The Zero Point Entropy of Nitrogen Adsorbed on Titanium Dioxide[1]

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The heat capacities of approximately a half layer of nitrogen on titanium dioxide have been measured from 19 to 88°K. These data along with the heat capacity of a full layer and the differential heat of adsorption data have been used to obtain information on the difference in zero point entropy between a full layer and 0.6 of a layer. The result is compared with the zero point entropy required by a distribution of molecules on sites.

This Laboratory has been carrying out an investigation of the thermodynamic properties of adsorbed films, in the course of which a detailed study has been made of nitrogen adsorbed on titanium dioxide. The present paper is concerned with some information on the zero point entropy of this system.

Previous publications from this Laboratory have reported data for the identical system. The heat capacity of a monolayer was given by Morrison and Szasz.[3] The differential heat of adsorption was discussed by Kington and Aston[4] and some thermodynamic functions required by the system have also been examined and compared with the requirements of the B.E.T. theory.[5] The additional experimental data reported in the present paper are concerned with the heat capacity of a half layer.

TABLE I

THE HEAT CAPACITY OF NITROGEN (0.005267 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.$^{-1}$	C_p adsorbed nitrogen cal. deg.$^{-1}$ mole^{-1}
19.281	0.942	0.924	0.018	3.4
25.861	2.028	2.003	.025	4.7
31.206	3.207	3.180	.027	5.1
37.040	4.607	4.569	.038	7.2
42.854	6.030	5.990	.040	7.6
48.489	7.378	7.334	.044	8.4
54.911	8.851	8.807	.044	8.4
55.858	9.055	9.017	.038	7.2
57.906	9.506	9.466	.040	7.6
58.316	9.596	9.554	.042	8.0
60.433	10.054	10.009	.045	8.5
60.863	10.148	10.101	.047	9.1
61.150	10.211	10.162	.049	9.3
61.376	10.251	10.209	.042	8.0
63.580	10.718	10.666	.052	9.8
66.399	11.293	11.229	.064	12.2
67.007	11.405	11.348	.057	10.8
68.791	11.744	11.695	.049	9.3
69.660	11.912	11.862	.050	9.5
72.447	12.429	12.384	.045	8.5
72.959	12.518	12.478	.040	7.6
76.099	13.112	13.048	.064	12.2
79.096	13.645	13.589	.056	10.6
81.918	14.137	14.093	.044	8.3
84.421	14.564	14.524	.040	7.6
87.597	15.095	15.032	.063	11.9

Experimental

The materials, apparatus and experimental technique have been described previously.[3] We now present the heat capacity data for 0.005267 mole of nitrogen adsorbed on approximately 96.8 g. of titanium dioxide (rutile). This amount corresponds to about one-half of the amount necessary to complete the monolayer with an adsorbent surface area of 10.4 m.²/g. as calculated using the equation of Brunauer, Emmett and Teller.[6]

The results of the heat capacity measurements are summarized in Table I and are also reproduced in Fig. 1. The continuous line in this figure is the best smooth curve through these points, while the dotted curves indicate the changes caused in these results by an error of 0.1% in the heat capacity measurement of the system N₂ plus TiO₂ plus calorimeter. As can be seen by comparison with the previous work the molal heat capacity of the adsorbed film is the same (within the accuracy of these measurements) for ½ V_m as it is for V_m. The accuracy of the heat capacity values obtained for the film is estimated to be about ±10%. Anomalous warm drifts of the type previously discussed have also been encountered in this work. However, the results reported were obtained on an "equilibrium" film, i.e., on a film which did not exhibit such an anomalous emission of energy. Only one set of heat capacity measurements was obtained below 50°K. because only in one run was such an "equilibrium" film present. This was during the first run, in which the system was cooled from liquid air temperatures to liquid hydrogen temperatures rapidly whereupon the heat capacity measurements progressed normally. During the
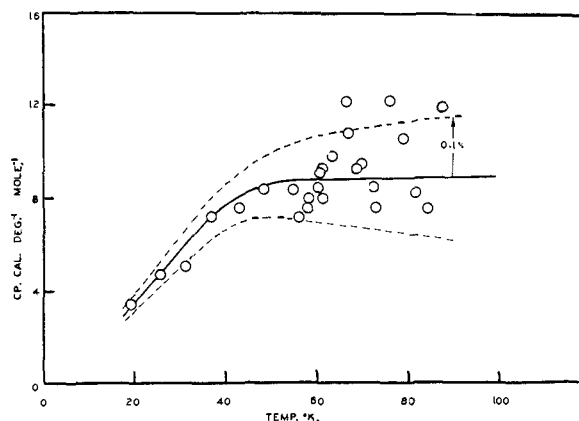

Fig. 1.—The molal heat capacity of nitrogen absorbed on titanium dioxide (0.005267 mole of N₂ adsorbed on 96.8 g. of TiO₂.

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(3) Morrison and Szasz, J. Chem. Phys., 16, 280 (1948).

(4) Kington and Aston, THIS JOURNAL, 73, 1929 (1951).

(5) Kington and Aston, ibid., 73, 1934 (1951).

(6) Brunauer, Emmett and Teller, ibid., 60, 309 (1938).

next run, which was performed in an essentially identical manner, a large warm drift appeared around 34°K. Unfortunately circumstances prevented us from making a detailed study of the warm drift in this case. It should be noted, however, that the heat capacity results obtained on the "non-equilibrium" film, agreed within experimental error with the results given in Fig. 1.

Results

The contribution to the thermal entropy per mole of adsorbed nitrogen, defined as $\int_0^T \mathrm{d}H/T$, of a half layer and a monolayer are shown in Table II. The extrapolation from 19°K. down to the absolute zero was made using a value of 106° for the Debye θ, and 5 degrees of freedom. The Debye function reproduces our heat capacity curve between 20 and 32°K. within experimental error. This function was only a mathematical device used in obtaining the entropy between 0 and 19°K. It was, of course, assumed that no phase transitions take place in the interval. The estimated uncertainties in the integrated quantity correspond to an accuracy of 10% in the heat capacity values of the film.

From Table II it is seen that the molal thermal entropy of a half layer is essentially the same as that for a complete layer.

TABLE II

MOLAL THERMAL ENTROPY POSSESSED BY A FILM AT 77.3°K.

Temp. interval, °K.	0.005267 mole (≈ half layer) cal. deg.$^{-1}$ mole^{-1}	0.00996 mole (≈ monolayer) cal. deg.$^{-1}$ mole^{-1}
0–19 (Debye θ = 106, 5 degrees of freedom)	1.3 ± 0.2	1.2 ± 0.2
19–77.3 $\left(\int_T^{C_p} \mathrm{d}T\right)$	9.7 ± 1.0	9.7 ± 0.5
0–77.3	11.0 ± 1.2	10.9 ± 0.7

The data[5] previously reported give the value of $S_{s(\theta)} - S_{s(0.6)}$. It was found that

$$S_{s(1.0)} - S_{s(0.6)} = 60 \times 10^{-3} \text{ cal./deg.} \pm 2 \times 10^{-3} \text{ cal./deg.} \quad (1)$$

We know from the molal thermal entropy $S_{77.3\ ^\circ K.} - S_0\ _{^\circ K.}$ (Table II) at two coverages that there is little change with coverage and this quantity is 11.0 ± 1.0 cal. deg.$^{-1}$ mole^{-1}. Since the monolayer contains 0.996 × 10^{-2} mole, the extent to which the entropy difference between a monolayer at 77.3°K. and 0.6 monolayer at the same temperature exceeds the equivalent difference at 0°K. is this quantity multiplied by 0.398 × 10^{-2}.

$$(S_{s(1.0)} - S_{s(0.6)}) - (S_{s(1.0)} - S_{s(0.6)})_0 = 44 \times 10^{-3} \pm 4 \times 10^{-3} \text{ cal./deg.} \quad (2)$$

where the subscript zero refers to the quantity at 0°K. Subtracting this result from the value given by equation (1) for the entropy difference at 77.3°K., the difference between the entropies at the two coverages at 0°K. is

$$(S_{s(1.0)} - S_{s(0.6)})_0 = +16 \times 10^{-3} (\pm 6 \times 10^{-3}) \text{ cal./deg.} \quad (3)$$

i.e., the zero point entropy of a monolayer is probably somewhat greater than the zero point entropy of 0.6 of a layer. On a molar basis this is 1.6 ± 0.6 cal./deg./mole, for a system of such a size that the monolayer held one mole.

In other words the value of the total entropy of a monolayer exceeds that of 0.6 monolayer by an amount between 1.0 and 2.2 e.u., but is not less than zero.

It should be noted that this is not the result indicated by a consideration of the distribution of molecules on sites, with adsorption restricted to one layer. At low temperatures the number of molecules in the second and higher layers is negligible until the first layer is complete, providing slow rate processes do not retard the establishment of the equilibrium between layers as required by the Boltzmann distribution law. A slow rate for such a process might be regarded as unlikely—(small barriers between layers). However, a slow rate of movement to equilibrium sites (unoccupied sites of lower energy) in the first layer is indicated by the abnormal thermal drifts observed in the thermal measurements. Such a situation would be that of a glass in two dimensions and of a mobile liquid in the third direction. In the extreme case of sites of nearly equal energy, the energy difference at high temperatures is essentially zero and at lower temperatures, where this difference becomes significant because of the Boltzmann distribution law, equilibrium is frozen. Thus the entropy would correspond to a distribution of X molecules between B equally probable sites which is

$$S = R \ln \frac{B!}{X![B - X]!} \quad (4)$$

Were equilibrium completely established rapidly, the entropy at the absolute zero must, of course, be zero. Equation (4) reduces to

$$S = R[1/\theta \ln 1/\theta - (1/\theta - 1) \ln (1/\theta - 1)] \quad (5)$$

This expression requires that the molal configurational entropy be zero for a complete monolayer and 2.2 e.u. at θ = 0.6, so that

$$(S_{s(1.0)} - S_{s(0.6)})_0 = -0.6 \times 2.22 = -1.33 \text{ cal./deg./mole} \quad (6)$$

for the system having one mole in the monolayer. According to our estimated error, the value obtained experimentally might be as low as 1.0. It would take five times our experimental error to give the calculated result.