A comparison of the transfer constants of styrene and *p*-chlorostyrene (Table V) illustrates the sensitivity of the transfer constants toward small changes in the polarity of the monomer. Alfrey, *et al.*,[10] bring attention to the fact that the Q, e scheme is not very useful in analyzing small changes in reactivity such as would be caused by the introduction of a halogen atom into the ring of styrene. They determined as the "best" values of Q and e for *p*-chlorostyrene, $Q = 1.3$, $e = -1$; however, the shift from the values for styrene ($Q = 1$, $e = -0.8$) is of the same order of magnitude as the experimental uncertainties in Q and e. The question is raised, therefore, as to whether or not the substitution of a chlorine atom in the *para* position of styrene actually confers a more electron donating character to the monomer. Our studies reveal an appreciably greater transfer constant for *p*-chlorostyrene than styrene and thereby indicate a higher electron donating character for the *p*-chlorostyryl radical. The higher transfer constant for *p*-chlorostyrene is not associated with the change in monomer reactivity (the Q term) since this factor should tend to lower the transfer constant for the more resonance stabilized *p*-chlorostyryl radical.

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[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Heat of Adsorption of Argon Adsorbed on Titanium Dioxide between 60 and 90°K.

BY E. L. PACE AND S. A. GREENE

RECEIVED JANUARY 11, 1954

The heat of adsorption of argon on titanium dioxide has been measured with a modified Nernst–Giauque calorimeter at temperatures of 63.5, 73.0, 78.5 and 86.5°K. for concentrations ranging to a maximum value of the order of a monolayer. The heat capacity of the adsorbed phase was determined between 55 and 90°K. in the same range of concentrations. By using the heat capacity data it was found possible to reduce the experimentally determined differential heats of adsorption at 73.0, 78.5 and 86.5 to a single curve at 63.5°K. within the experimental error. Therefore, at these temperatures, it is believed that the experimental method has yielded thermodynamically reversible results. The results of the experimental measurements at 63.5°K. do not fall on the single curve, and consequently the adsorption process appears to be metastable at this temperature. The differential heat curves for the equilibrium and non-equilibrium processes have been used to determine the corresponding energy distribution at the sites of adsorption.

Introduction

The present work is concerned with a calorimetric investigation of the heat of adsorption of argon adsorbed on a sample of titanium dioxide between 60 and 90°K. The concentrations of the adsorbed argon were dilute, the maximum value being approximately the monolayer capacity. The results of such measurements are of interest because of the knowledge they provide on the distribution of energy among the adsorbent sites.

The heat of adsorption and the heat capacity of argon adsorbed on another sample of titanium dioxide has been measured calorimetrically by Morrison and co-workers[1,2] in the 85 to 140°K. range. Coverages in both the monolayer and multilayer region were used. Good agreement was obtained between the heat capacity as measured directly or as derived from the temperature coefficient of the integral heats of adsorption. Consequently, there is good reason to believe that the properties measured in this case were the reversible thermodynamic properties of the system.

No measurements of the heats of adsorption below 85°K. were made by the group above, because thermal equilibrium at the lowest coverages was reached only after a period of several hours. We have also noted this slow approach to equilibrium for low coverages at temperatures around 70°K. but at temperatures above and below this value, an *apparent* equilibrium is attained rapidly even at low concentrations of adsorbed argon. This is of interest because of the bearing it may have on two studies which have utilized argon adsorbed on graphite, the results of which appear contradictory at this time. Jura and Criddle[3] have reported stepwise isotherms for argon adsorbed on graphite between 60 and 65°K. On the other hand, Crowell and Young[4] have observed only smooth isotherms at low coverages of argon adsorbed on graphite from 80 to 90°K. Even though the present work employs a different surface, our results, which overlap the range of temperatures used in the preceding two studies, may help provide an explanation for the phenomena which have been observed.

Experimental

The calorimeter is a modification of the Nernst–Giauque type.[5,6] A schematic drawing of the apparatus is shown in Fig. 1.

The calorimeter vessel of about 100-ml. capacity was filled with 60 g. of finely divided titanium dioxide in the rutile form. The sample of rutile was designated as No. MP 578-3 by the National Lead Company. It was 94.3% titanium dioxide with the remainder being water, adsorbed or coördinately bound. The sample was activated under a high vacuum at 180° for 72 hours until the pressure dropped below 10^{-6} mm. The monolayer capacity of the sample as determined by the BET method[7] at 77.6°K. was 0.0541 mole using argon as the adsorbate.

Temperatures and temperature differences during the measurements were determined by a four-lead, strain-free platinum resistance thermometer. The resistance thermometer was calibrated between 55 and 90°K. against a copper–constantan thermocouple which previously had been

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calibrated against oxygen vapor pressures, the oxygen having been condensed into the empty calorimeter vessel.

Energy inputs to the calorimeter were determined with a constantan heater in a conventional standard resistor and White potentiometer set-up.

The thermometer and heater were inserted into a reentrant well in the body of the calorimeter. Wood's metal was used for obtaining thermal contact.

Technical grade argon of 99.6% purity was used in the measurements as received with no further attempts to purify it and no spectroscopic analysis. The heat capacity of the calorimeter plus clean adsorbent was determined with a few tenths of a millimeter of helium pressure in the calorimeter to provide conduction between the calorimeter wall and the solid adsorbent, thus reducing the time necessary for the onset of steady state conditions in the fore and after period of the measurement. Temperature rises of the calorimeter during these determinations varied from 2.0 to 3.5 degrees. A precision of about 0.1% was realized.

We have defined the integral heat of adsorption, Q_{N_s}, as

$$Q_{N_s} = -\int_0^{N_s} q_{st}\,dN_s = N_s(E_G - E_{N_s}) + N_sRT \quad (1)$$

in which q_{st} is the isosteric heat of adsorption; N_s, number of moles of adsorbate; E_G, the molar energy of the gas; and E_{N_s}, the molar energy of adsorbate. The integral heats were obtained from the experimental data by use of

$$Q_N = (c_{pG} + c_{pcal} + c_{N_s})\Delta T - V_G P \quad (2)$$

in which c_{pG} is the heat capacity of the gas phase in the calorimeter; c_{pcal} is the heat capacity of the calorimeter vessel plus adsorbent; c_{N_s}, the heat capacity of the adsorbed phase; ΔT, the temperature rise for adsorption; V_G, the dead space volume of the calorimeter; and P_0, the equilibrium pressure. Any temperature adjustment in the integral heats was made by using

$$\left(\frac{dQ_{N_s}}{dT}\right)_{N_s} = c_{pG} - c_{N_s} \quad (3)$$

The definition of the heat of adsorption requires that the gas being adsorbed be at the same temperature as the calorimeter–adsorbent–adsorbate system. This is not exactly realized in a Nernst–Giauque calorimeter, so that a correction should be applied for the amount of heat liberated in or extracted from the system in bringing the temperature of the incoming gas to that of the system. Under the usual experimental conditions, the gas filling tube which is coiled around and soldered to the massive shield admits the incoming gas at the average temperature of the measurement. For the temperature rises of from 0.6 to 3.0° observed in the measurements, a correction of the above kind would be second order.

It was quite important to ascertain that all the argon entering the filling tube passed directly into the calorimeter vessel without solidifying in the tube. This was a real danger since the samples of argon were prepared in a buret at pressures of 100 to 400 millimeters. For adsorptions below 78.5°K. these pressures were above saturation values. Therefore, a throttling tube, 1 millimeter in internal diameter and 1 meter in length, was inserted in the gas filling line at a point between the volumetric apparatus and the calorimeter. The pressure was reduced by alternately opening and closing the stopcock that connected the throttle to the volumetric system. From the precision and consistency of the data, it was presumed that the throttle had served its purpose and no gas had condensed in the filling tube.

Results and Discussion

Experimental integral heat of adsorption data were obtained at 63.5, 73.0, 78.5 and 86.5°K. Successive small increments of argon were admitted to the calorimetric vessel containing the titanium dioxide and the heat effects thus produced were summed in a cumulative manner. At 69.5°K., it was not feasible to obtain data at low surface coverages because of the slowness of the equilibrium process. The precision of the data was ±0.5% of the heat liberated during the adsorption process.

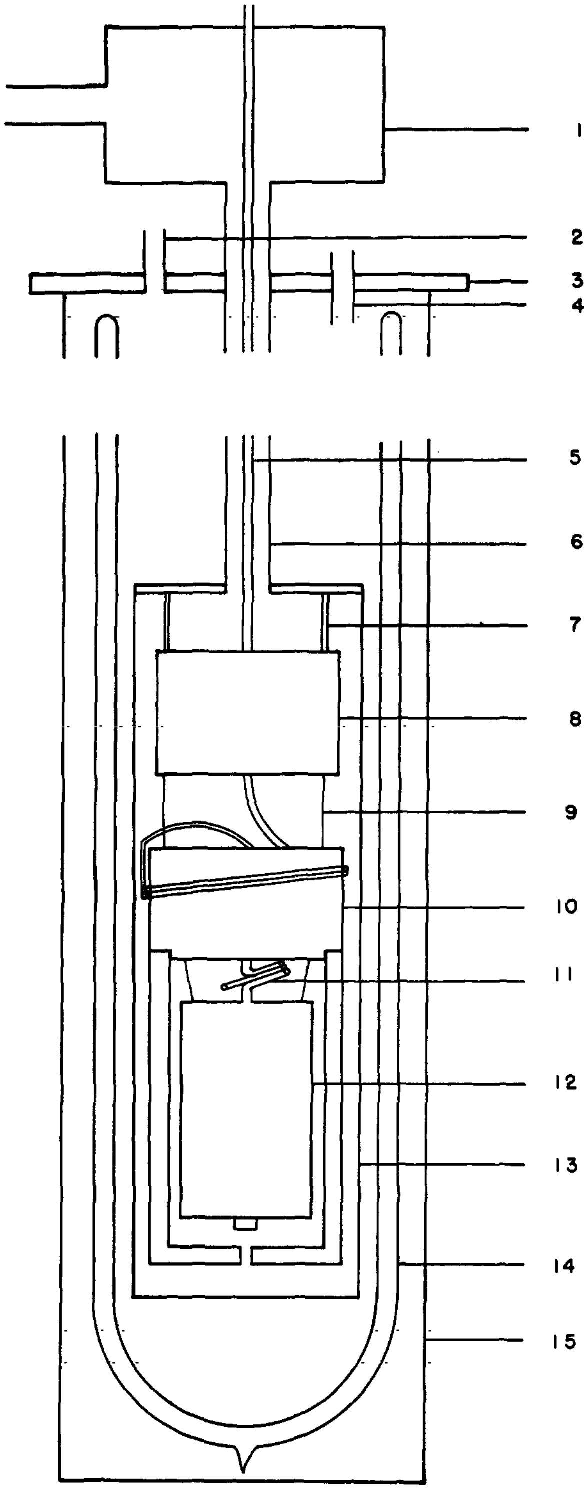

Fig. 1.—1, cup; 2, liquid nitrogen filling tube; 3, monel plate; 4, liquid nitrogen pumping tube; 5, gas filling tube; 6, can evacuation tube; 7, monel pin; 8, auxiliary block; 9, nylon cord; 10, massive radiation shield; 11, coiled filling tube; 12, calorimeter vessel; 13, calorimeter can; 14, glass dewar; 15, monel dewar can.

The molar differential heat of adsorption, $(dQ_{N_s}/dN_s)_T$, can be evaluated as the slope of the curve of integral heat (Q_{N_s}) *versus* moles adsorbed (N_s).

However, it was found that the average value, $(\Delta Q_{N_s}/\Delta N_s)_T$, for the mean number of moles adsorbed was the same as the true value within the experimental error. Consequently, the integral heat data were used directly to evaluate the differential heat of adsorption at each temperature.

The differential heats of adsorption at the various temperatures were reduced to a temperature of 63.5°K. by employing the relation

$$\frac{d}{dT}\left(\frac{dQ_{N_s}}{dN_s}\right)_T = C_{pG} - C_{N_s} - N_s\left(\frac{dC_{N_s}}{dN_s}\right)_T \quad (4)$$

in which C_{pG} and C_{N_s} are, respectively, the molar heat capacity of the gas phase and the adsorbed phase and N_s is the number of moles of argon adsorbed on the surface. The results are presented in Fig. 2.

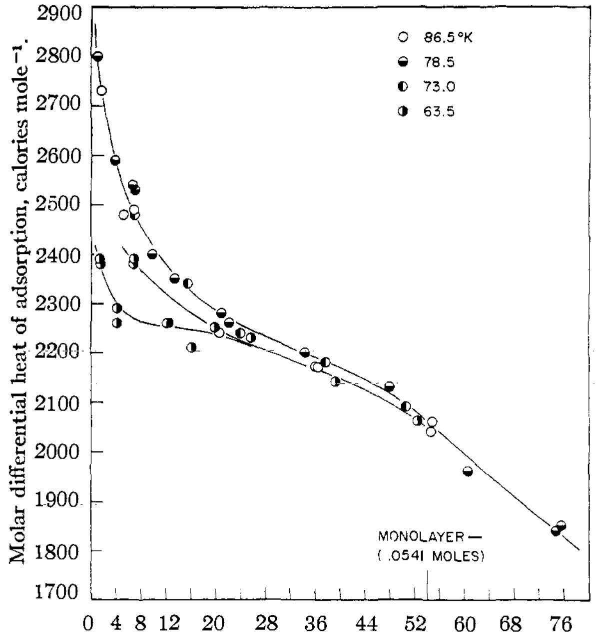

Fig. 2.—Differential heats of adsorption reduced to 63.5°K.

Heat capacity data for the adsorbed argon were necessary in order to make corrections to the heats of adsorption implied in equations 3 and 4. Therefore, the heat capacity was determined between 55 and 90°K. at concentrations of 0.0198, 0.0303, 0.0449, 0.0571 and 0.0695 mole corresponding to monolayer fractions of 0.37, 0.56, 0.83, 1.1 and 1.3. The data are shown in Fig. 3. The precision ranged from 3% at the highest coverage to 10% at the lowest. The heat capacity results are in fair agreement with those obtained by Morrison and co-workers.[1,2]

In reducing the differential heat of adsorption to the common temperature of 63.5°K., we find that the values determined experimentally at 73.0, 78.5 and 86.5°K. fall upon a single curve within the experimental error. Because of this correlation between the heat capacity and differential heat of adsorption, we believe that the experimental conditions have yielded thermodynamically reversible results in these cases. On the other hand, the differential heat of adsorption

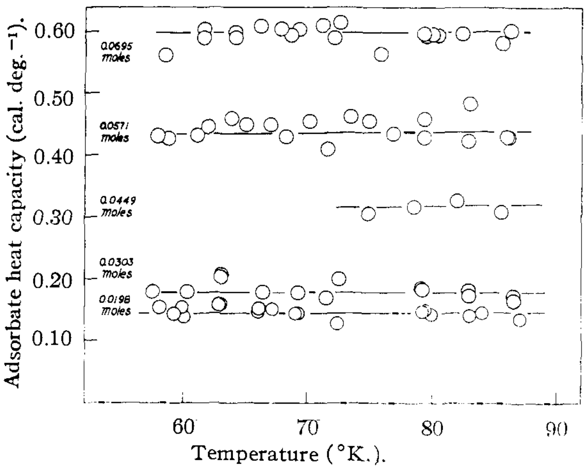

Fig. 3.—Heat capacity of adsorbed argon: argon–rutile system.

determined experimentally at 63.5°K. deviates considerably from the single curve for the heats at the other temperatures, particularly at low coverages. Two curves are shown in Fig. 2 for the measurements at 63.5°K. The initial volume increments used in obtaining the lower curve were smaller than those used for the upper curve. However, it was found possible to reproduce each curve within the experimental error provided that the adsorption path was duplicated with respect to order and size of volume increment used. Consequently, we believe that the adsorption process in this case is metastable. The argon adsorbed on the surface apparently requires a time interval to reach equilibrium which is long with respect to the length of the experiment (of the order of 4 to 8 hours). Since the calorimeter used in the measurements is sensitive to heat effects as small as 0.001 cal. per minute, it would appear that the rate of drift to equilibrium is small indeed.

It is interesting to note in relation to the above that it was not feasible to measure the heat of adsorption calorimetrically at 69.5°K. because of the warm drifts of several hours in length which followed the admission of a sample of argon.

The distribution of energy at the sites of adsorption can be derived from the shape of the differential heat curve. In order to determine this distribution the differential heats should be reduced to 0°K. so that the molecules can be assigned to the lowest energy level of the site. The corrective term for this is relatively small because of the crossing of the curves for the heat capacity of the gas phase and adsorbed phase at low temperatures. In any case, its influence on the shape of the heat curve is negligible. Hence, to a good order of approximation, the single differential heat curve at 63.5°K. can be used to determine the equilibrium distribution of energy. This has been done in the graph shown in Fig. 4. The ordinate f(ε) represents the number of moles of adsorbed gas to be found with energies between $-\epsilon$ and $-(\epsilon + d\epsilon)$. The energy zero has been taken as that of a molecule of the gas at infinite separation. We have also used the same procedure in obtaining a distribution curve for the non-equilibrium case using the differential heat curve at 63.5°K. resulting from the addition of small volume increments. This is included in Fig. 4.

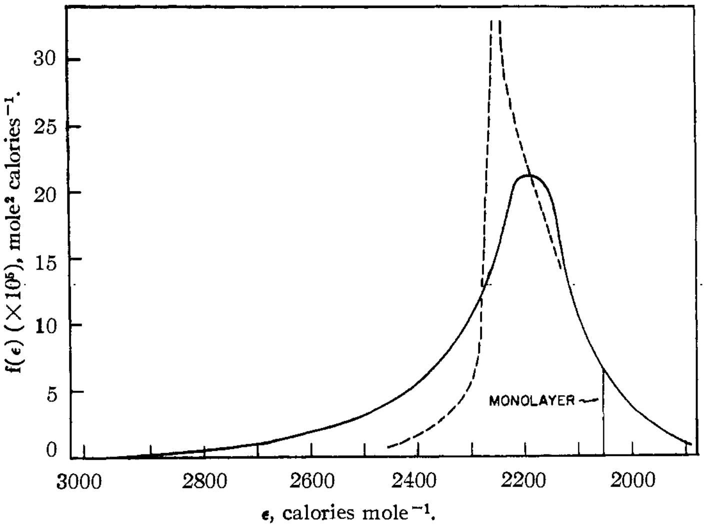

Fig. 4.—Energy distribution for argon adsorbed on rutile: — equilibrium distribution; ---, non-equilibrium distribution.

The heterogeneity of the surface is reflected in the exponential decrease of population of the sites with the increase in energy for the sites of high energy in the equilibrium curve. However, it is interesting to note that the bulk of the sites are grouped in an energy band which is not more than five hundred calories wide. One would expect a distribution of this type for a surface consisting predominantly of sites derived from the possible crystal faces for titanium dioxide.[8]

The distributions are based essentially on a simple model of unimolecular, localized adsorption with negligible molecular interaction. At coverages above 0.5 of a monolayer, the inflection point in the curve for the differential heat is probably caused by the appearance of attractive molecular interaction. Consequently, the simple model used above is inadequate and, at coverages approaching the monolayer capacity, the distribution curve would require a more detailed interpretation.

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CLEVELAND, OHIO

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[8] Dr. Walter K. Nelson of the National Lead Company has informed us that the titanium dioxide used is acicular and shows a predominance of 100 and 110 planes.

[CONTRIBUTION FROM THE MINERALS THERMODYNAMICS BRANCH, REGION III, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Low-temperature Heat Capacities and Entropies at 298.16°K. of Manganese Sesquioxide and Niobium Pentoxide

BY E. G. KING

RECEIVED FEBRUARY 6, 1954

Low temperature heat capacity measurements of manganese sesquioxide (Mn_2O_3) and niobium pentoxide (Nb_2O_5) were conducted throughout the temperature range 51–298°K. The heat capacity of manganese sesquioxide shows a pronounced maximum at 79.4°K. The entropies at 298.16°K. are 26.4 ± 0.5 cal./deg. mole for manganese sesquioxide and 32.8 ± 0.2 cal./deg. mole for niobium pentoxide.

This paper reports heat capacity measurements throughout the temperature range from 50 to 298°K. and entropy evaluations of crystalline manganese sesquioxide (Mn_2O_3) and niobium pentoxide (Nb_2O_5). No previous similar data exist for either of these substances, except a rather uncertain value of the entropy of manganese sesquioxide derived from dissociation pressure data by Kapustinsky and Bayuskina.[1] Data for manganese oxides of composition MnO, Mn_3O_4 and MnO_2 were published previously from this Laboratory.[2–4]

Materials

The manganese sesquioxide was part of the sample described by Orr[5] and used by him in high temperature heat content measurements. It analyzed 69.64% manganese and 10.13% available oxygen, as compared with the theoretical 69.59 and 10.14%. The X-ray diffraction pattern showed only lines corresponding to those for bixbyite as listed in the A.S.T.M. catalog.

The niobium pentoxide also was described by Orr.[6] The impurities, estimated spectrographically, totaled less than 0.10%. X-Ray diffraction showed the substance to be the high-temperature modification reported by Brauer.[7]

Measurements and Results

The heat capacity measurements were conducted with previously described[8] apparatus and methods. The results are expressed in defined calories (1 cal. = 4.1840 abs. joules) per deg. mole. Molecular

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