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ADSORPTION STUDIES ON PORAPAK S AT VARIOUS TEMPERATURES
BY GAS CHROMATOGRAPHIC AND STATIC METHODS

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SUMMARY

The distribution coefficients of Ar, CH₄, CO₂, O₂ and N₂ in Porapak S were obtained by Gas chromatography and by adsorption studies at various temperatures and a comparison was made between the two methods. Discontinuities in the curves are explained by a glassy transition in the polymer support.

INTRODUCTION

In the previous two articles dealing with the study that has been carried out on a 200 ft., $\frac{1}{8}$ in. O.D., Porapak S (50–80 mesh) column^{1,2} we have discussed (1) the effect of the carrier gas nonideality and adsorption on the net retention volume; (2) the gas flow properties of this type of column. This final article is concerned with the temperature dependence of (a) the net retention volume (obtained by the gas chromatographic (GC) method) and (b) the distribution coefficient (obtained by the static method). For convenience of discussion, this article is separated into two parts one dealing with the GC system and the other with the static system.

GAS CHROMATOGRAPHIC SYSTEM

Theoretical

It is a simple matter to show that the partition or distribution coefficient (K) is related to the partial molar free energy (ΔG^0) by

$$\Delta G^0 = -RT \ln K \quad (1)$$

For a gas–solid GC system, K is related to the net retention volume V_N by

$$V_N = KW_s \quad (2)$$

where W_s is the weight of the packing material. As it has been pointed out in the previous article¹, eqn. 2 can also be expressed in terms of surface area (S) accompanied

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by the appropriate change in the units of K . Substitution of eqn. 2 into eqn. 1 gives

$$\Delta G^0 = -RT \ln V_N + RT \ln W_s \quad (3)$$

But since

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (4)$$

then after this substitution and rearrangement we can write

$$\ln V_N = \frac{-\Delta H^0}{RT} + q \quad (5)$$

where

$$q = \frac{\Delta S^0}{R} + \ln W_s \quad (6)$$

As according to eqn. 5, a plot of $\ln V_N$ or under suitable conditions $\ln t_R$ against $1/T$ (where t_R is the retention time) should give a straight line from whose slope ΔH^0 can be extracted³⁻⁸. Furthermore, if K is known then both ΔS^0 and ΔG^0 can also be calculated.

Experimental apparatus and procedure

The experimental apparatus and procedure has already been described in the first article¹, but the present experiments were carried out under the following set of conditions:

Carrier gas, helium; temperature bath, (a) $t = 0^\circ$ (ice-water mixture) and (b) $t > 0^\circ$ (paraffin oil and heater); detector, electron capture (used in the "helium detector" mode).

Results and discussion

A sample (ca. 0.45 μ l) containing approximately equal parts of H_2 , N_2 , O_2 , Ar, CH_4 and CO_2 was subjected to a gas chromatographic separation at various column temperatures. The net retention volumes were calculated by the method described in the previous article and are given in Table I. The $\log V_N$ vs. $1/T$ plots for N_2 , O_2 , and Ar are shown in Fig. 1 and for CH_4 and CO_2 in Fig. 2 and Fig. 3, respectively. A plot similar (though not included) was obtained for H_2 .

TABLE I

NET RETENTION VOLUMES OF VARIOUS GASES AT DIFFERENT TEMPERATURES

$V_N(CO_2)/V_N(CH_4) = 5.99$ at $T = 273^\circ K$.

| Gas | $T = 351^\circ K^a$ | $T = 335^\circ K^a$ | $T = 320^\circ K^a$ | $T = 306^\circ K^a$ | $T = 273^\circ K^a$ |
|--------|---------------------|---------------------|---------------------|---------------------|---------------------|
| H_2 | 8.4 | 9.0 | 9.6 | 10.3 | 12.4 |
| N_2 | 19.2 | 22.1 | 25.6 | 29.6 | 46.2 |
| Ar | 24.8 | 28.9 | 33.5 | 39.9 | 62.3 |
| O_2 | 26.0 | 30.0 | 34.4 | 38.9 | 56.6 |
| CH_4 | 53.3 | 65.5 | 81.4 | 103.1 | 210.1 |
| CO_2 | 139.9 | 193.0 | 273.8 | 400.1 | 1258.2 |

^a $\pm \frac{1}{2}^\circ$.

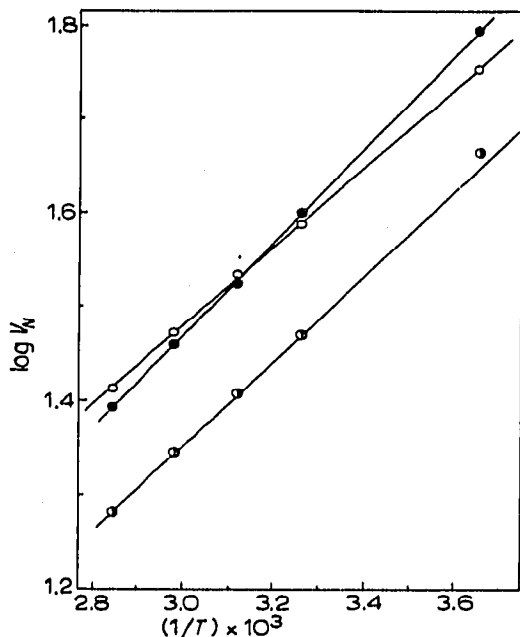


Fig. 1. Plot of $\log V_N$ against $1/T$ for N_2 , Ar, and O_2 . ● = N_2 ; ○ = O_2 ; ● = Ar.

On the whole, the results expressed in Figs. 1, 2 and 3 are more or less typical. There are however two points which should be noted. The first is found in Fig. 1. The crossing of the Ar and O_2 plots indicates that at $1/T = 3.2 \times 10^{-3}$ ($\sim 316^\circ K$) both Ar and O_2 have the same net retention volume and that the separation of these two constituents at this temperature is impossible on this column. Also, by working either above or below this temperature the elution order can be reversed.

The second and perhaps the more important point refers to the N_2 , CH_4 , and

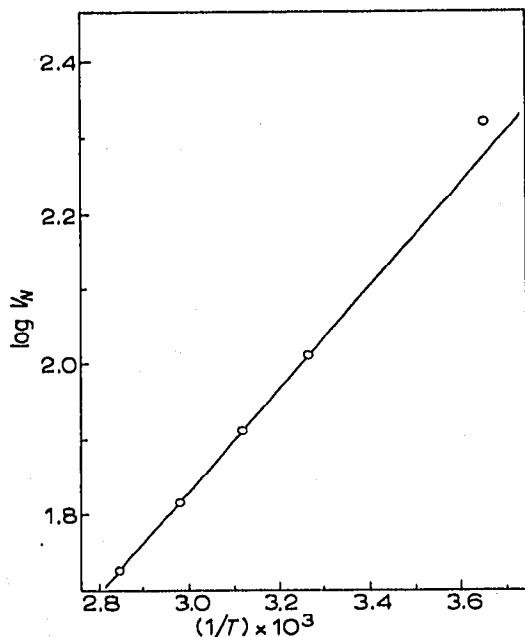


Fig. 2. Plot of $\log V_N$ against $1/T$ for CH_4 .

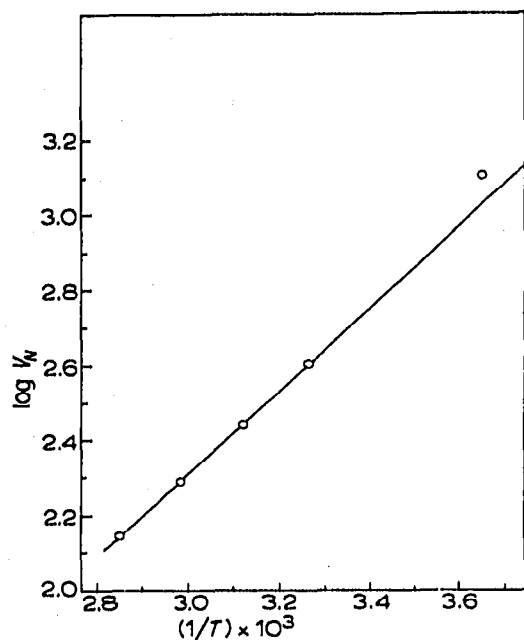


Fig. 3. Plot of $\log V_N$ against $1/T$ for CO_2 .

CO_2 plots. It can be noted that there exists a rather large deviation at $1/T = 3.66 \times 10^{-3}$ (273°K). Repeated experiments (CH_4 and CO_2 case) showed very high degree of reproducibility at this temperature (the spread in the experimental data would be insignificant in this type of a plot) and consequently these deviations cannot be attributed to experimental error, and will be discussed later when other facts are presented.

The ΔH^0 and q values were calculated by the least squares method from the linear portions of the plots and are tabulated in Table II.

$\text{K}(\text{CH}_4)$ AND $\text{K}(\text{CO}_2)$ AS A FUNCTION OF T BY THE STATIC METHOD

Introduction

The large deviations found at 273°K made it imperative that the temperature range should be extended below 273° . This however was not to be a simple task since even at 273°K using moderate carrier gas flow rates, the retention times of CH_4 and CO_2 were about 1 and 6.5 h, respectively. A further drop of 20° would at least double

TABLE II

THE ΔH^0 AND THE q VALUES FOR VARIOUS GAS SAMPLES USING HELIUM AS THE CARRIER GAS

| Gas | ΔH^0 (calc.) | q |
|---------------|----------------------|---------|
| H_2 | -940 | 0.7858 |
| N_2 | -2063 | -0.0026 |
| Ar | -2239 | -0.0009 |
| O_2 | -1917 | 0.5156 |
| CH_4 | -3125 | -0.5087 |
| CO_2 | -4984 | -2.2148 |

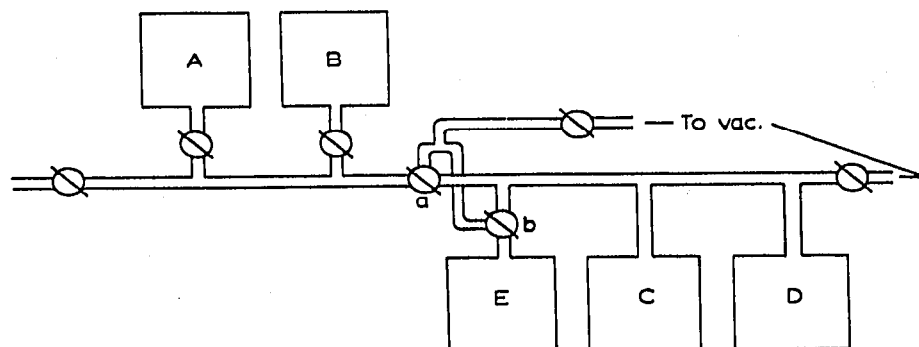


Fig. 4. Block diagram of the static system.

or perhaps even triple these retention times, making the study impractical. A static method could be made to serve a dual purpose. It would allow the study to be extended to the lower temperature region, and could serve as an independent check on the thermodynamic data obtained by the GC method.

Experimental

The apparatus used in this study consisted of a typical high vacuum glass

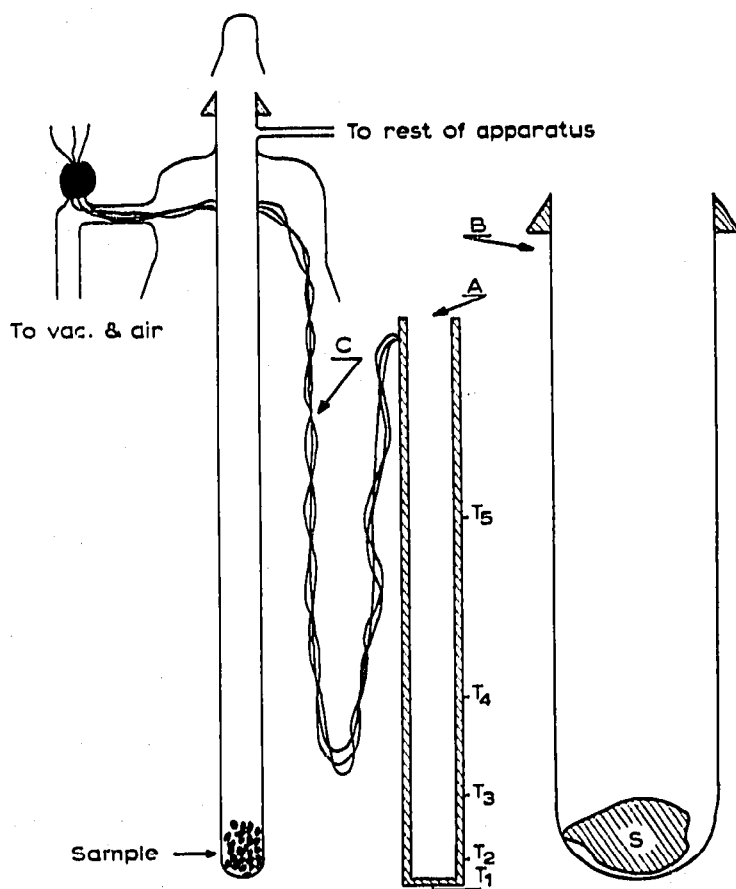


Fig. 5. Modified LeRoy still. A = brass tube on which the sample heating coil and thermocouples are mounted; B = outer jacket; C = heating and thermocouple wires; T₁, T₂, T₃, T₄, T₅ = thermocouples; S = styrofoam.

apparatus. For clarity, only the essential parts are shown in a block form in Fig. 4. A and B are each 1-l gas storage bulbs. C is a modified LEROY still⁹ which could be assembled or disassembled so that solid material could be introduced into it, degassed and studied within it. A more detailed description of the LEROY still is shown in Fig. 5. The outside jacket and the brass tube (closed at the bottom end) on which the heating coil and the thermocouples were mounted could be removed prior to degassing. The role of the styrofoam was to ensure a good contact between the sample tube and the brass jacket when the still was assembled.

D is a thermocouple pressure gauge (R.C.A.-model 1946). During operation it was maintained at 0°C with ice-water mixture. A 6-V battery served as a source of constant current and a Heathkit millivolt source (Model EUW-16) was used to buck the e.m.f. so that a 12 MV signal (stick vacuum) could be accommodated on the 5 MV span of a potentiometric recorder. The purpose of this gauge was only to indicate whether or not equilibrium conditions had been reached.

E is a McLeod gauge with the lowest limit of pressure indications of *ca.* 10^{-5} T. The volume of the McLeod gauge (mercury in the down position) was calibrated so that it may serve both as a pressure measuring device and as a constant known volume. The presence of mercury necessitated this calibration to be carried out at low pressure, *ca.* 0.1 mm pressure of helium gas.

The volume including the sample tube (the inner tube of the LEROY still), the thermocouple pressure gauge, and the interconnecting tubing was also calibrated. Stopcocks a and b were both three way stopcocks, as indicated in the diagram.

Both CO₂ and CH₄ were degassed by a number of repeated freeze-pump-expand cycles before they were stored in the storage bulbs.

The solid sample was 0.442 g of the identical material which was used in the column preparation. The treatment of this material prior to use has been described¹.

Experimental procedure

Prior to each experiment, the solid sample was heated under vacuum at 180°C for approximately 12 h. After the entire system (except storage bulbs A and B) was evacuated, the gas which was contained in one of the storage bulbs was allowed to expand only into the McLeod gauge (E) by means of stopcocks a and b. After sufficient time was allowed for pressure equilibration (about 15–20 min) the pressure was then measured with the McLeod gauge. In the event the pressure was higher than required, some of the gas was vented out of the system. The McLeod gauge was then brought to its down position and after 15–20 min stopcocks a and b and the one leading to the storage bulb were turned off. It should be pointed out that the 15–20 min pressure equilibration time was required in order to get good reproducibility in the pressure measurements.

The LEROY still and the sample contained within were cooled down to about –190°C after which the air jacket was evacuated. The gas contained in the McLeod gauge was then allowed to expand only into chamber C and D and the interconnecting tubing by means of stopcock b. The pressure was monitored with the thermocouple pressure gauge. After the gas had frozen out on the solid sample, the final pressure was checked with the McLeod gauge.

The temperature of the sample was raised by applying a predetermined voltage to the heating coils of the LEROY still. The temperature and pressure were monitored

on the recorder, and when equilibrium conditions were reached, at least six pressure measurements were made with the McLeod gauge. The temperature was then raised further and the cycle repeated. It should be mentioned that it required about 1.5 h to reach each temperature and pressure equilibrium.

Calculations of K

If one operates in a very low pressure region, it can be assumed that (a) Henry's Law is obeyed; (b) the gas behaves ideally; (c) the distribution coefficient (K) can be expressed in terms of concentrations¹⁰, that is

$$K = C_s/C_m = \left(\frac{N_s}{W_s}\right) / \left(\frac{N_x}{V_x}\right) \quad (7)$$

where

W_s is the weight of the adsorbent

N_s is the number of moles of gas adsorbed on the surface at some temperature T_x

V_x is the volume containing the non adsorbed gas which is also at temperature T_x

N_x is the number of moles of gas contained in V_x .

With the aid of the ideal gas law, eqn. 7 can be rewritten to read

$$K = \frac{N_s}{W_s} \cdot \frac{RT_x}{P} \quad (8)$$

Since R and W_s are known constants, and T_x and P are measurable variables, it remains now to determine N_s . This can be done if one knows the initial number of moles of gas that are introduced into the system and the final number of moles of non-adsorbed gas after equilibration since

$$N_s = N_0 - N_f \quad (9)$$

where 0 and f refer to the initial and the final quantities. N_0 like W_s is a known constant adjusted by the experimenter. N_f on the other hand is not directly accessible and can only be calculated from the two variables T_x and P . The problem now reduces to relating N_f to P and T_x .

If the entire system was to be kept at the same temperature T_x , then it would be a simple matter to relate N_f to P and T_x . Generally this is not the case and consequently there will be at least one temperature gradient present in the system. The present system has two temperature gradients (one between the LEROY still and the interconnecting tubing and the other between the thermocouple pressure gauge and the interconnecting tubing), but other systems may have more. The presence of these gradients and the different temperature that may be found in the system, make it necessary to discuss the system in parts.

At any particular point in the system where the temperature is T_i , the number of moles of gas bounded by the infinitesimal volume dV is

$$dN = \frac{P}{R} \cdot \frac{dV}{T_i} \quad (10)$$

If the temperature T_i is constant over a volume V_i , then integration of eqn. 10 gives

$$N_i = \frac{P}{R} \cdot \frac{V_i}{T_i} = a_i \frac{P}{R} \quad (11)$$

Also, if T_i remains constant for the duration of the entire experiment, then a_i can be considered as a constant of the system. This is true for all parts of the system where the above conditions are met. In the case where $T_i = T_x$; a_x is a variable and it is preferable to express N_x by

$$\frac{P}{R} \cdot \frac{V_x}{T_x}$$

The number of moles contained in the volume defined by the temperature gradient is

$$N_i = \frac{P}{R} \int \frac{dV}{T} \quad (12)$$

Now, if the extreme temperatures of the gradient are held constant, so will be the volume. No matter how complex the integral may be, the final expression will be

$$N_i = b_i \frac{P}{R} \quad (13)$$

where all b_i like a_i will be constants of the system. Finally, the number of moles of gas contained in the volume V defined by the temperature gradient between T_x and say T (the ambient temperature), will be some function of T_x . The exact function may vary from system to system but if V is kept constant, we can write that

$$n = \frac{PV}{R} f(T_a, T_x) \quad (14)$$

where $f(T_a, T_x)$ is some function involving both T_a and T_x .

N_f can now be expressed in terms of the various contributions and in turn eqn. 9 can be rewritten to give

$$N_s = N_0 - \frac{P}{R} \left[\sum a_i + \sum b_i + \frac{V_x}{T_x} + Vf(T_a, T_x) \right] \quad (15)$$

In practice it would require considerable effort to determine V and $f(T_a, T_x)$. It is preferable then to minimize the last term of eqn. 15 to the point where it can be neglected. This can be done by designing the apparatus so that V constitutes about 1% or less of the entire volume. If these conditions are met, eqn. 15 reduces to

$$N_s = N_0 - \frac{P}{R} F_x \quad (16)$$

where

$$F_x = k + \frac{V_x}{T_x} \quad (17)$$

and

$$k = \sum a_i + \sum b_i \quad (18)$$

V_x and k can be determined from a non-sorbing gas such as helium. Since the gas is non-sorbing, $N_s = 0$ and eqn. 16 can be rewritten to give

$$\frac{N_0R}{P} = F_x \tag{19}$$

If the assumptions made leading to eqn. 16 are correct, a plot of N_0R/P vs. $1/T_x$ should give a straight line with an intercept equal to k and with a slope of V_x .

It remains now to substitute eqn. 16 into eqn. 8 in order to get the final expression for K , that is

$$K = \frac{1}{W_s} \left[\frac{N_0R}{P} - F_x \right] T_x \tag{20}$$

RESULTS AND DISCUSSION

In the present system the volume V was small (2-3 ml) compared to the entire volume (about 500 ml). Calculations showed that if a linear temperature gradient was assumed along a tube of uniform cross-sectional area, then

$$f(T_a, T_x) = \frac{1}{(T_a - T_x)} \ln \frac{T_a}{T_x} \tag{21}$$

and that on the average the $Vf(T_a, T_x)$ term would contribute only about 0.5% with respect to the other two terms namely k and V_x/T_x . Under these conditions the omission of the $Vf(T_a, T_x)$ term is justified.

In the first article¹, it was shown that at elevated pressures and a 273°K there is a measurable interaction between helium and the solid material under investigation. In order to minimize this interaction, the system was calibrated (V_x and k determined) with helium under low pressure. On the average the helium pressure was about 3×10^{-2} T. The data was plotted as $(N_0R/P)T_x$ vs. T_x and is shown in Fig. 6. Under these conditions k is the slope and V_x is the intercept. As can be seen the plot is linear indicating that the assumptions made are reasonable.

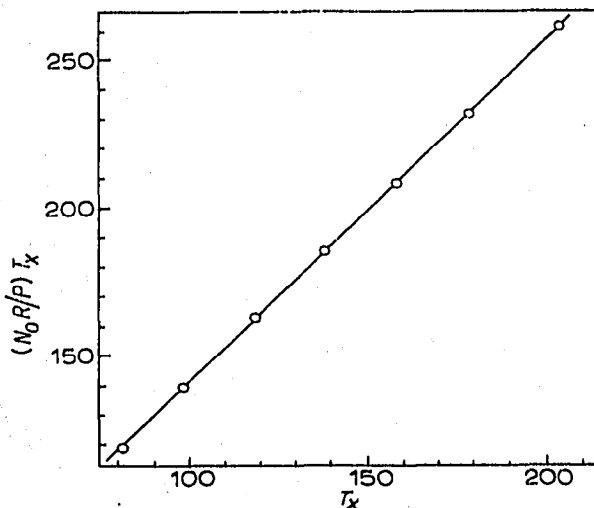


Fig. 6. $(N_0R/P)T_x$ as a function of T_x .

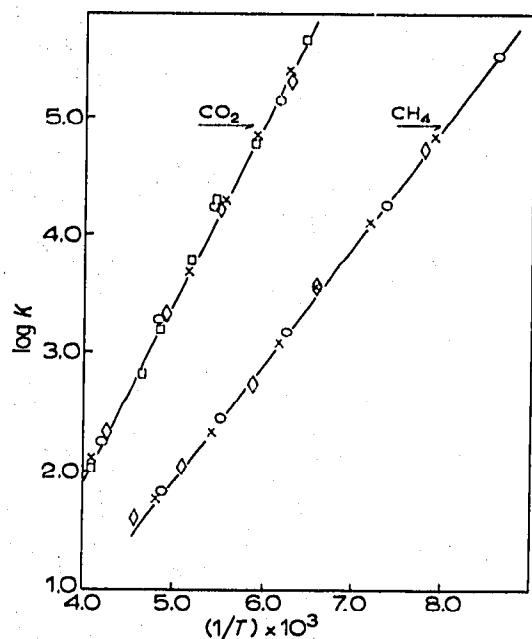


Fig. 7. Plot of $\log K$ against $1/T$ for CH_4 and CO_2 .

CH_4 : \diamond , $P_0 = 23.03 \times 10^{-3}$ mm; \circ , $P_0 = 51.49 \times 10^{-3}$ mm; \times , $P_0 = 88.62 \times 10^{-3}$ mm.

CO_2 : \square , $P_0 = 23.40 \times 10^{-3}$ mm; \circ , $P_0 = 54.92 \times 10^{-3}$ mm; \times , $P_0 = 97.10 \times 10^{-3}$ mm;
 \diamond , $P_0 = 136.10 \times 10^{-3}$ mm.

The distribution coefficients of CH_4 and CO_2 were measured in the temperature range 116° to 240°K with a fourfold initial pressure (P_0) variation and 155° to 240°K with a sixfold P_0 variation, respectively. The initial pressure refers to the pressure of the gas in the McLeod gauge before it is allowed to expand into the rest of the system. The lower temperature limit is governed by the appearance of sufficient gas pressure so that accurate pressure measurements can be made.

The results of these experiments are summarized in Fig. 7 where $\log K$ is plotted against $1/T$. Both lines are linear and in each case the variation of P_0 does not seem to affect the distribution coefficients indicating that under these low pressure conditions the adsorption isotherms are essentially linear. From the least square, the two lines can be characterized as follows:

| | CH_4 | CO_2 |
|-----------|---------------|---------------|
| slope | 975.7 | 1,502 |
| intercept | -2.942 | -4.095 |

Extrapolation to 273°K gave the following distribution coefficients $K(\text{CH}_4) = 4.25$ ml/g; $K(\text{CO}_2) = 25.44$ ml/g.

The ratio of $K(\text{CO}_2)/K(\text{CH}_4)$ is then 5.99. From the GC study it was found that at 273°K , $V_N(\text{CO}_2)/V_N(\text{CH}_4)$ was also 5.99. Although these ratios are in excellent agreement, it is more important to determine how the GC and the static system data correspond numerically. This can be tested utilizing eqn. 2 which relates K and V_N . Calculations show that the total weight of the packing material in the column (W_s) should be 49.3 g. Unfortunately due to several accidents during the column prepara-

ration the exact weight of the material is not known, but from the bulk density measurements and the volume of the empty column (calculated assuming uniform cross sectional area) this quantity was calculated to be 48.6 g. The close agreement between these two values adds credence to the following: (a) the method of determining V_m as described in the first article¹; (b) the assumptions made leading to eqn. 20; (c) the method of determining V_x and k ; (d) the deviations observed at 273° in Figs. 1, 2 and 3.

The ΔH^0 values were calculated from the slopes of the two lines and are compared below with those obtained from the GC data.

| | Static | GC |
|--|--------|------|
| $\Delta H^0(\text{CH}_4)(\text{kcal})$ | 4.46 | 3.12 |
| $\Delta H^0(\text{CO}_2)(\text{kcal})$ | 6.87 | 5.00 |

On first inspection it appears that the static system gives higher ΔH^0 , but since (as it has been shown) the two systems give virtually identical results this difference cannot be a by-product of the systems but must result from the difference in the temperature range employed. What this implies is that there is a change in the partial molar heat of adsorption as one goes from one temperature range to the other. This point is well supported by the GC data obtained at 273°K, in that the data does not fall on the $\ln V_N$ vs. $1/T$ line, but when it is converted to $\log K$, it fits well the extrapolated $\log K$ vs. $1/T$ line obtained from the static system. This then means that the change of slope occurs somewhere just above 273°K. This transition point was determined by first converting $\ln V_N$ to $\log K$ or *vice versa* and calculating where the two lines intersect. The CH_4 and the CO_2 data show these temperatures to be 284.7° and 286.6°K, respectively. Again the agreement is very good with the average value at $285.6 \pm 1^\circ\text{K}$. However, this transition could not be detected on a differential scanning calorimeter (Perkin-Elmer Model DSC-1B). The reason for this may be that the transition is slow and/or the heat of transition is negligible. The temperature at which this transition occurs and the inability to observe this transition on the calorimeter strongly suggest this to be the β -transition which for polystyrene ranges from 5° to 25°C (ref. 11).

In Table III are the ΔG^0 and the ΔS^0 values as computed at 273°K. The ΔS^0

TABLE III

THE ΔG^0 AND THE ΔS^0 VALUES FOR VARIOUS GASES AT 273°K

| Gas | $\Delta G^0(\text{Kcal.})$ | $\Delta S^0(\text{e.u.})$ |
|---|----------------------------|---------------------------|
| Gas chromatography (Helium carrier gas) | | |
| H_2 | 0.762 | -6.23 |
| N_2 | 0.048 | -7.80 |
| Ar | -0.114 | -7.80 |
| O_2 | -0.062 | -6.77 |
| CH_4 | -0.790 | -13.44 |
| CO_2 | -1.746 | -18.71 |
| Static method | | |
| CH_4 | -0.790 | -13.46 |
| CO_2 | -1.751 | -18.73 |

values for CH_4 and CO_2 (GC) were calculated using the ΔH^0 values obtained from the static system since the experimental points fall on the steeper part of the $\ln V_N$ or $\log K$ vs. $1/T$ plot. There is some error in the ΔS^0 for N_2 since the ΔH^0 obtained from the higher temperature region was used in the calculation.

It thus appears possible to use gas chromatography to determine the temperature of glassy state transitions in polymers.

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