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Manuscript received February 24, 1978; revision received June 4, and accepted June 18, 1979.

Diffusivities of Low-Volatility Species in Light Gases

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Gas-phase diffusivities for high boiling point organics in common gases are determined by evaporating a single submicron aerosol droplet of the organic species, while it is suspended in an electric field in the path of a polarized laser beam. The droplet size is measured as a function of time by using Mie theory to determine the size from the light scattering data of intensity versus angle. In addition to diffusivities, the Lennard-Jones molecular interaction potential parameter, ϵ_{ii}, and the collision diameter σ_{ii}, are found, by applying the molecular theory of gases to interpret the evaporation rate data. Results are compared with available empirical and semi-theoretical correlations for diffusivities and Lennard-Jones parameters. The low vapor pressure organics used here are dioctyl phthalate (DOP), dibutyl sebacate (DBS) and dibutyl phthalate (DBP), and the carrier gases are helium, nitrogen and carbon dioxide.

SCOPE

Predictions of mass transfer rates in a wide variety of gas phase chemical processes require knowledge of diffusion coefficients. Furthermore, the prediction of the lifetime of low-volatility aerosol droplets in the atmosphere requires knowledge of their vapor pressure and the diffusivity of their vapor in the surrounding air. As indicated by Fuller et al. (1966), a large amount of data is available on binary gas phase systems of relatively low molecular weight, for example, ethanol in air, nonane in nitrogen, etc. Further, the kinetic theory of gases, as presented by Hirschfelder, Curtiss and Bird (1954), provides a rigorous theoretical method for predicting gas phase diffusivities for systems whose Lennard-Jones molecular interaction parameters are known or can be obtained from viscosity data.

Numerous empirical and semi-theoretical correlations have been proposed for the estimation of diffusivities. Among these are the equations of Arnold (1930), Gilliland (1934), Andrussow (1950), Chen and Othmer (1962) and Fuller et al. (1966). Correlations are available for predicting the Lennard-Jones parameters, and these include the methods of Hirschfelder, Bird and Spotz (1949), Wilke and Lee (1955), Chen and Othmer (1962), Stiel and Thodos (1962) and Viswanath and Kuloor (1967). Recently Reid, Prausnitz and Sherwood (1977) reviewed some of the proposed methods of parameter estimation and compared some of the methods of estimating gas-phase diffusion coefficients.

Most of the correlations have been compared with data for systems involving relatively low molecular weight species with low boiling points in common gases. Data are scarce for large molecular weight species with high

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boiling points. It is the purpose of this article to describe a new method for determining diffusivities and Lennard-Jones Parameters, which is well-suited to systems involving extremely low vapor pressure species diffusing in common gases. The results for dioctyl phthalate (DOP) and dibutyl sebacate (DBS) evaporating into helium, nitrogen and carbon dioxide and for dibutyl phthalate (DBP) evaporating into nitrogen are compared with available empirical and semi-theoretical equations to assess the suitability of the equations for binary systems—in which the two molecular species have appreciably different molecular weights and collision diameters.

CONCLUSIONS AND SIGNIFICANCE

Precise measurements of submicron droplet evaporation rates are made by means of light scattering measurements for a charged droplet suspended in an electric field. For diffusion-controlled evaporation, the rate data can be used to determine the Lennard-Jones molecular interaction potential parameter, ϵ_{ii}, and the collision diameter, σ_{ii}, from which the diffusivity, D_{ij}, can be calculated by using the results of the molecular theory of gases.

The equations for ϵ_{ii}/k proposed by Hirschfelder, Curtiss and Bird (1954) are in reasonably good agreement with the results for DOP, DBS and DBP obtained from our experiments. The correlations of Chen and Othmer (1962), Stiel and Thodos (1962) and Viswanath and Kuloor (1967) significantly underpredict ϵ_{ii}/k. Existing correlations for σ_{ii} do not agree well with the results of this study, but the correlation of Chen and Othmer (1962) comes closest to our values.

Diffusivities predicted by five existing correlations do not yield the observed variation of D_{ij} with the molecular weight of the carrier gas, and they tend to overpredict the diffusivities in CO_2 appreciably. The correlation of Chen and Othmer (1962) appears to be the best, although it overpredicts the diffusivities of DBS in all three carrier gases (He, N_2 and CO_2).

The diffusion-controlled evaporation of small liquid droplets was first analyzed by Maxwell (1880), who solved the problem of isothermal, quasi-steady state evaporation into an infinite medium of constant vapor concentration far from the droplet interface. He obtained the following expression for the mass flux of the volatile species

$$J_i = -\frac{D_{ij}}{a}(C_o - C_\infty) \tag{1}$$

where i refers to the evaporating species, and j refers to the carrier gas. If the surrounding gas initially contains none of species i and if no accumulation of species i is permitted to occur in the gas phase, we can write $C_\infty = 0$. If the evaporation is isothermal and the dilute vapor is an ideal gas, we can write

$$C_o = p^o M_i/RT \tag{2}$$

Chang and Davis (1974) showed that if the droplet evaporation is sufficiently slow, the interfacial temperature quickly attains a value very close to the temperature of the surrounding gas. They solved the unsteady state equations for the temperature fields inside and outside the drop, coupled with the unsteady state diffusion equation describing the concentration field outside the drop, to show that for small droplets evaporating slowly, the isothermal assumption is closely followed.

With the mass flux defined by

$$J = \frac{1}{4\pi a^2}\frac{d}{dt}\left(\frac{4}{3}\pi a^3 \rho\right) \tag{3}$$

for constant droplet density Equation (1), using Equation (2), becomes

$$\frac{da}{dt} = -\frac{D_{ij}}{a\rho}\frac{p^o M_i}{RT} \tag{4}$$

Equation (4) can be integrated to give

$$a^2 = a_o^2 + S_{ij}(t - t_o) \tag{5}$$

where $S_{ij} = -2D_{ij}p^o M_i/\rho RT$, and a_o is the droplet radius at time t_o. Equation (5) indicates that, for isothermal droplet evaporation, a plot of a^2 versus $(t - t_o)$ should yield a straight line with slope S_{ij}. Provided that the vapor pressure, p^o, and the other physical constants and parameters in S_{ij} are known, the diffusivity, D_{ij}, can be determined by measuring the slope of the a^2 versus $(t - t_o)$ plot.

Davis and his associates (1977, 1978) showed how this technique can be applied to extract a considerable amount of physical chemical information from evaporation rate data. A brief recapitulation of their procedure is in order here, for this work is an extension of their work to expand the amount of data available for testing correlations.

ANALYSIS OF SLOPE DATA

When the vapor pressure and diffusivity are both unknown, the determination of both parameters is not trivial. In this event, the vapor pressure can be eliminated by performing two different experiments at the same temperature, using the same evaporating species but two different carrier gases. Taking the ratios of the slopes for the two experiments we obtain

$$\frac{S_{12}}{S_{13}} = \frac{D_{12}}{D_{13}} \tag{6}$$

Now from the molecular theory of gases [Hirschfelder, Curtiss and Bird (1954)] we obtain

$$D_{ij} = \frac{2.628 \times 10^{-7}[T^3(M_i + M_j)/2M_iM_j]^{1/2}}{P\sigma_{ij}^2\Omega_{ij}^{*(1,1)}(T_{ij}^*)} \text{ in m}^2\text{/s} \tag{7}$$

where the collision integral $\Omega_{ij}^{*(1,1)}$, is a function of reduced temperature, $T_{ij}^* = kT/\epsilon_{ij}$. The Lennard-Jones parameters, σ_{ij} and ϵ_{ij}, arise from the use of the Lennard-Jones interaction potential, ϕ_{ij}, given by

TABLE 1. LENNARD-JONES PARAMETERS FOR THE CARRIER GASES

Collision diameter, Å	Potential parameter, K
$\sigma_{22} = \sigma_{He} = 2.576\ (2.551)$	$\epsilon_{22}/k = \epsilon_{He}/k = 10.2\ (10.22)$
$\sigma_{33} = \sigma_{N_2} = 3.681\ (3.798)$	$\epsilon_{33}/k = \epsilon_{N_2}/k = 91.5\ (71.4)$
$\sigma_{44} = \sigma_{CO_2} = 3.996\ (3.941)$	$\epsilon_{44}/k = \epsilon_{CO_2}/k = 190\ (195.2)$

$$\phi_{ij} = 4\epsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - \left(\frac{\sigma_{ij}}{r}\right)^{6}\right] \tag{8}$$

The molecular interaction parameters for unlike-molecule interactions can be related to those for like-molecule interactions by application of the following combining rules

$$\epsilon_{ij} = (\epsilon_{ii}\epsilon_{jj})^{1/2} \tag{9}$$

and

$$\sigma_{ij} = (\sigma_{ii} + \sigma_{jj})/2 \tag{10}$$

Other combining rules which have been proposed have been evaluated by Good and Hope (1970, 1971). Equations (9) and (10) are the most frequently applied rules, are reasonably accurate according to Good and Hope, and have the virtue of simplicity.

Introducing Equations (7), (9) and (10) in Equation (6) yields

$$\frac{S_{12}}{S_{13}} = \left(\frac{\sigma_{11} + \sigma_{33}}{\sigma_{11} + \sigma_{22}}\right)^2 \frac{\Omega_{13}^{*(1,1)}(T_{13}^*)}{\Omega_{12}^{*(1,1)}(T_{12}^*)}\left[\frac{(M_1 + M_2)M_3}{(M_1 + M_3)M_2}\right]^{1/2} \tag{11}$$

where $T_{ij}^* = kT/(\epsilon_{ii}\epsilon_{jj})^{1/2}$. The experimentally determined ratio, S_{12}/S_{13}, can be written in terms of the two unknown like-molecule parameters, σ_{11} and ϵ_{11}. It is assumed that σ_{22}, ϵ_{22}, σ_{33} and ϵ_{33} for the carrier gases are known. Hirschfelder, Curtiss and Bird (1954) and Svehla (1962) have tabulated these parameters for many common gases, including the three carrier gases used in our experiments—He, N_2 and CO_2. The numerical values used here, those of Hirschfelder et al., are given in Table 1. Svehla's values are given in parentheses in the table. Except for N_2, the values of σ_{jj} and ϵ_{jj}/k from the two sources are in very close agreement. Since $\sigma_{ii} > \sigma_{jj}$ in our studies and since the collision integral is not highly sensitive to ϵ_{jj}/k, here it makes little difference whether we use the values of Hirschfelder et al. or Svehla's in the computations. For N_2 the differences are less than 2% in the calculated diffusivities.

To solve for σ_{11} and ϵ_{11} it is clear that a second equation is needed. This is obtained by performing a third experiment at the same temperature using yet another carrier gas. The result is

$$\frac{S_{12}}{S_{14}} = \left(\frac{\sigma_{11} + \sigma_{44}}{\sigma_{11} + \sigma_{22}}\right)^2 \frac{\Omega_{14}^{*(1,1)}(T_{14}^*)}{\Omega_{12}^{*(1,1)}(T_{12}^*)}\left[\frac{(M_1 + M_2)M_4}{(M_1 + M_4)M_2}\right]^{1/2} \tag{12}$$

In the experiments described below, species 1 refers to either DBP, DOP or DBS, 2 refers to He, 3 refers to N_2 and 4 refers to CO_2.

Equations (11) and (12) can be solved for σ_{11} and ϵ_{11} by the iterative procedure outlined by Davis and Ray (1977), and once these molecular interaction parameters have been calculated the appropriate diffusivity is obtained from Equation (7) together with the combining laws, Equations (9) and (10).

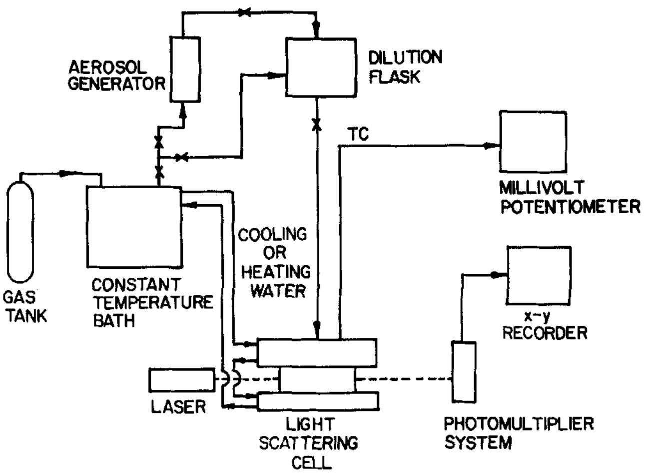

Figure 1. The experimental system.

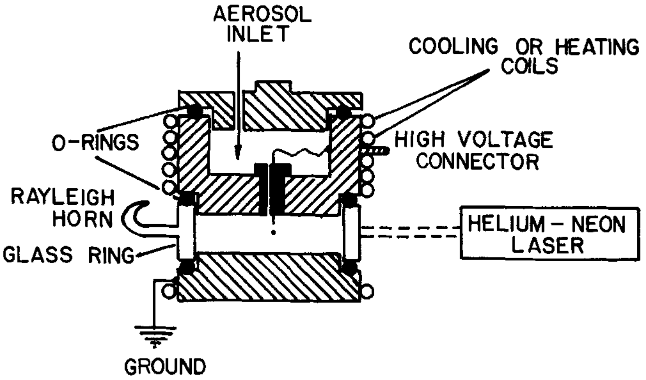

Figure 2. The light scattering cell.

An alternate method can also be used to determine the Lennard-Jones parameters from the measured slopes of a^2 versus $(t - t_o)$ data. Rather than carrying out three experiments at the same temperature in three different carrier gases, three experiments can be performed with the same carrier gas at three different temperatures. In this case, it is convenient to write the vapor pressure as a function of temperature using the Clausius-Clapeyron equation,

$$p^o(T) = p^o(T_o)\exp\left[\frac{(-\Delta H_{vap})}{R}\left(\frac{1}{T_o} - \frac{1}{T}\right)\right] \tag{13}$$

where T_o is a reference temperature, say the lowest temperature level used. Using Equations (7), (9), (10) and (13), and assuming ΔH_{vap} to be known, we obtain the slope ratio

$$\frac{S_{12}(T_1)}{S_{12}(T_o)} = \left(\frac{T_1}{T_o}\right)^{3/2} \frac{\Omega_{12}^{*(1,1)}\{kT_o/(\epsilon_{11}\epsilon_{22})^{1/2}\}}{\Omega_{12}^{*(1,1)}\{kT_1/(\epsilon_{11}\epsilon_{22})^{1/2}\}} \exp\left[\frac{(-\Delta H_{vap})(T_1 - T_o)}{RT_oT_1}\right] \tag{14}$$

from which ϵ_{11} can be calculated. When ΔH_{vap} is known only two experiments are required to determine ϵ_{11}. If ΔH_{vap} is unknown, then a third experiment can be used to provide the second equation,

$$\frac{S_{12}(T_2)}{S_{12}(T_o)} = \left(\frac{T_2}{T_o}\right)^{3/2} \frac{\Omega_{12}^{*(1,1)}\{kT_o/(\epsilon_{11}\epsilon_{22})^{1/2}\}}{\Omega_{12}^{*(1,1)}\{kT_2/(\epsilon_{11}\epsilon_{22})^{1/2}\}} \exp\left[\frac{(-\Delta H_{vap})(T_2 - T_o)}{RT_oT_2}\right] \tag{15}$$

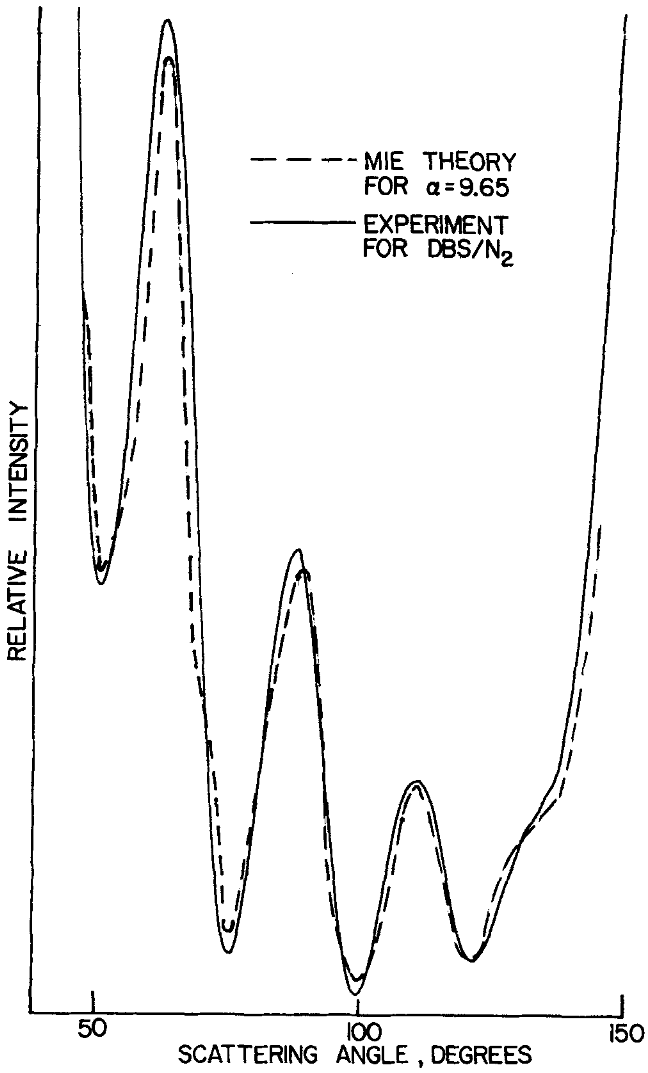

Figure 3. A comparison between the light scattering profiles and Mie theory, for DBS in N$_2$ for $t - t_0 = 0$ s.

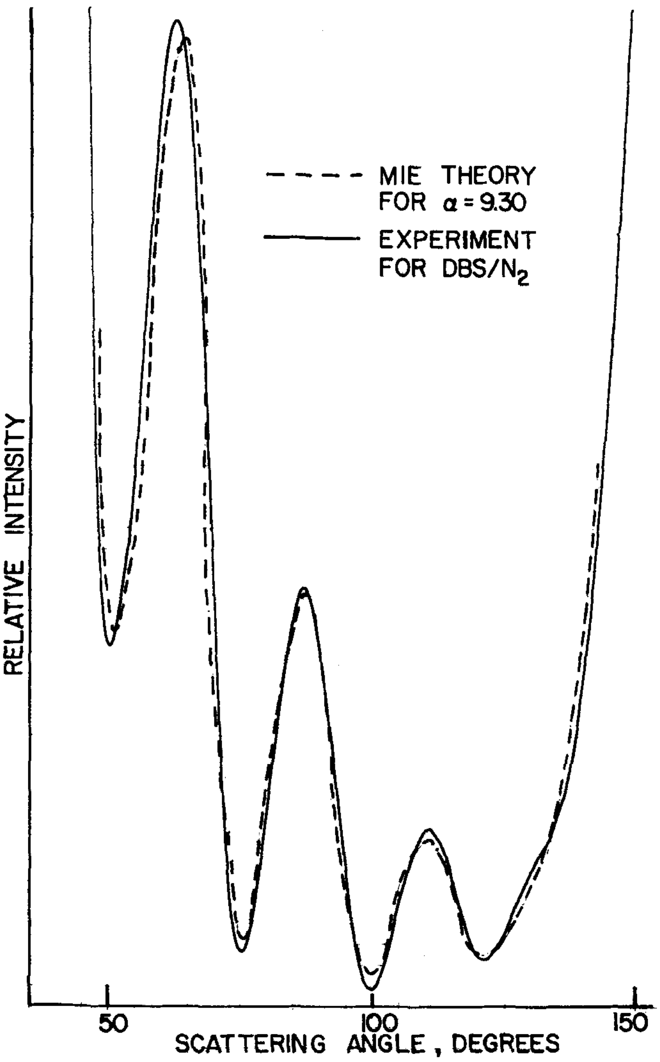

Figure 4. A comparison between the light scattering profiles and Mie theory for DBS in N$_2$ $t - t_0 = 350$ s.

Davis, Ravindran and Ray (1978) used this technique to measure the heat of vaporization as well as the Lennard-Jones parameters. To obtain the collision diameter by the variable temperature method we employ the definition of the slope, S_{ij}, together with Equations (7), (9) and (13) to give the equations

$$S_{ij}(T_o) = -\frac{\beta_{ij}}{\sigma_{ij}^2}\frac{p^o(T_o)T_o^{3/2}}{\Omega_{ij}^{*(1,1)}\{kT_o/(\epsilon_{ii}\epsilon_{jj})^{1/2}\}} \quad (16)$$

and

$$S_{ij}(T) = -\frac{\beta_{ij}}{\sigma_{ij}^2}\frac{p^o(T_o)T^{3/2}\exp[-\Delta H_{vap}(T - T_o)/RT_oT]}{\Omega_{ij}^{*(1,1)}\{kT/(\epsilon_{ii}\epsilon_{jj})^{1/2}\}} \quad (17)$$

where β_{ij} is given by

$$\beta_{ij} = 5.256 \times 10^{-7}[(M_i + M_j)/2M_iM_j]^{1/2}/\rho RP \quad (18)$$

when D_{ij} has units of m^2/s.

Since ϵ_{ii} and ΔH_{vap} are known from above the vapor pressure at reference temperature T_o, $p^o(T_o)$, and σ_{ij} can be obtained from the slope data at temperatures T_o and T using Equations (16) and (17). Finally, σ_{ii} is obtained by applying the mixing rule, Equation (10).

Thus, three experiments at the same temperature in three carrier gases provide sufficient information to calculate σ_{ii}, ϵ_{ii} and p^o. We refer to this method as the VCG (variable carrier gas) method. Alternatively, four experiments in the same carrier gas at four temperatures provide information to calculate the above three parameters plus ΔH_{vap}. The latter method we call the VT (variable temperature) method. Both the VCG and VT methods have been applied here, and the results are compared below.

EXPERIMENTAL SYSTEM

The experimental apparatus and procedures have been described in considerable detail by Davis and Chorbajian (1974), Chang and Davis (1976) and Davis and Ray (1977), so only a brief outline of the experimental aspects of the research is needed here.

A Science Spectrum Differential II light scattering photometer is modified to provide temperature and pressure control of the light scattering cell. A schematic diagram of the experimental equipment is shown in Figure 1. The aerosol is generated and charged by atomization of an emulsion of the organic in distilled and deionized water. No emulsifier is used, to avoid contamination of the organic droplets. The aerosol is then diluted with additional carrier gas, and the small amount of water surrounding the droplets evaporated, leaving the charge on the organic droplets. The dilute aerosol is then introduced into the upper chamber of the light scattering cell, shown in Figure 2, and a small amount

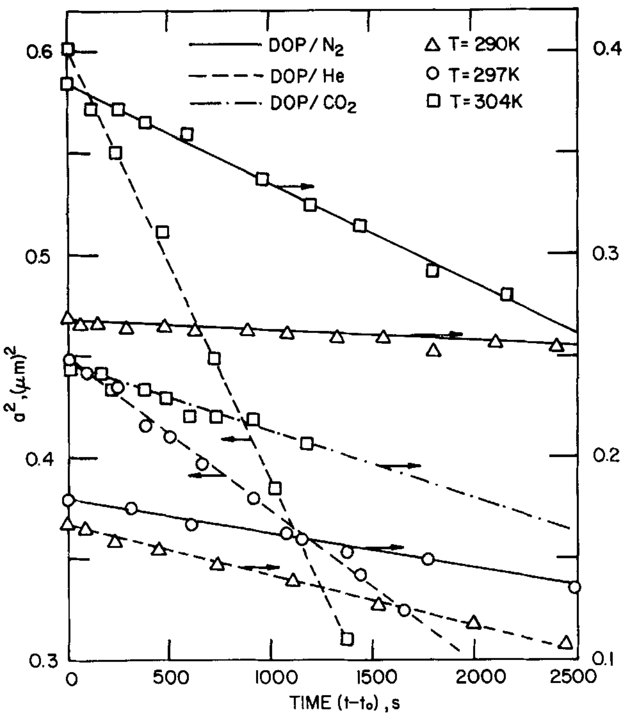

Figure 5. Evaporation rate data for DOP in the various carrier gases at various temperatures.

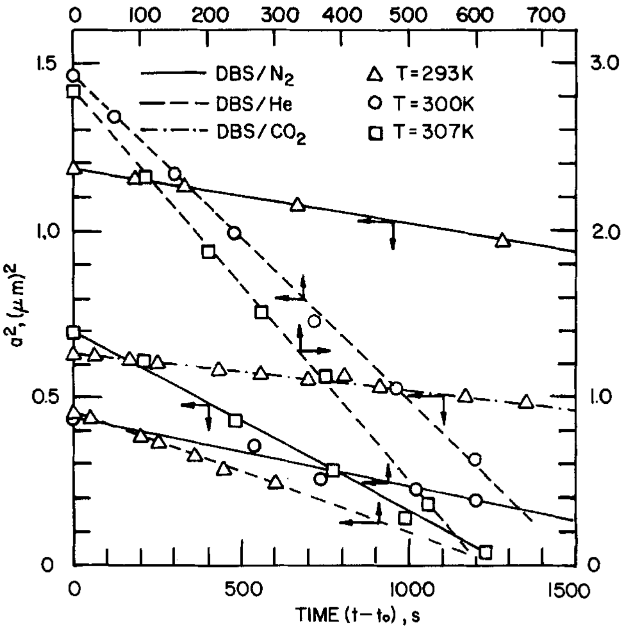

Figure 6. Evaporation rate data for DBS in the various carrier gases at various temperatures.

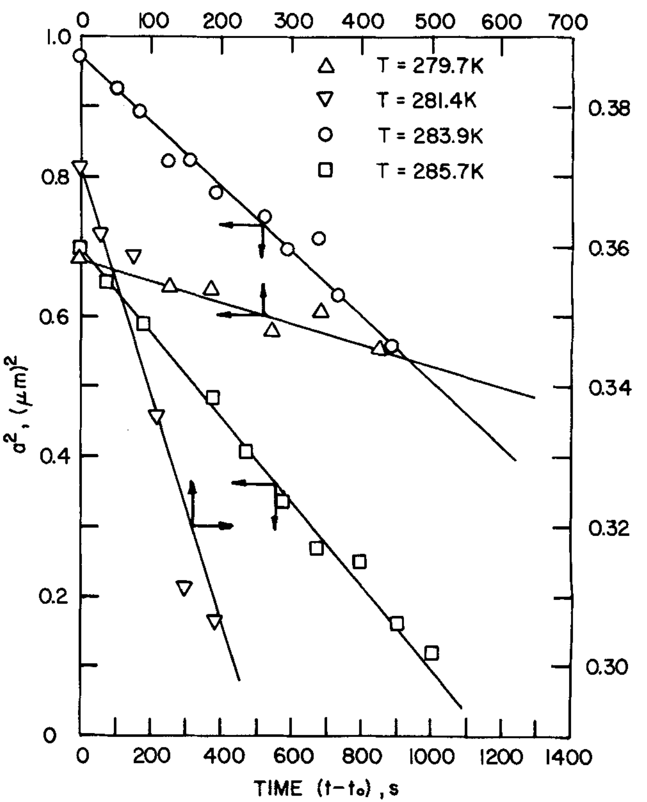

Figure 7. Evaporation rate data for DBP in N_2 at various temperatures.

of aerosol drawn through the small hole in the insulation around the electrified pin by means of a bellows attached to the exit line. The electric field set up by the electrified pin and the grounded lower plate tended to center the charged droplet along the vertical axis. The voltage and polarity are adjusted manually, until a droplet is "caught," and at this point in time, the automatic control features of the Science Spectrum device are activated to suspend the droplet automatically.

Once a droplet is suspended, a photomultiplier is traversed in the horizontal plane, to measure the intensity of the scattered light as a function of angle. Repeated traverses over the range $40° \leq \theta \leq 150°$ are made during the course of an evaporation run to determine the size as a function of time. Since a typical run exceeded 10 minutes in length and a traverse required only 14 seconds, numerous traverses could be taken before a droplet is either reduced to a size where significant vertical oscillations occurred or the run is intentionally terminated.

The output of the traversing photomultiplier is recorded on a stripchart recorder which was synchronized with the traversing mechanism, to produce a plot of intensity versus angle. Typical tracings of this type are shown in Figures 3 and 4.

From the Mie theory of light scattering the intensity of the scattered light is a function of the droplet radius, a, the wavelength, λ, of the light source, the refractive index

Table 2. Slopes of the a^2 Versus $(t - t_0)$ Data

$-S_{ij} \times 10^5$ $(\mu m)^2/s$	DOP			DBS			
	$T_0 = 290K$	$T_1 = 297K$	$T_2 = 304K$	$T_0 = 293K$	$T_1 = 300K$	$T_2 = 307K$	$T_0 = 279.7K$
$-S_{12}$	2.47	7.48	21.5	75.4	194	475	—
$-S_{13}$	0.559	1.70	4.91	17.0	44.0	108	24.5
$-S_{14}$	—	—	3.22	—	—	11.0	—
			He = 2		N_2 = 3		CO_2 = 4

of the medium, m, and the scattering angle, θ. The wavelength of the helium-neon laser used here was 632.8 nm, and the refractive indices of DBP, DOP and DBS are known as a function of temperature for this wavelength. Davis and Ray (1977) discussed the Mie theory more fully than we need here. Suffice it to point out that for nondimensional size $\alpha = 2\pi a/\lambda$ the intensity can be calculated as a function of θ for a specific refractive index. Because the Mie theory equations cannot be inverted to determine α directly from the light scattering profiles (intensity versus angle) it is necessary to match theory with data to establish the α which best fits the data. Chang and Davis (1976) developed an optimization technique to determine α to within 1% from data of the type shown in Figures 3 and 4, and we have used their optimization routine here. The "best fit" curves from Mie theory are also plotted on Figures 3 and 4 to show the close agreement between Mie theory and the experimental results obtained here.

EXPERIMENTAL RESULTS

Evaporation rates for DOP were measured in He and N_2 at temperatures of 290K, 297K and 304K, and at 304K a third carrier gas, CO_2, is used. For DBS, data are taken in He and N_2 at 293K, 300K and 307K and in CO_2 at 307K. For DBP, only N_2 is used as the carrier gas at 279.7K, 281.4K, 283.9K and 285.7K. Temperatures near room temperature are used to avoid undesirable temperature gradients in the light scattering chamber.

Typical results of a^2 versus $(t - t_o)$ are presented in Figures 5, 6 and 7 for DOP, DBS and DBP, respectively. The straight lines obtained confirm that the evaporation was, indeed, diffusion-controlled. The slopes obtained by least squares fitting of the data are given in Table 2.

Note that, as expected, the evaporation rate for a particular organic species at a specified temperature decreases as the molecular weight of the carrier gas increases. For a specified binary system, for example DOP in N_2, the evaporation rate increases with increasing temperature.

The data base of Table 2 provides sufficient information to calculate the diffusion parameters and vapor pressures of DBS and DOP by three independent methods, that is, using the VCG method at 304K and the VT method for the He and N_2 data. The parameters for DBP are obtained using the VT method for DBP in N_2. The reproducibility determined by using the different methods is better than the uncertainties associated with the solution procedure would suggest likely. This point requires some clarification.

In the iterative solution procedure used to solve the appropriate equations for the unknown parameters, a trial value of ϵ_{11} was selected to start the calculations. For example, in the solution of Equations (14) and (15), substitution of the trial value for ϵ_{11} in Equation (14) permits one to solve for ΔH_{vap} using the experimentally measured value of $S_{12}(T_1)/S_{12}(T_o)$. If these values of ϵ_{11} and ΔH_{vap} do not satisfy Equation (15) to within some specified criterion of accuracy, a new value of ϵ_{11} is assumed and the procedure repeated. In principle, this straightforward method should yield unique solutions for the unknown parameters, but because the collision integral is a weak function of ϵ_{11} in the range of values of T_{ij}^* encountered here the difference $|S_{12}(T_2)/S_{12}(T_o)_{\text{measured}} - S_{12}(T_2)/S_{12}(T_o)_{\text{calculated}}|$ does not have a well-defined minimum considered as a function of ϵ_{11} and ΔH_{vap}. That is, for a specified non-zero value of the above function, there is more than one set of values of ϵ_{11} and ΔH_{vap} which satisfy that value of the function.

DBP

$T_1 = 281.4K$	$T_2 = 283.9K$	$T_3 = 285.7K$
—	—	—
32.2	46.6	60.6
—	—	—

TABLE 3. CALCULATED VALUES OF THE PARAMETERS WHICH SATISFY EQUATIONS (14) AND (15) WITH THE SAME ACCURACY

DOP/N_2

	ϵ_{11}/k, K	ΔH_{vap}, — MJ/kmol	σ_{11}, Å	p^0(290K), μPa
	598	111.33	10.0	5.404
	694	111.34	9.91	5.516
	711	111.34	9.70	5.379
	763	111.27	9.90	5.635
Average	692	111.32	9.88	5.484

DOP/He

	ϵ_{11}/k, K	ΔH_{vap}, — MJ/kmol	σ_{11}, Å	p^0(290K), μPa
	585	111.39	10.1	5.791
	780	111.33	10.1	6.000
Average	683	111.36	10.1	5.896

Table 3 shows typical results calculated from the DOP data for various values of ϵ_{11}/k and ΔH_{vap} which satisfy Equations (14) and (15) with the same accuracy. Also given in the table are the values of σ_{11} and $p^0(T_o)$ computed from the data. From the DOP/N_2 data ϵ_{11}/k varies from 598K to 763K, and from the DOP/He data nearly the same range is encountered, that is $585K \leq \epsilon_{11}/k \leq 780K$. The averages for these data sets are quite close, 692K and 683K. There is very little variation in the calculated heat of vaporization, and the average value calculated for DOP is -111.34 MJ/kmol, which is in excellent agreement with the values -110.0 MJ/kmol and -107.1 MJ/kmol reported by Small et al. (1948) and Hickman et al. (1937), respectively, near the boiling point of DOP.

The collision diameter shows considerably less variation than ϵ_{11}/k, ranging from 9.70 Å to 10.1 Å, and the vapor pressure at 290K varies from 5.379 μPa from these calculations. The vapor pressure is a very strong function of temperature here, so slight errors in the measurement of the cell temperature could easily account for the differences between the calculated average vapor pressures for the N_2 and He runs.

A more sophisticated statistical analysis of the data will be reported elsewhere, but from the results of the present calculations, we can estimate average absolute errors. Results of all of our calculations are reported in Table 4. Also included in the table are the diffusivities calculated from the average values of σ_{11} and ϵ_{11}/k for atmospheric pressure and 298K.

Table 4. A Summary of Experimental Results

Lennard-Jones parameters

DOP		DBS		DBP	
σ_{DOP}, Å	ϵ_{DOP}/k, K	σ_{DBS}, Å	ϵ_{DBS}/k, K	σ_{DBP}, Å	ϵ_{DBP}/k, K
9.95 ± 0.12	689 ± 65	9.97 ± 0.26	688 ± 72	8.84 ± 0.13	672 ± 74

Diffusivities at 298K and 1 atm

	DOP/He	DOP/N_2	DOP/CO_2	DBS/He	DBS/N_2	DBS/CO_2	DBP/N_2
$D_{ij} \times 10^6$, m^2/s	13.2	3.08	1.98	13.6	3.02	1.95	3.67

COMPARISON OF RESULTS WITH CORRELATIONS

Lennard-Jones Parameters

Hirschfelder, Bird and Spotz (1949) obtained the following approximate relations for σ_{ii} and ϵ_{ii}/k from the Lennard-Jones and Devonshire (1937) theory of gases and liquids:

$$\sigma_{ii} = 0.833\, V_c^{1/3} \tag{19}$$

$$\epsilon_{ii}/k = 0.75\, T_c \tag{20}$$

$$\epsilon_{ii}/k = 1.39\, T_b \tag{21}$$

They compared these approximations with parameters calculated from viscosity data for 33 gases, the largest molecular weight species being *n*-nonane. As pointed out by Wilke and Lee (1955), the constant 1.21 is preferable to 1.39 in Equation (21).

Hirschfelder, Curtiss and Bird (1954) proposed the following equations to supersede Equations (20) and (21):

$$\epsilon_{ii}/k = 0.77\, T_c \tag{22}$$

$$\epsilon_{ii}/k = 1.15\, T_b \tag{23}$$

$$\epsilon_{ii}/k = 1.92\, T_m \tag{24}$$

Wilke and Lee (1955) recommended replacing the frequently unknown critical volume, V_c, by the molal volume at the normal boiling point, V_b, to give

$$\sigma_{ii} = 1.18\, V_b^{1/3} \tag{25}$$

They also found the equation,

$$\epsilon_{ii}/k = 1.21\, T_b \tag{26}$$

to be better for the prediction of diffusivities than other empirical relations tried. They pointed out that since the collision integral, $\Omega_{12}^{*(1,1)}$, is relatively insensitive to small errors in ϵ_{ii}/k, Equations (23) and (26) are nearly equivalent. The molal volume, V_b, can be estimated by the method of Le Bas (1915), which gives $V_b = 524.8$ cm^3/g-mole for DOP, 421.2 cm^3/g-mole for DBS and 347.2 cm^3/g-mole for DBP. The normal boiling points for these three species are approximately 600K, 618K and 614K, respectively.

Table 5. Estimated Critical Properties by the Method of Lydersen (1955)

	DOP	DBS	DBP
T_c, K	735	772	782
P_c, atm	11.47	15.0	17.2
V_c, cm^3/g-mole	1,300	988	860
Z_c	0.2473	0.2343	0.2305

In the absence of critical temperature data, T_c can be estimated from

$$T_c = 1.50\, T_b \tag{27}$$

More recently Fuller, Schettler and Giddings (1966) tabulated atomic diffusion volumes, v_i, for simple molecules and for the contributions of individual atoms in molecules which can be used to estimate σ_{ii} from a modification of Equation (25),

$$\sigma_{ii} = 1.18\, (\Sigma v_i)^{1/3} \tag{28}$$

From their tabulations, we obtain $\Sigma v_i = 473.0$ cm^3/g-mole for DOP, 366.2 cm^3/g-mole for DBS and 309.3 cm^3/g-mole for DBP. As pointed out by Fuller et al, these volumes are about 10% lower than the equivalent Le Bas volumes.

Chen and Othmer (1962) examined the relationship between ϵ_{ii}/k and T_c and that between σ_{ii} and V_c, and they applied the method of least squares to available data to give

$$\sigma_{ii} = 0.5894\, V_c^{0.4006} \tag{29}$$

$$\epsilon_{ii}/k = 1.276\, T_c^{0.9061} \tag{30}$$

In the same year, Stiel and Thodos (1962) proposed correlations in terms of the critical properties of the chemical species. Their equations are:

$$\sigma_{ii} = 0.1866\, V_c^{1/3} Z_c^{-6/5} \tag{31}$$

$$\epsilon_{ii}/k = 65.3\, T_c Z_c^{18/5} \tag{32}$$

The critical properties, T_c, P_c and V_c, and the critical compressibility, Z_c, can be estimated by the method of Lydersen (1955). Lydersen employs structural contributions to estimate the critical properties from the equations,

$$T_c = T_b[0.567 + \Sigma\Delta_T - (\Sigma\Delta_T)^2]^{-1} \tag{33}$$

$$P_c = M_i[0.34 + \Sigma\Delta_p]^{-2} \tag{34}$$

$$V_c = 40 + \Sigma\Delta_v \tag{35}$$

The delta quantities represent contributions due to individual atoms or groups of atoms, and they have been tabulated by Lydersen. For DOP, we obtain: $\Sigma\Delta_T = 0.48$, $\Sigma\Delta_p = 5.496$ and $\Sigma\Delta_v = 1260$. For DBS, the corresponding contributions are 0.37, 4.236 and 948. For DBP, we estimate 0.32, 3.680 and 820. The calculated critical properties are listed in Table 5.

Viswanath and Kuloor (1967) suggested eliminating V_c, which is not usually available, and they correlated the Lennard-Jones parameters with the ideal critical volume, V_{ci}, defined by

$$V_{ci} = RT_c/P_c \tag{36}$$

They proposed the relations

Table 6. Comparison Between Experimental and Predicted Values of Lennard-Jones Parameters

Source	σ_{DOP}, Å	σ_{DBS}, Å	σ_{DBP}, Å
This work	9.95 ± 0.12	9.97 ± 0.26	8.84 ± 0.13
Hirschfelder, Bird and Spotz (1949)	9.07	8.28	7.90
Wilke and Lee (1955)	9.50	8.83	8.28
Chen and Othmer (1962)	10.4	9.33	8.83
Stiel and Thodos (1962)	10.9	10.6	10.3
Viswanath and Kuloor (1967)	11.3	10.4	9.87
Equation (28)	9.2	8.43	7.97
	ϵ_{DOP}/k, K	ϵ_{DBS}/k, K	ϵ_{DBP}/k, K
This work	689 ± 65	688 ± 72	672 ± 74
Equations (22) and (27)	695	713	709
Equation (25)	—	505	—
Equation (23)	690	710	706
Equation (26)	726	747	743
Chen and Othmer (1962)	505	528	534
Stiel and Thodos (1962)	314	271	259
Viswanath and Kuloor (1967)	322	353	367

$$\sigma_{ii} = 0.3676\, V_{c_i}^{0.4} \qquad (37)$$

$$\epsilon_{ii}/k = 2.43\, T_c V_{c_i}^{-0.2} \qquad (38)$$

The various correlations discussed above are compared with the average experimental values of σ_{ii} and ϵ_{ii}/k in Table 6.

Diffusivities

Arnold (1930) extended Sutherland's (1893) hard sphere model of the kinetic theory of gases to give

$$D_{ij} = \frac{8.37 \times 10^{-7} T^{3/2}[(M_i + M_j)/M_i M_j]^{1/2}}{P(V_{b_i}^{1/3} + V_{b_j}^{1/3})^2 (1 + C^*/T)} \qquad (39)$$

where

$$C^* = 1.47 \left[\frac{2(V_{b_i}^{1/3} \cdot V_{b_j}^{1/3})^{1/2}}{V_{b_i}^{1/3} + V_{b_j}^{1/3}} \right]^3 (T_{b_i} T_{b_j})^{1/2} \qquad (40)$$

Again, the molal volumes at the boiling point, V_{b_i} and V_{b_j}, can be estimated by the method of Le Bas (1915).

Gilliland (1934) proposed a simple correlation based on the hard sphere model, which is

$$D_{ij} = \frac{4.3 \times 10^{-7} T^{3/2}[(M_i + M_j)/M_i M_j]^{1/2}}{P(V_{b_i}^{1/3} + V_{b_j}^{1/3})^2} \qquad (41)$$

Andrussow (1950) improved the temperature dependence on Gilliland's correlation to give

$$D_{ij} = \frac{6.06 \times 10^{-5} T^{1.78}\{[(M_i + M_j)/M_i M_j]^{1/2} + (M_i M_j)^{-1/2}\}}{P(V_{b_i}^{1/3} + V_{b_j}^{1/3})^2} \qquad (42)$$

where P is in units of torr.

Yet another correlation was proposed by Chen and Othmer (1962) by modifying the theoretical equation of Hirschfelder, Bird and Spotz. They eliminated the collision integral, replacing it by an empirical correlation for it, to give

$$D_{ij} = \frac{4.3 \times 10^{-5} (T/100)^{1.81} [(M_i + M_j)/M_i M_j]^{1/2}}{P\left(\dfrac{T_{c_i} T_{c_j}}{10{,}000}\right)^{0.1406} \left[\left(\dfrac{V_{c_i}}{100}\right)^{0.4} + \left(\dfrac{V_{c_j}}{100}\right)^{0.4}\right]} \qquad (43)$$

This equation gives much the same results as the equation of Hirschfelder, Bird and Spotz, but at high temperatures it predicts higher diffusivities due to the 1.81 power temperature dependence.

Fuller, Schettler and Giddings (1966) developed an empirical correlation for D_{ij} and compared it with eight other methods, including the above, and with 340 experimental values of the diffusivity available in the literature. Their correlation, which agreed with the data better than other empirical correlations examined, is

Table 7. Comparison Between the Diffusivities Obtained Here and Empirical Correlations

	$D_{ij} \times 10^6$, m²/s						
Source	DOP/He	DOP/N$_2$	DOP/CO$_2$	DBS/He	DBS/N$_2$	DBS/CO$_2$	DBP/N$_2$
This work	13.2	3.08	1.98	13.6	3.02	1.95	3.67
Arnold (1930)	19.3	3.79	2.39	21.6	4.13	2.60	3.95
Gilliland (1934)	11.2	3.45	2.76	12.6	3.86	3.10	3.87
Andrussow (1950)	10.7	3.31	2.65	12.1	3.72	2.98	3.67
Chen and Othmer (1962)	13.8	3.16	2.25	16.3	3.72	2.65	3.60
Fuller et al. (1966)	12.7	3.88	2.93	14.3	4.43	3.35	4.33

$$D_{ij} = \frac{1.00 \times 10^{-7} T^{1.75} [(M_i + M_j)/M_i M_j]^{1/2}}{P\left[\left(\sum_i v_l\right)^{1/3} + \left(\sum_j v_k\right)^{1/3}\right]^2} \quad (44)$$

where the atomic diffusion volumes, v_l and v_k, were tabulated by the authors as mentioned above.

It should be pointed out that the systems for which diffusivities were available did not involve a high boiling species.

Table 7 compares the diffusivities obtained in this study with the above correlations. The diffusivities tabulated are for 298K and atmospheric pressure.

DISCUSSION OF RESULTS

Table 6 shows that the predicted collision diameters scatter about the values obtained here for all three evaporating species. The predictions of the Chen and Othmer correlation appear to agree best with the experimental results, and the correlations of Stiel and Thodos and Viswanath and Kuloor significantly overpredict the collision diameters. The correlations of Hirschfelder et al. (1949) and Wilke and Lee tend to underpredict σ_{11}.

For the molecular interaction potential parameter, ϵ_{11}/k, Equation (22) with (27) and Equation (23) agree reasonably well with the results obtained here. Equation (26), due to Wilke and Lee, slightly overpredicts ϵ_{11}/k, and Equation (25) and the correlation of Chen and Othmer underpredict ϵ_{11}/k. Again the correlations of Stiel and Thodos and Viswanath and Kuloor are in poorest agreement with our results, for they predict values of ϵ_{11}/k equal to about one-half our values.

Predicted diffusivities vary appreciably from correlation to correlation. Not surprisingly, Arnold's equation based on a hard sphere model tends to overpredict diffusivities by as much as 46%. All of the correlations tend to overpredict the diffusivities in CO_2 even when they are reasonably close to the results for He and N_2. The correlation of Chen and Othmer shows the best agreement with our results, although it overpredicts the diffusivities for DBS by as much as 35.9% for DBS in CO_2 and 19.9% for DBS in He.

The correlation of Fuller et al., which is in good agreement with a large amount of data for lower molecular weight species, does not satisfactorily predict the molecular weight dependence. That is, the error in the predicted diffusivity is seen to increase with increasing molecular weight of the carrier gas. For DOP in CO_2 and DBS in CO_2, the errors are +48.0% and +71.8%, respectively. For DOP and DBS in He, the errors are −3.8% and 5.2%, respectively.

Part of the discrepancy between predicted diffusivities and those reported here can be due to the fact that in the development of the kinetic theory of gases leading to Equation (7) and in the semi-theoretical correlations based on kinetic theory, the only mode of energy exchange between molecules is assumed to be translational. In polyatomic atoms such as those encountered here, it is possible that rotational modes are affected. In this case, Equation (7) is not rigorously correct, and the application of Equation (7) to the analysis and interpretation of the data is not precise. The resulting values of σ_{11} and ϵ_{11} calculated from the evaporation rate would include the effects of translational-rotational interaction in a nonrigorous manner. The results for DOP and DBS in CO_2 would be the most questionable in this case, and none of the semi-theoretical equations would be suitable either.

ACKNOWLEDGMENT

The authors are grateful to the National Science Foundation for Grants CHE 76-18586 and CHE 78-20945 which supported this work.

NOTATION

a = droplet radius, μm
C = concentration of vapor, kg/m^3
C^* = constant defined in Equation (40)
D_{ij} = diffusivity, m^2/s
ΔH_{vap} = heat of vaporization, MJ/kmol
J_i = flux of species i, kg/m^2-s
k = Boltzmann's constant, J/kmol
M = molecular weight
p^o = vapor pressure, μPa
P = total pressure, atm. or Pa
r = distance between molecules, Å
R = gas constant
S_{ij} = slope of the a^2 versus $(t - t_o)$ line, $(\mu m)^2/s$
t = time, s
T = temperature, K
T_{ij}^* = reduced temperature, dimensionless
v, V = molecular volumes, cm^3/mole
Z = compressibility factor = PV/RT

Greek Letters

α = dimensionless droplet size
β_{ij} = group of parameters defined by Equation (18)
Δ = group contributions
ϵ = Lennard-Jones molecular interaction parameter, J/kmol
θ = light scattering angle
λ = wavelength of laser light, nm
ρ = liquid density, kg/m^3
σ = collision diameter, Å
ϕ_{ij} = Lennard-Jones potential, J/kmol
$\Omega_{ij}^{*(1,1)}$ = collision integral

Subscripts

b = boiling point value of property
c = critical value of property
i = the i^{th} or evaporating species
j = the carrier gas
m = melting point value of property
o = reference state

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Manuscript received February 9, 1979; revision received June 4, and accepted June 18, 1979.

Sweetening of Sour Natural Gases by Mixed-Solvent Absorption: Solubilities of Ethane, Carbon Dioxide, and Hydrogen Sulfide in Mixtures of Physical and Chemical Solvents

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Solubilities of ethane, carbon dioxide, and hydrogen sulfide have been measured in propylene carbonate, N-methyl-2-pyrrolidone and tetramethylene sulfone (sulfolane); and in mixtures of these physical solvents with monoethanolamine and diglycolamine, in the range −10 to 100°C. Thermodynamically consistent equations are given for gas absorption with chemical reaction at equilibrium. Henry's law describes physical equilibrium between the acidic gas in the vapor phase and free acid solute in the liquid phase. Equilibrium constants describe chemical equilibria for the absorbed gas and the chemical solvent.

Preliminary design calculations for sweetening natural gases by absorption with mixed solvents suggest that, under some circumstances, mixed-solvent absorption may be more economical than using conventional aqueous alkanolamine.

SCOPE

Since natural gases frequently contain appreciable quantities of carbon dioxide and hydrogen sulfide, it is necessary to remove these acidic components. Absorption with a polar solvent provides a convenient method for removal; both chemical and physical solvents are commonly used. This work provides some fundamental solubility data for possible absorption processes using mixed solvents, i.e., an organic physical solvent mixed with a relatively small amount (5-15%) of chemical solvent. Solubility data in mixed solutions are reported for carbon di-

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