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ADSORPTION EQUILIBRIUM OF HYDROGEN ISOTOPES ON ALUMINA ADSORBENTS FOR GAS–SOLID CHROMATOGRAPHY

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SUMMARY

The adsorption equilibrium of an alumina–hydrogen system was studied, in the context of the use of alumina adsorbents for hydrogen isotope separation by gas chromatography. Both the amount of hydrogen adsorbed at low equilibrium pressure and the heat of adsorption observed for an alumina adsorbent dried above 473 K increased due to the appearance of active adsorption sites associated with oxide (O^{2-}) and aluminium (Al^{3+}) ions. The surface of the alumina adsorbent was partially deactivated by coating with $MnCl_2$, but the deactivation effect was lost when the alumina was dried above 473 K, owing to the appearance of active adsorption sites. Chromatographic experiments performed on the alumina adsorbents with and without coating indicated that the separation performance of the column was strongly affected by the adsorption equilibrium of hydrogen isotopes on alumina. The retention time of hydrogen isotopes agreed approximately with the predicted time calculated from the adsorption equilibrium data obtained.

INTRODUCTION

A gas chromatograph is a simple and adequate tool in analytical chemistry of hydrogen isotopes. Six hydrogen isotopes (H_2 , H^2H , H^3H , 2H_2 , $^2H^3H$ and 3H_2) are sufficiently separated using alumina as well as molecular sieve adsorbents cooled with liquid nitrogen^{1–9}. Recently, increasing interest has been showing this separation method for fuel processing in nuclear fusion reactors. A mixture of deuterium and tritium is used as a fuel of fusion reactors, and the control of the fuel composition and purification of the fuel exhaust are current problems to be solved. Although cryogenic separation of hydrogen isotopes is likely to be used in the fuel processing system of fusion reactors, gas chromatography (GC) would be an attractive option in the process control and monitoring.

There is a possibility of applying GC to the enrichment of tritium fuel if a separation column capable of separating large volumes of hydrogen can be developed, e.g., 1 g or 4 dm³ of tritium gas. In this respect, efforts have been made to develop a rotating column with two-dimensional separation systems¹⁰ and a separation column to be used for fairly large amounts of tritium gas¹¹.

For separation of hydrogen isotopes by gas–solid chromatography (GSC),

alumina is a convenient column packing material and is commonly used at liquid nitrogen temperature¹⁻⁸. Although it is practical to maintain the temperature sufficiently low and constant during the separation by immersing the column in liquid nitrogen, we have to use partially deactivated alumina adsorbents because highly activated alumina has too strong adsorbability for hydrogen at liquid nitrogen temperature^{1,3-5}. One might use alumina adsorbents at a slightly higher temperature (≈ 100 K), but the temperature control would become difficult. A number of papers have been published on the partial deactivation of alumina adsorbents^{2,5-8}, and an alumina adsorbent coated with MnCl_2 was reported to be an excellent adsorbent for hydrogen isotope separation at liquid nitrogen temperature¹². In addition, on alumina adsorbents coated with salts, the overlap of *ortho*-hydrogen and hydrogen deuteride bands in chromatograms due to the interconversion of nuclear spin isomers was eliminated^{2,3,5,8}. However, detailed knowledge of the fundamental adsorption characteristics of the alumina adsorbents is not yet available, although there are some data on the adsorption equilibrium between alumina catalysts and hydrogen isotopes¹³.

Since it is essential to understand the adsorption equilibrium of hydrogen on solid adsorbents in order to design and develop a sophisticated column packing material for separation of hydrogen isotopes by GSC, the present study aims to obtain insight into the adsorption equilibria of H_2 and $^2\text{H}_2$ on alumina adsorbents with and without a coating of MnCl_2 and to examine further the effect of coating, drying and deactivation of alumina adsorbents used in GC.

EXPERIMENTAL

Alumina adsorbents coated with 19% (w/w) of MnCl_2 (60-80 mesh) from Shimadzu (Kyoto, Japan) and the same adsorbents, from which the coating had been removed by washing with HCl were used after heat treatment in a vacuum. The alumina adsorbents were prepared by heating a mixture of activated alumina and MnCl_2 at 400 K. Hydrogen (99.99999% pure) and deuterium with 99.7% isotopic purity (99.99% chemical purity) were used after passing through a column packed with molecular sieves 5A cooled with liquid nitrogen. Argon gas (99.999% pure) was used after passing through a column packed with molecular sieves 5A at room temperature.

Thermogravimetry (TG) and differential thermal analysis (DTA) of these alumina adsorbents were carried out with a Seiko SSC/560GH TG-DTA system, the samples being heated in a stream of argon. Hydrogen and argon adsorption isotherms on alumina adsorbents were measured with a conventional volumetric apparatus, shown in Fig. 1, consisting of a gas burette, a constant-temperature bath, pressure gauges and an evacuation system. The volume of the apparatus enclosing the sample was 72 cm³. The temperature of the sample was kept constant using the low-temperature bath filled with liquid nitrogen or mixtures such as isopentane-nitrogen (113 K), *n*-pentane-nitrogen (142 K), CS_2 - N_2 (163 K), toluene-nitrogen (178 K) and solid carbon dioxide-acetone (196 K).

An Yanagimoto G-30 gas chromatograph with a thermal conductivity detector was used to examine the performance characteristics of alumina adsorbents as column packing materials. The stainless-steel column (2 m \times 3 mm I.D.) packed with adsorbents was immersed in liquid nitrogen when used for the separation of hydrogen isotopes. Neon (99.99% pure) was used as the carrier gas.

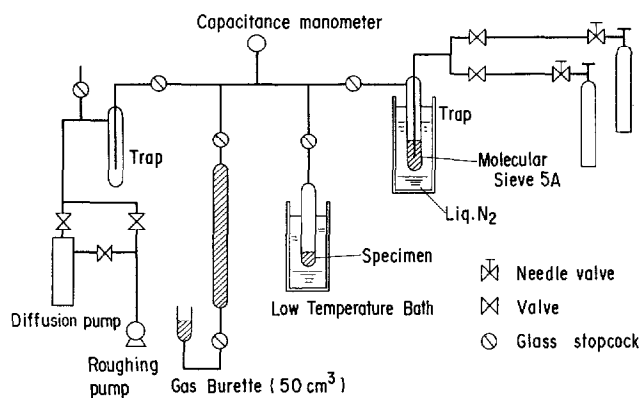


Fig. 1. Schematic diagram of the experimental apparatus.

RESULTS AND DISCUSSION

Effect of heat treatment on adsorption characteristics

The surface area of alumina adsorbents was found to change slightly depending upon the temperature of the heat treatment in a vacuum. Fig. 2 shows the variation of the surface area for the alumina adsorbents without coating, heated for 5 h at a prescribed temperature between 300 and 1100 K. The surface area determined from the BET equation for argon adsorption at liquid nitrogen temperature increased slightly with increasing temperature up to 900 K. It is generally known that alumina adsorbents chemisorb at least a monolayer of water when exposed to moisture at room temperature and that the water forms hydroxyl groups (OH^-) on the surface^{14,15}. The hydroxyl groups might be removed by the heat treatment and the decrease in the amount of residual hydroxyl groups depended on the temperature of the heat treatment¹⁴. The change in the surface area was not attributed to the sintering of the sample but to removal of hydroxyl groups, because no particular signal was observed in the DTA measurement.

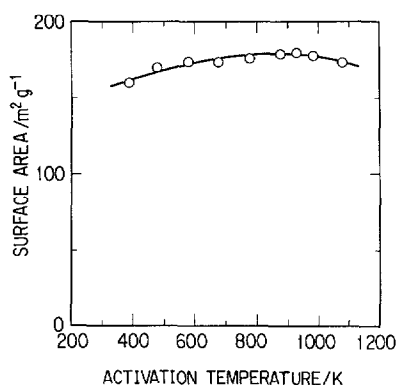


Fig. 2. Change in the surface area of an alumina adsorbent upon heat treatment.

Fig. 3 illustrates the hydrogen adsorption isotherms observed at liquid nitrogen temperature for alumina adsorbents dried at 383, 473 and 773 K. The Freundlich equation is commonly used for adsorption isotherms of gases¹³; however the present results did not obey this. Namely, relationship between the logarithm of the amount of adsorbed hydrogen and that of the equilibrium pressure was not linear. In the present study, therefore, an equation derived by Suwanayuen and Danner¹⁶ based on vacancy solution theory was applied to the adsorption equilibrium data

$$P = [n_1^{s,\infty}/K(1-\theta)]f(A_{13}, A_{31}, \theta) \quad (1)$$

with $\theta = n_1^s/n_1^{s,\infty}$ where P is the pressure of the gas phase, K the Henry law constant, n_1^s the number of moles of component 1 on the surface, $n_1^{s,\infty}$ the maximum number of moles of component 1 on the surface, θ the fractional coverage and A_{13} and A_{31} the Wilson equation parameters for surface interaction between components 1 and 3 (adsorbent). The four independent parameters, $n_1^{s,\infty}$, K , A_{13} and A_{31} , were obtained by fitting the isotherm equation to the observed data using a simplex method. The calculated curve, the solid line in Fig. 3, was well superimposed on the experimental values over a wide range of the equilibrium pressure. This indicates that physisorption of hydrogen was dominant on the surface of alumina adsorbents dried below 383 K.

On the other hand, the hydrogen adsorption isotherms observed for alumina adsorbents dried at 473 and 773 K did not necessarily agree with the calculated isotherms in the low equilibrium pressure range (1–100 Pa). The amounts of hydrogen adsorbed in the low equilibrium pressure range were larger than expected from the calculation and increased with drying temperature up to 1073 K. The amounts of

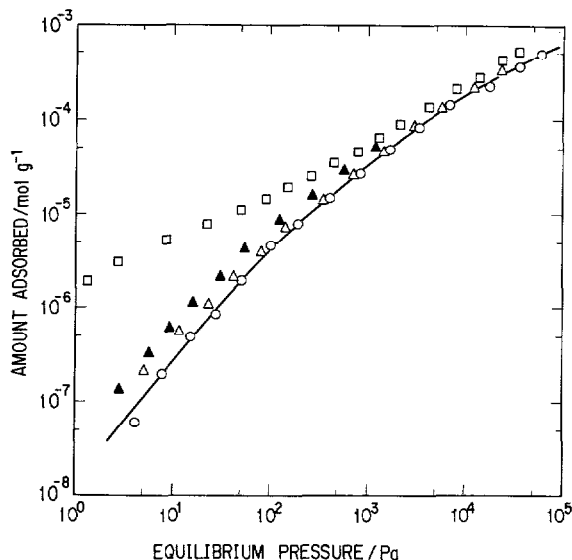


Fig. 3. Adsorption isotherms of H_2 and D_2 on alumina adsorbents: \circ , H_2 on alumina dried at 383 K; \triangle , H_2 on alumina dried at 473 K; \square , H_2 on alumina adsorbent dried at 773 K; \blacktriangle , 2H_2 on alumina dried at 473 K. The continuous line is the predicted curve.

deuterium adsorbed on the alumina adsorbents were larger than that of hydrogen. The same tendency was observed for the effect of the drying temperature. A comparison of the adsorption equilibria between H_2 and D_2 is also shown in Fig. 3 for an alumina adsorbent dried at 473 K.

These results suggest that a stronger effect than physisorption is involved in the hydrogen adsorption on alumina adsorbents dried at temperatures above 473 K. Namely, it is implied that the appearance of both oxide (O^{2-}) and aluminium ions (Al^{3+}) on the surface of alumina adsorbents associated with the removal of hydroxyl groups¹³ through the heat treatment above 473 K played important roles in the hydrogen adsorption in the low equilibrium pressure range.

The heat of adsorption of hydrogen evaluated from the Clausis–Clapeyron equation at constant volume adsorbed is shown in Fig. 4. The values obtained for alumina adsorbents dried at 773 K were about ten times as large as the latent heat of vaporization (0.9 kJ/mol)¹⁷ and decreased with increasing amount of adsorbed hydrogen. These phenomena were not observed for alumina dried at 383 K. The results also reveal that active adsorption sites for hydrogen (O^{2-} and Al^{3+}) were formed by the removal of hydroxyl groups.

Effect of coating with $MnCl_2$ on adsorption characteristics

Table I shows the amount of hydrogen adsorbed on alumina adsorbents with and without coating. Table II shows the BET surface areas and the parameters of the isotherm equation of Suwanayuen and Danner obtained by fitting the adsorption equilibrium data for hydrogen on the alumina adsorbents with and without coating, dried at 383 K. The BET surface area of the coated alumina adsorbent was the same as that of the alumina adsorbent without coating. However, the latter adsorbed larger amounts of hydrogen when dried at 383 K. In addition, all the values of the parameters in eqn. 1 decreased upon coating; a remarkable difference was observed especially for the Henry law constant, which is a parameter related to the adsorption characteristics at low equilibrium pressure. The heat of adsorption of hydrogen was also measured for the coated alumina adsorbent. The values obtained were smaller than those for the

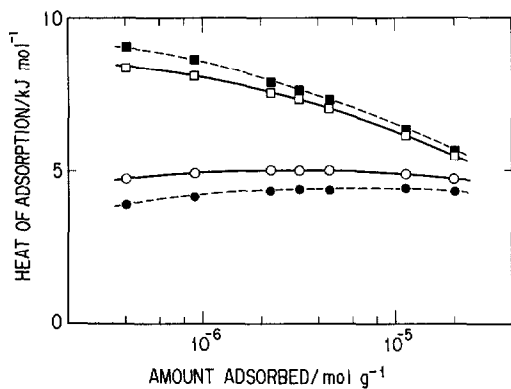


Fig. 4. Effect of the activation temperature and coating by $MnCl_2$ on the heat of adsorption of hydrogen on alumina adsorbents: ○, alumina adsorbent without coating dried at 383 K; ●, adsorbent with coating dried at 383 K; □, adsorbent without coating dried at 773 K; ■, adsorbent with coating dried at 773 K.

TABLE I
AMOUNTS OF HYDROGEN ADSORBED ON ALUMINA ADSORBENTS WITH AND WITHOUT COATING WITH MnCl_2

	Drying temperature (K)	Amount of hydrogen adsorbed (mol/g alumina)	Equilibrium pressure (kPa)
Without coating	383	0.40	0.013
		5.5	0.133
		40	1.33
		190	13.3
With coating	383	0.36	0.013
		3.5	0.133
		26	1.33
		150	13.3
Without coating	473	0.58	0.013
		5.8	0.133
		41	1.33
		220	13.3
With coating	473	0.54	0.013
		5.0	0.133
		35	1.33
		230	13.3

alumina adsorbent without coating when the drying temperature was 383 K as shown in Fig. 4. These results indicate that the adsorption site for hydrogen on the surface of alumina is deactivated by the coating with MnCl_2 .

As seen in Table I, no apparent difference was observed in the amount of hydrogen adsorbed when the alumina adsorbents were dried at 473 K before measurement. As shown in Fig. 4, the heat of adsorption of hydrogen on the coated alumina adsorbent dried at 773 K was slightly larger than that on the alumina adsorbent without coating. As described in the preceding section, the O^{2-} and Al^{3+} formed by the heat treatment would govern the adsorption behaviour of hydrogen on alumina adsorbents dried above 473 K. Alternatively, the coating with MnCl_2 did not inhibit the removal of hydroxyl groups as well as the appearance of the active adsorption sites on the surface when dried above 473 K.

TABLE II
PARAMETERS OF THE ADSORPTION ISOTHERM EQUATION FOR HYDROGEN ON ALUMINA ADSORBENTS WITH AND WITHOUT COATING WITH MnCl_2 DRIED AT 383 K

	Without coating	With coating
$n_1^{s,\infty}$ (mmol/g alumina)	4.91	3.37
K (mol/g alumina kPa)	23.7	12.6
A_{13}	0.42	0.39
A_{31}	4.4	2.7
Surface area (m^2/g alumina)	161.1	169.1

Chromatographic performance and adsorption characteristics of hydrogen on alumina adsorbents

In a number of reports on chromatographic experiments, two simulation models have been used for the analysis of experimental data: (1) the series-of-stirred-tanks model⁹ and (2) the dispersion model¹⁸⁻²⁰. Applying these two models, we evaluated parameters for the separation performance such as the retention time.

The series-of-stirred-tanks model gives

$$v = K'V_s(N-1)/t'_R \quad (2)$$

$$t'_R = t_R - (t_R)_{\text{inert}} \quad (3)$$

$$(t_R)_{\text{inert}} = (N-1)V_G/v \quad (4)$$

where v is the flow-rate of carrier gas, K' the Henry law constant of the alumina-hydrogen system in a neon carrier, V_s the hold-up of the adsorbent in a stage, N the total number of theoretical stages, t_R the mean residence time of the adsorbate gas, $(t_R)_{\text{inert}}$ the mean residence time of inert gas and V_G the hold-up of gas in a stage. From the dispersion model, a set of partial differential equations is derived for chromatograms¹⁸⁻²⁰. A moment method¹⁹ was used for modification of these equations because of its simplicity and adequate reliability for the analysis of chromatograms²¹ in the present study

$$(t'_R - t_{\text{oi}}/2)/(\varepsilon_p/\varepsilon_b - \varepsilon_p) = (\rho_p K'/\varepsilon_p)(z\varepsilon_b/u) \quad (5)$$

$$t'_R = t_R - (t_R)_{\text{inert}} \quad (3)$$

$$(t_R)_{\text{inert}} = (1 + \varepsilon_p/\varepsilon_b - \varepsilon_p)(z\varepsilon_b/u) \quad (6)$$

where t_{oi} is the time required for injection of adsorbate, ε_p the void fraction of the adsorbent, ε_b the void fraction of the column, z the column length, u the superficial velocity of the carrier gas and ρ_p the apparent particle density of the adsorbent. In the derivation of eqns. 2 and 6, it was assumed that the adsorption isotherm expressed by eqn. 1 could be simplified to a linear relationship at low equilibrium pressure important for the chromatography

$$n_1^s = K'c \quad (7)$$

where c is the molar concentration of adsorbate.

The chromatograms for H_2 and $^2\text{H}_2$ on the alumina adsorbents with and without coating were measured at several flow-rates of the carrier gas. Fig. 5 shows an example. It is clear that the chromatographic performance was strongly affected by the adsorption equilibrium between the alumina adsorbents and hydrogen isotopes. The deactivation by the coating with MnCl_2 reduced the retention time and sharpened the peak in the chromatogram. Since the peaks in the chromatogram were approximately symmetric, the mean residence time in eqn. 2 and 5 would correspond to the retention time. A plot of v against $V_s(N-1)/t'_R$ shown in Fig. 6 is almost linear as suggested by

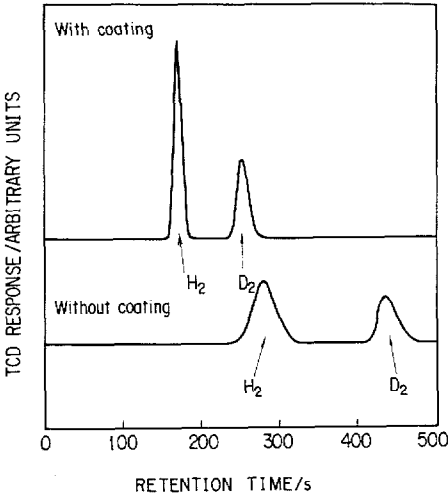


Fig. 5. Typical chromatogram of a mixture of H₂-²H₂ and packing materials: alumina adsorbent and alumina adsorbent coated with MnCl₂ dried at 383 K. Packed weight: 11 g. Neon flow-rate: 1.933 cm³/s. Sample volume: 0.02 cm³ H₂ + 0.02 cm³ ²H₂.

eqn. 2. Fig. 7 shows chromatographic data for H₂ and D₂ linearized by eqn. 5. Eqns. 2 and 5 seem to be valid for analysis of the chromatogram. The small deviation from the straight lines passing through the origin of the coordinate axes observed in both figures might be due to the error resulting from the assumption of eqn. 7 in which a linear approximation for the adsorption equilibrium was adopted. The degree of this deviation depended on the flow-rate of the carrier gas which affected the equilibrium pressure of adsorbate gas within the column.

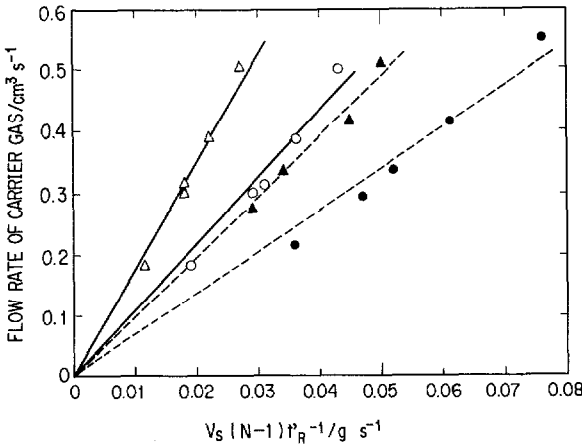


Fig. 6. Plots of the chromatographic parameters for H₂ and ²H₂ in the series-of-stirred-tanks model (eqn. 2). Relationship between the carrier gas and the total number of theoretical stages of the column: ○, H₂ on alumina adsorbent without coating; ●, H₂ on adsorbent coated with MnCl₂; △, ²H₂ on adsorbent without coating; ▲, ²H₂ on adsorbent coated with MnCl₂.

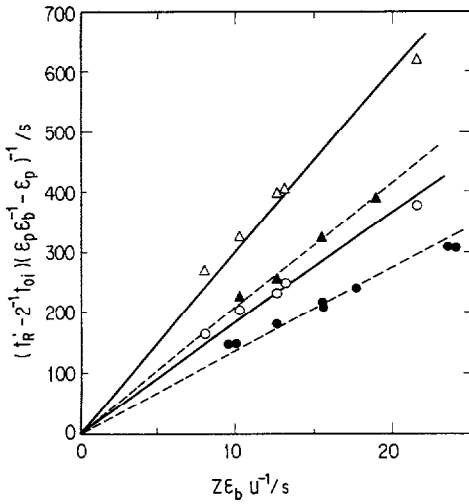


Fig. 7. Chromatographic parameters for H₂ and ²H₂ on alumina obtained from the moment method (eqn. 5). Dependence of the retention time on the flow-rate of carrier gas: ○, H₂ on alumina adsorbent without coating; ●, H₂ on adsorbent coated with MnCl₂; △, ²H₂ on adsorbent without coating; ▲, ²H₂ on adsorbent coated with MnCl₂.

The retention time can be calculated from eqns. 2 and 5 and the Henry law constants obtained in the present adsorption isotherm measurement. Table III lists the calculated and observed retention times under the analytical conditions used for the chromatograms shown in Fig. 5. No significant difference was observed between the retention times calculated with the series-of-stirred-tanks and dispersion models. The calculated retention time agreed approximately with the observed retention time,

TABLE III
RETENTION TIMES OF H₂ AND ²H₂ ON ALUMINA ADSORBENTS DRIED AT 383 K

		<i>Retention time (s)</i>	
		<i>H₂</i>	<i>²H₂</i>
With coating	Experimental observation	171	252
	Calculated value using Henry law constant of adsorption equilibrium		
	Series-of-stirred-tanks model	173	309
	Dispersion model	174	310
Without coating	Experimental observation	276	435
	Calculated value using Henry law constant of adsorption equilibrium		
	Series-of-stirred-tanks model	347	526
	Dispersion model	351	532

although the chromatographic experiments were performed on the alumina adsorbents packed in the stainless-steel column with neon as the carrier gas under conditions different from those used for the adsorption isotherm measurement by the volumetric method.

CONCLUSIONS

Remarkable increases in both the amount of hydrogen adsorbed at low equilibrium pressure and the heat of adsorption observed for alumina dried above 473 K were ascribed to the formation of active adsorption sites due to the appearance of O^{2-} and Al^{3+} on the surface resulting from the removal of hydroxyl groups.

The coating of alumina adsorbents with $MnCl_2$ made the surface deactivated, and it was elucidated that such adsorbents were suitable column packing materials at liquid nitrogen temperature for the separation of hydrogen isotopes by GSC. However, the deactivation effect disappeared with the alumina adsorbent dried above 473 K, since active adsorption sites of O^{2-} and Al^{3+} were formed with drying above 473 K regardless of the coating.

The adsorption equilibrium of the alumina-hydrogen system was a key parameter which determined the chromatographic performance. The present data for the adsorption equilibrium would lead to the selection of optimum conditions for column treatment as well as the design of a new adsorbent for GSC.

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REFERENCES

- 1 H. A. Smith and P. P. Hunt, *J. Phys. Chem.*, 64 (1960) 383.
- 2 W. R. Moore and H. R. Ward, *J. Phys. Chem.*, 64 (1960) 832.
- 3 P. P. Hunt and H. A. Smith, *J. Phys. Chem.*, 65 (1961) 87.
- 4 J. King, Jr., *J. Phys. Chem.*, 67 (1963) 1397.
- 5 E. H. Carter, Jr. and H. A. Smith, *J. Phys. Chem.*, 67 (1963) 1512.
- 6 M. Z. Gersh, *Anal. Chem.*, 37 (1965) 1786.
- 7 C. Genty and R. Schott, *Anal. Chem.*, 42 (1970) 7.
- 8 P. Urk and L. Linder, *Int. J. Appl. Radiat. Isot.*, 23 (1972) 239.
- 9 M. L. Conti and M. Lesimple, *J. Chromatogr.*, 29 (1967) 32.
- 10 M. Fujic, M. Kato and M. Tanase, *J. Appl. Radiat. Isot.*, 38 (1987) 1047.
- 11 H. Frischmuth, J. Perchermeier, A. Stimmelmayer and H. Weichselgartner, *Fifth Topical Meeting on the Technology of Fusion Energy, April 26-28, Knoxville, 1983*, p. 267.
- 12 K. Fujita and T. Kwan, *Bunseki Kagaku*, 12 (1963) 15.
- 13 W. S. Millman, F. H. Van Cauwelaert and W. Keith Hall, *J. Phys. Chem.*, 83 (1979) 2764.
- 14 J. B. Peri, *J. Phys. Chem.*, 69 (1965) 211.
- 15 J. M. Bather and R. A. C. Gray, *J. Chromatogr.*, 156 (1978) 21.
- 16 S. Suwanayuen and R. P. Danner, *AIChE J.*, 26 (1980) 68.
- 17 R. B. Stewart and H. M. Roder, *Technology and Use of Liquid Hydrogen*, Pergamon, New York, 1964, Ch. 11, p. 379.
- 18 E. Kucera, *J. Chromatogr.*, 19 (1965) 237.
- 19 P. Schneider and J. M. Smith, *AIChE J.*, 14 (1968) 762.
- 20 Y. W. Wong and F. B. Hill, *AIChE J.*, 25 (1979) 592.
- 21 R. S. Anderson and E. T. White, *Chem. Eng. Sci.*, 25 (1970) 1015.