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Binary Gaseous Diffusion Coefficients, III:

Sulfur Hexafluoride with Cyclohexane, Methylcyclohexane and Toluene at 1 Atm Pressure and 10–70 °C

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The binary gaseous diffusion coefficients at 1 atm pressure of sulfur hexafluoride with cyclohexane, methylcyclohexane, benzene, and toluene were measured at 10, 25, 40, 55 and 70 °C by the capillary tube method of *Stefan*[1]. Diffusion coefficients were calculated (a) by using *Lennard-Jones* (6, 12) pair potential parameters in conjunction with the *Hudson-McCoubrey* combining rule[2], and (b) with a semiempirical method somewhat similar to that suggested by *Chen* and *Othmer*[3]. Diffusion coefficients calculated via method (b) were in much better agreement with experiment than those obtained via method (a).

Introduction

The binary gaseous diffusion coefficient is an important property in a multitude of engineering problems since it is one of the factors governing the rate at which molecules of a species can leave one phase and penetrate into the bulk of another. However, data involving hydrocarbons and either SF_6, CF_4 or CH_4, resp., are rare (see, for example, the critical compilations by *Marrero* and *Mason*[4, 5]) and only quite recently substantial amounts of information on diffusional behavior of such systems have been accumulated[6–9]. The experimental results presented in this paper are a continuation of our earlier work[6, 7] on the diffusion of various hydrocarbons in gases consisting of simple nonpolar multiatomic molecules of almost spherical shape.

References [6] and [7] dealt with diffusion in methane and carbon tetrafluoride. This paper extends the investigation to sulfur hexafluoride. Using a modification of the method of *Stefan*[1], we determined the binary gaseous diffusion coefficients D_{12} at 1 atm pressure as a function of temperature for cyclohexane, methylcyclohexane, benzene, and toluene in SF_6. The temperature range extended from 10 to 70 °C.

Experimental

All measurements were performed in a modified *Stefan* apparatus similar to that reported by *Kohn* and *Romero*[10]. The experimental procedure was identical to that described earlier[6, 7]. Care was taken to satisfy the quasi-steady-state condition which will be approached within 1 per cent for diffusion times greater than $0.5\,L^2/D_{12}$, where L denotes the axial distance between the gas liquid interface and the tube outlet[5, 11]. Pressure was controlled to $\pm$ 2 Torr ($= \pm$ 267 Pa) by using a mercury filled cartesian manostat, and read via an open tube mercury manometer on the system in conjunction with a *Fortin*-type barometer. The temperature of the thermostat was controlled to $\pm$ 2 mK with a Tronac thermoregulator, and temperatures were determined to $\pm$ 2 mK by use of a calibrated platinum resistance thermometer and a *Müller* resistance bridge. Times were measured by a synchronous digital timer which was checked against the time standard of NBS station WWV. For further details the reader is referred to paper 1 of this series[6].

A check at 25 °C for the system N_2/H_2O for four different initial values of L yielded a value $D_{12} = 0.250$ vs. a "best" literature value[4] of 0.251. The agreement is quite satisfactory, esp. since *Marrero* and *Mason*[4, 5] consider the very best diffusion work to be precise to $\pm$ 1 per cent. The solvents used were all Phillips pure grade (99 moles per cent minimum purity) and were used straight from the bottle. SF_6 was the purest grade available from the Matheson Gas Products, Inc. Its composition was greater than 99 moles per cent of the major constituent and the gas was used without further purification.

Results

Measurements were performed from 10 to 70 °C in intervals of approx. 15 °C. From the observations of the lenght of the diffusion path (that is, the distance between liquid level and opening of the diffusion tube), the corresponding time, the barometric pressure and the experimental temperature, the binary diffusion coefficients D_{12} in cm^2 s^{-1} were calculated[12] from

$$D_{12} = \frac{L_\theta^2 - L_0^2}{2\,\theta} \cdot \frac{RT\,\rho_L}{PM_L} \cdot \frac{1}{2.303 \log\{P/(P - P_L)\}} \,. \qquad (1)$$

Here, L_0 and L_θ are the diffusion paths at time zero and θ, resp., R is the gas constant, T is the thermodynamic temperature, P is the total experimental pressure of the system, P_L is the saturation vapor pressure

Table 1. *Experimental and Calculated Binary Gaseous Diffusion Coefficients* D_{12} *at 1 Atm Pressure*

t/°C		D_{12}/cm^2 s^{-1}			D_{12}/cm^2 s^{-1}	
	exptl.	calc. Method (a)	calc. Method (b)	exptl.	calc. Method (a)	calc. Method (b)
		$C_6H_{12} + SF_6$			$C_6H_{11}CH_3 + SF_6$	
9.98	0.0292	0.0253	0.0282	0.0250	0.0225	0.0247
25.07	0.0324	0.0280	0.0313	0.0281	0.0249	0.0274
40.02	0.0358	0.0309	0.0345	0.0315	0.0275	0.0302
55.02	0.0392	0.0340	0.0379	0.0345	0.0302	0.0332
70.02	0.0426	0.0371	0.0414	0.0383	0.0330	0.0362
		$C_6H_6 + SF_6$			$C_6H_5CH_3 + SF_6$	
9.98	0.0330	0.0286	0.0311	—	0.0249	0.0268
25.07	0.0363	0.0318	0.0345	0.0306	0.0276	0.0297
40.02	0.0400	0.0350	0.0380	0.0344	0.0304	0.0327
55.02	0.0439	0.0384	0.0417	0.0384	0.0334	0.0359
70.02	0.0478	0.0420	0.0455	0.0418	0.0365	0.0392

of the liquid at temperature T, P_L is the liquid density, and M_L is the relative molecular mass of the liquid. Densities and vapor pressure were taken from standard references[13, 14].

According to Eq. (1), the binary diffusion coefficient may be obtained from the slope of a plot (L_θ^2–L_0^2) vs. θ. We chose to obtain D_{12} by determining the average of the slopes for each datum point at time θ referred back to time zero. Thus, each point is treated as a discrete experiment. The average deviation of the slopes determined in this manner were of the order of $\pm$ 1 per cent, the high temperature values being more precise than the low temperature values. Deviation plots showed no systematic bias.

Diffusion coefficients determined by this method were corrected to a pressure of 1 atm by making use of the fact that for moderate pressures the magnitude of the diffusion coefficient is inversely proportional to the pressure (cf. also *Slattery*[15] and Ref. [16]). This correction did not exceed 2% for any case. The resulting values of D_{12} at 1 atm at various temperatures are given in Table 1.

The temperature dependence of the diffusion coefficient for each system studied was obtained by fitting the experimental results to the logarithmic form of the equation $D_{12} = D_0 T^n$, i.e.

$$\log D_{12} = \log D_0 + n \log T \tag{2}$$

where D_0 is a constant and n is, in general, a non-integral exponent. Values of D_0 and n for each system are given in Table 2, together with the average deviation. The overall pattern of behavior of the parameters D_0 and n is strikingly similar to that found in systems with CF_4[7].

Table 2. *Constants in Eq. (2) for Diffusion of Stated Component in* SF_6 *in the Temperature Range 10–70 °C and at 1 Atm Pressure*

Component	$10^6 D_0/\mathrm{cm^2 s^{-1}}$	n	*RMS* deviation/$\mathrm{cm^2 s^{-1}}$
Cyclohexane	0.4317	1.970	0.0001
Methylcyclohexane	0.0988	2.204	0.0002
Benzene	0.5824	1.938	0.0001
Toluene	0.0897	2.237	0.0003

Discussion

The kinetic theory of gases[17] provides the following expression for D_{12} at low pressures (first approximation):

$$D_{12} = \frac{0.0018583\, T^{3/2}}{P\sigma_{12}^2\, \Omega_{12}^{(1,1)*}(T_{12}^*)} \left(\frac{M_1 + M_2}{M_1 M_2}\right)^{1/2} . \tag{3}$$

The details of the collision dynamics are represented by the collision integral $\Omega_{12}^{(1,1)*}(T_{12}^*)$ at a reduced temperature $T_{12}^* = kT/\varepsilon_{12}$. M_1 and M_2 are the relative molecular masses of species 1 and 2. The molecular potential energy parameters characteristic of a 1–2 interaction are denoted by σ_{12} and ε_{12}, resp. Two methods were used in computing these mixed parameters:

(a) *Lennard—Jones* (6, 12) potential parameters for the pure components with subscripts 1 and 2 (taken from Ref. [12] and [18]) were used in conjunction with the *Hudson—McCoubrey*[2, 19, 20] combining rule, that is

Table 3. *Data Used in Calculations for Table 1*

Substance	σ/Å	(ε/k)/K	I/eV	V_c/cm^{3}mol^{-1} [a]	T_c/K [a]
SF_6	5.51 [b]	201 [b]	19.3 [c]	199.0	318.7
Cyclohexane	5.63 [d]	573 [d]	11.0 [c]	308.3	553.5
Methylcyclohexane	5.99 [d]	599 [d]	10.7 [e]	367.8	572.1
Benzene	5.26 [d]	531 [d]	9.24 [c]	258.7	562.1
Toluene	5.64 [d]	575 [d]	8.92 [c]	315.6	591.7

[a] All critical data have been taken from: *A. P. Kudchadkar, G. H. Alani,* and *B. J. Zwolinski,* Chem. Rev. **68**, 659 (1968).

[b] Ref. [17].

[c] Ref. [21].

[d] Ref. [18].

[e] Estimated.

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2$$

and

$$\varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2} \frac{2\,(I_1 I_2)^{1/2}}{I_1 + I_2} \, \frac{\sigma_1{}^3\,\sigma_2{}^3}{\sigma_{12}{}^6} \, . \tag{4}$$

Ionization potentials I were obtained from *Landolt—Börnstein*[21] and *Reed*[22, 23]. The value of I for methylcyclohexane was estimated from data pertaining to similar compounds (cf. also Refs. [22, 23]). Pertinent data are given in Table 3.

(b) *Chen* and *Othmer*[3] have used the following expression for the potential parameters of the pure compounds (with i being either 1 or 2):

$$\varepsilon_i/k = 1.276\, T_{c,i}^{0.9061}$$

and

$$\sigma_i = 0.5894\, V_{c,i}^{0.4006}, \tag{5}$$

where T_c and V_c is the critical temperature and volume, resp. For the mixed parameters, they suggested the simple conventional combining rules $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ and $\varepsilon_{12} = (\varepsilon_1\varepsilon_2)^{1/2}$. Hence, using rounded figures, one obtains

$$\varepsilon_{12}/k = 1.276\ (T_{c,1}\, T_{c,2})^{0.453}$$

and

$$\sigma_{12} = 0.2947\ (V_{c,1}^{0.4} + V_{c,2}^{0.4}). \tag{6}$$

Combination of Eqs. (6) with Eq. (3) yields (at 1 atm pressure)

$$D_{12} = \Gamma\, T^{3/2}/\Omega_{12}^{(1,1)*}(T_{12}^*)\,, \tag{7}$$

where

$$\Gamma = \frac{0.021397}{\{V_{c,1}^{0.4} + V_{c,2}^{0.4}\}^2} \left(\frac{M_1 + M_2}{M_1 M_2}\right)^{1/2}$$

is a constant characteristic of the system under consideration. In our opinion Eq. (7) offers some advantages over the original *Chen—Othmer* equation[3, 24] in that its temperature dependence is not always the same, but may vary with the nature of the binary system.

In both approaches (a) and (b) collision integrals were taken from the tables of *Hirschfelder* et al.[17] which for the relevant temperature range are virtually identical with the more accurate tables of *Monchick* and *Mason*[25]. Diffusion coefficients calculated via Eqs. (3) and (4) [that is method (a)] did not agree well with experiment (cf. Table 1). The predicted values were substantially lower, deviations being of the order of 12%. On the other hand, the semiempirical approach (b) yielded quite satisfactory results as demonstrated in Table 1.

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