Binary Gaseous Diffusion Coefficients
II. Methane and Carbon Tetrafluoride with Cyclohexane, Methylcyclohexane, Benzene, and Toluene at 1 Atm at 10–70°C

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The binary gaseous diffusion coefficients D_{12} at 1-atm pressure of CH_4 and CF_4 with cyclohexane, methylcyclohexane, benzene, and toluene were measured at 10°, 25°, 40°, 55°, and 70°C by the capillary tube method of Stefan. The predicted diffusion coefficients calculated with Lennard-Jones (6,12) potential parameters in the Chapman-Enskog approximate kinetic theory in conjunction with the Hudson-McCoubrey combining rule were in satisfactory agreement with experiment.

The measurements reported in this paper constitute a continuation of our earlier work (*17*) on the diffusion of hydrocarbons in methane and carbon tetrafluoride. The previous results were for CH_4 and CF_4 with *n*-hexane, *n*-heptane, *n*-octane, and 2,2,4-trimethylpentane (10–70°C). Data involving hydrocarbons and CH_4 or CF_4 are rare or nonexistent [see, for example, the critical compilations by Marrero and Mason (*7, 8*)].

Using a modified form of the method of Stefan (*13*), we determined the binary diffusion coefficients, D_{12}, at 1-atm pressure as a function of temperature for the alicyclic compounds cyclohexane and methylcyclohexane and their aromatic counterparts benzene and toluene with these two gases. The systems investigated were selected to correlate to our work on gas solubility in liquids (*1, 2, 18–20, 22*). Specifically, we intended to check whether the pair potential parameters derived via application of scaled particle theory to gas solubility (*21*) can also be applied for the calculation of transport coefficients in the gaseous state.

Experimental

The experimental procedure was identical to that described earlier (*17*) except that for the measurements reported herein, all readings were taken in triplicate. Care was taken to satisfy the quasi-steady-state condition which will be approached within 1% for diffusion times greater than $L^2/2\ D_{12}$, where L denotes the axial distance between the gas-liquid interface and the tube outlet (*6, 8*). The pressure was controlled to ±2 mm Hg by using a mercury-filled cartesian manostat. For details, the reader is referred to paper I of this series (*17*). A check at 25° for the system N_2/H_2O for four different initial values of L yielded a value for D_{12} of 0.250 vs. a "best" literature value (*7*) of 0.251.

The benzene used was thiophene-free Baker analyzed reagent grade (99.9 mol %). The other solvents were all Phillips pure grade (99 mol % minimum purity). All were used straight from the bottle. Methane (99.0 mol % minimum purity) and carbon tetrafluoride (99.7 mol % minimum purity) were from Matheson Gas Products.

Results

Measurements were performed from 10° to 70°C in intervals of 15°C. From the observations made on the liquid level, the barometric pressure, the experimental temperature, and the corresponding time, the binary diffusion coefficients D_{12} (cm^2 sec^{-1}) were calculated (*12*) from Equation 1:

$$D_{12} = \frac{L_\theta^2 - L_0^2}{2\,\theta} \times \frac{RT\rho_L}{PM_L} \times \frac{1}{2.303 \log\left[P/(P - P_L)\right]} \quad (1)$$

Here, L_0 and L_θ are the diffusion paths at time zero and θ, respectively; R is the gas constant; T is the Kelvin temperature; P is the total experimental pressure of the system; P_L is the saturation vapor pressure of the liquid at temperature T; ρ_L is the liquid density; and M_L is the molecular weight of the liquid. Liquid vapor pressure and densities were obtained from standard references (*14, 23*).

As usual (*17*), D_{12} was obtained by determining the average of the slopes for each datum point at time θ referred back to time zero. Thus, in this procedure each point is treated as a discrete experiment. Diffusion coefficients calculated in this manner were corrected to a

Table I. Experimental and Calculated Coefficients D_{12} (cm^2 sec^{-1}) at 1-Atm Pressure

t, °C	D_{12}, exptl	D_{12}, calcd	D_{12}, exptl	D_{12}, calcd
	CH_4–cyclohexane		CF_4–cyclohexane	
10	0.0793	0.0799	0.0406	0.0368
25	0.0883	0.0885	0.0444	0.0407
40	0.0927	0.0975	0.0491	0.0448
55	0.1042	0.1068	0.0529	0.0491
70	0.1109	0.1165	0.0574	0.0534
	CH_4–methylcyclohexane		CF_4–methylcyclohexane	
10	0.0724	0.0740	0.0341	0.0331
25	0.0817	0.0819	0.0384	0.0366
40	0.0860	0.0902	0.0443	0.0403
55	0.0951	0.0988	0.0475	0.0442
70	0.1031	0.1077	0.0516	0.0482
	CH_4–benzene		CF_4–benzene	
10	0.0900	0.0877	0.0456	0.0412
25	0.1018	0.0971	0.0494	0.0456
40	0.1062	0.1069	0.0554	0.0502
55	0.1188	0.1171	0.0597	0.0550
70	0.1272	0.1277	0.0647	0.0600
	CH_4–toluene		CF_4–toluene	
10	0.0809	0.0791	0.0387	0.0364
25	0.0917	0.0883	0.0435	0.0403
40	0.0956	0.0972	0.0481	0.0443
55	0.1065	0.1065	0.0526	0.0485
70	0.1146	0.1161	0.0578	0.0529

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Table II. Constants in Equation 3 for Diffusion of Stated Component in Methane and Carbon Tetrafluoride, Respectively, in Temperature Range 10–70°C and 1-Atm Pressure

		CH_4	RMS	Max		CF_4	RMS	Max
Component	$D_0 \times 10^6$	n	dev	dev	$D_0 \times 10^6$	n	dev	dev
Cyclohexane	4.3171	1.7413	0.0014	0.0024	1.4946	1.8083	0.0002	0.0003
Methylcyclohexane	3.0763	1.7843	0.0011	0.0016	0.16156	2.1734	0.0006	0.0011
Benzene	4.2985	1.7638	0.0017	0.0026	1.3729	1.8435	0.0005	0.0007
Toluene	3.8730	1.7635	0.0016	0.0023	0.35159	2.0572	0.0002	0.0003

Table III. Data Used in Calculations for Table I

Substance	σ, Å	ϵ/k, K	I, eV
CH_4	3.70[a]	157[a]	13.2[b]
CF_4	4.66[c]	134[c]	17.8[b]
Cyclohexane	5.63[d]	573[a]	11.0[e]
Methylcyclohexane	5.99[d]	599[d]	10.7[f]
Benzene	5.26[d]	531[d]	9.24[e]
Toluene	5.64[d]	575[d]	8.92[e]

[a] (3). [b] (*11*). [c] (*12*). [d] (*21*). [e] (5). [f] Estimated.

pressure $P_1 = 1$ atm by making use of the fact that the magnitude of the diffusion coefficient is inversely proportional to the pressure, viz.:

$$(D_{12})_P/(D_{12})_{P_1} = P_1/P \qquad (2)$$

where $(D_{12})(P_1)$ denotes the diffusion coefficient at 1 atm. The resulting values of D_{12} at 1 atm at various temperatures are given in Table I. The average deviation of the slopes determined in this way was of the order of ±1%; maximum deviations on individual points for a given run ranged from 0.4 to 2.5% (the latter at low temperatures where the precision was poorer), and the overall imprecision of our diffusion coefficients we consider to be about ±1%. Deviation plots showed no systematic bias.

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 $D_{12} = D_0T^n$, i.e.,

$$\log D_{12} = \log D_0 + n \log T \qquad (3)$$

where D_0 is a constant, and n is, in general, a nonintegral exponent. Values of D_0 and n for each system are given in Table II, together with the root-mean-square deviations of experimental diffusion coefficients from the fitted line. However, as pointed out earlier (*17*) [cf. also O'Connell et al. (9)], in this rather narrow temperature range (10–70°C), plots of D_{12} vs. T were also quite linear. In contrast to our results (*17*) with CH_4, CF_4, and various alkanes, the n values differed considerably for the two gases with cyclic hydrocarbons. The increment $\Delta(n(CF_4) - n(CH_4)$ for one particular solvent was 0.08 and 0.29 for benzene and toulene, respectively, and 0.07 and 0.39 for cyclohexane and methylcyclohexane, respectively.

Discussion

Diffusion coefficients for the compounds studied in this paper were calculated by a kinetic theory equation (3) with the Lennard-Jones (6,12) potential function, for which values of the collision integral have been tabulated (3). In computing values of the molecular interaction parameters for like–unlike interactions, parameters for the pure components compiled by Wilhelm and Battino (*21*) and Reid and Sherwood (*12*), respectively, were used in conjunction with the Hudson-McCoubrey combining rules (*4*). Ionization potentials were obtained from Landolt-Börnstein (5) and Reed (*10, 11*). The value for the ionization potential of toluene was estimated from data pertaining to other aromatic compounds (cf. also refs. *10* and *11*). The necessary data are given in Table III, and the relevant equations are summarized below:

$$D_{12} = \frac{0.0018583\, T^{3/2}}{P\sigma_{12}^2\Omega_{12}^{(1,1)*}(T_{12}^*)}\left[\frac{1}{M_1} + \frac{1}{M_2}\right]^{1/2} \qquad (4)$$

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \qquad (5)$$

$$\epsilon_{12} = (\epsilon_1\epsilon_2)^{1/2}\,\frac{2(I_1I_2)^{1/2}}{I_1 + I_2}\,\frac{\sigma_1^3\sigma_2^3}{\sigma_{12}^6} \qquad (6)$$

Here, the subscripts 1 and 2 refer to the two pure compounds, D_{12} is the first approximation to the binary diffusion coefficient, and $\Omega_{12}^{(1,1)*}(T_{12}^*)$ is a collision integral at a reduced temperature $T_{12}^* = kT/\epsilon_{12}$. The molecular potential energy parameters characteristic of a 1–2 interaction are denoted by σ_{12} and ϵ_{12}, respectively, and I is the ionization potential. The combination rule Equation 6 was used extensively by Watts (*15, 16*) for calculating diffusion coefficients.

Diffusion coefficients calculated from theory (Equations 4–6) are compared with those obtained from experiment in Table I. In general, the agreement must be regarded as being satisfactory for the systems with CH_4 and only fair for the systems with CF_4. However, the results indicate that reasonable estimates for diffusion constants are obtainable by using molecular parameters obtained from applications of scaled particle theory to liquids (*21*), although, certainly, more data are needed to fully test this. We are currently collecting more data on selected systems for this purpose.

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Hydrogen Solubility in Aqueous Solutions of Sugars and Sugar Alcohols

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The solubility of hydrogen in aqueous solutions of sugars and their alcohols is determined at temperatures between 80° and 120°C, pressures between 100 and 800 psig, and molar concentrations between 0.5 and 3. Henry's Law is observed in every case, and the proper coefficients are reported.

The purpose of this study is to determine the solubility of hydrogen in aqueous solutions of sugars and sugar alcohols, under various conditions of pressure, temperature, and solute concentration. The data are important for obtaining a better estimate of the hydrogen concentration at the catalyst surface when hydrogenating the sugars, as well as determining the solute influence on solubility.

The solubility of hydrogen in water and organic and inorganic solutions has been studied extensively (*1*), although not with the compounds employed in this work. Lyashch (2) reported that the solubility of CO_2 in sucrose solutions decreased strongly with an increase in solute concentration, whereas an opposite effect was observed with citric acid. Wiebe et al. (*4*) found that the isothermal solubility of hydrogen in water showed a minimum between 40° and 60°C for pressures up to 1000 atm.

Experimental

Solubility effects were studied in the range of interest for hydrogenation, namely, 80–120°C, 100–800 psig, and 0.5–3.0*M* concentration. The solutions were prepared from distilled water and commercially available solutes (Sigma), 99.9% pure as reported by the manufacturer.

The equilibrium cell used in this work consisted of a ¾ gal, high-pressure autoclave manufactured by Autoclave Engineers, provided with automatic heating control instrument and an internal cooling coil. By proper use of both elements, it was possible to control the solution temperature to ±1°C. The autoclave was connected to a solubility measuring train similar to that used by Wiebe et al. (*4*) for the determination of the solubility of hydrogen in water at high pressures.

The apparatus (Figure 1) consisted essentially of two gas burets (1, 2) immersed in a water bath (4) that could be controlled to ±0.1°C. Both burets had a capacity of 100 ml with 0.2-ml graduations. The buret on the right (2), or solution buret, was connected through its bottom end to a tee. One opening of the tee connected to a leveling bulb (6) filled with solution of the appropiate concentration, and the other opening of the tee was connected to a high-pressure valve (B). The leveling bulb line was provided with a stopcock (D) so that the liquid level inside the solution buret could be adjusted to any level. A ⅜-in. diameter, high-pressure stainless-steel tubing (10) connected the high-pressure valve (B) to the sample line of the autoclave. This high-pressure line also had a branch with another high-pressure valve (A) so that the autoclave connecting line could be purged when desired.

The buret on the left (1), or hydrogen buret, was also provided with a stopcock (C) and a leveling bulb filled with mercury (5). The burets were connected at the top to a glass tee that led to a two-way stopcock (E). One opening of the stopcock (E) connected the buret system to the atmosphere while the other opening connected the system to a mercury manometer (3).

The autoclave was loaded with a solution of the proper molarity, pressurized to the desired level (±10 psig), and heated under agitation until the proper temperature, ±1°C, was attained for at least 15 min. The solubility ap-

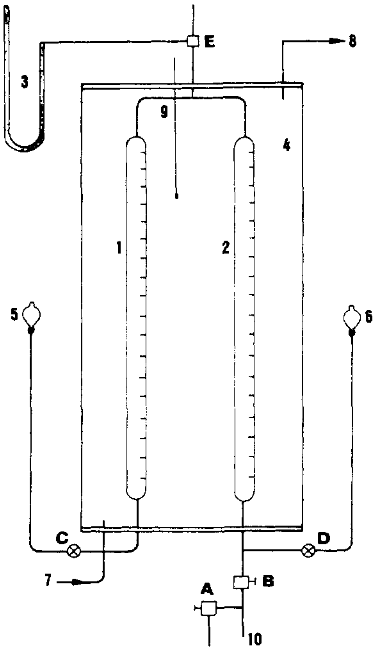

Figure 1. Solubility apparatus

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