

# ADSORPTION ISOTHERMS FOR TRITIUM ON VARIOUS ADSORBENTS AT LIQUID NITROGEN TEMPERATURE

TRITIUM SYSTEMS

**KEYWORDS:** tritium recovery, helium glow discharge exhaust gas, blanket sweep gas

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*The cryosorption method is useful for extracting hydrogen isotopes from a helium gas stream with a small amount of hydrogen isotopes. Therefore, in fusion reactors, this method is expected to be applied for the helium glow discharge exhaust gas processing system and the blanket tritium recovery system. To design these systems, adsorption isotherms for each hydrogen isotope are needed, making it possible to estimate the amount of adsorption in a wide pressure range. The amount of tritium adsorption on molecular sieve 5A, molecular sieve 4A, and activated carbon, which are potential adsorbents in the cryosorption bed, at liquid nitrogen temperature were quantified using the volumetric method. It was found that adsorption isotherms of tritium were also expressed with the two-site Langmuir model and that the obtained isotherms were close to the reported isotherms, the Langmuir coefficients for which were estimated using a reduced mass of hydrogen isotopes.*

## I. INTRODUCTION

The cryosorption method is useful for extracting hydrogen isotopes from a helium gas stream containing a

small amount of hydrogen isotopes. When a gas mixture containing hydrogen isotopes and He is introduced into the adsorption bed that is kept at cryogenic temperature using a refrigerant such as liquid nitrogen, hydrogen isotopes are adsorbed on the adsorbent, and only He flows out from the adsorption bed. In fusion reactors, this method is expected to be applied for the tritium recovery system such as the helium glow discharge (He GDC) exhaust gas processing system or the blanket tritium recovery system. In both systems, hydrogen isotopes including tritium must be extracted from the He gas stream efficiently. To design these systems, adsorption isotherms for each hydrogen isotope are needed, making it possible to estimate the amount of adsorption in a wide pressure range. Potential adsorbents for He GDC or the blanket tritium recovery system are molecular sieve 5A (MS5A), molecular sieve 4A (MS4A), and activated carbon. MS4A is expected to have a somewhat smaller amount of adsorption and a larger isotopic effect than MS5A, and activated carbon is expected to have larger adsorption capacity and a smaller isotopic effect than MS5A (Refs. 1 and 2). Adsorption isotherms for hydrogen isotopes on these materials at 77 K have been studied, but further study is still needed, especially concerning tritium (HT, DT, and T<sub>2</sub>). It has been reported that isotherms for T<sub>2</sub> can be estimated from H<sub>2</sub> and D<sub>2</sub> isotherms using a reduced mass of hydrogen isotopes,<sup>3</sup> but this has not yet been confirmed experimentally. Therefore, adsorption isotherms for T<sub>2</sub> on MS5A, MS4A, and activated carbon are planned and studied in the framework of U.S.-Japanese collaboration on fusion research and development.

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## II. THEORETICAL CONSIDERATIONS

Cryosorption experiments using MS5A, MS4A, and activated carbon with the breakthrough method have been performed by Nishikawa et al.<sup>1,2</sup> using H<sub>2</sub>, HD, and/or D<sub>2</sub> balanced with helium. Assuming that the amounts of He adsorption on these adsorbents are much smaller than those of hydrogen isotopes at 77 K, Nishikawa et al. have proposed the two-site Langmuir model for the adsorption isotherms for hydrogen isotopes on molecular sieves and activated carbon at 77 K. The two-site Langmuir model is based on the following assumptions:

1. Molecular sieves or activated carbon have two kinds of adsorption sites with different adsorption energies.
2. The Langmuir equation can be applied at each adsorption site.

Thus, the following equation is applied for the adsorption isotherm at a single adsorbate system:

$$Q_i = \frac{a_1^i P_i}{1 + b_1^i P_i} + \frac{a_2^i P_i}{1 + b_2^i P_i}, \quad (1)$$

where

$Q_i$  = adsorbed amount of hydrogen isotope ( $i$ ) per unit weight of adsorbent (mol  $Q_2/g$ )

$P_i$  = partial pressure of the hydrogen isotope (Pa)

$a^i, b^i$  = Langmuir coefficients for the hydrogen isotope.

The two-site Langmuir model can be easily extended to a multiadsorbate system using the Markham-Benton correlation.<sup>2,4</sup> For the multiadsorbate system, adsorption isotherms are expressed as

$$Q_i = \frac{a_1^i P_i}{1 + \sum_{i=1}^n b_1^i P_i} + \frac{a_2^i P_i}{1 + \sum_{i=1}^n b_2^i P_i}. \quad (2)$$

The Langmuir coefficients were reported for H<sub>2</sub>, HD, and D<sub>2</sub> on MS5A, MS4A, and activated carbon at 77 K (Refs. 1 and 2) and for HT on MS5A at 77 K (Ref. 5). In this work, the Langmuir coefficients for T<sub>2</sub> on MS5A, MS4A, and activated carbon at 77 K are investigated experimentally, and the aforementioned model is verified.

Langmuir coefficients and parameters concerned with the adsorption rate of hydrogen isotopes at 77 K have been reported to relate to the reduced mass of hydrogen isotopes.<sup>3</sup> Figure 1 shows the reported Langmuir coefficients  $a_1, b_1, a_2,$  and  $b_2$  for H<sub>2</sub>, HD, HT, and D<sub>2</sub>, respectively, for MS5A (Refs. 1, 2, and 5) plotted against the reduced mass of hydrogen isotopes, and the logarithmic plot shows that they seem to be proportional to the reduced mass. This model has the advantages of having a

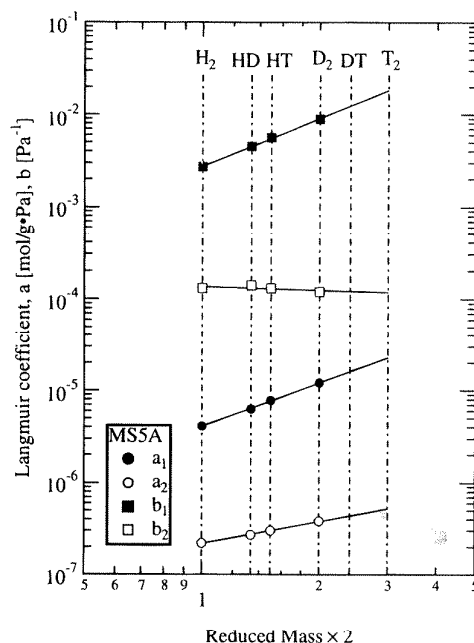


Fig. 1. The reported Langmuir coefficients for H<sub>2</sub>, HD, HT, and D<sub>2</sub> for MS5A plotted against the reduced mass in the logarithmic form.

simple form and being easily extended to a multiadsorbate system. Furthermore, if it is confirmed that the adsorption isotherms for T<sub>2</sub> obtained in this work are in good agreement with calculated ones using reduced mass, it may become possible to estimate the Langmuir coefficient for all hydrogen isotopes from the data of only two hydrogen isotopes.

## III. EXPERIMENTAL

Experiments on the isotherm with T<sub>2</sub> were performed at the Tritium System Test Assembly at Los Alamos National Laboratory as part of the U.S.-Japanese collaboration on fusion research and development.

Figure 2 shows a schematic diagram of the experimental apparatus. The experiments were performed using a volumetric method. Samples used in this work were MS5A ( $\frac{1}{16}$ -in. pellet) and MS4A ( $\frac{1}{16}$ -in. pellet) made by Wako Pure Chemical Industry, and activated carbon (12 to 30 mesh) made by Calgon Carbon. Weights of the charged samples after drying were 14.0, 14.3, and 9.96 g, respectively. Tritium stored in the zirconium-cobalt alloy packed bed (ZrCo bed) was introduced into the experimental apparatus by heating the bed. Experimental procedures were as follows:

1. After the volume measurements of the piping, reservoir tank, and sample cell, the sample was charged into

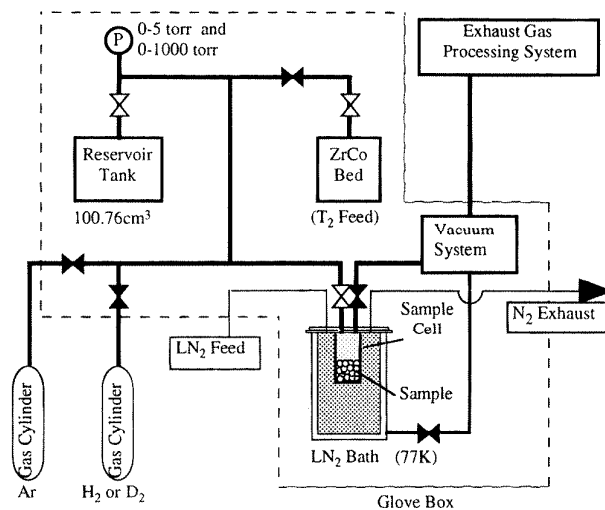


Fig. 2. A schematic diagram of an experimental apparatus.

the sample cell, and it was heated to 500 K under vacuum for >12 h to remove impurities.

2. After heat treatment, the sample was cooled to 77 K by supplying liquid nitrogen (LN<sub>2</sub>) into the LN<sub>2</sub> bath.

3. After confirmation that the temperature of the sample reached 77 K, the vacuum pump was stopped and the system pressure was recorded. This pressure was to be the base pressure of the experimental system.

4. After closing the valve of the sample cell, the prescribed amount of T<sub>2</sub> was introduced into the system (piping and reservoir tank), and the system pressure was recorded.

5. The sample was exposed to the gas. It took ~20 min or more to reach equilibrium.

6. After the equilibrium state was attained, the system pressure was recorded.

7. Steps 4 through 6 were repeated until the system pressure approached the atmospheric pressure.

The amounts of adsorbed hydrogen isotopes were estimated from the difference of the system pressure. The system pressure, which was measured with pressure transducers made by MKS Instruments, was in the ranges of 0 to 5 and 0 to 1000 Torr. After each experiment, the sample was heated to 500 K under vacuum to remove adsorbed hydrogen isotopes and impurities and was held until the next run. Isotherms were also taken with H<sub>2</sub> and D<sub>2</sub> to compare with that of T<sub>2</sub>.

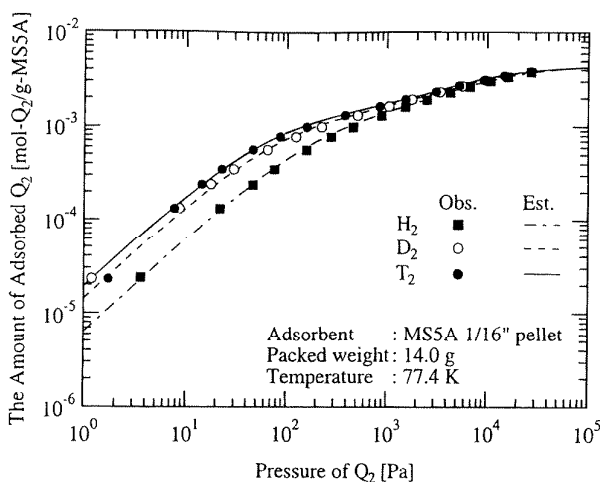
In this work, the effect of <sup>3</sup>He generation during the experiment was ignored because the amount of <sup>3</sup>He generated from tritium was estimated to be <0.0045% during an experiment that took ~7 h. Major experimental conditions are listed in Table I.

#### IV. RESULTS AND DISCUSSION

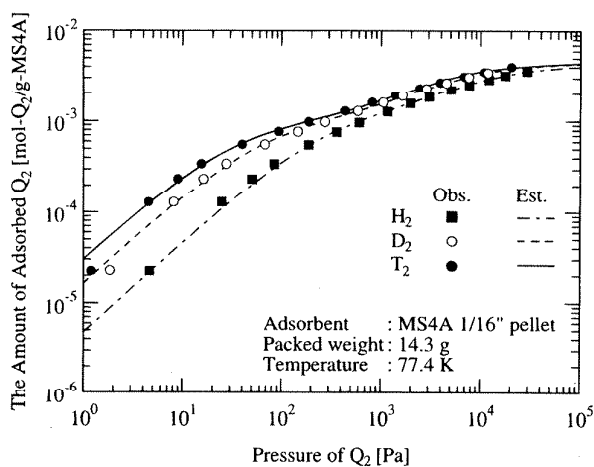
Figure 3a shows the adsorption isotherms obtained in this work for H<sub>2</sub>, D<sub>2</sub>, and T<sub>2</sub> for MS5A at 77 K. The adsorption isotherms were expressed well with the two-site Langmuir model [Eq. (1)], and Langmuir coefficients were obtained from the fitting of Eq. (1) to the data. The adsorbed amount of T<sub>2</sub> was the largest among the hydrogen isotopes. The isotopic effect on the adsorbed amount was large at low pressure, and it became smaller with increased pressure of hydrogen isotopes in the range up to atmospheric pressure. Figure 3b shows the adsorption isotherms obtained in this work for H<sub>2</sub>, D<sub>2</sub>, and T<sub>2</sub> for MS4A at 77 K. The adsorption isotherms

TABLE I  
Major Experimental Conditions

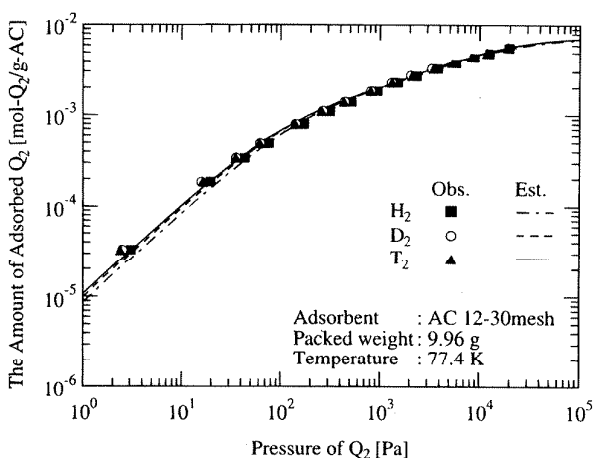
Sample	MS5A $\frac{1}{16}$ -in. Pellet (Wako Pure Chemical Industry)	MS4A $\frac{1}{16}$ -in. Pellet (Wako Pure Chemical Industry)	Activated Carbon 12 to 30 Mesh (American Society for Testing and Materials) (Calgon Carbon)
Charged weight (g)	14.0	14.3	9.96
Temperature	77 K		
Adsorbate	H <sub>2</sub> , D <sub>2</sub> , T <sub>2</sub>		
Reservoir tank	100.76 cm <sup>3</sup> (295 K)		
Pipeline	180.77 cm <sup>3</sup> (295 K)		
Sample cell	144.34 cm <sup>3</sup> (77 K)		



(a)



(b)



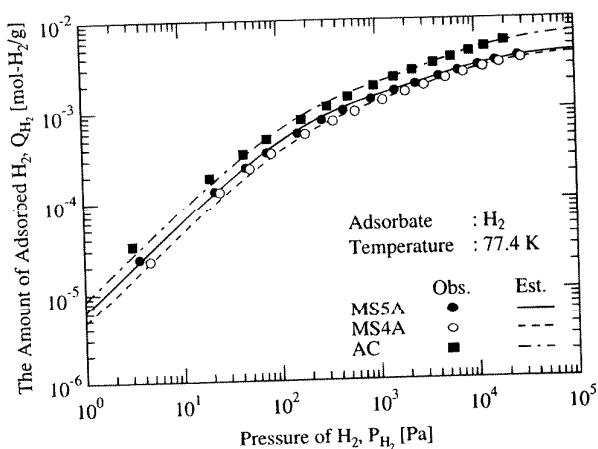
(c)

Fig. 3. Adsorption isotherms at 77 K for H<sub>2</sub>, D<sub>2</sub>, and T<sub>2</sub> on (a) MS5A, (b) MS4A, and (c) activated carbon.

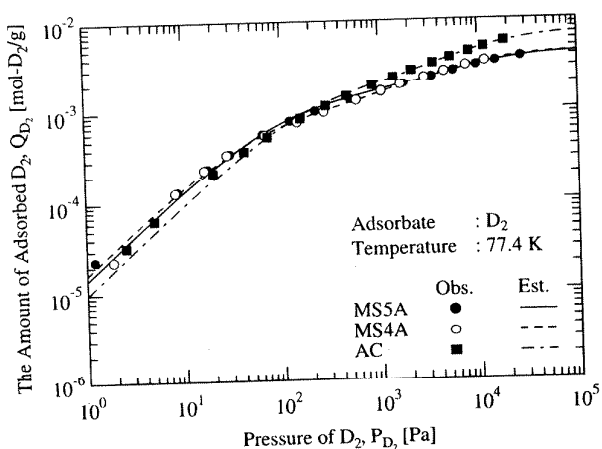
could also be expressed well with the two-site Langmuir model, and Langmuir coefficients were obtained. The adsorbed amount of T<sub>2</sub> was also the largest among the hydrogen isotopes. The isotopic effects on the adsorbed amount were also large at low pressure, and it became smaller with increased pressure of hydrogen isotopes, just as for MS5A. Figure 3c shows the obtained isotherms for activated carbon. Results were similar to those obtained for MS5A and MS4A, but the isotopic effect on the adsorbed amount on activated carbon was smaller than for MS5A and MS4A.

Figures 4a, 4b, and 4c show the same data but for the comparison of the adsorption capacity of MS5A, MS4A, and activated carbon. In the case of H<sub>2</sub>, the adsorbed amount is the largest for activated carbon and the smallest for MS4A under the given pressure region. In the case of T<sub>2</sub>, however, the adsorbed amount is the largest for MS4A only in the region <100 Pa. So, the isotopic effect on the adsorbed amount is the largest for MS4A among the samples tested in this work. From the viewpoint of the adsorbed amount and its isotopic effect, MS4A is a more suitable material for the blanket tritium recovery system than MS5A or activated carbon because the partial pressure of hydrogen isotopes in the blanket sweep gas is considered to be ~100 Pa.

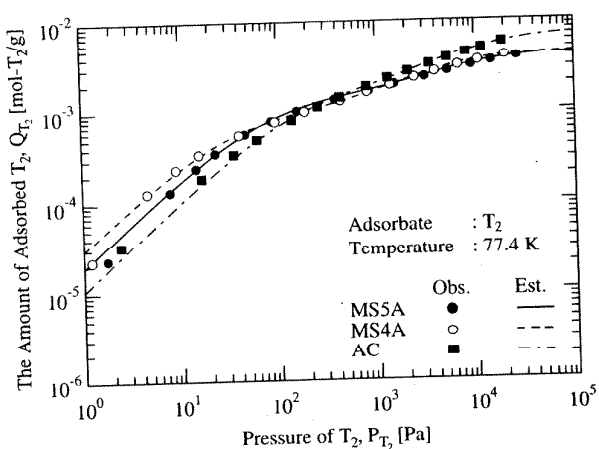
Figures 5a, 5b, and 5c show the comparison of adsorption isotherms obtained in this work and those reported by Nishikawa et al.<sup>1</sup> In each figure, the isotherm line for T<sub>2</sub> was estimated using extrapolated Langmuir coefficients with the reduced mass. In the case of MS5A, Nishikawa et al.'s isotherms can express the present data with fairly good accuracy, but they are slightly different above ~1000 Pa. Our work shows that the isotopic effect on the adsorbed amount becomes smaller with increasing pressure, but Nishikawa et al.'s work indicates that the effect increases again at higher pressure. In the case of MS4A, Nishikawa et al.'s isotherms agree with our data with fairly good accuracy, but they are slightly different above ~1000 Pa, as seen in the case of MS5A. Our work shows that the isotopic effect on the adsorbed amount becomes smaller with increasing pressure, but the effect increases again at higher pressure in Nishikawa et al.'s report. In the case of activated carbon, the reported isotherms become larger than experimental observation above ~1000 Pa. A possible cause of these differences is the pressure range of hydrogen isotopes. Nishikawa et al.<sup>1,2</sup> have performed experiments with the breakthrough method using He as the carrier gas under atmospheric pressure. The ranges of the partial pressure of hydrogen isotopes were <1000 Pa in their experiments. Isotherms reported by them are based on the data obtained <1000 Pa of partial pressure. This may explain why these isotherms disagree with our data >1000 Pa. On the other hand, in the case of activated carbon, their isotherms are smaller than our data at lower pressures. Also, in the cases of other adsorbents, Nishikawa et al.'s isotherms are slightly smaller than our data at lower



(a)

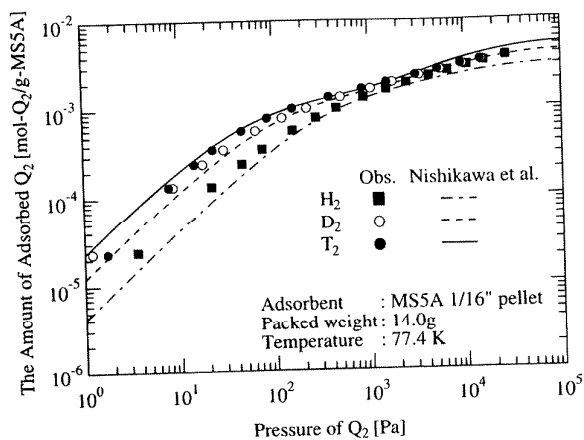


(b)

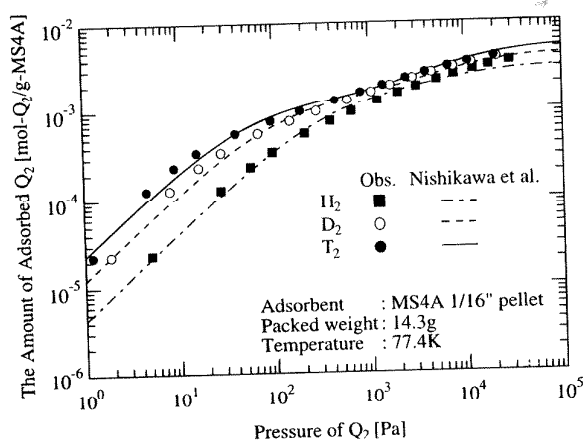


(c)

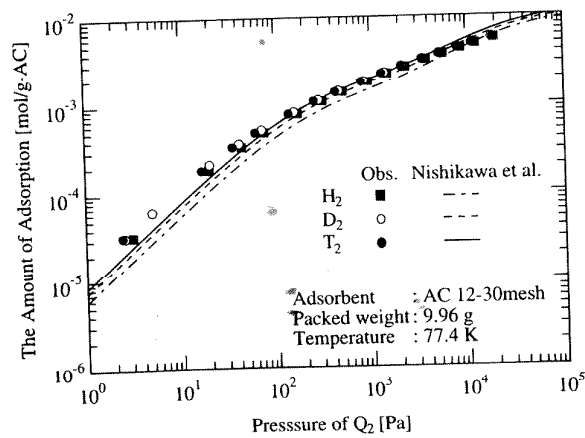
Fig. 4. Comparison of the adsorption capacity of MS5A, MS4A, and activated carbon for (a) H<sub>2</sub>, (b) D<sub>2</sub>, and (c) T<sub>2</sub>.



(a)



(b)



(c)

Fig. 5. Comparison between isotherms reported by Nishikawa et al. in Refs. 1 and data obtained in this work for (a) MS5A, (b) MS4A, and (c) activated carbon.

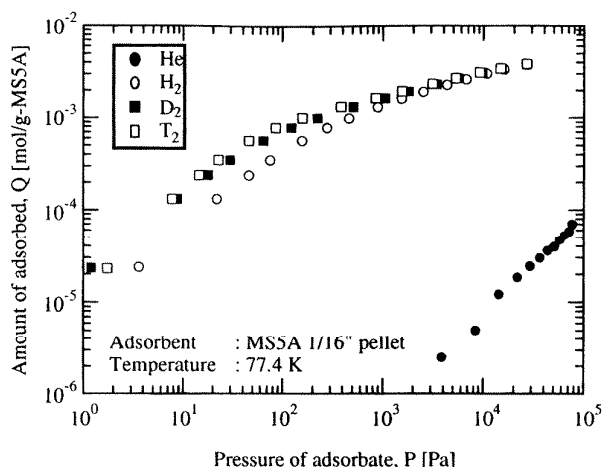


Fig. 6. Comparison between amount of adsorbed hydrogen isotopes and helium for MS5A at 77 K.

pressures. A possible cause is the adsorption of He mixed in the stream. Figure 6 shows a comparison of isotherm data obtained in this work for He and hydrogen isotopes for MS5A. The amount of adsorbed He at nearly atmospheric pressure is almost same as that of hydrogen isotopes at ~10 Pa. This condition is almost same as the experimental condition reported by Nishikawa et al.<sup>1,2</sup> It may not be realistic to discuss the adsorption capacity in a multiadsorbate system using that in a single adsorbate system, as shown in Fig. 6, but this adsorbed amount of He is considered to be significant.

As mentioned earlier, isotherms for T<sub>2</sub> obtained in this work agree with fairly good accuracy with calculated ones using Langmuir coefficients estimated from the reduced mass of hydrogen isotopes. Therefore, as described in the report by Nishikawa et al.,<sup>3</sup> Langmuir coefficients for hydrogen isotopes can be known without experiments only if they are first obtained experimentally for two other hydrogen isotopes. The

TABLE II  
Langmuir Coefficients Obtained in This Work for Hydrogen Isotopes for MS5A at 77 K

	$a_1$ (mol/g·Pa)	$b_1$ (Pa <sup>-1</sup> )	$a_2$ (mol/g·Pa)	$b_2$ (Pa <sup>-1</sup> )
MS5A				
H <sub>2</sub>	$6.0 \times 10^{-6}$	$4.4 \times 10^{-3}$	$3.5 \times 10^{-7}$	$1.1 \times 10^{-4}$
HD <sup>a</sup>	$8.4 \times 10^{-6}$	$6.0 \times 10^{-3}$	$3.7 \times 10^{-7}$	$1.2 \times 10^{-4}$
HT <sup>a</sup>	$9.5 \times 10^{-6}$	$6.8 \times 10^{-3}$	$3.8 \times 10^{-7}$	$1.2 \times 10^{-4}$
D <sub>2</sub>	$1.4 \times 10^{-5}$	$9.8 \times 10^{-3}$	$4.0 \times 10^{-7}$	$1.3 \times 10^{-4}$
DT <sup>a</sup>	$1.6 \times 10^{-5}$	$1.1 \times 10^{-2}$	$4.2 \times 10^{-7}$	$1.4 \times 10^{-4}$
T <sub>2</sub>	$1.9 \times 10^{-5}$	$1.3 \times 10^{-2}$	$4.5 \times 10^{-7}$	$1.5 \times 10^{-4}$

<sup>a</sup>Interpolation using reduced mass.

TABLE III  
Langmuir Coefficients Obtained in This Work for Hydrogen Isotopes for MS4A at 77 K

	$a_1$ (mol/g·Pa)	$b_1$ (Pa <sup>-1</sup> )	$a_2$ (mol/g·Pa)	$b_2$ (Pa <sup>-1</sup> )
MS4A				
H <sub>2</sub>	$4.4 \times 10^{-6}$	$3.9 \times 10^{-3}$	$3.5 \times 10^{-7}$	$1.1 \times 10^{-4}$
HD <sup>a</sup>	$7.4 \times 10^{-6}$	$6.9 \times 10^{-3}$	$4.6 \times 10^{-7}$	$1.4 \times 10^{-4}$
HT <sup>a</sup>	$9.2 \times 10^{-6}$	$8.6 \times 10^{-3}$	$5.1 \times 10^{-7}$	$1.5 \times 10^{-4}$
D <sub>2</sub>	$1.6 \times 10^{-5}$	$1.6 \times 10^{-2}$	$7.0 \times 10^{-7}$	$2.0 \times 10^{-4}$
DT <sup>a</sup>	$2.1 \times 10^{-5}$	$2.1 \times 10^{-2}$	$7.8 \times 10^{-7}$	$2.2 \times 10^{-4}$
T <sub>2</sub>	$3.0 \times 10^{-5}$	$3.1 \times 10^{-2}$	$9.2 \times 10^{-7}$	$2.6 \times 10^{-4}$

<sup>a</sup>Interpolation using reduced mass.

TABLE IV

Langmuir Coefficients Obtained in This Work for Hydrogen Isotopes for Activated Carbon at 77 K

	$a_1$ (mol/g·Pa)	$b_1$ (Pa <sup>-1</sup> )	$a_2$ (mol/g·Pa)	$b_2$ (Pa <sup>-1</sup> )
Activated carbon				
H <sub>2</sub>	$8.1 \times 10^{-6}$	$4.6 \times 10^{-3}$	$5.7 \times 10^{-7}$	$1.0 \times 10^{-4}$
HD <sup>a</sup>	$8.6 \times 10^{-6}$	$5.0 \times 10^{-3}$	$6.0 \times 10^{-7}$	$1.0 \times 10^{-4}$
HT <sup>a</sup>	$8.8 \times 10^{-6}$	$5.1 \times 10^{-3}$	$6.2 \times 10^{-7}$	$1.1 \times 10^{-4}$
D <sub>2</sub>	$9.3 \times 10^{-6}$	$5.5 \times 10^{-3}$	$6.5 \times 10^{-7}$	$1.1 \times 10^{-4}$
DT <sup>a</sup>	$9.6 \times 10^{-6}$	$5.9 \times 10^{-3}$	$6.8 \times 10^{-7}$	$1.1 \times 10^{-4}$
T <sub>2</sub>	$1.0 \times 10^{-5}$	$6.4 \times 10^{-3}$	$7.2 \times 10^{-7}$	$1.2 \times 10^{-4}$

<sup>a</sup>Interpolation using reduced mass.

Langmuir coefficients of H<sub>2</sub>, D<sub>2</sub>, and T<sub>2</sub> obtained in this work are listed in Tables II, III, and IV. The Langmuir coefficients for HD, HT, and DT estimated using interpolation with the reduced mass are also listed in these tables.

## V. CONCLUSION

Measurements of adsorption isotherms for hydrogen isotopes, particularly pure tritium for MS5A, MS4A, and activated carbon at 77 K, were performed. Measured adsorption isotherms were found to be expressed with the two-site Langmuir model, and Langmuir coefficients were obtained.

As a result, it was verified that Langmuir coefficients correlate with the reduced mass, even for tritium. This indicates that adsorption isotherms need to be obtained experimentally for only two of six hydrogen isotopes to know all of them.

## REFERENCES

1. M. NISHIKAWA, K. TANAKA, and M. UETAKE, "Study on a Method to Recover Tritium from Blanket Sweep Gas," *Fusion Technol.*, **26**, 17 (1994).
2. M. NISHIKAWA, K. TANAKA, M. UETAKE, M. ENOEDA, Y. KAWAMURA, and K. OKUNO, "Adsorption Isotherm and Separation Factor for Multicomponent Hydrogen Isotopes in Cryosorption Method for Recovery of Tritium from Blanket Sweep Gas," *Fusion Technol.*, **28**, 711 (1995).
3. M. NISHIKAWA, K. TANAKA, M. UETAKE, and T. SHIRAISHI, "Isotope Effect in Cryosorption of Tritium to Molecular Sieves and Activated Carbon at 77 K," *Fusion Technol.*, **34**, 234 (1998).
4. E. C. MARKHAM and A. F. BENTON, "The Adsorption of Gas Mixtures by Silica," *J. Am. Chem. Soc.*, **53**, 497 (1931).
5. M. ENOEDA, Y. KAWAMURA, K. OKUNO, K. TANAKA, M. UETAKE, and M. NISHIKAWA, "Recovery of Hydrogen Isotopes and Impurity Mixture by Cryogenic Molecular Sieve Bed for GDC Gas Cleanup," *Fusion Technol.*, **28**, 591 (1995).

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