mole/deg., or 8.6% higher than the value of Nilson and Pettersson. It is not possible to explain this deviation in the light of the little which is known of the experimental procedure and history of the sample used by Nilson and Pettersson.

Examination of the results reveals that the heat capacity of $Nd_2O_3$, while about equal to that of $La_2O_3$ at room temperature, lies well above that of $La_2O_3$ at higher temperatures. In view of the similarity in crystal structure and ionic character of these two oxides,[15] it seems likely that the contribution to the heat capacity arising from the lattice is probably very nearly the same for both oxides—that is, the Debye $\theta$'s for the two oxides are nearly equal. Furthermore, the contribution ($C_p - C_v$) may be expected to be small and approximately equal throughout the temperature range under consideration. It seems reasonable, therefore, to assume that the difference between the heat capacities of $Nd_2O_3$ and $La_2O_3$ is to be ascribed to an electronic transition (or transitions) within the $Nd^{+++}$ ion.

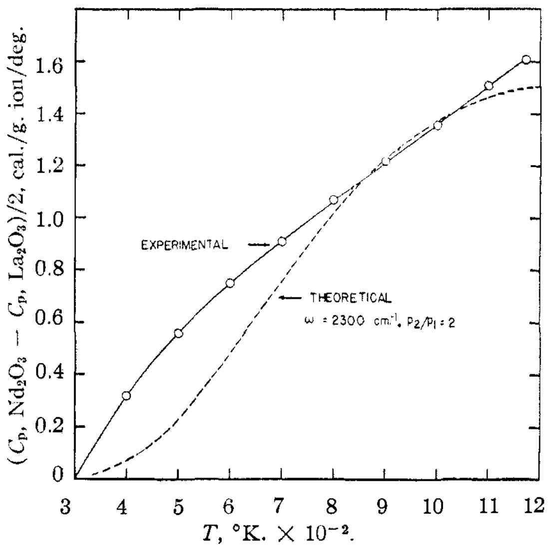

Fig. 2.—Difference in heat capacity of $Nd_2O_3$ and $La_2O_3$.

Figure 2 is a plot of the difference in $C_p$ of $La_2O_3$ and $Nd_2O_3$, expressed per gram ion of metal ion. The spectroscopic terms for the $Nd^{+++}$ appear not to have been worked out. However, calculations show that this heat capacity difference may be approximated by assuming an electronic transition between two states having an energy separation of about 2300 cm.$^{-1}$, the degeneracies of the states having a ratio $p_2/p_1 = 2$. The calculations can be made to fit the difference curve somewhat better at lower temperatures if lower energy states such as have been shown to be present in $Nd_2(SO_4)_3 \cdot 8H_2O$[16] are taken into account.

**Acknowledgment.**—The authors wish to express their appreciation to Dr. W. M. Spicer for performing the spectrographic analyses; to Mr. J. T. Roberts, Jr., for aid in the electrical calibration; and to Mr. G. W. D. Cook for his help and suggestions relating to the construction of the calorimeter. One of us (J. O. B.) wishes to acknowledge the assistance provided by a Tennessee Eastman Corporation fellowship.

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[15] V. H. Bommer, *Z. anorg. allgem. Chem.*, **241**, 273 (1939).

[16] J. E. Ahlberg, E. R. Blanchard and W. O. Lundberg, *J. Chem. Phys.*, **5**, 552 (1937).

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[CONTRIBUTION FROM THE NAVAL MEDICAL RESEARCH INSTITUTE AND THE MELLON INSTITUTE]

# Calculation of Thermodynamic Functions of Adsorbed Molecules from Adsorption Isotherm Measurements: Nitrogen on Graphon[1,2]

BY TERRELL L. HILL, P. H. EMMETT AND L. G. JOYNER

If isotherm measurements are available at neighboring temperatures down to relatively low pressures, it is possible to calculate not only the conventional (isosteric) differential energy and entropy of adsorption but also the integral energy and entropy of adsorption. The latter quantities give the energy and entropy of the adsorbed molecules which are directly comparable with the usual statistical mechanical quantities.

In the present paper the distinction between differential and integral entropies is illustrated and emphasized using the Brunauer, Emmett and Teller theory. The complete set of thermodynamic functions is calculated and discussed for the system nitrogen on graphon, using the data of Joyner and Emmett. The effects of uncertainties in low-pressure measurements on these calculations are pointed out.

In physical adsorption of a gas on a solid it is probably an excellent approximation to assume that the adsorbed molecules do not alter the thermodynamic properties of the solid.[3] It is therefore of interest to attempt to interpret experimental data for systems of this type in terms of the thermodynamic functions of the adsorbed molecules treated as a one-component system in the potential field presented by the solid adsorbent. Thus, one is interested in the energy $E_s$, entropy $S_s$, etc., of the system of $N_s$ adsorbed molecules on an adsorbent surface of area $\mathfrak{A}$. These are the thermodynamic functions implicit in statistical mechanical theories of adsorption.

A detailed discussion of the above thermodynamic system has been given in earlier papers.[4-6]

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[1] Some preliminary work on this subject was done by one of us (T. L. H.) while at the University of Rochester, Rochester, N. Y.

[2] Presented at an American Chemical Society Meeting, Boston, Mass., April, 1951; also in part at an A. A. A. S. Gordon Research Conference, New London, New Hampshire, June, 1948, and at the National Colloid Symposium, American Chemical Society, June, 1950.

[3] See, however, the recent paper by M. A. Cook, D. H. Pack and A. G. Oblad, *J. Chem. Phys.*, **19**, 367 (1951).

[4] T. L. Hill, *ibid.*, **17**, 520 (1949). Hereafter referred to as V.

[5] T. L. Hill, *ibid.*, **18**, 246 (1950). Hereafter referred to as IX (see also T. L. Hill, *ibid.*, **17**, 507 (1949)). Among other things, paper IX removes the above restriction to adsorbents which are unperturbed by adsorbed molecules and which have an "area"; but this generalization is probably not important here.[4] Paper IX shows that if adsorbent perturbations are present they are automatically included in thermodynamic calculations of the type carried out in this paper.

[6] T. L. Hill, *Trans. Faraday Soc.*, **47**, 376 (1951).

In the present paper we shall apply the methods of V and IX to the data of Joyner and Emmett[7] for the system nitrogen–Graphon (Section II). Also, in Section I, we shall make some remarks of a statistical thermodynamical nature which we believe will help to clarify the relations between the different entropies of adsorption.

## I. Entropies of Adsorption

From[8] V and IX

$$\left(\frac{\partial \ln p}{\partial T}\right)_\Gamma = \frac{\mathrm{s}_\mathrm{G} - \bar{\mathrm{s}}_s}{kT} = \frac{q_{st}}{kT^2} \qquad (1)$$

$$\left(\frac{\partial \ln p}{\partial T}\right)_\varphi = \frac{\mathrm{s}_\mathrm{G} - \mathrm{s}_s}{kT} \qquad (2)$$

The subscripts G and S refer to the adsorbate in the gaseous and adsorbed states, respectively. Also

$$\mathrm{s}_\mathrm{G} = S_\mathrm{G}/N_\mathrm{G},\ \mathrm{s}_s = S_s/N_s,\ \mathrm{s}_s = (\partial S_s/\partial N_s)_{\mathcal{A},T}$$

$$q_{st} = \text{“isosteric” heat of adsorption}$$

$$\Gamma = N_s/\mathcal{A}$$

$$\varphi = kT\int_0^p \Gamma \,\mathrm{d} \ln p \ (T \text{ constant}) \qquad (3)$$

Thus Equation 1, the isosteric equation, gives a *differential* entropy, $\bar{\mathrm{s}}_s$, whereas Equation 2, the iso-$\varphi$ equation, gives the integral entropy[5] per molecule, $\mathrm{s}_s$. It should be emphasized that the usual entropy discussed qualitatively or quantitatively (statistical mechanics) in terms of order–disorder, randomness of motion, etc., of the adsorbed molecules is the integral entropy (per molecule or mole) of Equation 2 and not the differential entropy of Equation 1 (*i.e.*, $N_s\mathrm{s}_s = S_s = k \ln \Omega$ where $\Omega$ is the number of quantum states of the system). Furthermore, it is not only incorrect to use a theoretical (qualitative or quantitative) argument based on the integral entropy per molecule (or mole) to "explain" an experimental differential entropy curve (from $q_{st}$) but, as will be seen below (Figs. 1–4), it is often completely misleading. It is much easier[9] to get values for the differential entropy, $\bar{\mathrm{s}}_s$, than for the integral entropy per molecule, $\mathrm{s}_s$, from experimental isotherm data, but in the majority of cases it should be easier to *understand* curves[6] representing the variation in $\mathrm{s}_s$ with extent of surface coverage or relative pressure than it is to understand such curves for $\bar{\mathrm{s}}_s$. Hence it is of considerable interest to compute curves for $\mathrm{s}_s$ as well as for $\bar{\mathrm{s}}_s$.

We now wish to point out a few elementary relations between integral and differential entropies and energies of adsorption. These relations provide useful checks on numerical computations. First we note that

$$S_s = N_s\mathrm{s}_s$$

$$\bar{\mathrm{s}}_s = N_s\left(\frac{\partial \mathrm{s}_s}{\partial N_s}\right)_{\mathcal{A},T} + \mathrm{s}_s \qquad (4)$$

Hence, when

$$\begin{aligned} \partial \mathrm{s}_s/\partial N_s > 0,\ \bar{\mathrm{s}}_s > \mathrm{s}_s \\ \partial \mathrm{s}_s/\partial N_s = 0,\ \bar{\mathrm{s}}_s = \mathrm{s}_s \\ \partial \mathrm{s}_s/\partial N_s < 0,\ \bar{\mathrm{s}}_s < \mathrm{s}_s \end{aligned} \qquad (5)$$

Thus, when $\mathrm{s}_s$ and $\bar{\mathrm{s}}_s$ are plotted against $N_s$, the curves cross whenever $\mathrm{s}_s$ has a maximum or a minimum. The relationships of Equation 5 are illustrated below in Figs. 1–5.

Similar relations hold for the energy of adsorption[5]

$$\bar{\mathrm{H}}_s = (\partial E_s/\partial N_s)_{\mathcal{A},T} = \mathrm{E}_s + N_s\left(\frac{\partial \mathrm{E}_s}{\partial N_s}\right)_{\mathcal{A},T} \qquad (6)$$

$$q_{st} = \mathrm{H}_\mathrm{G} - \mathrm{H}_s$$

(strictly speaking[5]

$$\mathrm{H}_s = [\partial(E_s + PV_s)/\partial N_s]_{P,\mathcal{A},T} \qquad (7)$$

but the pressure effects are negligible). Thus, in Equation 5, we may replace $\mathrm{s}_s$ by $\mathrm{E}_s$ and $\bar{\mathrm{s}}_s$ by $\bar{\mathrm{H}}_s$. The crossing of $\mathrm{E}_s$ and $\bar{\mathrm{H}}_s$ curves at a maximum in $-\mathrm{E}_s$ is illustrated in Figs. 6 and 7. Also, from Equation 6

$$\bar{\mathrm{H}}_s \longrightarrow \mathrm{E}_s \text{ as } N_s \longrightarrow 0 \qquad (8)$$

From Equations IX-18 and 19

$$\mathcal{H}_s - \bar{\mathrm{H}}_s = T(\mathrm{s}_s - \bar{\mathrm{s}}_s),\ \mathcal{H}_s = \mathrm{E}_s + (\varphi/\Gamma) = \mathcal{H}/N_s \qquad (9)$$

so that,[10] for example, $\mathcal{H}_s$ and $\bar{\mathrm{H}}_s$ curves cross whenever $\mathrm{s}_s$ and $\bar{\mathrm{s}}_s$ curves cross, etc. (Figs. 3, 4, 6, 7).

Finally, in this section, we wish to compare, as helpful illustrations, a few integral and differential entropy curves calculated from the (statistical) B.E.T. theory.[11] We consider for simplicity the special case in which the partition function,[12] $j_s$, for an adsorbate molecule on the surface of the adsorbent is equal to the partition function, $j_\mathrm{L}$, of a molecule in the liquid adsorbate. Consider first the case in which the constant $c$ of the B.E.T. equation equals infinity and in which accordingly the first layer will fill completely before higher layers start.

The first layer thus follows a Langmuir isotherm and[12]

$$S_s = k \ln \Omega_1$$

$$\Omega_1 = B!/N_s!(B - N_s)! \qquad (10)$$

where $B$ is the number of adsorption sites in the area $\mathcal{A}$. Hence, recalling that $j_s = j_\mathrm{L}$

$$(S_s - S_\mathrm{L}')/Bk = (\mathrm{s}_s - \mathrm{s}_\mathrm{L}')\theta/k \ (\theta \leqslant 1) \qquad (11)$$

$$(\mathrm{s}_s - \mathrm{s}_\mathrm{L}')/k = \frac{1}{\theta}\ln\frac{1}{1-\theta} + \ln\frac{1-\theta}{\theta} \ (\theta \leqslant 1) \qquad (12)$$

$$(\bar{\mathrm{s}}_s - \mathrm{s}_\mathrm{L}')/k = \ln\frac{1-\theta}{\theta} \ (\theta \leqslant 1) \qquad (13)$$

where $\theta = N_s/B$ and $\mathrm{s}_\mathrm{L}'$ ($= S_\mathrm{L}'/N_\mathrm{L}$) is the entropy of the liquid (in equilibrium with vapor) per molecule. After completion of the first layer (recall $c = \infty$), higher layers will begin to fill, and[12]

$$S_s = k \ln \Omega_2$$

$$\Omega_2 = N_s!/(N_s - B)!B! \qquad (14)$$

where $\Omega_2$ is the number of ways of distributing $N_s - B$ molecules on top of the $B$ molecules of the first layer, there being no restriction on the number of molecules in a pile. Then

$$(S_s - S_\mathrm{L}')/Bk = (\mathrm{s}_s - \mathrm{s}_\mathrm{L})\theta/k \ (\theta \geqslant 1) \qquad (15)$$

$$(\mathrm{s}_s - \mathrm{s}_\mathrm{L}')/k = \ln\frac{\theta}{\theta - 1} + \frac{1}{\theta}\ln(\theta - 1) \ (\theta \geqslant 1) \qquad (16)$$

$$(\bar{\mathrm{s}}_s - \mathrm{s}_\mathrm{L}')/k = \ln\frac{\theta}{\theta - 1} \ (\theta \geqslant 1) \qquad (17)$$

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[7] L. G. Joyner and P. H. Emmett, THIS JOURNAL, **70**, 2353 (1948).

[8] Equation 1, which follows practically immediately from solution thermodynamics (see Equations IX-9 and IX-33), has also been obtained by C. J. Gorter and H. P. R. Frederikse (*Physica*, **15**, 891 (1949)) and by R. S. Hansen (*J. Phys. Colloid Chem.*, **54**, 411 (1950)). Hansen's derivation amounts to deriving Equation 1 from Equations V-66, V-69 and V-70. Hansen also found Equation 2, but did not discuss its relation to Equation 3. The work of Rowley and Innes has already been mentioned in V in this connection. See also D. H. Everett, *Trans. Faraday Soc.*, **46**, 453 (1950). As a matter of fact, it has only recently come to our attention that H. M. Cassel (*Physik. Z.*, **26**, 862 (1925); **28**, 152 (1927)) anticipated some of the two-dimensional thermodynamics of Rowley and Innes. Also Cassel actually applied a Clausius–Clapeyron equation at constant spreading pressure $\varphi$ (or the equivalent Equation V-112) to obtain heats of adsorption from experimental data (*Z. Elektrochem.*, **37**, 642 (1931); (with K. Neugebauer) *J. Phys. Chem.*, **40**, 523 (1936)), but does not seem to have discussed in any of his papers the entropy of adsorbed molecules. In Cassel's applications $\varphi$ was obtained from direct measurement of the surface tension of the liquid adsorbent (mercury), with and without adsorbate. It was not necessary to use Equation 3. Finally, we might add here that we believe the Clausius–Clapeyron equation suggested by Wilkins (*Proc. Roy. Soc.* (*London*), **A164**, 496 (1938)) has by now been completely discredited[4,5] as a thermodynamic equation.

[9] This is because accurate low-pressure measurements are needed for use in conjunction with Equation 3 before one is in a position to apply Equation 2.

[10] In order to distinguish clearly between the two different heat contents, $H_s = E_s + PV_s$ and $\mathcal{H}_s = E_s + PV_s + \varphi\mathcal{A}$, we use the notation of reference 6, rather than that of V,VII (see below) or IX. The negligible term $PV_s/N_s$ has been omitted in Equation 9. Errata: H should be replaced by $\mathcal{H}$ in lines 29, 31, 33 and 34, p. 378, reference 6.

[11] T. L. Hill, *J. Chem. Phys.*, **17**, 772 (1949). Hereafter referred to as VII.

[12] T. L. Hill, *ibid.*, **14**, 263 (1946).

These functions (Equations 11-13 and 15-17) for $c = \infty$ are shown in Fig. 1. Figure 2 contains curves for $c = 100$, calculated from Equations VII-21 and VII-24.[13] $s_s - s_L'$ is of course just the slope of $S_s - S_L'$. For large enough values of $c$ the integral entropy per molecule has a minimum, which falls near[11] $\theta = 1$ (see also Fig. 4 of VII). The minimum is clearly due to the relatively small number of configurations of the system possible as the first layer is completed.[14] The occurrence of such a minimum may in fact be expected in systems where there is strong binding of adsorbate to adsorbent, quite aside from the particular considerations of the B.E.T. theory.[15]

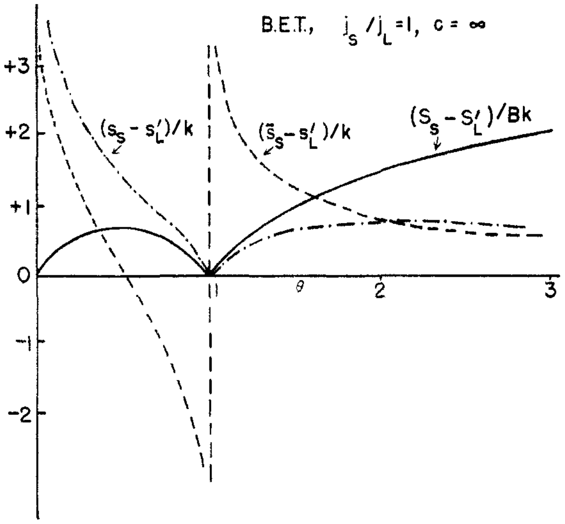

Fig. 1.—Entropy curves according to the B.E.T. theory. $c = \infty, jS/j_L = 1$.

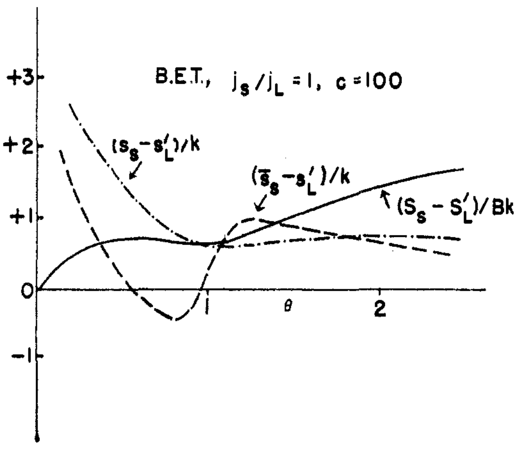

Fig. 2.—Entropy curves according to the B.E.T. theory, $c = 100, jS/j_L = 1$.

The fact that $s_s$ is greater than $s_L'$ for all values of $\theta$ in the curves of Figs. 1 and 2 is a property of the B.E.T. theory and the particular choice of $j_s/j_L$. This is not necessarily to be expected in real systems. Of course for any system, as pointed out in V,[4] as $\theta \to 0$, $s_s \to +\infty$, $E_s \to$ finite and $\mu$ (the chemical potential of the adsorbed molecules) $\to -\infty$.

The origin of the loop in the differential entropy curve for $c = 100$ is obvious from the $c = \infty$ curve. For $c < \infty$, the extreme behavior of the $c = \infty$ curve is modified somewhat owing to the overlapping[14] of $\Omega_1$ and $\Omega_2$. It will be noticed in these figures that integral and differential entropy curves can have completely different appearances.

## II. Calculations for Nitrogen Adsorbed on Graphon

Joyner and Emmett[7] measured adsorption isotherms for nitrogen on Graphon and on Grade 6 Spheron down to very low pressures. Calculations of $\varphi$ and related quantities from these data appear possible. We consider, however, that only the two higher temperature isotherms (78.3 and 90.3°K.) for Graphon are actually accurate enough at low coverages to justify making such calculations.

Joyner and Emmett[7] have already calculated isosteric heats and differential entropies from these data but for purposes of checking self-consistency (see below) we have recalculated these quantities, obtaining similar results.

We now proceed to discuss the methods used in the present calculations. We have actually used two different sets of extrapolations and smooth curves in the low-pressure region; we describe first the complete calculations based on the first set ("Computation I"). Thermodynamic functions for the second set of extrapolations and smooth curves can be found rather easily over part of the range in $\theta$ by "correcting" the first group of results (see "Computation II" below).

**Calculation of Spreading Pressure.**—Perhaps the most fundamental calculation is that of $\varphi$, given by (Equation V-94)

$$\varphi = KkT \int_0^x v \,\mathrm{d} \ln x \tag{18}$$

where $x = p/p_0$ as usual, $v$ is the volume of gas adsorbed (in cc., for a perfect gas at N.T.P.) per gram of adsorbent, $\Gamma = vK$, which defines the constant $K$, and $\Gamma = N_s/\mathcal{A}$, where $N_s$ and $\mathcal{A}$ refer to a gram of adsorbent.

Although the spreading pressure $\varphi$ has been calculated by a number of authors, it is not obvious at the present time which of the various possible detailed procedures is the most satisfactory. Jura and Harkins[16] have discussed this question recently. In this work we have used numerical integration (Simpson's rule) and Equation 3 as follows. The experimental points for $v$ are plotted against $x$ on large graph paper (using several different scales), and a smooth curve is drawn through these points. The smooth curve is extended down to a very low pressure, but a straight line, $v = ax$, is used as an analytical expression for the *lowest* pressures ($x < 2 \times 10^{-4}$). Values of $v$ are then read off the smooth curve for convenient values of $x$, and $v/x$ calculated. Analytical integration ($v = ax$) is then used for $0 \leqslant x \leqslant 2 \times 10^{-4}$ and numerical integration at higher pressures. The calculated values of $\varphi$ (Computation I) are given in Table I, using 80.42 m.²/g. for the surface area.[7,17]

**Calculation of $H_L' - \mathcal{H}_s$ and $s_s - s_L'$.**—To calculate $H_L' - \mathcal{H}_s$ from (Equation V-86)

$$(\partial \ln x/\partial T)_\varphi = (H_L' - \mathcal{H}_s)/kT^2 \tag{19}$$

we first plot on large graph paper $\varphi$ *versus* $x$ for each of the two temperatures, using several scales. Smooth curves are drawn. For a convenient value of $\varphi$, $x$ is read off each of the smooth curves, and hence $\Delta \ln x = \ln x_2 - \ln x_1$ is obtained for use in

$$k \Delta \ln x = (H_L' - \mathcal{H}_s)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{20}$$

We define $\bar{x}$ by (see V)

$$\ln \bar{x} = \frac{1}{2}(\ln x_1 + \ln x_2) \tag{21}$$

and $\bar{T}$ by

$$1/\bar{T} = \frac{1}{2}\left(\frac{1}{T_1} + \frac{1}{T_2}\right) \tag{22}$$

---

(13) The factor $kT$ in Equation VII-24 should be omitted to make the equation correct. As mentioned in VII, this equation (or its equivalent) was obtained independently by Gregg and Jacobs and by Davis and De Witt. It has also been published and used by Gorter and Frederikse.[8]

(14) When $c < \infty$, $\Omega_1$ and $\Omega_2$ of course overlap. But it is possible[11] to separate the two contributions explicitly, if desired.

(15) This property might form the basis of an absolute method of surface-area determination, as is pointed out in a forthcoming paper by G. Jura and T. L. Hill. However, the particular minimum in a different but related function discussed some time ago by Harkins and Jura (THIS JOURNAL, **66**, 919 (1944); see p. 926) would *not* be expected to occur at $\theta = 1$ (see Jura and Hill).

(16) G. Jura and W. D. Harkins, THIS JOURNAL, **66**, 1356 (1944).

(17) $\varphi\mathcal{A}$ is a true thermodynamic quantity but the absolute values of $\varphi$ given depend on the value chosen for $\mathcal{A}$ (a non-thermodynamic quantity, strictly speaking).

Then $\mathrm{S}_s - \mathrm{S}'_L$ is found from

$$\mathrm{S}_s - \mathrm{S}'_L = \frac{\mathcal{H}_s - \mathrm{H}'_L}{\bar{T}} - k \ln \bar{x} \tag{23}$$

**Calculation of $Q_{st}$ (Defined as $\mathrm{H}'_L - \bar{\mathrm{H}}_s$) and $\bar{\mathrm{S}}_s - \mathrm{S}'_L$.**—From the large smooth curves (several scales) drawn through the experimental *v versus x* points, $x_1$ and $x_2$ are read off for a convenient $v$. This gives $\Delta \ln x$ and hence the isosteric heat[11] $Q_{st}$ by analogy with Equation 20, and then $\bar{\mathrm{S}}_s - \mathrm{S}'_L$ by analogy with Equation 23.

**Calculation of $\mathrm{E}'_L - \mathrm{E}_s$.**—$\varphi/T$ is plotted on large paper against $x$ (several scales) for the two temperatures. Smooth curves are drawn. For a convenient $\varphi/T$, $x_1$ and $x_2$ are read off. This gives $\Delta \ln x$ and hence $\mathrm{E}'_L - \mathrm{E}_s$ by analogy with Equation 20 (see Equation V-89).

**Checks on the Above Calculations.**—A number of self-consistency checks are possible; we mention two here.

(1) We can use the equation

$$\mathrm{E}'_L - \mathrm{E}_s = (\mathrm{H}'_L - \mathcal{H}_s) + (\varphi/\Gamma) \tag{24}$$

to obtain $\mathrm{E}'_L - \mathrm{E}_s$ from $\mathrm{H}'_L - \mathcal{H}_s$. The procedure is the following. From the $\mathrm{H}'_L - \mathcal{H}_s$ calculation we have values of $\bar{x}$ corresponding to various values of $\varphi$. Similarly, from the $Q_{st}$ calculation we have associated values of $v$ and $\bar{x}$. A smooth plot is made of the *v versus* $\bar{x}$ values. For a given $\varphi$, the corresponding value of $\bar{x}$ is found on the *v versus* $\bar{x}$ curve, and $v$ read off. The pair of values $\varphi$ and $v$ gives, then, $\varphi/v$, which is essentially $\varphi/\Gamma$ for use in Equation 24.

(2) The equation

$$\mathrm{H}'_L - \mathcal{H}_s = Q_{st} - \frac{T}{\Gamma}\left(\frac{\partial \varphi}{\partial T}\right)_\Gamma \tag{25}$$

can be used to calculate $\mathrm{H}'_L - \mathcal{H}_s$ from $Q_{st}$. Procedure: the smooth plot of *φ versus x* and pairs of points $v$, $x$ (from the $Q_{st}$ calculation) for *each* temperature in both cases are combined to obtain $\varphi_1$ and $\varphi_2$ for a given $v$. One then has $\Delta\varphi = \varphi_2 - \varphi_1$, $\bar{T}$ (for $T$) and $v$ (for $\Gamma$) to use in Equation 25.

**Calculations Based on Second Set of Extrapolations and Smooth Curves (Computation II).**—Depending on the accuracy and number of experimental points, there is of course a certain amount of arbitrariness in the drawing of a smooth curve of *v versus x* and in the extrapolation to $v = x = 0$. We have, therefore, in addition to the above-described calculations, carried out a second group of computations. These are based on: (1) at 90.3°K., a different smooth curve from $v = 0$ to $v = 6$ cc., *not* forcing the curve to be a straight line below $x = 2 \times 10^{-4}$ ($v \cong 2.4$ cc.); (2) at 78.3°K., a different smooth curve from $v = 0$ to $v = 14$ cc., also *not* using a straight line below $x = 2 \times 10^{-4}$ ($v \cong 6.5$ cc.).

A complete repeat calculation must be carried out for $v \leqslant 14$ cc. ($\theta \leqslant 0.78$; see below). However, above $v = 14$ cc., $Q_{st}$ and $\bar{\mathrm{S}}_s - \mathrm{S}'_L$ are of course unchanged while $\mathrm{E}_s - \mathrm{E}'_L$, $\mathcal{H}_s - \mathrm{H}'_L$ and $\mathrm{S}_s - \mathrm{S}'_L$ may be found simply by "correcting" the first set of results, as follows.

Suppose $\Phi = \varphi + a(T)$, where $a(T)$ is the "error" in the spreading pressure, arising from the low-pressure ($v \leqslant 14$ cc.) region. $\varphi$ is the "true" spreading pressure (that is, $\Phi$ is here the surface pressure found in Computation I; $\varphi$ is the surface pressure of Computation II). Let $\mathrm{S}_s^*$ be the "incorrect" entropy found from $\Phi$ and Equation 2 (Computation 1). Then[4,15] the "error" in the entropy is

$$\mathrm{S}_s - \mathrm{S}_s^* = -\frac{1}{\Gamma}\frac{\mathrm{d}a}{\mathrm{d}T} \tag{26}$$

and

$$\mathcal{H}_s - \mathrm{H}_s^* = T(\mathrm{S}_s - \mathrm{S}_s^*) \tag{27}$$

Similarly[4]

$$\mathrm{E}_s - \mathrm{E}_s^* = -\frac{T}{\Gamma}\left(\frac{\mathrm{d}a}{\mathrm{d}T} - \frac{a}{T}\right) \tag{28}$$

In this case it turns out on recalculating $\varphi$ at low pressures, that $a_{90.3} = -0.02$ erg cm.$^{-2}$, $a_{78.3} = -0.38$ erg cm.$^{-2}$, and $\Delta a = 0.36$ erg cm.$^{-2}$ (see Table I). We use $\Delta a$ and the average value of $a$, $\bar{a} = -0.20$ erg cm.$^{-2}$ in Eq. (26) and (28) to obtain $\mathrm{E}_s - \mathrm{E}'_L$, $\mathcal{H}_s - \mathrm{H}_L$ and $\mathrm{S}_s - \mathrm{S}_L$ for $v > 14$ cc. (Computation II).

As checks we have here the facts that the two parts of each of the various curves "join" as they should at $\theta \cong 0.78$ and also the "crossing" requirements of Equations 4–9 are satisfied (see Figs. 4 and 7, below).

TABLE I

$\varphi$ FOR $N_2$ ON GRAPHON, ERG CM.$^{-2}$ ($\mathcal{A}$ = 80.42 M.$^2$/G.)

| $x$ | 90.3°K. Computation I and II | 78.3°K. Computation I | 78.3°K. Computation II |
|---|---|---|---|
| 0.0002 | 1.0 | 2.35 | 2.6 |
| .0008 | 3.7 | 7.2 | 7.6 |
| .002 | 7.3 | 11.7 | 12.1 |
| .005 | 12.1 | 16.75 | 17.1 |
| .011 | 16.9 | 21.35 | 21.7 |
| .02 | 20.7 | 25.0 | 25.4 |
| .04 | 25.5 | 29.5 | 29.9 |
| .07 | 29.6 | 33.2 | 33.6 |
| .13 | 34.4 | 37.6 | 38.0 |
| .19 | 37.6 | 40.55 | 40.9 |
| .25 | 40.2 | 42.9 | 43.25 |
| .31 | 42.35 | ... | ... |
| .33 | ... | 45.5 | 45.9 |
| .37 | 44.3 | ... | ... |
| .41 | ... | 48.0 | 48.4 |
| .43 | 46.2 | ... | ... |
| .49 | ... | 50.2 | 50.6 |
| .57 | ... | 52.3 | 52.7 |
| .65 | ... | 54.3 | 54.7 |
| .73 | ... | 56.35 | 56.7 |
| .81 | ... | 58.5 | 58.9 |

## Results and Discussion

In Figs. 3 and 4 we show the molar integral and differential entropy curves according to Computations I and II, respectively. In these and other figures it is instructive to plot the thermodynamic functions against $\theta = v/v_m$, although $v_m$ is not a thermodynamic quantity. We use[7] $v_m = 17.88$ cc./g., from the B.E.T. surface area method.

The qualitative similarity between Figs. 3 and 4 on the one hand, and Figs. 1 and 2, on the other, is striking when one recalls that Joyner and Emmett[7] found $c \cong 280$ for nitrogen on Graphon. Thus, regardless of specific details, there is strong binding of nitrogen to the surface and hence the first layer is virtually filled in before adsorption in higher layers gets appreciably under way. This leads to a minimum in $\mathrm{S}_s$ near $\theta = 1$ (as in Figs. 1 and 2) and a corresponding loop in $\bar{\mathrm{S}}_s$ centered near $\theta = 1$ (as in Figs. 1 and 2). There is, of course, little point in attempting a quantitative interpretation of Figs. 3 and 4 using the B.E.T. theory because of the theory's great over-simplification of the actual problem (uniform surface and localized adsorption assumed, horizontal interactions between adsorbed molecules neglected, etc.). But it should be emphasized that the present thermodynamic computations (using the criterion of a minimum in the molar entropy to locate $\theta = 1$) do provide interesting justification of the use of the B.E.T. equation at least as a *surface area method*.

It would be interesting to try to calculate theoretically the minimum value of $\mathrm{S}_s - \mathrm{S}'_L$ ($\theta \cong 1$) in Figs. 3 and 4. However, quite aside from the obvious uncertainty (compare the two figures) in this calculated experimental value, in the present state of the theory of liquids and of the theory of physical adsorption we believe such an attempt would not be of much significance.

We do not wish to give the impression that all entropy curves will resemble those of Figs. 1–4.

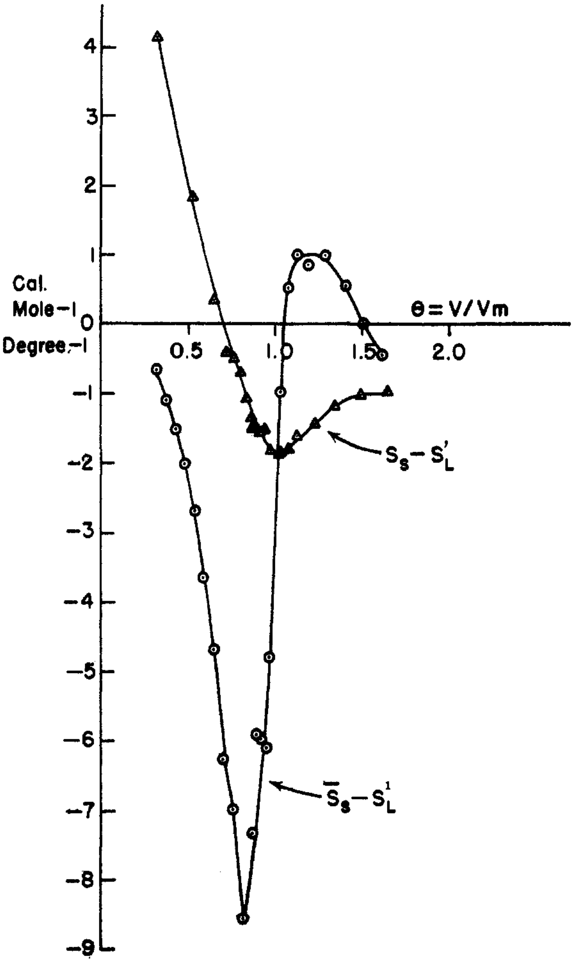

Fig. 3.—Entropy curves for $N_2$ on graphon, $\bar{T}$ = 83.9°K., computation I.

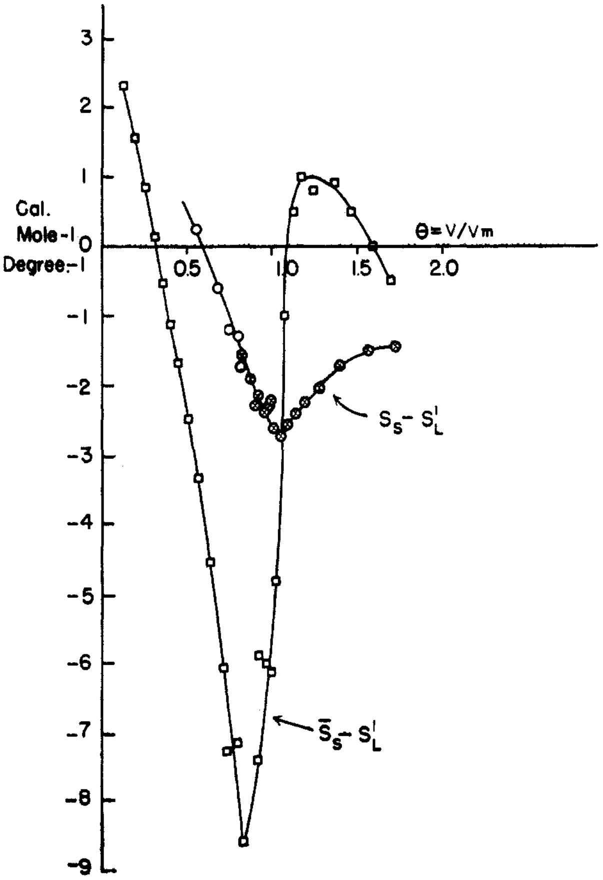

Fig. 4.—Entropy curves for $N_2$ on graphon, $\bar{T}$ = 83.9°K., computation II, with "joining" in the molar integral entropy curve at about $\theta$ = 0.78 (O and ⊗).

Among other possibilities, curves of the type shown *schematically* in Fig. 5 may be expected.

In Figs. 6 and 7 (Computation I and II, respectively) we give $H_L' - \bar{H}_s = Q_{st}$, $E_L' - E_s$ and $H_L' - \mathcal{H}_s$ plotted against $\theta$. In Fig. 6, $H_L' - \mathcal{H}_s$ has been calculated (see above) from Equation 19 and, as a check, from Equation 25, and $E_L' - E_s$ from Equation 24, and, as a check, V-89 (using values of $H_L' - \mathcal{H}_s$ from Equation 19 in Equation 24). It will be seen in Fig. 6 that the checks so obtained are quite satisfactory for $\theta > 0.6$. Below $\theta = 0.6$, low pressure difficulties (see below) become appreciable. The significance of checks of this type is discussed in V. In Fig. 7 the checks available are those discussed in connection with Equations 26–28.

The difference in results in the two sets (I and II) of calculations is an indication of the possible error owing to low pressure uncertainties. The two $v$ *versus* $x$ curves probably bracket the correct one, although we believe the second extrapolation to be less arbitrary and more trustworthy. The curves already published by Beebe, *et al.*,[18] and by Joyner and Emmett[7] show a slight *rise* in $Q_{st}$ as $\theta \rightarrow 0$, as contrasted with the *decrease* in Figs. 6 and 7. This discrepancy is further evidence of limited reliability in the low-pressure region (in both isotherm and calorimetric measurements). Incidentally, at $\theta = 0$, $E_L' - E_s = Q_{st}$ and $H_L' - \mathcal{H}_s$ is smaller by $kT$ = 167 cal./mole.

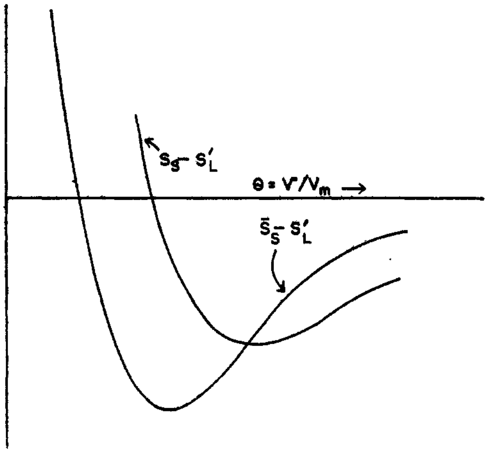

Fig. 5.—Schematic entropy curves.

The interpretation of the $E_L' - E_s$ curve is clearly that the surface is quite uniform[18] and that the rise as $\theta \rightarrow 0.85$ is due to attractive interactions between adsorbed nitrogen molecules. There are of course also reflections of this in the $Q_{st}$ and $H_L' - \mathcal{H}_s$ curves. Incidentally, $Q_{st}$, $\bar{S}_s - S_L'$ and the ad-

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(18) R. A. Beebe, J. Biscoe, W. R. Smith and C. B. Wendell, This Journal, **69**, 95 (1947).

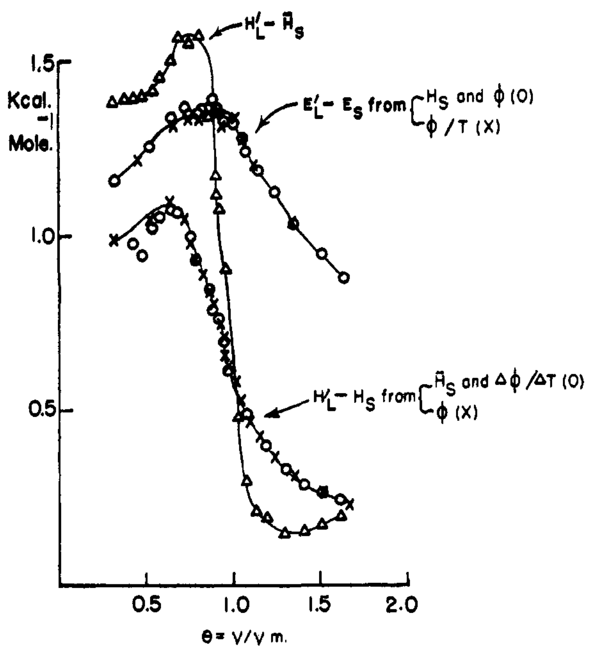

Fig. 6.—Heats of adsorption for $N_2$ on graphon, $\bar{T}$ = 83.9°K., computation I. Read $\mathcal{H}_s$ for $H_s$ in the figure.

sorption isotherms themselves all show signs[7] of coöperative filling in of the second layer ($1 < \theta < 2$) as well as the first, owing to attractive interactions (and probably recognizable only because of the relatively uniform surface[19]).

This similarity in the first and second layers was emphasized by Joyner and Emmett,[7] and Halsey[20] has further remarked that the same "configurational" argument used in Figs. 1 and 2 for the first layer could also apply, to some extent, in the second layer. There are, therefore, probably both "coöperative" and "configurational" contributions to the observed unusual effects in the range $1 < \theta < 2$, in this particular system.

As a final indication of the sensitivity of the calculations to the inaccuracy of low-pressure measurements, we might mention some results based on use of the *low* temperature pair of isotherms (68.4 and 78.3°K.). If we use the first (Computation I) extrapolation and smooth curve for 78.3°K., and an analogous smooth curve and linear extrapolation to $v = 0$ at 68.4°K., one gets an entropy curve $S_s - S_L'$ ($\bar{T}$ = 73.0°K.) which is everywhere positive ($0 < \theta < 2.5$). At $\theta = 1$, $S_s - S_L' \cong 1.8$ e.u. compared to the analogous $S_s - S_L \cong -1.85$ e.u. of Fig. 3 ($\bar{T}$ = 83.9°K.). Correcting for the change of $S_L$ with temperature, it is easy to see that these two results are thermodynamically incompatible since they indicate that $S_s$ *decreases* with increase in temperature, at constant $\theta$. If, on the other hand, the dotted curve[21] of Joyner and Emmett's Fig. 4 is used at 68.4°K. one finds that the lower temperature pair of isotherms now give a much lower entropy curve which is at least approximately the same as the curve for the higher temperature pair. Thus (referring to Joyner and Emmett's Fig. 4) a discrepancy of 0.01 or 0.02 mm. in the lowest pressures measured can markedly alter the calculated results.

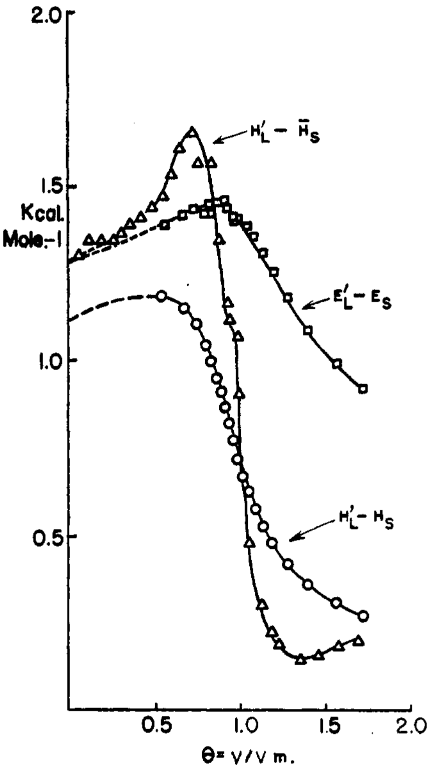

Fig. 7.—Heats of adsorption for $N_2$ on graphon, $\bar{T}$ = 83.9°K., computation II. Read $\mathcal{H}_s$ for $H_s$ in the figure.

We believe the qualitative conclusions reached and the methods used here to be of interest and importance, but recognize that quantitative errors of the order of magnitude indicated by a comparison of the curves in Fig. 3 with those in Fig. 4, and of the curves in Fig. 6 with those in Fig. 7, are possible with the present data. However, the calculations in this paper are probably the first of this type that have been made and we hope and expect that with further refinements in experimental techniques and the use of heats of immersion or calorimetric heats of adsorption, future attempts to calculate the complete set of thermodynamic functions of adsorbed molecules will be more accurate.[22]

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(19) G. Halsey, *J. Chem. Phys.*, **16**, 931 (1948).

(20) G. Halsey, American Chemical Society symposium at Boston, April, 1951.

(21) The three points shown on this dotted extension of the smooth curve for 68.4°K. are *not* experimental points and should have been omitted from the figure.

(22) We might remark that extrapolation of the isotherms to $p = 0$ should be much more precise in cases in which $c$ is near the order of unity. In the present case, unfortunately, $c \cong 280$.