Some Molecular Transport Characteristics in Binary Homogeneous Systems

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The behaviors of several diffusion coefficients are shown for the methane-*n*-butane system under conditions such that solutions are very nonideal and the concentrations of both components are significant. The coefficient proposed by Chapman and Cowling shows the least variation with state and is recommended for use under such conditions in hydrocarbon systems. Several other coefficients commonly used show large variations with state and coefficients using concentration as a potential are even negative in certain regions.

Diffusion or molecular transport is often carried out under conditions where the concentration of one of the components is small. Under these circumstances the treatment of such processes is relatively simple, and the choice of potential and the associated diffusion coefficient is relatively immaterial. In the case of hydrocarbons however many industrial processes are encountered where the molecular transport is at states where the concentration of the component of interest is not small and numerous additional factors associated with such transport processes must be taken into account.

It is the purpose of this discussion to present some of the more important relationships that apply to such situations in which there are two components, hereafter called *binary systems,* and to indicate the situations where negative Fick diffusion coefficients would be encountered. Such behavior is rather commonplace in binary hydrocarbon systems near the critical state. There is no thought that the material presented here involves any basically new concepts, but it does bring together material that has not to the authors' knowledge been heretofore assembled, and particular attention is given to the singularities that exist in a number of the diffusion coefficients in common use.

It does not appear necessary to review the background of molecular transport which was described by Fick (*1*) and Maxwell (*2*) and extended by the treatment of Chapman and Cowling (*3*). A brief summary of the more important relationships among and between certain coefficients and the limitations imposed upon these coefficients by the assumption of relatively simple equations of state is available (*4*). Jost (*5*) has summarized much of the experimental work available on the molecular transport in liquids. More recent measurements of the molecular transport in the liquid phase of hydrocarbons (*6*) have brought out the limitations of the Fick diffusion coefficient in describing the molecular transport in these binary systems near the critical state.

Recently there has been some additional interest in material transport phenomena, and the work of Bird, Stewart, and Lightfoot (*7*) presents some of the basic concepts in an admirable fashion. Kirkwood et al. (*8*) have indicated some of the various frames of reference that are of importance in isothermal diffusion, while Toor (*9*) has also emphasized the several frames of reference available in diffusion. However, these authors are primarily concerned with setting the framework for ternary and multicomponent diffusion, while the current effort was directed to an understanding of the behavior of the several coefficients currently used in the engineering profession under conditions where wide deviations from ideal solutions (*10*) exist and where the concentration of both of the components involved in the molecular transport process is significant.

BASIC RELATIONSHIPS

Before the behavior of several different diffusion coefficients in a typical binary hydrocarbon system is described,

TABLE 1. EQUILIBRIUM RELATIONSHIPS

General

$$V = 1/\sigma \tag{1-1}$$

$$\underline{V} = mV \tag{1-2}$$

$$\sigma_k = n_k\sigma = n_k/V \tag{1-3}$$

$$m_k = n_k m \tag{1-4}$$

$$\underset{\cdot}{\sigma} = 1/\underset{\cdot}{V} = \sigma/M \tag{1-5}$$

$$\underset{\cdot}{\sigma}_k = \underset{\cdot}{n}_k\underset{\cdot}{\sigma} = \sigma_k/M_k \tag{1-6}$$

$$M = 1\Big/\sum_{1}^{k} \frac{n_i}{M_i} \tag{1-7}$$

$$\underset{\cdot}{n}_k = Mn_k/M_k \tag{1-8}$$

$$\overline{V}_k = \left(\frac{\partial \underline{V}}{\partial m_k}\right)_{P,T,m_1,m_2,\ldots m_{k-1}} \tag{1-9}$$

$$\underset{\cdot}{\overline{V}}_k = M_k\overline{V}_k \tag{1-10}$$

$$\mu_k = \left(\frac{\partial F}{\partial m_k}\right)_{P,T,m_1,m_2,\ldots m_{k-1}} \tag{1-11}$$

$$\underset{\cdot}{\mu}_k = M_k\mu_k = RT\ln f_k + \beta(T) \tag{1-12}$$

Binary system

$$n_j + n_k = 1 \tag{1-13}$$

$$V = n_j\overline{V}_j + n_k\overline{V}_k \tag{1-14}$$

$$M = \frac{M_jM_k}{M_jn_k + M_kn_j} = M_j\underset{\cdot}{n}_j + M_k\underset{\cdot}{n}_k \tag{1-15}$$

$$\overline{V}_j = V - n_k\left(\frac{\partial V}{\partial n_k}\right)_{P,T} \tag{1-16}$$

$$n_k d\mu_k + n_j d\mu_j = 0 \tag{1-17}$$

Ideal solutions

$$\overline{V}_i = V_i^o \tag{1-18}$$

$$f_i = \underset{\cdot}{n}_i f_i^o \tag{1-19}$$

Perfect gases

$$\overline{V}_i = V_i^o = RT/M_iP \tag{1-20}$$

$$f_i^o = P \tag{1-21}$$

TABLE 2. VELOCITIES AND FLUXES

General

Weight flux
$$\dot{\mathbf{m}}_k = \sigma_k \mathbf{u}_k = \sigma_k \mathbf{u} + \dot{\mathbf{m}}_{dk} = M_k \underset{\cdot}{\dot{\mathbf{m}}}_k \tag{2-1}$$

Molal flux
$$\underset{\cdot}{\dot{\mathbf{m}}}_k = \underset{\cdot}{\sigma}_k \mathbf{u}_k = \underset{\cdot}{\sigma}_k \underset{\cdot}{\mathbf{u}} + \underset{\cdot}{\dot{\mathbf{m}}}_{dk} \tag{2-2}$$

Weight average or hydrodynamic velocity
$$\mathbf{u} = n_k \mathbf{u}_k + n_j \mathbf{u}_j \tag{2-3}$$

Molal average velocity
$$\underset{\cdot}{\mathbf{u}} = \underset{\cdot}{n}_k \mathbf{u}_k + \underset{\cdot}{n}_j \mathbf{u}_j \tag{2-4}$$

Difference between average velocities
$$\underset{\cdot}{\mathbf{u}} - \mathbf{u} = \frac{\dot{\mathbf{m}}_{dk}}{\sigma_k}\left(1 - \frac{M}{M_j}\right) = \frac{\underset{\cdot}{\dot{\mathbf{m}}}_{dk}}{\underset{\cdot}{\sigma}_k}\left(\frac{M_j}{M} - 1\right) \tag{2-5}$$

Molal diffusional flux
$$\underset{\cdot}{\dot{\mathbf{m}}}_{dk} = \frac{M}{M_j M_k}\dot{\mathbf{m}}_{dk} = \underset{\cdot}{\sigma}\,\underset{\cdot}{n}_j \underset{\cdot}{n}_k (\mathbf{u}_k - \mathbf{u}_j) \tag{2-6}$$

Weight diffusional flux
$$\dot{\mathbf{m}}_{dk} = \frac{M_j M_k}{M}\underset{\cdot}{\dot{\mathbf{m}}}_{dk} = \sigma n_j n_k (\mathbf{u}_k - \mathbf{u}_j) \tag{2-7}$$

Sum of weight diffusional fluxes
$$\dot{\mathbf{m}}_{dk} + \dot{\mathbf{m}}_{dj} = 0 \tag{2-8}$$

Sum of molal diffusional fluxes
$$\underset{\cdot}{\dot{\mathbf{m}}}_{dk} + \underset{\cdot}{\dot{\mathbf{m}}}_{dj} = 0 \tag{2-9}$$

Component *j* stagnant

$$\dot{\mathbf{m}}_j = \underset{\cdot}{\dot{\mathbf{m}}}_j = 0 \text{ as } \mathbf{u}_j = 0 \tag{2-10}$$

$$\dot{\mathbf{m}}_k = \sigma_k \mathbf{u}_k = \frac{1}{n_j}\dot{\mathbf{m}}_{dk} = \sigma \mathbf{u} \tag{2-11}$$

$$\underset{\cdot}{\dot{\mathbf{m}}}_k = \underset{\cdot}{\sigma}_k \mathbf{u}_k = \frac{1}{n_j}\underset{\cdot}{\dot{\mathbf{m}}}_{dk} = \underset{\cdot}{\sigma}\underset{\cdot}{\mathbf{u}} \tag{2-12}$$

Equal molal diffusion

$$\underset{\cdot}{\dot{\mathbf{m}}}_j = -\underset{\cdot}{\dot{\mathbf{m}}}_k \tag{2-13}$$

$$\underset{\cdot}{\mathbf{u}} = 0 \tag{2-14}$$

$$\underset{\cdot}{\dot{\mathbf{m}}}_k = \underset{\cdot}{\dot{\mathbf{m}}}_{dk} \tag{2-15}$$

$$\dot{\mathbf{m}}_k = \frac{M}{M_j}\dot{\mathbf{m}}_{dk} = \frac{\dot{\mathbf{m}}_{dk}}{1 - n_k\left(1 - \frac{M_j}{M_k}\right)} \tag{2-16}$$

$$\mathbf{u} = \frac{\dot{\mathbf{m}}_{dk}}{\sigma_k}\left(\frac{M}{M_j} - 1\right) = \frac{\dot{\mathbf{m}}_k}{\sigma}\left(1 - \frac{M_j}{M_k}\right) \tag{2-17}$$

Equal weight diffusion

$$\dot{\mathbf{m}}_j = -\dot{\mathbf{m}}_k \tag{2-18}$$

$$\mathbf{u} = 0 \tag{2-19}$$

$$\dot{\mathbf{m}}_k = \dot{\mathbf{m}}_{dk} \tag{2-20}$$

$$\underset{\cdot}{\dot{\mathbf{m}}}_k = \frac{1}{M_k}\dot{\mathbf{m}}_{dk} = \frac{M_j}{M}\underset{\cdot}{\dot{\mathbf{m}}}_{dk} = \frac{\underset{\cdot}{\dot{\mathbf{m}}}_{dk}}{1 - \underset{\cdot}{n}_k\left(1 - \frac{M_k}{M_j}\right)} \tag{2-21}$$

$$\underset{\cdot}{\mathbf{u}} = \frac{\dot{\mathbf{m}}_{dk}}{\sigma_k}\left(1 - \frac{M}{M_j}\right) = \frac{\underset{\cdot}{\dot{\mathbf{m}}}_k}{\underset{\cdot}{\sigma}}\left(1 - \frac{M_k}{M_j}\right) \tag{2-22}$$

TABLE 3. RELATIONSHIPS BETWEEN POTENTIAL GRADIENTS AT CONSTANT TEMPERATURE AND PRESSURE

General

$$\mathcal{D}\underset{\cdot}{n}_k = \frac{M^2}{M_j M_k}\mathcal{D}n_k \tag{3-1}$$

$$\mathcal{D}\sigma_k = \sigma^2 \overline{V}_j \mathcal{D}n_k \tag{3-2}$$

$$\mathcal{D}\underset{\cdot}{\mu}_k = M_k \mathcal{D}\mu_k = \frac{RTM^2}{\underset{\cdot}{n}_k M_j M_k}\left(\frac{\partial \ln f_k}{\partial \ln \underset{\cdot}{n}_k}\right)_{P,T}\mathcal{D}n_k \tag{3-3}$$

$$\mathcal{D}f_k = \frac{M^2}{M_j M_k}\left(\frac{\partial f_k}{\partial \underset{\cdot}{n}_k}\right)_{P,T}\mathcal{D}n_k \tag{3-4}$$

Ideal solutions

$$\mathcal{D}\sigma_k = \sigma^2 V_j{}^{\circ}\mathcal{D}n_k \tag{3-5}$$

$$\mathcal{D}\underset{\cdot}{\mu}_k = \frac{RTM^2}{\underset{\cdot}{n}_k M_j M_k}\mathcal{D}n_k \tag{3-6}$$

$$\mathcal{D}f_k = \frac{M^2 f_k{}^{\circ}}{M_j M_k}\mathcal{D}n_k \tag{3-7}$$

Perfect gases

$$\mathcal{D}\sigma_k = \frac{\sigma M}{M_j}\mathcal{D}n_k \tag{3-8}$$

$$\mathcal{D}f_k = \frac{M^2 P}{M_j M_k}\mathcal{D}n_k \tag{3-9}$$

it is desirable to set forth briefly the basic relationships. The equilibrium relationships which are needed in the further treatment are shown in Table 1. The first relations shown are general in application and are essentially definitions. Equations (1-13) through (1-17) are useful relations which apply only to binary systems. The relationships associated with ideal solutions, and perfect gases are also included.

The basic relationships between fluxes and velocities are known. However, in the interest of providing the reader with a summary of the more important relationships of this type, several of these relationships for binary systems are shown in Table 2. The more general relations are shown first, and it should be recognized that the weight diffusional fluxes shown in Equations (2-7) and (2-8) are with respect to a frame of reference moving at the momentum velocity, while the molal diffusional fluxes in Equations (2-6) and (2-9) are with respect to a frame of reference moving with the molal average velocity as defined in Equation (2-4) and are related to the momentum velocity by Equation (2-5). Fluxes defined with respect to frames of reference moving with other velocities, such as the volume average velocity, are also useful under some circumstances, but have not been described here.

Supplementary sets of relationships associated with special cases often treated in diffusion processes are included in the latter part of Table 2. The situations existing under conditions where one component is stagnant for equal molal diffusion and for equal weight diffusion are included in Table 2.

The relationships between the potential gradients often used in describing diffusional processes in binary systems are set forth as Table 3. Such relationships are not as commonly available as are those of Tables 1 and 2. The relations in Table 3 can be derived from the expressions shown in Table 1, and therefore are premised on the concept of local equilibrium (*11*). Equation (3-2), which leads to the rather unusual behavior of certain diffusion coefficients, is obtained in the following manner. Differentiation of Equation (1-3) at constant temperature and

TABLE 4. DIFFUSION COEFFICIENTS AT CONSTANT TEMPERATURE AND PRESSURE

Name	Symbol	Reciprocal relation	Usual definition	Simple definition	Relation to D_{Ckj}	
Fick (*1*)	D_{Fk}	$= \frac{\overline{V}_k}{\overline{V}_j} D_{Fj}$	$= -\frac{\dot{\mathbf{m}}_{dk}}{\mathfrak{D}\sigma_k}$		$= \frac{V}{\overline{V}_j} D_{Ckj}$	(4-1)
Chapman-Cowling (*3*)	D_{Ckj}	$= D_{Cjk}$	$= -\frac{\underset{\cdot}{n}_j \underset{\cdot}{n}_k (\mathbf{u}_k - \mathbf{u}_j)}{\mathfrak{D}\underset{\cdot}{n}_k}$	$= -\frac{\dot{\mathbf{m}}_{dk}}{\sigma \mathfrak{D} n_k}$	$= D_{Ckj}$	(4-2)
Bird (*12*)	D_{Bkj}	$= D_{Bjk}$	$= -\frac{\sigma R T \dot{\mathbf{m}}_{dk}}{\underset{\cdot}{\sigma}^2 M_k \underset{\cdot}{M}_j \underset{\cdot}{n}_k \mathfrak{D}\mu_k}$	$= -\frac{\underset{\cdot}{\dot{\mathbf{m}}}_{dk}}{\underset{\cdot}{\sigma}_k \mathfrak{D}\underset{\cdot}{\mu}_k}$	$= \left[\frac{\partial \ln \underset{\cdot}{n}_k}{\partial \ln f_k}\right]_{P,T} D_{Ckj}$	(4-3)
Maxwell (2)	D_{Mkj}	$= D_{Mjk}$	$= -\frac{R^2T^2\underset{\cdot}{\sigma}_k \underset{\cdot}{\sigma}_j (\mathbf{u}_k - \mathbf{u}_j)}{\mathfrak{D}(\underset{\cdot}{n}_k P)}$	$= -\frac{\underset{\cdot}{\sigma} R^2T^2 \underset{\cdot}{\dot{\mathbf{m}}}_{dk}}{P \mathfrak{D}\underset{\cdot}{n}_k}$	$= \frac{R^2T^2\underset{\cdot}{\sigma}^2}{P} D_{Ckj}$	(4-4)
Modified Maxwell (*4*)	D_{Mk}'	$= -\left(\frac{\partial f_j}{\partial f_k}\right)_{P,T} D_{Mj}'$	$= -\frac{R^2T^2\underset{\cdot}{\sigma}_k \underset{\cdot}{\sigma}_j (\mathbf{u}_k - \mathbf{u}_j)}{\mathfrak{D} f_k}$	$= -\frac{\underset{\cdot}{\sigma} R^2T^2 \underset{\cdot}{\dot{\mathbf{m}}}_{dk}}{\mathfrak{D} f_k}$	$= R^2T^2\underset{\cdot}{\sigma}^2 \left[\frac{\partial \underset{\cdot}{n}_k}{\partial f_k}\right]_{P,T} D_{Ckj}$	(4-5)
Volumetric (*13*)	D_{Vk}	$= \frac{\underset{\cdot}{\overline{V}}_k}{\underset{\cdot}{\overline{V}}_j} D_{Vj}$	$= -\frac{\underset{\cdot}{\sigma}_k \underset{\cdot}{\sigma}_j (\mathbf{u}_k - \mathbf{u}_j)}{\underset{\cdot}{\sigma} \mathfrak{D}\underset{\cdot}{\sigma}_k}$	$= -\frac{\underset{\cdot}{\dot{\mathbf{m}}}_{dk}}{\mathfrak{D}\underset{\cdot}{\sigma}_k}$	$= \frac{\underset{\cdot}{V}}{\underset{\cdot}{\overline{V}}_j} D_{Ckj}$	(4-6)

Note that $\dot{\mathbf{m}}_{dk}$ is referred to coordinates moving at velocity $\mathbf{u}$, while $\underset{\cdot}{\dot{\mathbf{m}}}_{dk}$ is referred to coordinates moving at velocity $\underset{\cdot}{\mathbf{u}}$.

pressure gives

$$\left(\frac{\partial \sigma_k}{\partial n_k}\right)_{T,P} = \frac{1}{V^2}\left[V - n_k\left(\frac{\partial V}{\partial n_k}\right)_{T,P}\right] \tag{1}$$

Combination with Equation (1-16) yields

$$\left(\frac{\partial \sigma_k}{\partial n_k}\right)_{T,P} = \overline{V}_j/V^2 = \sigma^2\,\overline{V}_j \tag{2}$$

Equation (3-2) can be obtained directly from Equation (2).

Several of the relationships are simplified when applied to binary systems which are ideal solutions (*10*), or when the gas phase follows the equation of state of a perfect gas. The resulting expressions are shown under Table 3.

The choice of an appropriate diffusion coefficient which describes the molecular transport in terms of the product of a potential gradient and the coefficient is sometimes difficult. It is not important which coefficient is employed as long as the data necessary for its application are at hand. However, it is desirable to employ a coefficient that does not undergo large changes over the range of conditions involved in a particular molecular transport problem. Under such conditions the ease of application is significantly improved, and a detailed tabulation of the coefficient as a function of the state of the system is not required.

The defining relationships of six different diffusion coefficients are shown in Table 4 (*1, 2, 3, 4, 12, 13*). It should be recognized that as discussed above the concept of local equilibrium set forth by Kirkwood (*11*) has been assumed in arriving at these relations. The authors have applied names to the coefficients, but there is a lack of uniformity in this regard, and the defining algebraic expression should be employed to establish the precise meaning of each of these coefficients. Table 4 also shows the relation between the coefficient in question and a symmetric coefficient which has been called by the authors the *Chapman-Cowling coefficient*. As a result of its symmetry with respect to each of the components of a binary system and its lack of a singularity in the composition field, the Chapman-Cowling coefficient as defined in Table 4 is believed to be a useful coefficient to describe molecular transport in hydrocarbon systems (*6*). This coefficient is variously referred to in the literature as the *binary diffusion coefficient* or *mutual diffusion coefficient, mass diffusivity* (*7*), and *coefficient of mutual diffusion* (*3*).

It will be noted that three of the coefficients are unsymmetrical. These are the Fick, modified Maxwell, and volumetric coefficients. The relationships of the corresponding coefficients for the two components are shown in Table 4. The defining relations for the six different diffusion coefficients are all equally applicable in describing the molecular transport with respect to a particular frame of reference. For example, the Fick and Chapman-Cowling coefficients in the simple definition are with respect to a frame of reference moving at the momentum velocity, $\mathbf{u}$, while the remaining coefficients in the simple definition are referred to coordinates moving at the molal average velocity $\underset{\cdot}{\mathbf{u}}$ which is related to the momentum velocity by Equation (2-5).

Each of the diffusion coefficients has been related to the Chapman-Cowling coefficient, and this relationship is valid insofar as the concept of local equilibrium (*11*) is applicable. In establishing fluxes it is usually convenient to combine Equation (2-1) with the appropriate relationship in

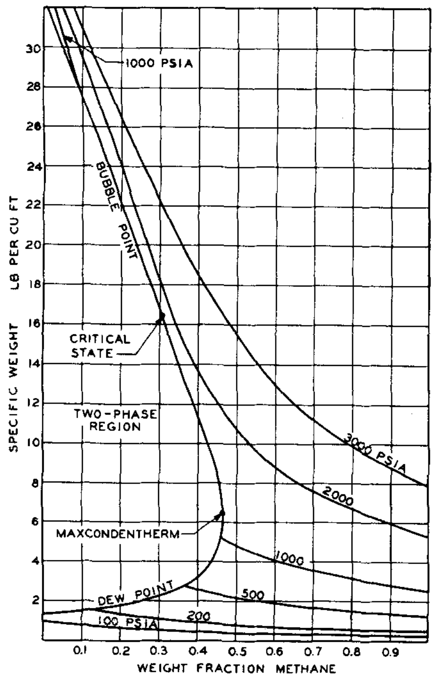

Fig. 1. Specific weight in the methane-*n*-butane system at 160°F.

Table 4 which, in the case of the Chapman-Cowling coefficient applied to one-dimensional transport, reduces to

$$\dot{\mathbf{m}}_{kx} = \sigma_k u_x - \sigma D_{Ckj} \frac{\partial n_k}{\partial x} \tag{3}$$

In a similar fashion the molal flux of component *k* can be expressed in terms of the Maxwell coefficient in the following way by using Equation (2-2):

$$\dot{\mathbf{m}}_{kx} = \sigma_k u_x - D_{Mkj} \frac{P}{\sigma R^2 T^2} \frac{\partial n_k}{\partial x} \tag{4}$$

Equations (3) and (4) illustrate how the flux with respect to a frame of reference which is fixed with respect to the observer can be evaluated from the diffusional flux with respect to a frame of reference moving with the momentum velocity in the case of Equation (3), and with the molal average velocity in the case of Equation (4).

From a practical standpoint it is desirable that a diffusion coefficient remains relatively invariant with respect to changes in state and involves a gradient that can be established readily. The Chapman-Cowling coefficient has been found not to possess singularities and to be relatively insensitive to changes in state at least for hydrocarbons. Likewise it employs the weight fraction as a potential, and gradients in the latter quantity are usually known. On the other hand, both the Bird and the modified Maxwell coefficients require a knowledge of the gradients of the chemical potential or of the fugacity which are often not known and are found to vary significantly with state. It is possible to express the gradients of fugacity or chemical potential in other forms such as is indicated in the following expression for a binary system:

$$\mathcal{D}\mu_k = \left[M_k \int_0^P \left(\frac{\partial \overline{V}_k}{\partial n_k} \right)_{T,P} dP + \frac{RTM}{n_k M_j} \right] \mathcal{D}\, n_k \tag{5}$$

There are few systems for which it is possible to evaluate Equation (5), and therefore rearrangement of the defining relations for the Bird coefficient does not make them more readily applicable to transport problems encountered in practice.

If simplifying assumptions are appropriate, some of the relations between coefficients are correspondingly simplified. For instance, if the solutions are ideal, the Bird coefficient becomes equal to the Chapman-Cowling coefficient, and for perfect gases, the volumetric coefficient is equal to the Chapman-Cowling coefficient. However, it is the purpose of this paper to consider cases which are not ideal (*14*).

EQUILIBRIUM BEHAVIOR

Before the transport characteristics of binary systems are considered, the equilibrium properties which play such an important part in the transport processes will be reviewed. With full realization that the material to be described is already available (*15, 16*), a brief review of the volumetric behavior of the methane-*n*-butane system at a temperature of 160°F. is presented.

Figure 1 depicts the specific weight as a function of composition at 160°F. The positions of the critical state and of the maxcondentherm are indicated.

It is clear that the specific weight does not vary linearly with composition, even though the specific volume is nearly linear with respect to composition at the lower pressures (*15*). No information is presented for the behavior in the heterogeneous region as this is not of concern.

The concentration of methane in the methane-*n*-butane system at 160°F. constitutes Figure 2. Again, the maxcondentherm and the critical state have been indicated, and it is of interest to note that the concentration of methane does not increase significantly with the increase in weight fraction methane above 0.5. In the upper part of the diagram, the behavior in the liquid phase has been indicated in some detail. Figure 3 portrays the concentration of *n*-butane. In this case there is a regular decrease in the concentration of *n*-butane with weight fraction methane.

The partial specific volume of methane in the methane-*n*-butane system at 160°F. is shown for both the liquid and gas phases in Figure 4. Similar information for *n*-butane is shown in Figure 5. Again, the locations of the critical state and the maxcondentherm have been included. It is apparent that, in the gas phase throughout most of the composition interval, there is relatively small variation

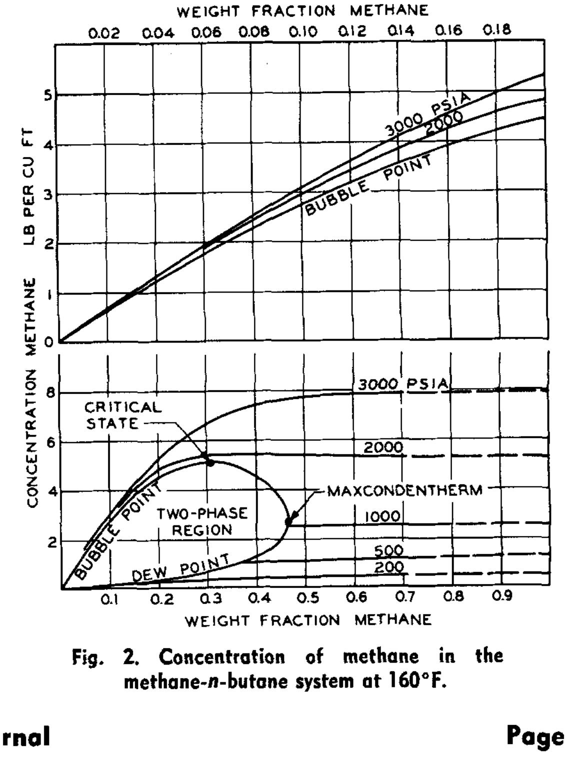

Fig. 2. Concentration of methane in the methane-*n*-butane system at 160°F.

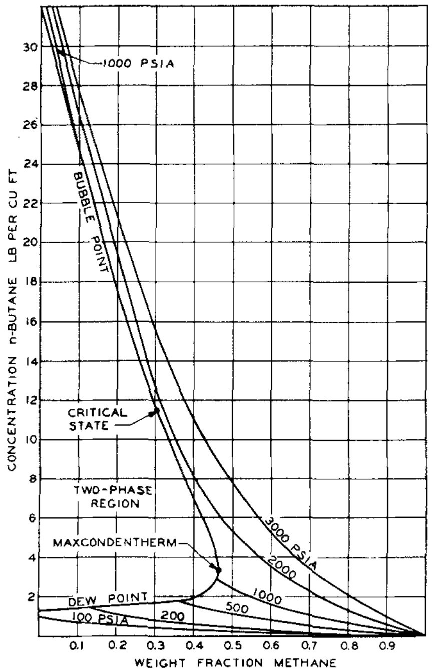

Fig. 3. Concentration of *n*-butane in the methane-*n*-butane system at 160°F.

in the partial volume of methane with composition. Likewise, in the liquid phase at weight fractions methane greater than 0.5, the variation in the partial volume of methane with composition is relatively small. The partial volume of *n*-butane decreases with an increase in the weight fraction of methane and reaches zero for bubble point at a weight fraction methane of 0.31. It is negative for weight fraction methane from 0.31 to 0.46 along the dew-point curve. The values of the partial volumes shown in Figures 4 and 5 were calculated from the volumetric data (*15, 16*) by application of Equation (1-16) and an analogous equation written for $\overline{V}_k$.

In accordance with Equation (2), whenever the partial volume of component j is zero, there is no change in the concentration of component k with a change in weight fraction. For example, in Figure 5 at a pressure of 2,000 lb./sq.in. it is seen that the partial volume of *n*-butane is zero at a weight fraction methane of approximately 0.362. Inspection of Figure 2 shows that the change in the concentration of methane with respect to the weight fraction methane at 2,000 lb./sq.in. and a composition 0.362 weight fraction methane is zero.

DIFFUSION COEFFICIENTS

The Chapman-Cowling coefficient at 160°F. and bubble point is shown as a function of composition in Figure 6. These data were obtained from the experimental measurements (*17*). The dashed line is an extrapolation of the data beyond the range of experimental measurements, and, although the exact value of the Chapman-Cowling coefficient close to the critical state is not known, there is no trend in the experimental data which would indicate any unusual behavior of this coefficient. Although coefficients for the dew-point gas would be of interest, they are not available. The full curve shown in Figure 6 was based upon an interpolation of the data obtained at five different temperatures and therefore does not necessarily reflect optimum agreement with the four points shown in the figure for 160°F. The extrapolation shown by the dashed curve is open to some uncertainty, but any probable form of the curve will not significantly change the discussion to follow.

The relations in Table 4 and the data of Figures 1, 4, and 5 allow calculation of the values of other diffusion coefficients from the data of Figure 6. Fick coefficients are shown in Figure 7. The smooth curve was calculated by the appropriate relationships relating the Chapman-Cowling and the Fick diffusion coefficients from the smooth curve of Figure 6. The points shown were computed directly from the experimental values of the Chapman-Cowling diffusion coefficient shown in Figure 6. The Fick coefficient for methane shows large variation and becomes infinite near the critical state where the partial volume of *n*-butane is zero. On the other hand, the Fick coefficient for *n*-butane shows rather simple behavior. It is presumed that a negative Fick coefficient for methane would be obtained at dew point for weight fraction methane higher than at the critical state for relatively high pressures, as Figure 5 shows *n*-butane to have a negative partial volume in this region. In illustration of this, Figure 8 shows the Fick diffusion coefficients which are calculated for methane if the Chapman-Cowling coefficient is taken to be 15×10^{-8} sq.ft./sec. for dew point, that is for weight fractions methane larger than critical. Singularities are found at both the critical state and at approximately 0.46 weight fraction methane. Region 1 of Figure 8 is at bubble point, while regions 2 and 3 are at dew point, and the arrows represent travel along the bubble point-dew point curve of Figure 5. Very large negative values of the Fick coefficient are found for the states corresponding to the negative partial volume of *n*-butane in Figure 5.

The Bird diffusion coefficient is based upon chemical potential as a driving force and thus satisfies the requirements of the relationship of fluxes and potential to yield the entropy production that is the essence of the applicability of the Onsager reciprocity relations (*18, 19*). However, since these reciprocity relations apply only in the proximity of equilibrium and there is no theoretical reason why the Bird coefficient should be less dependent upon composition than the Chapman-Cowling coefficient, there does not appear to be any basic advantage in utilizing the chemical potential as a driving force for molecular transport. From a practical standpoint it is shown in Figure 9 that the variation in this coefficient is large in the range of experimental measurement. Fugacity or chemical potential data (*15, 16*) were not available for compositions of bubble-point liquid higher than 0.17 weight fraction methane, so calculations were not extended to higher compositions. However, this coefficient is believed to become large in the vicinity of the critical state.

The Maxwell coefficient, shown in Figure 10, exhibits simple behavior near the critical state but undergoes large variation at low weight fraction methane. Figure 11 shows the modified Maxwell coefficients which also vary greatly

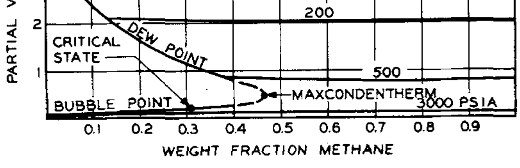

Fig. 4. Partial volume of methane in the methane-*n*-butane system at 160°F.

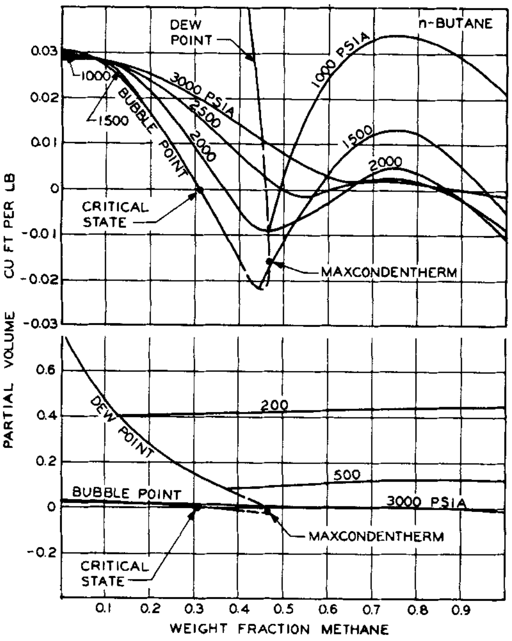

Fig. 5. Partial volume of *n*-butane in the methane-*n*-butane system at 160°F.

over the range of composition shown. Fugacity data were not available for higher compositions than those shown in Figure 11. Volumetric coefficients are depicted in Figure 12. Their behavior is similar to that of the Fick coefficients, and the coefficient for methane becomes infinite near the critical state in the same manner as does the Fick coefficient.

Review of Figures 6 through 12 shows that, of the coefficients considered, the Chapman-Cowling coefficient undergoes the smallest change with state. In addition, it is symmetric with respect to both components and uses a simple and readily determined potential. The latter is an important advantage as the weight or mole fraction is ordinarily known, but the chemical potential or fugacity of the components is often not known. Thus it appears that the Chapman-Cowling coefficient is a suitable coefficient to use and that there are no general advantages in using the other coefficients, although in some situations a given diffusion coefficient may yield a simpler transport equation.

One way of considering diffusion relationships which

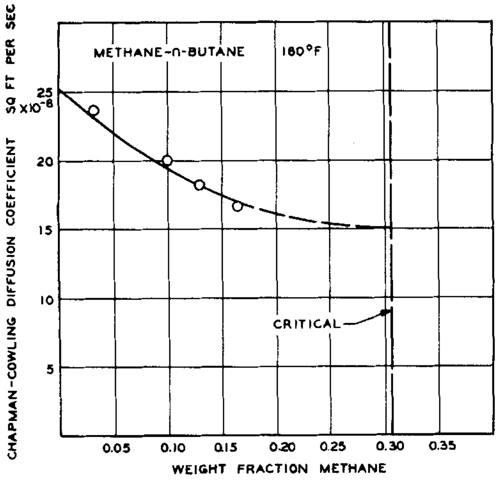

Fig. 6. Chapman-Cowling diffusion coefficient at bubble point in the methane-*n*-butane system.

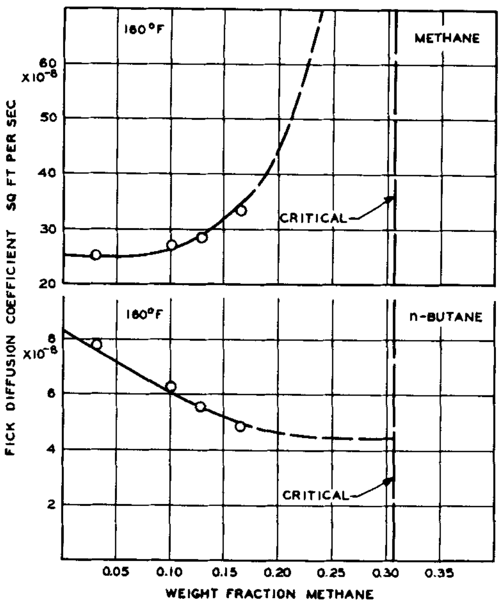

Fig. 7. Fick diffusion coefficients at bubble point in the methane-*n*-butane system.

gives insight into the relative behavior of nonsymmetric and symmetric coefficients is the following, illustrated by the Fick and the Chapman-Cowling coefficients. Upon the assumption that the diffusional flux is a linear function of the potential gradients for each component, there are obtained, with concentration as the potential

$$\dot{m}_{dk} = -D_k \mathfrak{D}\sigma_k + D_j \mathfrak{D}\sigma_j \tag{6}$$

and

$$\dot{m}_{dj} = -D_j \mathfrak{D}\sigma_j + D_k \mathfrak{D}\sigma_k \tag{7}$$

It will be noted that Equations (6) and (7) are symmetric relations. Simple manipulations with Equation (3-2) show that

$$D_{Fk} = D_k + D_j \frac{\overline{V}_k}{\overline{V}_j} \tag{8}$$

$$D_{Fj} = D_j + D_k \frac{\overline{V}_j}{\overline{V}_k} \tag{9}$$

and

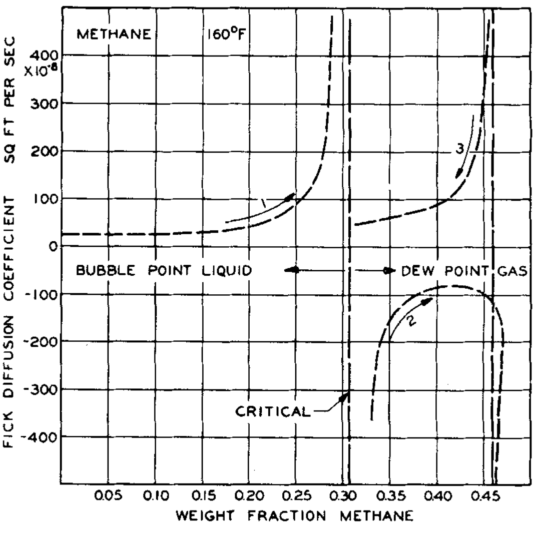

Fig. 8. Estimated Fick diffusion coefficient for methane in the methane-*n*-butane system.

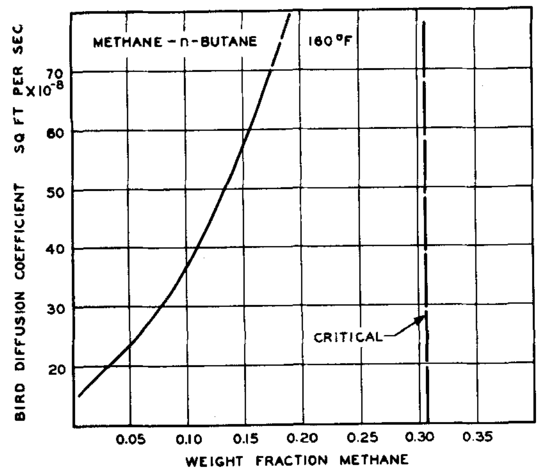

Fig. 9. Bird diffusion coefficient at bubble point in the methane-*n*-butane system.

$$D_{Ckj} = D_k \frac{\overline{V}_j}{V} + D_j \frac{\overline{V}_k}{V} \tag{10}$$

In the cases studied it appears that values of D_k and D_j which are simply related to state can be found which will give the poorly behaved Fick coefficient found in Equation (8). Therefore, the rapid variation of the Fick coefficient with state can be considered as due to an improper definition which neglects the gradient in concentration of the second component.

On the other hand, if weight fractions are selected as the potential, there is obtained

$$\dot{\mathbf{m}}_{dk} = - D_k' \mathcal{D} n_k + D_j' \mathcal{D} n_j \tag{11}$$

A corresponding expression for $\dot{\mathbf{m}}_{dj}$ exists. For a binary system

$$\mathcal{D} n_j = - \mathcal{D} n_k \tag{12}$$

and use of Equation (12) allows Equation (11) to be written as

$$\dot{\mathbf{m}}_{dk} = - (D_k' + D_j') \mathcal{D} n_k \tag{13}$$

Therefore

$$D_{Ckj} = V(D_k' + D_j') \tag{14}$$

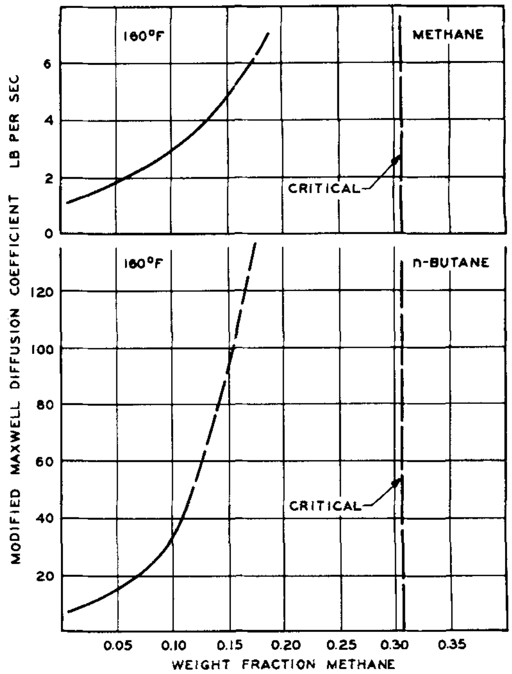

Fig. 11. Modified Maxwell diffusion coefficients at bubble point in the methane-*n*-butane system.

Thus only one coefficient need be used, as the nature of the potential chosen is such that gradients for both components are automatically accounted for. This gives another reason for selecting a symmetrical coefficient.

A similar demonstration can be used for the Bird coefficient. The molal diffusional flux can be taken as

$$\begin{aligned} \underset{\cdot}{\dot{\mathbf{m}}}_{dk} &= - D_k'' \underset{\cdot}{\sigma}_k \mathcal{D} \underset{\cdot}{\mu}_k + D_j'' \underset{\cdot}{\sigma}_j \mathcal{D} \underset{\cdot}{\mu}_j \\ &= - D_k'' \underset{\cdot}{\sigma} \underset{\cdot}{n}_k \mathcal{D} \underset{\cdot}{\mu}_k + D_j'' \underset{\cdot}{\sigma} \underset{\cdot}{n}_j \mathcal{D} \underset{\cdot}{\mu}_j \end{aligned} \tag{15}$$

The Gibbs-Duhem relation is, from Equation (1-17)

$$\underset{\cdot}{n}_k \, d\underset{\cdot}{\mu}_k + \underset{\cdot}{n}_j \, d\underset{\cdot}{\mu}_j = 0 \tag{16}$$

and substitution of Equation (16) in Equation (15) gives

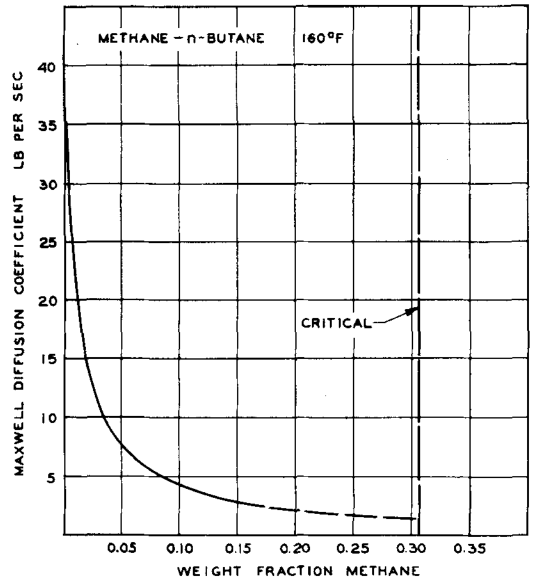

Fig. 10. Maxwell diffusion coefficient at bubble point in the methane-*n*-butane system.

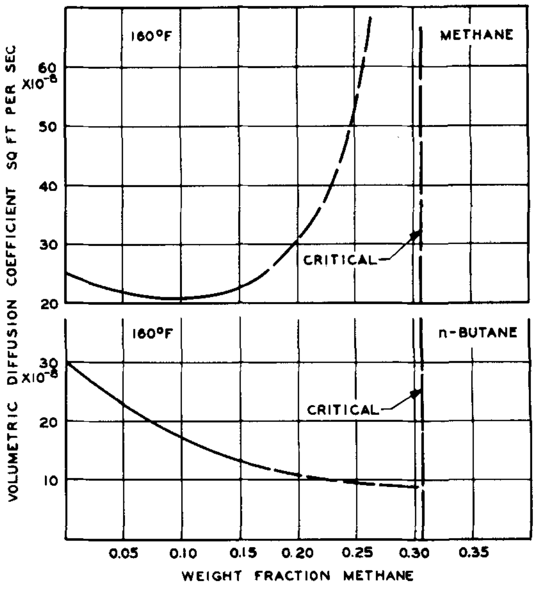

Fig. 12. Volumetric diffusion coefficients at bubble point in the methane-*n*-butane system.

$$\mathbf{m}_{dk} = -\,(D_k'' + D_j'')\;\sigma_k\,\mathcal{D}\,\mu_k \tag{17}$$

so

$$D_{Bkj} = D_k'' + D_j'' \tag{18}$$

In this case also the nature of the potential gradient expression $n_k\,\mathcal{D}\,\mu_k$ is such that the gradients for both components are accounted for, and the diffusion coefficient is symmetrical.

CONCLUSIONS

Any diffusion coefficient can be used to calculate material transport if the values of the coefficient and all the necessary volumetric and thermodynamic data are known throughout the states of interest. However, in many situations not all properties of the system are known, and there is obvious advantage in using a diffusion coefficient which itself remains relatively constant and which does not require thermodynamic properties for its application, as the latter are often not easily available.

The Chapman-Cowling coefficient is simple in application and shows the least variation with state of those coefficients examined for the methane-*n*-butane system. Other work has shown it to have a simple behavior in other binary hydrocarbon systems (*20*). It is concluded that the Chapman-Cowling coefficient is the most suitable of those investigated for application to binary hydrocarbon systems, and it is believed that it should be advantageous in application to other types of binary systems under conditions where the departure from ideal solution behavior is significant.

ACKNOWLEDGMENT

The helpful interest of Dr. J. L. Duda, of the Dow Chemical Company, is acknowledged.

NOTATION

The force-length-time system of units is used.

$\mathcal{D}$ = gradient operator
D_{Bkj} = Bird diffusion coefficient for components k and j, sq.ft./sec.
D_{Ckj} = Chapman-Cowling diffusion coefficient for components k and j, sq.ft./sec.
D_{Fk} = Fick diffusion coefficient for component k, sq.ft./sec.
D_k = diffusion coefficient for component k defined in Equation (6)
D_k' = diffusion coefficient for component k defined in Equation (11)
D_k'' = diffusion coefficient for component k defined in Equation (15)
D_{Mkj} = Maxwell diffusion coefficient for components k and j, lb./sec.
D_{Mk}' = modified Maxwell diffusion coefficient for component k, lb./sec.
D_{Vk} = volumetric diffusion coefficient for component k, sq.ft./sec.
F = free energy, B.t.u./lb.
f = fugacity, lb./sq.ft.
M = molecular weight, lb./lb.-mole
m = weight of material, lb.
$\dot{\mathbf{m}}$ = flux, lb./(sec.)(sq.ft.), referred to stationary coordinates
$\underset{\cdot}{\dot{\mathbf{m}}}$ = molal flux, lb.-mole/(sec.)(sq.ft.), referred to stationary coordinates
$\dot{\mathbf{m}}_d$ = flux due to molecular diffusion, lb./(sec.)(sq.ft.), referred to coordinates moving at the hydrodynamic or momentum velocity **u**
$\mathbf{m}_d$ = flux due to molecular diffusion, lb.-mole/(sec.)(sq.ft.), referred to coordinates moving at the molal average velocity **u**
n = weight fraction
$\underset{\cdot}{n}$ = mole fraction
P = absolute pressure, lb./sq.ft.
R = universal gas constant, (lb./sq.ft.)(cu.ft.)/(lb.-mole)(°R.); B.t.u./(lb.-mole)(°R.)
T = temperature, °R.
$\mathbf{u}$ = hydrodynamic, or momentum velocity, which is weight average velocity, ft./sec.
$\underset{\cdot}{\mathbf{u}}$ = molal average velocity, ft./sec.
V = specific volume, cu.ft./lb.
$\underset{\cdot}{V}$ = molal volume, cu.ft./lb.-mole
$\underline{V}$ = total volume, cu.ft.
$\bar{V}$ = partial specific volume, cu.ft./lb.
$\underset{\cdot}{\bar{V}}$ = partial molal volume, cu.ft./lb.-mole

Greek Letters

β = function
μ = chemical potential, B.t.u./lb.
$\underset{\cdot}{\mu}$ = chemical potential, B.t.u./lb.-mole
σ = specific weight, lb./cu.ft.
$\underset{\cdot}{\sigma}$ = reciprocal molal volume, lb.-mole/cu.ft.
σ_k = concentration of component k
∂ = partial differential operator
Σ = summation operator

Subscripts

i = index, component i
j = component j
k = component k
m = at constant weight
P = at constant pressure
T = at constant temperature
x = component in x direction
1, 2 . . . = components 1, 2 . . .

Superscript

o = pure component at same temperature and pressure

LITERATURE CITED

1. Fick, Adolf, *Ann. Phys., Ser. 2,* **94,** 59 (1855).
2. Maxwell, J. C., "Scientific Papers," Vol. 2, p. 625, University Press, Cambridge, England (1890).
3. Chapman, Sydney, and T. G. Cowling, "The Mathematical Theory of Non-Uniform Gases," 2 ed., University Press, Cambridge, England (1952).
4. Opfell, J. B., and B. H. Sage, *Ind. Eng. Chem.,* **47,** 918 (1955).
5. Jost, Wilhelm, "Diffusion in Solids, Liquids, Gases," Academic Press, New York (1952).
6. Reamer, H. H., J. H. Lower, and B. H. Sage, *J. Chem. Eng. Data,* **9,** 54 (1964).
7. Bird, R. B., W. E. Stewart, and E. N. Lightfoot, "Transport Phenomena," Wiley, New York (1960).
8. Kirkwood, J. G., R. L. Baldwin, P. J. Dunlop, L. J. Gosting, and Gerson Kegeles, *J. Chem. Phys.,* **33,** 1505 (1960).
9. Toor, H. L., *A.I.Ch.E. Journal,* **8,** 561 (1962).
10. Lewis, G. N., *J. Am. Chem. Soc.,* **30,** 668 (1908).
11. Kirkwood, J. G., and Bryce Crawford, Jr., *J. Phys. Chem.,* **56,** 1048 (1952).
12. Bird, R. B., "Theory of Diffusion, Advances in Chemical Engineering," Vol. 1, pp. 155-239, Academic Press, New York (1956).
13. Sherwood, T. K., and R. L. Pigford, "Absorption and Extraction," McGraw-Hill, New York (1952).

14. Lewis, G. N., and Merle Randall, "Thermodynamics", revised by K. S. Pitzer and Leo Brewer, 2 ed., McGraw-Hill, New York (1961).
15. Sage, B. H., B. L. Hicks, and W. N. Lacey, *Ind. Eng. Chem.*, 32, 1085 (1940).
16. ———, R. A. Budenholzer, and W. N. Lacey, *ibid.*, p. 1262.
17. Reamer, H. H., and B. H. Sage, *ibid., Chem. Eng. Data Ser.*, 1, 71 (1956).
18. Onsager, Lars, *Phys. Rev.*, 37, 405 (1931).
19. *Ibid.*, 38, 2265 (1931).
20. Sage, Bruce H., "Some Material Transport Properties of the Lighter Hydrocarbons in the Liquid Phase," Am. Petrol. Inst., New York (1964).

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Effective Binary Diffusion Coefficients in Mixed Solvents

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The diffusion of carbon dioxide through ethanol-water, benzene toluene, and carbon tetrachloride benzene was studied over the entire range of compositions for the solvent pairs. The results were interpreted in terms of an effective binary diffusion coefficient. Two semiempirical correlations were derived with the aid of absolute reaction rate theory to predict the effective binary diffusion coefficient from the binary diffusion coefficients of the solute in the individual pure solvents. These equations, although only crude approximations, reproduced the experimental data for six diffusion systems fairly well, including the highly nonideal solvent mixture ethanol-water.

Many absorption and extraction processes employ mixed solvents instead of a pure solvent. Since the theoretical treatment of such multicomponent diffusion processes on a rigorous basis is very complicated, it is desirable to be able to define and employ an effective binary diffusion coefficient (2) for the diffusing substance in mixed solvents by considering the mixed solvent as a pseudo pure liquid. One would like to have a simple method which permits the estimation of this effective binary diffusion coefficient from the binary diffusion coefficients of the solute in the individual solvents. Several empirical or semiempirical methods have been given in the literature for the diffusion of a dilute liquid component in mixed solvents (*18*, *25*). None of these methods apply to the case where the mixed solvent is highly nonideal.

The objective of this investigation was to develop a suitable approximate method for predicting the effective binary diffusion coefficient. The absorption of carbon dioxide into three mixed solvents, benzene-toluene, CCl_4-benzene, and ethanol-water, was measured and the results compared with a number of predictive methods. The third solvent system, ethanol-water, is known to be a highly nonideal mixture.

PREVIOUS PREDICTIVE RELATIONS

In a binary system, the diffusion coefficient is well defined; it is the mutual diffusion coefficient of the binary system. In multicomponent systems, however, there are many diffusion coefficients, and therefore it is desirable for practical purposes to define an effective binary diffusion coefficient for the component being absorbed or extracted. The idea of an effective binary diffusion coefficient is also useful in the analogies between momentum, heat, and mass transfer where a diffusion coefficient appears in the Chilton-Colburn j factor for mass transfer (*5*).

Historically, since most of the experimental work on diffusion has been for binary systems, it is desirable to have some methods which enable the prediction of the effective binary diffusion coefficient from the binary diffusion coefficients of component i in systems $i - j$. For the diffusion of a single gas into a stagnant multicomponent gas mixture, Wilke (*43*) derived from the Stefan-Maxwell equations the following expression for the effective binary diffusion coefficient

$$D_{1m} = (1 - x_1) \Big/ \sum_{j=2}^{n} (x_j / D_{1j}) \qquad (1)$$

where the subscript 1 refers to the diffusing gas and D_{1j} is the mutual diffusion coefficient of the binary system $1 - j$. The same expression was also obtained by Hsu and Bird (*19*) for the evaporation of a pure liquid into a multicomponent gas mixture. Fairbanks and Wilke (*10*) applied this equation with success to the diffusion of toluene vapor into a hydrogen-argon mixture and the diffusion of ethyl propionate into a hydrogen-air mixture.

No satisfactory method has been given in the literature for the prediction of the effective binary diffusion coefficient in a liquid phase. Bhat (*1*) studied the diffusion of some organic acids in ethanol-water mixtures of various compositions at 25°C. and proposed the following correlation:

$$D = 0.0104 \frac{\left(\dfrac{1}{M_A} + \dfrac{1}{M_B}\right)^{1/2}}{\eta (V_A^{1/3} + V_B^{1/3})^2} \qquad (2)$$