligible for solids in air but not for solids in water.) When one takes 0.001 sec. as an arbitrary low value for the time scale in Equation (2), the slip velocity of the resin particles would be about 2% of the fluctuating velocity for 50-μ particles and would be nearly the maximum value (14%) for particles larger than 300 μ.

The assumptions made in deriving Equation (2) would limit its usefulness for quantitative predictions even if exact values of the turbulence parameters were available. Most important is the assumption that the particle is always surrounded by fluid moving in the same direction, which means that the particle must be small relative to the smallest eddies of the turbulence. The energy of turbulent liquids is dissipated mainly in eddies about 50 μ in size (*12*), which might seem to place a severe restriction on the use of Equation (2). However the velocity fluctuations associated with such small eddies are probably much smaller than the fluctuations associated with large eddies, and it seems reasonable to expect Equation (2) to hold fairly well for particles up to a few hundred microns in diameter. Other assumptions made in the derivation are that Stokes' law holds, the Basset term can be neglected, and the effect of gravity is unimportant. The use of Stokes' law for the drag force is justified for most

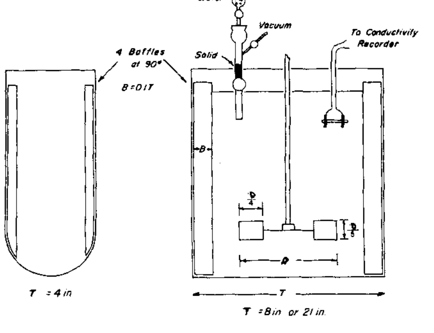

Fig. 2. Apparatus for stirred-tank studies.

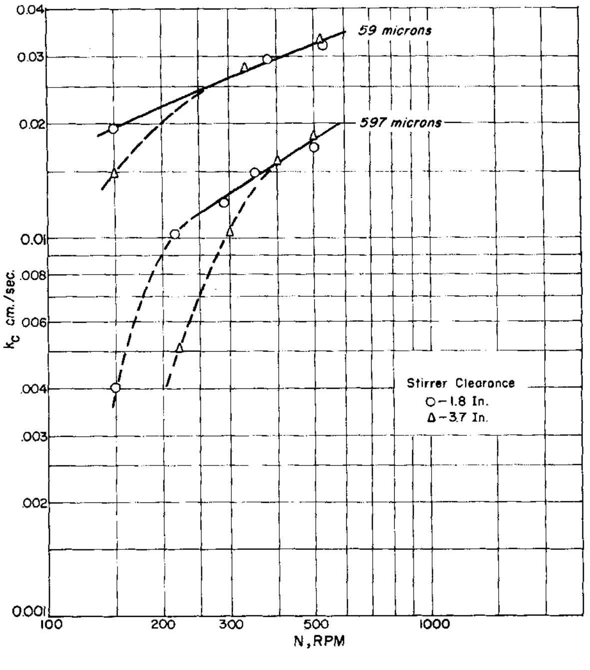

Fig. 3. Effect of stirrer position on transfer coefficient NaOH-H_2O-HR; 8-in. tank, 3-in. turbine, 7.4-in. depth.

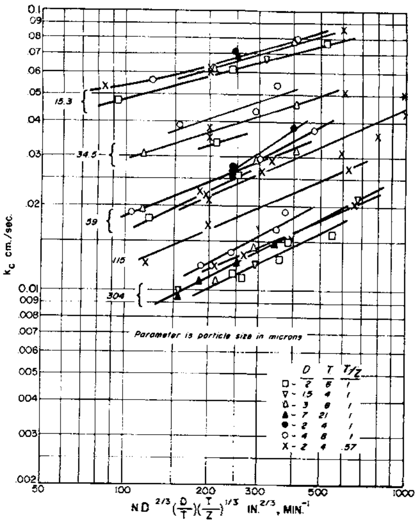

Fig. 4. Coefficients for ion exchange beads in water as a function of (power per unit volume)$^{1/3}$.

particles up to a few hundred microns in size, and a correction factor could probably be applied for large or very dense particles. The Basset term depends on the viscosity and the deviation in flow pattern from steady state, and the calculations of Hughes and Gilliland (*11*) for freely falling particles show that the acceleration is appreciably less because of this effect. Hinze gives no justification for neglecting the Basset term, but it would be difficult to calculate when both the fluid and the particle are accelerating. The gravity effect is important when the terminal velocity is the same order of magnitude as the fluctuating velocity given by Equation (2). Adding the two velocities vectorially one would get a rough value of the effective slip velocity. Use of a root-mean-square fluctuating velocity as the effective slip velocity for mass transfer is really not correct, since the rate of transfer depends at most on the 0.5 power of the velocity and not the 2.0 power. The effective velocity is therefore slightly less than given by Equations (2) and (4), but the correction is probably small compared with the other uncertainties in the use of these equations.

For particles which are larger than a sizable fraction of the eddies the fluid velocities near different parts of the surface will often be unrelated. The drag forces which tend to accelerate the particle will partially cancel, and the instantaneous relative velocity over a part of the surface could be greater than given by Equations (2) to (4). For large particles the local slip velocity averaged over the surface might approach the fluctuating velocity of the fluid, instead of the lower limit given by Equation (4). Of course Equation (1) no longer applies if the flow past the particle is not uniform, and only an order of magnitude estimate of the transfer coefficient for such cases is possible.

To summarize the slip-velocity theories they are all based on the use of an effective slip velocity in the steady state correlations for transfer to fixed particles. Using the terminal velocity one gets the minimum coefficient. For particles up to a few hundred microns the slip velocity can be estimated from the fluctuating fluid velocity and the time scale of the turbulence. For large particles the slip velocity is probably greater than predicted from the theory for small particles.

UNSTEADY STATE THEORY

In using the average slip velocity to calculate the transfer coefficient it must be remembered that Equation (1) is for steady state transfer. To prove that transient effects can be important, consider a small particle of the same density as the fluid. The terminal velocity is zero and the turbulent slip velocity is also zero, according to Equation (2). The particle moves with the fluid, but it is not always surrounded by the same fluid, which is an important distinction for mass transfer. The Sherwood number would be larger than the limiting value of 2 because the transfer rate would be momentarily higher each time the particle moved into a new fluid environment. When one takes an extreme case, if all the fluid surrounding the particle were replaced with fresh fluid, the transfer coefficient would vary with time according to the equation (*27*):

$$k_c = \frac{D_v}{r} + \sqrt{\frac{D_v}{\pi t}} \qquad (5)$$

For $D_v = 10^{-5}$ sq. cm./sec. and $r = 10^{-2}$ cm. the transient term exceeds the steady state term for times up to 3.2 sec. If the particle environment were changed several times a second, the transfer rate would be governed just by the transient term, which is the same as Higbie's formulation of the penetration theory (*8*).

A more realistic model for the unsteady state theory would consider that only part of the surrounding fluid was replaced as the particle moved from one location to another. The result would be about the same as if random eddies moved inside the concentration boundary layer but didn't go all the way to the surface. Calculated transfer rates for this modification of the penetration theory are presented in a separate paper (*7*). For eddies moving to within H units of a plane surface every t seconds the average transfer rate is given to within 5% by the approximate equation

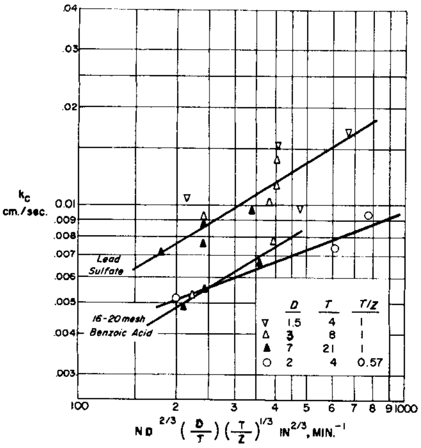

Fig. 5. Transfer coefficients for benzoic acid and lead sulfate at 20°C.

$$\frac{1}{k_c} = \frac{H}{D_v} + \frac{1}{2}\sqrt{\frac{\pi t}{D_v}} \qquad (6)$$

Allowance for a distribution of eddy lifetimes makes little difference, but allowance for a distribution of distances of approach increases the rate up to twice that given by Equation (6). Another important feature of this modified penetration theory is the gradual change in the exponent for the diffusivity, in contrast to the constant exponent of 0.5 in the usual penetration theories.

This modified theory of course holds only for no net flow past the surface, but when flow is present the transient effects produced by eddies would tend to increase the rate above that given by the slip-velocity theory. If the slip velocity is small, the transient effects might predominate. Though quantitative predictions for the modified penetration theory are even more difficult than for the slip-velocity theory, measurements of the diffusivity effect and the density effect for small particles should help to determine the relative importance of the two theories. The transient effects are most important for cases of very low diffusivity, so the effect of diffusivity on the transfer coefficient would be less than predicted by Equation (1) if transient effects are important. Similarly a smaller effect of density difference than predicted by Equations (1) to (4) would also indicate significant transient effects.

APPARATUS, PROCEDURE, AND CALCULATIONS

The equipment for the tank studies is shown in Figure 2. Most of the runs were made in the 4 in. round-bottom resin flask, which was filled to a depth of 5 or 8 in. The runs in the 8 and 21 in. flat-bottom tanks were made with a liquid depth equal to the tank diameter. All three tanks had four symmetrically-located baffles whose width was 10% of the tank diameter. The baffles were set about ⅛ in. out from the wall and ⅛ in. up from the bottom to eliminate dead pockets. The impellers were six-blade turbines 1½, 2, 3, 4, and 7 in. in diameter.

The ion exchange beads were obtained by separating into narrower size fractions standard grades of Dowex 50-WX8, a moderately cross linked, strong-acid resin. In the usual procedure for the ion-exchange runs enough caustic was added to a suspension of the resin in deionized water to give a pH of 11, and the reaction was followed either by the decrease in pH or, for more accurate work, by the decrease in conductivity:

$$HR + NaOH \rightarrow NaR + H_2O$$

The coefficient was calculated from the equation

$$\frac{A\, k_c\, (t_2 - t_1)}{V} = pH_1 - pH_2 \qquad (7)$$

The transfer area was determined from the weight of resin charged and the measured density and mean diameter of the swollen beads. Tests at pH values of 9 to 12 showed no effect of concentration on the transfer coefficient, which proved that only the external resistance was important. Most of the runs were at room temperature, and the coefficients presented in Figures 4 to 14 are corrected to 20°C. with the data in Figure 11 used.* The results for small particles in the large tank may be influenced slightly by the mixing lag. Appendix II shows that the mixing times are only a few seconds for the small tanks but 10 to 20 sec. for the 21-in. tank.

The particles of benzoic acid and *p, t*-butyl benzoic acid were prepared by spraying the molten acids into a shot tower. This produced spherical particles with about 10% internal voids; these voids were filled with water before the particles were charged to the tank. The samples of boric acid, zinc, and lead sulfate were screened from reagent grade material. The coefficients for particles dissolving in water were determined by following the change in conductivity with time. For tests with zinc a few cubic centimeters of dilute hydrochloric acid were added to the suspension, and the linear rise in pH with time was recorded.

The physical properties of the solids and solutions are given in Table 1. Most of the diffusivities were calculated from conductivity measurements, with the extra contribution of undissociated molecules in the case of the organic acids taken into account. Details of these calculations are available.*

RESULTS

Effect of Stirrer Location

Since this study deals primarily with transfer to suspended particles, a few tests were made to explore the conditions needed for complete suspension. Figure 3 shows transfer coefficients for two turbine positions in the 8-in. tank. The dotted lines indicate regions where clusters or layers of particles were seen on the bottom of the tank. The minimum speed at which the particles were completely suspended coincides with the break in the transfer coefficient graph. The minimum speed definitely decreases as the turbine is moved closer to the bottom, though no such effect was found by Zweitering (*30*). The minimum speeds range from 0.3 to 0.7 of the values predicted by Zweitering's correlation. All subsequent tests were made with a stirrer clearance of 1/4 or 1/3 the liquid depth, but as Figure 3 shows, the coefficients are probably the same for any stirrer location if the particles are completely suspended.

TABLE 1. PHYSICAL PROPERTIES AT 20°C.

ρ_p	ρ_p, g,/cc.	$\Delta\rho$, g./cc.	μ, centipoises	D_v, sq. cm./sec. × 10^5	N_{Sc}
NaOH + HR in water	1.24	0.24	1.0	1.93	518
NaOH + HR in 0.2% methocel* solution	1.24	0.24	6.7	1.83	3,670
NaOH + HR in 0.35% methocel* solution	1.24	0.24	20	1.78	11,300
NaOH + HR in 67% glycerine solution	1.34	0.17	17.9	0.142	107,500
Benzoic acid in water	1.28	0.28	1.0	0.77	1,300
Butyl-benzoic acid in water	1.13	0.13	1.0	0.74	1,350
Butyl-benzoic acid in 30% dextrose solution	1.145	0.014	3.02	0.34	7,700
Butyl-benzoic acid in 33% dextrose solution	1.146	0.006	3.58	0.30	11,400
Boric acid in water	1.43	0.43	1.0	1.00	1,000
Lead sulfate in water (5 to 10μ)	6.2	5.2	1.0	0.90	1,110
Zinc in dilute HCl	7.14	6.14	1.0	3.08	325

* A commercial thickener.

Effect of Stirrer Speed and Power Consumption

Most of the data for ion exchange particles in water are shown in Figures 3 and 4. Complete data are tabulated in Appendix IV.* Each line in Figure 4 shows the effect of turbine speed for a given system geometry. With a liquid depth equal to the tank diameter, the transfer coefficient is proportional to the 0.5 power of the turbine speed for particles larger than 100 μ. For smaller particles the exponent decreases gradually, becoming about 0.3 for 15-μ particles. Most of the tests in the 4-in. tank were made with an effective depth 1.75 times the tank diameter, and the exponents for the speed effect are about 10% less than the above values. When one considers this difference, the data for large dissolving particles (Figures 5 and 7*) which gave exponents of 0.4 to 0.5, are in good agreement with the ion exchange data. Figure 7 shows that correct results are obtained with boric acid only over a relatively narrow range of stirrer speeds, since the particles are not suspended at low speeds and are easily broken at high speeds.

The abscissa in Figures 4 and 5 is proportional to the cube root of the power per unit volume. The power was not measured, but an abscissa of 200 corresponds to about 0.96 hp./1,000 gal., based on a power number of 6.3[24]. (A value of 200 is obtained at 260 rev./min. with a 3-in. turbine in an 8-in. tank and Z/T = 1.0, or at 300 rev./min. with D = 2 in., T = 4, and Z/T = 1.75). For all particle sizes and a fivefold range of tank sizes the coefficients for similar systems are satisfactorily correlated on this basis. For the same power input the coefficients for D/T = 0.5 are 10 to 20% higher than for D/T = 0.25. Since the coefficient depends only on the 1/10 to 1/6 power of the energy input, two to three times as much power must be used to get the same coefficient with a small impeller as with a large impeller. The explanation for this difference must lie either in the more uniform dissipation of energy or the higher flow rates associated with the large impeller.

Effect of Particle Size

The effect of particle size is shown in Figure 8. For small ion exchange beads in water the coefficient decreases with increasing size, but the coefficient is almost independent of size for particles larger than 200 μ. For particles smaller than 100 μ the coefficients are plotted against a weighted mean diameter $D_p = \Sigma n D_p^2 / \Sigma n D_p$, which was derived on the assumption that k_c varied inversely with D_p. This over corrects somewhat, since the slope of Figure 8 in this region is only −0.7 instead of −1.0. The surface mean diameters and the weighted means are given in Table 2.

---

* Tabular material has been deposited as document 6958 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $5.00 for photoprints or $2.25 for 35-mm. microfilm.

* See footnote in column 1.

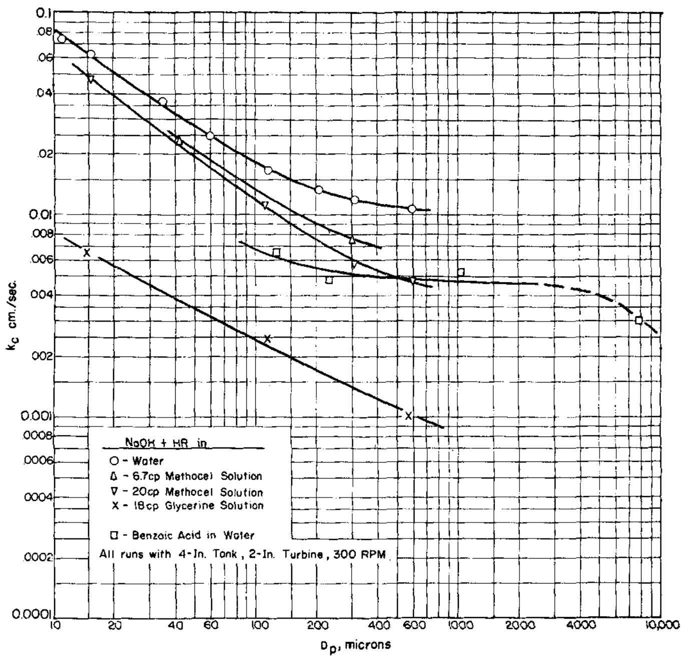

Fig. 8. Effect of particle size on the mass transfer coefficient.

For benzoic acid in water the increase in coefficient with decreasing diameter could not be as clearly demonstrated. With 80-μ particles agglomerates were seen even at high speeds, and the coefficients (not plotted here) were less than those for larger particles. Agglomeration may also have influenced the results for 130-μ particles. The benzoic acid tests do show that the region of nearly constant coefficient extends out to particles several milimeters in diameter. The 7.8-mm. spheres are suspended only part of the time at the standard conditions of 300 rev./min., and the average coefficient is only half that for smaller sizes. However at 500 rev./min. the coefficient is only 10% less than for 1-mm. particles. The lead sulfate data, Figure 5, were also expected to provide additional evidence of the size effect. However the coefficients are only 20 to 30% of the value expected for 5- to 10-μ particles, partly because the BET area is not realistic and partly because of particle agglomeration.

For viscous solutions the effect of particle diameter extends to larger sizes, as predicted by the slip-velocity theory. With a 20-centipoise methocel solution, the graph seems about to level off at 600 μ, but with the glycerine solution no similar trend is apparent. The values of k_c^* for the glycerine solution level off at about 1,000 μ, and the measured coefficients would probably show the same trend if extended to larger sizes.

The curves in Figure 8 are roughly parallel to those in Figure 1, and the ratio of the measured coefficient k_c to that predicted for freely falling spheres k_c^* is shown in Figure 9. For Reynolds numbers less than 1, k_c^* was obtained from Friedlander's (3) correlation rather than from Equation (1). While one curve fits the data for mass transfer in water or in methocel solutions, the ratio k_c/k_c^* for glycerine solutions is 1.5 to 2 times as great. The lower diffusivity is the most likely reason for the difference.

Effect of Diffusivity

The approximate effect of diffusivity was determined by comparing data for systems which had about the same density difference and viscosity. For 200- to 600-μ particles of benzoic acid or ion exchange beads the data of Figure 8 correspond to an exponent of about 0.8 for the diffusivity. A value of 0.7 is predicted from Equation (1), and the difference in this case is attributed to experimental error or to the effect of a rough surface on the benzoic acid particles. However the results for the large ion exchange beads in methocel solution and in glycerine solution correspond to an exponent of only 0.60 for the diffusivity, and this low value is considered significant, since the diffusivity was changed 12.5 fold. This decrease in the exponent with decreasing diffusivity is consistent with the unsteady state theory, which states that transient contributions to the flux become more important at low diffusivities.

When one compares the results for 15-μ particles in the two viscous solutions, the coefficients differ by a factor of 7.4, corresponding to an exponent of 0.79 for the diffusivity. For such small particles the slip-velocity theory predicts an exponent of 1.0, since the predicted Sherwood number is about 2.0.

Effect of Viscosity

To show that viscosity has only a small effect on the transfer coefficient, (apart from the usual effect of viscosity on the diffusivity), ion exchange rates were measured in dilute methocel solutions, where the diffusivity is almost as great as in water. The coefficients, corrected to the same diffusivity, are shown in Figure 10. The viscosities were measured with a viscometer at 60 rev./min. For large particles the coefficient varies with about the —0.22 power of the viscosity, and for small particles, the exponent is —0.06. Both graphs are nearly parallel to the corresponding curves for k_c^+. Figure 6 shows that the effect of speed is about the same in the viscous solutions as in water.[*]

The effects of viscosity changes caused by temperature changes are shown in Figure 11. The large apparent effect is primarily an effect of diffusivity, as is shown by the calculations in Table 2. The calculated exponents for viscosity are slightly greater than those obtained from the methocel tests, indicating that the effective viscosities of the methocel solutions in the agitated tank are less than the nominal values.

Effect of Density Difference

To determine the effect of density difference the coefficients for 300- to 500-μ particles at 300 rev./min. were corrected to a diffusivity of 10^{-5} sq. cm./sec. and a viscosity of 1 centipoise. The zinc particles were not suspended at this speed, so the data were extrapolated as shown in Figure 7.[*] The corrections factors used for butyl benzoic acid in dextrose solutions were 2.8 and 3.2, and the error in the corrected coefficients may be 10 to 20%. Even allowing for the maximum error Figure 12 shows that density difference has no significant effect below values of about 0.4 g./cc. At higher values the coefficient increases with the 0.3 to 0.4 power of the density difference, and the graph is nearly parallel to the curve for k_c^*. A plot for a higher speed, say 900 rev./min. would show the same trend, since the effect of speed was the same for both light and heavy particles once the particles became suspended.

Effect of Volume Fraction Solids

Transfer coefficients were measured for 16- to 50-mesh resin with a 3-in. turbine operating at 460 rev./min. in the 8-in. tank. Nine runs were made

---

[*] See footnote on page 96.

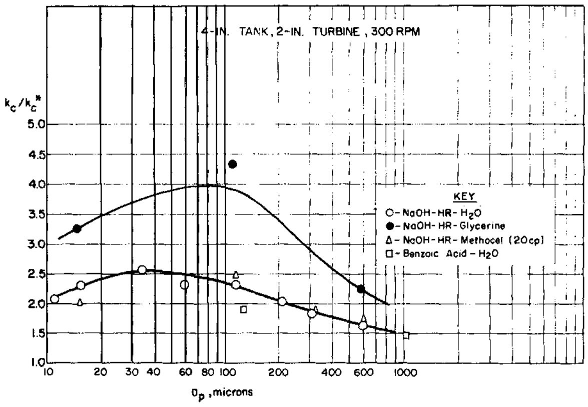

Fig. 9. Effect of particle size and difusivity on the ratio k_c/k_c^*.

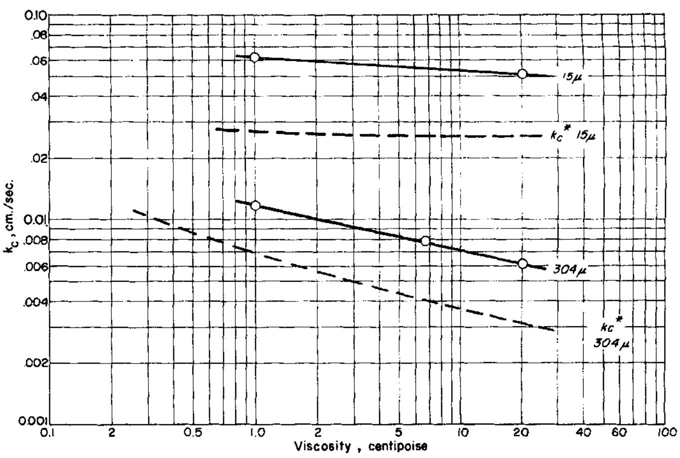

Fig. 10. Effect of viscosity on the mass transfer coefficient.

at six concentrations between 0.12 and 5.53 volume % resin. All nine coefficients were between 0.0145 and 0.0149 cm./sec., with no apparent trend. When one considers the precision of the data, it seems safe to extrapolate and say that there would be no appreciable concentration effect at concentrations up to at least 15% for particles of this size.

For particles small enough to have a low Sherwood number (large ratio of film thickness to particle diameter) an increase in coefficient with increasing concentration would be expected. In Appendix I calculations are presented to show the effect of nearby particles on diffusion in a stagnant medium.* For a volume concentration of 6.4% the Sherwood number is increased from 2 to 4.33, partly because the diffusion distance is decreased and partly because the coefficients are based on the average concentration, which is higher than the concentration midway between two spheres. For 30% particles the Sherwood number is increased to 9.4. It would be hard to measure this effect, since the solution concentration would change very rapidly with a high concentration of fine particles.

Effect of Shape and Solubility

The effects of shape and solubility were not determined, but they should be of minor importance. Pasternak and Gauvin (*21*) showed that the transfer rates to stationary cubes were 10 to 20% less than to stationary spheres of the same nominal size. Since cubes fall more slowly than spheres, a somewhat greater difference would be expected in the coefficients for suspended particles, but values of the ratio k_c/k_c^* would probably differ by less than 20%. It would be difficult to get exact data on the shape effect, since dissolving cubes or prisms soon became rounded because of the high transfer rate at the edges. Also solids like rock salt or sugar, often used for rate studies, are so soluble that the solubility corrections may be greater than the shape effect.

For very soluble salts the rate of solution is increased significantly by the one-way diffusion effect, or the flow of solution with respect to the surface. Humphrey and VanNess (*13*) corrected their data for this effect using a formula derived for flat surfaces and steady state conditions. However the shrinkage of the particle tends to decrease the transfer rate from that predicted for flat surfaces, and the combined effects have never been treated theoretically. An added complication is the change in diffusivity with concentration in the concentrated solution surrounding highly soluble particles.

Tests in Unbaffled Tanks

The coefficients in unbaffled tanks increased with only the 0.3 power of the stirrer speed, as shown in Figure 13.* At the speed needed for complete suspension in a baffled tank the coefficients are about the same with or without baffles. At lower speeds the coefficients are higher if no baffles are used because a higher fraction of the particles are suspended. At higher speeds the more uniform dispersion of the particles and the greater velocity fluctuations make the coefficients greater with baffles present. The coefficient at the same power consumption is higher without baffles except at very high speeds (900 rev./min. for 2 in./4 in. baffled system), but, of course, baffles are desirable anyway in most cases.

DISCUSSION OF RESULTS

General Correlations

A general correlation of the results might be attempted with the slip-velocity theory with the terminal velocity used to calculate the particle Reynolds number. The coefficients reported here cover one hundredfold range, but the ratio k_c/k_c^* varies only from 1.5 to 8. A plot of k_c/k_c^* vs. $(P/V)^{1/3}$ would be a band of points with an average deviation of perhaps 30%. For more accurate predictions separate lines could be drawn for different diffusivities and particle sizes, but the following procedure seems simpler and more accurate.

The recommended method of predicting the transfer coefficient for particles suspended in baffled tanks is:

1. Calculate the terminal velocity and the corresponding Reynolds number based on the particle diameter. Use a density difference of 0.3 g./cc. rather than the true value for very light particles.
2. Calculate k_c^* from Equation (1) or reference *3*.
3. Get the ratio k/k_c^* for standard agitation conditions $ND^{2/3}$ (D/T) $(T/z)^{1/8}$ = 200 in.$^{2/3}$ min.$^{-1}$, $D/T = 0.5$ with Figure 9. Use the lower curve for $D_v \geqq 10^{-5}$ sq. cm./sec. and the upper curve for $D_v = 10^{-6}$ sq. cm./sec.
4. Extrapolate to the given stirrer speed with the slopes of the lines in Figure 4 (0.5 for particles larger than 100 μ and 0.3 for 15-μ particles). A slight correction can be made for low values of D/T). This procedure should work fairly well for unbaffled vessels if a lower slope is used to extrapolate to other speeds (see Figure 13).* For other impellers the coefficients are probably between the values predicted for a turbine operating at the same speed and operating at the same power consumption. For vessels where there is no impeller (mixing done by recirculating the liquid) or only intermittent stirring, the coefficient is probably 1.2 to 1.5 k_c^*.

---

* See footnote on page 96.

* See footnote in column 1.

* See footnote in column 1.

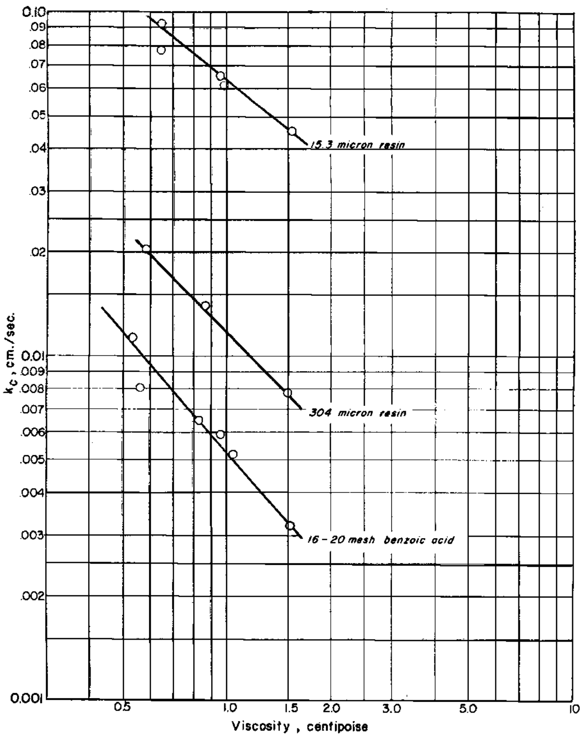

Fig. 11. Effect of viscosity on transfer coefficient (viscosity changed by changing temperature).

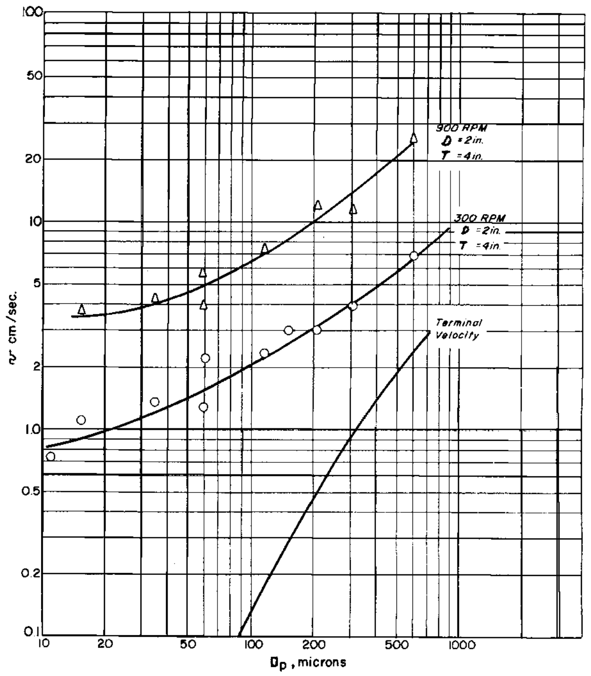

Fig. 14. Effective slip velocity based on mass transfer coefficient system, NaOH-H_2O-Hr.

The conventional correlations which use a turbine tip Reynolds number seem unsatisfactorily in several respects. Since the coefficient for large particles depends on $N^{0.5}\ D_v^{0.7}\ \mu^{-0.3}$, a plot of the coefficients against the Reynolds number gives separate parallel lines for each viscosity and each diffusivity. Addition of the Schmidt number brings these lines closer together, but a plot of $(kD)/(D_v)\ (\mu/pD_v)^{-0.3}$ vs. $(ND^2\rho)/(\mu)$ still requires separate lines for different stirrer sizes and tank sizes, since k_c varies approximately with $D^{1.1}/T^{0.8}$. To correct these deficiencies and also include the effect of particle size in a dimensionless correlation both the Sherwood number and the Reynolds number would have to be based on the particle diameter. The velocity in the Reynolds number would be replaced by a complex expression including the terminal velocity and some measure of the fluctuating velocity of the fluid. Separate lines would be needed for high Schmidt numbers and perhaps also for low density differences.

COMPARISON WITH THEORY

The data for large heavy particles in water can be cited in support of the slip-velocity theory. The coefficients depend approximately on $D_v^{0.7}$, as predicted by Equation (1), and the effects of viscosity and density difference are the same as those predicted for freely falling particles. The coefficients also vary with $N^{0.5}$, which agrees with the exponent for the Reynolds number in Equation (1). (The fluctuating fluid velocity and the slip velocity would presumably vary directly with N.)

The following evidence shows that the slip-velocity theory by itself is not adequate. The coefficients are nearly the same for very low and for moderate density differences, and the effect of diffusivity for systems with low diffusivity is also less than predicted. Furthermore the coefficients for small particles are greater than would be predicted from a slip-velocity theory. Figure 14 shows the effective slip velocity for several particle sizes at two stirrer speeds. These velocities were calculated from the measured Sherwood numbers and either Equation (1) or the correlation in reference 3. The true slip velocities should decrease rapidly with decreasing particle size, roughly paralleling the drop in terminal velocity. The values of 1 to 4 cm./sec. for 20-μ particles are very much larger than those corresponding to reasonable values of the turbulence parameters in Equation (2). Even the values for 600-μ particles seem too high. From streak photographs of particles in the 8-in. tank the average velocity in the region above the impeller was estimated to be 0.2 to 0.3 of the tip velocity (details in Appendix III).* For an average fluid velocity of

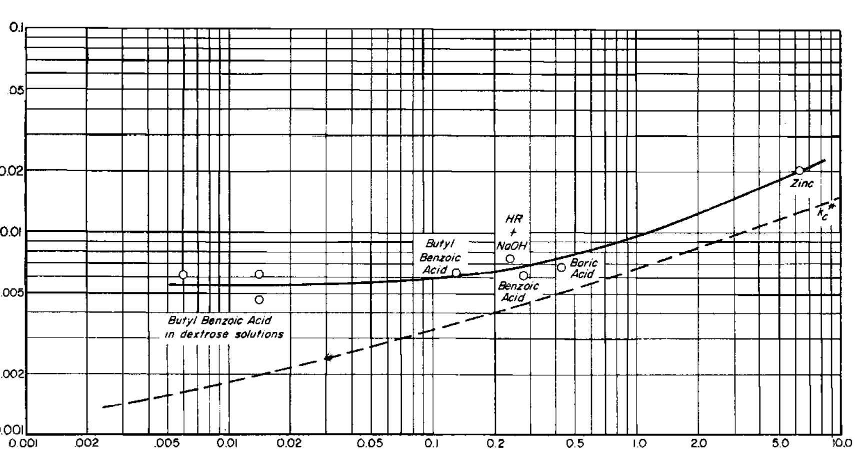

Fig. 12. Effect of density difference on mass transfer coefficient; results for 4-in. tank, 2-in. turbine, 300 rev./min.

---

* See footnote on page 96.

50 to 80 cm./sec. a slip velocity of 26 cm./sec. is unlikely, though perhaps not impossible.

A combination of the slip-velocity theory and the unsteady state theory can explain all the above results. The transfer rate depends primarily on the average slip velocity when this velocity is high enough to make the boundary layer or effective film thickness small relative to the diameter (large Sherwood number). The transfer rate for a given slip velocity is somewhat higher than predicted from steady state correlations because of the transient effects of eddies coming near the surface. When the slip velocity and the Sherwood number are small, the transient effects predominate because the eddies don't have to approach as close to the surface to affect the transfer rate. Thus the coefficients for very small particles or low density particles are much greater than predicted by the slip-velocity theory. The transient effects are also more important when the diffusivity is very low, as shown by Equation (5).

The fact that the coefficients for similar tanks are the same at the same power per unit volume is not evidence for either the slip-velocity theory or the unsteady state theory. It might be argued that only the very small-scale eddies influence the transfer rate, since the properties of the small eddies are determined only by the local energy dissipation rate (*26*). The average velocity in a tank and presumably the large velocity fluctuations that influence the slip velocity increase with $(D)^{1/3}$ at constant power per unit volume. However in larger tanks the major changes in particle velocity occur less frequently, and this may by coincidence offset the effect of the larger velocity fluctuations.

COMPARISONS WITH PREVIOUS WORK

The most extensive previous study of transfer in baffled tanks is that of Barker and Treybal (*1*). They said the coefficient varied with the 0.8 to 0.9 power of the stirrer speed, in contrast to the 0.5 power reported here. The high exponents may have resulted partly from incomplete suspension at low speeds and particle attrition at high speeds, with enough scatter so that the region of low slope at intermediate speeds was not apparent (see Figure 7 of this report). From the author's experience 16 to 20-mesh particles of boric acid would not be completely suspended in water at the lowest speeds used by Barker, even though many of the particles would be circulating with the fluid. The fact that some of Barker's coefficients are less than k_c^* is further evidence of incomplete suspension. The high exponents are also a result of plotting the coefficients against a turbine-tip Reynolds number and drawing a single line through the results for water and viscous solutions. As mentioned earlier such a plot should give separate parallel lines for each viscosity, and forcing one line through all the data gives the apparent effect of viscosity and not the effect of speed. Barker and Treybal found no effect of particle size or density difference, which is correct for the range of variables they covered, but it is not true in general. For tests in sugar solutions a particle size effect would have been evident for sizes less than 1 mm., just below the smallest sizes tested. Their statement that Schmidt number or molecular diffusivity has no effect on the transfer coefficient is incorrect. A comparison of their data for water and for sugar solutions indicates an apparent exponent of about —0.8 for the viscosity, but most of this effect comes from the change in diffusivity. Plotting k_c/k_c^* against $(P/V)^{1/3}$ for their boric acid data one gets a set of closely spaced lines similar to those of Figures 5 and 6, with higher coefficients obtained with the larger turbines. Their data do not seem accurate enough to justify any statement about the change in coefficient with tank size at the same power per unit volume. Most of the values of k_c/k_c^* for water solutions are within 20% of those predicted from the author's data for boric acid or for ion exchange resins. The values of k_c/k_c^* for sugar solution are 1.5 fold higher, in agreement with the trend shown in Figure 9.

Humphrey and Van Ness (*13*) also found a large effect of turbine speed, but their coefficients are all smaller than k_c^*, indicating incomplete suspension.

The coefficients reported by Mattern, Bilous, and Piret (*17*) for a propeller stirrer are about 0.4 to 2 times the values expected for freely falling particles. Above 1,000 rev./min. no effect of speed was noted for either batch or continuous runs, but an unexplained dependence on holdup time was found. The absence of a speed effect is probably a result of experimental error rather than a characteristic of the impeller.

Calderbank (*2*) said there is no effect of speed for either small gas bubbles or ion exchange particles, but in the published discussion Richards reported that k_c for ion exchange beads depends on the 0.15 power of the energy input, in good agreement with the 0.4 to 0.5 exponents reported here for the speed effect. Calderbank also claimed that the diffusivity was the only important variable for solid particles, though the different diffusivities were probably obtained by changing the viscosity. When one assumes a viscosity of 1 centipoise his coefficients for various D_v's are about 1.5 times k_c^*, which is reasonable for low or moderate stirrer speeds.

Attempts to allow for an expected effect of particle size by the use of dimensionless groups have generally led to unreliable correlations which indicate a size effect even though none exists over the size range covered. The correlation of Oyama and Endoh (20) corresponds to an exponent of —0.4 and that of Nagata (*18*) to an exponent of 3.08 for the effect of size on the transfer coefficient.

TABLE 2. CALCULATED EFFECT OF VISCOSITY ON TRANSFER COEFFICIENT

System	Slope from Figure 11	Slope corrected for expansion of solid	Effect of μ on D_v	Assumed effect of D_v on k_c	Exponent for viscosity, $k_c \propto \mu^n$ n
16- to 20-mesh benzoic acid	—1.15	—1.12	$\left(\frac{T}{\mu}\right)^{1.0}$ or $\left(\frac{1}{\mu}\right)^{1.15}$ (*29*)	$D_v^{0.7}$	—0.32
304-μ resin	—1.0	—0.97	$\left(\frac{1}{\mu}\right)^{0.85}$ (from conductivity tests)	$D_v^{0.7}$	—0.37
15-μ resin	—0.80	—0.77	$\left(\frac{1}{\mu}\right)^{0.85}$	$D_v^{0.8}$	—0.09

The effect of density difference has not been demonstrated by any previous workers. Kneule (*15*) used $(\Delta p/p)^{1/3}$ in his correlation for the transfer coefficient at the point of minimum suspension; since a higher speed is required to suspend heavy particles, much or all of the effect may have been a speed effect.

Only a few studies have been made with particles small enough to show a definite effect of particle size. Roller (23) dissolved gypsum and anhydrite particles and found the rate of solution per unit area to increase as the size was decreased from 25 to 3 μ. For still smaller particles the rate was lower, presumably because of agglomeration. The rate of mass transfer of hydrogen to 7-μ catalyst particles was estimated by an extrapolation technique in a recent study of diffusion-controlled hydrogenation (*14*). However the reported coefficients depend on the 0.75 power of the stirrer speed and are all less than k_c^*, which indicates extensive agglomeration. Nielson studies the kinetics of crystal growth in barium sulfate precipitation, a process which is diffusion controlled at high supersaturations (*19*). He reported an effective diffusivity 1.8 times the expected value for particles 2 to 5 μ in diameter. Though the solution was only stirred intermittently, the coefficient for these sizes is not very sensitive to stirrer speed, and the value of 1.8 agrees quite well with the value extrapolated from Figure 9 of this study.

The data of Hixson and Baum (*10*) are probably typical of the studies in unbaffled tanks. Individual runs show an exponent of 0.3 to 0.4 for the speed, once the particles are suspended, but the final empirical equation has an exponent twice as great because a single line was drawn through all the data on a Reynolds number plot. The coefficients for benzoic acid are 1.3 to 1.6 times k_c^* at speeds where a value of 1.5 to 1.6 would be predicted from the author's data. At the same conditions the heat transfer coefficient for melting ice cubes is about 1.6 times h^*, which shows that one correlation should suffice for both heat and mass transfer. Hixson and Baum got separate equations because they assumed an exponent of 0.5 for the Prandtl number and the Schmidt number. An exponent of 0.6 would have brought the correlations together. The coefficients for dimensionally similar systems were correlated by plotting against the tip velocity *ND*, but closer examination shows that these plots should really have a series of parallel lines; plotting the coefficients against $ND^{2/3}$, (or $(P/V)^{1/3}$), results in a better correlation.

Part II. Suspended in a Pipeline

Mass transfer coefficients are reported for particles of boric acid and benzoic acid dissolving in water in a 2-in. pipeline. For water velocities of 1 to 4 ft./sec. the coefficients are 1.2 to 2 times the values predicted for freely falling particles. The coefficients are slightly less than those obtained in agitated tanks at the same power per unit volume.

Part I gave a general discussion of the theories for mass transfer to suspended particles and specific results for particles in agitated tanks. For a given system the coefficients depended primarily on the power dissipated per unit volume, with a slight effect of relative stirrer size. It seemed of theoretical interest to study some of the same systems in a pipeline with turbulent flow. The results may also have practical significance, since processes such as crystallization, extraction, and reactions with suspended catalysts might be carried out in pipelines as well as in tanks.

The systems used were boric acid and benzoic acid dissolving in water. These systems were picked as the simplest ones to handle, and the properties are not different enough for an accurate measure of the effect of diffusivity or density difference. However the effects of these variables as well as viscosity and particle size should be nearly the same in the pipeline as in the tanks. The main purpose of these tests was to determine the magnitude of the coefficients and the effect of water velocity or power consumption on the coefficients.

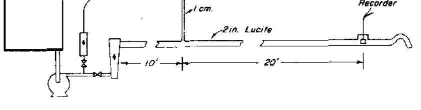

Fig. 1. Pipeline apparatus.

APPARATUS AND PROCEDURE

A diagram of the pipeline apparatus is shown in Figure 1. Deionized water at 20°C. was fed from a stainless steel tank through a rotameter to a horizontal Lucite pipe, 2 in. inside diameter. A small stream was bypassed to the solid injection line, a vertical glass tube 10 ft. downstream from the main rotameter. The solids were fed through a vibrating funnel which discharged into the flowing bypass stream. Four funnels were used to get different flow rates, and the rates were independent of the amount of solid in the funnel. The bypass stream was fed tangentially to the enlarged upper section of the feed tube to create a vortex so that the particles would be quickly dispersed and not stick to the wall of the feed tube. To prevent agglomeration the spheres of benzoic acid were coated with a wetting agent. Tests in stirred tanks showed that this amount of wetting agent had no significant effect on the measured coefficient. However the density of the particles for these tests was about 1.18 g./cc., compared with the solid density of 1.28 g./cc., since the internal voids were still filled with air.

In a typical run enough solid was charged to the funnel to give a pulse of about 10 sec. duration. The conductivity was recorded 20 ft. downstream except for tests with boric acid at the lowest velocity, when the distance was 10 ft. The recorded

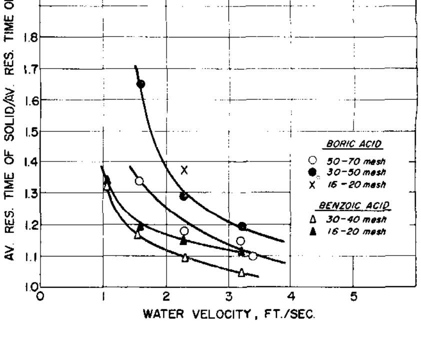

Fig. 2. Residence times for solids in 2-in. pipe.