maxima. The $\overline{\Delta H}_2$ and $T\overline{\Delta S}_2$ curves are nearly superimposable, and it is of interest to note how the large values of $\overline{\Delta H}_2$ and $T\overline{\Delta S}_2$ compensate to give very low values of $\overline{\Delta F}_2$.

The positive values of $\overline{\Delta H}_2$ and $\overline{\Delta S}_2$ indicate that less order may be created by the structure-making esters in water-rich DMSO than in pure water. If indeed moderate quantities of DMSO enhance the structure of water in some way, there should be relatively less structure to make as a result of the transfer of the structure-making esters. This is in agreement with observed results. Similar behavior takes place in the transfer of HCl from water to water-rich low molecular weight alcohols and ethylene glycol (*11, 15, 16*).

The series of three esters represents successive substitutions of methyl groups for hydrogen on the methylene carbon of ethyl acetate, and the data clearly show the effect of these substitutions. All maxima, and consequently the interaction differences, increase with increasing ester size. Both ethyl and isopropyl acetate show maxima at $X_3 \simeq 0.3$ in the region of maximum interaction or structure observed in other experiments (*3–5*). Those for *t*-butyl acetate occur at lower mole fractions. This is similar to other evidence showing differences in behavior between solutes with *t*-butyl and those with smaller primary and secondary alkyl groups in aqueous solutions (*1*).

LITERATURE CITED

(1) Arnett, E. M., in "Physicochemical Processes in Mixed Aqueous Solvents," p 105, F. Franks, Ed., Elsevier, New York, N. Y., 1967.
(2) Brink, G., Falk, M., *J. Mol. Struct.*, **5**, 27 (1970).
(3) Cowie, J. M. G., Toporowski, P. M., *Can. J. Chem.*, **39**, 2240 (1969).
(4) Fort, R. J., Moore, W. R., *Trans. Faraday Soc.*, **61**, 2102 (1965).
(5) Fort, R. J., Moore, W. R., *ibid.*, **62**, 1112 (1966).
(6) O'Connor, M. E., MS thesis, California State College at Long Beach, 1971.
(7) Parker, A. J., *Chem. Rev.*, **69**, 6 (1969).
(8) Safford, G. J., Schaffer, D. C., Leung, P. S., Doebler, G. W., Lynden, E. F. X., *J. Chem. Phys.*, **50**, 2140 (1969).
(9) Schichman, S. A., Amey, A. L., *J. Phys. Chem.*, **75**, 98 (1971).
(10) Stern, J. H., Anderson, C. W., *ibid.*, **68**, 2528 (1964).
(11) Stern, J. H., Hansen, S. L., *J. Chem. Eng. Data*, **16**, 360 (1971).
(12) Stern, J. H., Hermann, A., *J. Phys. Chem.*, **71**, 306 (1967).
(13) Stern, J. H., Hermann, A., *ibid.*, **72**, 364 (1968).
(14) Stern, J. H., Kulluk, J. D., *ibid.*, **73**, 2795 (1969).
(15) Stern, J. H., Nobilione, J. M., *ibid.*, **72**, 3937 (1968).
(16) Stern, J. H., Nobilione, J. M., *ibid.*, **73**, 928 (1969).

RECEIVED for review August 9, 1971. Accepted December 10, 1971. Work supported by the National Science Foundation.

Binary Gaseous Diffusion Coefficients

I. Methane and Carbon Tetrafluoride with *n*-Hexane, *n*-Heptane, *n*-Octane, and 2,2,4-Trimethylpentane at One-Atmosphere Pressure at 10–70°C

EMMERICH WILHELM[1] and RUBIN BATTINO[2]
Department of Chemistry, Wright State University, Dayton, Ohio 45431

The binary gaseous diffusion coefficients of methane and carbon tetrafluoride with *n*-hexane, *n*-heptane, *n*-octane, and 2,2,4-trimethylpentane were measured at one-atmosphere pressure and 10°, 25°, 40°, 55°, and 70°C by the capillary tube method of Stefan. The predicted diffusion coefficients calculated using Lennard-Jones potential parameters in the Chapman-Enskog approximate kinetic theory were about 2–6% low for the systems with methane and about 10–13% low for the systems with carbon tetrafluoride

Accurate knowledge of gaseous diffusion coefficients and their temperature dependence is important not only in obtaining fundamental information on forces between molecules, but also in process design calculations. Most of the large number of experimental diffusion coefficients reported were determined from diffusion experiments into air or one of the permanent gases. Measurements involving hydrocarbons and CH_4 and CF_4 are very rare or nonexistent [see, for example, the recent critical compilation by Marrero (*5–7*)]. Using a modified form of the method of Stefan (*12*), we determined the binary diffusion coefficients as a function of temperature for *n*-hexane, *n*-heptane, *n*-octane, and isooctane (2,2,4-trimethylpentane) with methane and carbon tetrafluoride.

EXPERIMENTAL

We used the Stefan (*12*) method in an apparatus similar to that reported by Kohn and Romero (*4, 11*). Our diffusion tubes were made of 2-mm i.d. precision bore tubing, 20 cm long. The open end of the tube had specially ground long tapers to provide greater reproducibility in sighting the edge of the open tube. The ends of the diffusion cells were fitted with 18/9 O-ring joints which made changing systems easy. Four diffusion tubes (each with a different liquid) were run simultaneously with one gas by connecting the diffusion cells in parallel with a manifold. This procedure greatly facilitated the measurements since we could run four systems at one time. The diffusion path lengths were read to the nearest 0.01 mm on a cathetometer; however, the reproducibility in reading heights was between 0.05 and 0.10 mm. The tubes were back-lit with diffuse white light, and the bottom of the meniscus was read for liquid height.

---

[1] Senior Fulbright Research Scholar, on leave from the University of Vienna, Austria.
[2] To whom correspondence should be addressed.

The temperature of the insulated 20-gal. water bath was controlled to ±0.002°C with a Tronac thermoregulator, and temperatures were determined to ±0.002°C by use of a calibrated platinum resistance thermometer and a Mueller bridge. A constant level device was needed for proper functioning of the thermostat above room temperature. Evaporation and heat losses were minimized by floating a 5–6-cm layer of plastic foam packing material on the surface of the bath. In addition to their excellent insulating properties, these little pieces of plastic provide a form-fitting cover for the bath.

Pressure in the system was controlled to ±2 mm Hg for all runs by using a mercury filled cartesian manostat. Pressures were read using an open tube mercury manometer on the system and a Fortin-type barometer (with all corrections applied). The system was pressure tight at about 790 mm Hg to a few mm/hr. Flow rates of the gases were determined using a soap bubble flow meter and a stop watch. Flow rates ranged from 30–130 ml/min. Times were determined on a synchronous digital timer at ±0.1 min. The timer showed a variation of ±0.1 min in 5 days when checked against NBS station WWV.

The liquids were saturated with the gas to be used before transferring them to the diffusion tubes. Above room temperature, the saturated liquids were equilibrated for 1–2 hr in the thermostat before transfer. This latter procedure assured that no out-gassing would occur during a run. The runs took 2–5 days. We detected no end effects when we used *n*-hexane (into CH_4) at 25°C in four tubes with initial diffusion paths of 4.1, 6.6, 10.4, and 12.7 cm and final diffusion paths of 6.0, 7.9, 11.3, and 13.4 cm, respectively.

The solvents used were all Phillips pure grade (99 mol % minimum purity) and were used straight from the bottle. Methane was from Matheson Gas Products (99.0% minimum purity) and carbon tetrafluoride was from Matheson Gas Products (99.7% min) or Air Products and Chemicals (99.7% min).

RESULTS

The results are given in Table I for 10, 25, 40, 55, and 70°C. The diffusion coefficients, D_{12} (cm²/sec), were calculated from Equation 1 (*10*).

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

θ is the time in sec, L_0 the diffusion path at time zero, and L_θ the diffusion path at time θ in cm, R is the gas constant, T is the Kelvin temperature, P is the total system pressure in atm, ρ_L is the density of the liquid (g/cm³), M_L is the molecular weight of the liquid (g/mol), and P_L is the saturated vapor pressure of the liquid at T. It was assumed for Equation 1 that the vapor pressure of the liquid was P_L at the surface of the meniscus and zero at the open end of the tube. The derivation of Equation 1 assumes ideal gas behavior. We did not apply corrections for the nonideality of the vapor phase, but will do so in a subsequent paper. The D_{12} values in Table I are for 1 atm. Liquid vapor pressure, densities, and molecular weights were taken from Timmermans (*13*) or Dreisbach (*1, 2*).

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. In this procedure each point is treated as a discrete experiment. The average deviation of the slopes determined in this way ranged from ±0.2% to an extreme of ±7%, with almost all of the values being of the order of ±1%. The 7% value was for the *n*-octane–CF_4 system at 10°C where the change in path from the beginning to the end of the run was only 0.58 mm. Our values are about 3% lower than Kohn and Romero's (*4*) for the *n*-hexane–CH_4 system. A test run with air at 25°C gave the following results: water 0.240 (0.259), benzene 0.0930 (0.093), *n*-hexane 0.0786, and *n*-heptane 0.0705. The values in parentheses are from Nagata and Hasegawa (*8*). Marrero (*5–7*) gives the following as a "best" value for water–N_2 (air) at 25°C: 0.251. The agreement is good, especially since Marrero (*5–7*) considers the very best diffusion work to be precise to ±1%. We consider the overall precision in our diffusion coefficients to be of the order of ±1%. A few values with poorer precision are placed in parentheses in Table I.

A further indication of the reliability of the measurements comes from a least-squares treatment of log D_{12} vs. log T. (In the range 10–70°C plots of D_{12} vs. T were also quite linear.) The average deviation for all systems for log D_{12} was 0.42% and for D_{12} 1.2%. The slopes of these plots, n (from the equation $D_{12} = T^n$), were solvent dependent giving almost identical values for both gases. The n values are: *n*-hexane 1.95, *n*-heptane 1.63, *n*-octane 1.62, and isooctane 1.84.

DISCUSSION

Calculated values of the diffusion coefficients were obtained from Equation 2 (*3*) where $\sigma_{12} = (\sigma_{11} + \sigma_{22})/2$,

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

$\epsilon_{12}/k = (\epsilon_{11}\epsilon_{22})^{1/2}/k$, and the collision integrals $\Omega_{12}{}^{*(1,1)}$ were taken from ref. *3*. Table II gives the two sets of values of σ_{11} and ϵ_{11}/k used for calculating the values of D_{12} appearing in Table I. The Set A values were taken from ref. *7* for CH_4 and CF_4 and from Wilhelm and Battino (*14*) for the solvents. These latter values are derived from gas solubility data via the scaled particle theory and strictly apply to the solvents in the liquid state. The Set B values came from ref. *10* for CH_4 and

Table I. Experimental and Calculated Diffusion Coefficients

t, °C	D_{12} (exptl), cm²/sec	D_{12} (calcd),[a] cm²/sec	D_{12} (calcd),[b] cm²/sec	D_{12} (exptl), cm²/sec	D_{12} (calcd),[a] cm²/sec	D_{12} (calcd),[b] cm²/sec
	CH_4[c] + *n*-Hexane			CF_4[d] + *n*-Hexane		
10	0.0754	0.0721	0.0761	0.0389	0.0345	0.0351
25	0.0819	0.0799	0.0841	0.0435	0.0382	0.0394
40	0.0921	0.0880	0.0926	0.0481	0.0421	0.0428
55	0.0993	0.0965	0.1013	0.0522	0.0461	0.0470
70		0.1053	0.1106		0.0503	0.0511
	CH_4 + *n*-Heptane			CF_4 + *n*-Heptane		
10	0.0716	0.0650	0.0690	(0.0375)	0.0305	0.0313
25	0.0792	0.0720	0.0763	0.0387	0.0338	0.0346
40	0.0839	0.0794	0.0840	0.0425	0.0372	0.0381
55	0.0905	0.0870	0.0919	0.0470	0.0408	0.0417
70	0.0986	0.0951	0.1003	0.0504	0.0445	0.0426
	CH_4 + *n*-Octane			CF_4 + *n*-Octane		
10	0.0659	0.0598	0.0640	(0.0275)	0.0279	0.0285
25	0.0722	0.0664	0.0708	0.0361	0.0307	0.0316
40	0.0783	0.0731	0.0780	0.0419	0.0338	0.0348
55	0.0822	0.0803	0.0854	0.0435	0.0371	0.0381
70	0.0907	0.0877	0.0931	0.0463	0.0404	0.0416
	CH_4 + Isooctane			CF_4 + Isooctane		
10	0.0664	0.0603	0.0664	0.0317	0.0279	0.0296
25	0.0731	0.0669	0.0735	0.0364	0.0309	0.0327
40	0.0772	0.0737	0.0809	0.0390	0.0340	0.0360
55	0.0873	0.0809	0.0885	0.0430	0.0373	0.0394
70	0.0942	0.0883	0.0964	0.0453	0.0407	0.0430

[a] Calculated using parameters marked Set A in Table II. [b] Calculated using parameters marked Set B in Table II. [c] Average deviation for all systems with CH_4 was 5.5% for Set A and 2.0% for Set B. [d] Average deviation for all systems with CF_4 was 13% for Set A and 10% for Set B.

Table II. Pair Potential Parameters Used in Calculations for Table I

Substance	Set A σ, Å	 ϵ/k, K	Set B σ, Å	 ϵ/k, K
CH_4	3.70[a]	157[a]	3.81[b]	144[b]
CF_4	4.66[a]	134[a]	4.70[b]	152[b]
n-Hexane	5.92[c]	517[c]	5.91[d]	413[d]
n-Heptane	6.25[c]	573[c]	6.33[d]	416[d]
n-Octane	6.54[c]	611[c]	6.61[d]	438[d]
Isooctane	6.52[c]	602[c]	6.52[e]	402[e]

[a] Ref. *10*. [b] Ref. *3*. [c] Ref. *14*. [d] Ref. *9*. [e] Estimated from $\epsilon/k = 0.74\ T_c$ and $\sigma^3 = 0.59\ V_c$.

CF_4, a consistent set for the *n*-alkanes from Nelson and DeLigny (*9*), and the values for isooctane were estimated. The agreement (average deviation) for all systems with CH_4 was 5.5% for Set A and 2.0% for Set B. The agreement with CF_4 was 13% for Set A and 10% for Set B. Considering the great variations reported in the literature for ϵ/k and σ values (see ref. *3*, for example), we find the agreement between experimental and calculated values of D_{12} to be reasonable.

The much greater difference for the systems with CF_4 is certainly beyond experimental error. An ϵ/k for CF_4 of about 70K would give about 1% agreement between experimental and theory. This is of the order one would expect if Kihara core potentials were used. We intend examining the situation in more detail in a subsequent paper when we have more data available.

ACKNOWLEDGMENT

We gratefully acknowledge several helpful discussions with Dr. Stanley Weissman.

LITERATURE CITED

(1) Dreisbach, R. R., *Advan. Chem. Ser.*, **15**, 3–536 (1955).
(2) Dreisbach, R. R., *ibid.*, 22, 3–491 (1959).
(3) Hirschfelder, J. O., Curtiss, C. F., Bird, R. B., "Molecular Theory of Gases and Liquids," Wiley, New York, N.Y., 1964.
(4) Kohn, J. P., Romero, N., *J. Chem. Eng. Data*, **10**, 125 (1965).
(5) Marrero, T. R., PhD thesis, University of Maryland, College Park, Md., 1970.
(6) Marrero, T. R., Mason, E. A., "Gaseous Diffusion Coefficients," NSRDS-NBS 38 (1971).
(7) Mason, E. A., Marrero, T. R., *Adv. At. Mol. Phys.*, **6**, 155 (1970).
(8) Nagata, I., Hasegawa, T., *J. Chem. Eng., Japan*, **3**, 143 (1970).
(9) Nelson, W. D., DeLigny, C. L., *Rec. Trav. Chim.*, **87**, 623 (1968).
(10) Reid, R. C., Sherwood, T. K., "The Properties of Gases and Liquids," 2nd ed., McGraw-Hill, New York, N.Y., 1966.
(11) Romero, N., MS thesis, University of Notre Dame, Notre Dame, Ind. (1962).
(12) Stefan, J. *Wien. Akad. Sitzungber.*, **63**, 63 (1871).
(13) Timmermans, J., "Physico-chemical Constants of Pure Organic Compounds," Elsevier Amsterdam, 1950.
(14) Wilhelm, E., Battino, R., *J. Chem. Phys.*, **55**, 4012 (1971).

RECEIVED for review August 12, 1971. Accepted December 3, 1971. This work was partially supported for certain portions by Public Health Service Grant No. GM14710-04.

Excess Enthalpy of Gaseous Mixtures of Nitrogen and Carbon Dioxide

JONG IL LEE and ALAN E. MATHER[1]
Department of Chemical and Petroleum Engineering, University of Alberta, Edmonton 7, Alta., Canada

The excess enthalpies of binary mixtures of nitrogen and carbon dioxide have been measured for six isotherms in the temperature range 10–80°C at pressures up to 110 atm over the complete range of compositions.

A number of methods can be used to obtain information regarding the dependence of the enthalpy of mixtures on pressure, temperature, and composition. A direct method is the determination of the excess enthalpy (heat of mixing). The excess enthalpy, H^E is defined by:

$$H^E \equiv \left\{ H_m - \sum_i x_i H_i \right\}_{P,T} \qquad (1)$$

where H_m is the enthalpy of the mixture, H_i the enthalpy of pure component i, and x_i the mole fraction of component i in the mixture.

Many studies have been made of the excess enthalpy of liquid mixtures, but only a few workers have applied this method to gases. The earliest work on gases was performed by Beenakker and co-workers (*1, 2, 5*) on the systems H_2–N_2, H_2–Ar, Ar–N_2, CH_4–H_2, and CH_4–Ar. Later Van Eijnsbergen and Beenakker (*7*) studied the systems CH_4–N_2, He–CH_4, and He–Ar as well as extended the range of data in some of the systems studied earlier. Hejmadi (*3*) obtained some data in the systems N_2–CO_2, N_2–C_2H_6, and N_2–O_2, and Klein et al. (*4*) made extensive measurements in the system CH_4–N_2. Earlier in this laboratory, the system N_2–CO_2 was studied in a flow calorimeter at 40°C (*6*). In the present work results in this system have been obtained along six isotherms between 10° and 80°C at pressures up to 110 atm.

THERMODYNAMIC RELATIONS

The first law of thermodynamics, applied to a flow calorimeter in which two pure gases mix, reduces to:

$$H_m(T_2,P_2) - xH_1(T_1,P_1) - (1-x)H_2(T_1,P_1) = \frac{\dot{Q} - \dot{W}}{F} \qquad (2)$$

---

[1] To whom correspondence should be addressed.