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GAS–SOLID CHROMATOGRAPHY ON OPEN-TUBULAR COLUMNS: AN ISOTOPE EFFECT

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SUMMARY

Attempts to provide porous-layer open-tubular (PLOT) columns with Chromosorb 102, molecular sieve 5A, molecular sieve 13X and activated charcoal are described. The high separation performance of these PLOT columns at relatively high separation temperatures and shorter separation times is demonstrated by the example of the separation of low-boiling gases and isotope molecules. Precise measurements of the temperature dependence of separation factors and specific retention volumes supply the basis for the calculation of differences in the enthalpy and entropy of adsorption. A model of a molecular size isotope effect is proposed and validated experimentally.

INTRODUCTION

Isotope effects in adsorption are now generally understood, but there is no analytic expression for the interaction of each kind of gas with particular adsorbents. One of the main difficulties in this connection is the absence of spectroscopic methods for the detection of molecular physical changes in chemical compounds in the adsorption state. Therefore, it is necessary to establish isotope effects in model tests simulating the various special interactions and to interpret them theoretically.

One of the possible model situations for the investigation of isotope effects in adsorption is gas chromatography, which permits the determination of physico-chemical quantities such as enthalpy of adsorption and separation factors from measurable quantities such as retention times as a function of test parameters such as temperature. Consequently, it was the aim of this study to produce appropriate separation columns that might provide information on isotope effects by enabling the required quantities to be determined experimentally. The main field of application of gas chromatography is, of course, analytical chemistry. Hence insights gained from

this study into adsorption and isotope effects occurring on adsorption may also provide important conclusions for isotope gas chromatography.

The high separation efficiency of capillary columns allows separations that are not practicable with packed columns. We therefore attempted to use capillaries to test the separation of isotope molecules, which is one of the most difficult tasks.

For the gas chromatographic separation of isotope systems of low-boiling substances such as $^1H_2-^2H_2-^3H_2$, $^{16}O_2-^{18}O_2$. $^{14}N_2-^{15}N_2$, $^{20}Ne-^{22}Ne$, $^{36}Ar-^{40}Ar$, $^{82}Kr-^{86}Kr$, $^{12}CO-^{13}CO$ and $^{12}CH_4-^{13}CH_4$, no suitable liquid stationary phase has been found so far. On the one hand, a suitable stationary phase should be applicable at room temperature so that the columns are durable, and on the other it ought to provide a sufficient solvent power for different substances and a sufficiently large separation factor for isotope systems. As the physical condition of the stationary phase may be either liquid or solid, only those solids that are durable when applied on the inner wall of a capillary column for high quality separation are applicable.

So far, only silica gels produced by alkaline corrosion of glass have been used as sorbents in gas–solid chromatographic capillaries[1-5]. Such columns provide high capacity ratios and high performance only at low temperatures. Possibilities of coating them with adsorbents such as molecular sieves, carbon molecular sieve, activated charcoal, porous polymers or alumina were lacking. However, the application of such stationary phases permits work at high temperature and high capacity ratio, if it is possible to produce thick coatings (about 30 μm). Sharp, symmetrical peaks would be achieved within short separation times.

For the $CH_4-C^2H_4$ separation, for example, the separation factor inverts with temperature. For the logarithm of the retention volumes of methane and deutero-methane, Bruner et al.[2] found

$$\ln\left[\frac{V_R(CH_4)}{V_R(C^2H_4)}\right] = \frac{A}{T^2} - \frac{B}{T} \tag{1}$$

an expression having the same analytical form as the logarithm of the vapour pressure ratio of the two isotope-substituted substances. The isotope effect results from the sum of two constituents with opposite signs, and with increasing temperature a positive "normal" isotope effect may turn into a negative "inverse" effect. The plot of the expression $T \ln[V_R(CH_4)/V_R(C^2H_4)]$ vs. $1/T$ provides straight lines that intersect the abscissa at the so-called inversion point, from which the constants A and B can easily be determined. The result is inversion of the peak sequence. At high temperatures (e.g., room temperature) first C^2H_4 then CH_4 is eluted. This is important for the determination of traces of $CH_3{}^2H$ in CH_4 as main component, as the demands on the separation performance in the reverse case are considerably higher. A column that separates the deuteromethanes is also applicable to studies of the deuterium isotope effect of methane.

The only possibility for the high-performance separation of low-boiling isotopic species seems to be to use capillaries with a thick coating of suitable adsorbents. For this purpose, the development of a coating method for providing high-performance columns of high permeability and great length is necessary. Glass or fused silica should be used as the capillary material for reasons of low surface activity and transparency.

EXPERIMENTAL

Coating experiments

For making pure adsorption capillaries only the corrosion techniques mentioned were successful. A static method has been suggested by Halasz and Horváth[6–8] and used successfully for many separations. They filled long steel capillaries (up to 50 m) with stable suspensions of many solids and liquid stationary phases, closed the capillaries at one end and passed them through a micro-furnace, where the solvent evaporated through the open end, then into a large furnace to prevent recondensation of the solvent. In this process the solid that settles on the capillary wall is retained, while the solvent vapour flowing continuously over the already settled solid coating has an smoothing effect. The same technique was used by Ettre and co-workers[9,10] to produce 45-m separation columns with 57 000 plates. For this purpose, stable suspensions with particle sizes between 1 and 10 μm are necessary.

Adhesiveness of dispersed adsorbents

The greatest problem encountered in the production of sorbent-coated capillary columns is the durability of the solid coatings on smooth walls. The adhesiveness of these solid particles is partly based on adhesion between the particles and the surface to be coated, and partly on cohesion between the particles themselves. It is known from experience that adhesion is lower with larger particles. With finely dispersed substances, effectively adhering coats are obtained, as in thin-layer chromatography. According to Patat and Schmid[11], the binding between the particles results from Van der Waals forces, whose influence decreases with the sixth power of distance. Further, according to Cremer[12], adhesiveness depends on the kind and pretreatment of the dispersed solid, its grain size and the pretreatment of the supporting surface. Rumpf[13] found that tensile strengths up to 1 MPa result from Van der Waals forces at particle sizes between 0.01 and 1 μm and at a grain distance of 0.01 μm. Compact solids have tensile strengths of more than 100 MPa. The durability of a settled layer of finely dispersed particles depends largely on the radius of curvature of the support surface. As the radius of curvature is very small in capillary columns, a highly curved ring of high stability is produced, comparable to an arched bridge under load. This ring will break down only if sections are removed from inside.

Layer thickness

The thickness of the adsorbent layer in porous-layer open-tubular (PLOT) columns must be suitable for the particular task to be fulfilled. The minimum layer thickness required depends mainly on the distribution coefficient of the components to be separated and hence on the kind of adsorbent and on the separation temperature. On the other hand, the layer must not be too thick, otherwise diffusion in its stationary phase will contribute to peak broadening, *i.e.*, increase the height equivalent to a theoretical plate (HETP). Hence it is an optimization problem to find the correct layer thickness. The layer thickness may be controlled with the help of the concentration of the solid in the suspension. In addition, it is possible to vary the radius of the uncoated capillary, R_K, as the column diameter influences the loading capacity.

From the relationship

$$\frac{R_K^2 \pi}{100} = \frac{(R_K^2 - r^2)\pi}{c} \tag{2}$$

where c is the solid concentration (vol.-%) the free radius r of the coated capillary is calculated as

$$r = R_K \sqrt{1 - \frac{c}{100}} \tag{3}$$

As $R_K = r + d_s$ where d_s is the layer thickness, we obtain

$$d_s = R_K \left(1 - \sqrt{1 - \frac{c}{100}} \right) \tag{4}$$

Fig. 1A shows the layer thickness as a function of the solid concentration for the radii $R_K = 125$, 160 and 265 μm. The ratio between the gas volume and the volume of
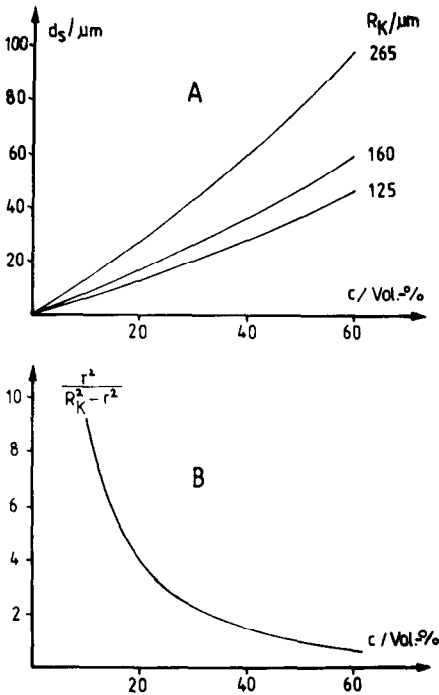

Fig. 1. (A) Layer thickness (d_s) as a function of the concentration of adsorbent (c) in the suspension. (B) Cross-sectional area ratio (gas/adsorbent) as a function of the content of adsorbent in suspensions.

the stationary phase is proportional to the value $r^2/(R_K^2 - r^2)$. From eqn. 3, the cross-section ratio may be calculated:

$$\frac{r^2}{R_K^2 - r^2} = \frac{100}{c} - 1 \tag{5}$$

Fig. 1B shows the plot of this function against c. The large increase in the cross-section ratio with decrease in the amount of solid in the suspension indicates that the application of high solid concentrations, *e.g.*, 20–50 vol.-%, will be necessary. From eqn. 5,

$$c = 100\left(1 - \frac{r^2}{R_K^2}\right) \tag{6}$$

and, as $r = R_K - d_s$,

$$c = 100\left[1 - \frac{(R_K - d_s)^2}{R_K^2}\right] \tag{7}$$

Preparation of suspensions

It was observed in all coating experiments that the suspension must meet the highest demands. This holds, in particular, for the mentioned tendency for sedimendation, the evaporation behaviour and the filling capacity of the capillaries. It was observed with all suspensions that even fine solids, owing to their high surface energy and the high collision density of the particles, produce particle enlargement and consequently sedimentation at high solid concentrations after various times. Particle enlargement before evaporation results in solid layers with low packing densities and hence produces loose layers of low durability. As during evaporation of the dispersion medium linear vapour flow-rates amounting to a few metres per second occur in the capillary, clogging of the inside is a frequent consequence. To prevent particle enlargement due to movement of particles and consequences such as sedimentation, clogging, non-uniform layer thickness and poor durability of the layers, it is advantageous to add thickeners to the suspensions. These greatly reduce the translation movements of the particles.

The thickener should meet the following demands: it must be soluble in the dispersion medium or able to swell; the necessary concentration must be as low as possible; the micropores of the adsorbent must not be clogged; when the adsorbent is activated (200–500°C), decomposition products must not affect the surface, or there must be no decomposition; and it should not have a tendency to foam during evaporation. Suitable substances are colloids, which in addition should be thixotropic. They make the filling of very long capillaries feasible.

The dispersion medium must also meet certain demands: viscosity, density and polarity greatly influence the sedimentation tendency; low boiling point and high evaporation speed simplify evaporation; and low surface tension and low foaming tendency prevent clogging. Many empirical experiments are necessary in order to select a suitable dispersion medium for a given solid, as little experience has been

gained in this field so far. In fact, the preparation of the suspension decides the success of the coating procedure.

RESULTS AND DISCUSSION

Separation with Chromosorb 102

A glass capillary (15 m × 0.30 mm I.D.) was coated with Chromosorb 102 using the static method. The layer thickness was about 25 μm. For activating the stationary phase, a heating rate of 2°C min^{-1} from 20 to 190°C was used under a stream of pure hydrogen. After an activation period of 3 h at 190°C it was just possible at -46°C to separate C^2H_4 from CH_4 in this sequence with a resolution of about 10%. The capacity ratio for CH_4 was 1.06 and the separation factor $\alpha(CH_4/C^2H_4)$ could be determined, in good agreement with Czubryt and Gesser[14], to be 1.065. The separation time was about 2.5 min. An attempt to determine the function log α *versus* $1/T$ for this system failed owing to poor separation at both lower and higher temperatures.

For substances having a higher value of k from the beginning, *e.g.*, water, this separation column is possibly appropriate. Considering that the vapour pressure ratio is $p_{H_2^{16}O}/p_{H^2H^{16}O} = 1.062$ at 46°C, then 13 000 theoretical plates would be sufficient for the complete separation of these molecules for $k = 10$. Later, De Zeeuw[15,16] succeeded in coating fused-silica PLOT columns with Porapak Q for the separation of gases and low-boiling polar and non-polar liquids. Such columns are now available from Chrompack as PoraPLOT Q.

Separation with molecular sieve 5A

By applying an aqueous suspension containing molecular sieve crystals about 1 μm in size at a concentration of 35 vol.-%, a capillary column was coated with a uniform, thick porcelain-like rigid layer of 30 μm thickness with good adhesiveness using the static method. A typical cross-section is shown (1:100) in Fig. 2. Even at gas speeds of 1 m s^{-1}, blow-out of molecular sieve was not observed. Glass capillaries having a molecular sieve layer may be straightened, and column parts may be assembled manually. As the molecular sieve contains a lot of water in the micropores and hollow spaces, heating must begin carefully. Heating proceeded at a rate of 1°C min^{-1} from 20 to 100°C and was kept at the latter value for 8 h. Then the column was heated at the same rate to 350°C and subsequently activated for 2 h, always under a flow of pure hydrogen. Fast heating of the newly prepared column with a high water content may easily produce considerable hydrolysis of the molecular sieve and lead to its destruction.

For checking and optimizing the separation efficiency, chromatograms were obtained at gas speeds between 22.4 and 61.5 cm s^{-1} for samples containing He, Ar, O_2, N_2, C^2H_4 and CH_4. Fig. 3 shows a typical chromatogram. At room temperature all the components mentioned were completely separated. It should be noted that the whole chromatogram takes only about 25 min to acquire and for methane at the peak width at half-height is only 10 s. The peak symmetry is good; the tailing of the C^2H_4 peak is due to CH^2H_3 still contained in the sample, produced during the formation of C^2H_4 from aluminium carbide and ^2H_2O. Even Ar and O_2 are completely separated. The optimum mean linear velocity for hydrogen is 31.3 cm s^{-1} measured with CH_4.

Table I gives the separation factors and their logarithms calculated for the pairs
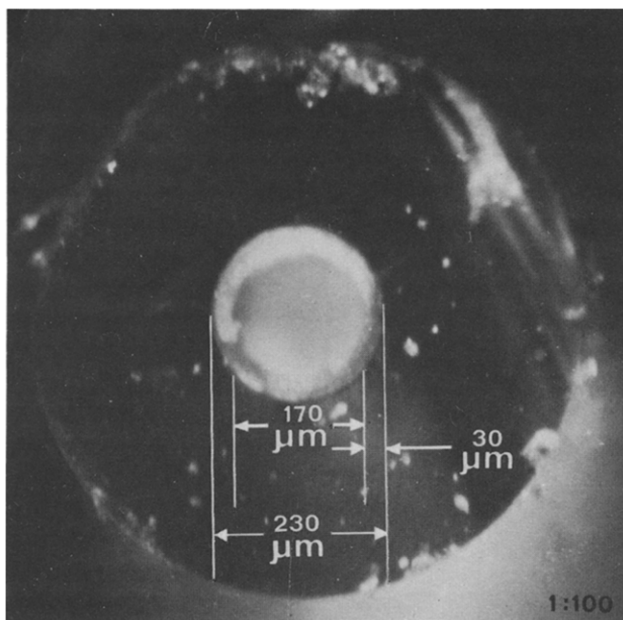
Fig. 2. Cross-section of a molecular sieve 5A capillary (1:100). Capillary I.D. = 230 μm; layer thickness = 30 μm.

O_2–Ar, N_2–O_2, CH_4–N_2 and CH_4–C^2H_4, positioned close to each other in the chromatogram. Fig. 4 shows that the separation factor for N_2–O_2 increases strongly and that for Ar–O_2 increases slightly in a linear fashion with $1/T$. Over the whole temperature range, however, α remains constant, within experimental error, for CH_4–C^2H_4 (the error is smaller than $\pm 0.1\%$). It must be added that above 50°C separation is no longer complete, which leads to errors in retention time determina-
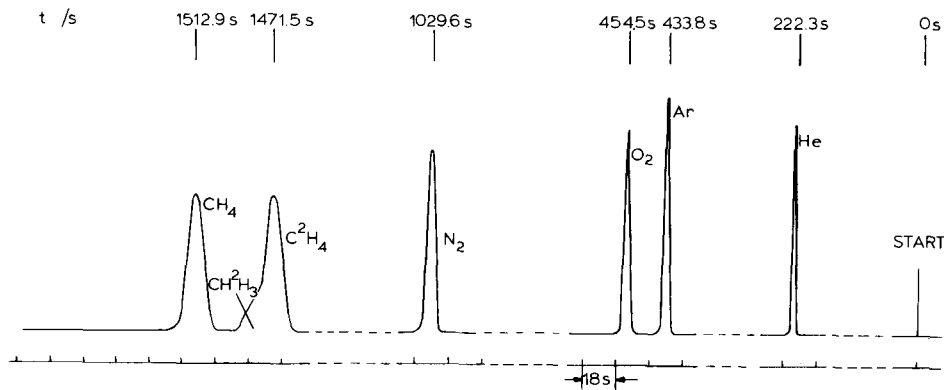

Fig. 3. Molecular sieve 5A PLOT column. I.D. = 330 μm; layer thickness = 30 μm; length = 67 m; temperature = 22.3°C; 1.4 bar H_2; microthermal conductivity detector; $HETP_{eff.}$ = 0.71 mm; effective plate number = 94 150; capacity ratio (CH_4) = 5.8; α_{CH_4/C^2H_4} = 1.0336.

TABLE I

DEPENDENCE OF RELATIVE RETENTION (α) AND LN α ON THE SEPARATION TEMPERATURE

| Temperature		$10^3/T \ (K^{-1})$	$\alpha_{O_2/Ar}$	ln α	α_{N_2/O_2}	ln α	α_{CH_4/N_2}	ln α	α_{CH_4/C^2H_4}	ln α
°C	K									
−45	228.2	4.38	1.21	0.191	11.04	2.40	1.19	0.17	1.03185	0.031
−24	249.2	4.01	1.18	0.166	6.36	1.85	1.35	0.30	1.03374	0.033
− 5.0	268.2	3.73	1.12	0.113	4.44	1.49	1.49	0.40	1.03407	0.034
0.0	273.2	3.66	1.12	0.113	4.55	1.52	1.49	0.40	1.03359	0.033
10.0	283.2	3.53	1.11	0.104	4.02	1.39	1.53	0.425	1.03446	0.034
30.3	303.5	3.30	1.09	0.086	3.28	1.19	1.62	0.48	1.03414	0.034
30.3	303.5	3.30	1.10	0.095	3.26	1.18	1.62	0.48	1.03279	0.032
40.2	313.4	3.19	1.08	0.077	3.00	1.10	1.65	0.50	1.03392	0.033
50.2	323.4	3.09	1.08	0.077	2.77	1.02	1.68	0.52	1.03390	0.033
60.0	333.2	3.00	1.06	0.058	2.59	0.95	1.71	0.54	1.03015	0.030
70.2	343.4	2.91	1.05	0.049	2.43	0.89	1.73	0.55	1.03198	0.031
80.1	353.3	2.83	−	−	−	−	1.74	0.55	1.03053	0.030
95	368.2	2.72	−	−	−	−	1.75	0.56	−	−
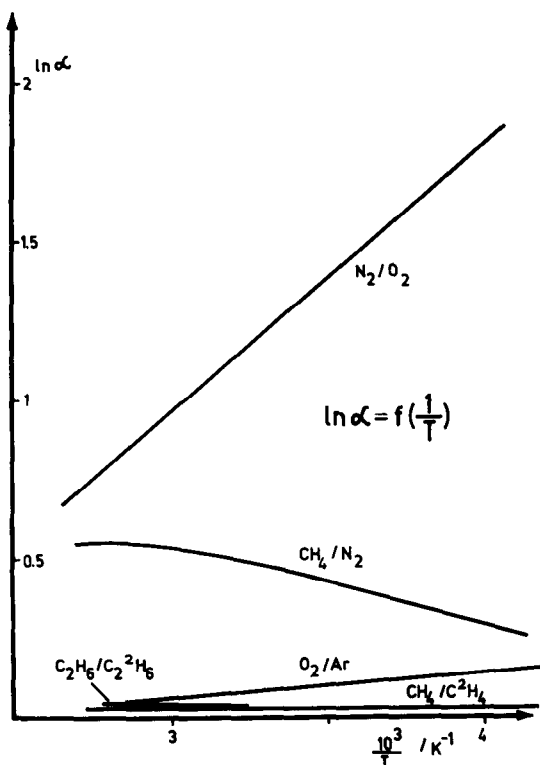
Fig. 4. Plots of ln α *versus* 1/T.

TABLE II

DIFFERENTIAL ENTHALPIES OF ADSORPTION $(\Delta H)_{GC}$ CALCULATED FROM LINEAR PLOTS OF LN V_g VERSUS $1/T$

m = slope, b = intercept on the ordinate, r^2 = regression coefficient.

Gas	m	b	r^2	ΔH_{GC} (kcal mol^{-1})
Ar	547.57	−1.311	0.9996	−2.505
O$_2$	583.70	−1.393	0.9998	−2.670
N$_2$	964.57	−2.125	0.9996	−4.413
C^{2}H$_4$	869.41	−1.621	0.9998	−3.978
CH$_4$	868.26	−1.602	0.9996	−3.972

tions. The constancy of the α value, which seems surprising, indicates an abnormal behaviour of methane towards the absorbent, as can also be seen from the plot for CH$_4$–N$_2$. For this pair, the separation factor even decreases with decreasing temperature. That the separation of argon and oxygen is almost as difficult as the separation of isotope molecules is shown by the separation factors at room temperature.

Evaluation of separation factors for the system CH$_4$–C^{2}H$_4$ between 228.2 and 323.4 K results in a mean value of α = 1.0336 ± 0.0008. At this separation factor and a value of k = 5.75 (measured at 22.3°C), complete separation requires 47 000 plates; the performance of a 67-m capillary is more than twice as efficient.

From the slopes of the straight lines of log V_g^{PT} versus $1/T$ (where V_g^{PT} is the corrected specific retention volume), the differential enthalpies of adsorption, ΔH_{GC}, can be calculated. In order to achieve the highest possible precision, linear regression calculations were carried out. The results are given in Table II. The parallel course of
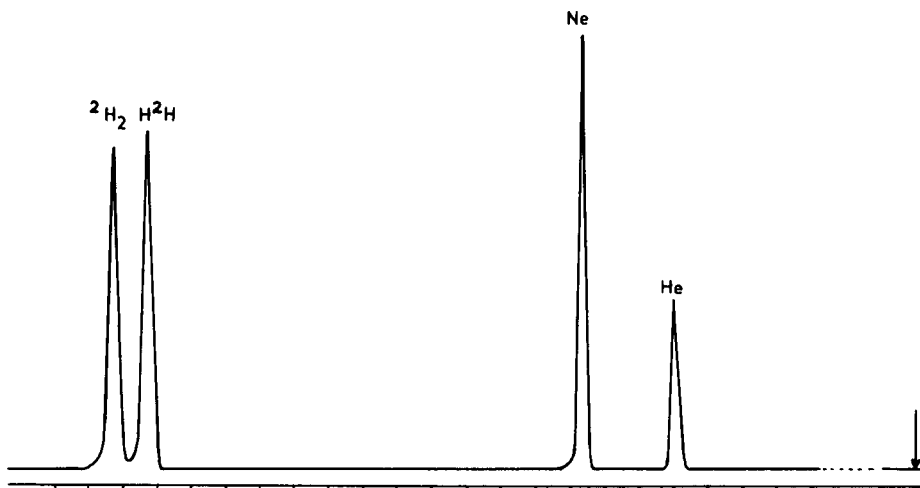

Fig. 5. Separation of H^{2}H and ^{2}H$_2$. PLOT column (see Fig. 3). Temperature = −78.5°C; $\alpha_{^2H_2/H^2H}$ = 1.0622; capacity ratio (^{2}H$_2$) = 0.574; separation time = 4.6 min (1 cm = 6 s).

the straight lines for CH_4 and C^2H_4 shows that the ΔH values are identical for both substances (the slight difference of 0.006 kcal mol^{-1} is within the measurement tolerance).

The high separation efficiency of the molecular sieve 5A PLOT column may also be demonstrated by the complete separation of H^2H and $^2H_2$ (Fig. 5) in an extremely short time and at a high separation temperature that was previously impossible. Recently, molecular sieve PLOT columns have been successfully produced with fused silica[17,18] and are now available in high quality.

The constancy of the separation factor α in the molecular sieve 5A column for CH_4 and C^2H_4 over a wide range of temperatures is at first glance an unexpected result. All previous gas chromatographic work on these isotopic species[4,14,19–22] yielded a distinctive dependence of the relative retention on temperature. In the usual representation,

$$\ln \alpha = \ln\left(\frac{K}{K'}\right) = \ln\left(\frac{k}{k'}\right) = \ln\left(\frac{t_R}{t'_R}\right) = -\frac{\Delta(\Delta H)}{RT} + \frac{\Delta(\Delta S)}{R} \tag{8}$$

where K = distribution coefficient, k = capacity ratio, t_R = net retention time, the quantity $\Delta(\Delta H) = \Delta H - \Delta H'$ is assigned to the difference in the changes in enthalpy of the isotopic species passing from the mobile to the stationary phase and the quantity $\Delta(\Delta S) = \Delta S - \Delta S'$ to the difference in the changes in entropy; the primed symbols apply to the heavier isotope. Lack of temperature dependence of the separation factor α,

$$\ln \alpha = \ln\left(\frac{K_{CH_4}}{K_{C^2H_4}}\right) = \ln\left(\frac{t_{R\,CH_4}}{t_{R\,C^2H_4}}\right) = \frac{\Delta(\Delta S)}{R} \tag{9}$$

means that no difference in the enthalpy of adsorption of the isotopic species can be observed and that an entropic term, perhaps purely steric in nature, is responsible for the fractionation. The gas chromatographic process comprises not only the establishment of a local thermodynamic equilibrium but also a kinetic process, in our case the movement of the molecules to be separated through the framework of the molecular sieve, that is, through the windows, channels and cavities of the zeolite. Therefore, $\Delta(\Delta S)$ need not be an entropic difference in the common thermodynamic sense. We suggest that the difference in the retention times of methane and methane-d_4 can be explained by means of the difference in the molecular sizes of the two isotopic species.

Kuchitsu and Bartell[23] investigated the effect of the anharmonicity of the internal vibrations on the bond length of polyatomic molecules and showed that the molecular dimensions of C^2H_4 must be some thousandth parts smaller than those of CH_4. The theoretical analysis was supported by experimental spectroscopic constants, diffraction data and scattering experiments. Grigor and Steele[24] explained the differences in the physical properties of liquid methane and methane-d_4 (including the vapour pressure isotope effect) by means of the assumption that the C^2H_4 molecule is 0.4% smaller than that of CH_4. In the same way, Gainar et al.[25] succeeded in interpreting the isotope effect on the virial coefficient. The diameter of the CH_4 molecule, estimated at $4.0 \cdot 10^{-8}$ cm, is nearly as the pore width of molecular sieve 5A

$(5.0 \cdot 10^{-8} \text{ cm})$. The difference of $0.016 \cdot 10^{-8}$ cm between the diameters of CH_4 and C^2H_4 probably leads to a sieve effect. This may be shown by the following simple consideration.

The entrance windows of the zeolite should be nearly circular openings of diameter D. The nearly spherical CH_4 molecule of diameter σ and the C^2H_4 molecules with a smaller diameter $\sigma - \Delta\sigma$ must pass through. For this the centres of the molecules have to go through a circular area of diameter $D - \sigma$ or $D - (\sigma - \Delta\sigma)$, respectively (Fig. 6, dotted areas). The probability of passing through the windows is proportional to these areas, and if this quantity controls the stay in the zeolite framework, the ratio of the retention times of the isotopic species must be the reciprocal of the ratio of these areas. Hence

$$\alpha = \frac{t_{R\ CH_4}}{t_{R\ C^2H_4}} = \frac{F_{C^2H_4}}{F_{CH_4}} = \frac{\frac{\pi}{4}[D - (\sigma - \Delta\sigma)]^2}{\frac{\pi}{4}(D - \sigma)^2} \tag{10}$$

The heavier isotopic molecule has the greater chance of passing through the pores and therefore has the shorter retention time. Simple mathematical operations yield

$$\ln \alpha = \frac{2\Delta\sigma}{D - \sigma} = \frac{\Delta(\Delta S)}{R} \tag{11}$$

(valid for $|\Delta\sigma| \ll |D - \sigma|$).

Fig. 7 shows the strong dependence of the separation factor on the quantity $D - \sigma$; the difference in molecular diameters is assumed to be $\Delta\sigma = 0.016 \cdot 10^{-8}$ cm. The separation factor $\alpha = 1.0336 \pm 0.0008$ for methane and methane-d_4 in the 5A column corresponds to $D - \sigma = (0.97 \pm 0.1) \cdot 10^{-8}$ cm (see Fig. 7). Hence we obtain a pore
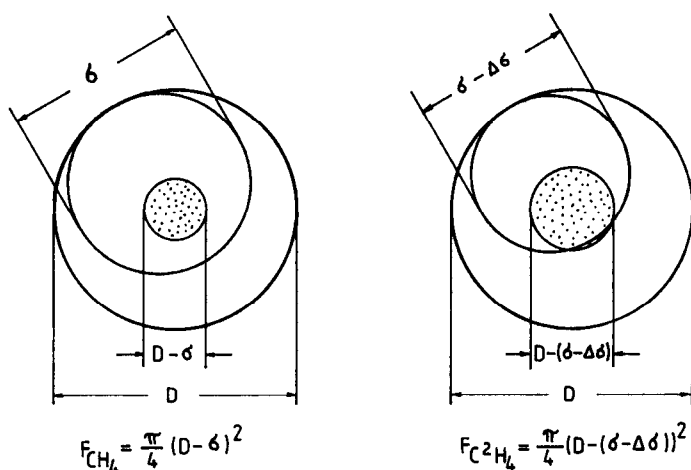

$$F_{CH_4} = \frac{\pi}{4}(D - \sigma)^2 \qquad F_{C^2H_4} = \frac{\pi}{4}(D - (\sigma - \Delta\sigma))^2$$

Fig. 6. Comparison of the available areas (dotted circles) for CH_4 and C^2H_4 to pass through pore openings.
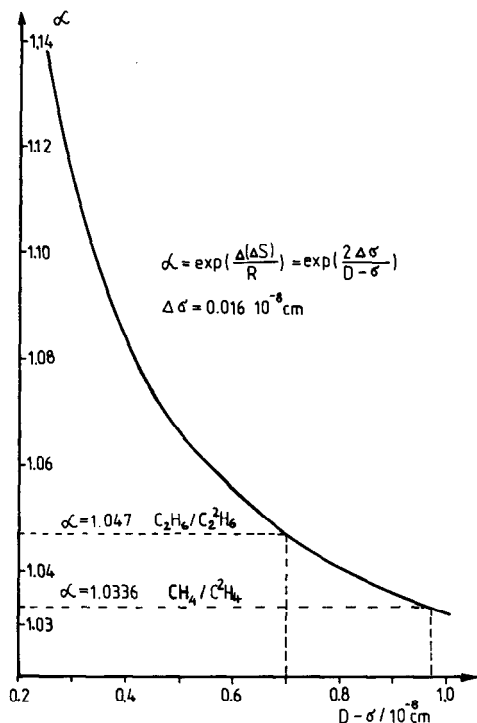
Fig. 7. Increase in separation factor α with diminishing difference between pore width and molecular diameter.

width of $(4.97 \pm 0.1) \cdot 10^{-8}$ cm for molecular sieve 5A. This value demonstrates consistency with the common picture of 5A zeolite. Eqn. 11 gives $\Delta(\Delta S) = R \ln \alpha = 0.0657$ cal mol^{-1} K^{-1}, which is a reasonable value for the differential entropy of adsorption for the CH_4–C^2H_4 separation.

In order to check our explanation of the abnormal isotope fractionation in zeolites, we tried to reduce the difference $D - \sigma$ by choosing isotopic molecules with a greater diameter. The pair C_2H_6–$C_2{}^2H_6$ seemed to be suitable; gas chromatographic conditions allowed evaluations in a high temperature range, from 44.5 to 80°C. The observed separation factor decreases only insignificantly with increasing temperature (see Fig. 4), which may result from the non-spherical form or (in comparison with the CH_4 molecule) additional intermolecular motions of the C_2H_6 molecule. Inserting the measured isotope separation factor $\alpha = 1.047$ at 44.5°C and the value $\Delta \sigma = 0.016 \cdot 10^{-8}$ cm (which seems reliable[26] also for the difference in the mean diameters of the C_2H_6 and $C_2{}^2H_6$ molecules) into eqn. 11, one obtains $D - \sigma = 0.7 \cdot 10^{-8}$ cm. This corresponds to an effective diameter $\sigma = 5.0 - 0.7 = 4.3 \cdot 10^{-8}$ cm of the C_2H_6 molecule, which is in good accord with the common value obtained, $e.g.$, from the transport properties of C_2H_6.

The gas chromatographic separation of isotopic compounds in connection with the very simple model of a molecular sieve has served as a means of determining effective pore widths from known effective molecule diameters and $vice\ versa$. Of

course, the reliability and range of applicability of the model should be investigated. With the estimated separation factor $\alpha_{C_2H_6/C_2^2H_6} = 1.047$ and a value $k = 49.3$, complete separation should require 19 000 plates. The column had a length of 18.8 m and for $C_2^2H_6$ an effective performance of 29 500 plates at 44.5°C. Therefore, complete separation was easily obtained (Fig. 8). In spite of the relatively high temperature, the separation of argon and oxygen is also complete, in a separation time of less than 3 min. The same effect was achieved by Heylmun[27] with a 4.5-m column packed with 5A molecular sieve at -72°C and a separation time of 30 min. Our capillary separates N_2 and Kr in less than 6 min.

Methane and methane-d₄ on a zeolite 13X capillary

In order to avoid the limiting influence of steric hindrance to the movement of methane molecules in zeolite 5A on the isotope fractionation, a zeolite 13X capillary column of length 53 m was prepared using an aqueous suspension. It should utilize the well known differences in polarizability of isotopic compounds[20]. In order to use eqn. 8 for a rough calculation of the expected separation factor for CH_4/C^2H_4, the zeolite 13X was modelled by an adsorbing area, which could be the surface of the supercages. The smaller C^2H_4 molecules take up slightly less area than the larger CH_4 molecules, so the probability of settling on the surface is greater for C^2H_4 than for CH_4 molecules. This leads to a contribution to the entropic term:

$$\frac{\Delta(\Delta S)}{R} = \ln\left[\frac{(\sigma - \Delta\sigma)^2}{\sigma^2}\right] = -2 \cdot \frac{\Delta\sigma}{\sigma} \tag{12}$$

On the other hand, the relative differences in the polarizability, $\Delta a = a - a'$, of isotopic pairs are connected with the relative differences in the adsorption energies[28]. The equation

$$\frac{\Delta(\Delta H)}{\Delta H} = \frac{\Delta a}{a} - f\left(\frac{\Delta\sigma}{\sigma}\right) \tag{13}$$
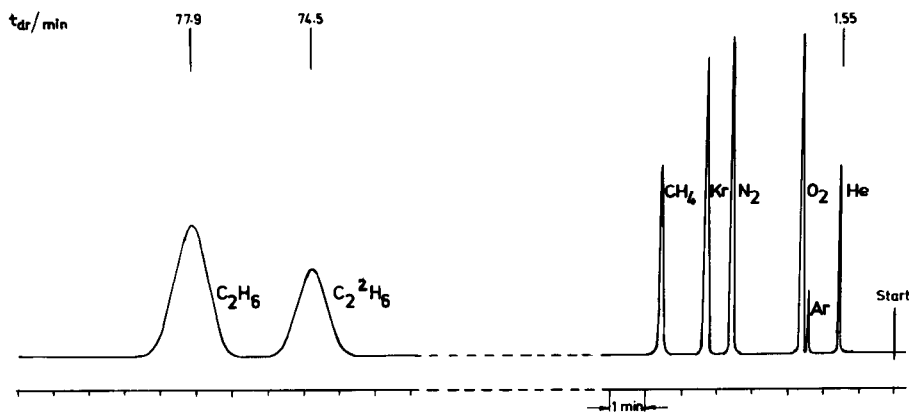

Fig. 8. Separation of C_2H_6–$C_2^2H_6$. Molecular sieve PLOT column (18.8 m × 0.31 mm I.D.); layer thickness $= 30 \mu$m; temperature $= 44.5$°C; effective plate number $= 29\,500$; capacity ratio $(C_2H_6) = 49.3$; $\alpha_{C_2H_6/C_2^2H_6} = 1.047$.

takes account of the fact that the distances of the centres of isotopic molecules from the adsorbing surface are different. The enthalpy of adsorption is related to the minimum value φ_0 of the potential function of the interaction of a molecule with the surface[28]. This quantity is proportional to a and mostly in a good approximation to a negative power of the equilibrium distance z_0. Analogously to that power exponent the factor f depends on the structure of the surface, ranging from $ca.$ 0.5 to $ca.$ 3; in our case, $f = 3$ is suggested by theoretical reasons (London dispersion theory[26]) but $f = 2$ fit better the experimental results. For the pair CH_4–C^2H_4 we have $\Delta\sigma/\sigma = 0.004$ and $\Delta a/a = 0.014$ and $-\Delta H \approx 4$ kcal mol^{-1}. Eqns. 13 and 8 yield

$$-\Delta(\Delta H) \approx 24 \text{ cal mol}^{-1} = 0.012R \cdot 10^3 \text{ K}$$

and

$$\ln \alpha = -0.008 + \frac{0.012}{T/10^3} \tag{14}$$

The study of the fractionation of isotopic methanes by means of zeolite 13X capillary shows a completely unexpected result (Fig. 9, Table III). Above 20°C the separation factor decreases, corresponding to the difference in adsorption energies of the isotopes, but below 20°C the separation factor remains constant at a value that is nearly the same as that with zeolite 5A. There must be a change in the state of adsorbed molecules in the zeolite 13X at 20°C. Below this characteristic temperature, the large adsorbing cavities (supercages) could be filled with a kind of scarcely moveable (condensed) molecules or the larger openings are in some sense rimmed with them, so that only windows of dimensions similar to those in zeolite 5A are available for the isotopic methane species to pass.

Deuterated methanes on an activated charcoal PLOT column
    Gant and Yang[19] tried to separate the different deuterated methane species by means of a 15.3 m × 0.152 cm I.D. packed charcoal column. Although they did not succeed in achieving a complete separation, they were able to determine the
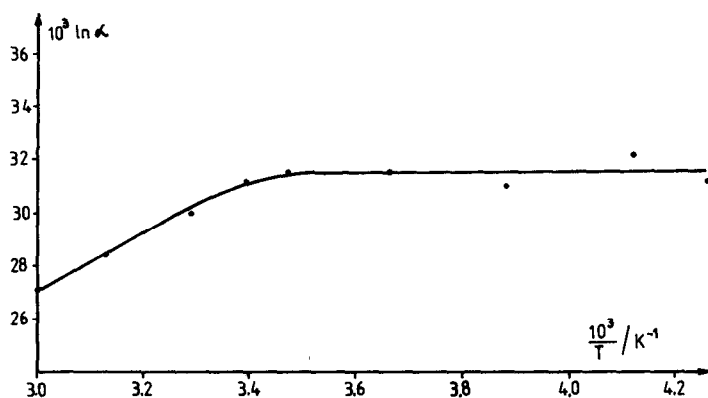

Fig. 9. Separation factor for CH_4/C^2H_4 on zeolite 13X column as a function of temperature.

TABLE III

SEPARATION FACTORS FOR $CH_4-C^2H_4$ ON THE CHARCOAL COLUMN: COMPARISON BETWEEN EXPERIMENTAL VALUES AND VALUES GIVEN BY A ROUGH CALCULATION VIA EQN. 14

Temperature (°C)	$10^3/T$ (K^{-1})	$10^3 \ln \alpha$ (calc.) (eqn. 14)	$10^3 \ln \alpha$ (meas.) (Fig. 9)
60	3.001	28.0	27.0
40	3.193	30.3	29.2
20	3.411	32.9	31.4
0	3.660	36.0	31.6
−20	3.950	39.4	31.5
−40	4.307	43.7	31.6

dependence of the separation factor on temperature for the system $CH_4-C^2H_4$. A measurable difference in the enthalpies of adsorption of the isotopic compounds was found, indicating that wide pores must exist. The separation factor for the pair $CH_4-CH_3{}^2H$ was calculated to be 1.016 at 280 K[19]. The reported values encouraged us to work with charcoal-coated capillaries.

In order to remove remaining metal oxides and sulphides, technical charcoal was boiled several times with concentrated hydrochloric acid, washed until neutral and dried. After crushing by hand, the charcoal was dried for 24 h and pulverized in a vibration mill to a grain size of 1–3 μm. It was difficult to prepare stable suspensions. Aqueous systems also with addition of wetting agents failed. Organic solvents, e.g., cyclohexanone led to stable suspensions but not to layers that adhered durably to the capillary. Good results were obtained by means of ethanol–water (4:1). We succeeded in coating about 30-m PLOT columns with a stable 30-μm layer. Several sections of this type were joined manually under the microscope by fusing. Fig. 10 shows that the separation of the single partially deuterated methanes is nearly complete at −9.5°C.
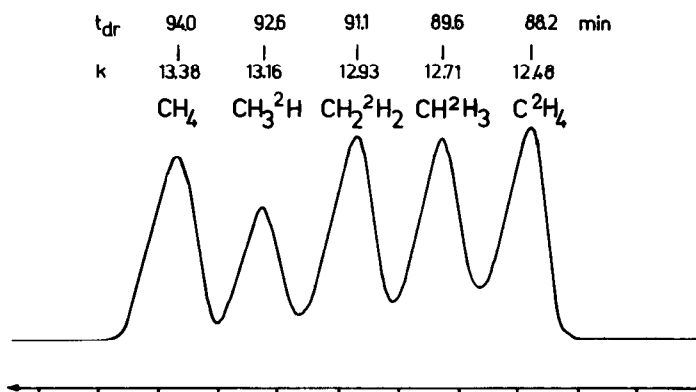

t_{dr}	94.0	92.6	91.1	89.6	88.2	min
k	13.38	13.16	12.93	12.71	12.48	
	CH_4	$CH_3{}^2H$	$CH_2{}^2H_2$	CH^2H_3	C^2H_4	

Fig. 10. Separation of deuterated methanes. Active charcoal PLOT column (98 m × 0.28 mm I.D.); layer thickness ≈ 30 μm; temperature = −9.5°C; effective plate number = 66 500.
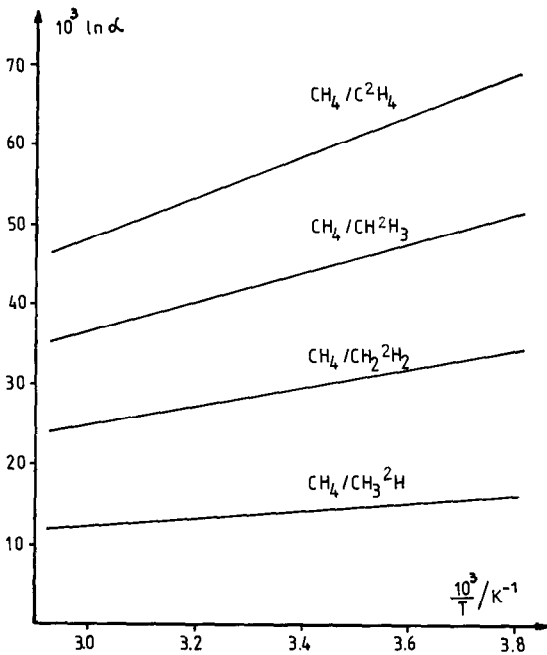
Fig. 11. Separation factor for different deuterated methanes as a function of temperature (-9.5 to $74.7°C$).

The separation factor for the pair CH_4–C^2H_4 is given by

$$\ln \alpha = -0.0284 + \frac{0.0256}{T/10^3} \tag{15}$$

This gives $\Delta(\Delta S) = -0.056 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $\Delta(\Delta H) = 50.8 \text{ cal mol}^{-1}$. ΔH_{CH_4} was calculated to be $4.32 \text{ kcal mol}^{-1}$. These values correspond fairly well with differential thermodynamic properties found by other workers[20,21]. We again see that according to eqn. 13 the relative difference of 1.17% in the enthalpies of adsorption is smaller than the relative difference in the polarizabilities. Fig. 11 demonstrates the validity of the law of the mean also for the fractionation of the partially deuterated methanes:

$$\ln \alpha(CH_4/CH_{4-n}{}^2H_n) = \frac{n}{4} \ln \alpha(CH_4/C^2H_4) \tag{16}$$

(n = number of H nuclei in CH_4 which are replaced with ^2H). Only the species $CH_3{}^2H$ shows a very slightly deviation in the lower temperature range. Such a behaviour was also observed by Fang and Van Hook[29] for isotope effects on the vapour-phase second virial coefficients of the deuterated methanes and may be connected with the quantum effects on the rotational degrees of freedom.

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