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The Heat Capacity of Nitrogen Adsorbed on Titanium Dioxide Between 20°K and 80°K

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A low temperature adiabatic calorimeter suitable for thermal measurements on adsorbed gases has been developed. Heat capacity values for two amounts of nitrogen adsorbed on titanium dioxide (rutile) are presented. While the measurements were complicated by the appearance of warm drifts in the calorimeter over part of the temperature range when nitrogen was present, it appears that at the concentrations used the adsorbate was present as a condensed phase.

INTRODUCTION

WHILE considerable information is available concerning the adsorption of gases and vapors on solid surfaces, relatively little of it is concerned with the properties of the adsorbate.³ Since these properties are in general determined as differences, the lack of data is probably attributable to experimental difficulties. The need for such data is twofold; firstly, to augment state data for two-dimensional films derived from measurements of adsorption isotherms⁴ and, secondly, to permit treatment of the adsorption process from known properties of both the adsorbate and the adsorbent. For both requirements, evaluation of the thermal properties of the adsorbed films would be desirable. In the present paper are described experiments in which measurements have been made of the heat capacity of nitrogen adsorbed on titanium dioxide.

The only previous comparable measurements are those of Simon,^{5,6} who determined the heat capacity of argon adsorbed on chabasite and on charcoal, and of hydrogen adsorbed on charcoal. The latter experiments were confused by the setting in of the *ortho-para* hydrogen conversion on the surface of the charcoal at low temperatures. With argon adsorbed on charcoal, the

results were better defined. Simon and Swain⁶ suggested that the results indicated the argon to be present as a two-dimensional gaseous film, but Cassel⁷ contends that rather the adsorbed argon atoms behave as one-dimensional oscillators. The recent development of highly precise adiabatic calorimeters^{8,9} now makes possible the investigation of somewhat simpler systems with crystalline solids, whose surface areas are much less than those of porous solids such as charcoal and silica gel, and where the adsorption is less complex because of the absence of capillary effects.

The utility of heat capacity values alone in determining the state of adsorbed films is restricted to the extent that only the heat capacity of the two-dimensional gaseous state may be predicted with any definiteness from theoretical considerations. However, first-order phase changes would be expected to appear as discontinuities in the heat capacity-temperature curves.

EXPERIMENTAL

Materials

The nitrogen for the experiments was prepared by the reaction of ammonia with bromine following the method of Giauque and Clayton.¹⁰ A stock of one kilogram of titanium dioxide in the rutile crystalline form was obtained through the courtesy of Dr. R. Dahlstrom of the Na-

¹ National Research Fellow in Chemistry, 1945-46. Present address: National Research Laboratories, Ottawa, Canada.

² Phillips Petroleum Fellow, 1945-47.

³ S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, New Jersey, 1943), Chap. XII.

⁴ G. Jura and W. D. Harkins, *J. Am. Chem. Soc.* **68**, 1941 (1946).

⁵ F. Simon, *Zeits. f. Electrochemie* **34**, 528 (1928).

⁶ F. Simon and R. C. Swain, *Zeits. f. physik. Chemie* **28B**, 189 (1935).

⁷ H. Cassel, *J. Am. Chem. Soc.* **57**, 2724 (1935).

⁸ J. G. Aston and M. L. Eidinoff, *J. Am. Chem. Soc.* **61**, 1533 (1939).

⁹ R. B. Scott, C. H. Meyers, R. D. Rands, F. G. Brickwedde, and N. Bekkedahl, *J. Research Nat. Bur. Stand.* **35**, 39 (1945).

¹⁰ W. F. Giauque and J. O. Clayton, *J. Am. Chem. Soc.* **55**, 4875 (1933).

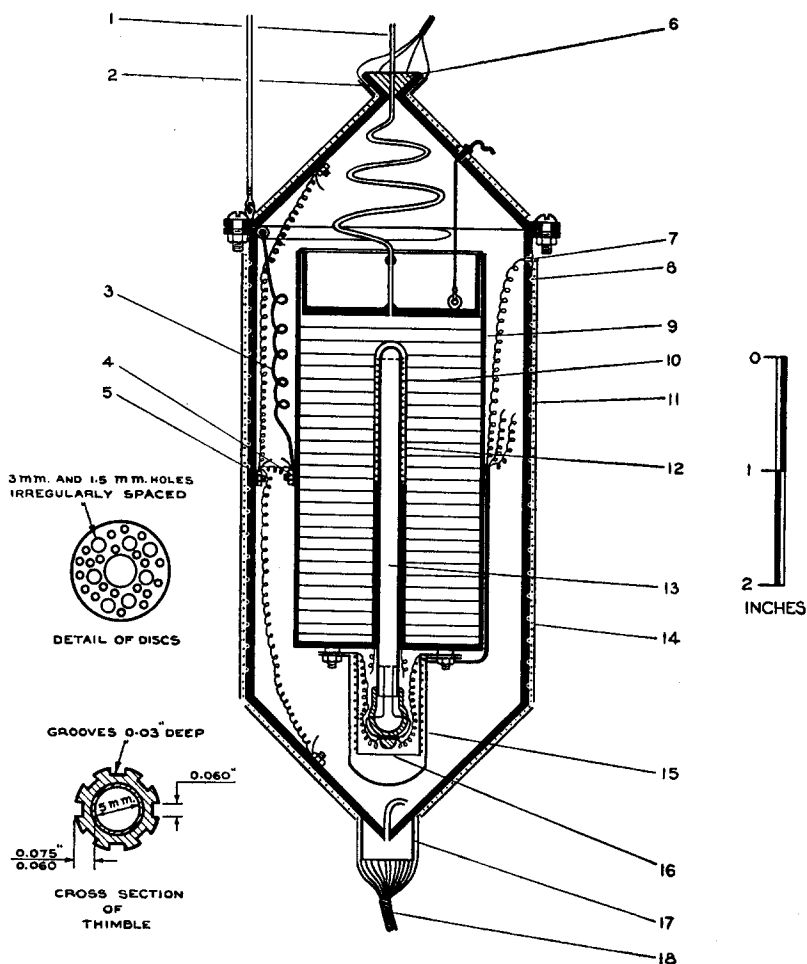
tional Lead Company. From this stock two representative samples were cut. One of approximately 30 grams was used in the surface area measurements, and the other of approximately 100 grams, in the heat capacity measurements. The surface area of the titanium dioxide, as determined by nitrogen adsorption at the boiling point of nitrogen, was found to be 10.2 m²/g.

Calorimeter Assembly

The design of the calorimeter and the adiabatic shield assembly was based on that of Scott *et al.*⁹ However, the need to degas the titanium dioxide at an elevated temperature made necessary a somewhat new design for the calorimeter vessel. A scale drawing of the principal parts of the assembly is shown in Fig. 1. The calorimeter, 9, was made of platinum approximately 0.020"

thick, and carried a re-entrant well, in which the platinum resistance thermometer, 13, was held. To the bottom of the calorimeter was welded a platinum ring attached to which were eight platinum machine screws which held in place the copper cylinder, 16, and the radiation trap, 15. The titanium dioxide was packed into the calorimeter between thirty disks, 10, made of No. 40 B. and S. platinum sheet, which made a spring fit with the re-entrant well and with the wall of the calorimeter. Irregularly spaced holes were drilled in the disks as shown at the left (not to scale) in Fig. 1. The disks were spaced regularly by coiled strips of platinum sheet, 2 mm wide, placed on edge. The lid of the calorimeter was dished to a depth of $\frac{1}{2}$ " and made a snug fit inside the cylindrical wall of the calorimeter. The vessel was closed by welding around the rim. With this type of seal the calorimeter could be

FIG. 1. Calorimeter and adiabatic shield assembly: 1, stainless steel filling tube; 2, copper cone containing Wood's metal thermal contact; 3, standard copper-constantan thermocouple S-8; 4, calorimeter thermocouple junction; 5, adiabatic shield thermocouple junction; 6, Wood's metal thermal contact; 7, Bakelite inserts; 8, adiabatic shield; 9, platinum calorimeter; 10, perforated platinum disks; 11, adiabatic shield heater; 12, calorimeter heater; 13, platinum resistance thermometer; 14, gold-plated copper foil; 15, radiation cap; 16, copper cylinder carrying leads from thermometer and heater; 17, copper cylinder carrying leads from adiabatic shield; 18, bundle of lead wires.



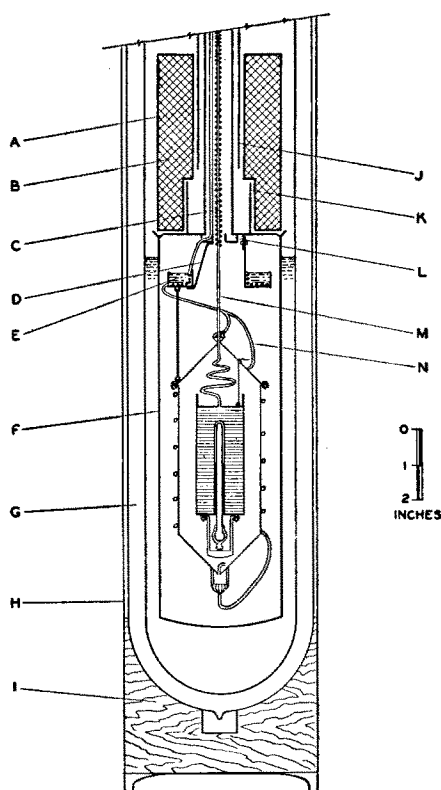


FIG. 2. Cryostat assembly: *A*, German silver support tube; *B*, lead block; *C*, filling tube heater; *D*, copper thermal shunt; *E*, copper trough; *F*, inner cryostat can; *G*, Pyrex Dewar flask; *H*, outer cryostat can; *I*, balsa wood block; *J*, mantle tube; *K*, monel metal cup; *L*, radiation trap; *M*, stainless steel filling tube; *N*, bundle of lead wires.

opened easily by turning off the rim in a lathe. To the lid were welded three platinum rings by which the calorimeter was suspended from the adiabatic shield on fish-line.

The platinum thimble of the resistance thermometer was made in three sections welded together, the inner diameter being 5 mm throughout. The upper closed-off section of the thimble was of wall thickness 0.015". The wall of the middle section, which averaged 0.068" in thickness, carried a 1° taper, which fitted a similarly tapered section of the re-entrant well. Eight longitudinal grooves, 0.030" deep, were cut in this portion of the thimble, as shown in section at the lower left of Fig. 1. The bottom section of the thimble was of 0.008" thickness, and to it was sealed the glass cap, through which the thermometer leads were brought. The thermometer was of platinum and was wound in the

conventional manner on a mica cross.¹¹ On the upper section of the thermometer thimble was wound the calorimeter heater, 12, of No. 40 B. and S.D.S.C. constantan (resistance 100 ohms). The thermometer assembly was set into the re-entrant well with stopcock grease. The excess grease and the residual air were forced out through the flutes of the middle section of the thimble.

The adiabatic shield, 8, was made of copper, 0.065" thick, and was gold-plated inside and out. Around the cylindrical side were cut shallow spiral grooves which carried the lead wires going to the calorimeter. The entire outer surface of the shield was covered with heaters, 11, of No. 30 B. and S.D.S.C. constantan wire, wound bifilarly. All of the leads to the side and to the bottom of the shield were separated and bound to the copper ring, 17, before being formed into a bundle, 18. Similarly, the leads from the top of the shield were bound at 2, formed into a bundle and joined to the bundle from the bottom. At a distance of four inches from the bottom of the shield, a heater of No. 40 B. and S.D.S.C. constantan (resistance 80 ohms) was wound bifilarly into the bundle of wires.

For the degassing of the titanium dioxide in the calorimeter at about 350°C, a furnace was placed around the calorimeter vessel. This operation necessitated the removal of the shield, the connecting wires, and the thermometer assembly. To accomplish this without severing any of the connections, the lead wires within the shield were assembled in the following manner: to the thermometer, 13, and to the calorimeter heater, 12, were attached leads of No. 40 B. and S.D.S.C. copper, which were wound twice around the copper cylinder, 16. At the point where the leads emerged from under the radiation cap, 15, the two heater leads were changed to No. 28 B. and S.D.S.C. copper. The No. 28 wires and the four thermometer leads were bound into a bundle, and carried up to about the midpoint of the calorimeter wall, where the bundle was bound firmly to the calorimeter with thread. At this point, two No. 40 B. and S.D.S.C. copper leads (one current lead and one potential lead) were attached to one of the No. 28 wires. To the other

¹¹ C. H. Meyers, *Bur. Stand. J. Research* **9**, 807 (1932).

was attached a single No. 40 copper wire, the second potential lead being taken off where this wire was joined to the external lead at the shield. Between the calorimeter and the side of the shield near the top, where the external leads entered through holes insulated with bakelite inserts, 7, the seven No. 40 wires were coiled into springs. The leads to the difference thermocouple junctions were coiled similarly. By this arrangement, then, the shield, the thermometer assembly, and the lead wires could be lowered from the calorimeter without any disconnection. The spiral in the stainless steel filling tube, 1, (2-mm o.d. and 1-mm i.d.) permitted the calorimeter to be lowered from the top shield when the furnace was in place.

The calorimeter and the shield assembly were suspended in the cryostat from tube A, as shown in Fig. 2. The lead wires from the shield were brought to the temperature of the refrigerant by intimate contact with the copper trough, *E*. At the top of the cryostat the wires emerged through a de Khotinsky seal. The upper section of the filling tube, *M*, was wound with a heater, *C*, of No. 30 B. and S.D.S.C. constantan (resistance 45 ohms). At the outside, connection of the filling tube to the nitrogen measuring system was made through a platinized glass seal.

The inner can, *F*, and the outer can, *H*, were made of monel metal, and both were sealed at the top with soft solder. During the soldering or unsoldering of the inner can, the cup, *K*, was filled with water to prevent damage to the lead wire assembly suspended from the can top. At the top of the outer can connections were made to a high capacity vacuum line and to a hydrogen gas holder. Through a special fitting a vacuum syphon was inserted for transferring liquid hydrogen into the cryostat. The technique of operation of the assembly was similar to that described by Scott *et al.*¹⁰

Temperature Scale

The temperature scale was derived in terms of one of the laboratory standard copper-constantan thermocouples.¹² Thermocouple S-8 (shown at 3 in Fig. 1) was soldered to a lug on the side of the calorimeter and passed through a semicircular

copper tube, which was soldered to the inside of the shield and filled with paraffin. The standard thermocouples had been calibrated with 72 cm at constant temperature,¹² so S-8 was wrapped on the outside of the shield until this length from the junction had been taken up. From the shield, the thermocouple passed directly up through the tube *A* (Fig. 2) without going through the trough, *E*.

During the course of the heat capacity measurements, some sixty comparisons were made between S-8 and the resistance thermometer, under conditions where there was no drift in the temperature of the calorimeter system. The initial temperature scale was derived using the original calibration data for S-8.¹² Also, the corresponding values of R/R_0 for the thermometer were converted to temperatures using the table of Hoge and Brickwedde.¹³ The difference between the two temperature scales, expressed as $\Delta R/R_0$, was plotted against the temperature as determined by the second scale¹³ and the best curve drawn through the points. Since the resistance of the thermometer at the boiling point of oxygen (90.19°K) was known, it was possible to place on the plot a point denoting the difference between the oxygen point and the value derived from the table of Hoge and Brickwedde. The final temperature scale was represented by a deviation curve parallel to the first deviation curve, but passing through this fixed point at 90.19°K. In effect then, it was assumed that the deviation of the thermometer indications from the table of Hoge and Brickwedde was proportional to the temperature. The difference between the initial scale based on the thermocouple and the final scale amounted to 0.05° at the boiling point of oxygen, and 0.15° at the boiling point of hydrogen. This difference is of the order of change of calibration to be expected if such a thermocouple is used at liquid hydrogen temperatures.¹⁴ While it would have been more satisfactory to check the indications of S-8 at fixed points below the oxygen point, time did not permit this. However, it seems unlikely that the temperature scale adopted is in error by more

¹³ H. J. Hoge and F. G. Brickwedde, *J. Research Nat. Bur. Stand.* **22**, 351 (1939).

¹⁴ J. G. Aston, in *Temperature, Its Measurement and Control in Science and Industry* (Reinhold Publishing Corporation, New York, 1941), p. 219.

¹² J. G. Aston, E. Willihnganz, and G. H. Messerly, *J. Am. Chem. Soc.* **57**, 1642 (1935).

TABLE I. The heat capacity of nitrogen (0.00996 mole) adsorbed on titanium dioxide (96.8 g).

T°K	C _p Total cal. deg. ⁻¹	C _p Calorimeter cal. deg. ⁻¹	C _p Adsorbed nitrogen cal. deg. ⁻¹	Moles adsorbed (mean)	C _p Adsorbed nitrogen cal. deg. ⁻¹ mole ⁻¹
22.057	1.360	1.321	0.039	0.00996	3.9
23.161	1.545	1.504	0.041	0.00996	4.1
27.511	2.402	2.350	0.052	0.00996	5.2
28.095	2.524	2.476	0.048	0.00996	4.8
32.417	3.527	3.464	0.063	0.00996	6.3
32.843	3.621	3.565	0.056	0.00996	5.6
37.781	4.827	4.749	0.078	0.00996	7.8
38.101	4.904	4.827	0.077	0.00996	7.7
42.365	5.949	5.871	0.078	0.00996	7.8
42.624	6.006	5.934	0.072	0.00996	7.2
46.613	6.984	6.893	0.091	0.00996	9.1
50.734	7.949	7.860	0.089	0.00996	8.9
55.513	9.023	8.941	0.082	0.00994	8.3
56.652	9.276	9.192	0.084	0.00993	8.5
62.116	10.460	10.365	0.095	0.00986	9.6
63.777	10.784	10.707	0.077	0.00983	7.8
67.478	11.538	11.440	0.098	0.00971	10.1
68.866	11.795	11.710	0.085	0.00966	8.8
73.039	12.579	12.493	0.086	0.00956	9.0
75.276	12.977	12.899	0.078	0.00933	8.4
78.417	13.554	13.467	0.087	0.00914	9.5

than 0.1°, which would not affect the heat capacities significantly.

EXPERIMENTAL RESULTS

Two series of measurements were made with 0.00996 mole and 0.01974 mole of nitrogen, respectively, adsorbed on the surface of the titanium dioxide. The first quantity of nitrogen corresponded closely to the value V_m^{15} for the adsorption on this particular sample of titanium dioxide. Heat capacity determinations with the smaller amount of nitrogen were made over the temperature range 20°K to 80°K in two parts, 20°K to 55°K with solid hydrogen as refrigerant and 55°K to 80°K with solid air as refrigerant.

TABLE II. The heat capacity of nitrogen (0.01974 mole) adsorbed on titanium dioxide (96.8 g).

T°K	C _p Total cal. deg. ⁻¹	C _p Calorimeter cal. deg. ⁻¹	C _p Adsorbed nitrogen cal. deg. ⁻¹	Moles adsorbed (mean)	C _p Adsorbed nitrogen cal. deg. ⁻¹ mole ⁻¹
57.043	9.485	9.278	0.207	0.01938	10.7
57.171	9.513	9.306	0.207	0.01938	10.7
62.323	10.634	10.408	0.226	0.01879	12.0
62.699	10.715	10.486	0.229	0.01872	12.2
68.007	11.775	11.543	0.232	0.01766	13.1
68.634	11.901	11.665	0.236	0.01752	13.5

¹⁵ S. Brunauer, P. H. Emmett, and E. Teller, J. Am. Chem. Soc. **60**, 309 (1938).

Upon first cooling the calorimeter system to the lower temperature range, apparently normal adiabatic determinations were made up to 35°K, at which point it was found that the temperature of the calorimeter drifted upwards at the rate of 0.0002°/min. This rate increased to about 0.001°/min. at 50°K. A second cooling of the system with a subsequent attempt at measurements gave similar results. In a third experiment, the system was cooled from solid air temperature and measurements attempted up to 48°K. At this temperature, adiabatic conditions were maintained within the system, and the upward drift of the temperature of the calorimeter was followed. After four hours, the drift slowed and stopped within a period of a few minutes. The calorimeter was then cooled and heat capacity measurements resumed. This time, equilibrium measurements were obtained in the temperature range 20° to 45°K. From 45°K, the system was again cooled and duplicate measurements obtained. Warm drifts were never observed when the system was cooled to just 55°K, nor were they observed at any temperature when there was no nitrogen in the calorimeter.

Table I summarizes the heat capacity measurements. All the values shown represent equilibrium measurements. Results obtained when the temperature of the calorimeter drifted upwards are not included because of the uncertainty of calculating the true temperature rise in these instances. The apparent equilibrium measurements below 35°K for the first two coolings to solid hydrogen temperatures were in agreement with the values in Table I within the limit of error. The temperatures in the first column are mean values for the determinations on the system containing the nitrogen (column 2). The heat capacities of the system without the nitrogen at these temperatures were calculated from a smoothed table prepared from experimental values.

Above 55°K, it was found necessary to correct the heat capacity determinations for the amount of nitrogen desorbed from the surface of the titanium dioxide during a heating period. Time did not permit a determination of the heat of desorption, so for purposes of the correction a value of 2100 cal./mole was derived from a BET¹⁵ plot of the adsorption data for the

system. This value takes no cognizance of the change of the heat of desorption with the amount adsorbed or with temperature. However, considering the range of concentration and of temperature, it seems probable that any change would not exceed 10 percent. The correction amounted to 0.15 percent of the heat input at 55°K, and 1.02 percent at 78°K. The average deviations of the experimental heat capacities from smoothed curves for the system with and without the nitrogen were 0.08 percent and 0.04 percent, respectively, which would suggest that the heat capacity of the adsorbed nitrogen is known to about 7 percent.

A second series of experiments were made with 0.01974 mole of nitrogen adsorbed in the calorimeter, but with less definite results. In this instance also, warm drifts of the calorimeter were encountered in the lower temperature range, starting at about 40°K. An attempt was made to follow the drift to completion, as in the first series of experiments, but this proved not possible. The drift had not stopped by the time all of the hydrogen refrigerant had disappeared from the cryostat, a period of about twenty-four hours. Due to the uncertainty of calculating the true temperature rise when the temperature of the calorimeter drifted, the heat capacity measurements up to 55°K were not considered reliable. Above 55°K, apparent equilibrium measurements were obtained, but desorption corrections became very much larger than for the first series. The reason for this is clear from a consideration of the adsorption isotherm of nitrogen on titanium dioxide. The first amount of nitrogen was adsorbed at a relative pressure of 0.15, and the second at a relative pressure of 0.7. The heat capacity measurements for the second filling of nitrogen over the temperature range 57° to 68°K are recorded in Table II. A value of 1400 cal./mole for the heat of desorption was assumed in correcting for the desorption of a portion of the nitrogen during the heating periods. An uncertainty of 10 percent in this value introduces an uncertainty of nearly 5 percent in the heat capacity at 57°K, and about 15 percent at 68°K. Reference to Fig. 3 shows that these heat capacity results are of the same order as the heat capacity of liquid nitrogen. This is at least in qualitative agreement with the pos-

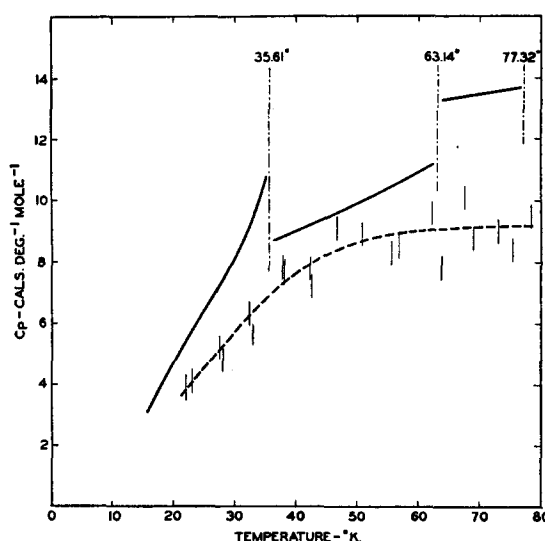


FIG. 3. Molal heat capacity of nitrogen. — data of Giauque and Clayton,¹⁰ ---- nitrogen (0.00996 mole) adsorbed on titanium dioxide (96.8 g).

tulate of the multimolecular adsorption theory,¹⁵ that at higher adsorptions the properties of the adsorbate approach those of the bulk liquid.

DISCUSSION

A plot of the data of Table I is shown in Fig. 3. The dotted curve relates the heat capacity values of the adsorbed nitrogen. The length of the vertical solid lines represents an estimate of the uncertainty of the individual values. The solid curves indicate the heat capacity of nitrogen in bulk as determined by Giauque and Clayton.¹⁰ The transition, fusion, and normal boiling points of nitrogen are indicated by vertical dashed lines.

At all temperatures the heat capacity of the adsorbed nitrogen appears less than that of bulk nitrogen. At 77°K, the heat capacity of the adsorbed nitrogen has attained the value of 9 cal./mole, which lies between the liquid heat capacity (approximately 14 cal./mole) and the gaseous heat capacity ($7/2 R$). For the two-dimensional gas one would estimate a maximum value of $6/2 R$. While the absolute value of the heat capacity of the adsorbed nitrogen above 55°K is influenced by the desorption correction, which could change the shape of the dotted curve in Fig. 3, it seems unlikely that the heat of desorption selected is sufficiently in error to bring the heat capacity at 77°K into agreement

either with that of liquid nitrogen or with that of the two-dimensional gas. If the value 2100 cal./mole were too small, then a maximum in the heat capacity curve would occur at about 55°K. It seems clear then that the nitrogen was present as a two-dimensional condensed phase. Indeed, such a conclusion is in agreement with the finding of Jura and Harkins⁴ for nitrogen adsorbed on titanium dioxide (anatase). Further speculation than this concerning the exact nature of the adsorbed phase must await the accumulation of additional data.

Consideration must also be given to the warm drifts which were observed when nitrogen was present in the calorimeter. While no complete explanation can be made on the basis of the available data, it is worth while to examine several possible mechanisms.

During the cooling of the calorimeter, nitrogen might have been desorbed from the surface of the titanium dioxide and condensed on the walls of the calorimeter, the readsorption process on heating the calorimeter giving rise to the temperature drifts. However, in a separate experiment, the magnitude of the temperature head established between the wall of the calorimeter and the interior during cooling was estimated. The temperature difference so calculated appeared quite insufficient to cause the nitrogen to condense on the walls. Also this explanation would seem to be precluded by the fact that the drifts were first observed in the temperature range 30° to 35°K, where the vapor pressure of nitrogen would be too small to permit sufficient transfer of nitrogen to account for the rate of rise of the temperature.

The possibility of rearrangement of the surface atoms of the titanium dioxide caused by the influence of the adsorbed nitrogen would appear unlikely since presumably only van der Waals' forces are involved in the adsorption of the nitrogen.

A more plausible suggestion is that the warm drifts represent a physical transition in the adsorbed film. On the occasion that the drift was followed to completion with the first nitrogen

filling, it was possible to calculate the energy evolved since the heat capacity of the system was known. This turned out to be 0.7 cal. In terms of the nitrogen in the system, the energy would be 70 cal./mole, which is of the order one would expect for a transition. Since titanium dioxide is an anisotropic solid, presumably the binding energy of the nitrogen would differ on the different crystal faces, so that one might expect a transition, if it occurs, to take place over an appreciable temperature range. However, a similar calculation with the second filling of nitrogen indicated an energy change of at least 250 cal./mole, because the drift was not followed to completion. This latter quantity is considerably less reliable because the drift was followed for an interval six times as long as in the first instance, and maintenance of strict adiabatic conditions within the system for that length of time proved quite difficult.

From this discussion it is evident that additional heat capacity data are required before a fuller interpretation of the results may be made. A complete understanding may not be obtained until measurements are made on a system containing an isotropic solid. The possibility of calculating the thermal properties of the adsorbed phase for a system of a monatomic gas adsorbed on such a solid is suggested by the recent work of Hill.¹⁶

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¹⁶ T. L. Hill, *J. Chem. Phys.* **14**, 441 (1946).