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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

A Correlation of the Thermodynamic Properties of Nitrogen Absorbed on Titanium Dioxide[1]

BY G. L. KINGTON AND J. G. ASTON

A comparison of the experimental thermodynamic properties with those calculated from the B.E.T. theory indicates that this or any other theory with such simplified assumptions will be inadequate to predict a set of thermodynamic properties which are even qualitatively consistent.

This paper is concerned with the adsorbed phase of nitrogen on titanium dioxide (rutile). Previous publications from this Laboratory have reported data for the identical system. The heat capacity of a monolayer was given by Morrison and Szasz.[2] The differential heat of adsorption was discussed by Kington and Aston.[3] We now present some thermodynamic functions derived from experimental data and the corresponding quantities required by the B.E.T. theory.

Method of Comparison and Results

Differential and Partial Molal Quantities.—The method of calculating the partial molal entropy of a film and the requirements of the B.E.T. theory for this quantity have been adequately discussed previously[4] for other systems, but hitherto the experimental data have not been sufficiently accurate to make anything but general conclusions. The partial molal entropy of the present system of nitrogen on rutile is shown in Fig. 1; curve 1 refers to the values obtained from the experimental data. These values were obtained by subtracting the quantity $\bar{H}_g - \bar{H}_s$ from the value of $\bar{F}_g - \bar{F}_s$. The former values were obtained from the measured differential heats, q_d, reported previously[3] by applying equation 28 of that paper[3] connecting the two quantities. They are graphed in Fig. 3. The values of $\bar{F}_g - \bar{F}_s$ were obtained from our own data on the isotherms plotted as $\bar{F}_l - \bar{F}_s$ in Fig. 2. In view of the fact that no two samples of rutile are alike, tabulated values of these data are of no particular use. It is seen that the curve for the partial molal entropy as a function of θ, obtained from the experimental data is in general agreement for the system reported previously,[4] *i.e.*, the partial molal entropy of the film is much lower than the entropy of the bulk liquid or solid phases at coverages less than a monolayer, the partial molal entropy of the film becoming approximately equal to the molal entropy for a liquid at coverages greater than a monolayer.

The thermodynamic functions required by the B.E.T. theory are dependent on the value of c and of j_s/j_l, since

$$c = (j_s/j_l)e^{(\epsilon_1 - \epsilon_l)/RT}$$

The value of c may be fixed from a knowledge of the experimental isotherm data, then the functions q, $\bar{S}_s$ and S_s required by the B.E.T. theory may be calculated if a value can be assigned to j_s/j_l.

In the absence of any information on this ratio, the original postulate of the B.E.T. theory was that $j_s = j_l$. However, there has been considerable discussion on the value to be given to j_s/j_l. Cassie[5] has suggested $j_s/j_l = 1/50$, Hill[6] has disagreed with this point of view and indicates that $j_s/j_l > 1$.

The value of c for our system has been determined as 120 from the isotherm data in the usual manner. Expressed in a somewhat different manner this means that the differential free energy required by the B.E.T. theory is in agreement with the free energy required by the experimental data (over a certain range of x) if c be chosen to be 120. A plot of the differential free energy from experimental data and using $c = 120$ in the B.E.T. theory is shown in Fig. 2. It is seen that there is good agreement above $\theta = 0.7$, but that below this surface coverage the B.E.T. theory departs from experiment rather markedly.

Having determined, for a certain range of θ, that the B.E.T. free energy requires $c = 120$, we will now use this value of c to calculate the partial molal entropy of a film required by B.E.T. theory. We can now take various values of j_s/j_l and investigate the behavior of the partial molal entropy of the B.E.T. film as a function of coverage. Values of j_s/j_l of 1, 75 $\times 10^{-3}$ and 6.3 $\times 10^{-3}$ have been taken and the respective values of $\bar{S}_s$ are shown in curves 2, 3 and 4 of Fig. 1. It is seen that taking a small value of j_s/j_l gives a much more realistic curve for $\bar{S}_s$, since the experimental curve (1), requires the value of this function to be less than the molal entropy of the liquid phase at coverages less than $\theta = 1$.

A further result of taking a small value for j_s/j_l is seen in its effect on the differential heat of adsorption required by the B.E.T. theory. Since the B.E.T. theory gives a fair indication of the free energy change in an adsorption process (see Fig. 2) then the wide divergence between the partial molal entropy required by the B.E.T. theory (assuming

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[1] This work was carried out under Office of Naval Research Contract N6-onr-269, Task Order X.

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

[3] Kington and Aston, THIS JOURNAL, **73**, 1929 (1951).

[4] Kington, Beebe, *et al.*, *ibid.*, **72**, 1775 (1950).

[5] Cassie, *Trans. Faraday Soc.*, **41**, 450 (1945).

[6] Hill, *J. Chem. Phys.*, **16**, 181 (1948).

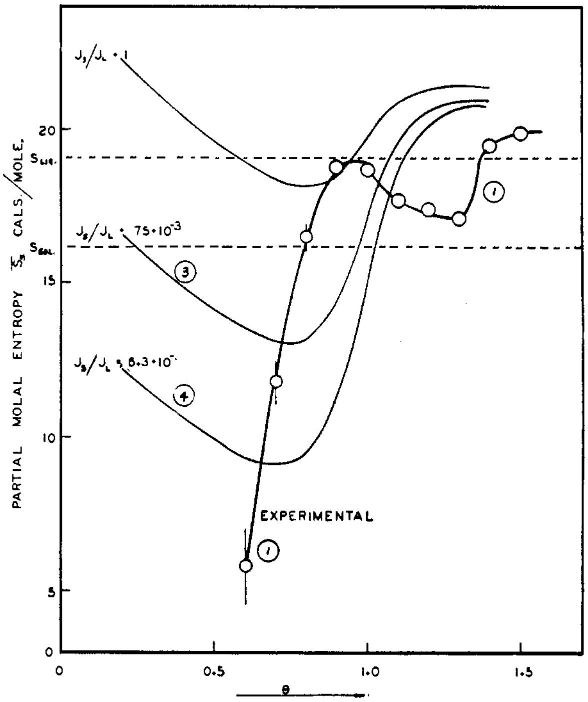

Fig. 1.—The partial molal entropy, $\bar{S}_s$, of nitrogen adsorbed on rutile at 77.3°K.: curve 1 is from experimental data, the length of the vertical line indicates the magnitude of the experimental error; for points with no vertical line, the diameter of the circle indicates the experimental error. Curves 2, 3 and 4 are from B.E.T. theory with $c = 120$. The dotted lines, S_{liq} and S_{sol}, indicate the molal entropy of the bulk liquid and solid nitrogen, respectively.

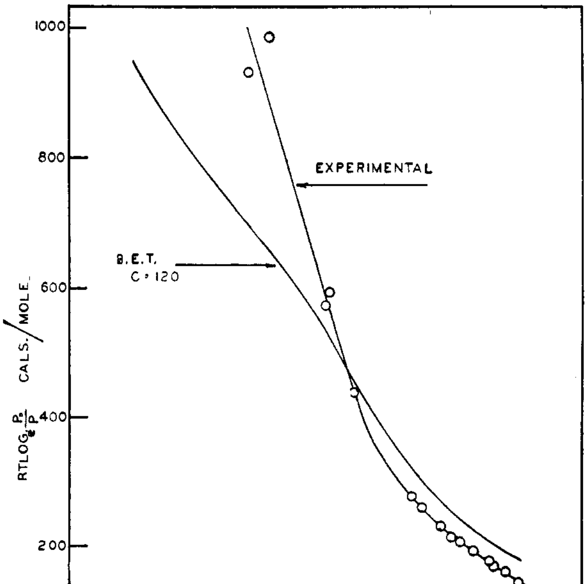

Fig. 2.—The differential free energy, $RT \ln p_0/p$.

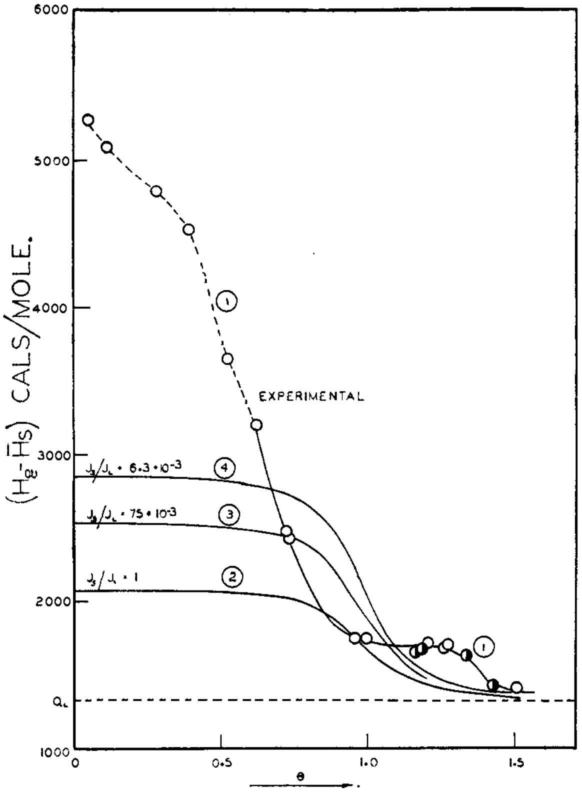

Fig. 3.—The differential heat of adsorption ($\bar{H}_g - \bar{H}_s$): curve 1 from experimental data, open circles from adsorption data, half-open circles from desorption data; curves 2, 3 and 4 from B.E.T. theory, $c = 120$.

$j_s/j_l = 1$) and that obtained from experimental data is mainly attributable to the differential heat of adsorption required by the B.E.T. theory. In Fig. 3 we have plotted the experimentally determined differential heat of adsorption (curve 1)[7] and the same quantity as derived from the B.E.T. theory in curves 2, 3 and 4. It is seen that if we take the usually accepted value of $j_s/j_l = 1$, then curve 2 is obtained, whereas if $j_s/j_l = 6.32 \times 10^{-3}$ then one gets curve 4, which is somewhat (but not a great deal) nearer the experimental facts.

However, it should be noted that no reasonable manipulation of the B.E.T. j_s/j_l can predict the high values of the heat of adsorption given by the experimental data in the region 0 to 0.5 θ and that of necessity, as will be seen later, such values will not predict the proper total entropy.

Considering the differential heat of adsorption between 1.0 and 1.4 v/v_m, it is seen that the experimental data require the heat to be greater than the B.E.T. value. This is reflected in the $\bar{S}_s$ (partial molal entropy) plot by the fact that the B.E.T. theory requires a greater partial molal entropy than is allowed by experimental data. Furthermore, it is seen that adjusting the value of j_s/j_l to be a small number does not give a small enough value to $\bar{S}_s$. It is therefore suggested that the B.E.T. requirement of $\epsilon_2 = \epsilon_1$ is not valid and that ϵ_2 should be greater than ϵ_1 in order to make the entropy change on adsorption greater than the entropy change in liquefaction.

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[7] It should be noted that these values have been corrected for the heat of compression by the method given by Kington and Aston, THIS JOURNAL, 73, 1929 (1951).

The Total Entropy of the Film.—By integration of the values for $\bar{S}_s$, a value for S_s, the total entropy of the film, is obtainable for any number of molecules on the surface. However, the accurate experimental determination of q_a proved impossible below $\theta = 0.5$, because of an extremely slow process lasting some hours which was associated with the adsorption. From our experimental data it is possible to obtain the quantity $S_{s(\theta)} - S_{s(0.6)}$, where $S_{s(\theta)}$ is the total entropy of the film of coverage θ, and $S_{s(0.6)}$ is the total entropy of a film of 6/10 of a layer. This function $S_{s(\theta)} - S_{s(0.6)}$ is plotted in Fig. 4. Curve 1 is required by the experimental data.

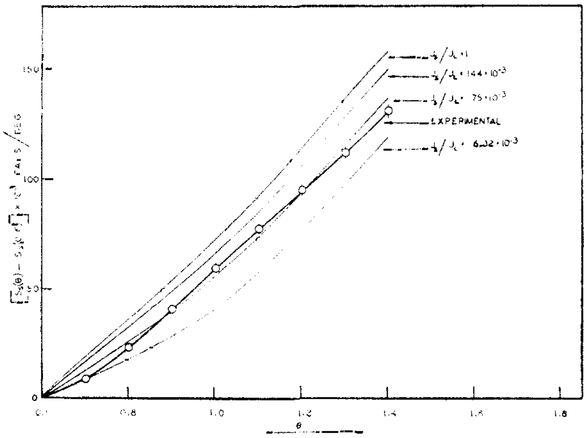

Fig. 4.—The quantity $S_{(s\theta)} - S_{s(0.6)}$. The length of the vertical line of the points on the experimental curve 1 indicates the magnitude of the experimental error. All theoretical curves are for B.E.T. theory, $c = 120$.

It has been shown by Hill[8] that the molal heat content change $(\bar{H}_s - \bar{H}_l)$ required by the B.E.T. theory is given by the expression (converting from a molecular to a molar basis)

$$(\bar{H}_s - \bar{H}_l) = -(\epsilon_1 - \epsilon_l)(1 - x) + \frac{(1 - x)(1 - x + cx)}{cx} \ln \left[\frac{(1 - x + cx)}{(1 - x)}\right]$$

and that the molal entropy change $(\bar{S}_s - \bar{S}_l)$ is given by

$$T(\bar{S}_s - \bar{S}_l) = (\bar{H}_s - \bar{H}_l) - RT \ln x$$

Using these equations one can then calculate $\bar{S}_s$ at any surface coverage and therefore the total entropy S_s for any film, according to the requirements of the B.E.T. theory.

Taking various values of j_s/j_l, the total entropy S_s is plotted as a function of θ, according to the B.E.T. theory in Fig. 5. From these curves the quantity $S_{s(\theta)} - S_{s(0.6)}$ can be evaluated and the results are shown with the experimental data in Fig. 4. It is seen that if $j_s/j_l = 1$ then the value for $S_{s(\theta)} - S_{s(0.6)}$ is too great, but if we take a small value for j_s/j_l, then a more reasonable figure for $S_{s(\theta)} - S_{s(0.6)}$ is obtained.

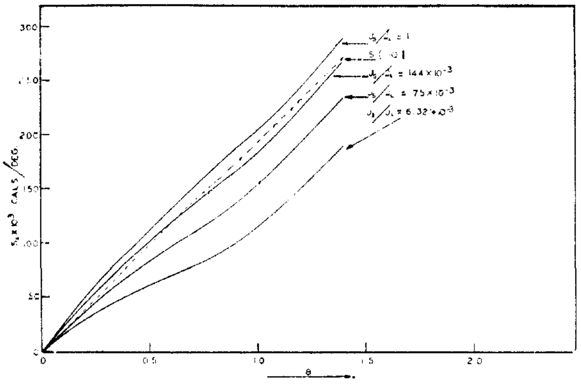

Fig. 5.—The total entropy of an adsorbed phase, S_s, as required by the B.E.T. theory, $c = 120$. The curve for S_{liq} indicates the total entropy of an adsorbed phase having a molal entropy equal to that of the bulk liquid.

Discussion

It is seen that any detailed treatment along the lines of Brunauer, Emmett and Teller requires $j_s/j_l \approx 10^{-3}$. It should be pointed out that this theory was developed to satisfy the only generally available thermodynamic quantity, namely, the partial molal free energy (the equilibrium adsorption pressure). The previous paper[2] has presented for the first time accurate experimental data from which the corresponding enthalpy and entropy can be obtained. It is now certain that these quantities do not correspond even qualitatively with the values predicted by the theory.

The modifications of the theory necessary can be seen to some extent. These are: (1) allowance for variation of ϵ_1 with coverage. (2) ϵ_2 must be greater than ϵ_1 and also a function of coverage (depending on the definition of ϵ_2 as discussed below). (3) j_s/j_l cannot be taken as unity.

It is not certain whether the value of j_s/j_l will be less or greater than unity until points (1) and (2) are settled, but if the arguments of Hill[5] are valid, it is the neglect of points (1) and (2) above which has led to our calculation of j_s/j_l less than unity. However, until a mechanism is proposed to account for the variation of ϵ_1 with coverage, j_s is singularly lacking in meaning. The fact that large thermal effects are noted for hours after adsorption at low coverages indicates large energies of activation for motion of molecules to new sites. Any computation of j_s requires a knowledge of a system of energy levels which will allow for this. Perhaps the facts could best be taken into account by the definition of an *i*th layer according to an energy ϵ_i rather than a geometric packing of the molecules over the surface in question, regarded as essentially plane and energetically homogeneous. If this be done, points (1) and (2) cease to be meaningful as ϵ_2 will then obviously be greater than ϵ_1.

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(8) Hill, *J. Chem. Phys.*, **17**, 772 (1949).