and

$$H_j = \sum_{1^n}^{M} H^m_{nj} y_{nj}$$

then,

$$\frac{\partial h_j}{\partial x_{nj}} = h^m_{nj}$$

and

$$\frac{\partial H_j}{\partial y_{nj}} = H^m_{nj}$$

It is always convenient to use these relationships (neglecting possible heats of mixing), when computing the derivatives.

7. Numerical computation of the derivatives $\partial K_{ij}/\partial T_j$ is more conveniently performed only on few selected trays. For the remaining ones, a very good approximation is obtained from the relation:

$$\frac{\partial K_{ij}}{\partial T_j} = a \frac{K_{ij}}{T_j^2}$$

where the parameter a is given by linear interpolation between two trays, where the computation has been performed numerically.

8. Strong dependence of K_{ij} on liquid and/or vapor composition may require the introduction of terms:

$$\frac{\partial K_{ij}}{\partial x_{nj}}, \frac{\partial K_{ij}}{\partial y_{nj}}$$

The evaluation time for these derivatives is relatively long; therefore, some loops without this computation may be more conveniently performed at the beginning. Then, the derivatives are evaluated only for a few selected stages, interpolating them linearly for the others. If convergence is not reached by this procedure, it may be useful to evaluate them for each stage. Not all interlinked columns show this problem. So, it is necessary only to use this procedure for those that require it.

NOTATION

A_j = submatrix of partial derivatives of linearized equations on stage j with respect to variables on stage $j-1$
B_j = submatrix of partial derivatives of linearized equations on stage j with respect to variables on stage j
C_j = submatrix of partial derivatives of linearized equations on stage j with respect to variables on stage $j+1$
D_j = submatrix of partial derivatives of linearized equations on stage j with respect to nonstandard variables
$E_{k,m}$ = submatrix of partial derivatives of linearized equations on stage k with respect to variables on stage m $(k>m+1)$
F_j = total feed to stage j
G = submatrix of partial derivatives of linearized specification equations with respect to nonstandard variables
h_j = molar enthalpy of the stream L_j
H_j = molar enthalpy of the stream V_j
K_{ij} = equilibrium constant for component i, tray j
K = row and column number for submatrices A,B,C
L_j = liquid stream to state $j+1$
L = number of new variables and of nonstandard specification equations
M = number of components
N = total number of trays for all the columns
P_j = submatrix of partial derivatives of linearized specification equations with respect to variables on stage j
Q_j = heat from stage j
$S_{n,r}$ = submatrix of partial derivatives of linearized equations on stage n with respect to variables on stage r $(r>n+1)$
T_j = temperature on stage j
t_j = residuals of the equations associated to the stage j, with the opposite sign
t_G = residuals of the nonstandard specification equations, with the opposite sign
U_j = liquid-side stream from stage j
$UX_{r,n}$ = liquid total flow rate from stage r to stage n
V_j = vapor stream to stage $j-1$
W_j = vapor-side stream from stage j
$WY_{r,n}$ = vapor total flow rate from stage r to stage n
z_{ij} = molar fraction of component i in F_j
x_{ij} = molar fraction of component i in L_j
y_{ij} = molar fraction of component i in V_j
δX = Newton correction to variable X
ϕ_{ij} = residual of equilibrium equation (component i, tray j)

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A Comment on the Equation of State by Hirschfelder et al.

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We find a flaw in the gas equation of state formulated by Hirschfelder et al. For densities somewhat smaller than the critical density and temperatures in the neighborhood of the critical temperature, $\partial P/\partial \rho$ at constant temperature is negative. This violates the requirement of mechanical stability. The importance of the violation depends on the use being made of the equation of state.

In previous articles, Hirschfelder, Buehler, McGee, and Sutton (1958) presented an analytic equation of state for gases and liquids which was designed to match the corresponding states

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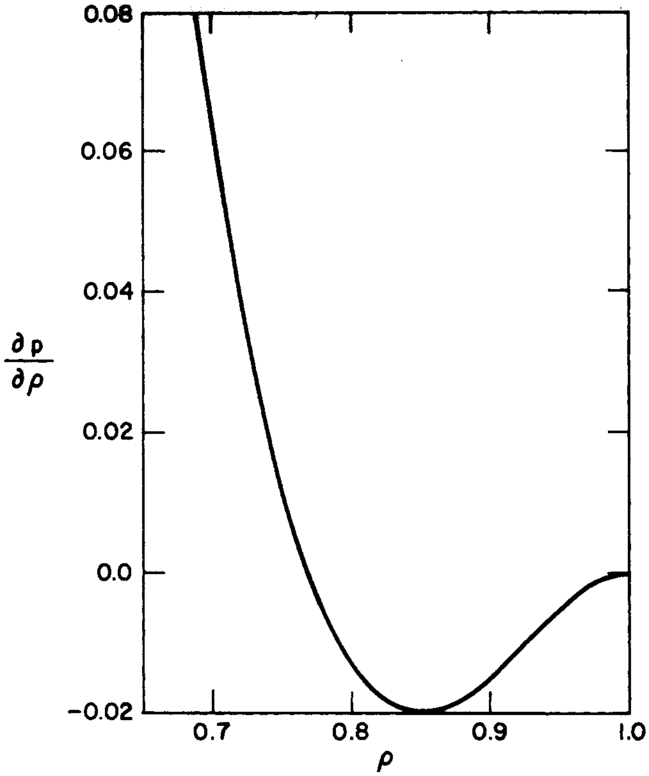

Figure 1. $\partial p/\partial\rho|_t$ as a function of ρ at $t = 1$ and for $\beta = 7.15$.

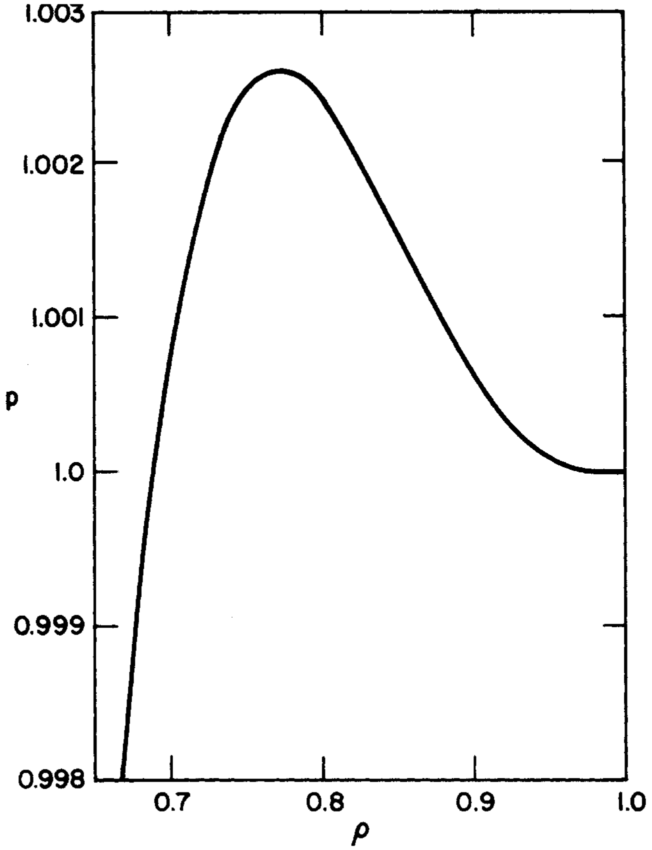

Figure 2. p as a function of ρ at $t = 1$ and for $\beta = 7.15$.

data of Hougen and Watson (1946). We are interested only in the analytic equation of state for the gas. They gave for the pressure:

$$p = -(k_o + k_1 t^{-1})\rho^2 + k_2(-t + t^{-1})\rho^3 + (\rho t/z_c)/(1 - b\rho + b'\rho^2) \quad (1)$$

where p, t, and ρ are the reduced pressure, temperature, and density, relative to the critical point; that is, $p = P/P_c$, $t = T/T_c$, and $\rho = V_c/V$. Eq. 1 is to be used for $\rho \leq 1$, but in the single-phase region. The other parameters in Eq. 1 are constants that are to be adjusted to give the best equation of state.

We know that at $\rho = 1$, $t = 1$, we have $p = 1$, $\partial p/\partial\rho|_t = 0$, and $\partial^2 p/\partial\rho^2|_t = 0$. These three conditions give three equations relating k_o, k_1, z_c, b, and b' to each other. If we define a parameter β such that $z_c = \beta(3\beta - 1)/(1 + \beta)^3$, then $k_1 = \beta - k_o$, $b = (1/\beta)(3\beta^2 - 6\beta - 1)/(3\beta - 1)$, and $b' = (\beta - 3)/(3\beta - 1)$. We now have three free parameters, β, k_o, and k_2. [This is the same parametrization as in Hirschfelder et al. (1958).]

On physical grounds $0 < z_c < 0.375$. This implies that β lies in one of three ranges; $1 - 2/\sqrt{3} < \beta < 0$, or $1/3 < \beta < 1 + 2/\sqrt{3}$, or $3 < \beta$. The lower and middle ranges of β imply that $b < 0$. Since b has an interpretation as an excluded volume, we identify $\beta < 0$ and $1/3 < \beta < 1 + 2/\sqrt{3}$ as unphysical. Therefore, $\beta > 3$. It is convenient for the remainder of this note to further restrict $\beta > 3 + 2\sqrt{2}$ or, equivalently, $0 < z_c \lesssim 0.3$. [This restriction is the same as in Hirschfelder et al. (1958).]

We now take Eq. 1 at $t = 1$ and compute the third derivative of p with respect to ρ. (Note that the k_o and k_2 dependences drop out of Eq. 1 at $t = 1$.) We find for $t = 1$, $\rho = 1$,

$$\partial^3 p/\partial\rho^3|_t = -6\beta(\beta^2 - 6\beta + 1)/(1 + \beta)^2 \quad (2)$$

For $3 + 2\sqrt{2} < \beta$, $\partial^3 p/\partial\rho^3|_t$ is negative at $t = 1$, $\rho = 1$. Since $\partial p/\partial\rho|_t$ and $\partial^2 p/\partial\rho^2|_t$ are zero at the critical point, this implies that for $\rho < 1$, but near 1, and t around 1, $\partial p/\partial\rho|_t$ will appear as shown in Figure 1. Namely, $\partial p/\partial\rho|_t$ will be negative over some gas region near the critical point, *outside* the two-phase region. This violates the requirement of mechanical stability. The appearance of p as implied by the above behavior of the derivative of p is shown in Figure 2. We wish to emphasize that this problem is caused, *not* by any particular values of the parameters β, k_o, or k_2, but by the functional form of Eq. 1.

To determine the magnitude of the violation, we plotted Eq. 1 and its density derivative for $\beta = 7.15$ ($z_c \simeq 0.27$) and $t = 1$. The curves are shown in Figure 1. As can be seen, the troublesome pressure rise, as ρ is lowered from 1, is small (of the order of 0.3%). Thus, one feels that this violation of thermodynamic stability will not be important for some uses. However, care must be exercised in using Eq. 1 to calculate derivatives in the neighborhood of the critical point. In particular, the isothermal compressibility and constant pressure specific heat are negative.

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NOTATION

P = pressure
P_c = pressure at critical point
T = temperature
T_c = temperature at critical point
V = volume
V_c = volume at critical point
b = fitting parameter (excluded volume)
b' = fitting parameter
k_o = fitting parameter
k_1 = fitting parameter
k_2 = fitting parameter
p = reduced pressure (= P/P_c)
t = reduced temperature (= T/T_c)
z_c = critical compressibility factor

Greek Letters

β = fitting parameter
ρ = reduced density (= V_c/V)

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Measurement of Fluid Resistance Correction Factor for a Sphere Moving through a Viscous Fluid toward a Plane Surface

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When the Reynolds number of the flow around the sphere is much less than 1.0, the fluid resistance is evaluated from the Stokes' formula:

$$F = 6\pi\mu r_p u_p$$

where r_p is the radius of a sphere, u_p is the sphere velocity, and μ is the fluid viscosity. This equation was obtained by neglecting the inertial terms in the Navier-Stokes equation for a rigid sphere in an unbounded fluid. Therefore, this relation applies only to fluid media which extend to infinity in all directions. In fact, when a sphere vertically approaches the rigid walls and/or a free surface, its velocity decreases as a result of an increase in the drag caused by additional friction between the fluid and the plane surface. Brenner (1961), therefore, calculated the correction factor to modify the form of Stokes' equation, solving the equation of creeping motion by use of bipolar coordinates.

Mackay and Mason (1961) measured the trajectories of single spheres approaching to the glass plate by using a 16-mm cine camera fitted with a 2.5-mm lens. Mackay et al. (1963) compared these experimental data with the theoretical values by Brenner. In this study, we experimentally examined the decreases in the velocity of single spheres in two cases that a sphere is approaching to the solid surface and the free surface, and the experimental results which are converted in the form of drag are compared in detail with the theoretical value given by Brenner.

The objective of this paper is to show that when a sphere approaches the vicinity of a plane surface (except the region where the London-Van der Waals attractive force is predominant), the drag of a sphere comes to about 50 or more times as large as that in an unbounded fluid and that the effect of increase in the drag should be considered when one analyzes the collection mechanism of particle such as in air and water filtration because the particle slowly moves toward the surface of the collector to be captured in those cases.

EXPERIMENT

When a sphere slowly approaches a plane surface with a velocity u_p in an unbounded and quiescent fluid, the form of Stokes' formula should be modified with the correction factor β calculated by Brenner (1961):

$$F = 6\pi\mu r_p \beta u_p \tag{1}$$

where β is a function of the separation h between the sphere and the plane surface only.

By use of Eq. 1, the equation of motion of a sedimentary sphere in the coordinate system as taken in Figure 1 is:

$$m_p\left(1-\frac{\rho_f}{\rho_p}\right)\frac{du_p}{dt} = -m_p\left(1-\frac{\rho_f}{\rho_p}\right)g - 6\pi\mu r_p\beta u_p \tag{2}$$

where ρ_p and ρ_f are the densities of the sphere and the fluid respectively; g is gravitational acceleration; m_p is the mass of a sphere; and t is time.

β is given from Eq. 2:

$$\beta = -\frac{2}{9}\cdot\frac{r_p^2 g}{\mu}\rho_p\left(1-\frac{\rho_f}{\rho_p}\right)\cdot\left(1+\frac{du_p}{dt}\frac{1}{g}\right)\Big/u_p \tag{3}$$

On the other hand, the terminal sedimentation or rise velocity u_∞ in the Stokes region is:

$$u_\infty = -\frac{2}{9}\cdot\frac{r_p^2 g}{\mu}\rho_p\left(1-\frac{\rho_f}{\rho_p}\right) \tag{4}$$

Accordingly, Eq. 3 is expressed as:

$$\beta = \frac{u_\infty}{u_p}\left(1+\frac{du_p}{dt}\cdot\frac{1}{g}\right) \tag{5}$$

Considering that $|du_p/dt| << 1$, the final form of β is:

$$\beta = \frac{u_\infty}{u_p} \tag{6}$$

This equation means that if u_p and u_∞ are experimentally evaluated, the value of β at an arbitrarily given position can be known.

Solid Surface

The schematic diagram of experimental setup is illustrated in Figure 2. An acrylic table of 100-mm height was laid at the bottom of a transparent acrylic vessel of 100 × 100 × 710mm^3 as is seen in Figure 2. After millet jelly whose density ($\rho = 1.185 - 1.421$ g/cm^3) and viscosity ($\mu = 0.698 - 47.8$ g/cm·s) had already been known was poured into the vessel and the homogeneity of its concentration was confirmed, a glass sphere ($r_p = 1.245$cm, $\rho_p = 2.500$g/cm^3) was gently dropped into it.

The sedimentation velocity was examined as follows. After recording the figure of the sedimentary sphere on the videotape through television camera with a ring for close-up photograph using an electronic flash (i.e., stroboscope), the videotape was slowly rerecorded on a monitor television. Its magnification was 24.0. The positions of bottom apex of the sphere were marked at on-and-off intervals of the electronic flash which could be known by the sudden shining of the photos on the monitor television.

Dividing the each distance s between two marks ($s \fallingdotseq 1/600\ r_p$, when the sphere was very near to the wall; $s = 0.07\ r_p$, when the sphere was far apart from the wall) by the flash time interval, the sphere velocity at each position was estimated. The rotation number of the stroboscope used was 300-500 rpm examined by

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