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THE EFFECT OF CARRIER GAS NONIDEALITY AND ADSORPTION ON THE NET RETENTION VOLUME IN GAS-SOLID CHROMATOGRAPHY

J. J. CZUBRYT*, H. D. GESSER AND E. BOCK
The University of Manitoba, Department of Chemistry, Winnipeg (Canada)

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SUMMARY

The effect of carrier gas nonideality and adsorption on the net retention volume has been considered and certain approximate relationships are developed. These in turn are applied to the net retention volumes of methane obtained on a 200-ft. (1/8 in. O.D.) Porapak S column at 0°C where He, Ar and CO_2 were employed as carrier gases. In all cases it was found that the effect of carrier gas nonideality on the net retention volume was much smaller than that arising from carrier gas adsorption. The relative degree of adsorption was found to be in the expected order, that is, He < Ar < CO_2. The adsorption of all three gases was found to be governed by a single pseudo adsorption isotherm of the form $\theta = k\bar{P}^n/(1 + k\bar{P}^n)$. All indications are that due to the uncertainty in the nature of the carrier gas adsorption isotherms, gas-solid chromatography is not a suitable method in the determination of the B_{12} terms.

INTRODUCTION

Since our previous report[1], dealing with the separation of CH_4–CD_4 mixtures on a Porapak S column using helium as a carrier gas, other carrier gases were employed in order to try and enhance this separation. Our preliminary experiments, carried out at constant temperature and flow rate, showed that the effect of carrier gases such as N_2, Ar, and CO_2 was to decrease dramatically both the retention times and the separation efficiency. This is illustrated in Fig. 1. In every case the heavy methane is eluted before the lighter one.

BROOKMAN *et al.*[2] have pointed out that if gas viscosity and compressibility are considered, then differential retention times are to be expected as one changes carrier gases and that the order would be in the same direction as the carrier gas viscosity. According to Fig. 1, the retention time order is $t(\mathrm{He}) > t(\mathrm{Ar}) > t(N_2) > t(CO_2)$ whereas the viscosity order for the gases is Ar > He > N_2 > CO_2 (ref. 3).

Rough calculations showed that neither this discrepancy nor the large decrease in the retention times could be accounted for by carrier gas nonideality alone. With the aid of an electron capture detector (used as a helium detector) it was found that N_2, Ar, and CO_2 could be separated on the same column under similar conditions. Un-

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* Holder of the National Research Council of Canada Studentship 1966–1968.

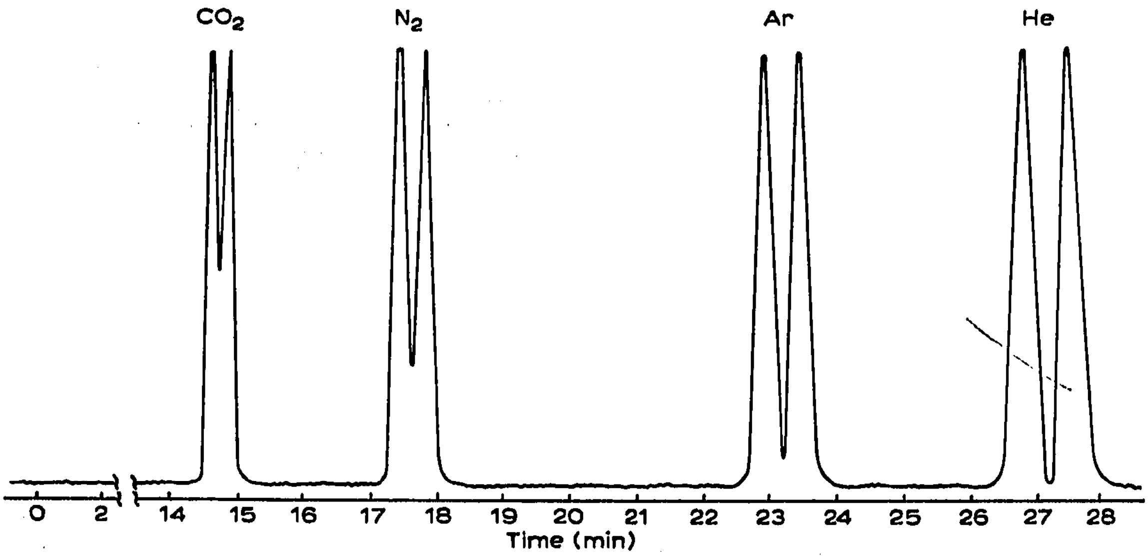


Fig. 1. Elution of CH_4–CD_4 mixtures with various carrier gases. Column, 80 ft. (1/8 in. O.D.) Porapak S (50–80 mesh); flow rate, 20 cm^3/min; temperature, $0 \pm 1/2\,°C$.

doubtedly this differential interaction between these gases and the packing material must also exist when these gases assume the role of a carrier gas. In the presence of an adsorbing carrier gas there will be competition between the solute and the carrier gas molecules for the active sites on which partitioning takes place, and consequently a reduction of both the retention times and the separation efficiency can be expected. The order of elution is now a function of carrier gas viscosity (and compressibility) and the degree of interaction between the carrier gas and the surface.

A study was initiated to determine the nature and degree of interaction between the carrier gas and the packing. The three carrier gases He, Ar, and CO_2 were chosen for this study since they exhibit a different degree of nonideality and a progressively stronger interaction with the packing.

THEORETICAL

The fundamental quantity in gas chromatography which relates the operating parameters to the thermodynamic properties is the net retention volume (V_N). For a gas–solid chromatography (GSC) system this relationship can be written as

$$V_N = KS \tag{1}$$

where K and S are respectively the distribution coefficient and the surface area on which partitioning can take place. The net retention volume in turn can be calculated by means of the following expression

$$V_N = t_R F_o j - V_M \tag{2}$$

where t_R, F_o, j, and V_M are the elution time of the solute, the flow rate at the column outlet, the Martin–James compressibility factor, and the column void accessible to the mobile phase respectively. Eqn. 2 is only valid under ideal gas conditions. In practice, however, one deals with real gases and eqn. 2 serves only as an approximation, the degree of which depends on the nonideality of the carrier gas and the operating pressure. The relationship expressed by eqn. 1 on the other hand is independent of the nature of the carrier gas or the pressure, but the magnitude of V_N certainly is.

The effect of pressure and the nature of the carrier gas on the net retention volume or the partition coefficient in gas–liquid chromatography (GLC) has been explored theoretically and/or experimentally by a number of workers[6–16], but virtually no work of this type has been done in the field of GSC. LOCKE[17] has considered this problem theoretically and has proposed several expressions relating the distribution coefficient to pressure and the carrier gas nonideality. Unfortunately these expressions are of limited use. In the first place he only considers two basic adsorption isotherms (linear and Langmuir). What is more important is the number of errors contained in these expressions. One of these has been pointed out by YOUNG[18] and refers to LOCKE's case III. Further perusal of these expressions reveals that for one reason or another the seven of the remaining nine expressions are also in error, namely cases II, IV, V, VI, VII, IX, and X.

Our approach to this problem is basically that used by LOCKE. Here it is also assumed that the solute samples are very small and consequently that their adsorption isotherms are linear.

In a very short section of column under pressure P where S is the available surface area of the packing material and V is the column void accessible to the mobile phase, the expression for the local distribution coefficient is defined as follows:

$$K = \frac{N_a V}{N_g S} \tag{3}$$

where N_a and N_g refer to the number of moles of solute adsorbed on the surface and in the mobile phase respectively. Following LOCKE, N_a can be expressed in terms of fugacity of the solute f by

$$N_a = kSf \tag{4}$$

where S has the same meaning as above and k is the solute adsorption constant. Now, the relationship between fugacity, f, the partial pressure p, and the local carrier gas pressure P is given by[19, 20],

$$\ln f = \ln p + \frac{P}{RT}[B_{22} - (1-y)^2(B_{11} - 2B_{12} + B_{22})] \tag{5}$$

where y is the mole fraction of the solute in the gas phase and B_{11} and B_{22} are the second virial coefficients of the pure carrier gas and the pure solute, respectively. B_{12} is the second virial cross coefficient, which is a measure of the interaction between the two types of molecules and is related to B_{11} and B_{22} by the following expression[21],

$$B_m = (1-y)^2 B_{11} + 2y(1-y)B_{12} + y^2 B_{22} \tag{6}$$

where B_m is the second virial coefficient of the mixture and in the limit as $y \to 0$ becomes equal to B_{11}. In the present system, where we are dealing with infinitely dilute mixtures, we can express N_g (eqn. 3) as

$$N_g = \frac{pV}{RT + B_{11}P} \tag{7}$$

After substituting this and eqn. 4 into eqn. 3 and taking natural logarithms we get

$$\ln K = \ln kRT + \ln \frac{f}{p} + \ln \left(1 + \frac{B_{11}P}{RT}\right) \tag{8}$$

Since normally $B_{11}P/RT \leqslant 1$, then the third term of the r.h.s. can be approximated by $B_{11}P/RT$. In the limit as $y \rightarrow 0$, eqn. 5 becomes

$$\ln \frac{f}{p} = (2B_{12} - B_{11}) \frac{P}{RT} \tag{9}$$

Substituting this into eqn. 8 we get

$$\ln K = \ln kRT + \frac{2B_{12}}{RT} P \tag{10}$$

It has been pointed out by DESTY *et al.*[7] that fugacity of the solute varies with pressure according to

$$\left(\frac{\partial \ln f}{\partial P}\right)_T = \frac{v}{RT} \tag{11}$$

where v is the molar volume of the solute which may be approximated to the molar volume of the pure solute (V_0). Intregration between limits between $P = P$ and $P = 0$ gives

$$\ln f(P = 0) = \ln f(P = P) - \frac{V_0P}{RT} \tag{12}$$

Following DESTY *et al.* and correcting eqn. 10 to the standard state, we obtain the desired expression

$$\ln K = \ln kRT + (2B_{12} - V_0) \frac{P}{RT} \tag{13}$$

or

$$\ln K = \ln K_0 + (2B_{12} - V_0) \frac{P}{RT} \tag{14}$$

where

$$K_0 = K(P = 0) = kRT \tag{15}$$

The relationship between K and P thus obtained for a GSC system is found to be identical to that of GLC systems when similar approximations are involved (here reference is made to GLC systems where factors such as carrier gas solubility, liquid phase compressibility etc. are ignored). This is expected if one considers that in both cases correction is being made for the effect of carrier gas nonideality and pressure on the fugacity of the solute in the mobile phase and consequently on K.

Eqn. 14 represents the distribution coefficient at any point in the column where the carrier gas pressure is P. The quantity of interest, however, is a particular value of K which is experimentally representative of the entire column (the mean value of K). In the field of GLC a number of above cited workers have chosen the representative value of K (or V_N) as that which is obtained at the mean column pressure $\bar{P}$ defined as

$$\bar{P} = P_o/j = P_oJ_2^3 \tag{16}$$

where P_o is the column outlet pressure and as before j is the Martin–James compressibility factor. EVERETT[8] questioned the use of $\bar{P}$ and has shown that a more representative value of pressure should be

$$P = P_o J_3^4 \tag{17}$$

where

$$J_n^m = \frac{n\left[\left(\frac{P_i}{P_o}\right)^m - 1\right]}{m\left[\left(\frac{P_i}{P_o}\right)^n - 1\right]} \tag{18}$$

and P_i is the column inlet pressure. In view of what has been said above, this can be extended to the GSC system and our final expression becomes

$$\ln K = \ln K_0 + (2B_{12} - V_0)\frac{P_o J_3^4}{RT} \tag{19}$$

where K of eqn. 19 no longer symbolizes the local value, but the column mean.

The carrier gas can further influence the magnitude of V_N in a GSC system by competing with the solute molecules for the active sites. This competition process leads to an effective loss of available surface area to the solute. If we define S as the available surface area and S_0 as the total surface area (no carrier gas adsorption) of the entire column, then the mean value of the fraction of the surface covered by the carrier gas is

$$\theta = 1 - \frac{S}{S_0} \tag{20}$$

It should be pointed out at this time that θ is only an apparent fraction since under ordinary conditions (no chemisorption) the solute molecules can displace the adsorbed carrier gas and the ease with which this can be done will be related to the relative magnitudes of the adsorption constants of the solute and the carrier gas. When the adsorption constant of the carrier gas becomes much greater than that of the solute, the θ (apparent) will approach θ (true).

Eqns. 1, 19 and 20 can be combined to give

$$V_N = K_0 S_0 (1 - \theta) \exp\left[(2B_{12} - V_0) P_o J_3^4\right] \tag{21}$$

In the limit as $P \to 0$ (and consequently $\theta \to 0$), $K_0 S_0$ represents the net retention volume at zero pressure ($V_N(0)$). Making this substitution and rearrangement of eqn. 21 gives

$$\frac{V_N}{\exp\left[(2B_{12} - V_0) P_o J_3^4\right]} = V_N(0)\,(1 - \theta) = V_N^* \tag{22}$$

and consequently θ can be expressed as

$$\theta = 1 - \frac{V_N^*}{V_N(0)} \tag{23}$$

Eqn. 23 allows one to determine the mean apparent value of θ in terms of the corrected net retention volume V_N^* of some suitable solute. Unfortunately, eqn. 23 does not allow for the determination of the nature of the adsorption isotherm of the carrier gas since in no way is it related to the proper pressure variable. To clarify this it must be realized that for any region of the column the local value of θ (θ_L) will be

$$\theta_L = \mathrm{f}(P) \tag{24}$$

Thus, if we assume the carrier gas to behave ideally so that $\mathrm{f} = P$ and that it has a linear adsorption isotherm, then

$$\theta_L = kP \tag{25}$$

In order to find the mean value of θ the following integration must be performed

$$\frac{\int \theta_L \,\mathrm{d}x}{\int \mathrm{d}x} = \frac{\int kP \,\mathrm{d}x}{\int \mathrm{d}x} = \bar{\theta}_L \tag{26}$$

But since[22]

$$\frac{x}{L} = \frac{P_i^2 - P^2}{P_i^2 - P_o^2} \tag{27}$$

where x is the distance along the column where the pressure is P, and L is the total length of the column, and consequently

$$\mathrm{d}x = \frac{-2LP\,\mathrm{d}P}{P_i^2 - P_o^2} \tag{28}$$

then eqn. 26 becomes

$$\bar{\theta}_L = \frac{k \int P^2 \,\mathrm{d}P}{\int P \,\mathrm{d}P} = \theta \tag{29}$$

and upon integration this gives

$$\theta = k\,\frac{2}{3}\left(\frac{P_i^3 - P_o^3}{p^2 - P_o^2}\right) = k\bar{P} \tag{30}$$

Eqn. 30 shows that for this particular case $\bar{P}$ is the proper pressure variable. Should the adsorption isotherm have been Langmuir then

$$\theta = \frac{k \int \frac{P^2 \,\mathrm{d}P}{1 + kP}}{\int P \,\mathrm{d}P} \tag{31}$$

and consequently $\bar{P}$ would no longer serve as the proper pressure variable, that is

$$\theta \neq \frac{k\bar{P}}{1 + k\bar{P}} \tag{32}$$

It follows that for every different carrier gas adsorption isotherm, θ will be a new function of P_i and P_o and consequently $\mathrm{f}(\bar{P})$ cannot be substituted for $\mathrm{f}(P)$. This means then that although it is possible to determine θ from GSC data, it is not possible to determine the nature of the adsorption isotherm and as a result the B_{12} terms cannot be obtained from GSC system unless the exact carrier gas adsorption isotherm is known in advance. The situation becomes more complex if one considers θ_L as a function of fugacity.

V_N and consequently $V_N{}^*$ must be calculated from the working parameters. It has been already pointed out that eqn. 2 is inadequate for systems using real carrier gases, particularly at elevated pressures. A more accurate expression can be arrived at by:

(a) Assuming that the carrier gas is governed by the following equation of state

$$PV = RT + B_{11}P \tag{33}$$

(b) By keeping a mass balance in the column (*i.e.* mass inflow = mass outflow). The final expression for V_N is

$$V_N = t_R F_o \left(\frac{P_o}{\bar{P}}\right)\left(\frac{1 + b\bar{P}}{1 + bP_o}\right) - V_M \tag{34}$$

where

$$b = \frac{B_{11}}{RT} \tag{35}$$

and $\bar{P}$ is the mean column pressure derived for a nonideal gas by MARTIRE AND LOCKE[23] and has the form

$$\bar{P} = \frac{\frac{1}{3}(a^3 - 1) - \frac{b}{4}(a^3 P_i - P_o)}{\frac{1}{2P_o}(a^2 - 1) - \frac{b}{3}(a^3 - 1)} \tag{36}$$

where

$$a = \frac{P_i}{P_o} \tag{37}$$

The ratio $P_o/\bar{P}$ has the same significance as the Martin–James compressibility factor. Under ideal gas conditions where $B_{11} = 0$, eqn. 34 reduces to eqn. 2.

EXPERIMENTAL

The packing material used in this study was 50–80 mesh Porapak S. Out of 100 random particles, the average particle diameter was measured to be 0.20 ± 0.02 mm by means of a Unitron (U-11) microscope having a micrometer scale in the eyepiece. A photomicrograph showed these particles to be smooth and generally quite spherical.

The packing material was first washed in tetrahydrofuran (THF) dried at 100°C, and degassed under vacuum while the temperature was slowly raised to 200°C and maintained there for about 5 min after which the heat was turned off. The cooled packing material was then added to a 10 % trimethylchlorosilane in benzene solution and after 20 min, the packing was filtered and washed with methyl alcohol and then dried at 100°C, under vacuum for three days.

The copper tubing (1/8 in. O.D. and 0.065 in. I.D.) was washed with acetone, THF, and methyl alcohol and then dried at room temperature by passing nitrogen gas through it.

The final 200-ft. column was made up of four 50-ft. sections which were packed separately. The ends of each section were terminated with approximately 1/16 in.-thick plug of G.E. Foametal. To prevent the plug from falling out, the ends of the copper tubing were gently filed towards the tube axis so as to form a slight lip over the plug. The four sections were joined together with Swagelok unions which were filled with the packing material. The final column was coiled on a length (~ 12 in.) of 4-in.-diameter brass pipe.

A Seiscor Model VIII high pressure and helium purge modified sampling valve having a sample volume of 0.5 μl was used throughout the study. In all experiments the sample pressure was below atmospheric and gave an effective sample size of 0.12 μl at S.T.P.

Most experiments were carried out at 0°C in a stirred and ice-filled bath or a temperature-controlled oil bath ($\pm$ 1/2°C).

The inlet pressure was measured with a 0–200 p.s.i. Marsh Master gauge which had an accuracy of better than 0.5 % of the pressure reading. The outlet pressure was measured with a mercury manometer to within $\pm$ 0.1 cm. Both pressures were measured before and after each experiment.

All gases except hydrogen were passed through a stainless steel enclosed Cu–CuO furnace maintained at about 850°C and through a molecular sieve (5A) trap.

Flow rate measurements were made by the method described elsewhere[24]. On the average the reproducibility was better than 0.01 %.

A 1-mV, 11-in. chart, 1-sec response Bristol recorder was used throughout. The chart drive motor was connected in parallel to a Lab-Chrom timer which served as a check on the accuracy of the chart advance.

A Beckman G.C.4 flame ionization detector was used in experiments where methane was the only constituent in the sample. In experiments involving other gases an Aerograph (250 mCi tritium source) electron capture detector was used in a "helium detector" mode. The voltage to the detectors was supplied by Keithley 240 power supply and the current through the detectors was measured by a Keithley 410 electrometer.

Further details of the precautions taken and experimental procedure are described elsewhere[25].

RESULTS AND DISCUSSION

Before the experimental data are presented, the manner in which $V_N{}^*$ were calculated will be discussed.

The net retention volume was calculated by means of eqn. 34, which requires that V_M be known. V_M is normally determined from the elution time of a non-sorbing solute, but in the present system the normal calibrating gases (air, methane) are known to interact quite strongly with the packing material. Of the several avenues open to overcome this problem, the following procedure was followed to determine V_M. Using helium as the carrier gas and an electron capture detector (used as helium detector) the corrected retention volume ($V_R{}^0$) of hydrogen was determined at several temperatures. It was found that there was a significant decrease in $V_R{}^0$ with increasing temperature, suggesting that hydrogen could not be regarded as non-sorbing solute. Unfortunately the limited temperature range covered did not allow extrapolation of $V_R{}^0$ *vs.* $1/T$ plot to $1/T = 0$, where $V_R{}^0 = V_M$ without an introduction of a large error.

Since $\log(V_R^0 - V_M)$ is a linear function of $1/T$ (ref. 26), this relationship was applied and $\log(V_R^0 - X)$ was plotted against $1/T$. The value of X was increased by 0.5 cc until a straight-line relationship was obtained. This particular value of X was chosen as V_M and was used in all the calculations.

The $B_{11}(T)$ values for He and Ar were calculated from a Beattie–Bridgeman type equation which has the form[27]

$$\frac{B_{11}}{V^*} = 0.461 - 1.158\left(\frac{T^*}{T}\right) - 0.503\left(\frac{T^*}{T}\right)^3 \tag{38}$$

where T^* and V^* are the characteristic temperature and volume, respectively. The values of T^* and V^* were obtained from the same source as eqn. 38.

$B_{11}(T)$ for CO_2 was calculated from eqn. 39 and the available tables[28].

$$B_{11}(T) = b_0 B_{11}^*(T^*) \tag{39}$$

where B_{11}^*, T^* and b_0 are the reduced second virial coefficient, the reduced temperature (as defined in ref. 28) and the steric parameter, respectively.

The second virial cross coefficients were calculated from an equation similar to that of eqn. 38 (ref. 27), that is

$$\frac{B_{12}}{V_{12}^*} = 0.461 - 1.158\left(\frac{T_{12}^*}{T}\right) - 0.503\left(\frac{T_{12}^*}{T}\right)^3 \tag{40}$$

where

$$T_{12}^* = (T_1^* \cdot T_2^*)^{1/2} \tag{41}$$

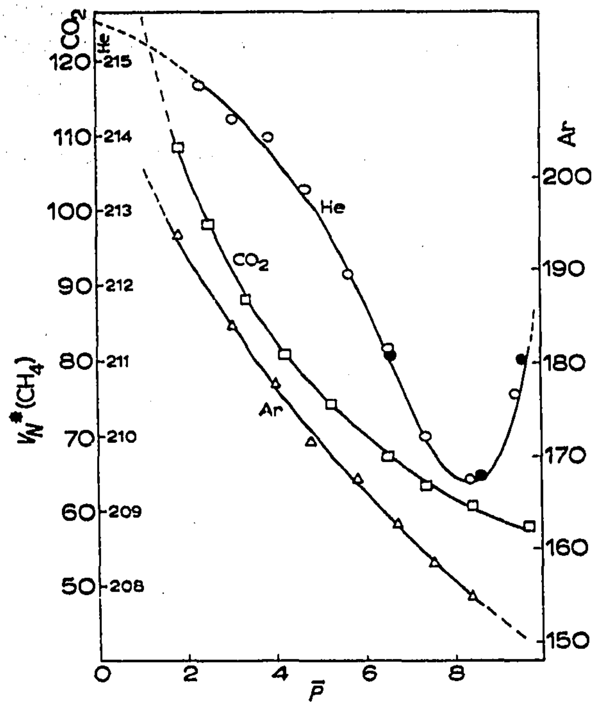
and

$$V_{12}^* = 1/2[(V_1^*)^{1/3} + (V_2^*)^{1/3}] \tag{42}$$

where as before subscripts 1 and 2 refer to the carrier gas and the solute.

According to eqn. 22, carrier gas adsorption is signaled by a decrease in V_N^* as the column pressure is increased. From what has been said before, the exact relationship between V_N^* and pressure cannot be determined unless the carrier gas adsorption isotherm is known. The trend, however, can be shown by plotting V_N^* against some suitable pressure variable which is related to P_i and P_o. For the present purpose we have chosen $\bar{P}$ (MARTIRE AND LOCKE's expression) as it best describes the condition of the column and most probably will be closer to the true pressure variable than pressure variables such as $[(P_i + P_o)]/2$ or P_i/P_o. Such plots of $V_N^*(CH_4)$ *vs.* $\bar{P}$ (mean column pressure) for He, Ar, and CO_2 are shown in Fig. 2. The helium plot shows that although helium gas is generally considered as being ideal, it does measurably interact with this surface even at 273°K. This plot is of considerable importance in that, unlike the other two, it allows extrapolation to the $P = 0$ region and consequently the determination of $V_N(0)$.

The unexpected minimum followed by a relative increase in V_N^* with increasing pressure is only observed in the helium plot. As it is indicated by the dark circles, this region is quite reproducible. The two experiments were performed independently, that is, they were interspersed by the Ar and CO_2 experiments. Consequently, this result is not an artifact of the working system and has to be accepted as genuine. The reason for this trend will be discussed elsewhere since it is related to other factors. It is suffi-



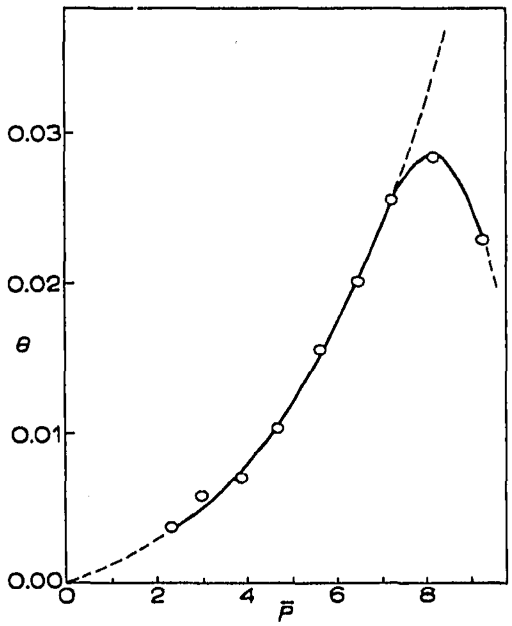
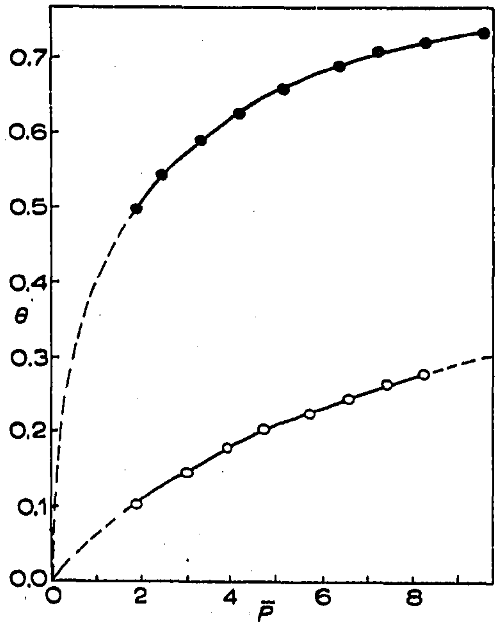


Fig. 2. $V_N^*(CH_4)$ as a function of $\bar{P}$ for He (○ and ●), Ar (△), and CO_2 (□). Carrier gas at 0 ± 1/2 °C.

Fig. 3. θ (He) as a function of $\bar{P}$.



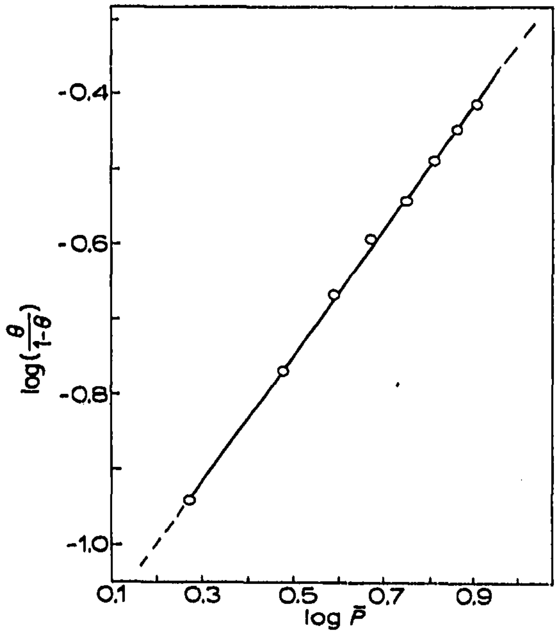


Fig. 4. θ (Ar, ○) and θ (CO_2, ●) as a function of $\bar{P}$.

Fig. 5. Log $\{\theta/(1 - \theta)\}$ *vs.* log $\bar{P}$ for Ar.

cient to say at the present time that this anomalous effect is a by-product of a secondary flow mechanism in which only helium can participate. Fig. 2 shows that at constant $\bar{P}$ the magnitude of V_N^* is in the opposite direction to the anticipated order of carrier gas interaction; this of course is expected if V_N^* is related to $(1-\theta)$.

The degree of interaction of the carrier is perhaps more meaningful in terms of θ. A plot of θ *vs.* $\bar{P}$ for helium is shown in Fig. 3, whereas those for Ar and CO_2 are shown in Fig. 4. It may be mentioned again that in the helium plot the results at the highest $\bar{P}$ become meaningless if the above comment is not considered. Fig. 4 shows that in the case of Ar almost 30 % of the surface is apparently covered at $\bar{P} \simeq 8.5$ atm whereas in the case of CO_2 coverage is about 75 % at the same $\bar{P}$. The actual values are probably somewhat higher.

It was found that for all three gases θ could be related to the variable $\bar{P}$ through the following expression

$$\log\left(\frac{\theta}{1-\theta}\right) = A + n \log \bar{P} \tag{43}$$

In all cases the fit was quite good, as it is illustrated by Fig. 5, where $\log\{\theta/(1-\theta)\}$ is plotted against $\log \bar{P}$ for Ar. After taking antilogs and rearrangement, eqn. 43 becomes

$$\theta = \frac{k\bar{P}^n}{1 + k\bar{P}^n} \tag{44}$$

This pseudo adsorption isotherm is neither Langmuir nor Freundlich, it is a combination of both. It has the property of reducing to the Freundlich form at low pressures, and exhibits the characteristic Langmuir plateau at high pressures. It, in fact, becomes the Langmuir adsorption isotherm when $n = 1$.

This equation has been used advantageously[29–31] and is preferred to the Freundlich or Langmuir equation in many cases.

The k and the n constants for the three carrier gases are given in Table I.

TABLE I

ADSORPTION PARAMETERS FOR THE CARRIER GASES IN TERMS OF CH_4 AS SOLUTE AT 273°K

	k	n
He	8.158×10^{-4}	1.7010
Ar	6.890×10^{-2}	0.8191
CO_2	6.523×10^{-1}	0.6438

According to SIPS[32] the maximum value that n can have is ± 1, but for physically real systems this can only be 1. According to Table I, n for helium is greater than 1 (1.7). This is probably in part an artifact from the choice of the pressure variable.

A comparison was made to determine the validity of these pseudo adsorption isotherms. For each working pressure of each gas, θ was calculated by two different methods. In the first case θ was calculated from eqn. 44. In the second case θ was calculated by assuming the relationship of eqn. 44 to hold but in the place of $\bar{P}$ the local value of P was substituted as a different segment of the column was considered (at intervals of 1 in.). The resulting θ's were then summed and divided by the total number of contributions (2,400). The expressions used to relate x (column distance) and θ were eqn. 44, 45 and 46.

$$P = \frac{yb}{2} + \left[2y + \left(\frac{yb}{2}\right)^2\right]^{1/2} \tag{45}$$

and

$$y = \frac{x}{L}\left(\frac{P_i^2}{2 + bP_i} - \frac{P_o^2}{2 + bP_o}\right) + \frac{P_o^2}{2 + bP_o} \tag{46}$$

where as before b is given by eqn. 35.

The expressions for P and y were derived from Darcy's Law, in which allowance is made for gas imperfections. If we relate θ_1 and θ_2 to the first case and the second case, respectively, then the percent deviation is expressed as

$$\frac{\theta_1 - \theta_2}{\theta_1} \times 100 = \%\ \text{deviation} \tag{47}$$

This relationship for all the three gases is given in Fig. 6. In the case of He, these deviations are positive and some ten times larger than Ar and CO_2, in which cases they are negative and have an average value of about $-1.5\,\%$. On first inspection it appears that at least for the Ar and the CO_2 case the adsorption isotherm may be well approximated by eqn. 44. Approximations of this magnitude cannot be made, however, if the GSC system is being used as a tool in determining the B_{12} terms as suggested by LOCKE. In support of this an example is drawn from the present study. For the argon experiment ($\bar{P} = 4.77$) the % deviation is about $-1.6\,\%$. Utilizing θ_2 rather than θ_1 to determine V_N^* from $V_N(0)$, and consequently the B_{12} term, it is found that there is a difference of some 67 % between the two values.

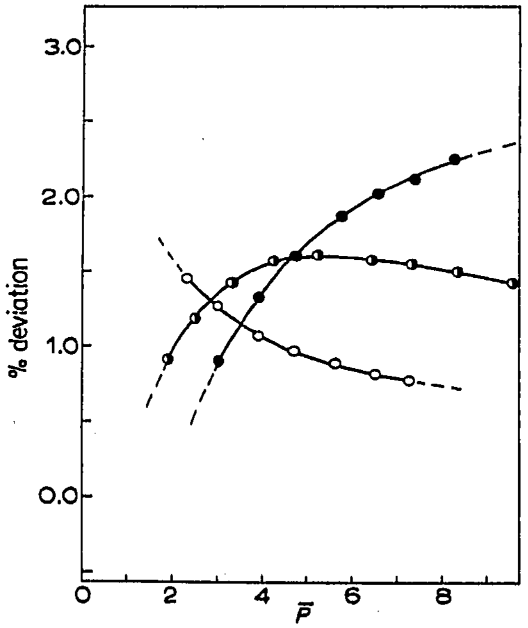


Fig. 6. $\{(\theta_1 - \theta_2)/\theta_1\} \times 100$ as a function of $\bar{P}$. ○, He (10 × ○); ◑, CO_2 (− 1 × ◑); ●, Ar (− 1 × ●).

In conclusion, it appears that GSC is not suitable for the determination of the B_{12} terms unless the exact expression for the carrier gas adsorption isotherm is known precisely but not from static systems where only the pure carrier gas is involved, but in terms of θ (apparent) where the relative adsorption of the solute and the carrier gas are taken into account. Such would be perhaps a fruitless task considering the effort involved and comparing this to the relative case offered by GLC.

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