Table VI. Entropies of the Liquid Methyl Alkyl Ketones at 298.15° K., Cal./(Mole ° K.)

	$S_{298.15^\circ \mathrm{K.}}$	$S_{\mathrm{increment}}$
Acetone	47.9[a] (49.28)[b]	7.80
2-Butanone	57.08[c]	8.03
2-Pentanone	65.11[d]	8.08
2-Hexanone	(73.19)	8.08
2-Heptanone	(81.27)	8.08
2-Octanone	89.35[d]	

[a] Reference (*3*). [b] R ln 2 is added because of symmetry. [c] Reference (*8*). [d] These data.

DISCUSSION

The low temperature heat capacity measurements on liquid acetone were taken by Kelley (*3*) from which he derived an entropy of 47.9 ± 0.3 cal./(mole ° K.) at 298.15° K. A recent publication from this laboratory (*8*) on liquid methyl ethyl ketone (2-butanone) gave the third law entropy as 57.08 ± 0.15 cal./(mole ° K.). From these two values, it is possible to establish the entropy increment owing to the addition of a methylene group. In comparisons of this kind, however, one must also take into consideration the symmetry of each molecule. Since the symmetry number for acetone is two, R ln 2 must be added giving an entropy value of 49.28 cal./(mole ° K.). As the ketone, 2-butanone, has a symmetry number of one, no additional entropy is added. In this case, then, the entropy increment owing to the addition of a methylene group going from acetone to 2-butanone is found to be 7.8 cal./(mole ° K.).

The next member in the series is methyl propyl ketone (2-pentanone), whose entropy, 65.11 cal./(mole ° K.), was established in the experimental section. The difference between 2-pentanone and 2-butanone is 8.03 cal./(mole ° K.) compared to the difference of 7.80 cal./(mole ° K.) between 2-butanone and acetone. The third law entropy of the sixth member of the series, 2-octanone, given earlier as 89.35 cal./(mole ° K.), shows the average entropy increment per methylene group to be 8.08 cal./(mole ° K.) from 2-pentanone through 2-octanone. The results of these measured and interpolated values of the entropy at 298.15° K. of the methyl alkyl ketone series are shown in Table VI.

Parks, Kelley, and Huffman (*6*) have found that the average entropy increment per methylene group is 8.0 cal./(mole ° K.) from formic acid to palmitic acid. The average increment for normal aldehydes is found to be 8.1 cal./(mole ° K.) from the work of Parks and coworkers (*7*) on *n*-butyraldehyde and *n*-heptaldehyde. The agreement between the entropy increment per methylene group of the normal ketones, acids, and aldehydes is considered to be satisfactory. It has been established, however, that the entropy increment is 7.72 cal./(mole ° K.) for the *n*-alkanes (*1*) and is 7.8 cal./(mole ° K.) for the normal alcohols (*6*). This significant difference in entropy increment most certainly lies in the fact that the ketone-acid-aldehyde class contains the carbonyl group which is not present in the alkane-alcohol class.

LITERATURE CITED

(1) Am. Petrol. Inst. Research Project 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbon and Related Compounds," Carnegie Press, Carnegie Institute of Technology, Pittsburgh, Pa., 1953.
(2) Hildenbrand, D.L., Kramer, W.R., McDonald, R.A., Stull, D.R., *J. Am. Chem. Soc.* **80**, 4129 (1958).
(3) Kelley, K.K., *Ibid.*, **51**, 1145 (1929).
(4) Oetting, F.L., *J. Phys. Chem.* **67**, 2757 (1963).
(5) Oetting, F.L., McDonald, R.A., *Ibid.*, **67**, 2737 (1963).
(6) Parks, G.S., Kelley, K.K., Huffman, H.M., *J. Am. Chem. Soc.* **51**, 1969 (1929).
(7) Parks, G.S., Kennedy, W.D., Gates, R.R., Moseley, J.D., Moore, G.E., Renquist, M.L., *Ibid.*, **78**, 56 (1956).
(8) Sinke, G.C., Oetting, F.L., *J. Phys. Chem.* **68**, 1354 (1964).
(9) Stull, D.R., *Anal. Chem. Acta* **17**, 133 (1957).

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Molecular Diffusion Coefficients in Binary Gaseous Systems at One Atmosphere Pressure

N-Hexane–Methane and 3-Methylpentane–Methane Systems

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THERE are relatively few data on binary diffusion coefficients in hydrocarbon gaseous systems. Such data are necessary in calculations involving steady and non-steady state mass transport. Few, if any studies on diffusion coefficients in isomeric systems have been reported. In the saturated hydrocarbon systems, it appears desirable to determine if there are measurable differences in the diffusion coefficients of isomeric compounds in the same gas. Data of these types are of considerable value in testing certain diffusional models such as those derived by use of intermolecular potential functions in conjunction with the kinetic theory.

EXPERIMENTAL

The experimental apparatus was an adaptation of the diffusion glass tube apparatus first described by Stefan (*8*), and which has been used extensively for measurement of gas diffusion coefficients. It consisted of the diffusion cell shown in Figure 1, which contained a capillary tube of 0.15 cm. I.D. The cell was thermostated in a well agitated water bath whose temperature was controlled to ±0.01° C. by a mercury temperature controller. The temperature of the bath was measured using a calibrated mercury in glass thermometer which was accurate within 0.1° C.

The capillary tube method of Stefan was used to measure the binary molecular coefficients of *n*-hexane diffusing in methane and 3-methylpentane diffusing in methane at one atmosphere pressure and at temperatures of 25°, 30°, 40°, 50°, and 60° C. The predicted diffusion coefficients based upon the Lennard-Jones force constants in the Chapman-Enskog approximate kinetic theory were in excellent agreement with the experimental data.

At discrete time intervals the liquid level in the capillary tube was measured with a cathetometer which could be read to a precision of ±0.005 cm. The time duration of the experimental runs varied between four and 26 hours depending upon the temperature level. The time was taken on a synchronous clock.

Different flow rates of methane through the cell showed no effect on the diffusion rate. The methane gas leaving the cell was bubbled through water at a nominal rate of 20 to 30 bubbles per minute.

The total pressure of the experiment was taken as the barometric pressure prevailing in the laboratory at the time of the experimental run. Since the barometric pressure sometimes changed during a run, the arithmetic average barometric pressure at the start and finish of a run was taken as the pressure of the system. The pressure was measured on a standard barometer to a precision of 0.1 mm. of mercury. The measured diffusion coefficients were corrected to a pressure of one standard atmosphere. An attempt to control accurately the pressure of the system with a Cartesian manostat device proved unsuccessful owing to insufficient control sensitivity of the device.

The materials employed in the study were all Phillips "pure grade" (99 mole % minimum purity) materials and were used without further purification.

RESULTS

An experimental run consisted of from five to 12 cathetometric measurements of the length of the vapor space above the liquid in the capillary tube at certain time intervals during a total run time of from four to 26 hours. Thirty-three experimental runs were made, and four of these were discarded because the barometric fluctuations during these particular runs were large enough to cause the data to exceed the maximum expected deviation. The raw data runs were initially smoothed by using a least squares treatment on the diffusion path length squared *vs.* time. The least square slopes of the resulting straight line equations were then used in conjunction with Equation 1 to calculate the molecular diffusion coefficient (*6*).

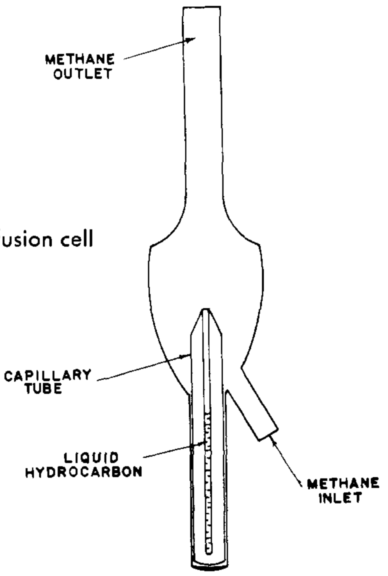

Figure 1. Diffusion cell

$$D_V = \frac{(Z_\theta^2 - Z_0^2)}{2\theta} \frac{RT\rho_L}{M_L} \frac{P_{BM}}{(P_{A1} - P_{A2})} \quad (1)$$

At least three experimental runs were made with each of the two binary systems at each of the five temperatures from 25° to 60° C. In several cases, four runs were made under identical conditions. The data from the multiple runs under identical conditions were averaged in order to compute the diffusion coefficient. The reproducibility of the experimental runs was excellent as the average deviation for all the runs from the average value was 0.77%, and the maximum observed deviation was 1.89%. The data were further smoothed by the method of least squares to determine the best straight line representation of the logarithm of the diffusion coefficient *vs.* the logarithm of the absolute temperature. The results of the final smoothing are shown in Table I. The standard deviation of the experimental points from the smoothed points for the *n*-hexane-methane system is 0.00086 cm.^{2}/sec. and for the 3-methylpentane system is 0.00126 cm.^{2}/sec. The smoothed data of Table I were compared with the approximate Chapman-Enskog kinetic theory in which the Lennard-Jones force parameters were employed. The specific equation used was the well known perfect gas law form (*1*):

$$D_V = \frac{0.0018583\, T^{3/2}}{P_T \sigma_{AB}^2 \Omega_{AB}} \left(\frac{1}{M_A} + \frac{1}{M_B}\right)^{1/2} \quad (2)$$

Equation 2 when applied to the *n*-hexane-methane system using the force constants for methane and *n*-hexane as given in Hirschfelder (*2*), the conventional mixture rules $[\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}$, $\sigma_{AB} = \frac{1}{2}(\sigma_A + \sigma_B)]$, and the values of the collision integrals (Ω_{AB}) taken from Liley (*3*) gave results which were somewhat lower than the experimental data. However, the average deviation of the equation from the smoothed data was only 1.62%. Since the Lennard-Jones parameters for 3-methylpentane are not reported in Hirschfelder, it was not possible to make a semirigorous comparison between the two binary systems. However, the Lennard-Jones parameters for *n*-hexane and 3-methylpentane were estimated by using the critical constants and the equations recommended by Hirschfelder (*1*) $[\sigma = 0.841\, V_c^{1/3}$ and $(\epsilon/k) = 0.77\, T_c]$, along with the Hirschfelder computed Lennard-Jones parameters for methane. Excellent comparison with the experimental data was obtained. The deviations of these calculated points from the experimental data are given in Table I.

The effect of temperature on the diffusion coefficient was obtained from the slope of the log D_v *vs.* log T plot. The slope for the *n*-hexane-methane system was 1.861 and for the 3-methylpentane-methane system was 1.852. An average slope of 1.857 fits the data of both systems within the experimental precision. The approximate kinetic theory in the same temperature range gives a slope of 1.945. The measured slopes are smaller than this by an amount which seems to exceed the effects which are strictly due to instrumental precision. However, at low temperature, the temperature effect on the diffusion coefficient is approximately given by an exponent of 2 on the temperature while at

Table I. Molecular Diffusion Coefficients in the *n*-Hexane–Methane and the 3-Methylpentane–Methane Systems at One Atmosphere Pressure

	n-Hexane–Methane			3-Methylpentane–Methane	
		Dev. of Eq. 2 from exp.			Dev. of Eq. 2 from exp.
Temp., °C.	D_v(exp.), cm.^{2}/sec.	%[a]	%[b]	D_v(exp.), cm.^{2}/sec.	%[b]
25	0.08664	−2.06	+0.46	0.08756	−0.02
30	0.08936	−1.78	+0.67	0.09028	+0.33
40	0.09493	−1.67	+0.95	0.09591	−0.31
50	0.10065	−1.45	+1.30	0.10164	+0.69
60	0.10650	−1.16	+1.41	0.10752	+1.21
		Av. 1.62	Av. 0.96		Av. 0.51

[a] Equation 2 with all Lennard-Jones parameters taken from reference (*2*). [b] Equation 2 with the Lennard-Jones parameter for methane taken from reference (*2*) and for *n*-hexane and 3-methyl pentane estimated from the critical constants.

high temperatures the exponent on the temperature is closer to 1.65.

Although the data of Table I indicate that the molecular diffusion coefficients of the 3-methylpentane–methane system are slightly higher than those of the *n*-hexane–methane system, this cannot be taken as an absolute fact. The standard deviation of the 3-methylpentane–methane system exceeds the absolute difference between the diffusion coefficients of the two systems. Thus, there is not a statistically significant difference between the diffusion coefficients of the two systems. However, the slightly larger diffusion coefficients obtained for the 3-methylpentane–methane system are in good agreement with the approximate kinetic theory.

During this experimental study, special emphasis was placed upon the investigation of any approximations involved in the physical model which might affect the accuracy of the calculated diffusion coefficients. The effects which could play some role in the experiments are as follows:

(*A*) Counter diffusion of methane toward the gas-liquid interface,
(*B*) Nonideality of the gas phase,
(*C*) Fugacity lowering of the interfacial solvent liquid by dissolved methane,
(*D*) Localized cooling by evaporation leading to a lower vaporization temperature than the thermostat temperature,
(*E*) Concavity of the liquid-gas interface

The experimental evidence which showed that effect *A* was negligible was obtained in a separate liquid phase diffusion study of the same two systems which is as yet unpublished. Effect *C* was deduced to be negligible from calculations involving the thermal flux necessary for the measured evaporation rate and the estimated thermal resistance owing to conduction and convection. Effect *E* was judged to be negligible because the concavity vertical dimension was of the order of 0.06 cm., and the diffusion path was never less than 2.0 cm. and generally averaged around 4.0 cm.

The corrections for effects *B* and *C* were obtained in vapor-liquid studies of these two systems (*7*) of which one study is not as yet published. Of the two effects, *B* was larger than *C* and in some cases affected the diffusion coefficient in excess of 1%. The corrections were not applied to the data of Table I but are discussed by Romero (*4*).

Additional contributions to absolute error of the measured diffusion coefficients are errors in the numerical values of the vapor pressures and densities of *n*-hexane and 3-methylpentane which were used in the calculations. These data were taken from Rossini (*5*) and are believed to be the best available.

The largest single cause of experimental error in this study appears to have been the barometric pressure fluctuations during the experimental runs. An error treatment indicated that a maximum error of 8.5% was possible from this source alone. If a sensitive enough manostat pressure controller were to be used, the pressure fluctuation problem could be circumvented.

No conclusive statement can be made regarding the possible effect of gas phase composition on the molecular diffusion coefficient. The interfacial concentration of methane varied from about 0.8 mole fraction at 25° C. to 0.1 mole fraction at 60° C. However, the logarithmic mean mole fraction of methane in the diffusion column only varied by a factor of 1.65 for the *n*-hexane–methane system and 2.3 for the 3-methylpentane–methane system. Concentration effects probably had only a nominal influence on the diffusion coefficients of this study.

NOMENCLATURE

D_v = gas phase molecular diffusion coefficient, cm.^{2}/sec.
k = Boltzmann constant, erg/° K.
M_L = molecular weight of pure liquid
P_A = partial pressure of the evaporating liquid, atm.
P_B = partial pressure of methane, atm.
P_{BM} = logarithmic mean partial pressure of methane, atm.
$= \dfrac{(P_{B2} - P_{B1})}{\ln(P_{B2}/P_{B1})}$
R = universal gas law constant, cm.^{3} × atm./gram mole × ° K.
T = absolute temperature, ° K.
T_c = critical temperature of pure evaporating liquid, ° K.
V_c = critical volume of pure evaporating liquid, ° K.
Y_B = mole fraction of methane
Y_{BM} = logarithmic mean mole fraction
$= \dfrac{(Y_{B2} - Y_{B1})}{\ln(Y_{B2}/Y_{B1})}$
Z = instantaneous length of diffusion path, cm.

Greek Letters

θ = time, sec.
ρ_L = liquid density, gram/cm.^{3}
ϵ_{AB} = energy at minimum of potential "well" in the Lennard-Jones "6–12" potential function, ergs
σ_{AB} = "collision diameter," distance between centers of molecules at zero potential energy, angstroms
Ω_{AB} = "collision integral" used in Chapman-Enskog kinetic theory

Subscripts

0 = zero time
1 = specifies the position at the gas-liquid interface
2 = specifies the position at the top of the capillary tube
θ = time after start of observations

LITERATURE CITED

(1) Bird, R.B., Stewart, W.E., Lightfoot, E.N., "Transport Phenomena," p. 511, Wiley, New York, 1960.
(2) Hirschfelder, J.O., Curtiss, C.F., Bird, R.B., "Molecular Theory of Gases and Liquids," pp. 245, 1111, 1112, Wiley, New York, 1954.
(3) Liley, P.E., Thermophysical Properties Research Center Rept. **15**, Purdue University, February 1963.
(4) Romero, N., M. S. thesis, Univ. of Notre Dame, Notre Dame, Ind., 1962.
(5) Rossini, F.D., Pitzer, K.S., Arnet, R.L., Brown, R.M., Pimentel, G.C., "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," pp. 300, 306, 380, 381, Carnegie Press, Pittsburgh, Pa., 1953.
(6) Sherwood, T.K., Pigford, R.L., "Absorption and Extraction," p. 17, McGraw-Hill, New York, 1952.
(7) Shim, J., Kohn, J.P., J. CHEM. ENG. DATA **7**, 3-8 (1962).
(8) Stefan, J., *Wien. Akad. Sitzungber.* **63**, 63 (1871).

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