only six are known with sufficient accuracy to permit their use in determining the structure. Taking into account also the fact that the moments of inertia are not very sensitive to the locations of the relatively light hydrogen and deuterium atoms, it seemed best to assume that the geometry of the molecule, CF_3CX_2Y, was completely unaffected by isotopic substitution. The configuration then depends on only five parameters which must be evaluated using a method of successive approximations.

The results of these considerations are presented in Table V in the form of a set of bond distances and angles giving the best agreement with the observed moments of inertia. Table VI compares the results of this set with the observed moments. It can be seen that the calculated values are in good agreement with the observed ones. The structural parameters determined in this work are in excellent agreement with the values obtained by Brandt and Livingston[5] (Table I).

TABLE V

MOLECULAR PARAMETERS

C-C, Å.	1.530 ± 0.005
C-F, Å.	1.335 ± 0.005
C-H, Å.	1.085 ± 0.008
∠CCF	111°02′ ± 17′
∠CCH	108°19′ ± 35′

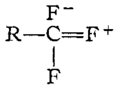
TABLE VI

MOMENTS OF INERTIA IN GCM.^{2} × 10^{40}

	Moment	Obsd.	Calcd.
CF_3CH_3	I_b	161.812	161.861
CF_3CD_3	I_b	182.177	182.177
CH_3CH_2D	I_a	151.3[a]	153.3
	I_b	168.618	168.610
	I_c	169.601	169.638
CF_3CD_2H	I_a	155.1[a]	155.3
	I_b	174.634	174.635
	I_c	176.900	176.918

[a] The uncertainty in these moments is ±6.8 whereas the uncertainty in all other moments is ±0.007.

The C–F bond distance and the CCF angle are consistent with those values found in other molecules containing the CF_3 group.[15] In particular, comparison with the fluoromethane series[16] shows that the C–F bond distance determined for CF_3CH_3 has about the expected value for a singly bonded CF_3 group (C–F = 1.385 Å. in CH_3F, 1.358 Å. in CH_2F_2 and 1.326 Å. in CHF_3). It has been postulated[16] that the slight shortening of the C–F bond and slight closing of the FCF angle in CHF_3 can be associated with the occurrence of resonance structures[17] of the type



$$R{-}\overset{F^-}{\underset{F}{C}}{=}F^+ \qquad \text{(I)}$$

It is certainly conceivable that structures of this type can also contribute to the slight closing of the tetrahedral umbrella of the CF_3 group in CF_3CH_3.

Since the C–H distance in Table V is based upon the assumption that C–H = C–D, it probably represents an average value lying somewhere between the true values of the C–H and C–D bond distances. By analogy with the results obtained by Miller, *et al.*,[18] for the methyl halides, the C–D bond could be expected to be shorter than the C–H bond by perhaps 0.009 Å.

Acknowledgment.—The authors wish to express their thanks to Dr. Norbert Muller for some helpful discussions. They are also grateful to the Proctor and Gamble Company and to the Purdue Research Foundation, acting under Contract AT-(11-1)-164 in coöperation with the Atomic Energy Commission, whose support has made this research possible.

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LAFAYETTE, INDIANA

[CONTRIBUTION NO. 89 FROM THE CRYOGENIC LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Heats of Adsorption of Hydrogen and Helium on Prepared Surfaces*

BY WILLIAM A. STEELE AND J. G. ASTON

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Measurements have been made of the heats of adsorption of helium on titanium dioxide powder which had varying amounts of argon preadsorbed on it. Some measurements of the heats of adsorption of hydrogen were also made on similar systems. It is assumed that high energy sites for physical adsorption occur at surface roughnesses and faults. The experimental data are discussed in terms of this model, and it is seen that this work provides an excellent confirmation of this hypothesis.

Introduction

In a recent publication by the authors and Tykodi,[1] an analysis was made of the isotherms and heats of adsorption of a number of rare gases on titanium dioxide. The data were fitted to a model in which lateral interaction in the adsorbate was neglected, but in which the surface heterogeneity of the adsorbent was taken into account. A single site distribution function was taken to characterize the titanium dioxide surface in all cases. The physical considerations underlying the choice of distribution function were as follows: the major portion of the adsorption sites (about 60%) were considered to be those formed by the flat surface of the adsorbent, having energies which could be estimated by calculating the energy due to dis-

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(*) This research was carried out under Contract DA-36—061-ORD-509 of the Office of Ordnance Research.

(1) J. G. Aston, R. J. Tykodi and W. A. Steele, *J. Phys. Chem.*, **59**, 1053 (1955).

persion forces between a gas atom and a planar titanium dioxide surface[2]; the remainder of the adsorption sites were then assumed to be due to imperfections in the surface structure (so-called topographical heterogeneity) such as cracks, holes, grain boundaries, etc. On such a site, an adsorbed atom would have a larger interaction with the solid than on a planar site, due to adjacent surfaces making angles (other than zero) with the planar surface.

This model for adsorption could not be expected to work too well for neon or argon, since these adsorbates exhibit appreciable lateral interaction near the monolayer. However, adsorbed helium, and to a lesser extent hydrogen, should give isotherms and heats which are determined almost exclusively by the site distribution of the adsorbent. The actual site distribution chosen was admittedly a rough approximation to reality, but agreement between experiment and theory was sufficient to inspire further investigation.

The present paper is concerned with an attempt to verify the assumptions made concerning the source of surface heterogeneity of the titanium dioxide used previously. To this end, the heats of adsorption of helium and hydrogen were measured on titanium dioxide powder which had had varying amounts of argon preadsorbed upon it. If the heterogeneity was actually due to imperfections in the surface, a sufficient amount of preadsorbed argon would be expected to fill in the high energy sites, effectively removing them and replacing them by a planar surface composed partly of argon atoms and partly of titanium dioxide molecules. The application of the Kirkwood–Müller formula[3] shows that the energy of interaction of a helium atom with an argon crystal is about the same as that of a helium atom with a titanium dioxide crystal. Thus, the preadsorption of argon on a titanium dioxide surface should produce a roughly uniform surface for helium adsorption. In a preliminary communication[4] it was shown that about one-half layer of argon is sufficient to remove almost all signs of heterogeneity in the heats of adsorption of helium. The results of an extensive investigation of this effect will be presented here, and also the experimental techniques used will be discussed in some detail.

Results and Discussion

Measurements were made of the heat of adsorption of helium on a bare titanium dioxide surface, on titanium dioxide plus 0.36 layer of argon, 0.60 layer and 1.05 layers. The temperatures of measurement were from 10–17°K., and the adsorption pressures of the helium were less than 100 cm. at all times. Under these conditions, no multilayer adsorption can occur, and the correlation of the measured heats with the site distribution in the surface is very nearly complete. The results of these experiments are shown in Fig. 1, where isosteric heats of adsorption of helium in cal./mole are plotted against the amount adsorbed in units of cc.-S.T.P. per gram of adsorbent. Some heats measured by Aston, Mastrangelo and Tykodi[5] on another sample of the same titanium dioxide as that used in this work are included for comparison. The precision of the data is within the estimated 5% (see Experimental), and the corrected calorimetric heats agree well with those calculated from the isotherms. Even the preadsorption of 0.36 layer of argon markedly reduces the heterogeneity of the surface and removes all sites with heat of 400 cal./mole or greater. The heat curves are such that in terms of the topographical model only a small number of sites of energy 250–400 cal./mole are left, and this residue of high energy sites is filled in by 0.25 additional layers of argon.

No significant change can be detected in the shape of the curve of heat of adsorption *versus* coverage when one adds 0.45 layer of argon to a surface which already holds 0.60 layer, although the curve is not quite flat. If the energy of interaction of a helium atom with a titanium dioxide surface was not essentially identical with the energy of interaction with a titanium dioxide substrate covered with a monomolecular layer of argon, one would expect that the heat of adsorption curve would change significantly upon the addition of argon to uncovered titanium dioxide surface. Thus, one may conclude, in agreement with the result calculated from the Kirkwood–Müller formula, that the energy of interaction of an adsorbed atom with titanium dioxide is identical to the interaction energy with titanium dioxide coated with argon, within the accuracy of these experiments.

There is, however, a small decrease in the heat of adsorption with coverage even in the system where a full layer of argon has been preadsorbed. It is suggested that this residual heterogeneity is due to the fact that preferred sites will occur on a perfectly planar surface, due to the periodic nature of the surface potential energy. For instance, the maximum calculated energy due to dispersion forces is roughly 100% greater for a helium atom over the center of a lattice cell in the surface of a simple cubic argon-like crystal than the energy of interaction when the helium atom is over a corner of the lattice cell.[6] Since the energy of interaction of helium with a solid such as titanium dioxide is due mainly to the dispersion energy of the adsorbed atom with the atoms in the solid, one would certainly expect some decrease in the differential molar heats of adsorption of helium on such a solid, independent of any topographic effects.

In Fig. 2 are displayed the heats of adsorption of hydrogen *versus* coverage for two surfaces: bare titanium dioxide and titanium dioxide plus 0.60 layer of preadsorbed argon.

The heats of adsorption of hydrogen on the titanium dioxide plus 0.6 layer of argon show no signs of topographical heterogeneity. The effect of the residual heterogeneity mentioned in the previous paragraph seems to be of the same order of magnitude for hydrogen as for helium. How-

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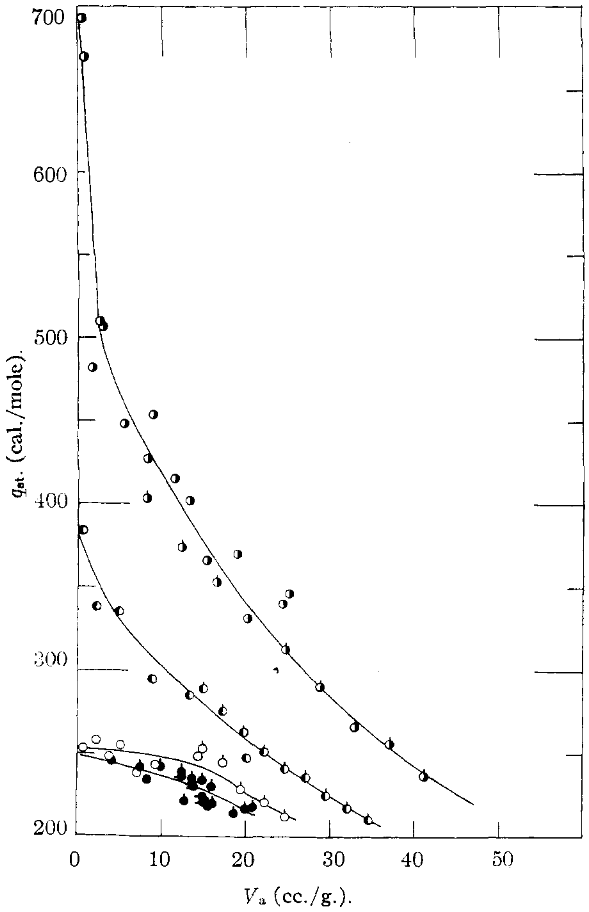

Fig. 1.—Isosteric heats of adsorption of helium on various surfaces: ◑, heats on bare titanium dioxide; ◐, heats on titanium dioxide plus 0.36 layer of preadsorbed argon; ○, heats on titanium dioxide plus 0.60 layer of preadsorbed argon; ●, heats of titanium dioxide plus 1.05 layers of preadsorbed argon. The points without tabs are calorimetric; those with tabs were calculated from the isotherms using the Clausius–Clapeyron equation.

ever, the higher energy sites fill in more rapidly in the case of hydrogen adsorption.

When the heat curves for helium and hydrogen adsorbed on bare titanium dioxide are compared, it is apparent that a large fraction of the high energy sites seems to be absent when the hydrogen is used as an adsorbate. For instance, the number of sites of energy two or more times the energy of adsorption on the flat surface is quite large when helium is adsorbed. However, almost no such states are available for hydrogen adsorption. At first glance, it would seem that such an effect is in contradiction to the hypothesis that the high energy sites are found in cracks or holes in the titanium dioxide crystals. It is unlikely that this unavailability of high energy sites for hydrogen could be due to any great extent to the difference in molecular dimensions, since the two molecules are very similar in size (the collision diameters of hydrogen and helium are 2.9 and 2.6 Å., respectively[7]).

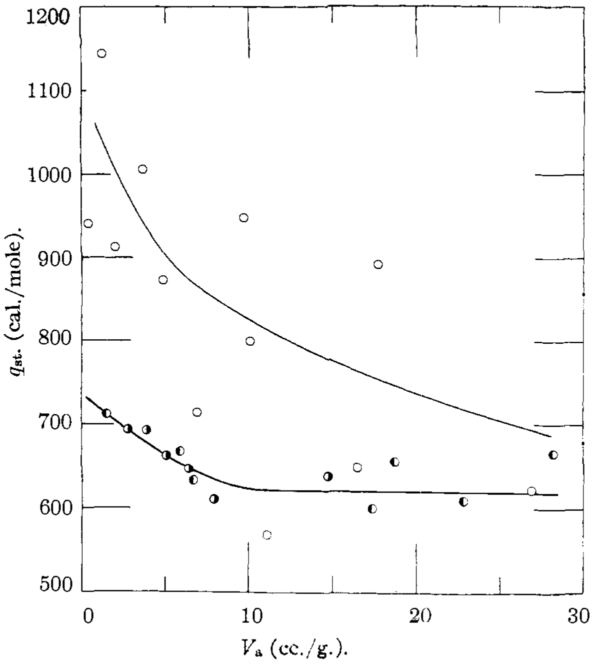

Fig. 2.—Isosteric heat of adsorption of hydrogen on various surfaces: ○, parahydrogen on bare titanium dioxide; ◑, parahydrogen on titanium dioxide plus 0.60 layer of preadsorbed argon; ◐, normal (room temperature equilibrium) hydrogen on titanium dioxide plus 0.60 layer of preadsorbed argon.

The most probable explanation has its basis in the fact that the thermal energy of hydrogen molecules at the temperatures of these experiments is quite small compared to the energy of binding to the surface. Thus, the hydrogen will be almost completely immobilized upon adsorption. In particular, the rate of diffusion into the surface faults which give rise to the high energy sites may be negligibly small. Indeed, the adsorbed phase is most probably in a metastable state during the time span of an experiment. This line of reasoning is further supported by the extremely long "equilibrium times" (see Experimental) and by the fact that the scatter of the data for the bare surface is considerably larger than the estimated precision of the method. (For these reasons, it did not seem worthwhile to make any more extensive measurements at low coverages of adsorbed hydrogen than those presented here.)

Experimental

The calorimeter used in this work was a modified version of the one used by Frederikse.[8] This system is designed to operate with the surroundings kept at a constant temperature close to that of the calorimeter by regulating the vapor pressure of the bath. The temperature rise during any process was then found by extrapolation of the equilibrium drift rates. Adequate thermal isolation of the calorimeter from the surroundings could be obtained by maintaining a good vacuum in the envelope which separated the calorimeter from the bath. Two german silver filling tubes were led through the bath space to the top of the vacuum envelope. These tubes make two loops in the bath just above the vacuum envelope to ensure that the incoming gas passes through at least one foot of tubing at the temperature of the bath. In this way, it is believed that the gas was brought sufficiently close to the temperature of the adsorbent that

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(7) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, Cambridge, England, 1952, p. 285.

(8) H. P. R. Frederikse, Thesis, Leiden, 1950.

the amount of heat absorbed or given off to the calorimeter by the gas in coming to the temperature of the calorimeter was a negligible quantity compared to the heat evolved on adsorption. After entering the vacuum envelope, the filling tubes made three more loops inside: thus, the calorimeter is connected to the bath through two one-foot lengths of german silver tube, and by the electrical leads. The eight electrical connections to the thermometer and heater are led through the top of the envelope *via* platinum-glass take-out caps, and come to the thermometer and heater proper *via* eight one-foot lengths of #29 constantan wire which are lacquered to the filling tubes in two groups of four. A phosphor bronze thermometer for work at 1–4°K. and a constantan heater were included (R = 106 ohms at 14°K.). The constantan heater also served as a thermometer ($\Delta T/\Delta R$ = 6.071°/ohm) in the range 10–20°K.

The calorimeter itself was filled with 83 g. of high surface area titanium dioxide (the B.E.T. nitrogen monolayer capacity was 52.4 cc. STP/g.). Twelve copper plates were placed in the powder at intervals along the length of the calorimeter in an attempt to decrease equilibrium times. The Dewar enclosing the bath space was set inside a second Dewar which contained liquid nitrogen. This served two purposes: the rate of evaporation of hydrogen in the inner Dewar due to radiation was greatly decreased; also, by breaking the vacuum in the inner Dewar and in the envelope, the calorimeter and its contents could be cooled easily to 80°K. with liquid nitrogen and 60°K. with solid nitrogen. As pointed out by Singleton and Halsey,[9] a long period of slow cooling is necessary to ensure that the preadsorbed layer is in an equilibrium distribution over the surface. Since these experiments were made with comparatively small amounts of preadsorbed gas, the gas was more firmly bound to the surface, and the equilibrium process was not quite as sensitive to variations in method as in the experiments of Singleton and Halsey. Allowing small variations in the time and technique of precooling, three runs were made on the system with one-half layer of preadsorbed argon, and two runs on the system with one layer. No significant difference could be detected in isotherms or isosteric heats. In general, the desired quantity of gas was admitted to the calorimeter at 80°K.; the system then was cooled slowly to 60°K. and held at that temperature for at least eight hours. The bath space subsequently was filled with liquid hydrogen and the remainder of the cooling done in 30 minutes or less.

The techniques used in the measurement of the helium heats differed in some respects from those used in the hydrogen work. In the helium experiments, the calorimeter was first cooled to 10°K. The heat capacity of the system was measured; following this, a measured amount of gas was admitted to the calorimeter. After the system had reached thermal equilibrium, a second heat capacity measurement was made. Since these determinations were made without cooling the calorimeter during the sequence, the final temperature was then about 17°. The system was then cooled to 10°K. and the cycle repeated. After applying the usual corrections,[10,11] curves of heat capacity *versus* coverage at two temperatures were constructed; a further correction was necessary to correct the measured heat capacities to two common temperatures. In order to determine partial molal heats of adsorption (often called "differential" heats or isosteric heats[10,11]), the heat capacity at the average temperature of measurement was obtained by interpolation. The partial molal heat of adsorption was then calculated in the customary manner. The conventional corrections for heat of compression were, of course, applied.[10,11] The largest source of error lay in the interpolation procedure, since the heat capacity changed by roughly a factor of two over the temperature range of the experiments. The estimated precision of the partial molal heats of adsorption of helium is 5%. The corrections for heat of compression become excessively great at coverages where the pressure is large (over 100 mm.). In this region, more accurate results were obtained by calculating the heats from the measured isotherms.

The procedure followed in the hydrogen experiments could be simplified somewhat due to two factors: the time required to pump out exchange gas is considerably less at 18°K. than at 10°K., and the heat capacity of the system is not so sensitive to temperature changes in this region. Thus the calorimeter was cooled to 18° and a heat capacity measurement was made. The calorimeter was then cooled to 18° again and the desired quantity of gas admitted. The corrections for heat of compression were negligible, since the adsorbed hydrogen had no appreciable vapor pressure at the temperatures and coverages of these experiments. The major source of error in these measurements was in the determination of the equilibrium drift rates after gas was admitted to the system and also, to a lesser extent, after a heat capacity. In these experiments, the time required for equilibrium was extremely long (of the order of 1.5 to 2 hours in some determinations). Thus, errors in the calculated temperature rise were quite appreciable if the equilibrium drift rate was in error by a small amount. The estimated precision of these heats is also about 5%.

In order to ensure that no spurious heat effects were present due to the conversion of the room temperature mixture to parahydrogen, the hydrogen used in all but one of these experiments was first converted to the 20°K. equilibrium mixture. The method followed was that of Squires and Stewart,[12] who used a catalyst of charcoal plus preadsorbed oxygen at 20°K. They estimated the half-time of the reaction to be 10–20 minutes. In the present work, the hydrogen was left in contact with the catalyst for a minimum of 60 minutes before it was used.

Room temperature equilibrium hydrogen was used in one of the runs on the titanium dioxide plus 0.60 layer of preadsorbed argon to ascertain whether the rotational state of the adsorbed hydrogen had an appreciable effect on the heat of adsorption. It is clear from the data shown in Fig. 2 that the difference in the heats is negligible insofar as these experiments are concerned.

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