Transient Diffusivity Measurements in Catalyst Pellets With Two Zones of Differing Diffusivities

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Transient pulse diffusivity measurements were carried out in a pellet string reactor. The outer skin of the catalyst spheres was partially obstructed by contaminants, and the objective was to determine the diffusivity both in this obstructed skin and also in the unobstructed core.

Conservation equations were formulated which describe the transient diffusion process in catalyst pellets with two interconnecting regions of differing diffusivities. The shape of the elution curve from a packed bed with axial dispersion was computed by numerical inversion of the Laplace transformed solutions for a Dirac delta function input.

The calculations indicated that if an appropriate residence time is chosen, the elution curve shape should be sensitive to the differing diffusivities of the two zones in the catalyst pellets.

The experimental peak shapes were analyzed by the Fourier analysis technique and the diffusivities were extracted by the Constrained Simplex optimization routine. The results showed good resolution of the different diffusivities in the skin and the core of the catalyst pellets.

SCOPE

Many industrial catalytic processes operate in the intrapellet diffusion controlled regime as a result of the high reaction rates required for commercial applications. Consequently, the diffusive properties of porous catalysts are often as important as their chemical composition.

A voluminous and rapidly growing literature deals with techniques to determine the diffusive characteristics of porous catalysts and to relate these to their pore structure. These are reviewed, for example, in the books of Satterfield (1970) and Smith (1970). It sometimes happens that the diffusive properties of porous catalysts change during their operation, for example, by the deposition of a contaminant which gradually blocks the pores and thus increases the catalyst's diffusional resistance. Such an example was recently discussed by Hegedus and Cavendish (1977), who found an automobile exhaust catalyst in which a thin outer shell of the pellets was partially obstructed by the deposition of lead and phosphorus. By comparing diffusion influenced integral reactor data with a mathematical model of such multizone catalysts, they were able to indirectly determine the diffusivity in this partially obstructed shell.

Catalyst pellets with two zones of differing diffusivities may be of interest beyond the example just mentioned. Partial pore plugging in a shell around the pellet may occur in cracking catalysis (Sampath and Hughes, 1973; Butt et al., 1975) and hydrodesulfurization (Schuit and Gates, 1973; Newson, 1975).

Two-zone catalysts with zones of differing diffusivities were also proposed in theoretical calculations to provide improved performance in certain applications (Wolf, 1977). Catalyst pellets with a skin of differing diffusivity have indeed been documented by several investigators (Satterfield and Saraf, 1965; Cadle and Satterfield, 1968; Butt et al., 1975; Androutsopoulos and Mann, 1976). It seems, then, that there is an interest in developing an experimental technique which is able to determine the effective diffusivity within catalyst pellets which have two distinct zones of differing diffusivities.

Several experimental techniques have been proposed to measure effective diffusivities in porous catalysts, and these will not be reviewed in detail here. The most frequently used static counterdiffusion technique was originally developed by Wicke and Kallenbach (1941). It was modified for spherical catalyst pellets by Weisz (1957). Geometric correction factors were recently developed for the Weisz diffusivity cell by Meyer et al. (1976) to account for the spherical geometry of the pellets. Experiments in our laboratory with static counterdiffusion techniques, however, failed to properly measure the diffusivity in a narrow skin surrounding the pellets because the contribution from the diffusional resistance of the shallow (5 to 20 μm) skin was much smaller than that of the bulk (about 3 600 μm) of the catalyst pellets.

The failure of the steady state counterdiffusion technique to sense the diffusivity in the outer skin suggests the application of some transient technique which may be more sensitive to the radial distribution of diffusivities in catalyst pellets. Although a variety of transient techniques have been proposed (for example, Suzuki and Smith, 1972; Dogu and Smith, 1976), we will concentrate our attention on the chromatographic (or pulse) technique which examines the eluted concentration pulse from a packed column after a tracer has been injected into the carrier gas stream.

Chromatographic techniques coupled with moment analysis were described by Haynes and Sarma (1973) and Hashimoto and Smith (1973). As pointed out by several authors (for example, Gangwal et al., 1971; Wakao and Tanaka, 1973), the errors in the higher moments which are required to compute diffusivities are large. This can be circumvented by employing Fourier analysis (Gangwal et al., 1971; Scott et al., 1974) which was claimed to greatly reduce the error originating from the uncertainty of the tail portion of the signal.

The purpose of this work was to extend the pulse diffusivity measuring technique, coupled with Fourier analysis, to catalyst pellets with two zones of differing diffusivities.

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CONCLUSIONS AND SIGNIFICANCE

A mathematical model was developed to describe the shape of an eluted concentration pulse from a column packed with porous catalyst pellets. In the model, the pellets were allowed to have two distinct zones of differing diffusivities.

Based on guidance obtained from the mathematical simulation, an apparatus was constructed and used to measure the diffusivity in a string of about 320 porous catalyst pellets. The diffusivity was determined by Fourier analysis of the eluted tracer peak after a plug of nitrogen was injected into a helium carrier stream.

The combination of the mathematical model and the experimental data demonstrated good resolution between the diffusivity in the interior of the catalyst pellets and in a narrow, partially plugged skin which surrounded them. The technique can be used to measure the effective diffusivity both in uniform catalyst pellets and also in pellets with two zones of differing diffusivities.

MATHEMATICAL ANALYSIS

The dispersion of the tracer in a pellet string reactor involves gas phase axial dispersion and diffusion in the porous catalyst pellets. A heterogeneous model was used to describe the transient behavior of the chromatographic signal with a pulse input.

The diffusion process in zones I and II of the catalyst pellets (Figure 1) can be characterized by the effective diffusivities D_{e1} and D_{e2}, respectively. The mass balance equations are

$$D_{e1}\left(\frac{\partial^2 C_1}{\partial r^2}+\frac{2}{r}\frac{\partial C_1}{\partial r}\right)=\beta_1\frac{\partial C_1}{\partial t} \tag{1}$$

for $o < r < a$, and

$$D_{e2}\left(\frac{\partial^2 C_2}{\partial r^2}+\frac{2}{r}\frac{\partial C_2}{\partial r}\right)=\beta_2\frac{\partial C_2}{\partial t} \tag{2}$$

for $a < r < R$.

Mass transfer processes in the bulk gas phase involve axial dispersion, convective mass transfer, and gas-solid interfacial transfer. The conservation equation for the pellet string reactor becomes

$$\frac{D_L}{\epsilon}\frac{\partial^2 C}{\partial x^2}-u\frac{\partial C}{\partial x}-\frac{3D_{e2}}{R}\left(\frac{1-\epsilon}{\epsilon}\right)\left(\frac{\partial C_2}{\partial r}\right)_{r=R}=\frac{\partial C}{\partial t} \tag{3}$$

Equations (1) to (3) with a Dirac delta input in gas concentration can be solved in the Laplace transformed domain (see appendix). The outlet concentration as a function of time was obtained by numerical inversion using the method of Dang and Gibilaro (1974).

By solving Equations (1) to (3) for typical system properties and operating conditions, a sensitivity study was conducted to check the conditions under which the pulse diffusivity technique would enable us to distinguish between catalyst pellets with uniform diffusivity and those with a partially obstructed skin.

The numerical simulation indicated that both increasing the carrier gas flow rate and decreasing the bed length enhanced the difference between the peak value of the residence time distribution curves for the two types of pellets (see Figures 2 and 3). Physically, this large difference in the peak value of the residence time distribution curves is attributed to the fact that at shorter residence times, the tracer penetrates a shallower depth of the pellets. Either increasing the gas flow rate or reducing the bed length shortens the residence time of the tracer in the column and thus reduces the tracer's penetration depth into the pellets. Therefore, a decrease in average residence time enhances the portion of the signal which is characteristic of the outer zone of the pellets. By varying the residence time of the tracer in the column, one can gain information on the effective diffusivity as a function of the radial position within the pellet.

The experimental apparatus was designed based upon the results obtained from the above sensitivity study, to obtain operating conditions which allow the most sensitive measurements.

EXPERIMENTAL APPARATUS AND DATA REDUCTION

A pellet string reactor similar to the one described by Scott et al. (1974) was constructed for the dynamic diffusivity measurements (Figure 4). A glass tube column with a total length of 100 cm and an inner diameter of 0.5 cm was used in which about 320 pellets were packed. The column to pellet diameter ratio was 1.40. [Scott et al. (1974) showed that the flow pattern in such a pellet string reactor is similar to that of a conventional packed bed.] Helium (99.999% purity) was the carrier gas, and about 25 μl of nitrogen (99.999% purity) was injected as tracer for each run. Measured by a soap bubble flow meter, the carrier gas flow rate was varied in range from 50 to 100 cm^3/min. The column and the thermal conductivity detector were located in an insulated box with a controlled temperature of 40 ± 0.2°C. Employing a Carle microbead thermistor, the detector had a response time of 0.04 s. The detector had inlet tubing of 0.058 cm inner diameter and was installed very close to the end of the column so that the displacement volume between the end of the bed and the detector cell was very small.

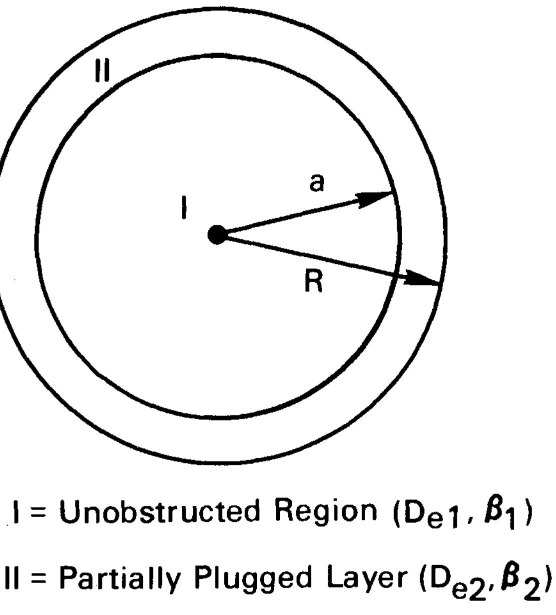


Fig. 1. Geometric configuration of a catalyst pellet with two zones of differing diffusivities.

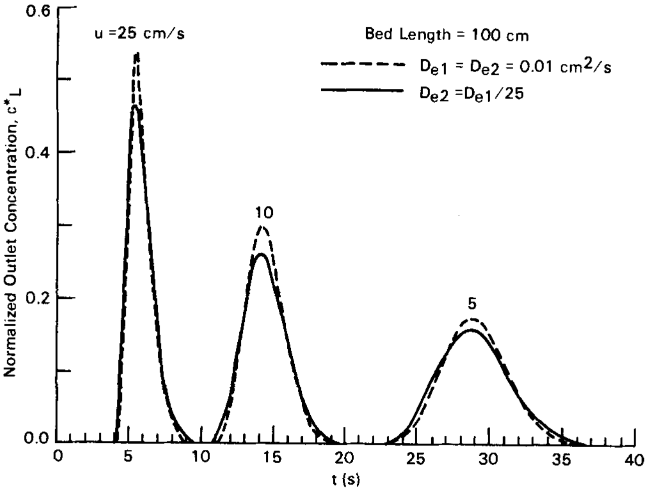


Fig. 2. Effect of carrier gas flow rate on the computed residence time distribution curves.

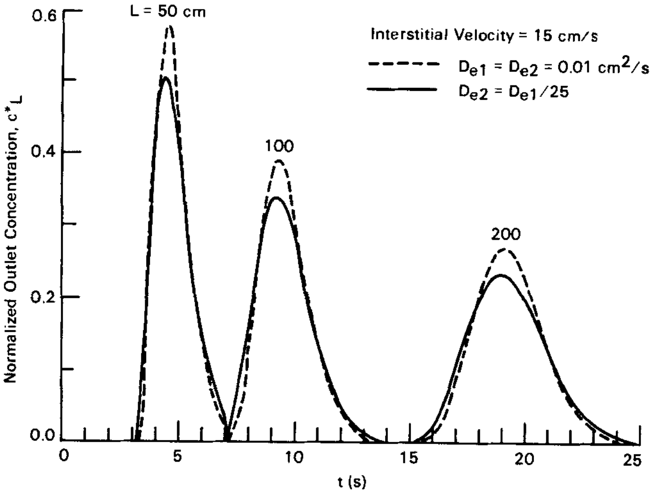


Fig. 3. Effect of bed length on the computed residence time distribution curves.

The chromatographic signal was sent directly to a minicomputer with an analog to digital converter of fourteen bits resolution (Tustin X-1500). The digitized data (sampling rate of 50 samples/s) were stored on a magnetic tape which was subsequently mounted on an IBM-370 computer's tape drive system for further processing.

The system parameters were extracted from the digitized data by Fourier analysis (for example, Gangwal et al., 1971). After subtracting the base line values from the data and normalizing to a unit peak area, the Fourier coefficients (also amplitude ratios and phase lags) were evaluated.

The Constrained Simplex method (Adelman and Stevens, 1972) was used to determine the diffusivity values which, when inserted in the model equations, best described the experimental data. The objective was to minimize the squared relative differences in amplitude ratio and phase lag between the model predictions and the experimental data:

$$\text{Obj. function} = \sum_{i=1}^{7}\left(\frac{AR_{\text{exp}} - AR_{\text{model}}}{AR_{\text{exp}}}\right)_i^2 + \left(\frac{PL_{\text{exp}} - PL_{\text{model}}}{PL_{\text{exp}}}\right)_i^2 \qquad (4)$$

The analysis of this work indicated that a very close agreement in residence time distribution could be obtained if the first seven harmonics were compared with the data in the optimization search scheme. The Constrained Simplex optimization technique has been found to be efficient and accurate in evaluating the system parameters.

Several model parameters were either directly measured or estimated from existing correlations as explained below.

The thickness of the partially plugged zone was measured by electron microprobe. For the partially plugged automobile catalyst employed in this work, the average value from ten pellets was used for the thickness of this zone. The pellet porosity in the unobstructed region was obtained from ultra high pressure mercury porosimetric measurements.

Gas-solid mass transfer coefficients were estimated from the correlation of Petrovic and Thodos (1968). Both this work and other reports (for example, Haynes, 1975) indicated that for high enough carrier gas flow rates, the external mass transfer resistance is so small that the errors introduced in the estimation of the mass transfer coefficient become unimportant.

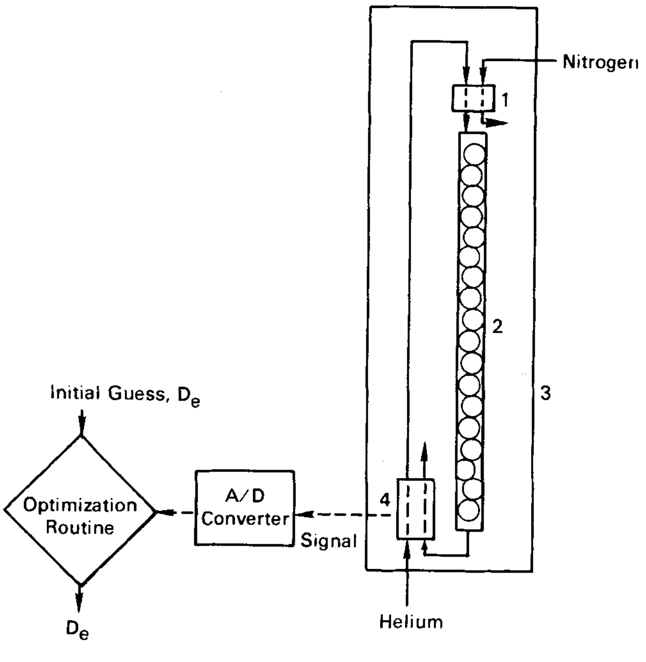
The axial dispersion coefficients were calculated from the dispersion correlation of Scott (1974), who used a pellet string reactor similar to the one discussed in this paper.

PARAMETRIC SENSITIVITY

Since each parameter may have a different influence on the diffusivities computed from the experimental data, we undertook an analysis to determine the sensitivity of the diffusivities in zones I and II to inaccuracies in the model parameters.

The pellet porosity in the partially plugged layer is the most questionable parameter, since no direct measurement is possible owing to the thinness of this layer. Scanning electron microscope observations (Figure 5) indicated that the porosity in this zone may be as low as 1 to 10%. To check for the importance of this parameter, several values of β_2 (0.01, 0.025, 0.05, and 0.10) were assigned to the model in analyzing the same experimental data. Surprisingly, less than 1% change in the diffusivity D_{e2} was obtained for a tenfold variation in β_2.

The lack of sensitivity to the porosity of the outer skin can be explained by considering the relative magnitude of the time constants for the diffusion process in zones I and II.



1 = Sampling Valve
2 = Pellet String Reactor, about 320 Pellets
3 = Electrically Heated Box, T = 40 ± .2°C
4 = Thermal Conductivity Detector

Fig. 4. Schematic diagram of the experimental apparatus and data processing system.

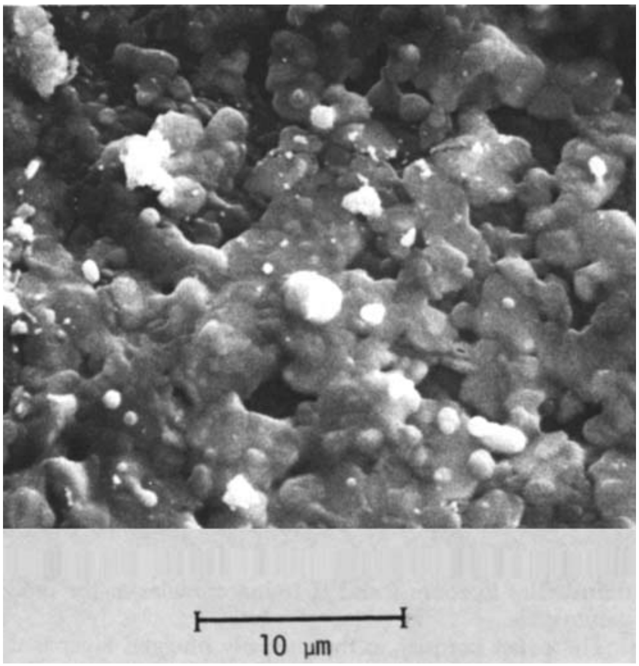


Fig. 5. Scanning electron photomicrograph (3000 X magnification) of the outer surface of a partially plugged catalyst pellet.

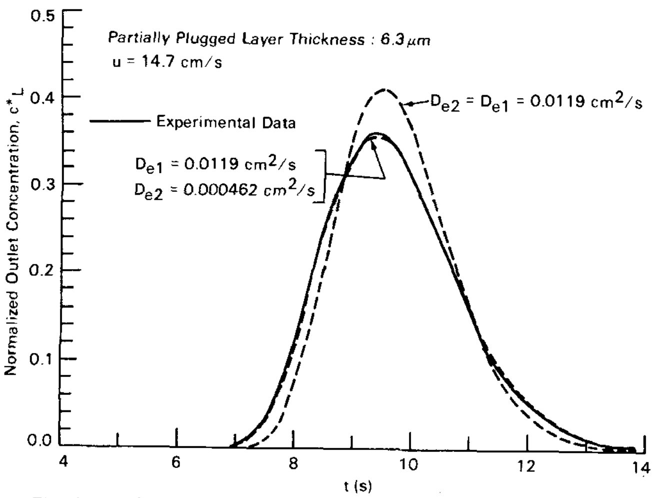


Fig. 6. Results for a partially plugged automobile exhaust catalyst.

In Equation (1), the time constant for the unobstructed region I is

$$\tau_I = \frac{\beta_1 a^2}{D_{e1}} \tag{5}$$

For the partially plugged zone II, the time constant is [Equation (2)]

$$\tau_{II} = \frac{\beta_2 (R - a)^2}{D_{e2}} \tag{6}$$

The ratio of time constants represents the relative rate of relaxation of the transient diffusion processes in the two zones:

$$\frac{\tau_{II}}{\tau_I} = \left(\frac{\beta_2}{\beta_1}\right) \frac{(R - a)^2 D_{e1}}{a^2 D_{e2}} \tag{7}$$

Introducing the parameters measured for our catalyst, Equation (7) becomes

$$\frac{\tau_{II}}{\tau_I} = \left(\frac{\beta_2}{\beta_1}\right) (3.15 \times 10^{-4}) \tag{8}$$

Since β_2 is smaller than β_1, one can conclude that the time constant for the outer skin is much smaller than that for the unobstructed region. This indicates that the transient response of the outer skin is so fast with respect to the transient response of the interior that a pseudo steady state approximation can be applied for the outer skin. Therefore, if zone II is thin, the right-hand side of Equation (2) can be neglected (that is the effect of the porosity disappears) without altering the model predictions. This explains why the effect of the partially plugged porosity does not show any significant influence on the diffusivity which is computed from the data obtained from the partially plugged catalyst at hand.

We also investigated the sensitivity of the diffusivity to the thickness of zone II. For a 10% error in the measured thickness of zone II, the outer skin diffusivity changed by about 8%.

As mentioned before, the axial dispersion coefficient was estimated from Scott's (1974) correlation for a pellet string reactor. The standard deviation of Scott's correlation was less than 10% of the averaged value of the axial dispersion coefficient. Our sensitivity analysis showed that a 10% perturbation in the axial dispersion coefficient causes about 15% change in the outer skin's diffusivity.

It is interesting to note that the diffusivity calculated for the inner zone D_{e1} changed less than 5% as a result of any of these parameter perturbations.

EXAMPLES

In order to demonstrate the technique, we show here the results we obtained on two catalysts: one with two zones of differing diffusivities and one with uniform diffusivity.

Figure 6 shows the experimental results for a partially plugged catalyst with an outer zone thickness of 6.3 µm. The results indicate that the diffusivity in the partially plugged layer was reduced by a factor of about 26 with respect to the unobstructed core of the catalyst pellet.

Very close agreement between the experimental data and model prediction is shown in Figure 6. This indicates that the combination of the Fourier analysis and the Constrained Simplex method provides a powerful tool for solving this particular problem. Figure 6 also shows the residence time distribution computed from the assumption that the entire pellet is uniform with the properties of its core. The large difference between the residence time distribution computed for the uniform diffusivity case and the measured curve shows the excellent resolution of D_{e1} and D_{e2} by this technique.

To provide additional support for these determinations of D_{e1} and D_{e2}, we characterized a sample similar to the one depicted in Figure 6, but without the contaminated outer layer. Its measured (uniform) diffusivity was 0.0140 cm²/s, in good agreement with the value of 0.0119 cm²/s determined for the core of the partially plugged sample.

ACKNOWLEDGMENT

The numerical inversion of the Laplace transformed solutions was kindly contributed by J. C. Cavendish of the Mathematics Department, General Motors Research Laboratories.

NOTATION

a = radius of the unobstructed region, cm
AR = amplitude ratio, dimensionless
C = tracer concentration in the bulk gas, mole/cm³
C_1 = tracer concentration in zone I of the pellets, mole/cm³

C_2 = tracer concentration in zone II of the pellets, mole/cm^3

C_L^* = normalized outlet concentration $\frac{C_L(t)}{\int_0^T C_L(t)\,dt}$, dimensionless

D_{e1} = effective diffusivity in zone I, cm^2/s

D_{e2} = effective diffusivity in zone II, cm^2/s

D_L = axial dispersion coefficient, cm^2/s

$h(s)$, k_1, k_2 = defined in the appendix

k_f = external mass transfer coefficient, cm/s

L = total column length, cm

PL = phase lag, rad

q_1, q_2 = defined in the appendix

R = pellet radius, cm

s = Laplace transform variable

t = time, s

T = period for Fourier analysis, s

u = interstitial velocity of the carrier gas, cm/s

u_1, u_2 = defined in the appendix

x = axial position in the bed, cm

Greek Letters

β_1 = pellet porosity in zone I

β_2 = pellet porosity in zone II

δ = Dirac delta function

ϵ = bed void fraction

Ψ_1, Ψ_2, Ψ_3, Ψ_4 = defined in the appendix

τ_I, τ_{II} = time constants, defined in Equations (5) and (6), s

APPENDIX

The mass balance equations for a nonadsorbing gas tracer in a two-zone catalyst pellet are

$$D_{e1}\left(\frac{\partial^2 C_1}{\partial r^2} + \frac{2}{r}\frac{\partial C_1}{\partial r}\right) = \beta_1 \frac{\partial C_1}{\partial t} \qquad \text{(A1)}$$

$$D_{e2}\left(\frac{\partial^2 C_2}{\partial r^2} + \frac{2}{r}\frac{\partial C_2}{\partial r}\right) = \beta_2 \frac{\partial C_2}{\partial t} \qquad \text{(A2)}$$

with boundary conditions

$$C_1(o, r) = 0 \qquad \text{(A3)}$$

$$C_2(o, r) = 0 \qquad \text{(A4)}$$

$$C_1(t, a) = C_2(t, a) \qquad \text{(A5)}$$

$$D_{e1}\frac{\partial C_1}{\partial r} = D_{e2}\frac{\partial C_2}{\partial r}, \quad \text{at} \quad r = a \qquad \text{(A6)}$$

$$D_{e2}\frac{\partial C_2}{\partial r} = k_f\,[C - C_2]\,, \quad \text{at} \quad r = R \qquad \text{(A7)}$$

$$\frac{\partial C_1}{\partial r} = 0, \quad \text{at} \quad r = 0 \qquad \text{(A8)}$$

The conservation equation for the gas phase is

$$\frac{D_L}{\epsilon}\frac{\partial^2 C}{\partial x^2} - u\frac{\partial C}{\partial x} - \frac{3D_{e2}}{R}\left(\frac{1-\epsilon}{\epsilon}\right)\left(\frac{\partial C_2}{\partial r}\right)_{r=R} = \frac{\partial C}{\partial t} \qquad \text{(A9)}$$

with boundary conditions

$$C(o, x) = 0 \qquad \text{(A10)}$$

$$C(t, 0) = \delta(t = 0) \qquad \text{(A11)}$$

$$C(t, \infty) = 0 \qquad \text{(A12)}$$

If we let $u_1 = rC_1$, $u_2 = rC_2$, $k_1 = D_{e1}/\beta_1$, and $k_2 = D_{e2}/\beta_2$, Equations (A1) to (A8) become

$$k_1\frac{\partial^2 u_1}{\partial r^2} = \frac{\partial u_1}{\partial t} \qquad \text{(A13)}$$

$$k_2\frac{\partial^2 u_2}{\partial r^2} = \frac{\partial u_2}{\partial t} \qquad \text{(A14)}$$

with boundary conditions

$$u_1(t, a) = u_2(t, a) \qquad \text{(A15)}$$

$$D_{e1}\left(\frac{1}{a}\frac{\partial u_1}{\partial r} - \frac{u_1}{a^2}\right) = D_{e2}\left(\frac{1}{a}\frac{\partial u_2}{\partial r} - \frac{u_2}{a^2}\right) \quad \text{at} \quad r = a \qquad \text{(A16)}$$

$$D_{e2}\left(\frac{1}{R}\frac{\partial u_2}{\partial r} - \frac{u_2}{R^2}\right) = k_f\left[C - \frac{u_2}{R}\right], \quad \text{at} \quad r = R \qquad \text{(A17)}$$

$$u_1(t, 0) = 0 \qquad \text{(A18)}$$

$$u_1(0, r) = 0 \qquad \text{(A19)}$$

$$u_2(0, r) = 0 \qquad \text{(A20)}$$

If we take Laplace transforms with respect to time of Equations (A9) to (A20) and solve the equations in the Laplace transformed domain, the effluent concentration becomes

$$\overline{C}(s, L) = \exp\left\{\frac{u\epsilon L}{2D_L} - \sqrt{\left(\frac{u\epsilon L}{2D_L}\right)^2 + \frac{s\epsilon L^2\,[1 + h(s)]}{D_L}}\right\} \qquad \text{(A21)}$$

where

$$h(s) = \frac{3\,k_f\,D_{e2}(1-\epsilon)}{sR\epsilon(\Psi_2\Psi_3 - \Psi_1\Psi_4)}\,[\Psi_2 q_2 R \cosh q_2 R - \Psi_1 q_2 R \sinh q_2 R - \Psi_2 \sinh q_2 R + \Psi_1 \cosh q_2 R] \qquad \text{(A22)}$$

and

$$\Psi_1 = q_2 a \cosh q_2 a - \sinh q_2 a + \frac{D_{e1}}{D_{e2}}\sinh q_2 a(1 - q_1 a \coth q_1 a) \qquad \text{(A23)}$$

$$\Psi_2 = q_2 a \sinh q_2 a - \cosh q_2 a + + \frac{D_{e1}}{D_{e2}}\cosh q_2 a(1 - q_1 a \coth q_1 a) \qquad \text{(A24)}$$

$$\Psi_3 = D_{e2}(q_2 R \cosh q_2 R - \sinh q_2 R) + k_f\,R \sinh q_2 R \qquad \text{(A25)}$$

$$\Psi_4 = D_{e2}(q_2 R \sinh q_2 R - \cosh q_2 R) + k_f\,R \cosh q_2 R \qquad \text{(A26)}$$

$$q_1 = \left(\frac{s\beta_1}{D_{e1}}\right)^{1/2} \qquad \text{(A27)}$$

$$q_2 = \left(\frac{s\beta_2}{D_{e2}}\right)^{1/2} \qquad \text{(A28)}$$

The time domain solution for Equation (A21) can be obtained by substituting $s = i\omega$, finding the real and imaginary parts of $\overline{C}$ (ω, L), and following the numerical inversion procedure recommended by Dang and Gibilaro (1974).

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Manuscript received July 13, 1977; revision received and accepted November 9, 1977.

The Homogeneous Nucleation of Bubbles in Superheated Binary Liquid Mixtures

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It is shown how to apply homogeneous nucleation theory to predict the limits of superheat of multicomponent liquid mixtures. Measurements of such limits for *n*-pentane-*n*-hexane, *n*-hexane-cyclohexane, benzene-cyclohexane, and benzene-*n*-hexane mixtures as a function of composition are presented and compared with theory.

SCOPE

Barriers to the nucleation of bubbles may lead to a superheating of liquids which is so large that when nucleation does occur, they boil with explosive violence. Such explosive boiling tends to occur whenever a low boiling nucleating liquid comes in contact with a much higher boiling host liquid if their temperature difference is sufficiently large. This limit of superheat is therefore readily attained and represents quite a significant hazard to industry.

In a recent review in this journal (Blander and Katz, 1975), it was shown that homogeneous nucleation theory was quite successful in predicting the measured limits of superheat of pure (that is, one component) substances. However, the low boiling liquid is often a mixture of two or more components. It is the purpose of this paper to show how to apply nucleation theory to multicomponent mixtures, to describe an improved version of the rising droplet column used to measure the limits of superheat, and to present results on an ideal and on several somewhat nonideal binary mixtures which were studied to test the validity of the theory.

CONCLUSIONS AND SIGNIFICANCE

The theory for the homogeneous nucleation of a superheated liquid was successfully generalized to multicomponent mixtures by employing the chemical equilibrium approximation; that is, the pressure and composition of the gas in the embryonic bubbles is determined by its being in equilibrium with the surrounding superheated liquid for bubbles of every size. With this approximation, the equation for the rate of nucleation of multicomponent mixtures

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