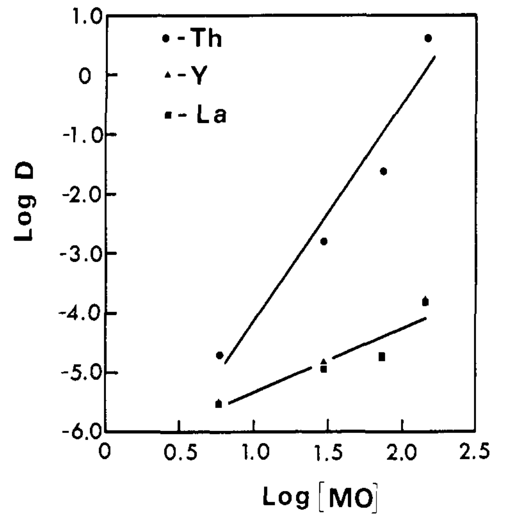

Figure 1. Log D vs. log [MO] for metal extraction (HNO_3 concn = 9.46N; O/A = 2.50; initial metal concn = 0.05M)

To obtain the value of n in the above equation, extractions of HNO_3 were carried out as a function of the solvent concentration with solutions containing no metal ions. The results are given as a log D vs. log [MO] plot shown in Figure 2, where the slope of the best line is 1.18. The species ($HNO_3 \cdot H_2O \cdot MO$) was either coextracted with the metal ions or could be formed first and then coordinated with the metal nitrates. In each of these experiments the acidity of the aqueous raffinate was practically the same as that of the corresponding experiment for the metal extraction.

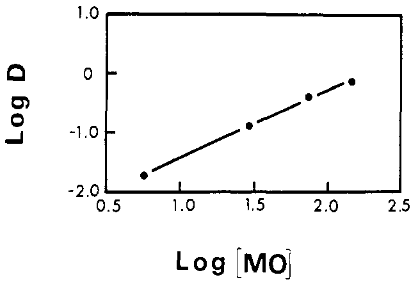

Figure 2. Log D vs. log [MO] for HNO_3 extraction (HNO_3 concn = 9.46N; O/A = 2.50; initial metal concn = 0.05M)

Although extraction of the metals is greater at higher HNO_3 concentration and O/A value, the largest separation factor between thorium and yttrium (D_{Th}/D_Y), 84.4, occurred at a HNO_3 concentration of 9.46N and an O/A value of 1.25. The separation factor between yttrium and lanthanum (D_Y/D_{La}) was less than 1.2 in all cases.

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Binary Diffusion Coefficients of *n*-Pentane in Gases

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The Stefan method was used to measure the binary gaseous diffusion coefficients of *n*-pentane (*n*Pe) in hydrogen, helium, nitrogen, air, and argon at 1 atm pressure and a temperature from −15° to 25°C at sec; *n*Pe-He, 0.3044 ± 0.0003 cm^2/sec; *n*Pe-N_2, 0.0885 ± 0.0001 cm^2/sec, *n*Pe-air, 0.0877 ± 0.0002 cm^2/sec; and *n*Pe-Ar, 0.0792 ± 0.0007 cm^2/sec. The 0.0885 ± 0.0001 cm^2/sec, 2*n*Pe-air, 0.0877 ■ 0.0002 cm^2/sec; and *n*Pe-Ar, 0.0792 ± 0.0007 cm^2/sec. The temperature exponent for each system lay between 1.778 and 1.971, in good agreement with the predicted values based upon the Lennard-Jones force constants in the Chapman-Enskog approximate kinetic theory.

Binary gaseous diffusion coefficients in hydrocarbon systems are important physical properties for chemical engineering. The temperature exponents of diffusion coefficients are also important for simplifying interpolation and (possibly) for extrapolation. There are relatively few such data in the literature, and those values differ in many cases. Therefore, we measured the diffusion coefficients by the Stefan method with hydrogen, helium, nitrogen, air, and argon as the carrier gases for *n*-pentane.

Experimental

The *n*-pentane was of pure grade (99 mol % minimum purity). The carrier gases—hydrogen, helium, nitrogen, air, and argon—were supplied by Hitachi Oxygen Co. (99.9 mol % minimum purity).

The Stefan method was used for the determination of the binary gaseous diffusion coefficients. Since the experimental method is well known, only a brief description will be given here. The apparatus consisted of the diffusion cell (Figure 1), which contained a capillary tube of 0.10-cm i.d., 0.60-cm o.d., and 10-cm length. The cell was immersed in a well-agitated water (or methanol solution) bath whose temperature was controlled to within 0.05°C. The temperature of the bath was measured to a precision of 0.01°C with a calibrated mercury thermometer with a magnifying glass. After steady state was reached, at certain time intervals the liquid level in the capillary tube was measured with a reading microscope which could be read to a precision of 0.001 cm.

The time duration of experimental runs varied between 1 and 25 hr, depending on the temperature level and carrier gases. Care was taken to ensure that the diffusion coefficients were not influenced by flow rates of carrier gases in the approximate range of 100-500 cm^3/min.

The gas flow rate was actually controlled at 250 cm³/min. A check was made to ensure that the diffusion coefficients did not change in the range of 2–8 cm of diffusion path.

The total pressure of the experiment was taken as barometric pressure in the laboratory at the time of the experimental run. Since the barometric pressure sometimes changed during a run, the arithmetic average of barometric pressures at the start and finish of the run was taken as the pressure of the system. The largest typical pressure change during a run was 2.0 mm Hg. The pressure was measured on a standard barometer to a precision of 0.01 cm of mercury.

The measured diffusion coefficients were corrected to a pressure of 1 standard atm.

Results

The molecular diffusion coefficients were calculated with Equation 1 (*7*).

$$D_{AB} = \frac{(z_\theta^2 - z_0^2)}{2\theta} \; \frac{RT\rho_L}{M_L} \; \frac{p_{BM}}{p_{A1} - p_{A2}} \qquad (1)$$

The density (ρ_L) and vapor pressure (p_A) of *n*-pentane used to calculate the diffusion coefficients were taken from the literature, and the precision of the density (ρ_L) and vapor pressure (p_A) were both within ±0.1% (*3, 5, 8*). The diffusion coefficients obtained in the experimental measurements are summarized in column 3 of Table I. The reproducibility of the experimental runs was excellent since the average deviation for all runs from the average value was 0.3%, and the maximum observed deviation was 0.7%.

The gaseous diffusion coefficients were represented with the following equation:

$$D_{AB} = D_{AB0} \left(\frac{T}{T_0}\right)^m \qquad (2)$$

The raw data were smoothed by a least-squares treatment on log D_{AB} vs. log T to give a straight line. The diffusion coefficients recalculated by the resulting straight line equation are given in column 4 of Table I. The temperature exponents in the range of −15° to 25°C for each system are also given in column 4 of Table II. The maximum standard deviation in these five systems was 0.5%. When the precision of the literature values (M_L, ρ_L, p_A) and original data (z, θ, T) were taken into account, the precision of the experimental values in column 3 of Table I was in most cases better than ±1.0%.

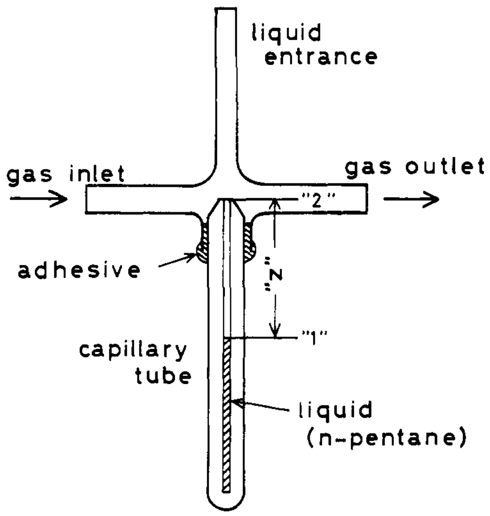

Figure 1. Diffusion cell

The diffusion coefficients of *n*-pentane in air at 25°C were investigated by Lugg (*6*) and Barr and Watts (*1*) and are shown in Table III along with the results of this work. Lugg used the Stefan method, and Barr and Watts used the method of infrared spectrophotometry. Their data were lower than that of this work by about 3%.

Table I. Experimental Diffusion Coefficients for *n*-Pentane in Gases at 1 atm

Temp, °C	No. of data	Diffusion coefficients, cm²/sec: Exptl	Recalcd
		H_2–*n*-pentane	
−15.0	2	0.2633 ± 0.0004[a]	0.2643[b]
−10.0	2	0.2741 ± 0.0006	0.2736
−5.0	4	0.2826 ± 0.0014	0.2830
0.0	6	0.2925 ± 0.0006	0.2925
5.0	2	0.3035 ± 0.0005	0.3021
10.0	9	0.3128 ± 0.0006	0.3119
15.0	5	0.3214 ± 0.0006	0.3218
20.0	6	0.3327 ± 0.0003	0.3319
25.0	2	0.3404 ± 0.0009	0.3421
		He–*n*-pentane	
−15.0	3	0.2343 ± 0.0010	0.2360
−10.0	3	0.2437 ± 0.0011	0.2442
−5.0	2	0.2535 ± 0.0006	0.2526
0.0	2	0.2632 ± 0.0013	0.2610
5.0	5	0.2707 ± 0.0005	0.2697
10.0	4	0.2786 ± 0.0014	0.2784
15.0	3	0.2865 ± 0.0006	0.2872
20.0	5	0.2957 ± 0.0004	0.2962
25.0	3	0.3044 ± 0.0003	0.3053
		N_2–*n*-pentane	
−15.0	2	0.0675 ± 0.0001	0.0675
−10.0	2	0.0702 ± 0.0000	0.0700
−5.0	2	0.0721 ± 0.0000	0.0725
0.0	3	0.0749 ± 0.0001	0.0751
5.0	2	0.0782 ± 0.0001	0.0778
10.0	3	0.0807 ± 0.0001	0.0804
15.0	2	0.0830 ± 0.0002	0.0831
20.0	4	0.0860 ± 0.0001	0.0859
25.0	2	0.0885 ± 0.0001	0.0887
		Air–*n*-pentane	
−15.0	2	0.0676 ± 0.0009	0.0679
−10.0	2	0.0703 ± 0.0000	0.0703
−5.0	4	0.0732 ± 0.0004	0.0727
0.0	4	0.0751 ± 0.0005	0.0751
5.0	4	0.0772 ± 0.0005	0.0776
10.0	4	0.0804 ± 0.0001	0.0801
15.0	4	0.0825 ± 0.0004	0.0826
20.0	4	0.0851 ± 0.0002	0.0852
25.0	4	0.0877 ± 0.0002	0.0878
		Ar–*n*-pentane	
−15.0	3	0.0597 ± 0.0005	0.0599
−10.0	3	0.0618 ± 0.0009	0.0622
−5.0	2	0.0649 ± 0.0003	0.0645
0.0	5	0.0670 ± 0.0000	0.0669
5.0	2	0.0695 ± 0.0001	0.0693
10.0	2	0.0720 ± 0.0002	0.0718
15.0	2	0.0743 ± 0.0000	0.0743
20.0	2	0.0770 ± 0.0001	0.0769
25.0	3	0.0792 ± 0.0007	0.0795

[a] Standard deviation. [b] Smoothed experimental data by use of the temperature exponent *m* for each system.

Table II. Temperature Exponents of Diffusion Coefficients for *n*-Pentane at 1 atm

Carrier gases	Temp range, °C	No. of data	Temp exponent	
			Exptl	Calcd
H_2	−15–25	38[a]	1.790 ± 0.006[b]	1.809[c]
He	−15–25	30	1.789 ± 0.009	1.710
N_2	−15–25	22	1.894 ± 0.007	1.902
Air	−15–25	32	1.778 ± 0.007	1.881
Ar	−15–25	24	1.971 ± 0.008	1.936

[a] Total number of data in temperature range of −15–25°C. [b] Standard deviation. [c] Calculated values by use of Equation 3.

Table III. Comparison of Diffusion Coefficients in *n*-Pentane–Air System at 25°C and 1 atm

This work	0.0877 ± 0.0002 cm^2/sec
Barr and Watts (*1*)	0.0856 ± 0.0035 cm^2/sec
Lugg (*6*)	0.0842 ± 0.00182 cm^2/sec

Since their standard deviations were 2–4%, the agreement with this work was within experimental error.

According to kinetic theory (*4*),

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

The temperature exponents (m) calculated with Equation 3 are listed in Table II. In calculating m by Equation 3, Ω_{AB} for Lennard-Jones (12, 6) potential model as a function of (kT/ϵ) was used, and σ_{AB} and ϵ_{AB} were calculated from the collision diameter σ and the energy at minimum potential well ϵ of each molecule, with the conventional combining rule [$\sigma_{AB} = (\sigma_A + \sigma_B)/2$, $\epsilon_{AB} = \sqrt{\epsilon_A\epsilon_B}$] (*2*). The temperature exponents agreed well with those calculated for each system, as shown in Table II.

Acknowledgment

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Nomenclature

D_{AB} = binary diffusion coefficient for A in B, cm^2/sec
M_L = molecular weight of pure liquid
m = temperature exponent, Equation 2
P = total pressure, atm
p_A = partial pressure of component A, atm
p_{BM} = logarithmic mean partial pressure of component B, atm
R = gas constant, cm^3 atm/g-mol K
T = absolute temperature, K
z = instantaneous length of diffusion path, cm

Greek Letters

θ = time, sec
ρ_L = liquid density, g/cm^3
σ_{AB} = collision diameter, distance between centers of molecules at zero potential energy, Å
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 observation

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