acid was subjected to ultrasonic irradiation. Also, adding excess alkali to the solution, which would prevent step 2, and then irradiating until all of the carbon tetrachloride was exhausted caused the total amount of chlorine produced to be only one-half as great as the normal amount obtained in neutral solution.

A third piece of evidence in favor of the proposed scheme is shown in Fig. 15. The first reaction, which is practically complete in ten minutes, produces hydrogen chloride; the second step destroys it. This implies that the acidity will increase to a maximum value at ten minutes, and then decrease gradually. Such a prediction was confirmed experimentally, by irradiating 8 mg. of carbon tetrachloride in 100 ml. of water. For this case the theoretical maximum acidity is a little over 0.10 milliequivalent; the value observed was a little below 0.10, because some destruction of HCl took place even in the first ten minutes.

However, infrared and mass-spectrometer analyses[13] showed that carbon dioxide is produced, not carbon monoxide, by irradiation of a mixture of water and excess carbon tetrachloride in a closed system from which all of the air has been replaced by helium. The carbon dioxide might arise from hydrolysis of some of the intermediate product phosgene, or else from an ultrasonic reaction between carbon monoxide and water. It was interesting to note that, after a few hours of irradiation, the characteristic odor and color of elemental chlorine were unmistakably present.

Summary

1. The amount of iodine liberated by ultrasonic waves from potassium iodide–carbon tetrachloride aqueous solutions depends on the dimensions and material of the reaction vessel.

2. Although dissolved oxygen has formerly been considered essential, nitrogen or helium are found to serve almost as well.

3. As the power input is increased, no iodine is produced until cavitation occurs. Then the yield increases almost linearly if the volume of solution is large enough, but for smaller volumes the yield first increases and then decreases sharply.

4. The main reaction is that between water and dissolved carbon tetrachloride, the potassium iodide being primarily an indicator of the oxidizing chlorine set free.

5. Rate studies indicate that the reaction takes place in two steps, each of which liberates two chlorine atoms per carbon tetrachloride molecule. The first step is approximately ten times faster than the second.

6. In the absence of carbon tetrachloride the oxidation of potassium iodide solution proceeds only about one-fifteenth as rapidly as in the presence of carbon tetrachloride.

WASHINGTON, D. C. RECEIVED JUNE 27, 1949

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[13] These analyses were performed by Dr. D. C. Smith of the Naval Research Laboratory and Mr. S. Schuhmann of the National Bureau of Standards, respectively.

[CONTRIBUTION FROM THE MOORE LABORATORY OF CHEMISTRY, AMHERST COLLEGE, AND THE RESEARCH LABORATORY OF GODFREY L. CABOT, INC.]

The Entropy of Adsorbed Molecules

BY G. L. KINGTON,[1] R. A. BEEBE,[1] M. H. POLLEY[1,2,3] AND W. R. SMITH[4]

It is of fundamental interest in a study of adsorption phenomena to investigate the state of the adsorbed phase. Lennard-Jones[5] and Hill[6] have suggested that we may consider two types of motion of adsorbed molecules, one a long range motion in which the molecules move relatively long distances and exchange places, or a more restricted type of motion in which each molecule oscillates laterally about a potential minimum and is thus confined to a particular region of the surface. Two states of adsorbed molecules are then distinguished, a mobile state and a vibrating state.

It is possible to determine the entropy of the adsorbed molecules from experimental data and also to estimate it from statistical considerations of possible models of the adsorbed state. A comparison of the two kinds of data makes it possible to select the model which produces results which most nearly conform to the experimental data.

Such a comparison was carried out by Barrer[7] for the occlusion system, gas–zeolite. Although the process considered is not one of adsorption but rather of solution, the method of statistical mechanical interpretation of the experimental thermodynamic data is similar to that employed in the present study. It is of interest to note that Barrer concluded that the solute molecules (ethane, propane, *n*-butane, hydrogen) approximate closely to three-dimensional oscillators within the framework of the zeolite, and that no large fraction of molecules could possess even one-dimensional translational freedom within the zeolite.

Kemball and Rideal[8,9] have investigated the

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[3] A part of this paper was presented as a thesis by M. H. Polley in partial fulfillment of the requirements for the Master's degree at Amherst College.

[4] Godfrey L. Cabot, Inc., Boston, Mass.

[5] Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1932).

[6] Hill, *J. Chem. Phys.*, **14**, 441 (1946).

[7] Barrer, *Trans. Faraday Soc.*, **40**, 374 (1944).

[8] Kemball and Rideal, *Proc. Roy. Soc.* (*London*), **187A**, 53 (1946).

[9] Kemball, *ibid.*, **190**, 117 (1947).

adsorption of several non-polar substances on a mercury surface by a similar treatment. For the system benzene on mercury at 25°, these authors found a striking agreement between the experimental entropy of adsorption and that calculated for molecules possessing two degrees of translational freedom and one degree of rotation in the plane of the ring.

The work in these laboratories has resulted in the accumulation of data[10,11,12] on the adsorption of gases on solid surfaces (in particular on carbon black). This information, consisting of isotherm and calorimetric heat data, can be treated to yield the thermodynamic quantities of adsorption, in particular ΔS, the differential entropy of adsorption. It is the purpose of this paper to describe the partial molal entropy obtained from such a treatment of the experimental data, and to compare it with the entropies of the bulk three-dimensional states and with the entropy requirements of the Brunauer, Emmett and Teller theory. In a future paper we hope to compare our experimentally measured values of the partial molal entropy with the entropy required by other models of the adsorbed state. We shall deal in the present paper with the adsorption of nitrogen and oxygen on the two adsorbents, carbon black and titanium dioxide (anatase).

Results

The Isotherms and Heats of Adsorption.—The calorimetrically determined differential heats of adsorption and the Brunauer, Emmett and Teller plots of the isotherm data for nitrogen and oxygen on carbon black[13] have been reported elsewhere. For the convenience of the reader the differential heats of nitrogen on carbon black are reproduced in Fig. 1. In this and in all subsequent figures, the values of v_m have been determined in the usual manner from the B.E.T. plots. Figures 1 and 4 also contain plots of the heats of adsorption required by the B.E.T. theory; these curves will be discussed in a later section. The same calorimetric technique as previously described[10] was used in the investigation of the elementary gas–anatase systems now reported.

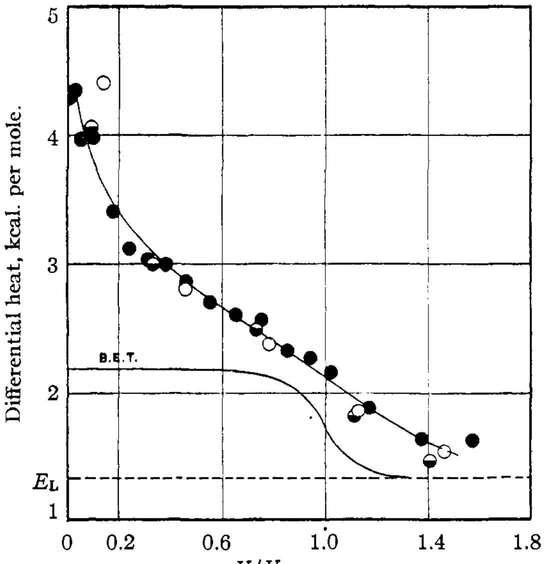

Fig. 1.—Differential heat of adsorption at 78.5°K., nitrogen on carbon black (Spheron 6): run 8 ○, run 14 ◒, run 16 ●.

The specific surface area of the anatase had been measured by different experimental methods by Brunauer, Emmett and Teller and by Harkins and Jura.[14] These two sets of investigators obtained the values 13.9 and 13.8 sq. m./g., respectively. Using this titanium dioxide we have conducted two runs with nitrogen and two with oxygen. The results are given in Figs. 2, 3, and 4. We obtain the value 13.9 sq. m./g. from our nitrogen data by the B.E.T. method.

A summary of the results obtained from a B.E.T. treatment of the systems nitrogen and oxygen on anatase and carbon black is given in Table I. On the basis of the v_m values given in Column 3 and the specific surface areas in Column 4, we have calculated the values of the area per molecule of oxygen on the two adsorbents. These values, given in Column 5 are 12.9 and 16.8 sq. Å. on the carbon black and the anatase, respectively. Methods for estimating the area occupied per adsorbed molecule in close packing on a surface have been suggested by Brunauer and Emmett[15] and more recently by Hill.[16] Both these methods yield values for the surface area per molecule which are about 2 sq. Å. lower for oxygen than for nitrogen. Thus the value 16.8 sq. Å. for oxygen compared to 16.2 sq. Å. for nitrogen on titanium dioxide, appears to be anomalous. It seems probable that in this case the substrate surface must be exercising a

TABLE I

RESULTS OBTAINED FROM THE APPLICATION OF B.E.T. THEORY TO CARBON BLACK AND TITANIUM DIOXIDE SYSTEMS

(1) Adsorbent	(2) Absorbate	(3) v_m, cc./g.	(4) Surface area[a] from v_m, sq. m./g.	(5) Area per molecule[b] sq. Å.
Carbon black	Nitrogen	25.6	111.2	16.2[a]
Carbon black	Oxygen	32.1	...	12.9
Anatase	Nitrogen	3.17	13.8	16.2[a]
Anatase	Oxygen	3.05	...	16.8

[a] Assuming cross-section of the nitrogen molecule is 16.2 sq. Å. [b] Assuming surface area as given by nitrogen adsorption.

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[10] Beebe, Biscoe, Smith and Wendell, THIS JOURNAL, **69**, 95 (1947).

[11] Beebe, Polley, Smith and Wendell, *ibid.*, **69**, 2294 (1947).

[12] Beebe and Smith, *Ind. Eng. Chem.*, **41**, 1431 (1949).

[13] The term carbon black is used throughout this paper to denote the product of Godfrey L. Cabot, Inc., known as "Spheron 6."

[14] Harkins and Jura, THIS JOURNAL, **66**, 1362 (1944).

[15] Brunauer and Emmett, *ibid.*, **59**, 1553 (1937).

[16] Hill, *J. Chem. Phys.*, **16**, 189 (1948).

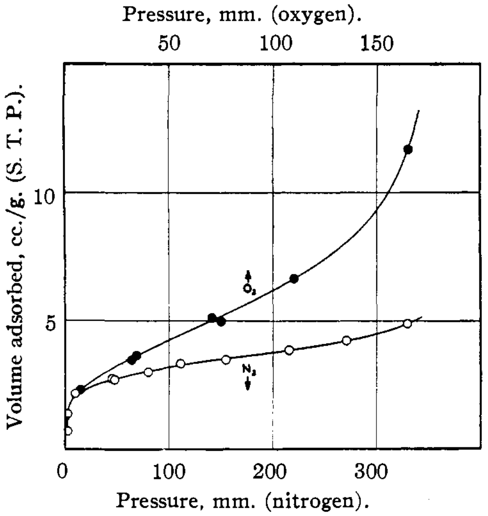

Fig. 2.—Isotherms of titanium dioxide (anatase) adsorption system at 78.5°K.: oxygen, ●; nitrogen, ○.

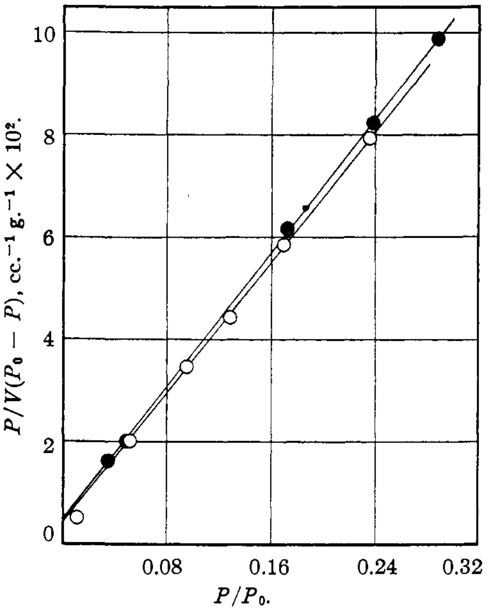

Fig. 3.—B. E. T. plots for titanium dioxide: oxygen, ●; nitrogen ○.

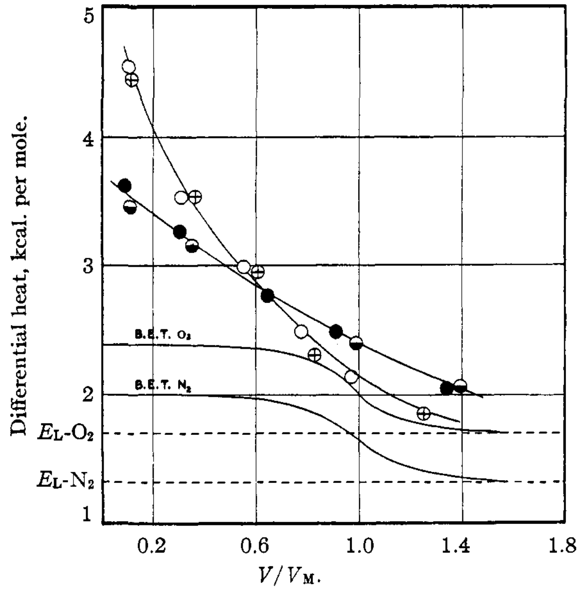

Fig. 4.—Differential heat of adsorption at 78.5°K., nitrogen and oxygen on titanium dioxide: nitrogen run 31 ○, run 35 ⊕; oxygen run 32 ●, run 36 ◒.

considerable specific effect on the spacing of the adsorbed molecules relative to each other. It is noteworthy that Arnold[17] likewise has reported an anomalously high value for oxygen on titanium dioxide.

The heats of adsorption of nitrogen and oxygen on titanium dioxide are compared in Fig. 4. From this figure it is seen that the calorimetrically determined differential heat of adsorption on anatase undergoes a large variation as successive fractions of the surface are covered. The magnitude of the heat of adsorption indicates that the adsorption of both oxygen and nitrogen is van der Waals in nature. A changing differential heat of adsorption with fraction of surface covered was noted on carbon black surfaces.[10] However, the differential heats of adsorption of nitrogen and oxygen in the first layer on carbon black were identical within the experimental error, whereas the heats of adsorption of these two gases on titanium dioxide show marked differences. It is apparent that the initial heat of adsorption of nitrogen is *ca.* 1 kcal. per mole higher than the initial oxygen value. The two curves cross at about $v/v_m = 0.6$ and then approach the respective heats of liquefaction.

It is of interest to compare the difference between the heats of adsorption of oxygen and nitrogen in the early increments, with Arnold's[17] findings on the adsorption of mixtures of nitrogen and oxygen on titanium dioxide. This author found that at a sufficiently low relative pressure the adsorbed phase always contained an excess of nitrogen over oxygen for all gas phase concentrations investigated. We may therefore correlate the higher heat of adsorption of nitrogen at low coverages on titanium dioxide with its preferential adsorption on this solid when mixed with oxygen.

The Entropy of the Adsorbed Layer.—Emmett and his co-workers[18,19] have shown that the differential entropy of adsorption may be obtained from a knowledge of the heat of adsorption and of the isotherm data. Davis and Dewitt[18] obtained information for the system butane on glass spheres at 0°, using isosteric heat data. Similar work has been carried out by Emmett and Joyner[19] on the system nitrogen–carbon black.

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[17] Arnold, THIS JOURNAL, **71**, 104 (1949).

[18] Davis and DeWitt, *ibid.*, **70**, 1135 (1948).

[19] Joyner and Emmett, *ibid.*, **70**, 2353 (1948).

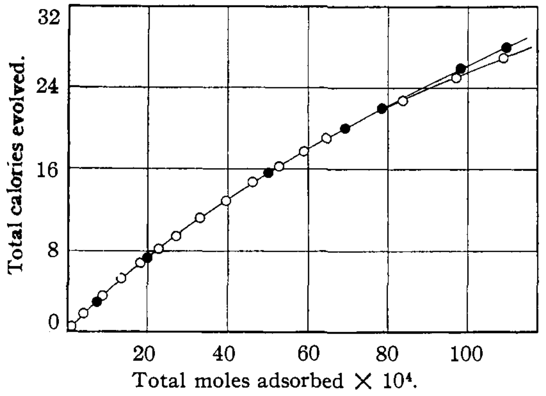

Fig. 5.—Integral heat of adsorption of nitrogen on Spheron 6 carbon black at 78.5°K.: experimental ○; empirical ●.

Consider a gas phase at pressure p in equilibrium with the adsorbed state; let the adsorption of one mole of gas onto an infinite surface change the heat content of the system by ΔH. Since we are considering an equilibrium process, then the change in entropy is given by $\Delta H/T$. The change in entropy in going from any *standard* gas state[20] to the adsorbed state is then

$$\Delta S = \Delta H/T - \mathrm{R} \ln p/p_0$$

S is the differential entropy of adsorption and is equal to $\bar{S}_A - \bar{S}_G$; where $\bar{S}_G$ is the molar entropy of the gas phase in the standard state p_0 and $\bar{S}_A$ is the partial molal entropy of the gas in the adsorbed phase at the coverage under consideration. Hence $\bar{S}_A$ is given by

$$\bar{S}_A = S_G + (\Delta H/T - R \ln p/p_0) \qquad (1)$$

Inasmuch as we experimentally determined p and ΔH as a function of v/v_m, we are able to calculate $\bar{S}_A$, the partial molal entropy of the gas in the adsorbed state at various surface coverages. Using the experimental ΔH values from the smoothed curves of Figs. 1 and 4 (this paper) and Fig. 7 of "Heats of Adsorption on Carbon Black. I,"[10] the partial molal entropies in the adsorbed state $\bar{S}_A$, were obtained and are plotted in Curve 1 of Fig. 6, and in Figs. 7, 8, 9.

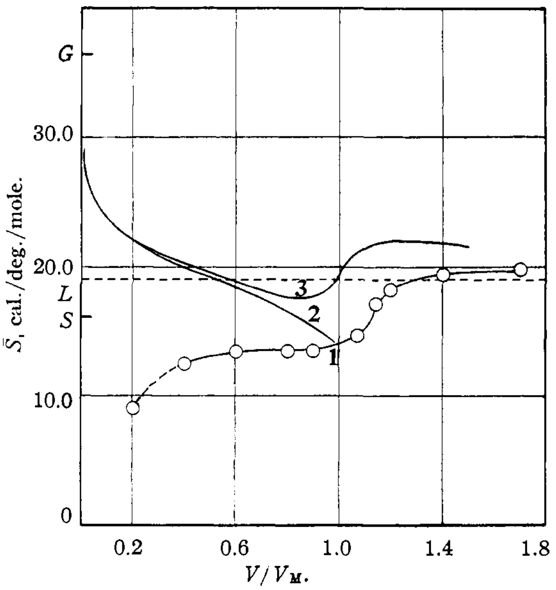

Fig. 6.—Partial molal entropy of nitrogen on carbon black at 78.5° K.: (1) experimental, (2) B. E. T., constant $\Delta H = E_1$, (3) B. E. T., variable ΔH.

An independent approach to the determination of the entropy of an adsorbed layer is provided by treatment of the heat capacity data of Morrison and Szasz.[21] Overcoming the considerable experimental difficulties associated with the measurement of the heat capacity of the adsorbed film, these authors have obtained data for a monolayer of nitrogen on titanium dioxide (rutile) from 23° to 80°K. We have obtained the entropy change from 23° to 78.5°K. by graphical integration of the data of Morrison and Szasz. Combining this result with the entropy calculated by means of the Debye function over the range 0 to 23.0°K., the molar entropy for a monolayer of nitrogen on rutile at 78.5°K. was found to be 10.9 ± 0.5 e.u. This is an integral quantity and to obtain a comparable value from our data, it is necessary to evaluate the quantity $\left(\int_0^{n_0} \bar{S}\, dn/n_0\right)$ by integration of our partial molal entropies shown in Curve 1 of Fig. 8.[22] As a result of this integration of our data

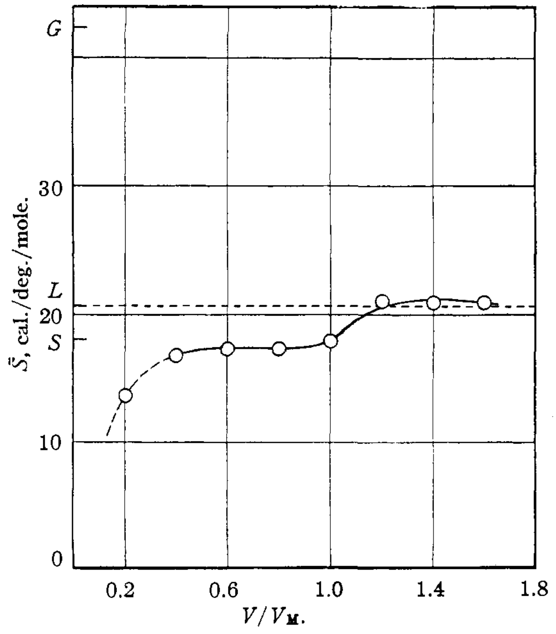

Fig. 7.—Partial molal entropy (from experimental data), of oxygen on carbon black at 78.5°K.

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[20] The standard state will be defined as that of one mole of gas at the saturation vapor pressure p_0 existing at the temperature of the experiment.

[21] Morrison and Szasz, *J. Chem. Phys.*, **16**, 280 (1948).

[22] n is defined as the number of moles adsorbed at any given coverage, n_0 as the number of moles adsorbed in a complete monolayer. Thus $n/n_0 = v/v_m$ used in Fig. 8.

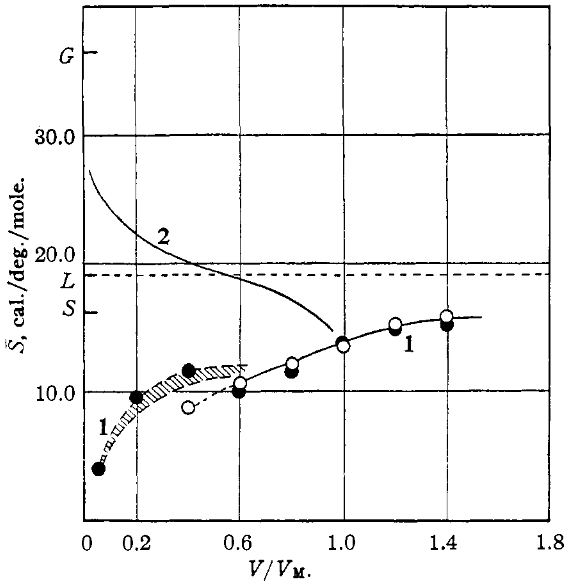

Fig. 8.—Partial molal entropy of nitrogen on titanium dioxide, at 78.5°K.: curve 1, ○ using Amherst heat and isotherm data; ● using Amherst heat data and Arnold's isotherm data; curve 2, from B. E. T. theory.

on anatase, the molar entropy for the monolayer of nitrogen is found to be 9.9 e.u. Obviously it would be indefensible to place undue emphasis on the agreement between the molar entropies arrived at by the two methods since different crystalline forms of titanium dioxide were employed, and since we cannot be too sure about Curve 1 for low coverages for the reasons discussed below. Furthermore, the film may possess zero point entropy and this has not been considered. However, we believe it worthy of note that these two independent approaches to the entropy determination are possible.

The Magnitude and the Influence of the Experimental Error.—The usefulness and value of the thermodynamic quantities obtained from experimental data is dependent upon the magnitude of the experimental error. In particular, the validity of any interpretation based on such values may be affected. The determination of the entropy of adsorption depends on the measurement of two quantities, first the calorimetric heat of adsorption and secondly the equilibrium pressure. We will consider each in turn.

It has been customary to obtain differential heat curves by taking the heat evolved per mole of gas adsorbed in an increment and plotting this quantity as a function of v/v_m at the mid-point of the increment. This is an approximation and is only valid if sufficiently small increments of gas are admitted. In an endeavor to make the best possible use of the data, a more exact method of obtaining differential heats was investigated. The total integral heat of adsorption was plotted as a function of the total volume of gas adsorbed and the slope of this curve was measured. In order to facilitate the determination of the slope of these integral heat curves, various empirical equations describing such curves were investigated. Lamb and Coolidge[23] have suggested that the variation of the heat of adsorption with the amount of gas adsorbed might be expressed by an exponential relationship

$$q = ma^n \qquad (2)$$

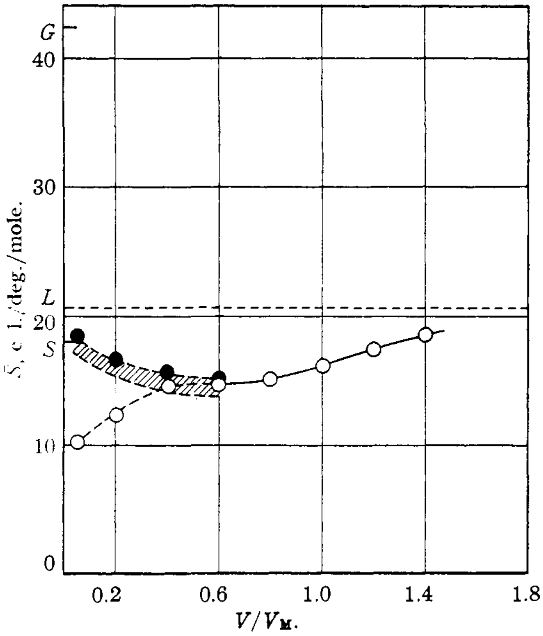

Fig. 9.—Partial molal entropy of oxygen on titanium dioxide at 78.5°K.: ○ using Amherst heat and isotherm data; ● using Amherst heat data and Arnold's isotherm data.

where q is the total heat evolved when the amount of gas adsorbed is a cc. per gram, and m and n are constants.

It was found in our present work that the integral heat curve was approximately a section of a parabola. An empirical equation of the form

$$(y + k)^2 = 4a(x + h)$$

was therefore set up and plotted with the experimental integral heat curve. In Fig. 5 is plotted the integral heat of adsorption for nitrogen on carbon black and also a plot of the equation

$$(y + 22.1)^2 = 18.5 \times 10^4(x + 26.5 \times 10^{-4}) \quad (3)$$

The more exact differential heats obtained by this type of treatment did not vary by more than ±2% from the differential heat curve obtained by the customary method. The treatment was not extended to other systems.

The maximum possible error in the determination of the heat of adsorption has been estimated as ±5%.[10] This is now regarded as a high estimate. However, if we accept this error in a heat of 4.0 kcal./mole at 78.5°K., then we would expect an uncertainty in the entropy of ±2.5 e.u.

The equilibrium pressure data reported in this paper were determined by direct observation of a simple mercury manometer. This method was satisfactory at pressures above one mm., but below this value an accurate determination of the equilibrium pressure was impossible with this device. This is an important factor governing the accuracy of the thermodynamic data derived from this source. Taking as an example the case of nitrogen on carbon black, it is found that the equilibrium pressure corresponding to $v/v_m = 0.24$, is 0.6 mm. Thus at coverages below about 0.3 v/v_m the accuracy of the pressure measurements and therefore of $R \ln p/p_0$ is in doubt. The experimental entropy curves 1, in Figs. 6, 7, 8, 9 are therefore dotted in over the region 0 to 0.3 coverage, and the entropy values over this range must be viewed with reservation.

A valuable check has been provided on the entropy at low coverage for the titanium dioxide system, by the use of isotherm data obtained by Arnold[17,24] on an identical

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[23] Lamb and Coolidge, THIS JOURNAL, **42**, 1146 (1920).

[24] Also private communication.

sample of the solid. This author had determined equilibrium pressures of nitrogen and oxygen, ranging from 10^{-4} mm. to 1 mm. by the use of a triple range calibrated McLeod gage. Using Arnold's pressure data in combination with the heats determined in these laboratories, the entropy was calculated and is shown in Figs. 8, 9. It is seen that above $v/v_m = 0.5$, the entropy as derived from this source is in excellent agreement with that obtained by the use of our own pressure data. At lower coverages however, there is some divergence. In the case of nitrogen on titanium dioxide the curves from the two sources are of the same general form. It is also apparent that there is a break in the curve derived from Arnold's pressure data at the point where there was a changeover in the method of measurement, *i. e.*, from manometer to McLeod. In the case of oxygen on titanium dioxide, it is seen that the use of Arnold's low pressure data results in a change in the direction of the entropy curve. It must be remembered, however, that because of the existence of the thermal transpiration effect,[25] the entropy values obtained from low pressure data are subject to an uncertainty of about 1.3 e.u. This uncertainty arises because of our inability to determine whether we should apply the thermal transpiration correction over a certain critical low pressure range for the temperature gradient and inlet tube diameter under consideration. The extent of this uncertainty translated into terms of entropy units is represented by the cross-hatching in Figs. 8 and 9. This is of particular importance when considering the finer details of the entropy curves such as in the case of oxygen on titanium dioxide at low coverages.

The B.E.T. Differential Heat and Entropy.—Davis and DeWitt[18] have discussed the B.E.T. heat of adsorption and have shown that the variation of the differential heat of adsorption with the fraction of the surface covered could be expressed by the relationship (using Hill's nomenclature)[6]

$$\Delta H = (E_1 - E_L)\,\mathrm{d}X/\mathrm{d}A + E_L \qquad (4)$$

where ΔH is the differential heat of adsorption, X is the number of molecules adsorbed in the first layer, A is the total number of molecules adsorbed and $\mathrm{d}X/\mathrm{d}A$ is obtained[26] by the differentiation of Hill's expression X/B for the number of molecules of adsorbate in the first layer as a function of the total amount adsorbed and of the value of c.[27] One therefore concludes that the B.E.T. theory requires the heat of adsorption to decrease because (considering any one increment) the fraction of molecules from that increment adsorbed in the first layer decreases with increasing surface coverage.

Assuming a_1b_2/a_2b_1 is unity, we have calculated $(E_1 - E_L)$ for the systems nitrogen–carbon black, nitrogen–titanium dioxide, and oxygen–titanium dioxide. ΔH was then obtained using equation 4, and the results are compared with the calorimetrically determined quantities in Figs. 1 and 4. It is seen that the B.E.T. theory requires a constant heat of adsorption up to 0.6 to 0.8 v/v_m. There is then a rapid decrease in ΔH which reaches E_L in the region 1.2–1.5 v/v_m (depending on c). When this behavior is compared with the case discussed by Davis and DeWitt it is seen that there is a marked difference. These authors examined the system *n*-butane on glass spheres at 0° and found that the B.E.T. theory predicted a markedly changing ΔH at all fractions of the surface covered. The relevant difference between the butane–glass sphere system at 0° and the systems under discussion in the present paper is in the value of the constant c. For a given value of v/v_m, $\mathrm{d}X/\mathrm{d}A$ is entirely dependent on c. If c is small, then $\mathrm{d}X/\mathrm{d}A$ is large; this is the situation in the case discussed by Davis and DeWitt, where $c = 5$. In the present case c is in the range 79 (nitrogen on titanium dioxide) to 244 (nitrogen on carbon black).

We may therefore conclude that the B.E.T. theory is capable of predicting a decreasing heat of adsorption which is significant for all coverages in the monolayer when c is small. For large values of c the B.E.T. theory still requires a constant heat of adsorption equal to E_1 for the major portion of the monolayer. We are therefore forced to assume that the most important factor governing a decreasing differential heat of adsorption is not the one offered by the B.E.T. theory (*i. e.*, dependence on $\mathrm{d}X/\mathrm{d}A$) and we must look elsewhere, perhaps to a heterogeneous surface involving varying heats of adsorption.

We have calculated the entropy of the adsorbed film of nitrogen according to the requirements of the B.E.T. theory on both carbon black and titanium dioxide surfaces. In making these calculations the term $R \ln p/p_0$ was found by use of the p values from the B.E.T. equation.

The above calculation has been made in two ways assuming, (1) a constant $\Delta H = E_1$, and (2) a ΔH varying between E_1 and E_L as required by equation 6 and shown in Figs. 1 and 4. The entropies for constant ΔH are shown in curve 2 of Figs. 6 and 8. In curve 3 of Fig. 6 we have shown the results obtained by assuming variable ΔH. It is seen that the refined B.E.T. theory (variable ΔH) shows little departure from the classical theory (constant $\Delta H = E_1$) up to a coverage of about 0.8 v/v_m. From 0.8 to 1.3 v/v_m the B.E.T. entropy curve, although not agreeing exactly in magnitude, does follow the experimental curve in shape.

Discussion

The entropies of the bulk three-dimensional phases of nitrogen and oxygen at 78.5°K. were obtained by integration of specific heat data of Giauque.[28,29] These entropy data are denoted by the letters G, L and S on the ordinates in Figs. 6 to 9, the values for the gaseous, liquid and solid states of nitrogen being 36, 19.1 and 16.2 e.u., respectively. It is obvious that our partial molal entropy values on both carbon black and anatase

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[25] Loeb, "Kinetic Theory of Gases," McGraw-Hill Book Company, Inc., New York, N. Y., 1927, p. 283.

[26] The equation given by Davis and DeWitt (*loc. cit.*), equation 9, p. 1138 should read

$$\frac{\mathrm{d}X}{\mathrm{d}A} = \frac{\mathrm{d}V_1}{\mathrm{d}V} = \frac{c}{2(c-1)}\left\{1 - \frac{\theta - 1 + 2/c}{[(1-\theta)^2 + 4\theta/c]^{1/2}}\right\}$$

where $\theta = v/v_m$.

[27] c is defined as $(a_1b_2/a_2b_1)e^{(E_1 - E_L)/RT}$.

[28] Giauque and Clayton, This Journal, **55**, 4875 (1933).

[29] Giauque and Johnson, *ibid.*, **51**, 2300 (1929).

fall far short of the molal entropy of the three dimensional gas at all coverages and that they approach the entropies of the solid and liquid bulk phases only when $v \geqq v_m$. The same observations could, of course, be made concerning the molal entropy value for nitrogen on rutile derived from the data of Morrison and Szasz.

The entropy as predicted by the B.E.T. theory is in fair agreement with the experimental entropy at a coverage defined by $v/v_m = 1$. At all coverages less than this value, the B.E.T. theory requires entropies which diverge increasingly, as v/v_m becomes smaller, from the entropies obtained from experimental evidence. At the monolayer the B.E.T. theory assumes a small configurational entropy. The fair agreement of the entropy values based on the B.E.T. theory and those calculated from the experimental data at the monolayer suggests that this assumption may well be a valid one at this coverage. At lower coverages than $v/v_m = 1$, the B.E.T. theory requires a considerable configurational entropy, because it postulates that the molecules favor all sites equally and therefore have a large choice of sites. This is seen by examining Hill's partition function for the B.E.T. theory. The factor $B!/(B - X)!X!$ in this partition function (where X molecules are adsorbed on B sites) will result in a maximum configurational entropy contribution, and is responsible for the extremely high entropies required by the B.E.T. theory at low coverages. The disagreement of the experimental evidence and B.E.T. theory at coverages less than $v/v_m = 1$ therefore indicates that this assumption of maximum configurational entropy is not correct and the B.E.T. theory is inadequate in this region for that reason. These conclusions might be derived from considerations of heat data alone. It has been shown that the E_1 as derived from the B.E.T. theory is in good agreement with the experimental differential heat only at $v/v_m = 1$. Therefore it may be suggested that the B.E.T. theory is valid at the completion of the monolayer, but not prior to the completion.

Summary

1. The differential heat of adsorption of nitrogen and oxygen on titanium dioxide has been determined calorimetrically at 78.5°K. The titanium dioxide used in both cases was a sample of anatase with a B.E.T. surface area of 13.9 sq. m. per g.

2. The magnitude of the heat in both cases indicates that the adsorption is van der Waals in nature. The initial increments of nitrogen showed a heat of adsorption approximately 1 kcal. per mole higher than the initial oxygen values.

3. The partial molal entropy of the adsorbed gas was determined from our experimental data for both nitrogen and oxygen adsorbed on carbon black and titanium dioxide (anatase) at 78.5°K.

4. The results show that the partial molal entropy of the adsorbed gas is less than the partial molal entropy of the bulk three-dimensional liquid or solid phases, at coverages less than a monolayer (as defined by the B.E.T. v_m), for all the systems investigated. At coverages greater than a monolayer, the partial molal entropy approaches the entropy of the three-dimensional liquid or solid.

5. The entropy requirements of the B.E.T. theory are shown to be incompatible with experimental evidence at coverages less than a monolayer.

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A Hydrous Manganese Oxide with Exchange Properties

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Although numerous attempts to form manganese dioxide by gaseous oxidation of alkaline suspensions of manganous hydroxide have been made, complete oxidation is apparently never achieved, and the products are reported to vary in composition between $MnO_{1.95}$ and $MnO_{1.60}$.[1-5] Nicholls and Walton[3] found that the oxidative products were amorphous to X-rays. Copeland, *et al.*,[5] observed the diffraction pattern ascribed to delta-MnO_2[6] on drying their preparation at 150°. Feitknecht and Marti[4] prepared an oxide varying in composition between $MnO_{1.7}$ and $MnO_{1.8}$ with a powder pattern derived from a new phase to which they gave the name manganous manganite.

In the course of an investigation of the structures and properties of the manganese oxides and minerals, the writer has had occasion to employ this method of preparation. It was found that products other than manganous manganite or delta-MnO_2 could be identified. Of these a hydrous oxide was obtained which appears not to have been described.

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