The Study of Gas-Solid Equilibrium at High Pressures by Gas-Chromatography: Part I. Ethane, Propane, and n-Butane at Essentially Infinite Dilutions in the Methane-Silica Gel System

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The measurement of vapor-solid distribution coefficients or *K* values of a solute distributed between a gas phase and an adsorbed phase at essentially infinite dilutions has been investigated. Gas-solid chromatography is the technique employed in which the solute of interest is eluted through a tube packed with a solid adsorbent by a flowing gas phase which may or may not be appreciably adsorbed. The data taken for the eluted solute samples were then related to the *K* value and isobaric heat of adsorption for the solutes in the vapor-solid system.

A previous mathematical solution describing the chromatographic process is extended to include the case of an appreciably adsorbed pure component elution gas. This theory allows the calculation of solute *K* values and heats of adsorption for a solute at essentially infinite dilution in the vapor-solid system. It is necessary to have adsorption data for the elution gas covering the range of interest. For this reason the necessary elution gas adsorption isotherms were determined gravimetrically for the temperature and pressure range of the study.

For comparison purposes a single ethylene adsorption isotherm at 25°C. was obtained along with retention volume data for methane, ethane, and propane at essentially infinite dilution in the ethylene-silica gel system at 25°C. Agreement of the data of this study and the literature was thought to be sufficiently good to warrant further use of the technique.

Methane adsorption isotherms on silica gel were gravimetrically measured at —40°, —20°, 0°, 20°, and 40°C. from 100 to 2,000 lb./sq.in.abs. Retention volume data over the same pressure and temperature ranges were taken for ethane, propane, and *n*-butane at essentially infinite dilution in the methane-silica gel system.

The purpose of this paper is to present the results of an investigation into the possibilities of using gas-solid chromatography (GSC) as an experimental means for determining gas-solid equilibrium data. If a GSC technique could be made applicable over a sufficiently wide range of conditions, the ease and rapidity of making GSC measurements would greatly simplify the procurement of gas-solid equilibrium data over presently used methods.

Little notice was taken of the chromatographic elution technique until the pioneering work of Martin and Synge (*20*) on liquid-liquid partition chromatography appeared in 1941. In this method the components to be separated are carried by a moving liquid phase through a bed of solid support impregnated with an immobile liquid. In 1952 the suggestion by the same authors to use a gas as the moving phase or eluent was carried out by James and Martin (*12*), and gas-liquid partition chromatagraphy (GLPC) was begun.

Although the main interest in GLPC has been as an analytical tool, it was established by Porter, Deal, and Stross (*23*) that partition coefficients calculated from GLPC data were consistent with those obtained previously by static methods. Introduction of the corrected retention volume as a characteristic parameter of the GLPC process was by Littlewood (*19*) who also obtained an expression for calculating heats of solution from the temperature variation of this quantity. Further substantiation of the method for obtaining equilibrium properties was found by several authors as reviewed by Stalkup and Kobayashi (*26*). However it was not until the work of Stalkup and Kobayashi that an elution gas which was appreciably soluble in the fixed liquid phase was used. Their work on methane-*n*-decane and other light hydrocarbons extended the method into the range of multicomponent mixtures in both phases showing good agreement with measurements made by classical methods.

Application of elution analysis to gas-solid chromatography was established by Janak and his co-workers beginning in 1953 (*13*), and by Ray (*24*). The principal interest was in the analysis of low boiling gases and vapors, athough an interest in applying the method to physical properties studies has been growing. Gregg and Stocke (*10*) were the first to attempt to determine the complete adsorption isotherm from elution data, although they used the detailed form of the elution chromatogram rather than the retention volume. At the same time White and Cowan (*28*) pointed out the possibility of using GSC to calculate thermodynamic quantities, since the necessary symmetrical peaks could be obtained.

Mathematical description of the adsorption chromatography was presented by Wilson (*29*) for a pure liquid

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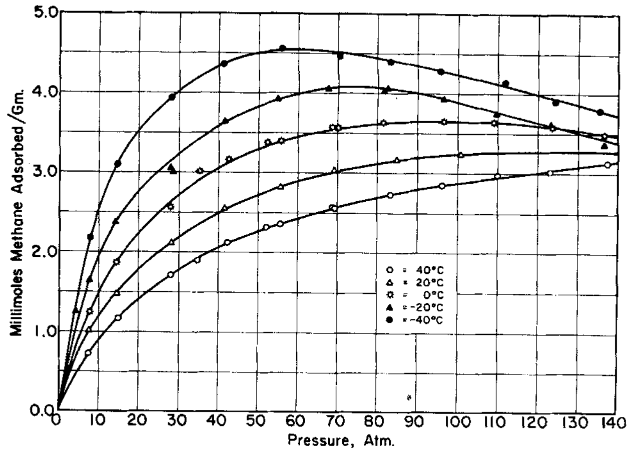

Fig. 1. Experimental isotherms for methane on silica gel.

eluent, was extended and elaborated upon by de Vault (*27*) to include mixtures, and further clarified by Glueckauf (*8*). The most general case for a linear adsorption isotherm was presented by Lapidus and Amundson (*16*) and their co-workers (*14*). Both plate and rate theories appeared in these articles.

In 1958 Greene and Pust (9) extended the method of Littlewood (*19*) to the determination of heats of adsorption by GSC. The application was considerably clarified by Habgood and Hanlan (*11*). The objection to asymmetrical peaks was discussed and found to be capable of being overcome particularly for the case of small samples. A fairly complete study of both elution and displacement studies as applied to calculate isotherms, surface areas, and heats of adsorption was reported by Eberly and his co-workers (*4, 5, 6*), although they were primarily interested in the high-temperature range. The mathematics of the process as derived by Eberly and Spencer (*6*) can easily be shown to agree completely with those presented here, even though the former used the rate theory rather than the plate theory used here.

As in the case of GLPC, the study of adsorption has been limited to the use of an elution gas which is not considered to be adsorbed, such as helium or hydrogen. It is the purpose of this work to extend the GSC method to the case of an adsorbable elution gas.

GAS-ADSORBED GAS DISTRIBUTION COEFFICIENTS AT INFINITE DILUTION FROM CHROMATOGRAPHIC DATA

The theoretical plate model was used by Martin and Synge (*20*) to develop an expression relating the retention volume V_{Ri} of the solute i to its partition coefficient. Several authors (*3, 15*) have since further explored and verified the solution with refinements. The basic relation is

$$V_{Ri} = V_g + V_a/H_{ai} \qquad (1)$$

In addition to the assumptions of point-by-point equilibrium, negligibility of axial diffusion, and large number of identical theoretical plates in the column (all of which can be met by proper choice of column and packing characteristics), it is also necessary to assume that the partition coefficient is constant over the entire column and that the sample volume at introduction is very small relative to the total gas volume in the column. It is felt that some justification is necessary to validate the last two assumptions for the case of an adsorbable elution gas with the adsorbed gas as the fixed phase.

The gas-solid equilibrium under study is characterized by a variable distribution coefficient, that is a curved isotherm. Hence Equation (1) applies strictly only to the limiting retention volume as the sample volume goes to zero (*2, 4, 11*), or the initial shape of adsorption isotherm for the component in question. As will be shown in the next paragraph, at 400 lb./sq.in.abs. and above, the samples used in this study were indeed small enough to be considered limiting. Also, as can be seen from Figure 1, the methane adsorption isotherms are not severely curved, over a limited pressure range, such as from base line to peak sample concentration. By using the small samples employed here, the operating range of the column for any particular run is very small; thus the isotherm can reasonably be assumed to be linear in this short range. The fact that the injected sample is but a small perturbation to the existing steady state equilibrium in all cases is essential to the application of this chromatographic technique.

In order to evaluate the effect of sample size, sample loop pressures of both ethane and propane were varied from 10 to 40 in. of mercury in a ¼-cc. sample and run on the −20°C. isotherm. These data are shown in Figures 2 and 3 for ethane and propane, respectively. Both pure solute and solute mixed with methane were used, with the solute partial pressure being varied over the cylinder pressure range for the case of the mixed samples. Above 400 lb./sq.in.abs. pressure the sample size variation gave rise to retention volume variation of no more than 2% of the 1 atm. sample pressure value. The values of ethane retention volume extrapolated to zero sample pressure are respectively 6, 3, and 2% larger than those at 1 atm. for the 100, 200, and 400 lb./sq.in.abs. runs, and the same extrapolated value for propane are 5 and 2% for the 200 and 400 lb./sq.in.abs. runs, respectively. It must be concluded that sample size effect was less than the experimental uncertainty of the data for all but the lowest pressure and that the lower pressure runs should have been corrected for sample size. The sample size studies were not conducted on *n*-butane, but the same general trend should exist.

Since mixed samples appear to give more consistent results in this study, all subsequent runs were made with 1 atm. sample partial pressure from the mixed samples in a ¼-cc. sample tube.

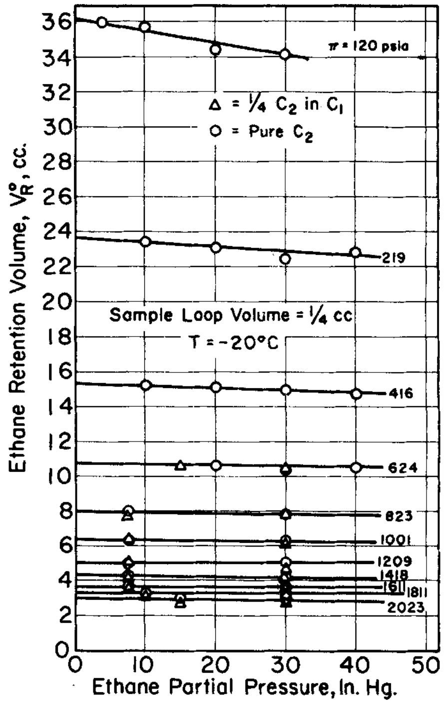

Fig. 2. Effect of sample size on ethane retention volume.

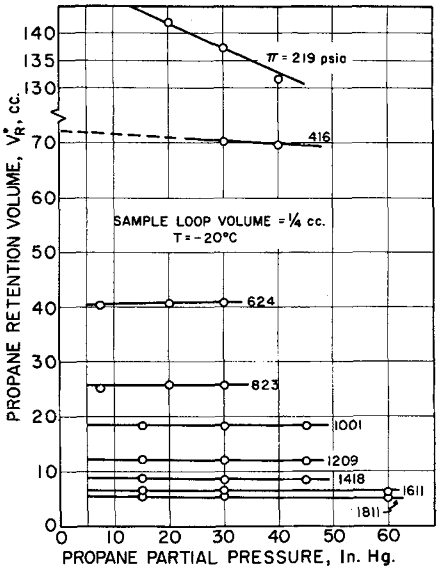

Fig. 3. Effect of sample size on propane retention volume.

In order to obtain the partition coefficient determined by Equation (1) in a more practical form, and to eliminate the complex problem of evaluating V_a, H_{ai} can be expressed as a K value. Here $K_i = y_i/x_i$ will be defined as the ratio of mole fraction in the gas to that in the adsorbed phase. Now $Y_i = \pi y_i/ZRT$ and $X_i = w x_i/V_a$. Thus

$$H_{ai} = \frac{Y_i}{X_i}$$

$$= \frac{\pi y_i}{ZRT} \bigg/ \frac{w\, x_i}{V_a}$$

or

$$H_{ai} = \frac{K_i\, \pi\, V_a}{ZRTw} \tag{2}$$

Substitution of (2) into (1) with rearranging yields

$$K_i = \frac{ZRTw}{\pi(V_{Ri} - V_g)} \tag{3}$$

where i is a component not present in the elution gas.

Since the retention volume measured is the product of the atmospheric flow rate and the retention time less a small apparatus response time correction C (7), it must be converted to column conditions of temperature and pressure. This quantity has been called the corrected retention volume, V^o_{Ri} and is obtained as follows:

$$V^o_{Ri} = (t_R - C)\, f_{LP} \frac{P_{\text{atm}}}{\pi} \frac{T}{T_{\text{atm}}} Z_{\pi,T} \tag{4}$$

This is the quantity desired in Equation (3), so that the final working equation can be written as

$$K_i = \frac{ZRTw}{\pi(V^o_{Ri} - V_g)} \tag{5}$$

With the assumptions of linear adsorption isotherm, large numbers of theoretical plates, small sample volume compared with column volume, constant plate characteristics and partition coefficient, and point-by-point equilibrium Equation (5) is proposed as valid for calculating infinite dilution K values for adsorption from experimental gas-solid elution data.

EXPERIMENTAL APPARATUS

A gas chromatographic apparatus modified for high-pressure operation which was operable at column temperatures above and below ambient was used for this investigation. A schematic diagram of the equipment as used is given elsewhere (*26*). The tubing, fittings, and valves were nominally ⅛-in. tubing size, except for the columns, which were ¼ and 3/16 in. for the adsorption and retention determinations, respectively. The tubing assembly was designed to minimize dead volume in the system.

The gas-sample valve used to inject small solute samples into the high-pressure elution gas stream was a modified commercial valve. It was a linear operating valve with six ports and a stem fitted with O rings to partition off the ports. Before the valve could be used at the higher pressures, it was necessary to replace the original stem with one having a closer clearance of 0.005 in. Also neoprene O rings were substituted for those supplied. The valve was located outside the bath to prevent sample condensation and to permit convenient replacement of the O rings. With these precautions, satisfactory service was obtained up to 2,000 lb./sq. in. abs.

Column pressure was accurately regulated by a loaded dome-type of diaphragm pressure regulator located just before the sample valve. Both reference and column carrier gas flow rates were controlled by stainless steel microneedle valves. These valves also served as expansion valves, breaking the pressure down from column conditions to 1 atm. A soap bubble flow meter was used to measure the column carrier gas flow rate at atmospheric conditions. An eight-filament pretzel diffusion type of katharometer was used as a detector.

DISCUSSION OF EXPERIMENTAL RESULTS

Comparative Studies with Published Data

In order to apply Equation (5), it was necessary to investigate values for w at all conditions. The method used for the determination of the pure component adsorption isotherms was a gravimetric one which consisted of first equilibrating the column by a steady flow of the pure gas through it at the desired temperature and pressure, then closing off the column with valves at both ends, removing the assembly from the system and weighing it on an analytical balance. If the evacuated volume weight is known, the mass of adsorbate plus equilibrium gas can be determined as the difference between the empty column weight and the weight of the assembly removed from the system. Finally, the mass adsorbed and the specific adsorption was obtained by subtracting from the difference obtained above the product of the column gas volume and the gas density at the equilibrium conditions of temperature and pressure.

The gravimetric method described above had never been applied over the pressure range studied here; therefore it was felt that some check on the method and technique was necessary. To this end an ethylene isotherm at 25°C. was run to compare with the work of Lewis, Gilliland, Chertow, and Cadogan (*18*). The agreement was found to be quite good at the lower pressures, with deviation increasing to a maximum of about 8% at the highest pressure of 400 lb./sq.in.abs. for their data. It was felt that the agreement was satisfactory considering that a detailed characterization of their silica gel was not available. The same regeneration procedure and Gibbs' definition of amount adsorbed was employed in both this study and the study of reference *18*. This definition states that the amount adsorbed is that amount present in excess of the amount which would be present under the same conditions of temperature and pressure if the adsorbing material would adsorb none of the component of interest (*1*). It should be emphasized that the Gibbs' definition of adsorption is implied in Equation (5), in the term w in particular.

As a check, particularly on the chromatographic method of obtaining distribution coefficients, elution data were taken for samples of methane, ethane, and propane at infinite dilution in an ethylene carrier gas, again at 25°C. These data were also compared with those of Lewis et al.

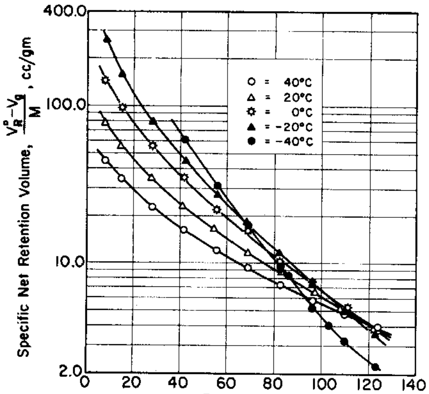

Fig. 4. Specific net retention volume for propane vs. pressure along isotherms.

(*17*) and shown to agree in regions were checks were possible. The *K* values from Lewis et al. were obtained by graphically taking the slope of their $x - y$ diagrams at the origin to compare with the infinite dilution values measured chromatographically and calculated from Equation (5). In view of the required extrapolation, the variation of the ethane *K* values with pressure at essentially infinite dilutions assumed the correct trend with deviations not exceeding 15% at pressures above 100 lb./sq.in.abs.

No correction was made for the decrease in gas volume due to volume occupied by the adsorbate, in accordance with the Gibbs' definition of adsorption which was employed throughout this study.

Determination of Pure Methane Adsorption Isotherms

In order to apply Equation (5) to the methane-silica gel system it was necessary to investigate values for w at all conditions. Accordingly, the methane adsorption isotherms were studied by the gravimetric method discussed above from methane compressibility data from the literature (*21, 22, 25*).

The adsorption isotherms for methane were run at −40°, −20°, 0°, 20°, and 40°C. in the pressure range 100 to 2,000 lb./sq.in.abs. The data are shown in Figure 1 and tabulated elsewhere (7). The relative maximum for the low temperature range follows from the Gibbs' definition of the amount adsorbed and the increased gas density.

K VALUES FOR THE SOLUTE PRESENT AT ESSENTIALLY INFINITE DILUTION IN THE ADSORBED PHASE

Applicability of the chromatographic elution technique to the study of gas-solid equilibria was tested experimentally by using an appreciably adsorbed elution gas, in this case methane, flowing through a silica gel packed column, and measuring retention times for solute samples of ethane, propane, and *n*-butane. Since the elution gas was pure methane and relatively small samples were injected, the solute concentration in the adsorbed phase was at essentially infinite dilution in the methane-silica gel system. In addition the experimental conditions were such that the assumptions inherent in Equation (5) were met. Retention times were measured for the solutes at −40°, −20°, 0°, 20°, and 40°C. over the pressure range of 100 to 2,000 lb./sq.in.abs.

The flow rates measured at atmospheric pressure varied from 63 to 85 cc./min., which corresponds to column flow variations from about 50 cc./min. to less than 2 cc./min., giving no apparent discrepancies in the data. The atmospheric flow rate was always selected to fall in the optimum performance range of the catharometers used. The flow rates resulted in extremely low flow rates for the high-pressure runs, favoring the assumption of point-by-point equilibrium. The data reported graphically were taken at different flow rates (7) and involve different directional approaches to equilibrium as regards pressure.

Since the two different columns were used for the retention volume determinations, the specific net retention volume $(V_R^o - V_g)/M$ was chosen as the quantity to be used for self-consistency comparisons. These values which were calculated from the measured retention volumes are presented in Figure 4 for propane along isotherms. Numerical values of the specific net retention volume for ethane, propane, *n*-butane on silica gel are tabulated elsewhere (7). As can be seen from the curves these data are quite consistent internally, up to the point at which they begin crossing. The crossing corresponds to the presence of maxima in the adsorption curves for mixtures of these components and methane, as the retention volume is proportional to the initial slope of the adsorption isotherm for the respective components in the methane silica gel system. Although the observed peaks were somewhat assymmetrical, in particular the *n*-butane peaks at the lower pressures and temperatures, the assymmetry was neglected in determining the peak maximums. The fact that the retention volume remains constant with varying sample size, as shown by the samples size study, is felt to cover this assumption (*11*). All the ethane and propane peaks were quite symmetrical, even at the elevated pressures.

Adsorption distribution coefficients or *K* values for ethane, propane, and *n*-butane at infinite dilution were calculated from the methane adsorption isotherms and the retention volumes discussed above in Equation (5). The *K* values are tabulated elsewhere with the observed data (7) and plotted in Figures 5 through 9 as log *K* vs. log *P*. The data agree quite well with the smooth curves drawn through the points, and only the highest pressure points for ethane and propane at −40°C. are in sufficient disagreement to warrant discussion. It is felt that these two points are lower than expected because the samples condensed upon injection and traveled through the column as liquid until diluted and vaporized. The *K* values for *n*-butane at −40° and −20°C. and propane at −40°C. at pressures below 1,000 lb./sq.in.abs. are not tabulated or plotted, as the sample peaks were not large enough to be detected. The extremely long retention times allow considerable diffusion and mixing in the axial directions which results in dilution of the samples below the detector sensitivity.

Pressure variation of the *K* values is as might be expected. As the pressure increases, the surface becomes

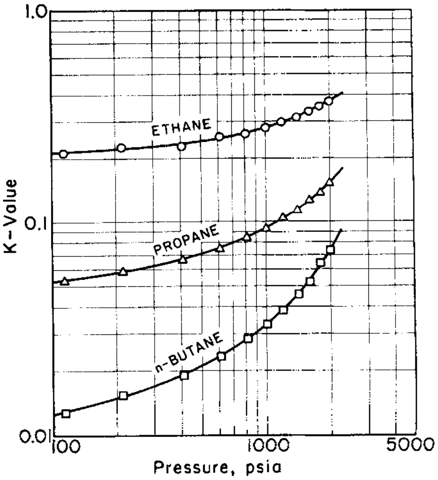

Fig. 5. K value at essentially infinite dilution, 40°C.

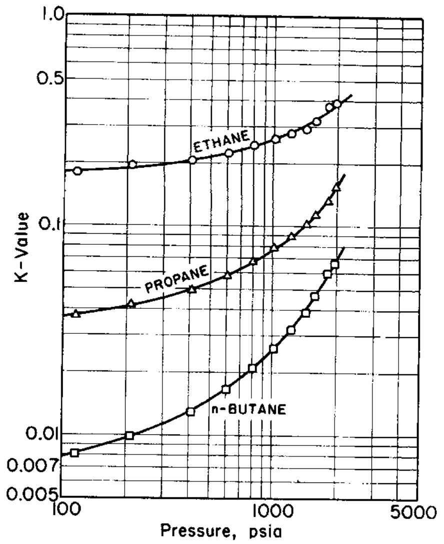

Fig. 6. K value at essentially infinite dilution, 20°C.

more completely covered by the methane carrier gas resulting in decreased adsorption of the eluted samples. Therefore the K values increase with increasing pressure, even beyond the methane isotherm maxima. Each K value curve seems to be approaching $K = 1.0$ at a pressure higher than the maximum pressure investigated in this study. This seems to indicate a critical pressure analogous to that observed in gas-liquid systems. Higher-pressure data will have to be taken to confirm this hypothesis, but a study of the K value vs. pressure curves gives strong evidence of such a phenomenon.

The error arising from temperature inaccuracies was negligible in this study. The pressure error, a maximum of 2 lb./sq.in. as given by the gauge calibration, varied from 2% at 100 lb./sq.in.abs. to 0.1% at 2,000 lb./sq.in.abs. Thus the overall error was lowered with increasing pressures by this effect. The same holds for the errors due to inaccuracies in the column weighing with the range being 1 to 0.05%.

Variations of flow rate during a run were noticed frequently, and in all cases an average value was used. Even though the variations were in all cases less than 1%, it is felt that this could be improved in future studies. The source of trouble is thought to be the expansion valve.

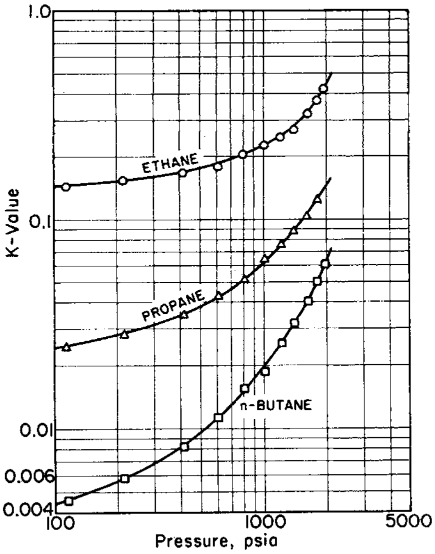

Fig. 7. K value at essentially infinite dilution, 0°C.

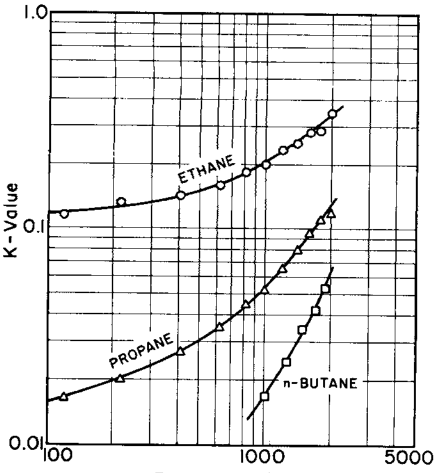

Fig. 8. K value at essentially infinite dilution, —20°C.

In order to estimate the effect of inaccuracy in V_g on the data the 20°C. adsorption isotherm and K values have been considered with the following results. This particular isotherm was chosen since there were two values for V_g available, that measured from radioactive methane retention volumes in Equation (5) with $K = 1$ and that calculated from the tubing and silica gel packing volumes. At 100 lb./sq.in.abs. the calculated value of V_g was high by 0.47 cc. or 15% of the value measured radioactively. This measured value is subject at 100 lb./sq.in.abs. to a 2% error from the pressure reading and a 1% flow rate error, as discussed earlier. Thus the total error of the calculated V_g could be 18% of that measured radioactively. This would result in a 0.54% error in X/M for the methane adsorption isotherm.

At 1,000 lb./sq.in.abs. the calculated value for V_g was 0.17 cc. or 5% high relative to the radioactively measured value. With a 1% flow rate error and a 0.2% pressure error the X/M value for the pure methane adsorption isotherm could be in error by 6.2%, since the gas density is greater.

The net errors, resulting from the 18% error in the calculated V_g and the 0.54% in the X/M value for pure methane, in the K values for ethane, propane, and n-butane at infinite dilution with Equation (5) would be 2.8, 0.3, and 0.39%, respectively, at 100 lb./sq.in.abs. At 1,000 lb./sq.in.abs. the infinite dilution K value errors for ethane, propane, and n-butane, respectively, would be 5, 1.25, and 3% for the 5% error in calculated V_g includ-

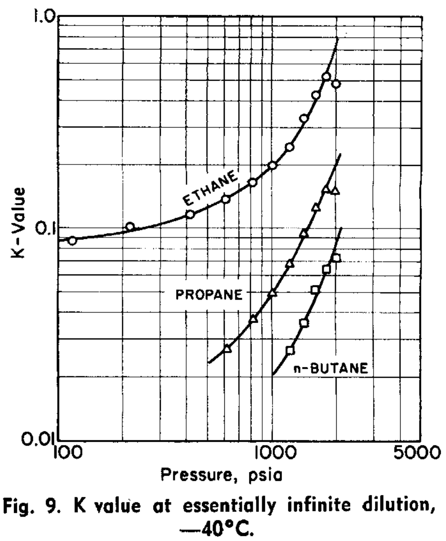

Fig. 9. K value at essentially infinite dilution, —40°C.

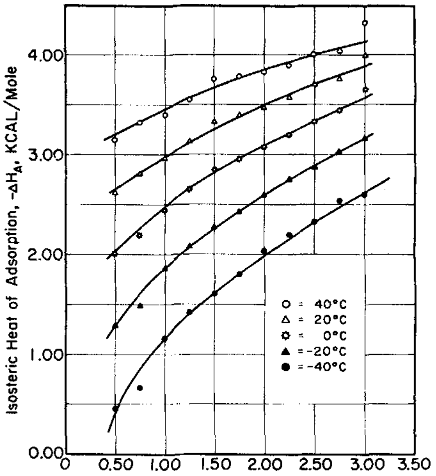

Fig. 10. Isosteric heats of adsorption of methane on silica vs. specific adsorption at various temperatures.

ing the 5% error in the methane X/M. The propane K value errors are low because of the cancellation of the V_g and the X/M errors, in accordance with Equation (5).

Thus, it can be seen that V_g plays an increasingly important part as the pressure is increased. Similarly the data for the lighter components are more influenced by V_g, since the retention volumes are lower for them.

The error from neglecting the sample size effect must also be included for the infinite dilution K values. This would be 6% for ethane at 100 lb./sq.in.abs. and 5% for propane at 200 lb./sq.in.abs. No n-butane sample size study was made. Above 400 lb./sq.in.abs. this error could not be separated from other experimental errors and is therefore included in the 1,000 lb./sq.in.abs. error analysis.

In summary, the errors are seen to vary widely with pressure and the component considered. The maximum error in X/M values for pure methane adsorption rises from 2.5% at 100 lb./sq.in.abs to 6.2% at 1,000 lb./sq.in.abs. Infinite dilution K value errors cover the following ranges from 100 to 1,000 lb./sq.in.abs.: for ethane 12 to 6.2%, for propane 8.3 to 2.5%, for n-butane 3.4 to 4%. In all cases these are the maximum errors possible, and it is felt that the experimental scatter is within these limits for all points The reproducibility was better than the maximum error stated for all data taken.

THERMODYNAMIC TREATMENT OF DATA

In order to study the thermodynamics of the system investigated here, it will be necessary to consider two cases: the pure methane adsorption and the elution of the essentially infinitely dilute solutes in the methane-silica gel system.

The adsorption of pure methane on silica gel can be considered as an equilibrium of a given component between two coexisting phases, the gas and the adsorbate. In this case Clausius-Clapeyron equation will apply along univariant equilibrium conditions in the form

$$\frac{dP}{dT} = \frac{\Delta H_A}{T \Delta V} \tag{6}$$

Here $V = \overline{V}$ ads $- \overline{V}$ gas, and $\overline{V}_g = ZRT/P$. At all but the lowest temperatures and highest pressures the molar volume of the adsorbate is much less than that of the gas, so that $\Delta V \simeq V_g$ except at the highest pressures. The adsorbate specific volume could be as much as 10% of the molar gas volume at extreme conditions, but since no data were available for evaluation of $\overline{V}$ ads, it was neglected throughout the heat of adsorption determination.

Substitution of $\overline{V}_g$ into Equation (6) and rearrangement gives

$$\frac{d(\ln P)}{d(1/T)} = \frac{\Delta H_A}{ZR} \tag{7}$$

From the experimental isotherms plots of log P vs. $1/T$ were made along isosteres, or constant X/M values. The methane isosteric heats of adsorption determined from the slopes of these curves and Equation (7) are tabulated elsewhere (7) and given in Figure 10. These H_A values are typical of physical or van der Waals adsorption (*1*), and the value of 2,800 cal./mole at 25°C. 1 atm. given by Greene and Pust is within the range of the values calculated here (*9*).

Determination of the heat of adsorption of the eluted samples has been studied previously (*5, 9, 11*), and all investigations here used the relation

$$H_A = C' \exp^{-\Delta H_A/RT} \tag{8}$$

Similarly it has been shown (*19, 23*) that in the GLPC case the partition coefficient is analogously proportional to the exponential heat of solution. Thus Equation (7) was used with the retention volume data obtained here.

Taking the log of Equation (8) and differentiating with respect to $1/T$ one gets

$$\frac{\partial \ln H_A}{\partial \left(\frac{1}{T}\right)} = -\frac{\Delta H_A}{R} \tag{9}$$

But using Equation (1) and substituting for H_a one obtains

$$\frac{\partial \ln [(V_R{}^0 - V_g)/M]}{\partial (1/T)} = -\frac{\Delta H_A}{R} \tag{10}$$

Thus from the slope of a plot of the log of the specific net retention volume $(V_R{}^0 - V_g)/M$, at constant pressure vs. $1/T$, the isobaric heat of adsorption can be calculated from Equation (10). This calculation was carried out for all the solutes run, and the results are tabulated elsewhere (*7*) and shown for ethane as Figure 10.

The heat of adsorption for the eluted samples is not expected to have the same meaning as previously reported values run with an elution gas which was nonadsorbable relative to the sample. Here the methane carrier is appreciably adsorbed, and the ΔH_A's must be interpreted as differential heats of adsorption for the solutes at infinite dilution in the methane-silica system.

DESCRIPTION OF MATERIALS USED

A chromatographic grade silica gel was used throughout this study. The 30 to 50 mesh gel as obtained had a

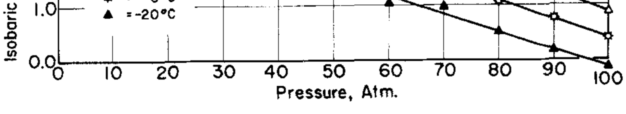

Fig. 11. Isobaric heat of adsorption vs. pressure at various temperatures for propane at infinite dilution in the methane-silica gel system.

specific surface area of 532 sq. m./g. and was used to pack the column for the isotherm determinations. The columns used for the retention data were packed with the same gel which had been crushed and screened to 100 to 140 mesh with a surface area of 543 sq. m./g. A more favorable tube diameter to particle ratio was thus obtained for the retention column.

The dried methane gas used in this study was found by analysis to be 99.7 mole % methane, 0.2 mole % nitrogen, and 0.1 mole % of other hydrocarbons, principally ethane. The ethylene, ethane, propane, and *n*-butane were instrument grade gases with 99.5 mole % minimum purity.

CONCLUSIONS

Although agreement with published data was not exact where comparisons were possible, it was sufficiently close to establish the gravimetric method of measuring adsorption. The internal consistency, appearance of the maximum, and reproducibility of the methane isotherms further support the applicability of gravimetric technique to the determination of high-pressure adsorption isotherms, at least to the isotherm maximum.

The sample size study and agreement with literature values of the heats of adsorption obtained from the retention volumes indicate that the chromatographic process is a true equilibrium steady state when the perturbations are minute. Thus the *K* values determined chromatographically for infinite dilution are characteristic of the adsorption equilibrium systems studied. The consistency of the *K* value data offers further support to the assumption of equilibrium and negligibility of the peak assymmetries.

It can be said that the chromatographic study of adsorption systems has been shown to be valid, and it should provide a simple and rapid method for further investigations into adsorption equilibrium. The chromatographic technique also offers a direct way of measuring infinite dilution data. However it is as yet applicable only to gaseous systems of light hydrocarbons.

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NOTATION

C = correction to observed retention time for response time and low-pressure dead volume, min.
H_a = adsorption partition coefficient, Y_i/X_i, $\dfrac{\text{moles/unit volume in gas}}{\text{moles/unit volume in adsorbate}}$
H_A = heat of adsorption: isosteric heat of adsorption for methane, *K* cal./mole; differential isobaric heat of adsorption at essentially infinite dilution for ethane, propane, and *n*-butane in the methane-silica gel system, *K* cal./mole
K = *K* value, y/x, ratio of mole fraction in gas to that in adsorbate
M = mass of silica gel packing, g.
P = pressure, atm., lb./sq.in.abs.
R = gas constant per mole
T = absolute temperature, °K.
V_a = total volume of adsorbed phase in column, cc.
V_g = total accessible gas volume of flow system cc.
V_R = retention volume, cc.
$V_R{}^o$ = retention volume corrected to column conditions, cc.
X_i = concentration of component *i* in adsorbate, moles/unit volume
X/M = specific adsorption, millimoles adsorbed/g. of silica gel
Y_i = concentration of component *i* in gas phase, moles/unit volume gas
Z = compressibility factor, PV/RT for gas
f_{LP} = low-pressure flow rate, cc./min. at 1 atm.
t_r = retention time, time from sample injection to peak emergence, min.
w = total moles adsorbed on column, moles
x_i = mole fraction of component *i* in adsorbate
y_i = mole fraction of component *i* in gas phase
π = total column pressure, lb./sq.in.abs. or atm.

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