LITERATURE CITED

Benson, B. B., and D. Krause, Jr., "Empirical Laws for Dilute Aqueous Solutions of Nonpolar Gases," *J. Chem. Phys.*, **64**, No. 2, 689 (1976).

Beuschlein, W. L., and L. O. Simenson, "Solubility of Sulfur Dioxide in Water," *J. Am. Chem. Soc.*, 62, 610 (1940).

Clarke, E. C. W., and D. N. Glew, "Aqueous Non Electrolyte Solutions—Part VIII—Deuterium and Hydrogene Sulfides Solubilities in Deuterium Oxyde and Water," *Can. J. Chem.*, 49, 691 (1971).

Cysewski, G. R., and J. M. Prausnitz, "Estimation of Gas Solubilities in Polar and Nonpolar Solvents," *Ind. Eng. Chem. Fundamentals*, 15, No. 4, 304 (1976).

Ellis, A. J., and R. M. Golding, *Am. J. Sci.*, 261, 47 (1963); Reproduced by H. C. Helgeson, in "Thermodynamics of Complex Dissociation in Aqueous Solution at Elevated Temperatures," *J. Phys. Chem.*, 71, No. 10, 3121 (1967).

Hala, E., "Vapor-Liquid Equilibrium in the Critical Region. Concentration Limits of Binary Systems," *Ind. Eng. Chem. Fundamentals*, 14, No. 2, 138 (1975).

———, J. Pick, V. Fried, and O. Vilim, *Vapour Liquid Equilibrium*, Pergamon Press, Oxford, England (1967).

Hayduk, W., and H. Laudie, "Solubilities of Gases in Water and Other Associated Solvents," *AIChE J.*, 19, No. 6, 1233 (1973).

Houghton, G., A. M. McLean, and P. D. Ritchie, "Compressibility, Fugacity and Water Solubility of Carbon Dioxyde in the Region 0-36 atm and 0-100°C," *Chem. Eng. Sci.*, 6, 132 (1957).

Jones, M. E., "Ammonia Equilibrium Between Vapour and Liquid Aqueous Phases at Elevated Temperatures," *J. Phys. Chem.*, 67, 1113 (1963).

Kozintseva, T. N., "Solubility of Hydrogen Sulfide in Water at Elevated Temperatures," *Geokhimiya*, 8, 758 (1964).

de Ligny, C. L., N. G. Van der Veen, and J. C. Van Houwelingen, "Correlation and Prediction of Solubility and Entropy of Solution of Gases in Liquids by Means of Factor Analysis," *Ind. Eng. Chem. Fundamentals*, 15, No. 4, 336 (1976).

Pierotti, R. A., "The Solubility of Gases in Liquids," *J. Phys. Chem.*, 67, No. 9, 1840 (1963).

Pray, H. A., C. E. Schweickert, and B. H. Minnich, "Solubility of Hydrogen, Oxygen, Nitrogen and Helium in Water," *Ind. Eng. Chem.*, 44, No. 4, 1146 (1952).

Rowlinson, J. S., *Liquids and Liquid Mixtures*, Butterworth, London, England (1969).

Selleck, F. T., L. T. Carmichael, and B. H. Sage, "Phase Behavior in the Hydrogen Sulfide-Water System," *Ind. Eng. Chem.*, 44, No. 9, 2219 (1952).

Manuscript received August 15, 1977; revision received December 8, and accepted December 16, 1978.

Effects of Convection and Brownian Motion on Particle Growth Rate in Colloidal Dispersions

TADAO SUGIMOTO

Department of Industrial Chemistry,
Faculty of Engineering
University of Tokyo,
Hongo, Bunkyo-ku, Tokyo 113, Japan

The particle growth rate due to the monomer diffusion in colloidal dispersions is known to be given by

$$\dot{r} = \frac{DV_m(C - C_r')}{r} \tag{1}$$

This equation has been used as the fundamental equation of particle growth or dissolution in the theories of Ostwald ripening (Wagner, 1961; Mullin, 1972; Sugimoto, 1971, 1978).

The effect of convection is not considered in Equation (1). It is, however, of practical importance to consider the effect of convection, since natural convection and/or forced convection (agitation) are almost always applied in real systems in order to accelerate the mass transfer.

Kahlweit (1975) has proposed use of the following Nernst's equation instead of Equation (1) for diffusion controlled Ostwald ripening under the influence of convection:

$$\dot{r} = \frac{DV_m(C - C_r')}{\delta} \tag{2}$$

where δ is assumed independent of r and implies the presence of convection. Although this equation is known to be valid for relatively large particles ($> 10^2$ μm), it seems unlikely that it is similarly applicable to the kinetics of Ostwald ripening which ordinarily involves small particles under a few microns in size. In such a small size range, the convection seems to become ineffective, and the Brownian motion of the particles is expected to become the determinant factor. Thus, the object of this work is to propose kinetic equations of $\dot{r}$ due to monomer diffusion when the effects of convection and Brownian motion may both be present.

EFFECTS OF CONVECTION AND BROWNIAN MOTION

The quantity of monomers diffusing per unit time through the spherical surface at x from the center of a particle ($x \geqq r$) is given by the Fick's law as

$$\dot{n} = 4\pi x^2 D \frac{\partial c(x, t)}{\partial x} \tag{3}$$

If the monomer stream is in the steady state, $\dot{n}$ is independent of x. Thus, it follows that

$$\dot{n} = 4\pi r^2 \dot{r}/V_m \tag{4}$$

and integration of Equation (3) over x gives

$$4\pi D\left[c(x, t) - c(r, t)\right] = -\dot{n}\left(\frac{1}{x} - \frac{1}{r}\right) \tag{5}$$

Since $c(x, t)$ at $x \geqq r + \delta$ is virtually equal to C from the

---

Tadao Sugimoto is at Clarkson College of Technology, Potsdam, New York 13676.

0001-1541-78-1014-1125-$00.75. © The American Institute of Chemical Engineers, 1978.

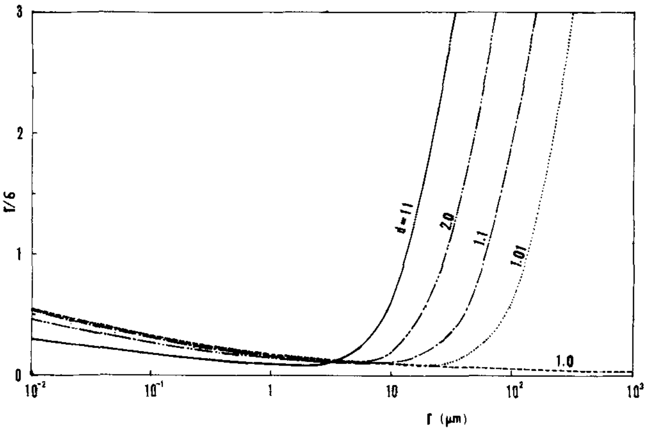

Fig. 1. Relationships between r/δ and r in aqueous dispersion.

definition of the stagnant boundary layer, it follows from Equations (4) and (5) and the boundary conditions of $c(r + \delta, t) = C$ and $c(r, t) = C_r'$ that

$$\dot{r} = \left(1 + \frac{r}{\delta}\right) \frac{DV_m(C - C_r')}{r} \tag{6}$$

Therefore, Equations (1) and (2) correspond to the extreme cases of $r/\delta << 1$ and $r/\delta >> 1$, respectively, for the general expression of Equation (6).

From the definition of mass transfer coefficient K

$$\frac{\dot{n}}{4\pi r^2} = K(C - C_r') \tag{7}$$

Combination of Equation (6) with (7) yields

$$Sh = \frac{2(r + \delta)}{\delta} \tag{8}$$

On the other hand, the mass transfer rate for single spheres is given by the semitheoretical equation (Ranz and Marshall, 1952)

$$Sh = 2 + \theta\, Re^{1/2} Sc^{1/3} \quad (\theta \simeq 0.60) \tag{9}$$

Comparing Equation (8) with (9), we get

$$\frac{r}{\delta} = \frac{\theta}{2} Re^{1/2} Sc^{1/3} \tag{10}$$

Here, we assume that effective mean velocity of the particle relative to the fluid in the Reynolds number is given by

$$u = \sqrt{\overline{u_c^2} + \overline{u_t^2}} \tag{11}$$

If the free falling velocity of particles in the fluid is used as $\sqrt{\overline{u_c^2}}$ owing to convection (Calderbank and Moo-Young, 1961; Nienow, 1969), and if the consideration is confined to the Stokes region ($Re < 1$), $\sqrt{\overline{u_c^2}}$ is given by the Stokes' law as

$$\sqrt{\overline{u_c^2}} = \frac{2\Delta d r^2 g}{9\mu} \tag{12}$$

The $\sqrt{\overline{u^2}_t}$ due to the thermal movement of the particle itself (Brownian motion) is given by

$$\sqrt{\overline{u_t^2}} = \sqrt{\frac{3kT}{m}} \tag{13}$$

Thus

$$\frac{r}{\delta} = \frac{\theta}{\sqrt{2}} \left(\frac{d_\infty}{D^2\mu}\right)^{1/6} \left[\left(\frac{2\Delta d g}{9\mu}\right)^2 r^6 + \frac{9kT}{4\pi r d}\right]^{1/4} \tag{14}$$

For an aqueous dispersion at 25°C, typically one has $d_\infty = 1\ \mathrm{g \cdot cm^{-3}}$, $\mu = 10^{-2}$ poise, and $D = 10^{-5}\ \mathrm{cm^2 \cdot s^{-1}}$. For these conditions, r/δ is shown as a function of r for various particle densities in Figure 1. Since the Schmidt number is about 10^3 under this condition, the Stokes region corresponds to $r/\delta < 3$ from Equation (10) and covers the range of r in Figure 1. It is found in this figure that the mass transfer process for particle growth is mainly governed by convection for particle radius above a few microns, and the effect drops drastically with the reduction of particle size. Below the threshold of a few microns, r/δ gradually rises with decrease in r, and the mass transfer gets controlled by Brownian motion. The critical radius between these two ranges is estimated by setting $\partial(r/\delta)/\partial r = 0$ as

$$r_c = \left(\frac{243kT}{32\pi d}\right)^{1/7} \left(\frac{\mu}{\Delta d g}\right)^{2/7} \tag{15}$$

except for $\Delta d = 0$, when there is no effect of convection.

In the convection range ($r >> r_c$), δ is given from Equation (14) as

$$\delta = \frac{3}{\theta} \left(\frac{D^2\mu}{d_\infty}\right)^{1/6} \left(\frac{\mu}{\Delta d g}\right)^{1/2} r^{-1/2} \tag{16}$$

and $\dot{r}$ is given by Equation (6) as

$$\dot{r} = \left[1 + \frac{\theta}{3}\left(\frac{d_\infty}{D^2\mu}\right)^{1/6} \left(\frac{\Delta d g}{\mu}\right)^{1/2} r^{3/2}\right] \frac{DV_m(C - C_r')}{r} \tag{17}$$

In this range, r/δ is strongly dependent on r because of the proportionality to $r^{3/2}$. In addition, since the condition $r/\delta >> 1$ for Equation (2) is by no means satisfied in the Stokes region ($r/\delta < 3$), and since δ depends on r, Equation (17) cannot be approximated by Equation (2) below 100 μm in diameter in aqueous dispersion.

In the Brownian motion range ($r << r_c$), Equation (14) gives

$$\delta = \frac{2}{\sqrt{3}\,\theta} \left(\frac{D^2\mu}{d_\infty}\right)^{1/6} \left(\frac{\pi d}{kT}\right)^{1/4} r^{5/4} \tag{18}$$

and Equation (6) yields

$$\dot{r} = \left[1 + \frac{\sqrt{3}\,\theta}{2}\left(\frac{d_\infty}{D^2\mu}\right)^{1/6} \left(\frac{kT}{\pi r d}\right)^{1/4}\right] \frac{DV_m(C - C_r')}{r} \tag{19}$$

If the particle size distribution range in a given colloidal dispersion is not so far from the minimum of r/δ in the Brownian motion range, r/δ can be practically approximated by the $(r/\delta)_{\min}$ throughout the distribution range, since the r dependence of r/δ is relatively small owing to its proportionality to $r^{-1/4}$, especially when d is high. In this case, $\dot{r}$ is given by

$$\dot{r} = \left[1 + 0.834\left(\frac{d_\infty}{D^2\mu}\right)^{1/6} \left(\frac{kT}{\pi d}\right)^{6/7} \left(\frac{\Delta d g}{\mu}\right)^{2/7}\right] \frac{DV_m(C - C_r')}{r} \tag{20}$$

where $[1 + 0.834(d_\infty/D^2\mu)^{1/6}(kT/\pi d)^{6/7}(\Delta d g/\mu)^{2/7}]\ D$ is the effective diffusion coefficient.

CONCLUSIONS

The expressions of δ and $\dot{r}$ under the influence of convection and Brownian motion have been obtained. In an aqueous colloidal dispersion, the particle growth and dissolution rate due to monomer diffusion are governed by Brownian motion below an order of micron in particle radius, while they are dominated by the convections above the order. Since the r dependence of r/δ is relatively small in the Brownian motion range, Equation (20) can be practically used instead of Equation (19) if the size distribution ranges not so far from the radius which gives the minimum of r/δ in the Brownian motion range.

ACKNOWLEDGMENT

The author wishes to express his sincere gratitude to Professor J. Estrin of Clarkson College of Technology for his valuable comments on this work.

NOTATION

C = concentration of monomers in bulk solution
C_r' = concentration of monomers at interface of solid/solution
$c(x, t)$ = concentration of monomers at radial distance x and time t
D = diffusion coefficient of monomers
d = density of a particle
d_∞ = density of fluid
Δd = density difference ($= |d - d_\infty|$)
g = acceleration of gravity
K = mass transfer coefficient of monomers
k = Boltzmann constant
m = mass of a particle
$\dot{n}$ = number of moles of monomers passing per unit time through the spherical surface at x from the center of a particle
Re = Reynolds number ($= 2rud_\infty/\mu$)
r = particle radius
$\dot{r}$ = dr/dt
r_c = critical radius between Brownian motion range and convection range
Sc = Schmidt number ($= \mu/Dd_\infty$)
Sh = Sherwood number ($= 2rK/D$)
T = absolute temperature
t = time
u = effective slip velocity of a particle
$\overline{u_c^2}$ = mean square relative velocity of a particle due to convections
$\overline{u_t^2}$ = mean square relative velocity of a particle due to thermal movement (Brownian motion) of the particle
V_m = molar volume of particle
x = distance from the center of a spherical particle
δ = thickness of a stagnant boundary layer (Mullin, 1972)
θ = dimensionless constant in Equation (9)
μ = viscosity of fluid

LITERATURE CITED

Calderbank, P. H., and M. B. Moo-Young, "The Continuous Phase Heat and Mass-Transfer Properties of Dispersions," *Chem. Eng. Sci.*, **16**, 39 (1961).

Kahlweit, M., "Ostwald Ripening of Precipitates," *Adv. Colloid Interface Sci.*, **5**, 1 (1975).

Mullin, J. W., *Crystallisation*, 2 ed., Butterworths, England (1972).

Nienow, A. W., "Dissolution Mass Transfer in a Turbine Agitated Baffled Vessel," *Can. J. Chem. Eng.*, **47**, 248 (1969).

Ranz, W. E., and W. E. Marshall, "Evaporation from Drops," *Chem. Eng. Progr.*, **48**, 141, 173 (1952).

Sugimoto, T., "General Kinetics of Ostwald Ripening of Precipitates," *J. Colloid Interface Sci.*, **63**, 16 (1978).

———, "Statistical Considerations on Kinetics of Particle Size Distribution Change in Colloidal Dispersion," *ibid.*, **62**, 286 (1977).

Wagner, C., "Theory of Precipitate Change by Redissolution," *Z. Elektrochem.*, **65**, 581 (1961).

Manuscript received June 10, 1977; revision received December 1, and accepted December 16, 1977.

Saturated Liquid Densities of Normal Fluids

VASANT L. BHIRUD

The Lummus Company
1515 Broad Street
Bloomfield, N.J. 07003

Process design calculations require liquid densities for estimating storage capacities, sizing pipelines, in calculating vapor-liquid equilibria, etc. Corresponding states theory correlations play an important role in predicting these densities at various conditions. Pitzer's corresponding states theory (Lewis and Randall, 1961) has been very successful in accurately correlating thermophysical properties of normal (nonpolar and a few slightly polar) fluids. However, his correlation for the saturated liquid compressibility factor was found to be poor by Lyckman et al. (1965). Improved correlation by Lyckman et al. (1965) and a recent development of Halm and Stiel (1970) were still considered to be somewhat less accurate by Spencer and Danner (1972) in their comprehensive study of saturated liquid density correlations. In a critical review of these correlations, Reid et al. (1977) recommend the correlation of Gunn and Yamada (1971) for its accuracy over a large temperature range. This correlation of Gunn and Yamada requires critical temperature, Pitzer's acentric factor, and an experimental density at a reduced temperature of 0.6 and thus is not purely predictive. They have also developed a predictive relationship (scaling volume as a function of T_c, P_c, and ω) whose accuracy is not available.

The objective of this study was to develop an accurate and predictive saturated liquid density correlation for

---

0001-1541-78-1229-1127-$00.75.