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.

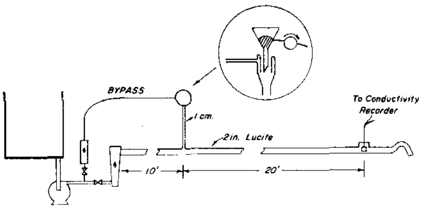

Fig. 1. Pipeline apparatus.

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

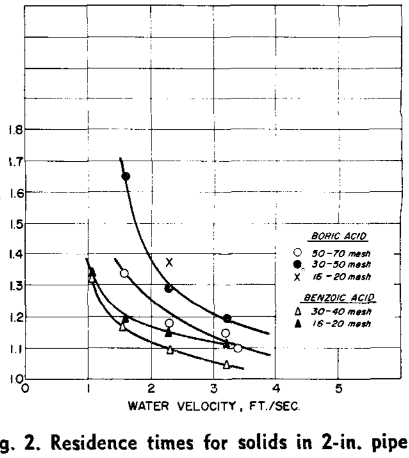

Fig. 2. Residence times for solids in 2-in. pipe.

pulse in conductivity was flat for 4 to 8 sec., but it had a total width greater than 10 sec. because of longitudinal dispersion of the solid. The minimum and maximum residence times of the solid were obtained from the initial and final times of the recorded pulse and the measured feed time for the solid charge. These values were checked by direct observation of the times for the first and last particle to pass the probe following a 0.3-sec. pulse of solids.

Transfer coefficients for the pipeline tests were calculated as follows:

$$kc = \frac{\text{solute concentration at probe}}{(\text{liq. res. time})\,(\text{avg. driving force})\,(\text{avg. area per vol. of liq.})}$$

To get the transfer area it was necessary to correct for the excess holdup of solids in the pipe. The ratio of solid feed rate to liquid feed rate was multiplied by the ratio of average residence time for the solid to residence time for the liquid. This corrected solids concentration was used to get the initial area per unit volume of solution. The final area and the arithmetic average area were calculated from the initial area and the fraction dissolved. The residence time was the time in the 20 ft. of 2-in. pipe plus the time in the feed line, which ranged from 5 to 15% of the total time.

RESULTS

Before the transfer coefficients are discussed it should be noted that the particles were not completely suspended at the lower velocities used. When the residence time ratio, shown in Figure 2, was 1.2 or greater, the solids were concentrated in the bottom portion of the pipeline, and particles were seen sliding along or bouncing off the bottom. At the highest velocity the minimum and maximum residence times were about 0.9 and 1.2 times the liqud residence times. At the lower velocities up to a twofold spread in residence times was observed.

The mass transfer coefficients are shown in Figure 3. The velocities used correspond to pipe Reynolds numbers of 20,000 to 75,000, and the volume concentration of solids was less than 1%. The coefficients for both solids are independent of size for particles larger than 70 mesh, in agreement with the results in stirred tanks. The higher coefficients for boric acid are attributed primarily to the higher diffusivity, though there might be some effect of density difference.

The coefficients for benzoic acid increase with velocity for velocities of 2 to 4 ft./sec., the region where the particles are fully suspended. At lower velocities the coefficients are nearly independent of velocity, in contrast to the results in stirred tanks, where the coefficients for partially suspended particles are greatly influenced by stirrer speed. The lowest coefficients in Figure 3 are still higher than the values expected for freely falling particles, 0.0035 cm./sec. for benzoic acid and 0.005 cm./sec. for boric acid.

The coefficients for fully suspended particles are 10 to 30% less than those obtained in a 4-in. agitated tank at the same power consumption. However tests in other pipe sizes would be needed to show if P/V is really the proper correlating parameter.

NOTATION

A = surface area
a = parameter in Equation (2)
b = parameter in Equation (2)
D = stirrer diameter, in.
D_p = particle diameter, μ or cm.
D_v = diffusivity, sq. cm./sec.
h = heat transfer coefficient
h^* = heat transfer coefficient for freely falling particles
H = distance between surface and approaching eddy
k_c = mass transfer coefficient, cm./sec.
k_c^* = transfer coefficient for a particle falling at its terminal velocity, cm./sec.
N = stirrer speed, rev./min.
P = power consumption
r = particle radius, cm.
t = time, sec.
T = tank diameter, in.
v_f = fluctuating component of fluid velocity
v_p = fluctuating component of particle velocity
v_s = slip velocity
v_t = terminal velocity
v_e = effective slip velocity (corresponding to k_c)
V = volume of solution
z = liquid depth, in.
μ = viscosity, centipoise
ρ_f = fluid density
ρ_p = particle density
$\Delta\rho$ = density difference
Tf_L = Lagrangian integral time scale [Equation (2)]
N_{Sh} = Sherwood number = $(k_c D_p)/(D_v)$
N_{Re} = Reynolds number for a particle = $(D_p\, v_s\, \rho)/(\mu)$
N_{Sc} = Schmidt number = $(\mu)/(\rho D_v)$

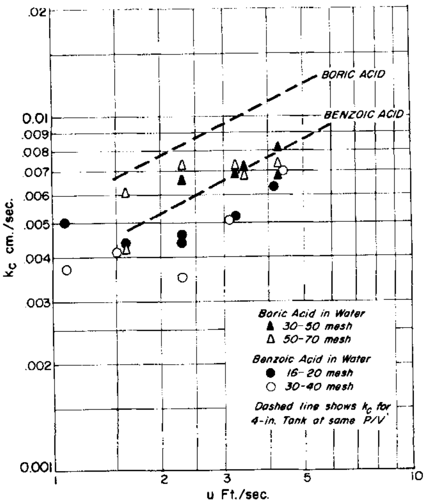

Fig. 3. Mass transfer coefficients in a 2-in. pipeline.

LITERATURE CITED

1. Barker, J. J., and R. E. Treybal, *A.I.Ch.E. Journal*, **6**, 289 (1960).
2. Calderbank, P. H., *Trans. Inst. Chem. Engrs.*, **37**, 173 (1959).
3. Friedlander, S. K., *A.I.Ch.E. Journal*, **3**, 43 (1957).
4. *Ibid.*, p. 381 (1957).
5. Griffith, R., *Chem. Eng. Sci.*, **12**, 198 (1960).
6. Harned, H. S., and B. B. Owen, "The Physical Chemistry of Electrolyte Solutions," p. 172, Reinhold, New York (1943).
7. Harriott, Peter, *Chem. Eng. Sci.*, to be published.
8. Higbie, Ralph, *Trans. Am. Inst. Chem. Engrs.*, **31**, 365 (1935).
9. Hinze, J. O., "Turbulence," p. 360, McGraw-Hill, New York (1959).
10. Hixson, A. W., and S. J. Baum, *Ind. Eng. Chem.*, **33**, 478, 1433 (1941).
11. Hughes, R. R., and E. R. Gilliland, *Chem. Eng. Progr.*, **48**, 497 (1952).
12. Hulbert, H., personal communication.
13. Humphrey, D. W., and H. C. Van Ness, *A.I.Ch.E. Journal*, **3**, 283 (1957).
14. Johnson, D. L., et al., *ibid.*, p. 411.
15. Kneule, F., *Chem. Eng. Tech.*, **28**, 221 (1956).
16. Manning, W. P., and W. H. Gauvin, *A.I.Ch.E. Journal*, **6**, 184 (1960).
17. Mattern, R. V., Olegh Bilous, and E. L. Piret, *ibid.*, **3**, 497 (1957).
18. Nagata, S., et al., *Mem. Fac. Eng. Kyoto Univ.*, **22**, 86 (1960).
19. Nielsen, A. E., *Acta Chem. Scand.*, **13**, 1680 (1959).
20. Oyama, Y., and K. Endoh, *Soc. Chem. Eng. (Japan)*, **20**, 575 (1956).
21. Pasternak, I. S., and W. H. Gauvin, *Can. J. Chem. Eng.*, **38**, 35 (1960).
22. Ranz, W. E., and W. R. Marshall, *Chem. Eng. Progr.*, **48**, 141 (1952).
23. Roller, P. S., *J. Phys. Chem.*, **35**, 1133 (1931); **36**, 1202 (1932).
24. Rushton, J. H., E. W. Costich, and H. J. Everett, *Chem. Eng. Progr.*, **46**, 467 (1960).
25. Saunders, A. R., Ph.D. thesis, Univ. Maryland, College Park, Maryland (1959).
26. Shinnar, R., and J. M. Church, *Ind. Eng. Chem.*, **52**, 253 (1960).
27. Smoluchowski, M. V., *Z. Physik, Chem.*, **92**, 129 (1918).
28. Van de Vusse, J. G., *Trans. Inst. Chem. Engrs.*, **S41**, (1957).
29. Wilke, C. R., *Chem. Eng. Progr.*, **45**, 218 (1949).
30. Zwietering, Th. N., *Chem. Eng. Sci.*, **8**, 244 (1958).

Manuscript received January 9, 1961; revision received July 23, 1961; paper accepted August 15, 1961.