perature. Over most of the temperature range, the deviation curve for Scatchard et al., who estimated their temperature uncertainty as ±0.01K, falls within these limits. The systematic difference between our results and theirs probably lies in the calibration of their 20-junction thermopile. The same comparator and scale were used in both studies.

The normal boiling temperature calculated from Equation 1 is 337.664K. This is in excellent agreement with the value calculated from the equation of Scatchard et al. (14), 337.65 on the current temperature scale. Wojciechowski (16) also obtained 337.65K in a careful study of the boiling temperature of methanol. Many other investigators have obtained higher boiling temperatures for methanol. We attribute higher boiling temperatures to higher water content in the methanol samples studied by these workers.

Ambrose and Sprake (1) have reported precise vapor-pressure measurements for a number of aliphatic alcohols. Their vapor pressures for methanol, obtained by comparative ebulliometry, are consistently lower than ours. The differences between the two sets of measurements can be explained, over the temperature range of the present work, by a water content of 0.07 wt % in their methanol. This explanation seems reasonable in view of the difficulty expressed by Ambrose and Sprake in removing the last traces of water from their samples.

Through the use of the Clapeyron equation, Dever et al. (2) attempted to show thermodynamic consistency of their vapor pressures with the precise calorimetric enthalpies of vaporization of Fiock et al. (3). Dever et al. calculated the volume of the vapor from the virial coefficients of Kretschmer and Wiebe (7). This procedure is unsatisfactory both because it requires at least a twofold extrapolation of Kretschmer and Wiebe's results to reach the saturation pressure, and because Kretschmer and Wiebe omitted the third virial coefficient but included the fourth in their equation of state. This unusual equation has recently been criticized by Kell and McLaurin (6) in a

study of the *PVT* behavior of methanol at high temperatures.

We have found that reasonable values for the third virial coefficients for methanol vapor can be calculated from the vapor-pressure measurements reported here, the enthalpy of vaporization (3) and literature values of the second virial coefficient (6–8). These calculations will be published elsewhere.

Acknowledgment

Literature Cited

(1) Ambrose, D., Sprake, C. H. S., *J. Chem. Thermodyn.*, **2**, 631 (1970).
(2) Dever, D. F., Finch, A., Grunwald, E., *J. Phys. Chem.*, **59**, 668 (1955).
(3) Fiock, E. F., Ginnings, D. C., Holton, W. B., *J. Res. Nat. Bur. Stand.*, **6**, 881 (1931).
(4) Gibbard, H. F., Creek, J. L., "*n*-Butyl Phthalate: An Isopiestic Standard for Methanol," presented at the 167th National Meeting, ACS, Los Angeles, Calif., April 1974.
(5) Gibbard, H. F., Scatchard, G., *J. Chem. Eng. Data*, **18**, 293 (1973).
(6) Kell, G. S., McLaurin, G. E., *J. Chem. Phys.*, **51**, 4345 (1969).
(7) Kretschmer, C. B., Wiebe, R., *J. Amer. Chem. Soc.*, **76**, 2579 (1954).
(8) Kudchadker, A. P., Eubank, P. T., *J. Chem. Eng. Data*, **15**, 7 (1970).
(9) Mitchell, J., Smith, M., "Aquametry," Interscience, New York, N.Y., 1948.
(10) Morton, A. A., Mark, J. G., *Ind. Eng. Chem.*, **6**, 151 (1934).
(11) Polak, J., Murakami, S., Lam, V. T., Pflug, H. D., Benson, G. C., *Can. J. Chem.*, **48**, 2457 (1970).
(12) Scatchard, G., Raymond, C. L., *J. Amer. Chem. Soc.*, **60**, 1278 (1938).
(13) Scatchard, G., Wilson, G. M., Satkiewicz, F. G., *ibid.*, **86**, 125 (1964).
(14) Scatchard, G., Wood, S. E., Mochel, J. M., *ibid.*, **68**, 1957 (1946).
(15) Taylor, R. K., *ibid.*, **52**, 3577 (1930).
(16) Wojciechowski, M., *J. Res. Nat. Bur. Stand.*, **17**, 721 (1936).

Adsorption of Hydrocarbons on Carbon Molecular Sieve

Tomoko Nakahara,[1] Mitsuho Hirata, and Toshiaki Omori
Department of Industrial Chemistry, Tokyo Metropolitan University, Tokyo, Japan

The adsorption equilibria for methane, ethylene, ethane, propylene, propane, *n*-butane, *n*-pentane, benzene, and cyclohexane on commercially available carbon molecular sieve were obtained by a gravimetric technique. Isotherms were measured for the pure gases in the temperature range from 5.4° to 50°C and pressures up to 1 atm. The isotherms show the Type I shape according to the classification by Brunauer et al., which is usually observed at adsorption on microporous adsorbents. The molecular sieving effect was clearly observed by the adsorption showing the strong discrimination of cyclohexane from benzene.

The data presented were obtained as a first part of a continuing study of adsorption of gases and vapors on microporous solids. The carbonaceous molecular sieve

materials are interesting as a separation medium in which zeolite sieves are not suitable. The carbon sieves are more stable at high temperatures than zeolite sieves and are quite stable in strong acid solutions. They also exhibit much less hydrophilic character than the zeolites (6).

The carbon molecular sieve used in this work is the Molecular Sieving Carbon-5A (MSC-5A) (a product of Takeda Chemical Industrial Co.) which has micropores of approximately 5 Å. The hydrocarbon adsorption on this material was reported by Kawazoe et al. (5) for ethylene, ethane, and benzene at several temperatures. But the raw data which made it possible to compare with our data were limited only to ethane adsorption data at 0° and 30°C.

Experimental Apparatus and Procedure

Adsorbent. A carbon molecular sieve sample was crushed into 28–42 mesh, which originally consisted of

[1] To whom correspondence should be addressed.

cylindrical particles, 5 mm in diameter and length. The apparent density, true density, macropore volume, micropore volume, and total pore volume of this material are 0.90 g/ml, 1.8 g/ml, 0.38 ml/g, 0.18 ml/g, and 0.56 ml/g, respectively (4). The surface area defined by the B-point method from the nitrogen isotherm at $-195.3°C$ was 650 m²/g.

Adsorbates. The adsorbates investigated were methane, ethylene, ethane, propylene, propane, n-butane, n-pentane, benzene, and cyclohexane. The purity and manufacturer of each adsorbate are as follows: methane: 99.95%, research grade (Takachiho Chemical Co.); ethylene: 99.95% (Nisseki Chemical Co.); ethane: 99.0% minimum purity, pure grade (Takachiho Chemical Co.); propylene: 99.7% (Tonen Petroleum Chemical Co.); propane: 99.7%, research grade (Takachiho Chemical Co.); n-butane: 99.7%, research grade (Takachiho Chemical Co.); n-pentane: 99%, distillate of 36.5–37.0°C, special grade reagent (Tokyo Kasei Ind. Co.); benzene: distillate of 79.5–81°C, special grade (Showa Chemical Co.); cyclohexane: distillate of 80–82°C, special grade reagent (Showa Chemical Co.). Prior to use in adsorption measurements, the methane, ethylene, and ethane were passed through a trap cooled by a Dry Ice–methanol mixture.

Apparatus. A static gravimetric adsorption apparatus with a McBain quartz spring balance of 0.189 mm/mg sensitivity was used. A schematic diagram of this apparatus is shown in Figure 1. The weight of adsorbed gas or vapor was determined by suspending the carbon sieve in a small bucket of aluminum foil from the spring and noting changes in the spring deflection measured by a cathetometer through the glass thermostat. The deflection could be read to 0.01 mm. Equilibrium pressures above the carbon sieve were measured by mercury manometer C. The meniscus of the mercury was read by a cathetometer when the pressure was lower than 10 mm Hg. Experimental temperatures were maintained constant within ±0.05°C by the regulator with the thermistor sensor. The adsorption chamber should be placed in a thermostat at least 17 cm deep from the water surface so that the sample bucket avoids heat convection and radiation.

Procedure. An approximately 0.5-gram carbon sieve sample was placed in a bucket suspended from the spring. Before the experimental run for obtaining the isotherm, the carbon sample was outgassed by heating at 360°C under high vacuum by electric furnace for 2 hr. The sample should be kept under high vacuum until cooled. The potential adsorbate gas was admitted to the
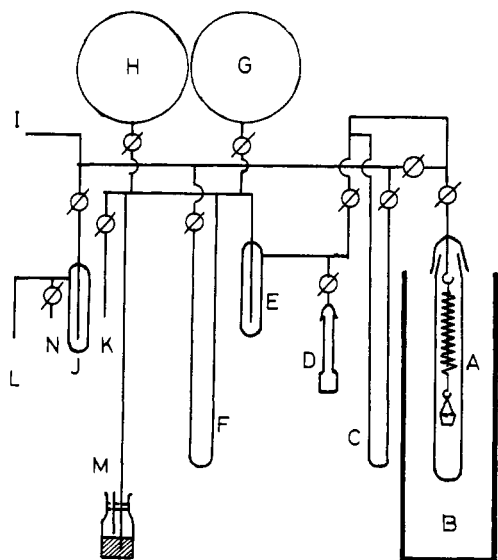

Figure 1. Gravimetric apparatus for adsorption measurement
A, adsorption chamber; B, water thermostat; C, F, mercury manometer; D, liquid adsorbate reservoir; E, J, cold trap; G, H, gas reservoir; I, MacLeod gage; K, gas supply; L, vacuum pump; M, mercury safety; N, vent

Table I. Adsorption Equilibrium Data (MSC-5A)

5.4°C		30.0°C			
Press, mm Hg	Amt adsorbed, g/g-adsorbent	Press, mm Hg	Amt adsorbed, g/g-adsorbent	Press, mm Hg	Amt adsorbed, g/g-adsorbent
		Methane			
5.0	0.0002	21.0	0.0006		
27.0	0.0023	50.0	0.0017		
43.0	0.0035	114.5	0.0037		
88.0	0.0060	196.0	0.0061		
153.0	0.0087	293.0	0.0081		
243.0	0.0121	405.0	0.0103		
327.0	0.0142	521.0	0.0118		
430.0	0.0160	622.0	0.0135		
530.0	0.0180				
654.0	0.0199				
		Ethylene			
5.5°C		**30.0°C**		**50.0°C**	
0.8	0.0044	12.5	0.0140	4.8	0.0036
2.2	0.0096	42.7	0.0260	11.8	0.0080
10.0	0.0217	72.6	0.0335	21.0	0.0116
28.0	0.0334	101.0	0.0376	53.0	0.0198
51.5	0.0412	150.0	0.0430	95.0	0.0263
81.5	0.0473	219.6	0.0483	146.0	0.0303
122.0	0.0530	307.0	0.0517	203.0	0.0354
163.5	0.0569	524.5	0.0589	299.0	0.0408
242.5	0.0613	648.5	0.0610	425.0	0.0462
350.0	0.0650			541.0	0.0485
538.0	0.0691			629.0	0.0506
681.0	0.0711				
		Ethane			
7.2	0.0261	11.0	0.0170	4.8	0.0046
21.7	0.0389	23.0	0.0258	13.0	0.0111
49.0	0.0487	43.0	0.0325	31.0	0.0184
80.0	0.0545	73.0	0.0394	48.0	0.0232
118.0	0.0591	113.5	0.0449	76.0	0.0290
178.5	0.0645	161.0	0.0496	102.0	0.0322
282.0	0.0686	209.0	0.0525	141.0	0.0364
376.0	0.0710	271.0	0.0560	203.0	0.0416
502.0	0.0738	338.5	0.0583	304.0	0.0466
629.0	0.0762	439.0	0.0609	412.0	0.0505
		622.5	0.0640	550.0	0.0532
				672.0	0.0571
		Propylene			
0.2	0.0202	1.5	0.0350	2.0	0.0228
1.4	0.0467	4.5	0.0484	29.0	0.0586
1.9	0.0516	22.0	0.0686	64.0	0.0700
2.7	0.0590	62.0	0.0808	100.0	0.0758
3.1	0.0622	107.0	0.0865	167.0	0.0804
4.0	0.0665	182.0	0.0908	277.0	0.0849
6.7	0.0718	288.0	0.0945	435.0	0.0900
11.6	0.0768	407.0	0.0966	556.0	0.0923
30.0	0.0858	511.0	0.0980	656.0	0.0937
64.0	0.0921	675.0	0.0995		
103.5	0.0958				
182.5	0.0997				
294.5	0.1023				
431.0	0.1038				
560.0	0.1048				
681.0	0.1059				

Table I. Continued

Press, mm Hg	Amt adsorbed, g/g-adsorbent	Press, mm Hg	Amt adsorbed, g/g-adsorbent	Press, mm Hg	Amt adsorbed, g/g-adsorbent
Propane					
5.4°C		30.0°C		50.0°C	
0.3	0.0151	0.6	0.0186	0.7	0.0120
1.7	0.0361	1.7	0.0249	5.0	0.0307
3.2	0.0456	6.7	0.0421	13.2	0.0418
5.4	0.0535	12.4	0.0546	25.5	0.0512
15.4	0.0630	30.0	0.0645	50.0	0.0586
37.0	0.0710	60.0	0.0711	90.5	0.0669
69.5	0.0763	102.0	0.0760	160.0	0.0723
122.0	0.0807	180.0	0.0795	256.0	0.0753
218.0	0.0855	296.0	0.0820	393.4	0.0788
389.0	0.0889	432.5	0.0838	640.0	0.0810
624.0	0.0913	630.0	0.0862		
n-Butane					
5.4°C		30.0°C		51.0°C	
1.7	0.0771	0.4	0.0431	0.2	0.0187
4.8	0.0885	0.9	0.0577	1.8	0.0411
12.0	0.0945	1.9	0.0694	3.9	0.0526
31.0	0.0999	4.0	0.0770	6.5	0.0614
70.3	0.1046	12.1	0.0859	12.0	0.0690
153.0	0.1085	29.6	0.0918	20.1	0.0742
304.0	0.1118	70.0	0.0969	28.1	0.0757
453.0	0.1136	171.0	0.1015	48.1	0.0802
644.0	0.1157	302.5	0.1040	64.1	0.0816
		453.0	0.1056	84.0	0.0860
		645.0	0.1072	149.0	0.0891
				232.9	0.0913
				539.6	0.0954
				642.7	0.0959

n-Pentane		Benzene			
30.0°C		5.4°C		30.0°C	
0.3	0.0648	1.0	0.1422	0.3	0.1219
2.1	0.0788	2.7	0.1484	2.0	0.1384
6.2	0.0890	6.4	0.1546	4.4	0.1443
15.0	0.0964	15.0	0.1606	14.2	0.1517
29.2	0.1005	23.0	0.1652	30.7	0.1574
62.5	0.1050	29.3	0.1680	46.0	0.1613
101.5	0.1083	36.0	0.1721	75.2	0.1649
183.0	0.1102			87.2	0.1665
291.0	0.1131				
538.5	0.1161				

Cyclohexane	
30.0°C	
2.0	0.0049
5.5	0.0068
15.6	0.0085
38.5	0.0098
65.3	0.0117
89.0	0.0137

adsorption chamber from the gas reservoir. If the adsorbate is liquid at normal state, such as n-pentane, benzene, or cyclohexane, the dissolved gas should be removed by freezing the liquid in a liquid air bath and pumping out. It was then melted, refrozen, and evacuated several times to remove the dissolved gas completely. The time for reaching equilibria changes from 10 to 40 min depending on the temperature, pressure, and adsorbate. It takes longer when the temperature is lower,

the pressure is lower, and the molecular weight of the hydrocarbon is higher.

Results and Discussion

The equilibrium data for methane, ethylene, ethane, propylene, propane, n-butane, n-pentane, benzene, and cyclohexane on MSC-5A are presented in Table I. Adsorption isotherms for methane, ethane, and n-butane are shown in Figures 2–4. For the systems at temperatures below the critical temperature of the gas, such as propylene and heavier hydrocarbons, the shape of the iso-
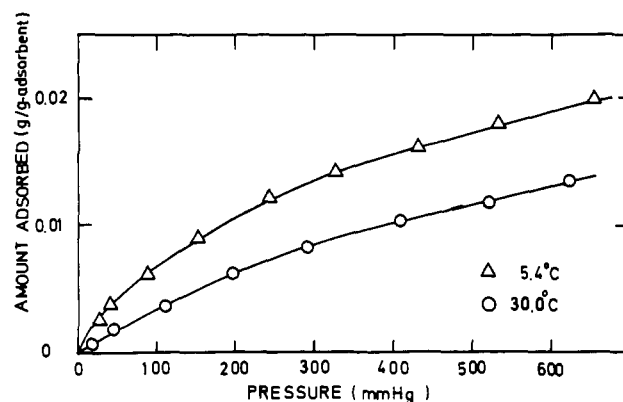
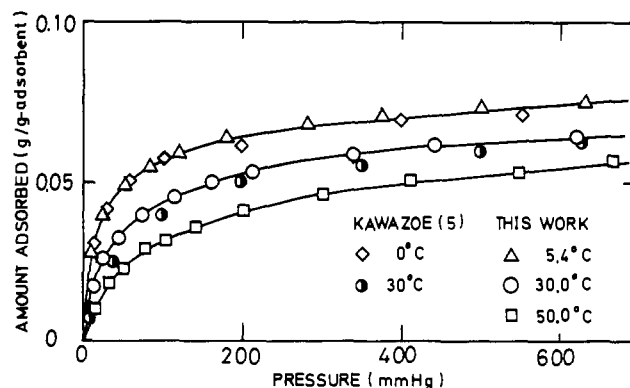**Figure 2.** Adsorption isotherms for methane (MSC-5A)

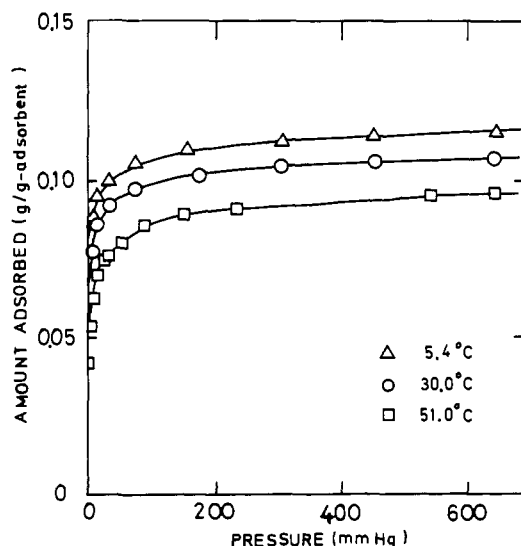**Figure 3.** Adsorption isotherms for ethane (MSC-5A)

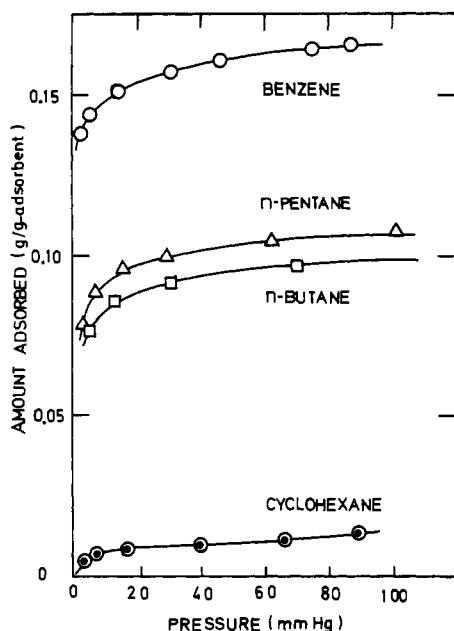**Figure 4.** Adsorption isotherms for n-butane (MSC-5A)

Figure 5. Molecular sieving effect for benzene and cyclohexane by MSC-5A at 30°C and isotherms of n-butane and n-pentane at 30°C as reference

therms shows the Type I isotherm according to the classification by Brunauer et al. (1). Figures 4 and 5 show this type of isotherm for n-butane and other hydrocarbons, respectively.

Isotherms of Type I are associated with the systems in which adsorption does not proceed beyond a monomolec-

ular layer. For the methane system, in which the temperatures are above the critical, the adsorption does not reach saturation at the pressure below 650 mm Hg (Figure 2). For the ethylene and ethane systems, in which the temperatures are both below and above the critical, the shape of the isotherms is also similar to Type I. For the adsorbent like MSC-5A having the pores of molecular size diameter, the pore volumes are filled with adsorbate at relatively low pressures, giving the same results as the monomolecular adsorption. It also means that the adsorption inside the macropores is almost negligible. Adsorption on saran charcoals, the molecular sieving action of which is well known, has typical Type I isotherms (3).

The data by Kawazoe et al. (5) for ethane at 0° and 30°C are presented together with our data in Figure 3. The molecular sieving effect is obvious because the adsorbed amount of cyclohexane is $\frac{1}{15}$ the benzene adsorption amount at 30°C (Figure 5). The n-butane and n-pentane adsorption at 30°C is shown in the same figure for comparison. Details of the molecular sieving action of this material are reported by Eguchi (2).

Literature Cited

(1) Brunauer, S., Deming, L. S., Deming, W. E., Teller, E., J. Amer. Chem. Soc., **62**, 1723 (1940).
(2) Eguchi, Y., J. Jap. Petrol. Inst., **13**, 2191 (1970).
(3) Gregg, S. T., Sing, K. S. W., "Adsorption, Surface Area and Porosity," Chap. 4, Academic Press, New York, N.Y., 1967.
(4) Kawazoe, K., Astakhov, V. A., Kawai, T., Bulletin of the Institute of Industrial Science, Tokyo University, Vol 22, p 491, 1970.
(5) Kawazoe, K., Astakhov, V. A., Kawai, T., Eguchi, Y., Chem. Eng. Jap., **35**, 1006 (1971).
(6) Walker, Jr., P. L., Austin, L. G., Nandi, S. P., "Chemistry and Physics of Carbon," Vol 2, p 260, Marcel Dekker, New York, N.Y., 1966.

Diffusion Thermoeffect in Gases

Ali Boushehri[1]

Department of Chemistry, St. Louis University, St. Louis, Mo. 63156

A study of the diffusion thermoeffect (the Dufour effect) was made for five different gas mixtures: H_2-N_2, H_2-CH_4, He-A, He-CO_2, and He-N_2. Measurements were made at several different temperatures and pressures. The values of the thermal diffusion factors were calculated for the five gas mixtures from the experimental data and were compared with the values obtained by other workers from direct thermal diffusion measurements.

The diffusion thermoeffect is of interest both in its own right as a little-investigated transport phenomenon and because it enables us to obtain quantitative information on other transport coefficients, particularly the thermal diffusion factor. In this work five different gas mixtures are investigated. No previous measurements of the temperature dependence of the diffusion thermoeffect are known to have been made for the H_2-N_2, CH_4-H_2, He-A, CO_2-He, and N_2-He mixtures.

[1] Present address, Department of Chemistry, Pahlavi University, Shiraz, Iran.

The Dufour effect involves the measurement of the transient temperature gradient which results from an initial concentration gradient, and it is therefore related to the phenomenon of thermal diffusion. The effect was discovered by Dufour (3) in 1872 but was not extensively investigated until after its rediscovery by Clusius and Waldmann (1) in 1942. Apart from the classic studies of Waldmann, little work has been done in this field. Rastogi and Madan (8) studied the Dufour effect with an apparatus similar to the one used in the present work. Sawford et al. (9) also recently published some measurements on this effect. A study of the pressure dependence of the diffusion thermoeffect was made by Mason et al. (7).

Suppose two gases (labeled with subscripts 1 and 2), initially at the same temperature, diffuse into each other. On the basis of irreversible thermodynamics (2), it may be shown that:

$$\lambda \frac{\Delta T}{\Delta x} + \frac{\rho_1 RTD_{12}\alpha}{C_1\left[M_1 - C_1(M_1 - M_2)\right]} \frac{\Delta C_1}{\Delta x} = K \quad (1)$$

where λ and D_{12} are the heat conductivity and diffusivity coefficients, respectively; α is the thermal diffusion fac-