lespie et al. are in quite reasonable correspondence, as viewed even on relative volatility axes which exaggerate any scatter.

Figure 10 shows data of Guillevic et al. (*29*) at two temperatures along with isotherms from our data at temperatures near their values. The temperature differences leave room for question, but there seem to be differences between their data and ours, particularly along the dew-point curve at 453.1 K. The difference in relative volatility may be around 25% at some compositions.

Correlation of Data. The data have been fitted with a number of equation-of-state models, as reported elsewhere by Rizvi (*31*) and Heidemann and Rizvi (*32*).

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Binary Gaseous Diffusion Coefficients. 5. Cyclooctane and *trans*-1,2-Dimethylcyclohexane with Helium, Argon, Methane, and Sulfur Hexafluoride at 1 atm and 313–343 K

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The binary gaseous diffusion coefficients for cyclooctane and *trans*-1,2-dimethylcyclohexane diffusing into helium, argon, methane, and sulfur hexafluoride were measured at about 313.15, 328.15, and 343.15 K and atmospheric pressure by the capillary tube method of Stefan. The experimental results are compared with diffusion coefficients calculated via the first-order Chapman–Enskog approximation. For the gases, effective Lennard-Jones (6, 12) pair potential parameters were taken from recent literature; for the liquids they were obtained from an extended corresponding-states correlation suggested by Tee, Gotoh, and Stewart.

Introduction

This study continues our earlier investigations (*1–4*) into binary gaseous diffusion coefficients. We now report on eight systems involving spherical molecules of a wide range of sizes (He, Ar, CH_4, SF_6) with two isomeric alicyclic C_8 compounds of different ring size, viz., cyclooctane (C_8H_{16}) and *trans*-1,2-dimethylcyclohexane (*trans*-1,2-$(CH_3)_2C_6H_{10}$). In particular, we wished to determine whether there were any discernible effects associated with differences in ring size of otherwise quite similar alicyclic isomers.

Experimental Section

The experimental procedures were identical with those described in detail in our earlier papers (*1–4*). Thus, only a brief summary will be presented. The Stefan capillary tube method (*5*) was used, running each solvent/gas pair in duplicate at about 313.15, 328.15, and 343.15 K and approximately atmospheric pressure. Temperature was controlled to better than ±0.01 K in a 80-L water bath over the periods of the measurements, which ranged from 2 to 10 days. Temperatures were measured with a calibrated platinum resistance thermometer on IPTS-68. The total pressure of about 1 atm (=101.325 kPa) was controlled with a mercury-filled Cartesian manostat to better than ±0.9 kPa for all runs except for helium

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at 313.17 K and argon at 328.15 K, both with cyclooctane, where pressure variations amounted to ±1.6 kPa. Flow rates of the gases past the ends of individual tubes ranged from 0.06 to 0.20 $cm^3 \cdot s^{-1}$. Care was taken to satisfy the quasi-steady-state condition (*6*, *7*), which will be approached within 1% for diffusion times greater than $0.5 l^2 D_{12}^{-1}$, where l denotes the axial distance between the gas–liquid interface and the tube outlet, and D_{12} is the binary diffusion coefficient. Within the limits of experimental error, the diffusion coefficients were found to be independent of the gas flow rate and the slight variations of the diffusion path lengths of the individual measurement runs (*1–4*).

A comparison measurement, at 313.15 K and 1 atm, of water diffusing into nitrogen yielded D_{12} = 0.273 $cm^2 \cdot s^{-1}$, which is in close agreement with reliable literature data (*8*, *9*). The inaccuracy of our diffusion coefficients is considered to be about ±1%, while the imprecision is less than 0.5% in most cases.

The *trans*-1,2-dimethylcyclohexane was from the Chemical Supply Co. (99% purity) and was used as received. Cyclooctane was reagent grade and was further purified by distillation through a 2-m packed vacuum-jacketed column at a reflux ratio of 20 or better. Water was purified by reverse osmosis followed by distillation. This purified water had a specific resistance of 0.5 × 10^6 Ω·m. Methane (99.0%) and sulfur hexafluoride (99.8%) were from Matheson Gas Products; helium (99.995%), argon (99.998%), and nitrogen (99.998%) were from Air Products.

Results

Binary gaseous diffusion coefficients $D_{12}(T,P)$ at thermodynamic temperature T and total pressure P (which was always close to atmospheric pressure) were obtained (*10*) as before (*1–4*) from the following expression:

$$D_{12}(T,P) = \frac{l_\theta^2 - l_0^2}{2\theta} \frac{RTd_1^{\mathrm{L}}}{PM_1} \frac{1}{\ln\,[P/(P - P_{s,1})]} \qquad (1)$$

Here, l_0 and l_θ are the measured diffusion paths at times zero and θ, R is the gas constant, d_1^{L} is the mass density of the liquid, M_1 is the molar mass of the liquid, and $P_{s,1}$ is its vapor pressure at T. Densities and vapor pressures were obtained from standard sources (*11*, *12*). The data obtained at experimental pressure P were converted to P_{ref} = 1 atm = 101 325 Pa by making use of the fact that at low to moderate pressures the product $PD_{12}(T,P)$ is practically independent of pressure, whence we obtained

$$D_{12}(T,P_{ref}) \equiv D_{12} = D_{12}(T,P)\,\frac{P}{P_{ref}} \qquad (2)$$

These pressure corrections were quite small, that is, usually less than 2%. The results shown in Table I are corrected diffusion coefficients D_{12}, at 101 325 Pa and various temperatures, of C_8H_{16} and (*trans*-1,2-$(CH_3)_2C_6H_{10}$) each in He, Ar, CH_4, and SF_6.

At low pressures and over not too large a temperature range, D_{12} varies as T^s, where s usually lies between $^3/_2$ and 2 (*9*, *13*). Accordingly, the data of Table I may be represented by an equation of the form

$$D_{12} = D_{12}(T_{ref},P_{ref}) \left(\frac{T}{T_{ref}}\right)^s \qquad (3)$$

where $D_{12}(T_{ref},P_{ref})$ is the binary diffusion coefficient at T_{ref} and P_{ref}. Table II summarizes the values of s and $D_{12}(T_{ref},P_{ref})$ for the eight pairs for T_{ref} = 273.15 K and P_{ref} = 101 325 Pa, as obtained from fitting ln D_{12} vs. ln T. The average deviations of the experimental diffusion coefficients from those calculated by using eq 3 are also tabulated: they are generally less than 1%.

Table I. Experimental and Calculated Binary Gaseous Diffusion Coefficients D_{12}, at 1 atm = 101 325 Pa Pressure, of Cyclooctane and *trans*-1,2-Dimethylcyclohexane with Helium, Argon, Methane, and Sulfur Hexafluoride

	$D_{12}/cm^2 \cdot s^{-1}$		$D_{12}/cm^2 \cdot s^{-1}$	
T/K	exptl	calcd[a]	exptl	calcd[a]
	C_8H_{16}/He		*trans*-1,2-$(CH_3)_2C_6H_{10}$/He	
313.17		0.3179	0.2615	0.3008
328.15	0.2934	0.3446	0.2857	0.3260
343.36	0.3192	0.3725	0.3000	0.3523
	C_8H_{16}/Ar		*trans*-1,2-$(CH_3)_2C_6H_{10}$/Ar	
313.15	0.0673	0.0631	0.0656	0.0606
328.15	0.0730	0.0692	0.0721	0.0664
343.26	0.0780	0.0756	0.0780	0.0725
	C_8H_{16}/CH_4		*trans*-1,2-$(CH_3)_2C_6H_{10}/CH_4$	
313.30	0.0826	0.0823	0.0818	0.0792
328.16	0.0900	0.0902	0.0903	0.0868
343.33	0.0972	0.0986	0.0962	0.0948
	C_8H_{16}/SF_6		*trans*-1,2-$(CH_3)_2C_6H_{10}/SF_6$	
313.15	0.0298	0.0272	0.0294	0.0264
328.14	0.0319	0.0299	0.0316	0.0290
343.29	0.0355	0.0327	0.0346	0.0317

[a] Calculated via eq 4 and 5. The pure-component Lennard-Jones parameters for He, Ar, CH_4, and SF_6 were taken from ref *19–21* (see Table III); those for cyclooctane and *trans*-1,2-dimethylcyclohexane were estimated via the Tee–Gotoh–Stewart correlations, eq 6 and 7 (*22*).

Table II. Parameters $D_{12}(T_{ref},P_{ref})$ and s of Eq 3, Where T_{ref} = 273.15 K and P_{ref} = 1 atm = 101 325 Pa, and the Average Percent Deviations[a] α of the Diffusion Coefficients

system	$D_{12}(T_{ref},P_{ref})/cm^2 \cdot s^{-1}$	s	α
C_8H_{16}			
+ He	0.2086	1.86	
+ Ar	0.0541	1.61	0.27
+ CH_4	0.0648	1.78	0.15
+ SF_6	0.0228	1.90	0.93
trans-1,2-$(CH_3)_2C_6H_{10}$			
+ He	0.2145	1.49	0.83
+ Ar	0.0508	1.89	0.28
+ CH_4	0.0645	1.77	0.73
+ SF_6	0.0230	1.77	0.47

[a] $\alpha = N^{-1}\sum_N|\Delta_i|$, where $\Delta_i = 100\,[D_{12}(\mathrm{exptl}) - D_{12}(\mathrm{smoothed})]/D_{12}(\mathrm{smoothed})$ is the percent deviation of an individual data point. N is the number of data points, and D_{12}(smoothed) is obtained from eq 3.

Discussion

The first-order approximation in the kinetic theory of dilute gases (*13*, *14*) gives the following expression for the binary diffusion coefficient:

$$D_{12}(T,P) = \frac{3}{8} \frac{1}{\rho^{\mathrm{V}} \sigma_{12}^2 \Omega_{12}^{(1,1)*}(T_{12}^*)} \left(\frac{N_{\mathrm{A}} k_{\mathrm{B}} T}{2\pi\mu}\right)^{1/2} \qquad (4)$$

Here, N_A is Avogadro's constant, k_B is Boltzmann's constant, $\mu = M_1M_2/(M_1 + M_2)$ is the reduced molar mass, M_1 and M_2 denote the molar masses of the liquid and the gas (*15*), respectively, σ_{12} is a characteristic molecular interaction size parameter, and ρ^{V} is the number density. To a good approximation (*9*, *13*, *14*) ρ^{V} may be expressed as P/k_BT. The details of the collision dynamics are represented by the reduced collision integral $\Omega_{12}^{(1,1)*}(T_{12}^*)$ at a reduced temperature $T_{12}^* = k_BT/\epsilon_{12}$, where ϵ_{12} is a characteristic molecular interaction energy parameter.

The reduced collision integral has been tabulated as a function of T_{12}^* for the Lennard-Jones (*6*, *12*) potential by several authors (*14*, *16*, *17*). We used the analytical relation of Neufeld et al. (*18*), which allows direct calculation of $\Omega_{12}^{(1,1)*}(T_{12}^*)$

Table III. Values for Some Molecular Parameters and Bulk Properties As Used in the Calculations: Lennard-Jones Parameters σ and ϵ/k_B, Critical Temperature T_c, Critical Pressure P_c, and Acentric Factor ω

substance	$10^{10}\sigma$/m	(ϵ/k_B)/K	T_c/K[b]	$10^{-6}P_c$/Pa[b]	ω[b]
He	2.570 (*19*)	10.8 (*19*)	5.19	0.227	−0.387
Ar	3.336 (*20*)	141.2 (*20*)	150.8	4.874	−0.004
CH_4	3.706 (*20*)	159.7 (*20*)	190.6	4.600	0.008
SF_6	5.128 (*21*)	222.1 (*21*)	318.7	3.759	0.286
C_8H_{16}	6.09[a]	535[a]	618.2	3.447	0.441
trans-1,2-$(CH_3)_2C_6H_{10}$	6.37[a]	496[a]	596.0	2.969	0.242

[a] TGS estimates, eq 6 and 7. [b] From Reid, Prausnitz, and Sherwood (*26*) (for He, Ar, CH_4, and SF_6) and Passut and Danner (*27*) (for cyclooctane and *trans*-1,2-dimethylcyclohexane).

with an accuracy comparable to that of the best tables to date (*17*):

$$\Omega_{12}^{(1,1)*}(T_{12}^*) = A/T_{12}^{*B} + C\exp(-DT_{12}^*) + E\exp(-FT_{12}^*) + G\exp(-HT_{12}^*) \quad (5)$$

The values of the eight coefficients *A* through *H* may be found in ref *16*.

Recent recommended (*6*, *12*) pair potential parameters for He, Ar, CH_4, and SF_6 are readily available (*19–21*). For the alicyclic compounds we used effective parameters obtained via correlations suggested by Tee, Gotoh, and Stewart (TGS) (*22*), and, for comparison's sake, parameters obtained from application of scaled particle theory (*23*) to gas solubilities (*24*, *25*). The former approach is based on an extended corresponding-states analysis of second virial coefficient and gas viscosity data for nonpolar molecules. In dimensionless form the TGS relations are

$$\sigma(P_c/k_BT_c)^{1/3} = 0.45767 - 0.01689\omega \quad (6)$$

$$\epsilon/k_BT_c = 0.7915 + 0.1693\omega \quad (7)$$

where P_c is the critical pressure, T_c is the critical temperature, and ω denotes the acentric factor (*26*, *27*). Table III shows the σ and ϵ/k_B values used in this work, together with P_c, T_c, and ω.

In order to actually use eq 4 and 5, combining rules for obtaining the interaction quantities σ_{12} and ϵ_{12} from the effective pure-component Lennard-Jones parameters must be selected (*28–30*). In view of the approach outlined above, with its inherent uncertainties, only the rather approximate conventional Lorentz–Berthelot prescription

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \quad (8)$$

$$\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2} \quad (9)$$

was used.

Diffusion coefficients obtained from eq 4, 8, and 9 have been included in Table I. Considering the relatively complex systems, agreement between experimental D_{12}'s and diffusion coefficients calculated with the parameters (for the alicycles) from the TGS relations is quite satisfactory, with the exception of the two helium systems, where the calculated diffusion coefficients are about 15–17% higher. A critical discussion of these differences is deferred until the D_{12}'s of several other mixtures of similar type have been measured. In general, both the temperature dependence and the slightly larger values observed for the cyclooctane systems, as compared to the *trans*-1,2-dimethylcyclohexane systems, are well reproduced. On the other hand, when using σ and ϵ for the cyclic compounds as obtained from gas solubility measurements (*24*, *25*), calculated diffusion coefficients are all smaller, by up to about 10%, than the corresponding D_{12}(TGS), whence no numerical details are given. This result is, however, not unexpected, since these parameters were obtained by fitting *liquid* bulk properties (Henry coefficients).

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