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Multicomponent Gaseous Diffusion in Porous Media in the Transition Region. A Matrix Method for Calculation of Steady-State Transport Rates

Rajamani Krishna[1]

Department of Chemical Engineering, University of Manchester Institute of Science and Technology, Manchester M60 1QD, England

Isothermal steady-state diffusion of n-component gaseous mixtures through porous media in the transition region is considered in the absence of viscous flow. The extended Maxwell–Stefan equations accounting for both molecular and Knudsen diffusion processes are represented in compact matrix notation and a general analytic solution obtained for the transfer rates N_i. Both the equimolar ($\sum_{i=1}^{n} N_i = 0$) and the Graham diffusion ($\sum_{i=1}^{n} N_i \sqrt{M_i} = 0$) restrictions on the transfer fluxes are considered in the analysis. The results generalize published analytic solutions for two components.

Introduction

Gaseous diffusion in porous solids occurs by two mechanisms. When the diameter of a pore is less than the mean free path of the gas, collision at the wall controls and Knudsen diffusion predominates. The diffusion flux is given by

$$N_i = -c\mathcal{D}_{Ki} \frac{dy_i}{dz} \qquad (i = 1, 2, \ldots, n) \qquad (1)$$

where $\mathcal{D}_{Ki}$ is the Knudsen diffusivity of species i in the porous solid.

On the other hand, when the pore diameter is much greater than the mean free path of the gas, the collisions are mainly between gas molecules, and bulk diffusion prevails. In this diffusion regime the fluxes are related to the composition gradients by the Maxwell–Stefan equations

$$\frac{dy_i}{dz} = \sum_{\substack{i=1 \\ j \neq i}}^{n} \frac{y_i N_j - y_j N_i}{c\mathcal{D}_{ij}} \qquad (i = 1, 2, \ldots, n) \qquad (2)$$

where $\mathcal{D}_{ij}$ represent the gas phase diffusivities of the binary pairs i–j in the mixture.

Many practical systems operate in the transition region, which can be described by a combination of the two mechanisms. Neglecting viscous flow phenomena, we may thus write the diffusion relationships in the transition region as (Feng and Stewart, 1973; Feng et al., 1974)

$$\frac{dy_i}{dz} = -\frac{N_i}{c\mathcal{D}_{Ki}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{y_i N_j - y_j N_i}{c\mathcal{D}_{ij}} \qquad (i = 1, 2, \ldots, n) \quad (3)$$

[1] Koninklijke/Shell-Laboratorium, Amsterdam, The Netherlands.

Only $n - 1$ of the composition gradients in (3) are independent for

$$\sum_{i=1}^{n} \frac{dy_i}{dz} = 0 \qquad (4)$$

and therefore the determination of the n fluxes N_i requires an additional "determinancy" condition. Two determinancy conditions are normally used in practice (Dullien and Scott, 1962; Rothfield, 1963): (i) equimolar counterdiffusion, valid for a closed system at constant total pressure, requiring

$$\sum_{i=1}^{n} N_i = 0 \qquad (5)$$

and (ii) the Graham diffusion relationship

$$\sum_{i=1}^{n} \sqrt{M_i}\, N_i = 0 \qquad (6)$$

For steady-state conditions ($dN_i/dz = 0$), eq 3 together with eq 5 or 6 may be solved for specified boundary conditions

$$\begin{aligned} \text{at } z &= 0, y_i = y_{i0} \\ \text{at } z &= \delta, y_i = y_{i\delta} \end{aligned} \qquad (i = 1, 2, \ldots, n) \qquad (7)$$

to yield the transfer rates N_i.

Analytic solutions for the binary ($n = 2$) case are easily obtained and are available in the literature (see, for example, Geankoplis, 1972). For the ternary case, solutions are available in parametric form (Cunningham and Geankoplis, 1968; Remick and Geankoplis, 1970). No general analytic solution for the n-component diffusion problem has been presented in the literature.

It is our object here to consider the general n-component problem and to obtain convenient analytic expressions for the transfer fluxes. The results of this study may be expected to

be useful in the analysis of experimental data and in the solution of practical diffusion problems.

Analysis

First we represent eq 5 and 6 in a common format. To do this we divide eq 6 by $\sqrt{M_n}$ to give

$$\sum_{i=1}^{n-1} \left(\frac{M_i}{M_n}\right)^{1/2} N_i + N_n = 0 \tag{8}$$

The nth flux N_n may therefore be written in a general form as

$$N_n = -\sum_{i=1}^{n-1} \nu_i N_i \tag{9}$$

where for the equimolar counterdiffusion case we have (cf. eq 5)

$$\nu_i = 1 \qquad (i = 1, 2, \dots, n-1) \tag{10}$$

and for the Graham diffusion relationship (6) the ratios ν_i are given as (cf. eq 8).

$$\nu_i = \left(\frac{M_i}{M_n}\right)^{1/2} \qquad (i = 1, 2, \dots, n-1) \tag{11}$$

Now, if we define the following parameters: (i) a dimensionless distance coordinate η as

$$\eta = z/\delta \tag{12}$$

(ii) transfer coefficients of the binary pairs k_{ij} as

$$k_{ij} = c\mathscr{D}_{ij}/\delta \qquad (i, j = 1, 2, \dots, n; i \neq j) \tag{13}$$

(iii) Knudsen transfer coefficients of the n species, k_{Ki}, by

$$k_{Ki} = c\mathscr{D}_{Ki}/\delta \qquad (i = 1, 2, \dots, n) \tag{14}$$

we may write the $n - 1$ independent eq 2 as

$$\frac{dy_i}{d\eta} = -\frac{N_i}{k_{Ki}} + y_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{N_j}{k_{ij}} - N_i \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{y_j}{k_{ij}}$$
$$(i = 1, 2, \dots, n-1) \tag{15}$$

Incorporating expression 9 for the nth flux, we may rewrite (15) in terms of the $n - 1$ independent fluxes N_i as

$$\frac{dy_i}{d\eta} = -\left(\frac{1}{k_{Ki}} + \frac{\nu_i y_i}{k_{in}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{y_j}{k_{ij}}\right) N_i$$
$$+ y_i \sum_{\substack{j=1 \\ j \neq i}}^{n-1} \left(\frac{1}{k_{ij}} - \frac{\nu_j}{k_{in}}\right) N_j \qquad (i = 1, 2, \dots, n-1) \tag{16}$$

The composition gradients may be obtained at the position $\eta = 0$ and written in $n - 1$ dimensional matrix notation as

$$\frac{d(y)}{d\eta}\bigg|_{\eta=0} = -[B](N) \tag{17}$$

where the elements of the square $n - 1 \times n - 1$ matrix $[B]$ are given by

$$B_{ii} = \frac{1}{k_{Ki}} + \frac{\nu_i y_{i0}}{k_{in}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{y_{j0}}{k_{ij}} \qquad (i = 1, 2, \dots, n-1) \tag{18}$$

$$B_{ij} = -y_{i0}\left(\frac{1}{k_{ij}} - \frac{\nu_j}{k_{in}}\right) \qquad (i, j = 1, 2, \dots n - 1; i \neq j) \tag{19}$$

The fluxes N_i can be obtained from eq 17 as

$$(N) = -[B]^{-1}\frac{d(y)}{d\eta}\bigg|_{\eta=0} \tag{20}$$

If the composition profiles are known, the composition gradients at $\eta = 0$ can be evaluated and the fluxes obtained from (20). In order to obtain the composition profiles we note that

$$\sum_{i=1}^{n} y_i = 1 \tag{21}$$

and therefore eq 15 may be written in terms of the $n - 1$ independent compositions as

$$\frac{dy_i}{d\eta} = \left(\frac{N_i}{k_{in}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{N_j}{k_{ij}}\right) y_i - N_i \sum_{\substack{j=1 \\ j \neq i}}^{n-1} \left(\frac{1}{k_{ij}} - \frac{1}{k_{in}}\right) y_j$$
$$- \frac{N_i}{k_{Ki}} - \frac{N_i}{k_{in}} \qquad (i = 1, 2, \dots, n-1) \tag{22}$$

Equations 22 represent a set of $n - 1$ linear first-order differential equations in the compositions y_j. To solve them it is convenient to represent them in matrix notation as

$$\frac{d(y)}{d\eta} = [\Phi](y) + (\zeta) \tag{23}$$

where the elements of the matrix $[\Phi]$ are given by

$$\Phi_{ii} = \frac{N_i}{k_{in}} + \sum_{\substack{j=1 \\ j \neq i}}^{n} \frac{N_j}{k_{ij}} \qquad (i = 1, 2, \dots, n-1) \tag{24}$$

$$\Phi_{ij} = -N_i\left(\frac{1}{k_{ij}} - \frac{1}{k_{in}}\right) \qquad (i, j = 1, 2, \dots, n - 1; i \neq j) \tag{25}$$

and the column matrix (ζ) has the elements

$$\zeta_i = -\frac{N_i}{k_{Ki}} - \frac{N_i}{k_{in}} \qquad (i = 1, 2, \dots, n-1) \tag{26}$$

The linear matrix differential equation (23) may be solved for the boundary conditions

$$\begin{aligned} \text{at } \eta = 0, \ (y) &= (y_0) \\ \text{at } \eta = 1, \ (y) &= (y_\delta) \end{aligned} \tag{27}$$

to give the composition profiles as (Amundson, 1966; Krishna and Standart, 1976)

$$(y_\eta - y_0) = \{\exp[\Phi]\eta - \lceil I_J\}\{\exp[\Phi] - \lceil I_J\}^{-1}(y_\delta - y_0) \tag{28}$$

The composition gradient at $\eta = 0$ may be obtained from equation (28) as

$$\frac{d(y)}{d\eta}\bigg|_{\eta=0} = -[\Phi]\{\exp[\Phi] - \lceil I_J\}^{-1}(y_0 - y_\delta) \tag{29}$$

which may be combined with eq 20 to give the desired expression for the fluxes N_i

$$(N) = [B]^{-1}[\Xi](y_0 - y_\delta) \tag{30}$$

where we have defined, for convenience, a matrix of "correction factors", $[\Xi]$, as

$$[\Xi] \equiv [\Phi]\{\exp[\Phi] - \lceil I_J\}^{-1} \tag{31}$$

Equation 30 is not truly explicit in the fluxes N_i for the matrix $[\Xi]$ is a function of the rates of transfer. We shall, however, see that the form (30) is a convenient representation.

In the limit of vanishing rates of transfer ($N_i \to 0$) the matrix $[\Phi]$ reduces to the null matrix, i.e.

$$\text{Limit}_{\substack{N_i \to 0, \\ i=1,2,.n}} [\Phi] = [0] \qquad (32)$$

and when this happens, the matrix of correction factors reduces to the identity matrix $\lceil I \rfloor$, i.e.

$$\text{Limit}_{\substack{N_i \to 0, \\ i=1,2,.n}} [\Xi] = \lceil I \rfloor \qquad (33)$$

The significance of the matrix $[\Xi]$ is that it corrects the matrix $[B]^{-1}$ for finite rates of transfer. From a physical point of view, we may therefore define a matrix of permeability coefficients, $[P^\bullet]$, by

$$(N) = [P^\bullet](y_0 - y_\delta) \qquad (34)$$

where the superscript black dot on the elements of $[P^\bullet]$ serves as a reminder that these permeabilities are dependent on the rates of transfer. For vanishing transfer rates therefore we have (cf. eq 30-34)

$$(N) = [P](y_0 - y_\delta) \qquad (35)$$

where the matrix of "zero flux" permeabilities, $[P]$, can be calculated straightforwardly from

$$[P] = [B]^{-1} \qquad (36)$$

where the elements of $[B]$ are given by eq 18 and 19 and depend only on the compositions at $\eta = 0$ and the transfer coefficients in the gas phase, k_{ij} and k_{Ki}.

For finite but low rates of transfer, eq 35 and 36 provide an approximate but good description of the transfer process. This approximation suggests a suitable iteration procedure for calculating the fluxes for finite transfer rates: (i) Calculate the elements of the matrix $[B]$ from eq 18 and 19 and obtain the matrix $[P]$ by suitable matrix inversion procedure. (ii) Calculate the fluxes N_i from (35). Only $n - 1$ of the fluxes are determined in this way, the nth flux being given by eq 9. (iii) With this estimate of N_i, the elements of $[\Phi]$ may be calculated from eq 24 and 25. The matrix of correction factors $[\Xi]$ is then obtained by use of Sylvester's theorem (Amundson, 1966; Krishna and Standart, 1976). (iv) The finite flux permeabilities $P^\bullet_{ij}$ are then calculated from

$$[P^\bullet] = [P][\Xi] \qquad (37)$$

and a better estimate of the fluxes obtained from eq 34 using eq 9 to calculate N_n. (v) The steps (iii) and (iv) are repeated till convergence is obtained for each individual N_i.

Discussion

For two-component systems the procedure outlined above simplifies considerably because all matrices degenerate to scalars. Thus we have

$$N_1 = P_{11}\Xi_{11}(y_{10} - y_{1\delta}) \qquad (38)$$

where

$$P_{11} = 1/B_{11} = \left(\frac{1}{k_{K1}} + \frac{1}{k_{12}} - \frac{y_{10}(1 - \nu_1)}{k_{12}}\right)^{-1} \qquad (39)$$

and

$$\Xi_{11} = \frac{\Phi_{11}}{\exp \Phi_{11} - 1} \qquad (40)$$

with the dimensionless mass transfer rate factor Φ_{11} given by

$$\Phi_{11} = \frac{N_1 + N_2}{k_{12}} = \frac{N_1(1 - \nu_1)}{k_{12}} \qquad (41)$$

Equations 38–41 may be combined to give N_1 explicitly in the form

$$N_1 = \frac{k_{12}}{1 - \nu_1} \ln \left(\frac{1 + k_{12}/k_{K1} - (1 - \nu_1)y_{1\delta}}{1 + k_{12}/k_{K1} - (1 - \nu_1)y_{10}}\right) \qquad (42)$$

which result is also available in the published literature (Geankoplis, 1972; Rothfield, 1963; Scott and Dullien, 1962). For the special case of equimolar diffusion, $\nu_1 = 1$, eq 38–41 simplify to give

$$N_1 = P_{11}(y_{10} - y_{1\delta}) \qquad (43)$$

where now

$$P_{11} = \left(\frac{1}{k_{K1}} + \frac{1}{k_{12}}\right)^{-1} \qquad (44)$$

The Knudsen diffusion coefficient $\mathcal{D}_{Ki}$ is independent of total system pressure whereas the gas-phase bulk diffusion coefficient $\mathcal{D}_{ij}$ is inversely proportional to the pressure. Therefore for a given porous solid, bulk diffusion will predominate at high pressures whereas at low pressures the diffusion fluxes will be governed by the Knudsen diffusion mechanism. Between these extremes the diffusion process will take place in the transition region where both Knudsen and bulk diffusion resistances will be important. Since the molar density of the diffusing gas mixture c is proportional to the total system pressure it can be seen from eq 13, 14, 39, and 44 that the effective transfer coefficient, or permeability, will increase with the system pressure and therefore the flux N_1 will increase till the pressure reaches a value at which bulk diffusion controls. Further increase in the pressure will have no effect on the transfer rate. These observations were confirmed by Cunningham and Geankoplis (1968) experimentally.

From eq 38–41 it can be seen that the molar flux N_1 will have the same sign as the constituent driving force $(y_{10} - y_{1\delta})$ and at a given pressure the flux N_1 increases monotonously with increased values of the driving force. The permeability $P_{11}^\bullet$ ($= P_{11}\Xi_{11}$) can only assume positive values for a two-component system.

The situation with regard to a three component system—the simplest multicomponent system—is much more complicated. The rate relations (34) are coupled and may be written explicitly as

$$N_1 = P^\bullet_{11}\Delta y_1 + P^\bullet_{12}\Delta y_2$$
$$N_2 = P^\bullet_{21}\Delta y_1 + P^\bullet_{22}\Delta y_2 \qquad (45)$$

where Δy_1 and Δy_2 are the constituent driving forces

$$\Delta y_i = y_{i0} - y_{i\delta} \qquad (i = 1, 2, 3) \qquad (46)$$

Since the cross coefficients $P^\bullet_{12}$ and $P^\bullet_{21}$ will be nonzero in general we cannot expect a simple dependence of N_i on Δy_i, as is true for a binary system. Further, as discussed by Toor (1957) for the ternary bulk gas diffusion case, three interesting possibilities exist for ternary gas diffusion in the transition regime: (i) osmotic diffusion (diffusion in the absence of a constituent driving force)

$$N_i \neq 0; \Delta y_i = 0 \qquad (47)$$

(ii) diffusion barrier (no diffusion even in the presence of a constituent driving force)

$$N_i = 0; \Delta y_i \neq 0 \qquad (48)$$

(iii) reverse diffusion (diffusion of a component in a direction opposite to that dictated by its driving force)

$$N_i \Delta y_i < 0 \qquad (49)$$

The above "interaction" phenomena are caused primarily by the cross coefficients B_{ij}. It is clear from eq 18 and 19 that

Table I. Equimolal Diffusion by Hydrogen (1)–Styrene (2)–Ethylbenzene (3) through Porous Solid. Effect of Total Pressure on Diffusion Fluxes[a]

p, bars	N_1, (kmol)/(s) (m²)	N_2, (kmol)/(s) (m²)	N_3, (kmol)/(s)(m²)
1.0	21.9818×10^{-6}	0.48976×10^{-6}	-22.4716×10^{-6}
3.0	28.2104×10^{-6}	0.15486×10^{-6}	-28.3653×10^{-6}
5.0	29.9058×10^{-6}	0.00267×10^{-6}	$-29.9084\ 8 \times 10^{-6}$
6.0	30.3620×10^{-6}	-0.04379×10^{-6}	-30.3182×10^{-6}

[a] The physical data chosen in the calculation of the fluxes are summarized as follows: molecular weights: $M_1 = 2$; $M_2 = 104$; $M_3 = 106$; gas phase compositions: $y_{10} = 0.88$; $y_{20} = 0.1$; $y_{1\delta} = 0.7$; $y_{2\delta} = 0.02$; length of diffusion path: $\delta = 0.01$ m; radius of pore: $r_p = 1.0 \times 10^{-7}$ m; temperature: $T = 500$ K; gas constant: $R = 0.083144$ (bar)(m³)/(kmol)(K); parameters in eq 9: $\nu_1 = 1$; $\nu_2 = 1$ (equimolal diffusion). Knudsen diffusion coefficients calculated from (Remick and Geankoplis, 1974): $\mathcal{D}_{K1} = 97r_p(T/M_1)^{1/2}$, m²/s; $\mathcal{D}_{K2} = 97r_p(T/M_2)^{1/2}$, m²/s; $\mathcal{D}_{K3} = 97r_p(T/M_3)^{1/2}$, m²/s. Bulk gas phase diffusion coefficients of the binary pairs estimated using the method of Fuller et al. (1966): $\mathcal{D}_{12} = 1.457 \times 10^{-9}T^{1.75}/p$, m²/s; $\mathcal{D}_{13} = 1.435 \times 10^{-9}T^{1.75}/p$, m²/s; $\mathcal{D}_{23} = 1.329 \times 10^{-10}\ T^{1.75}/p$, m²/s.

since the Knudsen transfer coefficients k_{Ki} do not contribute to the cross coefficients B_{ij}, the "interaction" or "coupling" effects are minimal in a Knudsen diffusion predominated regime. On the other hand, when bulk gas diffusion predominates the "interaction" effects will be at their maximum. Since with increasing system pressure, bulk gas diffusion assumes increasing importance we may also expect "interaction" effects to become increasingly important at higher system pressures. Table I presents the results of numerical calculations for equimolal diffusion of hydrogen (1)–styrene (2)–ethyl benzene (3) through a porous solid; the physical data used in the calculation are summarized in the table. The interesting point to note is that the molar flux of styrene, N_2, decreases in magnitude with increasing pressure. Further, on increasing the system pressure from 5 bars to 6 bars, the species styrene changes direction of transfer. The reason for this is that diffusional interactions become more significant with increasing pressure and at $p = 6.0$ bars, the permeabilities $P^\bullet_{ij}$ are calculated to be (units: kmol/(s)(m²))

$$P^\bullet_{11} = 1.69561 \times 10^{-4}; P^\bullet_{12} = -1.98774 \times 10^{-6}$$
$$P^\bullet_{21} = -6.02587 \times 10^{-5}; P^\bullet_{22} = 1.35035 \times 10^{-4} \qquad (50)$$

and therefore

$$N_2 = P^\bullet_{21}(0.18) + P^\bullet_{22}(0.08) = -4.379 \times 10^{-8} \qquad (51)$$

which is in a direction opposite to that of the driving force Δy_2; the species styrene experiences reverse diffusion under these conditions.

When the diffusion species in a ternary mixture are similar in size and nature, i.e.

$$k_{Ki} \simeq k_K; k_{ij} \simeq k \qquad (52)$$

the matrix $[B]$ will be diagonal and so will the matrices $[P]$ and $[P^\bullet]$. Under these conditions interaction effects will be absent and the dependence of the fluxes N_i on the constituent driving forces Δy_i will be a simple linear one. This is in fact confirmed by Remick and Geankoplis (1974) by experimental measurements for the system helium–neon–argon.

Conclusion

Analytic expressions for calculation of steady-state transfer rates for n-component diffusion through porous media in the transition region have been obtained in terms of an $n - 1$ dimensional square matrix of finite-flux permeability coeffi-

cients $[P^\bullet]$. The matrix $[P^\bullet]$ is further obtained as a product of a matrix of zero flux permeabilities, $[P]$, and a matrix of correction factors, $[\Xi]$, which account for finite transfer rates. The elements P_{ij} of $[P]$ can be calculated from the Knudsen diffusion coefficients of the individual species and the bulk gas diffusion coefficients of s the binary pairs. The calculation of the transfer rates involves a straightforward iteration procedure. The fundamental difference between transfer characteristics of binary and multicomponent systems have been emphasized by means of a numerical example involving diffusion in a three-component system. The results show that for an n-component system we should not expect a simple flux-driving force $(N_i - \Delta y_i)$ dependence unless the species making up the mixture are similar in size and nature.

Nomenclature

$[B]$ = matrix with elements given by eq 18 and 19
c = molar density of fluid mixture
$\mathcal{D}_{ij}$ = gas phase diffusivity of the binary pair i–j
$\mathcal{D}_{Ki}$ = Knudsen diffusivity of gaseous species i through porous medium
$\lceil I \rfloor$ = Identity matrix with elements δ_{ij}
k_{ij} = gas-phase transfer coefficients of binary i–j, defined by (13)
k_{Ki} = Knudsen transfer coefficient of species i, defined by (14)
M_i = molecular weight of species i
N_i = molar flux of species i
n = number of species in the mixture
p = total system pressure
$[P]$ = matrix of "zero flux" permeability coefficients
$[P^\bullet]$ = matrix of "finite flux" permeability coefficients
R = gas constant
y_i = mole fraction of species i in gaseous mixture
Δy_i = composition driving forces defined by eq 49
z = position coordinate

Greek Letters

δ = length of diffusion path
δ_{ij} = Kronecker delta
$(\hat{y})$ = matrix with elements given by eq 26
η = dimensionless position coordinate defined by eq 12
ν_i = ratio defined by eq 10 and 11
$[\Xi]$ = matrix of correction factors defined by eq 31
$[\Phi]$ = matrix of dimensionless rate factors defined by eq 24 and 25

Matrix Notation

( ) = column matrix of dimension $n - 1$
[ ] = square matrix of dimension $n - 1 \times n - 1$
[ ]$^{-1}$ = inverted matrix of dimension $n - 1 \times n - 1$
$\lceil \ \rfloor$ = diagonal matrix with $n - 1$ elements

Subscripts

i,j,k = indices
0 = evaluated at position $z = 0$
δ = evaluated at position $z = \delta$
n = nth species property or parameter

Superscript

$\bullet$ = coefficient corresponding to finite rates of transfer

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Use of an Annular Teflon Spinning-Band Distillation Column to Determine Practical Liquid–Vapor Equilibrium Data for Close-Boiling Systems. 1. The Carbon Tetrachloride–Benzene System

Edgar D. Smith* and D. M. Mathews

Department of Chemistry, Graduate Institute of Technology, University of Arkansas, Little Rock, Arkansas 72203

An annular Teflon spinning-band distillation column was used to magnify the differences in the liquid and vapor compositions in the carbon tetrachloride–benzene system. The data clearly showed that there is no azeotrope formed in this system. It was further shown that useful liquid–vapor equilibrium data could be calculated from the distillation column results.

Introduction

Because of the extremely small differences between the liquid and vapor compositions of binary systems where the boiling points of the components are within a few degrees of each other, it is difficult to obtain an accurate liquid–vapor equilibrium diagram. The analytical methods on which much of our present data is based—refractive index and/or density determinations—are relatively insensitive and are also subject to error due to the presence of trace impurities. In contrast, gas chromatography offers an accurate and precise method for the analysis of the liquid and vapor compositions. In addition, the analytical results are unaffected by impurities so long as they do not emerge with the components of interest. It was the authors' reasoning that the small differences in liquid and vapor compositions could be magnified by the use of an efficient distillation column rather than the usual one-plate distilling apparatus. The magnification factor (N) would depend on the number of plates in the distillation apparatus (column plus pot), and the enrichment due to a one-plate distillation could be approximated on the basis of the enrichment obtained with N plates. It is, of course, essential for these calculations to be valid that the efficiency of the still be reasonably constant and that N be known. It is also essential that the still have a very low hold-up so that reliable data could be obtained at the upper and lower concentration levels. The recently developed annular Teflon spinning-band stills are particularly suited to these applications because of their high efficiency, low hold-up, and short equilibration time.

Plate Value Determinations

A Nester-Faust NFT-50 annular Teflon spinning-band still was used in this work. The total number of plates in the distillation apparatus was established with a series of mixtures of especially purified n-heptane and methyl cyclohexane. The results are summarized in Table I and show that the plate values were reproducible over the wide range of pot compositions tested. (It should be noted that at this level of effi-

ciency, a 10% change in the plate value causes less than a 1% change in the calculated vapor composition for a one-plate distillation.) The α value of 1.07 reported by Beatty and Calingaert (1934) was used in these plate calculations. The constancy of the plate values obtained in this work strongly supports their finding that α does not change appreciably over the range of concentrations studied in this "ideal" system. It also follows that the one-plate vapor compositions calculated from these data via the Fenske equation (1932) *must* be in excellent agreement with the literature data. Thus, these data may be taken as proof that our proposed method for determining liquid vapor equilibrium diagrams works for an ideal system, where α is practically constant.

CCl4–Benzene Liquid–Vapor Equilibrium Data

The literature concerning this controversial system is reviewed by Fowler and Lim (1956) and will not be repeated here. Suffice it to say that Young (1922) and Ocon and Espantoso (1958) reported a minimum boiling azeotrope at 91.7 and 96.0 mol % CCl4 respectively, while Campbell and Dulmage (1948), Fowler and Lim (1956), and Rodger et al. (1969) failed to find any evidence of an azeotrope. It was generally agreed, however, that the liquid and vapor compositions were nearly identical above about 90 mol % CCl4. For this reason, the CCl4–benzene system is not recommended for the determination of theoretical plates in stills containing more than about 25 plates and even then pot compositions must be kept low to avoid the high CCl4 mole percent region in the vapor. Despite these limitations, the CCl4–benzene mixture has been a popular one to test distillation columns because the components are cheap, they are readily obtainable in the pure state, and analysis by refractive index or specific gravity measurements is easy. It was therefore felt that resolution of the over 70 year controversy as to the existence of an azeotropic composition should be attempted.

The vapor pressures of pure CCl4 and pure benzene were calculated from the Antoine equation (1888) over the boiling