

SEPARATION OF HYDROGEN ISOTOPES BY GAS-SOLID CHROMATOGRAPHY

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INTRODUCTION

Several methods of separating hydrogen isotopes and isomers by gas-solid chromatography have been published in the last few years¹⁻¹³.

In all these methods, excepting that studied by GANT AND YANG⁸, the separation is carried out at liquid nitrogen temperature.

At this temperature hydrogen is retained permanently with helium as carrier gas by several absorbant materials including Molecular Sieve 4A⁷. In a study of the static absorption of hydrogen isotopes by PANCHENKOV *et al.*¹⁴ this absorbant phase shows the best selection capacity with respect to the other Zeolites A and X, the Mordenites, the aluminosilicate catalyst, silica and aluminium oxide.

We studied the use of this stationary phase in the separation of hydrogen isotopes at temperatures above 77°K, using helium, argon and neon as carrier gases. We found that in the range -110 to -160°C, with helium as carrier, we obtain a total resolution for the six isotopic species in the region of -140°C. Argon gives a separation of hydrogen, hydrogen tritide and tritium, but with poorer resolution than that obtained with helium, while neon behaves in the same way as helium.

We were also able to calculate the heats of absorption for hydrogen deuteride, hydrogen tritide, deuterium, deuterium tritide, tritium.

EXPERIMENTAL

The diagram of the apparatus used is given in Fig. 1. It consists of a Perkin-Elmer chromatograph F6-3T with carrier gas flow-rate regulator and thermal conductivity detector employing thermistors, and a cryostat containing the column. This cryostat, the 2 ml ionisation chamber and the glass injector connecting the chromatograph to the vacuum apparatus, were built in the laboratory. The cryostat allows the temperature to be regulated to $\pm 1^\circ\text{C}$. The columns were prepared with Molecular Sieve 4A from the Union Carbide Corp. Two methods of activation were used: helium or nitrogen sweeping of the filled column for 4 to 8 h at 250°-300°C, and degassing of the sieve under vacuum at 450°-500°C before filling.

The columns are made of copper, with an internal diameter of 2 mm and length varying between 30 and 200 cm. The samples of isotopic mixtures were prepared with tritium produced by the Radioelements Department (Saclay), hydrogen from the "Air Liquide" Company, and deuterium from the Stable Isotope Section (Saclay), equilibrated by electric discharge. All the carrier gases were purified by passage over Molecular Sieve 5A at liquid nitrogen temperature.

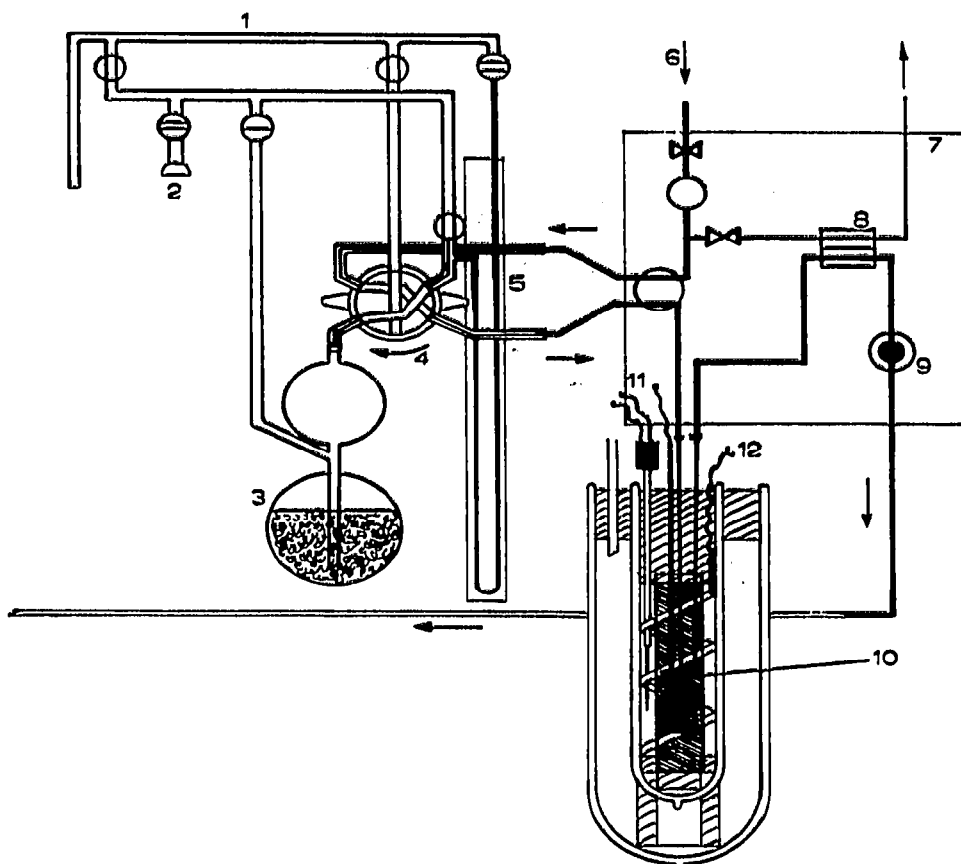


Fig. 1. Diagram of apparatus: 1 = vacuum apparatus; 2 = sample glass bulbs; 3 = Toeppler pump; 4 = injector; 5 = mercury manometer; 6 = carrier gas; 7 = Perkin-Elmer chromatograph; 8 = thermal conductivity detector; 9 = ionization chamber; 10 = column; 11 = probe and thermocouple; 12 = heating element.

RESULTS AND DISCUSSION

Helium carrier

Ortho-para hydrogen separation. The ortho-para hydrogen separation can be achieved in the temperature range from -135° to -160°C . Fig. 2 shows the chromatograms obtained on a column of Molecular Sieve 4A, 2 m long and 2 mm in diameter, activated at 250°C under a gas flow.

It can be seen that in spite of the distance between the peak maxima (the separation factor reaches $\alpha = 1.21$), we fail to obtain total resolution because of the presence of an intermediary plateau.

The presence and size of this plateau depends on the activation of the column. In highly activated columns (500°C under vacuum), no separation is obtained and the hydrogen appears as a single peak (Fig. 3). The rate of passage of the hydrogen through the column also has some influence on this separation. An incipient separation can be observed on a highly activated column with high flow rates, whereas with low flow rates a single peak is obtained (Fig. 4a and b). As a general rule a better separation is obtained at very low temperature with a fast flow. It seems that highly activated Molecular Sieve 4A (checked for absence of iron) can have a catalytic effect on the

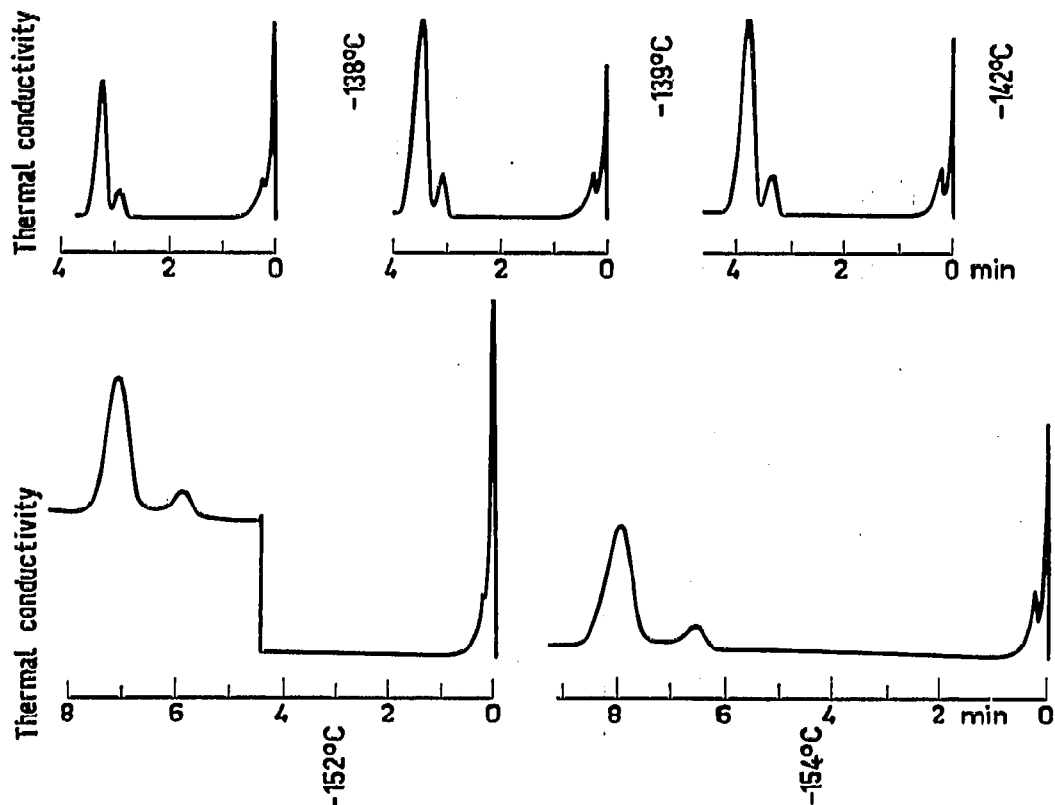


Fig. 2. Separation of ortho and para-hydrogen on a Molecular Sieve 4A column at different temperatures. Experimental conditions: column $2\text{ m} \times 2\text{ mm}$, particle size $0.31\text{--}0.4\text{ mm}$, activation at 250° under helium flow, carrier gas flow rate 85 ml/min .

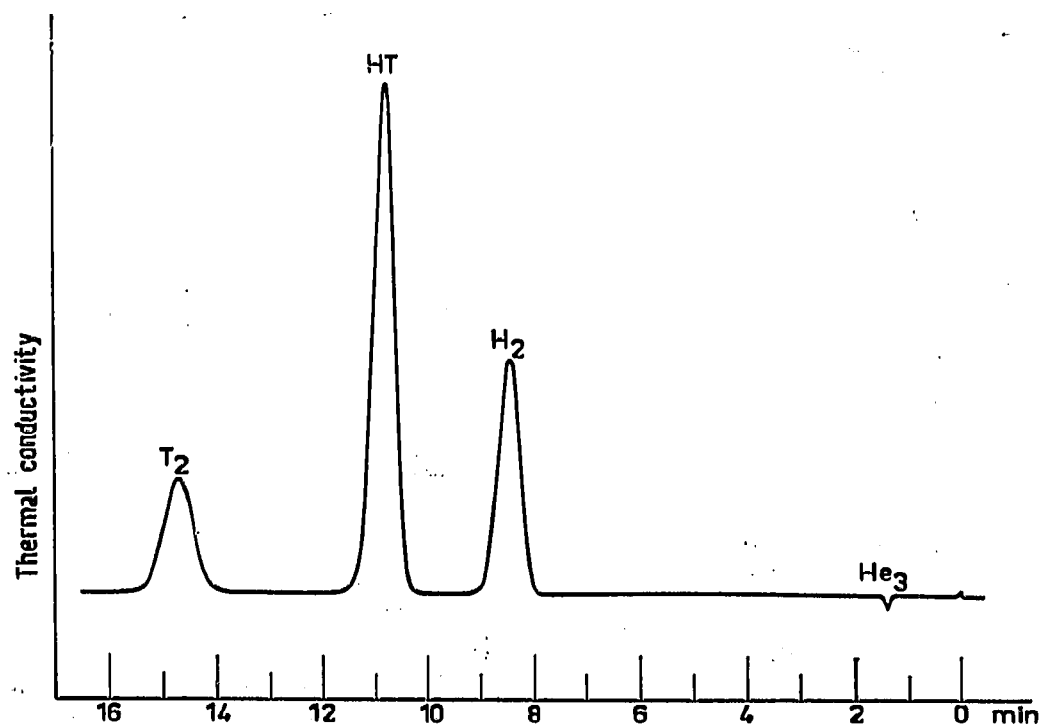


Fig. 3. Separation of H_2 , HT , T_2 on a Molecular Sieve 4A column. Experimental conditions: column, $2\text{ m} \times 2\text{ mm}$; particle size, $0.16\text{--}0.25\text{ mm}$; activation at 500°C under vacuum; carrier gas flow rate, 25 ml/min ; temperature, -133°C .

ortho-para hydrogen conversion. This effect has been observed by MOORE AND WARD and by SMITH AND CARTER³⁻⁵ with highly activated alumina.

Separation of isotopic species. Hydrogen, hydrogen tritide and tritium are completely separated between -125°C and -160°C with carrier gas flow rates between 10 and 90 ml/min on 2 m columns; even on moderately activated columns (250°C under gas flow) (Fig. 3).

It should be mentioned that between -115° and -125°C a separation is obtained, but the resolution is only complete with highly activated columns and very low flow rates. Below -160°C the separation cannot be used for an analysis because of the broadening of the peaks and the excessively long analysis time.

The six isotopic species: hydrogen, hydrogen deuteride, hydrogen tritide, deuterium, deuterium tritide, tritium are separated between -140°C and -160°C with flow rates between 15 and 50 ml/min; the resolution is complete.

Fig. 4 shows chromatograms of the separations obtained on two columns: one highly and the other moderately activated.

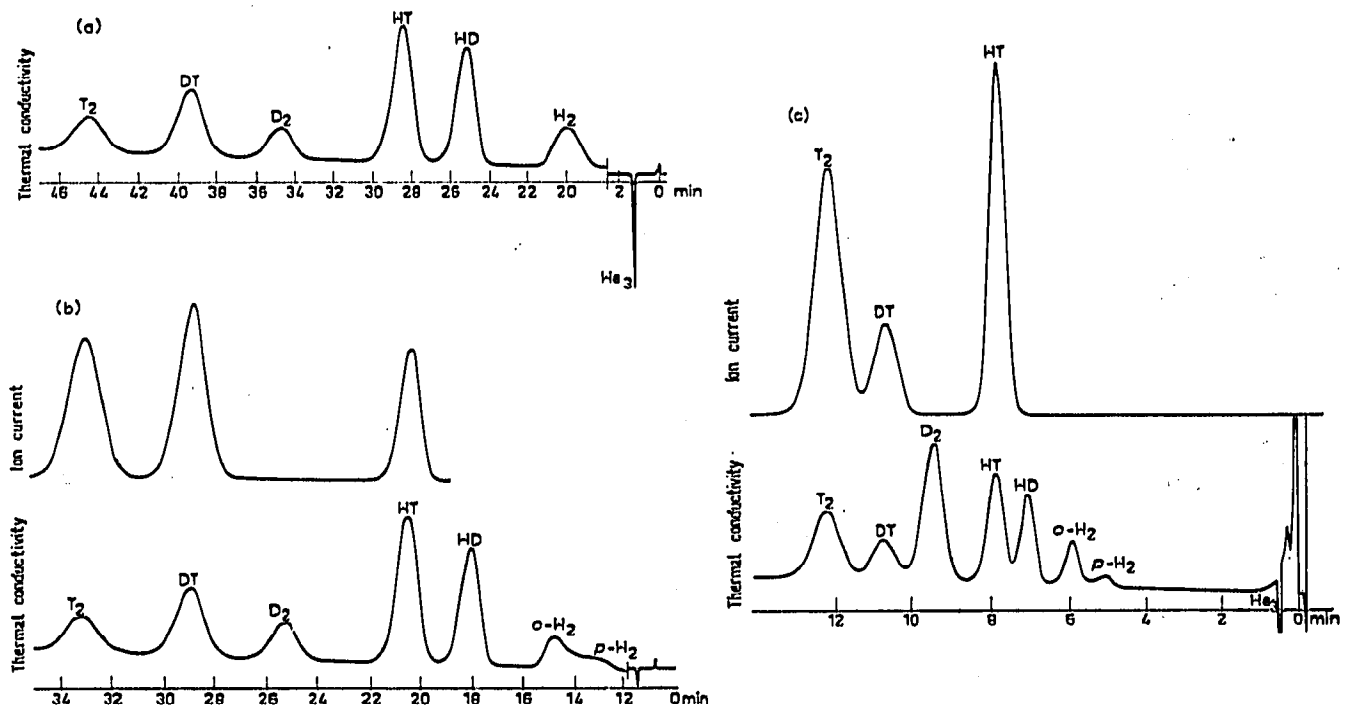


Fig. 4. Separation of $o\text{-H}_2$, $p\text{-H}_2$, HD, HT, D_2 , DT, T_2 on different columns of Molecular Sieve 4A. Experimental conditions: (a) column, 2 m \times 2 mm; particle size, 0.16-0.25 mm; activation at 500°C under vacuum; carrier gas flow rate, 28 ml/min; temperature, -149°C ; (b) column, 2.20 m \times 2 mm; particle size, 0.25-0.31 mm; activation at 500°C under vacuum; carrier gas flow rate, 55 ml/min; temperature -151°C ; (c) column, 2 m \times 2 mm; particle size, 0.25-0.31 mm; activation at 250°C under helium flow; carrier gas flow rate, 80 ml/min; temperature -148°C .

We noted that the HD peak is not superimposed on the $o\text{-H}_2$ peak as is the case with separation on alumina. On the other hand the HT-HD couple is only separated completely on highly activated columns. Table I shows the separation factors obtained for columns of different particle size, length and activation as a function of temperature. For purposes of comparison, the published values of separation factors obtained with other absorbants at 77°K are also given.

TABLE I

SEPARATION FACTORS

Columns: (a) 2 m column, particle size 0.25–0.31 mm (40–60 mesh), activation under gas flow at 250°C.
 (b) 2 m column, particle size 0.31–0.4 mm (35–40 mesh), activation under gas flow at 250°C.
 (c) 2 m column, particle size 0.16–0.25 mm (60–80 mesh), activation under vacuum at 500°C.
 (d) 2.20 m column, particle size 0.25–0.31 mm (40–60 mesh), activation under vacuum at 500°C.
 (e) 2 m column, particle size 0.31–0.4 mm (35–40 mesh), activation under vacuum at 500°C.

Temperature	α_{H_2}/ρ_{H_2}	HD/H_2	HT/H_2	D_2/H_2	DT/H_2	T_2/H_2	HT/HD	D_2/HD	
-119°C 154°K	(a)		1.21*			1.58*			
	(b)								
	(c)								
	(d)			1.24			1.57		
	(e)								
-130°C 143°K	(a)		1.25*			1.76*			
	(b)								
	(c)								
	(d)			1.27			1.74		
	(e)								
-133°C 140°K	(a)		1.24*			1.70*			
	(b)								
	(c)			1.33			1.89		
	(d)								
	(e)								
-135°C 138°K	(a)								
	(b)	1.12		1.29*	1.47*		1.84*		
	(c)								
	(d)								
	(e)								
-146°C 127°K	(a)								
	(b)	1.16		1.35*			2.15*		
	(c)		1.27	1.43	1.76	1.99	2.27	1.13	1.38
	(d)								
	(e)		1.22	1.38	1.69	1.91	2.18	1.12	1.38
-148°C 125°K	(a)								
	(b)	1.18	1.19*	1.35*	1.65*	1.88*	2.16*	1.13	1.37
	(c)		1.19*	1.34*	1.62*	1.83*	2.15*	1.12	1.35
	(d)		1.28	1.45	1.81	2.08	2.39	1.13	1.41
	(e)								
-151°C 122°K	(a)								
	(b)	1.21	1.20*	1.37*	1.66*		2.19*		
	(c)			1.36*	1.66*	1.90*	2.16*	1.13	1.37
	(d)		1.23	1.40	1.75	2.00	2.30	1.13	1.42
	(e)		1.26	1.44	1.82	2.10	2.45	1.14	1.44
-152°C 121°K	(a)								
	(b)			1.39*			2.23*		
	(c)								
	(d)		1.27	1.46	1.85	2.16	2.53	1.15	1.46
	(e)								
-153°C 120°K	(a)								
	(b)		1.22*	1.41*	1.77*	2.08*	2.46*	1.15	1.44
	(c)								
	(d)		1.24	1.42	1.78	2.07	2.40	1.14	1.44
	(e)								

DT/HD	T_2/HD	D_2/HT	DT/HT	T_2/HT	DT/D_2	T_2/D_2	T_2/DT
				1.30			
				1.27			
				1.33			
				1.33			
				1.36			
				1.31**			
				1.35			
				1.41			
		1.14		1.42		1.25	
				1.58			
				1.57			
1.57	1.79	1.23	1.39	1.58	1.13	1.29	1.14
1.56	1.78	1.22	1.38	1.58	1.13	1.29	1.14
1.57	1.80	1.22	1.39	1.60**			
1.53	1.72	1.21	1.37	1.59	1.14	1.31	1.14
1.63	1.87	1.24	1.43	1.58	1.13	1.27	1.12
				1.64	1.15	1.32	1.15
		1.22		1.60		1.32	
1.57	1.79	1.22	1.39	1.58	1.14	1.30	1.14
1.63	1.87	1.24	1.42	1.64	1.14	1.31	1.15
1.67	1.94	1.26	1.45	1.69	1.15	1.34	1.16
				1.61			
				1.54**			
1.70	1.99	1.26	1.47	1.73	1.16	1.36	1.17
1.70	2.00	1.25	1.48	1.70			
				1.74	1.17	1.38	1.17
1.66	1.93	1.25	1.45	1.68	1.15	1.34	1.16

(continued on p. 38)

TABLE I (continued)

Temperature	oH_2/pH_2	HD/H_2	HT/H_2	D_2/H_2	DT/H_2	T_2/H_2	HT/HD	D_2/HD	
-156°C 117°K	(a)		1.42*			2.42*			
	(b)								
	(c)								
	(d)		1.24	1.43	1.79	2.08	2.41	1.15	1.44
	(e)								
<i>Published values***</i>									
	(13)		1.09	1.20	1.26	1.45	1.66	1.10	1.15
-195.8°C 77°K	(6)		1.13	1.23	1.38		1.68	1.09	1.22
	(5)		1.22	1.42	1.49	1.85	2.08	1.22	1.17
	(7)	1.37							1.53
	(7)								1.39
	(11)		1.14	1.20					1.39
	(11)	1.19							1.23
	(11)								1.47

* These values refer to the separation with respect to ortho-hydrogen.

** Line (a) these values correspond to a column 80 cm long; line (b) the column was 30 cm.

*** The separation factors calculated here and those given in references 7 and 11 are obtained from the ratios of the retention times corrected for dead time, whilst those given in references 13, 6 and 5 are calculated from the retention times taken following injection.

The introduction of different quantities of the various components between $2 \cdot 10^{-4}$ and 0.2 ml NTP gave no measurable variations in the retention times for a given temperature and degree of activation.

In addition the absolute retention volumes at constant temperature are independent of the carrier gas flow rate. We are thus in the linear region of absorption isotherm.

Fig. 5 shows the $HETP_{eff}$ curve for HT and T_2 as a function of flow rate. The optimum flow rate is 25 ml/min. The efficiency (number of effective theoretical plates

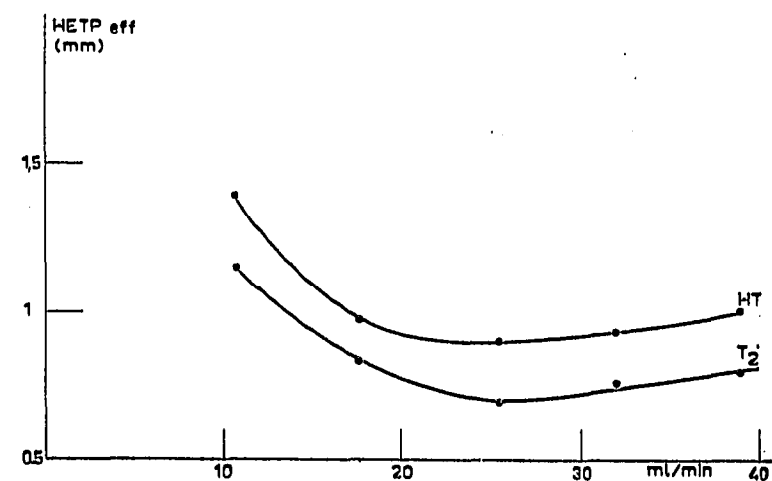


Fig. 5. Plots of $HETP_{eff}$ against carrier gas flow rate for the peaks of HT and T_2 .

DT/HD	T ₂ /HD	D ₂ /HT	DT/HT	T ₂ /HT	DT/D ₂	T ₂ /D ₂	T ₂ /DT	
				1.70 1.69**				
1.67	1.93	1.25	1.45	1.68	1.15	1.34	1.16	
								<i>Exptl. cond.</i>
1.33	1.52	1.05	1.21	1.38	1.15	1.32	1.14	Al ₂ O ₃ + Fe ₂ O ₃ - He carrier
	1.48	1.12		1.30		1.22		- d° -
1.52	1.71	1.05	1.30	1.47	1.24	1.40	1.13	- d° - M.S.13X-He carrier
				1.62		1.34		M.S. 5A - H ₂ carrier
				1.73	1.25		1.05	Al ₂ O ₃ -cap. col. He carrier M.S.13X-cap. col. He carrier M.S.5A-cap. col. He carrier

per metre) is a function of particle size and especially of activation. It increases slightly with decrease in temperature and reaches a maximum between -145° and -155°C . The values, which vary according to the isotopic species considered, are 500 (700–800 at the maximum point) for columns activated under a gas flow and 1000 (1300–1500 maximum) for those activated under vacuum.

Table II lists the resolutions obtained on a highly activated column of particle size 0.16–0.25 mm, with the corresponding capacity ratios and number of theoretical plates. This chromatographic separation method was used in the quantitative analysis of H₂, HT, and T₂ mixtures.

The calibration curves are linear up to 100 mm³ NTP for hydrogen, and over the whole range studied, *i.e.* up to 200 mm³ NTP, for HT and T₂. The minima detectable (we take as the detection limit an elongation of 10 mm equal to 0.08 mV) are 0.57 mm³ NTP of T₂, 0.5 mm³ NTP of HT and 3 mm³ NTP of H₂ (these figures were obtained with a 2 m column activated under vacuum at 500°C, carrier gas flow rate 37 ml/min, temperature -130°C , Perkin-Elmer thermistor detector).

If an ionization chamber is used as detector it is possible to determine down to 0.005 mm³ NTP of tritium in the form of HT or T₂.

Determination of heats of absorption. From the general equation

$$\frac{d \ln V_g}{d (1/T)} = \frac{\Delta H}{R}$$

the graph of $\ln V_g$ as a function of $1/T$ gives straight lines (Fig. 6) and the heats of

TABLE II
RESOLUTION FACTORS

Temperature	σ_{H_2}/ρ_{H_2}	HD/H_2	HT/H_2	HT/HD	D_2/HT	DT/D_2	T_2/DT	D_2/HD	T_2/HT	Flow rate	K_{HT} *	H_{T_2} *	$N_{eff}T_2^{**}$
-133			2.93						4.36	25.5 ml/min	6.71	9.51	2840
-146	2.23		3.38	1.38	2.50	1.58	1.65	3.98	5.56	24 ml/min	15.59	24.70	2700
-150		2.77	3.52	1.56	2.76	1.77	1.78	4.49	6.02	28 ml/min	20.82	33.55	3092

* Capacity ratio, $-K = t_{dr}/t_m$.

** Number of effective theoretical plates for T_2 peak.

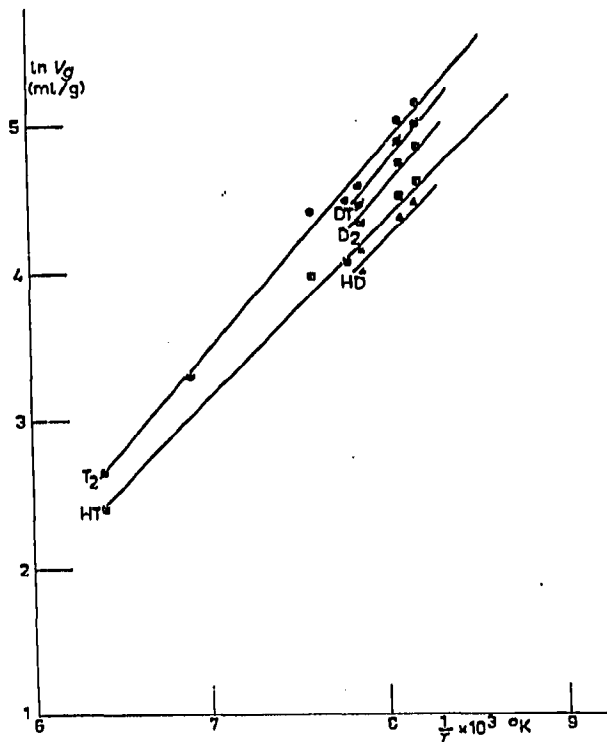


Fig. 6. Plot of $\ln V_g$ against inverse temperature.

absorption H can be calculated from their slopes^{15,16}. The heats of absorption thus obtained are as follows:

$$\Delta H_{HD} = 2.30 \pm 0.1 \text{ kcal}$$

$$\Delta H_{HT} = 2.40 \pm 0.05 \text{ kcal}$$

$$\Delta H_{D_2} = 2.64 \pm 0.1 \text{ kcal}$$

$$\Delta H_{DT} = 2.74 \pm 0.1 \text{ kcal}$$

$$\Delta H_{T_2} = 2.80 \pm 0.05 \text{ kcal}$$

The precision of the ΔH_{HT} and ΔH_{T_2} values is greater because of the larger number of experimental points obtained.

Argon carrier

The use of argon as carrier gas was studied because of the greater sensitivity obtainable with a thermal conductivity detector in the measurement of hydrogen and with an ionization chamber in the determination of HT and T₂.

This gas can be used down to -160°C and separates He, H₂, HT, T₂; because of its high absorption on Molecular Sieve 4A, the retention times for the same column and under the same flow rate and temperature conditions are shorter than with helium and the separation factors and resolutions are lower. Under the best temperature conditions, -143 – 150°C , with a flow rate of 40–50 ml/min, we obtain: $\alpha(T_2/HT) = 1.61$ – 1.69 ; $\alpha(HT/H_2) = 1.34$; $R(T_2/HT) = 2.09$ – 2.20 $R(HT/H_2) = 1.42$, (the columns used were moderately activated).

Neon carrier

With neon as carrier total separation of H₂, HT, D₂, DT, T₂ can be obtained.

The separation factors are slightly better than those obtained with helium for the same column and under the same temperature and flow-rate conditions.

At -155°C we obtain: $\alpha(\text{HD}/\text{H}_2) = 1.33$; $\alpha(\text{HT}/\text{HD}) = 1.17$; $\alpha(\text{D}_2/\text{HT}) = 1.30$; $\alpha(\text{DT}/\text{D}_2) = 1.18$; $\alpha(\text{T}_2/\text{DT}) = 1.15$; $\alpha(\text{T}_2/\text{HT}) = 1.77$.

Unfortunately because of the high cost of the gas this separation cannot be used for routine analysis.

CONCLUSION

Molecular Sieve 4A can be used as the stationary phase in gas-solid chromatographic separation of hydrogen isotopes. In the temperature range -140 – -150°C , with helium as carrier gas and flow-rates between 15 and 50 ml/min, total resolution of the six isotopic species is obtained.

SYMBOLS AND FORMULAE

t_r = retention time (injection measurement)

t_m = retention time of a non-absorbed component. In our system this dead time was determined from the retention time of He_3 , which is not absorbed in the temperature range studied.

t_{ar} = corrected retention time, $t_{ar} = t_r - t_m$

F = carrier gas flow rate in ml/min measured at room temperature and at the column output pressure P_s (atmospheric pressure under our experimental conditions).

V_c = retention volume, $V_c = t_r \times F$

V_m = dead volume, $V_m = t_m \times F$

V_n = absolute retention volume calculated thus:

$$V_n = (V_c - V_m) \times \frac{T_c}{T_s} \times j$$

where

T_c = temperature of column in $^{\circ}\text{K}$,

T_s = absolute temperature at which the flow rate is measured,

j = pressure gradient correction factor of JAMES AND MARTIN.

$$j = \frac{3(P_c/P_s)^2 - 1}{2(P_c/P_s)^3 - 1}$$

V_g = specific retention volume (brought to 273°C and 1 g of the stationary phase),

$$V_g = \frac{V_n \times 273}{m \times T_c}$$

α = separation factor,

$$\alpha = \frac{t_{ar1}}{t_{ar2}}$$

R = resolution,

$$R = 2 \frac{(t_{ar2} - t_{ar1})}{W_2 + W_1}$$

with t_{dr1} and t_{dr2} corrected retention times of components 1 and 2, and W_1 and W_2 widths at the base of peaks 1 and 2.

n = number of effective theoretical plates,

$$n = 16 \left(\frac{t_{dr}}{W} \right)^2$$

k = capacity ratio,

$$k = \frac{t_{dr}}{t_m} = \frac{t_r}{t_m} - 1$$

SUMMARY

Molecular Sieve 4A can be used as the stationary phase in the gas-solid chromatographic separation of hydrogen isotopes and isomers: the separation is studied as a function of the different factors involved (temperature, flow rate, activation of the stationary phase).

From the determination of the specific retention volumes as a function of temperature it was possible to calculate the heats of absorption of hydrogen deuteride, hydrogen tritide deuterium, deuterium tritide and tritium.

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