The Heat Capacity of and the Entropy Change in a Monolayer of Oxygen Chemisorbed on Platinum Black from 15 to 300°K

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The Heat Capacity of and the Entropy Change in a Monolayer of

Oxygen Chemisorbed on Platinum Black from 15 to 300°K.[1a]

by R. A. Fisher,[1b] H. Chon, and J. G. Aston

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The heat capacity of a monolayer of oxygen chemisorbed on platinum black has been measured from 15 to 300°K. These heat capacity data were used to evaluate the entropy change in the oxygen monolayer. A thermally indicated titration, using hydrogen to remove the chemisorbed oxygen, demonstrated that there was a one-to-one correspondence between the atoms of chemisorbed oxygen and the surface platinum atoms. An analysis of the heat capacity and entropy data showed that below 90°K. the chemisorbed oxygen was strongly localized on the platinum surface. Above 90°K., cooperative interactions between the adsorbed oxygen seemed to be involved in a transition from localized chemisorption to chemisorption where at least some of the oxygen molecules have restricted motion within the monolayer. Some evidence is presented that indicates hindered mobility would be expected for oxygen chemisorbed on platinum only at monolayer coverages where cooperative interactions are greatest, and, as a consequence, can operate to lower potential barriers to motions within the surface monolayer. On the basis of the heat capacity and entropy data, it was not possible to decide if the chemisorbed oxygen was present on the surface in a diatomic or monatomic form.

Introduction

In recent series of experiments in this laboratory, a technique was developed for cleaning a platinum surface, using the recombination of hydrogen and oxygen on platinum, by a thermally indicated titration.[2] This experimental technique allows the preparation of a platinum surface either free of chemisorbed molecules or with a known amount of adsorbed hydrogen or oxygen present. Since an adiabatic calorimeter, capable of high accuracy, had been used for the titration experiments, it was decided to attempt a measurement of the heat capacity of a monolayer of adsorbed oxygen. A subsequent analysis of the heat capacity data for the adsorbed monolayer has enabled some conclusions to be drawn concerning the mobility of the adsorbed molecules, as well as giving some insight into the nature of the surface bonding.

Experimental

Apparatus and Materials. The adiabatic calorimeter assembly and the related measuring apparatus and equipment, as well as the purification procedure used for the various gases used in the experiments, has been extensively described elsewhere.[2,3a,b] The temperature scale used was in terms of a strain-free platinum resistance thermometer (ice-point resistance, 25 absolute ohms) which had been compared with laboratory standards.[4a] Temperatures are given in terms of the NBS scale.[4b]

Surface Preparation. In the experiments described below, the surface of the 163.4-g. platinum black sample was always prepared using a thermally indicated titra-

(1) (a) This work was supported in part by the Office of Ordnance Research; (b) presently at the Low Temperature Laboratory of the University of California, Berkeley, Calif.

(2) H. Chon, R. A. Fisher, and J. G. Aston, *J. Am. Chem. Soc.*, **82**, 1055 (1960).

(3) (a) R. A. Fisher, Ph.D. Dissertation, The Pennsylvania State University, University Park, Pa., 1961; available from University Microfilms, Ann Arbor, Mich.; (b) J. Greyson and J. G. Aston, *J. Phys. Chem.*, **61**, 610 (1957).

(4) (a) G. W. Moessen, J. G. Aston, and R. H. Ascah, "Temperature," Reinhold Publishing Corp., New York, N. Y., 1962, p. 91; (b) H. J. Hoge and F. G. Brickwedde, *J. Res. Natl. Bur. Std.*, **22**, 362 (1939).

tion with hydrogen or oxygen, followed by water desorption, using the methods described previously.[2]

Determination of the surface area of the platinum black was accomplished using standard B.E.T. techniques to evaluate the area from a nitrogen isotherm taken at the boiling point of liquid nigrogen. (The area of a nitrogen molecule was taken as 16.3 $\text{Å}.^2$.) From B.E.T. surface area measurements the number of surface sites (platinum atoms present at the surface) could be estimated provided the area per surface site was known. The average area per platinum site is obtainable from the lattice constant and the indices of the surface crystallographic planes. The lattice constant for platinum (f.c.c.) is 3.91 Å. and the assumption was made that the platinum black surface had only low index (100, 110, and 111) crystallographic planes present, each with equal probability. Using this as a basis gave a calculated average area per platinum site of 8.37 $\text{Å}.^2$.

In estimating the number of surface platinum atoms and the volume of gas necessary to form a monolayer the following equations were used.

$$V_M(g) = 22.4(n_{Pt}/fN_0) \text{ (in l. at STP)} \quad (1)$$

$$n_{Pt} = S_{Pt}/s_{Pt} \quad (2)$$

$$S_{Pt} = (N_0 s_{N_2}/22.4)V_M(N_2) \text{ (in Å.}^2) \quad (3)$$

Here $V_M(N_2)$ is the nitrogen monolayer volume, $V_M(g)$ the monolayer volume of the chemisorbed gas, n_{Pt} the number of surface platinum sites, S_{Pt} the total platinum surface area, s_{Pt} the surface area of a single platinum site, s_{N_2} the area of an adsorbed nitrogen molecule, 22.4 the molar volume in l. mole^{-1}, N_0 Avogadro's number (6.023 $\times$ 10^{23} molecules mole^{-1}), and f the number of platinum sites needed for each adsorbed gas molecule.

Heat Capacity of Oxygen Chemisorbed on Platinum Black. A B.E.T. determination of the platinum black surface area yielded a monolayer volume for nitrogen of 1.09 l. of N_2 at STP. A calculation, using the procedure and equations outlined above, gave 1.06 l. at STP as the expected monolayer volume for O_2 or H_2 using the assumption that there was one adsorbed atom per surface site.

Following the B.E.T. determination, with a monolayer of oxygen adsorbed, the calorimeter was outgassed to a pressure of less than 10^{-6} mm. Purified helium gas was then admitted to the calorimeter to a pressure of 1 cm. at room temperature to serve as an exchange gas. Heat capacities for this system were then obtained between 15 and 300°K. Following these heat capacity determinations, the chemisorbed oxygen was removed by a thermally indicated titration with hydrogen.[2] The oxygen removal by this procedure resulted in a

40% decrease in the platinum black surface area as shown by a B.E.T. nitrogen surface area determination.

The heat capacity of the resulting platinum black sample, with an essentially clean surface, was determined in a manner similar to that for the sample with a monolayer of chemisorbed oxygen. It was assumed that the surface area reduction produced a negligible change in the heat capacity. This assumption was justified by the results.

To obtain the heat capacity due to the adsorbed oxygen, the data from both heat capacity determinations were plotted and smooth curves drawn through the points. Differences between these two curves were then taken at even temperature intervals. Between 15 and 90°K. there was no detectable heat capacity contribution from the chemisorbed oxygen. From 90 to 170°K. the heat capacity rose rapidly to a maximum and then fell off slowly in going from 170 to 300°K. The entropy change associated with the heat capacity for the chemisorbed oxygen was obtained from the relationship

$$\Delta S = \int_0^T C_p/T \, dT \quad (4)$$

using a Simpson's rule integration of the heat capacity data.

Table I lists the heat capacity and entropy data for the chemisorbed oxygen at even temperature intervals. Column two of the table gives the heat capacities for the actual amount of oxygen chemisorbed on the platinum surface (0.0473 mole of O_2). Columns one, three, and four list, respectively, temperature, molal heat capacities, and related molal entropies on the basis of 1 g. mole of chemisorbed oxygen. Columns five and six are the heat capacities and related entropies on the
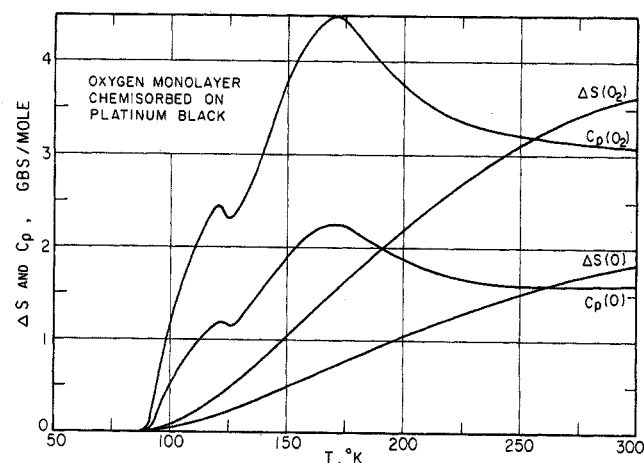

Figure 1. Experimental heat capacity and related entropy change data for oxygen chemisorbed on platinum black.

basis of 1 g.-atom of chemisorbed oxygen. Figure 1 is a graph of the molar data of Table I.

Table I: Experimental Heat Capacities and Related Entropy Changes for Oxygen Chemisorbed on Platinum Black[a]

$T,$ K°.	$\Delta C_p,$ gibbs	C_p —gibbs/mole of O_2—	ΔS	C_p —gibbs/g.-atom of O—	ΔS
0 to 90	0.000	0.00	0.00	0.00	0.00
92.5	0.015	0.33		0.16	
95	0.031	0.66	0.02	0.33	0.01
97.5	0.041	0.87		0.44	
100	0.051	1.09	0.06	0.55	0.03
105	0.067	1.42		0.71	
110	0.087	1.85	0.20	0.92	0.10
115	0.103	2.18		1.09	
120	0.113	2.39	0.39	1.20	0.20
125	0.111	2.28		1.14	
130	0.113	2.39	0.57	1.20	0.28
135	0.123	2.60		1.30	
140	0.144	3.02	0.77	1.51	0.39
145	0.164	3.48		1.74	
150	0.175	3.70	1.01	1.85	0.50
155	0.190	3.93		1.97	
160	0.206	4.35	1.26	2.18	0.63
165	0.211	4.46		2.23	
170	0.216	4.56	1.53	2.28	0.77
175	0.211	4.46		2.23	
180	0.206	4.35	1.79	2.18	0.90
190	0.195	4.14		2.07	
200	0.180	3.80	2.22	1.90	1.11
210	0.173	3.64		1.82	
220	0.170	3.58	2.56	1.79	1.28
230	0.164	3.48		1.74	
240	0.159	3.37	2.86	1.68	1.43
250	0.154	3.26		1.63	
260	0.152	3.21	3.13	1.60	1.56
270	0.150	3.17		1.58	
280	0.149	3.14	3.36	1.57	1.68
290	0.149	3.14		1.57	
300	0.148	3.13	3.58	1.56	1.79

[a] One monolayer equals 0.0473 mole of O_2.

The average deviations of the experimental data from smooth curves through them for the two sets of heat capacities is: 0.2% from 15 to about 20°K., 0.1% from 20 to about 190°K., and 0.2% from 190 to 300°K. The corresponding precision of the heat capacities for the chemisorbed oxygen is, on the average, 0.2 gibbs (mole of O_2)$^{-1}$. (Here the convention is used, as originated by Giauque[5] and used by him, of defining the gibbs as: 1 gibbs = 1 defined cal./defined °K.) The precision in all cases is understood to be both positive and negative.

Since the original particle size of the platinum black sample was about 100 Å. on a side before the oxygen removal,[2,3a] and because sintering occurred upon re-

moval of the chemisorbed oxygen, the question arises as to the possibility of heat capacity contributions due to surface and particle size effects.[6,7] Lien and Phillips[8] have shown that for MgO particles about 100 Å. on a side, the heat capacity at low temperatures (in the liquid helium range) is quite different than that for bulk MgO. Their results are in qualitative agreement with those predicted from theory.[6,7] For the present case of the platinum black–oxygen system, no detectable heat capacity existed for the chemisorbed oxygen below 90°K. It may be concluded from this that sintering of the platinum black to larger particles, with correspondingly lower surface areas, resulted in no detectable change in the heat capacity above 15°K. due to this effect.

Near room temperature, contributions to the heat capacity would be expected from any water adsorbed on the platinum surface. This water would be present because of incomplete removal following the thermally indicated hydrogen titration. In the event that any water were present and did lead to contributions to the heat capacity, then the heat capacity for the sample, with an assumed bare surface, would be too high. Consequently, the heat capacity due to chemisorbed oxygen would be too low. However, due to the outgassing conditions following the titration, it is unlikely that much water remained on the surface. From the measured quantity of water removed, the maximum amount remaining on the surface could have been no more than 50 cc. at STP (0.0002 mole of H_2O). Heat capacity contributions, in the temperature range of interest, from an amount of water this small would be expected to be low.

Discussion

Theoretical. Gas molecules adsorbed on a surface tend to occupy sites, or regions, of minimum potential energy. The variation of the potential energy from point to point on the surface leads to potential barriers V between adjacent sites. These potential barriers hinder motion from one site to another. Three cases arise: (I) $V \ll kT$, the variation in potential in passing from site to site is unimportant and the surface is effectively a continuum. Consequently, the adsorbed molecules have two-dimensional mobility. (II) $V \gg kT$, the variation of the potential from site to site is large. As a result, the adsorbed molecules are localized and vibrate about the minima of the potential wells.

(5) W. F. Giauque, E. W. Hornung, J. E. Kunzler, and T. R. Rubin, *J. Am. Chem. Soc.*, **82**, 62 (1960).

(6) E. W. Montroll, *J. Chem. Phys.*, **18**, 183 (1950).

(7) G. Jura and K. S. Pitzer, *J. Am. Chem. Soc.*, **74**, 6030 (1952).

(8) W. H. Lien and N. E. Phillips, *J. Chem. Phys.*, **29**, 1415 (1958).

(III) $V \approx kT$, hindered surface migration may take place from one site to another by passage over (or through by quantum mechanical tunneling) the potential barriers. Cooperative interactions between molecules adsorbed on a surface may lead to lowering of the potential barriers, V. That is, there may be a mutual interaction of the adsorbed molecules, due to their motions, so that the net result is a lowering of the potential barriers to this motion.

When a gas molecule is diatomic, the degrees of freedom relating to the internal motions of the atoms relative to one another are usually altered upon adsorption. In the extreme case dissociation will take place at the surface. For the nondissociative case the rotational degree of freedom for in-plane rotation may have a potential barrier associated with it so that free rotation is restricted. Likewise, the out-of-plane rotation and the vibrational motion of the atoms relative to one another may have barriers associated with them. These barriers related to the internal degrees of freedom of the molecule may all be lowered by cooperative interactions.

The heat capacity of adsorbed molecules will depend on the population changes with temperature of the various energy levels associated with external and internal degrees of freedom for the adsorbed molecules. The external degrees of freedom, which are related to motions of the centers of mass of the molecule, lead to translational and/or vibrational heat capacity contributions. Degrees of freedom associated with internal motions of the atoms of the molecule relative to one another, when the molecule is polyatomic, give rise to rotational and/or vibrational heat capacity contributions. Rotational and translational degrees of freedom may be so highly hindered that they go over into vibrational degrees of freedom. Cooperative phenomena involving a degree of freedom will lead to a rapid change with temperature of the heat capacity associated with the degree of freedom. A maximum in the heat capacity vs. temperature curve results from cooperative interactions. The sharpness of the curve increases with increasing cooperation, and, in the limit of complete cooperation, the heat capacity–temperature curve goes over into a λ-type anomaly.

The entropy change at temperature T accompanying the localization of gas molecules on an adsorbent surface may be represented by

$$\Delta S_{loc} = [S(g) - S_{loc}(ad)] \quad (5)$$

while the entropy change for mobile adsorption may be written as

$$\Delta S_{mob} = [S(g) - S_{mob}(ad)] \quad (6)$$

Here the subscripts loc and mob refer, respectively, to localized and mobile adsorbed phases, while $S(g)$ is the entropy of the molecules in the gas phase and $S(ad)$ the entropy of the adsorbed molecules. Transition from localized to mobile adsorption involves an entropy change which is given by

$$\Delta S_{m,l} = [\Delta S_{mob} - \Delta S_{loc}] =$$
$$[S_{mob}(ad) - S_{loc}(ad)] \quad (7)$$

For the entropy change to be expected in a transition from localized to mobile adsorption $\Delta S_{m,l}$ may be written as

$$\Delta S_{m,l} = [S_c(ad) - {}_2S_t(ad)] \quad (8)$$

where the term ${}_2S_t(ad)$ is the entropy associated with free two-dimensional translational motion and $S_c(ad)$ is the configurational entropy for the adsorbed molecules. $S_c(ad)$ is a function of the surface coverage θ and for monolayer coverages is equal to zero.

Heat Capacity and Entropy of Oxygen Chemisorbed on Platinum Black. From an examination of Fig. 1, several valuable conclusions can be drawn concerning the state of the chemisorbed oxygen on the platinum black surface. The negligible heat capacity contribution from the chemisorbed oxygen below 90°K., and the rapid rise in the heat capacity to a maximum in going from 90 to 170°K., points to hindered mobility, with cooperative interactions between oxygen atoms or molecules, above 90°K. Localized adsorption below 90°K. explains the negligible heat capacity contribution in this region of temperature.

From previous work[2] on the thermally indicated hydrogen titration of oxygen chemisorbed on platinum black, it was shown that the heat of reaction changed by about 11 kcal. (mole of H_2)$^{-1}$ in removing the first 10% of the adsorbed oxygen. Removal of the remaining 90% chemisorbed oxygen gave practically a constant heat of reaction. The high initial heats indicate less tightly bound oxygen. Removal of a small fraction of the chemisorbed oxygen decreases the cooperative interactions between the adsorbed oxygen. This causes the chemisorbed oxygen to become localized and, as a consequence, more tightly bound to the platinum surface. Thus, the drop in the heat of reaction by 11 kcal. (mole of H_2)$^{-1}$ shows that hindered motions within the layer loosen the surface bonds.

It is interesting to compare the experimental heat capacity and entropy change data at 300°K. with the heat capacity and entropy associated with various unhindered motions of oxygen molecules or atoms on the adsorbent surface. This comparison is made in Table II for both the case of diatomic and atomic oxygen

chemisorbed on the surface. In the table, the subscripts to the right (t, r, and v) refer, respectively, to translation, rotation, and vibration, while the subscripts to the left denote the number of degrees of freedom to be associated with each.

Table II: Comparison of Experimental Heat Capacity and Entropy for Oxygen Chemisorbed on Platinum Black, with the Heat Capacity and Entropy Associated with Various Unhindered Degrees of Freedom. The Comparison is Made at 300°K.

	Exptl.		Calcd.				
	C_p	S	$_2C_t$	$_1C_r$	$_1C_v$	$_2S_t$	$_1S_r$
Diatomic oxygen	$1.6R$	$1.8R$	R	$R/2$	R	$8.3R$	$1.4R$
Atomic oxygen	$0.8R$	$0.9R$	R	...	R	$6.9R$	...

The entropies $_2S_t$ and $_1S_r$ were calculated from equations taken from Trapnell[9]

$$_2S_t = R(\ln MTA + 33.12) \quad (9)$$

and

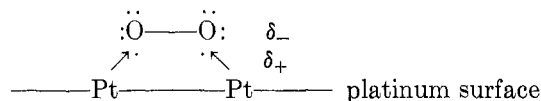$$_1S_r = R/2(1 + \ln IT - \ln \sigma + 87.28) \quad (10)$$

In the two above equations R is the gas constant (1.987 gibbs mole^{-1}), M the molecular weight of the adsorbed molecules, A the area in cm.^{2} occupied by each adsorbed molecule, I is the moment of inertia for the rotating group in g. cm.^{2}, and σ is the symmetry number for the rotation.

In the preparation of Table II the following constants were used. For atomically adsorbed oxygen, A was taken as 8.37×10^{-16} cm.^{2} and M as 16. For diatomically adsorbed oxygen, A was taken as 16.7×10^{-16} cm.^{2} (this is twice the average area per platinum site because of the experimentally found one-to-one correspondence between oxygen atoms and surface platinum atoms) and M as 32. The moment of inertia used was that of a gaseous oxygen molecule (7.3×10^{-40} g. cm.^{2}) with a rotational symmetry number of 2.

Since a monolayer of oxygen was chemisorbed on the platinum surface, $S_c(ad)$ is zero, and the *minimum* entropy change to be expected in a transition from localized to mobile adsorption would be $_2S_t(ad)$. From an examination of Table II it is clear that if the oxygen is chemisorbed as atoms, then only a fraction of them are on sites with potential barriers sufficiently low that a transition to hindered mobility can take place. If the oxygen is diatomically adsorbed, it is not possible to say

whether the entropy change is associated with hindered rotational degrees of freedom, hindered translational degrees of freedom, or a combination of both. Contributions from vibrational degrees of freedom, other than those associated with in-plane vibrations of the centers of mass (which go over into hindered translational or rotational motion), would be expected to be low for both diatomically and atomically chemisorbed oxygen at 300°K. This would also be expected for contributions from out-of-plane torsional vibrations associated with one of the rotational degrees of freedom for the diatomic case.

The question as to whether or not the chemisorbed oxygen is atomic or diatomic cannot, unfortunately, be answered by the heat capacity and entropy data. It is known that oxygen chemisorbed on most metals is dissociated into atoms.[10] On the other hand, an oxygen molecule in the gaseous state possesses two unpaired electron spins. Thus, it is possible that upon adsorption a platinum–oxygen complex could result from formation of bonds between the surface platinum orbitals and these unpaired electron spins. This picture of in-plane diatomic oxygen chemisorption is not inconsistent with the relative electronegativities for oxygen and platinum given by Pauling,[11] or with the sign of the surface dipole.[12] A type of surface compound which might be formed from diatomic chemisorption of oxygen on platinum can be schematically shown as

$$
\begin{array}{ccc}
\ddot{O} & —— & \ddot{O}: \quad \delta_- \\
\nearrow \cdot & & \cdot\nwarrow \quad \delta_+ \\
——Pt——&——Pt——& \text{platinum surface}
\end{array}
$$

where the arrows indicate electron transfer toward the oxygen atoms from the platinum atoms in the surface. For this type of configuration, the oxygen would be in the state of hybridization similar to that found in peroxides.

Appendix

A treatment of hindered two-dimensional surface translation has been given by Hill.[13] Hill's attack on the problem is analogous to Pitzer's treatment of the hindered rotation problem.[14]

(9) B. M. W. Trapnell, "Chemisorption," Academic Press, New York, N. Y., 1955, p. 210.

(10) B. M. W. Trapnell, *ibid.*, p. 180.

(11) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, New York, N. Y., 1945, p. 65.

(12) C. W. Oatley, *Proc. Phys. Soc.* (London), **51**, 318 (1939); see also ref. 9, p. 181.

(13) T. L. Hill, "Introduction to Statistical Thermodynamics," Addison-Wesley, New York, N. Y., 1960, p. 172.

(14) K. S. Pitzer, "Quantum Chemistry," Prentice-Hall, New York, N. Y., 1953, p. 492.

For the simple case of noninteracting, monatomic molecules, adsorbed on a simple cubic lattice, a periodic potential U_{XY} at the adsorbent surface may be approximated by

$$U_{XY} = U_Z{}^0 + V/2[1 - \cos (2\pi X/a - \cos (2\pi Y/a)] \quad (11)$$

In eq. 11, X and Y are coordinates in the surface plane and Z the coordinate perpendicular to the surface, $U_Z{}^0$ is the depth of the potential in U_{XY}, V the potential barrier separating potential minima, and a is the nearest neighbor spacing for the adsorbent lattice.

The partition function for a system of N noninteracting particles of mass m is given by

$$Q_{XY} = (q_{XY})^N/N! \quad (12)$$

where q_{XY} is the partition function for an individual particle. It may be calculated using the potential of eq. 11 and using the approximation that

$$q_{XY} = q_{\text{classical}}[q_{\text{HO-QM}}/q_{\text{HO-classical}}] \quad (13)$$

where HO stands for harmonic oscillator and QM means quantum mechanical.

After some mathematical manipulation q_{XY} is obtained

$$q_{XY} = \frac{(2\pi mu)I_0{}^2(u) \exp(-2u - 2Ku)}{(1 - \exp(-Ku))^2} \quad (14)$$

where

$$K = (2h^2/ma^2V)^{1/2} \quad (15)$$

and

$$u = V/2kT \quad (16)$$

In the above equations k is the Boltzmann constant $(1.380 \times 10^{-16} \text{ erg}/°\text{K.})$ and h Planck's constant $(6.625 \times 10^{-27} \text{ erg sec.})$.

Q_{XY} is evaluated, and in the usual way the heat capacity is found to be given by

$$_2C_t/Nk = -1 + 2u[u - I_1(u)/I_0(u) - u(I_1(u)/I_0(u))^2] + \frac{2K^2u^2 \exp(-Ku)}{(1 - \exp(-Ku))^2} \quad (17)$$

using the relationship

$$C/Nk = \frac{\partial}{\partial T}\left[T^2 \frac{\partial \ln Q}{\partial T}\right] \quad (18)$$

In the preceding, $I_0(u)$ and $I_1(u)$ are, respectively, the modified Bessel functions of the first and second kind.[15] The potential barrier V may be obtained from the relation

$$V = 5kT_M \quad (19)$$

T_M is the temperature where the heat capacity maximum of eq. 17 occurs.

Although the oxygen heat capacity data would not be expected to follow any such simple theoretical heat capacity curve as that obtained from eq. 17, it is interesting to see just how closely the data do fit.

Figure 2 shows the experimental heat capacity and entropy change data, as points, for a mole of chemisorbed O_2 molecules. Curve A is the theoretical heat capacity calculated from eq. 17. Taking T_M equal to
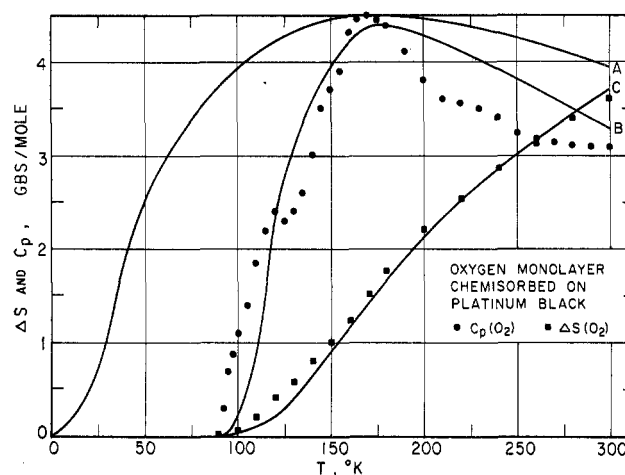

Figure 2. Comparison of experimental heat capacity and entropy change data with calculated values.

170°K., the potential barrier V is 1700 cal. (mole of O_2)$^{-1}$ using eq. 19. The parameter a for platinum is 2.76 Å. It is quite evident, as was to be expected, that curve A does not fit the experimental heat capacity data except at the maximum. Qualitatively, however, the calculated curve exhibits similar characteristics.

Since curve A has the general shape of the experimental heat capacity data, an empirical method for fitting the data suggests itself. Curve B was computed using the following artifice. Transformation of the temperature coordinate was made according to the following definition

$$T' = T - T_0 \quad (20)$$

where T_0 is taken as the experimental temperature where heat capacity contributions first become detectable. A potential barrier V' is then calculated using

$$V' = 5kT'_M \quad (21)$$

By use of eq. 20, 21, and 17 curve B was obtained. T_0

(15) A table of the various Bessel functions is given in "British Association Mathematical Tables X," Part II, Cambridge University Press, London, 1952.

was taken as 90°K. which gave T'_M as 80°K. The potential barrier V' was 800 cal. (mole of O_2)$^{-1}$.

The entropy change at 300°K., obtained from an integration of curve A, gave 8.5 gibbs (mole of O_2)$^{-1}$, while curve B gave 3.7 gibbs (mole of O_2)$^{-1}$. The experimental change of entropy at 300°K. is 3.6 gibbs (mole of O_2)$^{-1}$. Curve C is a plot of the entropy change obtained from an integration of curve B.

The fit of curves B and C to the experimental heat capacity and entropy change data on the basis of a mole of chemisorbed O_2 is surprisingly good. However, it must be emphasized that use of eq. 20 has no known theoretical justification, and it is used in an entirely empirical manner. (The introduction of T_0 is some-

what analogous to the introduction of the Weiss Δ into the equation for magnetic susceptibility, $\psi = C/(T - \Delta)$.)

If the assumption is made that the oxygen is atomically chemisorbed, and that only a fraction of it, about 50%, occupies sites with barriers which can become sufficiently lowered through cooperative interactions, then the heat capacity data can also be fit using the empirical method embodied in eq. 20 and 21.

The same empirical method may be applied to hindered rotational degrees of freedom which involve cooperative interactions. (For calculating hindered rotational heat capacities and associated entropy changes, the tables given by Pitzer are useful.[14])

A Calorimetric Study of the Transformation of Some Metastable

Modifications of Alumina to α-Alumina

by T. Yokokawa and O. J. Kleppa

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The heats of solution, in a lead–cadmium–borate melt at 705°, of α-alumina (corundum) and of several metastable modifications of aluminum oxide have been investigated. From the measured heats of solution we obtained the following enthalpies of transformation: $Al_2O_3(\gamma) = Al_2O_3(\alpha)$, $\Delta H = -5.3$ kcal./mole; $Al_2O_3(\kappa) = Al_2O_3(\alpha)$, $\Delta H = -3._6$ kcal./mole; $Al_2O_3(\delta) = Al_2O_3(\alpha)$, $\Delta H = -2.7$ kcal./mole.

Introduction

Crystalline alumina (Al_2O_3) is known to occur in a series of different structural modifications. Among these only the α-modification (corundum) is thermodynamically stable. The various metastable forms are denoted β, γ, δ, κ, η, θ, χ and have been characterized by X-ray powder diagrams only. The conditions under which they form are not well understood. Characteristically they are obtained on the ignition of aluminum compounds, and the appearance of a particular phase depends on a variety of factors such as im-

purity content, temperature, particle size, quenching speed, etc.[1]

All the various metastable modifications can be converted to the stable corundum form by ignition at sufficiently high temperatures. The conditions required for complete conversion change from one sample to another.

We have found no reliable information in the published literature on the heat of transformation of the

(1) See, *e.g.*, M. Plummer, *J. Appl. Chem.* (London), **8**, 35 (1958); H. P. Roothsby, *ibid.*, **8**, 44 (1958).