ically inconsistent singularity at $\alpha = 0.5$ so this model cannot be regarded as being fundamental in nature. This difficulty is resolved in the present model by the inclusion of a region of void space associated with the reference particle.

It is instructive to note that the predictions of the present model are asymptotic with those of Happel for small α (the differences being 2.5%, 1.4%, and 0.3% at $\alpha = 10^{-3}$, 10^{-4}, and 10^{-8}, respectively). This asymptotic behavior occurs not only in the present case involving cylinders but also in the case of spheres (Neale and Nader, 1974a), indicating further that the two models are fundamentally related.

It should be mentioned that the predictions of Kuwabara's model for the pressure drop across parallel staggered cylinders are in excellent agreement with experimental values (Kirsch and Fuchs, 1967). Moreover, in similar systems of parallel cylindrical fibers the diffusional collection efficiency of aerosol particles is predicted well by Kuwabara's model—such an efficiency is related to $D^{1/3}$ (Kirsch and Fuchs, 1968).

That there is such satisfactory agreement between the physically realistic model used in this paper and the more hypothetical cell models of Happel and Kuwabara does seem to indicate that these latter models possess considerable fundamental significance (the Happel model in particular) despite the fact that they do not actually represent any real physical situation. However, the overwhelming advantage of these cell models is that they are very easy to apply and provide good, physically consistent predictions in numerous diversified applications [for example, see Levine and Neale (1974) for an important application involving electrokinetic flow].

NOTATION

k = permeability of fiber mat
p = fluid pressure
$[r, \theta, z]$ = cylindrical coordinates
R = radius of reference fiber
S = outer radius of void shell
u_r, u_θ = velocity components
U^* = superficial flow velocity through mat
x = principal flow direction
W = drag force per unit length of fiber

Greek Letters

α = fiber mat concentration = R^2/S^2
μ = fluid viscosity
χ = dimensionless radial coordinate = r/R
ψ = stream function
τ = shear stress
ξ = dimensionless permeability = k/R^2
$*$ = denotes averaged quantities within porous medium

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Separation of Boron Isotopes by Direct Mode Thermal Parametric Pumping

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Results of boron isotope separation by direct mode thermal parametric pumping are presented in this R & D Note. Separation is based on the exchange reaction between gaseous BF_3 and solid $BF_3 \cdot DMSO$ (dimethyl sulfoxide) which can be written as

$$B^{10}F_3 + B^{11}F_3 \cdot DMSO \leftrightarrows B^{11}F_3 + B^{10}F_3 \cdot DMSO \tag{1}$$

with an equilibrium constant

$$K = \frac{[B^{11}F_3][B^{10}F_3 \cdot DMSO]}{[B^{10}F_3][B^{11}F_3 \cdot DMSO]} \tag{2}$$

This value is the ratio of B^{10}/B^{11} in the solid to that in the fluid phase. Parametric pumping separation is predicted on the variation of K with temperature so initial effort was focused on measuring this variation.

Palko et al. (1958, 1961, 1967), interested in obtaining the ${}_5B^{10}$ isotope because of its large neutron capture

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cross section, have been engaged in research work studying the behavior of boron isotope-complex systems. All their work was based on distillation as a separation method so they determined equilibrium constants (or separation factors) for BF_3-liquid complex systems. Temperature dependence was also measured. Lappert and Smith (1965) first prepared the solid complex used in this study.

THEORY

Pigford et al. (1969) presented a simplified model to describe parametric pumping based on instantaneous, local equilibrium. For the present system, equilibrium between the solid and gas phase concentration of B^{10} is obtained from Equation (2) as

$$[B^{10}F_3 \cdot \mathrm{DMSO}] = \left(\frac{[B^{11}F_3 \cdot \mathrm{DMSO}]}{[B^{11}F_3]} K \right) [B^{10}F_3] \quad (3)$$

This expression is analogous to the following in Pigford's notation

$$x = \frac{\rho_S}{\rho_F} M(T) y \quad (4)$$

and the dimensionless parameter m is defined

$$m(T) = \frac{\rho_S (1 - \epsilon) M(T)}{\epsilon \rho_F} \quad (5)$$

Once this value is established at the two temperatures of parametric pumping operation, the value of b, which determines separation, can be calculated from

$$b = \frac{|m_2 - m_1|}{2 + (m_1 + m_2)} \quad (6)$$

According to equilibrium theory, the mole fraction in the syringe is given by

$$y_n = y_0 \left(\frac{1 - b}{1 + b} \right)^n \quad (7)$$

for Region I operation. Operation in this region is assured by keeping the syringe volume less than the column void volume.

EXPERIMENT

The complex was prepared by allowing gaseous BF_3 to react with liquid DMSO in a stirred, one-liter Erlenmeyer flask especially adapted for this purpose. The reagents were obtained from Matheson and Crown Zellerbach, respectively, and were used without attempting to improve the stated purity. Gas flow was controlled by a needle valve so that the temperature of the reacting mixture did not exceed 348 K. Near the end of the reaction, heat was required to keep the mixture above 326 K, the melting point of the complex. Completion of the reaction was determined by shutting off the flow of BF_3 and observing the pressure of the system. If it did not drop after six to eight hours, the reaction was considered complete. The amount of BF_3 added was determined by the weight gain of the flask. The complex, still at a temperature above its melting point, was then poured into polyethylene ice trays, allowed to solidify, and crushed by means of an ice crusher. It was stored until further use under slight positive pressure of BF_3 to prevent decomposition.

The complex obtained by this method has a $B^{10}F_3$ concentration of that in the supply BF_3 gas since virtually all of it goes into the complex. The amount of leftover gas can be neglected compared to that reacted.

Equilibrium data were obtained in the jacketed column used for the actual parametric pumping experiment except for two points obtained in a similar glass column. Crushed complex of known isotope ratio was placed into the column. Air was purged by flushing with BF_3 and using a slight vacuum. BF_3 was then allowed to enter the column and kept for several hours in order to achieve equilibrium. The gas phase was sampled, analyzed, and the experiment was repeated at different temperatures.

After several exploratory runs with varying amounts of DMSO, the column was packed with glass beads, 4.76 mm diameter, and filled with liquid DMSO. After draining the column, it was observed that approximately 4 g of DMSO remained inside of it. Upon reaction in situ with BF_3, this yielded about 7 g of solid complex distributed fairly evenly along the column.

Using the spheres, the void volume was measured by water displacement to be 39 ml. The cycle time chosen was 40 min, which includes two stopping periods of 2 min each. The desired flow rate was achieved by adjusting the pump speed such that it displaced 39 ml in 18 min.

The displacement of gaseous BF_3 over the solid complex was performed by using a Harvard 944 dual-infusion/withdrawal syringe pump. The syringes (50 cm^3, gas-tight, Luer-Lock type) were connected to the column by means of the necessary Luer-Lock adapters and Swagelok fittings. The column used was a 12.7-mm inside diameter 316 stainless steel tube. All materials in contact with the gas were glass, teflon, or stainless steel, with the exception of the pressure gauge, which had a bronze Bourdon tube. The general setup is depicted schematically in Figure 1.

To begin a run air was displaced as in the equilibrium determination. BF_3 was allowed to enter the system until a pressure of about 2.1×10^4 n/m^2 was observed at the high temperature, with the top syringe filled and the bottom one empty. In order to assure uniform distribution, the gas was pumped back and forth by hand several times before starting the pumping operation but after cutting off the BF_3 supply by closing valve A.

The two baths ran at their respective high and low extreme temperatures at all times. A Nestlab LT-9 circulator was used for the low temperature reservoir which was kept at about 203 K. A Haake circulating bath was maintained at 303 K for the other reservoir. Methanol was the circulating fluid, and temperature was determined by a copper-constantan thermocouple referenced against ice water on a potentiometric recorder (Honeywell Elektronik 19). The change in temperature of the column was produced by connecting a set of 2

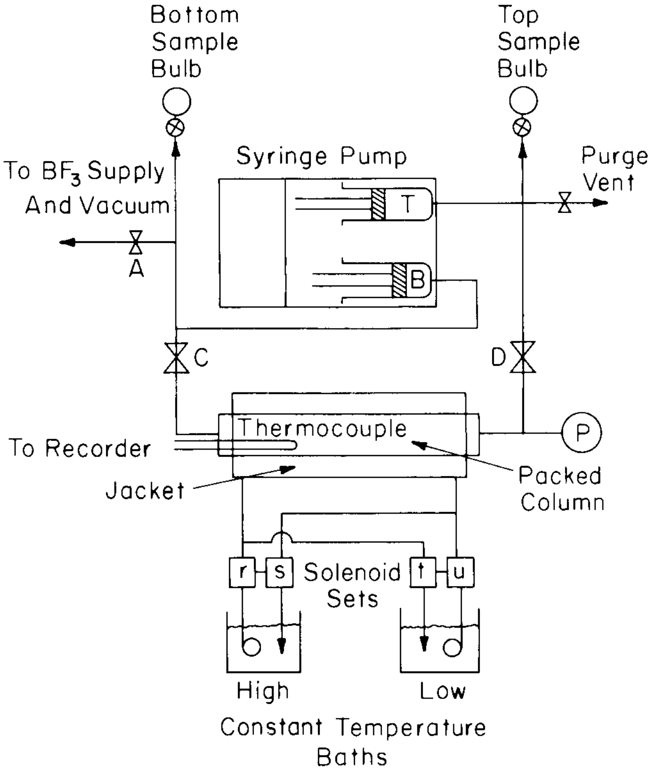

Fig. 1. Apparatus for pumping operation.

three-way directional flow, Valcor solenoid valves to each bath in such a way that the circulating fluid of one bath runs from one valve through the jacket and back to the other valve and bath when activated. Simultaneously the other bath fluid passes through one valve to the other and directly back to the bath, hence bypassing the jacket, when deactivated. The activation of the solenoid valves, as well as the direction of the movement of the pump, was accomplished by means of microswitches on a recycling can timer. The frequency of the temperature-flow cycles was changed by simply replacing a gear in the timer motor resulting in the desired angular velocity of the cams that activate the microswitches.

The top syringe is sampled first by closing valve D, opening the sample-bulb stopcock and pushing the contents of the top syringe into the bulb. The bottom sample was taken after letting the pump fill up the bottom syringe from the contents of the column, then closing valve C and proceeding as for the top sample. After taking the two samples, the experiment was repeated from the beginning since there is practically no BF_3 left.

Isotopic analysis was carried out at the Mass Spectrometry Center of the University of Kentucky. Peak heights of the BF_2^+ ions of weight 48.00974 and 49.00511 were measured and used to determine $B^{10}F_3$ mole fractions. Five determinations were made and standard deviations were calculated for each sample.

RESULTS AND DISCUSSION

The results obtained for the equilibrium determinations are presented in Figure 2 along with a least-squares line ($R^2 = 0.8$):

$$\ln K = \frac{-11.325}{T} + 0.077 \qquad (8)$$

Comparing this equation to

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \qquad (9)$$

one calculates the following molar quantities for the reaction at 293 K: $\Delta H = 94.1$ joules, $\Delta S = 0.62$ joules/K, and $\Delta F = -88.7$ joules. It should be pointed out that the temperature dependency observed is opposite to the results obtained by Palko and coworkers for several gas-liquid systems. This is reflected in the difference in algebraic sign of the enthalpy of the reaction associated with the postulated mechanism although the absolute values are of the same order of magnitude.

Results for parametric pumping runs of 10, 20, 40, and 60 cycles are shown in Figure 3. Each point is shown with its standard deviation.

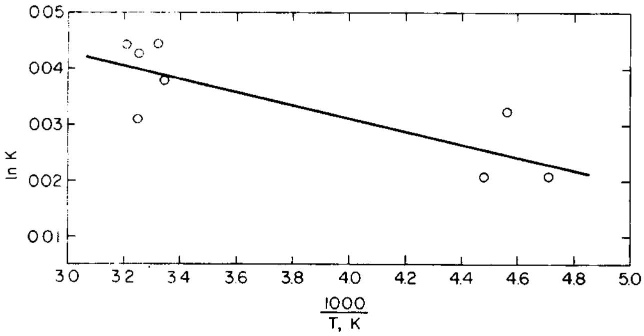

Fig. 2. Temperature variation of equilibrium constant for the reaction $B^{10}F_3 + B^{11}F_3 \cdot DMSO \leftrightarrows B^{11}F_3 + B^{10}F_3 \cdot DMSO$

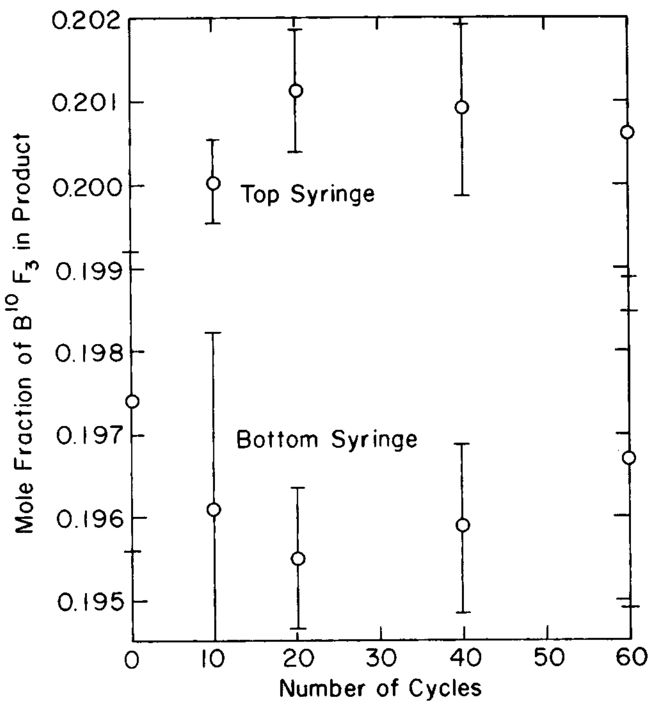

Fig. 3. Experimental composition of top and bottom products obtained by parametric pumping.

Statistically, the separation obtained is significant; a *t*-test showed that the probability of the top and bottom samples being of different concentration was above 95%. Separation factors ranged from 1.020 to 1.028.

As stated earlier, the equilibrium theory allows prediction of parametric pumping separations based on the parameter *b*. One way to compare theory and experiment is to compare the value of *b* calculated from equilibrium measurements with that calculated from parametric pumping experiments. To calculate a value from the latter, the mole fraction in the bottom syringe after 10 cycles is used in Equation (7) to give $b = 0.00033$.

From the equilibrium measurements a value of *b* is determined as follows:

$$M_1' = M_1 \frac{\rho_S}{\rho_F} = \frac{\left(\dfrac{7\text{g complex}}{39\text{cc solid}}\right)\left(\dfrac{\text{g}-\text{mole complex}}{145.94\text{ g complex}}\right)\left(\dfrac{1\text{ g}-\text{atom B}}{\text{g}-\text{mole complex}}\right)\left(\dfrac{0.7945\text{ g}-\text{atom B}^{11}}{\text{g}-\text{atom B}}\right)}{\left(\dfrac{4.35\times10^{-5}\text{ g}-\text{mole BF}_3}{\text{cc gas}}\right)\left(\dfrac{0.7945\text{ g}-\text{atom B}^{11}\text{F}_3}{\text{g}-\text{mole BF}_3}\right)} K_1 \qquad (10)$$

$$= 28.27\, K_1 \text{ (ml gas/ml solid)} \qquad (10a)$$

and

$$M_2' = 28.27\, K_2 \qquad (10b)$$

assuming the gas density is constant. Evaluating the equilibrium constants from Equation (8) at $T_1 = 298$ K and $T_2 = 214$ K, one gets from the above equations $M_1' = 29.40$ and $M_2' = 28.95$ ml gas/ml solid. For a void volume of $\epsilon = 0.5$, Equation (5) gives $m_1 = M_1'$ and $m_2 = M_2'$ so

$$b = \frac{|28.95 - 29.40|}{2 + (29.40 + 28.95)}$$

$$= 0.0075$$

As expected the value of *b* realized in the actual runs is lower than the above value primarily due to axial mixing which is significant in gas-solid systems (Jenczewski and Myers, 1970; Patrick et al., 1972), and the uncertainty in initial column conditions.

ACKNOWLEDGMENT

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NOTATION

b = equilibrium change parameter, dimensionless
ΔF = standard free energy of reaction, joules
ΔH = standard heat of reaction, joules
K = equilibrium constant given by Equation (2)
m = dimensionless equilibrium parameter
M = equilibrium constant in Equation (4), mole/g
M' = isotope equilibrium constant analogous to M, ml gas/ml solid
n = number of cycles
R = gas law constant, joules/K
ΔS = standard entropy of reaction, joules/K
t = time, s
T = temperature, K
x = composition of solute in stationary phase, g/g solid
y = composition of solute in mobile phase, g/mole

Greek Letters

ϵ = fractional void volume of column, ml void/ml column
ρ = density, g/ml (for solid) and mole/ml (for gas)

Subscripts

0 = refers to initial column conditions
1, 2 = refer to extreme conditions during cycle
S, F = refer to solid (stationary) and fluid (mobile) phases
n = conditions after n number of cycles

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Viscoelastic Effect of Polymers on Single Bubble Dynamics

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Single bubble dynamics is involved in many areas of chemical engineering such as evaporative transport of mass or energy, polymer processing technology, and foaming dynamics. Often when the bubbles are formed in environments where polymers are present, polymer viscoelasticity could significantly affect the bubble behavior and in turn the overall flow characteristic. Recently it was reported that high molecular weight polymers added to water could cause suppression of flow-generated cavitation on blunt-nosed bodies (Ellis et al., 1970) as well as jet and propeller cavitations (Hoyt, 1971). The appearance of the cavitation bubble was also changed by the presence of polymer and the bubbles seemed to collapse less violently (Brennen, 1970). While the basic mechanisms involved in these phenomena are not yet known, it was suggested that polymer viscoelasticity may have effects on the growth and collapse of individual cavitation bubbles. Experiments were carried out earlier to observe the growth (Ting and Ellis, 1974) and the collapse (Ellis and Ting, 1974) of individual bubbles in polymer solutions. These experiments indicated that the effect of polymers on single bubble dynamics seemed to be very small. In this report, some theoretical considerations will be given to determine the important parameters through which polymer viscoelasticity may affect the dynamics of single bubbles.

ANALYSIS

Consider the problem of a single bubble growing or collapsing in an incompressible liquid of infinite extent. The vapor bubble is taken to be spherical at all times and gravitational effects are neglected. A thermal equilibrium is assumed such that the vapor pressure inside the bubble is uniform and equal to the equilibrium vapor pressure of the liquid surrounding the bubble at the liquid temperature. Spherical coordinates (r, θ, ϕ) are chosen with the origin at the center of the bubble which is at rest. The only velocity component is in the radial direction, which, in order to satisfy the continuity equation, is generally given as

$$u = \frac{R^2(t)\dot{R}(t)}{r^2} \tag{1}$$

where $R(t)$ is the bubble radius at time t. The equation of motion is

$$\rho\frac{\partial u}{\partial t} + \rho u\frac{\partial u}{\partial r} = -\frac{\partial p}{\partial r} + \frac{\partial \sigma_{rr}}{\partial r} + \frac{2\sigma_{rr} - \sigma_{\theta\theta} - \sigma_{\phi\phi}}{r} \tag{2}$$

where p is the hydrostatic pressure, and σ_{rr}, $\sigma_{\theta\theta}$, and $\sigma_{\phi\phi}$ are the normal stress components. The Oldroyd 3-constant model for a viscoelastic liquid is used (Oldroyd, 1950)