The Molar Volume and Entropy of Adsorbed Methane on Porasil

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With the use of high-precision gas-chromatography, the multilayer adsorption of methane on fused silica beads was precisely measured between 145.0 K and 213.6 K. The molar volume and the partial molar entropy of the adsorbed methane were determined as a function of the temperature. The molar volume in the monolayer region depends much less on the temperature than that of the bulk liquid. However, the molar volume of multilayer adsorbed methane shows a dependence on the temperature similar to that of bulk liquid, which is at a lower temperature. The volume of the monolayer is practically constant under the present experimental conditions. The apparent thickness of the adsorbed monolayer was interpreted in terms of a simple collision model. The partial molar entropy of the adsorbed phase is much lower than that of the saturated bulk liquid. The lower dependence of the molar volume on the temperature and the lower entropy suggest that the freedom of motion of the adsorbed molecules is restricted as compared with those in bulk liquid.

The series perturbation technique,[1] a refined form of "Hypothetical perfect gas perturbation,"[2] was described in a previous paper and shown to be useful in the study of adsorption. The absolute adsorption and the molar volume of adsorbed methane can be measured by means of this technique. The molar volume of adsorbed methane was verified by the analysis of the dependence of Gibbs adsorption on the gas phase density, which was discussed previously.[1]

In order to measure the precise values of the molar volume of the adsorbed phase, a high-precision gas-chromatography was developed. The apparatus was equipped with a high-precision flow meter described elsewhere.[3] In addition to the molar volume of the adsorbed phase, the entropy of the adsorbed phase will be presented here.

Experimental

Apparatus. The high-pressure gas-chromatographic apparatus[1] was modified for the precise measurement of the retention volume. The apparatus consists of two sets of the ordinary gas-chromatographic apparatus. One has a column packed with an adsorbent for the measurement of the physical adsorption. The other is connected to the outlet of the former one and is used as a flow meter. A differentiator and a high-precision timer are combined with the latter chromatographic apparatus to give precise measurements of the flow rate of the carrier gas.[3] The general features of the apparatus are similar to the one described previously.[1] Therefore, only the modifications for precise measurement will be described here.

The pressure of the perturbation gases was kept equal to that of the carrier gas. The volume of the loop of the sample injection valve (a dose of perturbation gas) was about 50 μl. The carrier gas and all the perturbation gases were dried with magnesium perchlorate before entering the system. The column packed with the adsorbent was immersed in a thermostat filled with isohexane or isopentane. The thermostat was cooled by liquid nitrogen, and the temperature was maintained as constant as ±0.02° by means of a Thermotrol, Model 1053 A, manufactured by Hallikainen Instruments. The temperature distribution in the thermostat was uniform at any temperature in the present study in the range of ±4 inches from the column position. A flow-through thermal conductivity cell, Model 10-460 by Gow-Mac, was used. The gas volume of the thermal conductivity cell was 0.35 ml. The signal was recorded by means of a recorder, Speedomax W/L, made by Leeds & Northrup. The response time (full span) of the recorder was 0.5 s. The thermal conductivity cell and the expansion valves were immersed in the thermostat at 35.0 °C.

Materials. All the gases except radioactive methane and the adsorbent Porasil are the same as those used in the previous study.[1] The tritiated methane was purchased from New England Nuclear. The perturbation gases were diluted with the carrier gas (methane) in the following ratios: helium 1/32, neon 1/16, argon 1/32, and tritiated methane 0.5 curie in 560 ml of methane at 130 atm. The diluted perturbation gases were stored in 560 ml cylinders made of stainless steel.

Determination of Retention Time. The shape of an elution peak corresponds to the concentration distribution of a perturbation gas in the eluted carrier gas. The retention time is defined as the value averaged over this distribution curve:

$$t_r = \int_0^\infty y \cdot t\mathrm{d}t \bigg/ \int_0^\infty y\mathrm{d}t$$

Here, y is the height of the elution peak at time t. When a perturbation gas is injected, a precision timer is triggered by a microswitch attached to the sample injection valve. The precision timer is turned off manually in the vicinity of the top of the elution peak, and this turn-off signal is marked on the recorder chart by an event marker. The precision timer is used to minimize the effect of any possible shrinkage or expansion of the chart paper.

The retention time, t (min), was calculated as below:

$$t_r = t_0 + \frac{l_c - l_m}{u}$$

t_0 (min) is the time elapsed between the turning on and off of the timer described above. l_m (cm) is the position of the turn-off mark on the recorder chart with reference to the outset of the elution peak. u (cm/min) is the chart speed of the recorder. u was taken at 10.16 cm/min during the course of this work. l_c is the center of gravity of the eluted peak:

$$l_c = \int_0^{l_2} y \cdot x\mathrm{d}x \bigg/ \int_0^{l_2} y\mathrm{d}x = \sum_{i=0}^{s} x_i \cdot y_i \cdot \Delta x \bigg/ \sum_{i=0}^{s} y_i \cdot \Delta x$$

where x (cm) is the position in the chart with reference to the outset of the peak and where l_2 is the position of the end of the peak. The other values follow the usual substitution

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of an integration with summation. The value of *s* was taken between 25 and 40 for an elution peak.

Source of Experimental Error. The retention times for He, Ne, Ar, and CH_3T were reproducible within 0.1% in any experimental run in this apparatus. The precision of the flow meter was 0.06% as has been discussed elsewhere.[3) Therefore, there must be other sources of experimental error. As a matter of fact, the flow rate was found to change when an eluted perturbation gas passed through the expansion valve. The carrier gas flows through the expansion valve in a viscous flow across a great difference of pressure. On the other hand, the composition of the part of the carrier gas including an eluted perturbation gas is a little different from pure carrier gas. This difference in composition gives rise to a change in the viscosity, resulting in the slight change in the flow rate mentioned above. Since the retention volume is calculated as the difference between the column value and the by-pass one (see Eq. (1) in Ref. 1), the viscosity effect will be cancelled out in the first order approximation. However, a delicate difference in flow pattern may bring about some scattering of the retention volumes. This viscosity effect will cause the sample-size effect, which was minimized in the present study by choosing the concentration of the perturbation gases stated above.

Results and Discussion

Adsorption Isotherm. The experimental data obtained by means of present apparatus were treated according to the series perturbation method previously reported.1) The values of the absolute adsorption* of methane on Porasil between 145.0 K and 213.16 K are tabulated in Table 1. The isotherms show typical multilayer adsorption.

Table 1. Absolute adsorption of methane on porasil

T K	P atm	Abs. ads. mmol/g
213.16	3.00	0.930
	5.00	1.381
	10.00	2.051
	20.00	3.191
	40.00	5.293
193.16	5.00	1.977
	10.00	2.968
	20.00	4.658
	30.00	6.689
	40.00	9.672
181.23	5.00	2.530
	10.00	3.793
	15.96	5.206
	20.07	6.332
	26.62	8.979
171.69	3.00	2.374
	6.64	3.693
	10.47	4.908
	14.79	6.529
	18.42	8.606
	20.89	11.239
162.15	3.00	2.981
	4.00	3.491
	5.50	4.170
	8.00	5.303
	10.50	6.755
	13.00	8.921
	15.50	18.073
145.00	1.80	3.641
	2.50	4.306
	3.00	4.790
	4.00	5.774
	5.00	7.178
	6.00	9.325

Molar Volume of the Adsorbed Methane. The free gas volume of the chromatographic column varies with the amount of adsorption. Figure 1 shows this relation in the present study after the correction of the thermal expansion of the stainless steel column and Porasil. In the interests of simplicity, the results at 193.16 K and 181.23 K are not shown in Fig. 1. The free gas volume decreases linearly up to 7 mmol/g, but the plots become curved near 10 mmol/g. The slopes of the straight lines were computed by the least-squares method between 0 and 7 mmol/g. The results, shown in Fig. 2, show the molar volume of the adsorbed phase between 0 and 7 mmol/g, V_a. The average molar volume, V_m, of the adsorbed phase near 10 mmol/g was estimated by means of:

$$V_m = \{V_g(0) - V_g(N_A)\}/N_A$$

where $V_g(0)$ and $V_g(N_A)$ are the free gas volume at the amount of adsorption 0 and N_A mmol/g. The value of $V_g(0)$ was estimated from the extrapolation linearly to zero adsorption in Fig. 1. The molar volume, V_m, is also plotted against the temperature in Fig. 2, with the molar volume of saturated liquid methane4) shown for comparison. The data obtained from the previous paper are indicated by closed circles. The V_a is higher than that of liquid methane at lower temperatures and changes slowly with the temperature. On the other hand, V_m increases with the temperature in the linear extension of liquid methane at lower temperatures. These facts suggest that the adsorbed phase

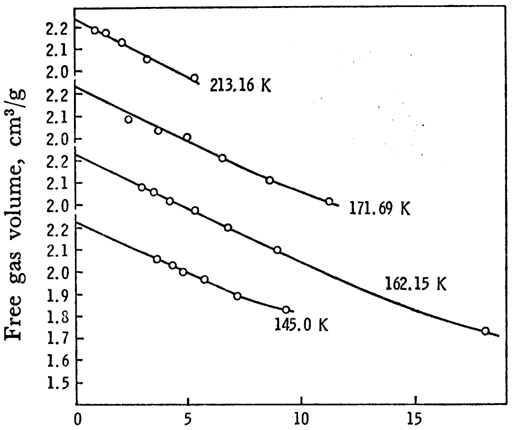

Fig. 1. Dependence of the free gas volume upon the amount of adsorption.

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* The amount of adsorption discussed in this paper is the "absolute adsorption" described previously.1)

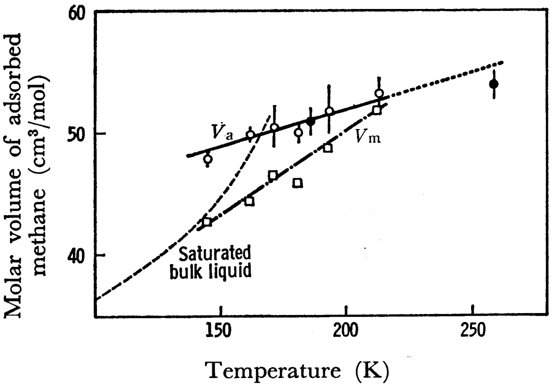

Fig. 2. Change of molar volumes of adsorbed methane with temperature. V_a is the molar volume near monolayer, and V_m is that averaged over 10 mmol/g of adsorption.

near the monolayer is quite different from the liquid phase, but that the multilayer adsorbed phase would be similar to the liquid phase at lower temperatures.

Temperature Dependence of the Monolayer Capacity. The adsorption data were processed according to a modified BET method which has three parameters:[5)]

$$\Phi/N_A = 1/(N_0 \cdot C) + \Theta/N_0$$

$$\Phi \equiv x[(1-x^n)-nx^n(1-x)]/(1-x)^2$$

$$\Theta \equiv x(1-x^n)/(1-x)$$

$$x \equiv P/P_0$$

N_0 is the monolayer capacity (mmol/g). P and P_0 are the adsorption pressure and the saturation pressure of the bulk liquid at the same temperature. n is a parameter adjustable so as to give the best straight line in the Φ/N_A *vs.* Θ plot. Straight lines were obtained where x was less than 0.6. The values of n lie between 5.5 and 6. In Table 2 are tabulated the values of N_0 obtained by this procedure. It is remarkable that the monolayer capacity changes very slowly with the temperature. The volume of the monolayer, V_0, can be evaluated by means of:

$$V_0 = V_a \cdot N_0$$

with the V_a as shown in Fig. 2. The V_0 value appears in the third column of Table 2. The monolayer volumes are apparently independent of the temperature.

Apparent Thickness of the Monolayer. One can estimate the apparent thickness of the monolayer, h_0, from this relationship:

Table 2. The monolayer properties of adsorbed methane on porasil

T K	N_0 mmol/g	V_0 cm³/g	h_0 Å
213.16	3.04±0.02	0.161	3.34
193.16	3.13±0.01	0.162	3.36
181.23	3.17±0.01	0.159	3.30
171.69	3.18±0.02	0.161	3.34
162.15	3.23±0.01	0.161	3.34
145.00	3.28±0.02	0.157	3.26

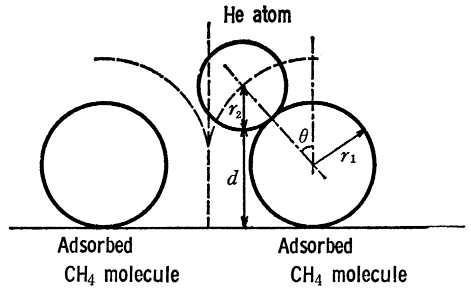

Fig. 3. A collision model of a perturbation gas atom and adsorbed methane molecules.

$$h_0 = V_0/A$$

where A is the surface area of the adsorbent, 482 m²/g according to conventional BET, using nitrogen with molecular cross-sectional area of 16.2 Å². The thickness of the monolayer, shown in the fourth column of Table 2, is virtually constant.

Since an adsorbed molecule will vibrate normal to the surface, the thickness of the monolayer must be larger than the collision diameter of the adsorbate molecule. Therefore, it seems to be contradictory that the apparent thickness of the monolayer is 3.31 Å, while the collision dimaeter of methane is 3.817 Å.[6)] This will now be explained. Let us take an example of a helium atom moving normal toward the surface (Fig. 3). The helium atom will hit an adsorbed methane molecule and fly back to the gas phase again. The distance between the center of the helium atom and the surface is r_2+d when a helium atom is in contact with a methane molecule (Fig. 3), where r_1 and r_2 are 1/2 of the collision diameters of methane and helium respectively. The contribution of r_2 has already been corrected to the steric effect in the series-perturbation theory by adding $A \cdot r_2$ to the retention volume of helium,[1)] where A is the surface area of the adsorbent. Thus, the thickness of the adsorbed layer may be observed to be d in that collision. The apparent thickness of the adsorbed layer can be estimated by averaging the d values over the surface of the adsorbed methane molecule. If adsorbed methane molecules are arranged in a hexagonal closed packing position, and if the monolayer capacity is assumed to be 3.20 mmol/g, the apparent thickness of the adsorbed layer can be estimated to be 3.0 Å by a simple calculation. In this estimation, the collision diameters of helium and methane are taken to be 2.56 Å and 3.82 Å respectively.[6)] If the helium atom moves parallel to the surface, the apparent thickness will be observed to be equal to 3.82 Å. Therefore, the actual value of the apparent thickness must be a certain value between 3.0 Å and 3.82 Å. If one takes into account the vibrational motion of adsorbed methane normal to the surface, the observed apparent thickness (3.31 Å) is in good agreement with the value estimated above.

Entropy of the Adsorbed Methane. The experimental data were treated according to a procedure described previously.[7)] Figure 4 shows the plots of $\log f$ *vs.* $1/T$ at fixed amounts of adsorption, where f

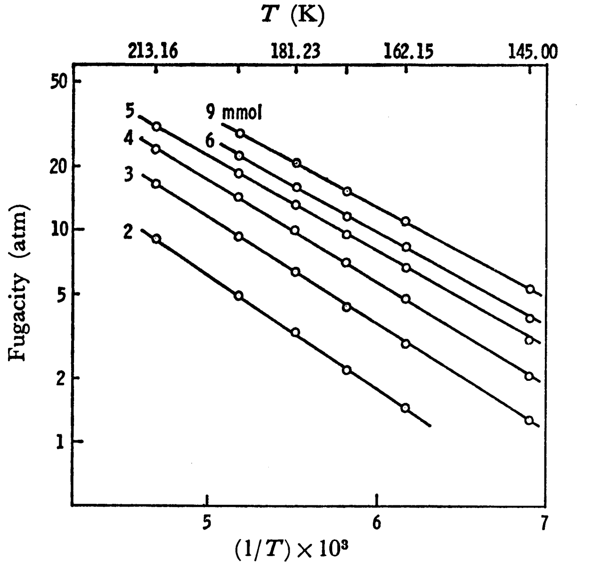

Fig. 4. Plots of log f *vs.* $1/T$ at fixed amounts of adsorption.

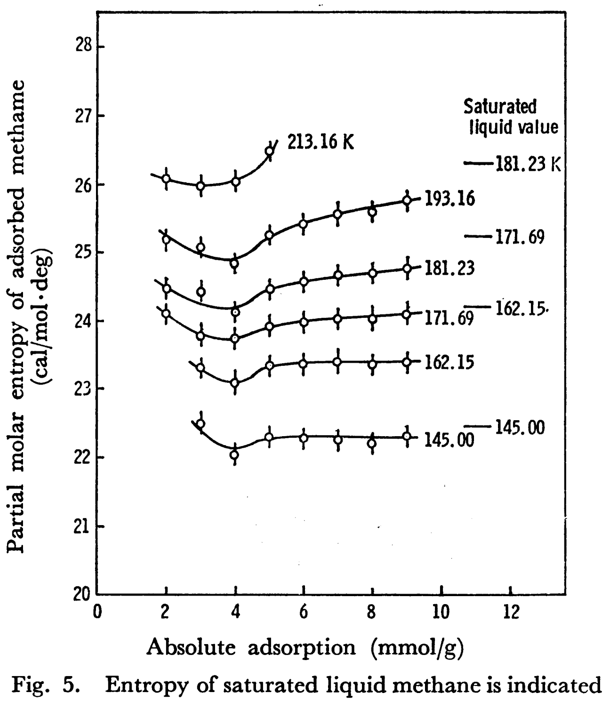

Fig. 5. Entropy of saturated liquid methane is indicated in the right-hand side.

is the equilibrium fugacity. The experimental points for 7 and 8 mmol/g are not shown for the sake of simplicity. Single straight lines can be drawn over all the range of temperatures. The slopes of the straight lines were determined by the least-squares method.

The partial molar entropy of the adsorbed methane was also calculated; it is shown in Fig. 5.** In Fig. 5 the molar entropy of saturated liquid methane is also shown at various temperatures. The partial molar entropy of the adsorbed phase at 145 K is nearly equal to the molar entropy of saturated liquid at the same temperature.*** However, above 145 K the partial molar entropy of the adsorbed methane is much lower than the molar entropy of the saturated liquid. As has been mentioned above, the temperature dependence of the molar volume of the adsorbed methane, $V_{\rm m}$, is much lower than that of the bulk liquid (Fig. 2). $V_{\rm m}$ increases linearly with the temperature near the critical temperature (190.9 K[8]), like an extension of the molar volume of saturated liquid methane at lower temperatures. This may be explained as follows. The surface will attract adsorbate molecules and prevent the intermolecular distance from increasing steeply near the critical temperature. These facts suggest that the freedom of motion of the adsorbed molecules is restricted above 145 K as compared with that in bulk liquid.

Grant and Manes[9] stated that the liquidlike state may persist on the adsorbent at temperatures far above the critical temperature of the free liquid. Their assumption was previously verified by the present authors.[7]

Brunauer[10] suggested that multilayer adsorption probably occurs at temperatures where molecular clusters can exist in the gas phase, *i. e.*, for temperatures up to 10 to 15° above the critical. However, the present authors investigated the high-pressure adsorption of methane on Porasil, and found that multilayer adsorption takes place as much as 40° above the critical temperature. The −19.9 °C isotherm, 60° higher than the critical, reaches about 1.6 times the monolayer coverage.[1]

These findings indicate that the surface attracts adsorbate molecules very strongly, even over the monolayer coverage, and that multilayer adsorbed molecules possess less freedom of motion than those of bulk liquid at the same temperature.

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** The values of entropy above 4 mmol/g of adsorption at 213.16 K and 193.16 K differ somewhat from those reported in the previous paper.[7] This disagreement comes from the different temperature ranges of measurement in the two studies. It is impossible at present to tell whether or not the discrepancy is meaningful.

*** The measurement could not be made below 145.0 K for the following reason. In order to obtain precise values of the retention time, the flow rate must not be two low at the detectors. On the other hand the pressure drop across the column is to be low enough to be negligible. Therefore the pressure should be appreciably higher inside the column than at the detector. (*i.e.* 1 atm) However, the vapor pressure of methane becomes very low below 145.0 K (for example, 2.67 atm at 125 K). Consequently, it is impossible to measure an appropriate adsorption isotherm.

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