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# The Nature of Silica-Alumina Surfaces III. Statistical Interpretation of the Adsorption of Ammonia on Alumina

ALFRED CLARK AND VERNON C. F. HOLM

*From the Phillips Petroleum Company, Bartlesville, Oklahoma*

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Statistical calculations have been made for the adsorption of ammonia on alumina in the region of fixed adsorption. There is a broad distribution of adsorption energies, and an expression for this distribution has been derived. Adsorption data fit the integral form of the Langmuir equation. Configurational entropies have been shown to be several-fold less than those for uniform sites. Evidence is given which indicates that the changes in vibrational entropies of adsorbent and adsorbate as a result of perturbations caused by adsorption are small. Below a coverage of $0.36 \times 10^{14}$ molecules/cm$^2$, adsorbed ammonia molecules have lost all translation and rotation. Above this value, it is possible that one degree of rotational freedom may have been regained.

## I. INTRODUCTION

In a previous paper (*1*), an account was given of the thermodynamics of adsorption of ammonia on eleven silica-alumina gels ranging in composition from pure alumina to pure silica. The data for alumina indicated a large region of fixed adsorption and an isosteric heat of adsorption that declined rapidly with increasing coverage. These data provided an opportunity for detailed study of the state of adsorbed ammonia. This paper reports the results of the calculations using the methods of statistical thermodynamics. The states of adsorbed molecules have been considered quantitatively for many systems (*2–7*). In calculations of this nature, it is often customary to calculate configurational entropies on the assumption that all sites have the same adsorption energy. We have endeavored in this paper to consider the effects of a distribution of adsorption energies on configurational entropies. Almost invariably in statistical and thermodynamic studies, perturbations of the adsorbent and adsorbate are neglected. We have attempted to justify this procedure in the present case. We have also limited the calculations to the region of immobile adsorption—the only region where the Langmuir equation is strictly useful. It is one of the objectives of this paper to show that the integral form of the Langmuir equation applies to the ammonia-alumina system in the region of immobile adsorption.

## II. EXPERIMENTAL METHODS

Experimental methods will be given only briefly here, since they were described in detail in a previous paper (*1*).

Alumina was obtained by heat treatment of high purity $\beta$-alumina trihydrate from Davison Chemical Corporation; the resulting material was $\eta$-alumina. Ammonia was obtained from the Matheson Company, and its specified purity (99.99%) was verified.

Adsorption measurements were made with a vacuum microbalance similar to one described by Gray and Jennings (*8*).

Isosteric heats of adsorption, $q_{st} = -\Delta \bar{H}_\Gamma$, and differential molar entropies of adsorbed ammonia, $\bar{S}_\Gamma$, as functions of surface coverage were calculated exactly as in Part I.

## III. METHODS OF CALCULATION

The Langmuir equation for immobile adsorption, with all sites of the same adsorption energy, no interaction between adsorbed molecules, and no more than one molecule per occupied site, is derived by the methods of statistical thermodynamics (*9*):

$$N = \frac{N_0}{1 + \dfrac{[(2\pi m)^{3/2}(kT)^{5/2}q_G \exp(-U_0/RT)]}{ph^3 q_a}} \quad (1)$$

where $N$ is the number of adsorbed molecules per cm$^2$; $N_0$, the total number of adsorption sites per cm$^2$; $m$, the mass of the ammonia molecule; $k$ and $R$, the gas constant per molecule and per mole, respectively; $p$, the equilibrium pressure; $h$, Planck's constant; $U_0$, the energy of adsorption per mole when both adsorbed and gaseous molecules are at rest in their electronic ground states and zero point vibrational levels; $q_G$, the partition function for internal degrees of freedom of the gas phase molecule; and $q_a$, the partition function for an adsorbed molecule with no freedom of translation.

If, as in the present case, there is a distribution of adsorption energies, Eq. (1) takes the integral form:

$$N = \int_0^\infty \frac{dN/dU_0}{1 + \dfrac{[(2\pi m)^{3/2}(kT)^{5/2}q_G \exp(-U_0/RT)]}{ph^3 q_a(U_0)}} dU_0 \quad (2)$$

where $dN/dU_0$ is the distribution function for adsorption energies, and $q_a$ becomes a function of $U_0$. The limits, 0 to $\infty$, are justifiable. It will be shown later that $dN/dU_0$, and thus the number of molecules adsorbed, rapidly approaches zero above the highest observed values of $U_0$, so that the upper limit, $\infty$, does not introduce a significant error. It will be shown later that the lower limit, 0, is justifiable because adsorption in the *immobile* region cuts off rather sharply at an energy of adsorption considerably in excess of the minimum heats observed. In order to utilize Eq. (2), $dN/dU_0$ and $q_a(U_0)$ must be determined.

### *Calculation of* $dN/dU_0$

The distribution function, $dN/dU_0$, is calculated from the isosteric heat of adsorption, $q_{st}$. This is equivalent to assuming that sites are filled in order of their decreasing adsorption energies in the region of immobile adsorption, and that there is not more than one molecule per occupied site. Filling the sites strictly in this order is tantamount to assuming that the configurational entropy is zero. This assumption will be justified in Section V.

The differential energy of adsorption, $q_{diff}$, is calculated from the isosteric heat of adsorption, $q_{st}$, by the equation:

$$q_{diff} = q_{st} - RT$$

where we have assumed a perfect gas.

In order to proceed further, it is necessary to consider the allowable modes of freedom of an adsorbed ammonia molecule in the immobile region. A gas phase molecule of ammonia has six modes of vibration, three of rotation, and three of translation. Upon immobile adsorption, it will lose at least all of its translational modes, which are transformed into three surface vibrational modes. It may also lose the three modes of rotation, which become surface vibrations—one torsional and two bending. First, $U_0$ will be calculated on the assumption that all translations and rotations have been lost, that the adsorbed ammonia molecule has six modes of surface vibration, in addition to six modes of internal vibration. It is also assumed that only the ground electronic state of the adsorption site–adsorbate complex has to be considered.

The differential energy of adsorption, $q_{diff}$, is related to $U_0$ by the following equation:

$$q_{diff} = U_0 - \bar{E}_v + (E_G{}^{kin} - E_{ads}{}^{kin})$$

where $\bar{E}_v$ is the differential energy per mole of surface vibrations of adsorbed ammonia in excess of the zero-point energy at a given concentration; and $(E_G^{\mathrm{kin}} - E_{\mathrm{ads}}^{\mathrm{kin}})$ is the loss of kinetic energy of rotation and translation upon adsorption. It has been assumed that the energy of internal vibrations of the ammonia molecule is not changed significantly on adsorption.

When the adsorbed molecules have only vibrational energy, $E_{\mathrm{ads}}^{\mathrm{kin}} = 0$. Rotational and translational energies are assumed to be classical. For each rotational and translational mode transformed into vibration on adsorption, ½ $RT$ calories are lost, and $U_0$ is therefore expressed by the equation:

$$U_0 = q_{\mathrm{diff}} + \bar{E}_v - 3RT = q_{\mathrm{st}} + \bar{E}_v - 4RT \qquad (3)$$

In order to calculate $\bar{E}_v$, use is made of the experimental differential surface entropy, $\bar{S}_\Gamma$ $(=\partial\tilde{S}_\Gamma/\partial n$, where $\tilde{S}_\Gamma$ is total integral entropy, and $n$ is moles adsorbed), given in Table 1. This entropy may be expressed as the sum of four quantities:

$$\bar{S} = \bar{S}_c + \bar{S}_v + \bar{S}_{v'} + \bar{S}_s \qquad (4)$$

where $\bar{S}_c$ is the partial molal configurational entropy; $\bar{S}_{v'}$, the internal vibrational differential entropy; $\bar{S}_v$, the differential entropy of surface vibrations; and $\bar{S}_s$, the perturbational differential entropy of the solid adsorbent. The partial molal configuration entropy is taken as zero at all coverages in the immobile range (see Section V). The internal vibrational differential entropy, $\bar{S}_{v'}$, is assumed to be the same as in the gas phase at all surface coverages. It is small (1.5 eu/mole at 400°C); and, since it is assumed to be constant with respect to surface coverage, it is equal to the molal vibrational entropy. The perturbational differential entropy of the solid—the result of distortion of the solid in the field of the adsorbate—should be greatest at low coverages where adsorption is strongest. At the lowest coverage investigated, the total differential surface entropy $(\bar{S}_\Gamma)$ is 2.7 eu/mole at 400°C. Approximately 1.5 eu/mole is accounted for by the entropy of internal vibrations leaving at most at any coverage in the immobile region 1.2 eu/mole which could be attributed to perturbations. On this basis, $\bar{S}_s$ is assumed to be negligible (see Section IV for further details).

Therefore, the differential entropy of surface vibrations, $\bar{S}_v$, was calculated from the equation:

$$\bar{S}_v = \bar{S}_\Gamma - \bar{S}_v'$$

It is not possible to calculate the six frequencies of surface vibrations of the ammonia molecule individually. But an "average" frequency, $\bar{\nu}_s$, may be obtained from the following equation for the entropy of an harmonic oscillator:

$$\bar{S}_v = R\left[\sum_{i=1}^{6} \frac{h\nu_i/kT}{\exp\,(h\nu_i/kT)_{-1}} - \ln\,(1 - \exp\,(-h\nu_i/kT)\right]$$

$$= 6R\left[\frac{(h\bar{\nu}_s/kT)_{-1}}{\exp h\bar{\nu}_s/kT} - \ln\,(1 - \exp\,(-h\bar{\nu}_s/kT)\right]$$

Values of $\bar{\nu}_s$ were obtained from a plot of $\bar{S}_v$ versus $\bar{\nu}_s$.

Using these same values, $\bar{\nu}_s$, it is not difficult to show that a good approximation to the surface vibrational energy in excess of the zero-point vibrational level can be obtained from the conventional equation of an harmonic oscillator:

$$\bar{E}_v = RT\sum_{i=1}^{6} \frac{h\nu_i/kT}{\exp\,(h\nu_i/kT)_{-1}} \cong \frac{6RTh\bar{\nu}_s/kT}{\exp\,(h\bar{\nu}_s/kT)_{-1}}$$

Values of $\bar{E}_v$ were obtained from a plot of $\bar{E}_v$ versus $\bar{\nu}_s$.

It is now possible to calculate $U_0$ as a function of surface coverage ($N$) using Eq. (3). Taking the derivative of the plot of $U_0$ versus $N$ gives the desired quantity, $dN/dU_0$, the distribution function.

Similarly, $U_0$, can be calculated when

TABLE 1

THERMODYNAMIC QUANTITIES[a] FOR $NH_3$ ADSORBED ON $Al_2O_3$

(Fixed adsorption, no translation or rotation)

| $N \times 10^{-14}$ $(cm^2)^{-1}$ | $p$ (mm) | $T$ (°C) | $\bar{S}_\Gamma$ (eu/mole) | $\bar{S}_{v'}$ (eu/mole) | $\bar{S}_v$ (eu/mole) | $\bar{E}_v$ (cal/mole) | $\bar{A}_v$ (cal/mole) | $\bar{\nu}_s \times 10^{-13}$ $(sec^{-1})$ | $q_v$ |
|---|---|---|---|---|---|---|---|---|---|
| 0.26 | 0.07 | 400 | $\sim$1.5 | 1.5 | $\sim$0.0 | $\sim$0.0 | $\sim$0.0 | >5.5 | $\sim$1.00 |
| 0.30 | 0.20 | 400 | $\sim$1.5 | 1.5 | $\sim$0.0 | $\sim$0.0 | $\sim$0.0 | >5.5 | $\sim$1.00 |
| 0.34 | 0.61 | 400 | 2.7 | 1.5 | 1.2 | 750 | −57 | 5.5 | 1.04 |
| 0.38 | 1.30 | 400 | 13.2 | 1.5 | 11.7 | 4450 | −3410 | 1.5 | 12.42 |
| 0.42 | 2.10 | 400 | 18.1 | 1.5 | 16.6 | 5550 | −5650 | 0.98 | 64.00 |
| 0.46 | 3.30 | 400 | 21.0 | 1.5 | 19.5 | 6100 | −7000 | 0.77 | 172.66 |
| 0.50 | 5.10 | 400 | 23.1 | 1.5 | 21.6 | 6400 | −8150 | 0.65 | 423.12 |
| 0.34 | 0.05 | 350 | $\sim$2.5 | 1.3 | $\sim$1.17 | $\sim$650 | $\sim$−78 | $\sim$5.5 | $\sim$1.06 |
| 0.38 | 0.14 | 350 | 12.4 | 1.3 | 11.1 | 3350 | −3600 | 1.5 | 17.81 |
| 0.42 | 0.34 | 350 | 19.7 | 1.3 | 15.8 | 5050 | −4820 | 1.0 | 47.80 |
| 0.46 | 0.72 | 350 | 19.7 | 1.3 | 18.4 | 5550 | −6050 | 0.80 | 129.00 |
| 0.50 | 1.20 | 350 | 21.9 | 1.3 | 20.6 | 5850 | −7040 | 0.66 | 285.90 |
| 0.54 | 1.74 | 350 | 23.4 | 1.3 | 22.1 | 6050 | −7700 | 0.59 | 484.00 |
| 0.58 | 2.40 | 350 | 24.5 | 1.3 | 23.2 | 6150 | −8350 | 0.53 | 806.00 |
| 0.62 | 3.30 | 350 | 25.5 | 1.3 | 24.2 | 6250 | −8750 | 0.49 | 1130.00 |
| 0.64 | 4.00 | 350 | 26.0 | 1.3 | 24.7 | 6300 | −9000 | 0.47 | 1360.0 |
| 0.34 | — | 300 | $\sim$1.02 | 1.02 | $\sim$0.0 | $\sim$0.0 | $\sim$0.0 | >2.2 | $\sim$1.0 |
| 0.36 | — | 300 | $\sim$7.01 | 1.02 | $\sim$5.99 | $\sim$2300 | $\sim$−1130 | $\sim$2.2 | $\sim$2.67 |
| 0.38 | 0.02 | 300 | 11.57 | 1.02 | 10.55 | 3550 | −2500 | 1.5 | 8.84 |
| 0.42 | 0.04 | 300 | 16.52 | 1.02 | 15.50 | 4500 | −4360 | 0.93 | 44.83 |
| 0.50 | 0.14 | 300 | 21.02 | 1.02 | 20.00 | 5200 | −6270 | 0.62 | 237.5 |
| 0.58 | 0.46 | 300 | 23.4 | 1.02 | 22.38 | 5525 | −7375 | 0.52 | 625.0 |
| 0.66 | 1.10 | 300 | 25.0 | 1.02 | 23.98 | 5700 | −8110 | 0.45 | 1189 |
| 0.74 | 2.20 | 300 | 26.4 | 1.02 | 25.38 | 5810 | −8790 | 0.41 | 2138 |
| 0.82 | 4.05 | 300 | 27.4 | 1.02 | 26.38 | 5870 | −9230 | 0.37 | 3170 |

[a] $N \times 10^{-14}$ = No. molecules adsorbed/cm² × $10^{-14}$.
$p$ = Equilibrium pressure of $NH_3$.
$\bar{S}_\Gamma$ = Differential surface entropy of $NH_3$.
$\bar{S}_{v'}$ = Entropy of internal vibrations of $NH_3$.
$\bar{S}_v$ = Differential entropy of surface vibrations.
$\bar{E}_v$ = Differential energy of surface vibrations in excess of zero point level.
$\bar{A}_v$ = Differential work function of surface vibrations in excess of zero point level.
$\bar{\nu}_s$ = Average frequency of surface vibrations of adsorbed $NH_3$.
$q_v$ = Differential partition function of surface vibrations of $NH_3$.

the adsorbed ammonia molecule may have five surface vibrations and one rotational degree of freedom. In that case,

$$U_0 = q_{st} + \bar{E}_v - (7/2)RT$$

and,

$$\bar{S}_\Gamma = \bar{S}_v + \bar{S}_v' + \bar{S}_{r_1}$$

where $\bar{S}_{r_1}$ is the entropy per mole of one degree of rotational freedom, and configurational and perturbational entropies have been neglected, as before.

### *Calculation of $q_a(U_0)$*

The partition function for fixed adsorbed molecules, $q_a(U_0)$, depends on the degrees of freedom of the adsorbed molecule, just as $U_0$ does. For fixed adsorption with no rotation or translation, $q_a(U_0)$ may be expressed as the product of the partition functions of internal and surface vibrations, $q_{v'}$ and $q_v$, respectively.

$$q_a(U_0) = q_v' q_v$$

The partition function for internal degrees of freedom of the gas phase molecule, $q_G$, is the product of the partition functions for three degrees of rotation and six modes of internal vibrations.

$$q_G = q_v' q_r$$

Since the quotient, $q_G/q_a$, occurs in the Langmuir equation (2), and since the internal vibrations are assumed unchanged upon adsorption, there is obtained:

$$q_G/q_a = q_r/q_v$$

The rotational partition function, $q_r$, is calculated from the standard statistical formula for classical rotation:

$$q_r = \frac{\pi^{1/2}}{\sigma} \frac{(8\pi^2 I_A kT)^{1/2}}{h^2} \cdot \frac{(8\pi^2 I_B kT)}{h^2}$$

where $\sigma$ (=3) is the symmetry number; $I_A$, the moment of inertia of one rotational degree of freedom of the ammonia molecule; and $I_B$, the moment of inertia of the two degenerate rotational degrees of freedom.

The partition function for surface vibrations, $q_v$, is calculated as follows:

From the values of $\bar{E}_v$, the vibrational energy in excess of the zero-point level, and $\bar{S}_v$, the corresponding entropy, determined as above, the work function, $\tilde{A}_v$, is calculated.

$$\tilde{A}_v = \bar{E}_v - T\bar{S}_v$$

From the values of $\tilde{A}_v$ as a function of surface coverage, $q_v$ is calculated:

$$\tilde{A}_v = -RT \ln q_v$$

For fixed adsorption, no translation, one degree of rotation, five modes of surface vibration, and six modes of internal vibration,

$$q_a(U_0) = q_{v'} q_v q_{r_1}$$

Following the procedure above, $q_v$ is easily calculated for this case.

### *Calculation of Configurational Entropy*

If all sites have the same adsorption energy, configurational entropy is obtained from the standard statistical equation:

$$\tilde{S}_c = k \ln N_0!/N!(N_0 - N)!$$

where $N_0$ is the total number of adsorption sites, and $N$, the number of adsorbed molecules per cm$^2$.

When a continuous distribution of adsorption energies exists, the procedure of Hill (*10*) can be used to obtain:

$$\tilde{S}_c = k \int_0^\infty \left\{ \ln \left[ \frac{[\exp(-U_0/RT)/ap] + 1}{\exp(-U_0/RT)/ap} \right] + \frac{\ln [\exp(-U_0/RT)/ap]}{[\exp(-U_0/RT)/ap] + 1} \right\} \frac{dN}{dU_0} dU_0 \quad (5)$$

where $\tilde{S}_c$ is the configurational entropy per unit area, and

$$a = \frac{q_v}{q_r} \cdot \frac{h^3}{(2\pi m)^{3/2}(kT)^{5/2}}$$

is a function of temperature and adsorption energy.

All terms in Eq. (5) can be evaluated by procedures already described. The partial molal configurational entropy was obtained by differentiation. It will be recalled that in the procedures for evaluating $q_v$ and $U_0$ from differential entropies, the configurational entropy, and therefore the partial molal configurational entropy, was assumed to be negligible at all coverages. It will be shown in Section IV that these entropies are negligibly small as a first approximation. If they were not, then by a process of iteration they could be introduced into all of the above procedures, and the process continued until consistent results were obtained.

## IV. Perturbations of Adsorbent and Adsorbate

The Langmuir equation can be expressed in the form *(11)*:

$$N = N_0 \Big/ 1 + \frac{\exp\,(\Delta H_\Gamma/RT)}{p\,\exp\,(\Delta \bar{S}_\Gamma/R)}$$

or in the integral form, if there is a distribution of adsorption energies. It holds regardless of perturbations of the adsorbent or adsorbate, and is equivalent to the statistical form, Eq. (1) or (2). In the statistical form, if it is desired to split the partition function, $q_a$, into its component parts, then some knowledge about the effects of perturbations is required. A knowledge of entropy effects is sufficient for this purpose according to the methods described in Section III. Zero-point vibrational energies and electronic energies are contained in the experimental quantity, $q_{st}$, and, therefore, in $U_0$. The usual assumption is made that there is no ligand–ligand or ligand–lattice vibrational coupling, so that statistical and thermodynamic quantities for the various bonds can be treated independently.

Pertinent information is given in review papers by Crawford and Eischens *(13)*. Some of the internal vibrations of ammonia have been shown to remain unperturbed on adsorption. Others have not been observed yet in the adsorbed state. The N–H stretching and unsymmetrical bending vibrations at 3.0 and 6.1 $\mu$, respectively, are not shifted significantly on adsorption on silica-alumina or alumina. The symmetrical N–H bending vibration at 10.5 $\mu$ is not seen in the adsorbed state; but this is not surprising because the region above 8.0 $\mu$ is obscured by a strong Si–O or Al–O bond.

Perturbations of the adsorbent are easily seen if the surface possesses functional groups. They are larger than perturbations of the adsorbate. For example, the average shift in O–H frequency produced by ammonia on the surface of porous glass is 640 cm$^{-1}$, from 3749 to 3109 cm$^{-1}$, at 150°C. Yet this frequency shift represents less than 1 eu change in entropy, according to the harmonic oscillator approximation. In this frequency range, entropy is insensitive to changes in frequency. There is no quantitative information about perturbations of OH bending vibrations, oxygen or hydroxyl bridges, etc., produced by adsorption of ammonia.

Though all observed frequency shifts for adsorbent and adsorbate give a negligible total entropy change, no conclusions can be reached from infrared data alone with regard to the vibrations which have not been observed yet.

An important point for the present discussion is that all observed shifts in frequencies are downward, and this would normally be expected in most cases *(12)*. Downward frequency shifts imply that $\tilde{S}_s$, the *total* integral entropy of solid perturbations, increases with increasing surface coverage. Consequently, $\bar{S}_s$, the perturbational differential entropy in Eq. (4) should be positive. Also $\bar{S}_v$ and $\bar{S}_{v'}$ are positive; and, at low coverages, $\bar{S}_c \geqslant 0$. Thus each component of $\bar{S}_\Gamma$ in Eq. (4) should be positive or zero, and less than 2.7 eu ($\bar{S}_\Gamma$ in Table 1) at the lowest coverage investigated at 400°C. If it is assumed that the small internal vibrational entropy of ammonia (1.5 eu at 400°C) is not changed significantly upon adsorption, then the sum, $\bar{S}_s + \bar{S}_c + \bar{S}_v)$, does not exceed 1.2 eu at the lowest coverage investigated. If all adsorption sites have the same energy, $\bar{S}_s$ should remain constant with increasing surface coverage. If adsorption energies decline, $\bar{S}_c$ (see Section V) and $\bar{S}_s$ should decrease with increasing coverage. For these reasons, $\bar{S}_s$ and $\bar{S}_c$ are presumed to be negligible within the limits of experimental accuracy over the range of coverages used in the calculations. The bulk of the entropy changes upon adsorption are therefore considered to be localized in the surface bonds and surface vibrations of the adsorbed molecule.

It is interesting to speculate under what conditions $\bar{S}_T$ might be negative even though all perturbations are accompanied by downward shifts in frequencies. At more than one-half coverage on a surface consisting of uniform high-strength sites exclusively, the partial molal configurational entropy, $\bar{S}_c$, becomes negative, and could conceivably exceed the positive sum of the vibrational differential entropies, $\bar{S}_v$, $\bar{S}_{v'}$, and $\bar{S}_s$.

## V. Results and Discussion

### *Adsorption Isotherms*

Isotherms were calculated for three temperatures, 400°, 350°, and 300°C. The maximum coverage included in these calculations is $0.82 \times 10^{14}$ molecules/cm$^2$. This is well below the mobile region as shown in a previous paper (*1*). The case of fixed adsorption with no rotation will be discussed first. The adsorbed ammonia molecule is considered to have six modes of surface vibrations and six internal vibrations.

In Fig. 1, the potential energy of adsorption, $U_0$, is plotted against surface coverage. Taking the derivative of this curve, the distribution function, $dN/dU_0$, is obtained:

$$dN/dU_0 = 0.1425 \exp(-.0544U_0)$$

The expression holds up to at least $1.2 \times 10^{14}$ molecules/cm$^2$, and $U_0$ is essentially independent of temperature at constant coverage.

In Table 1, the results of statistical and thermodynamic calculations using the methods of the previous sections are collected. The lowest observed coverage at 400°C was $0.34 \times 10^{14}$ molecules/cm$^2$. Data below this point were obtained by extrapolation of $\bar{S}_T$ on the assumption that the partition function, $q_v$, sinks to a value of 1 and then remains constant for all lower coverages. The lowest observed coverage at 350° and 300°C was $0.38 \times 10^{14}$ molecules/cm$^2$, and the curves of $\bar{S}_T$ versus $N$ were extrapolated to $0.34 \times 10^{14}$ molecules/cm$^2$.

It will be observed in Table 1, that adsorbed ammonia molecules are essentially at the zero-point vibrational level at coverages less than $0.34 \times 10^{14}$ molecules/cm$^2$. Values of average frequency, $\bar{\nu}_s$, remain essentially constant at a given coverage, independent of temperature. This relationship should hold, if there is no change in the mode of adsorption with temperature.

Using Eq. (2), the adsorption isotherms were determined. The integrand of Eq. (2)

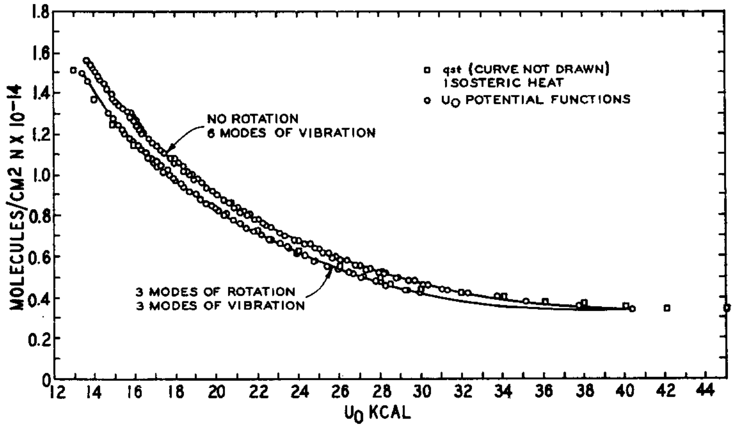

FIG. 1. Isosteric heat and potential functions of adsorption of $NH_3$ on $Al_2O_3$.

was plotted against $U_0$ for each pressure and temperature, using the appropriate values of $q_v$. The area under each curve gave one point on the isotherm. Typical curves are given in Figs. 2A and 2B for 400° and 350°C at an experimental coverage of $0.50 \times 10^{14}$ molecules/cm². Areas under the curves in both cases are $0.53 \times 10^{14}$ molecules/cm². In no case were values of $U_0$ used below the range for which the distribution function was shown to be valid. In the range of coverage calculated, adsorption had sunk to zero before lower values of $U_0$ were reached.

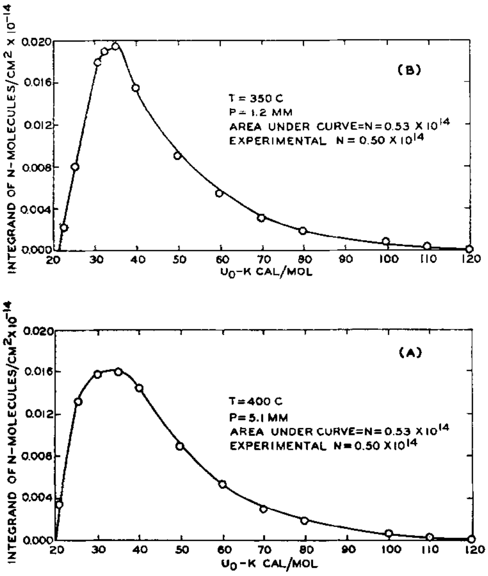

FIG. 2. Adsorption of $NH_3$ on $Al_2O_3$.

If the branch of these curves to the left of the maximum had dropped vertically from the maximum, this would have indicated that the configurational entropy was exactly zero; that is, the cutoff would have been sharp at some $U_0$ depending on temperature and pressure.

Figure 3 gives plots of experimental isotherms and those calculated from Eq. (2). The deviations are small and would have been less if the configurational entropy of zero assumed in the calculated curves were replaced by iterated values (see this section, Configurational Entropies). The sensitivity of $N$ to changes in the entropy of adsorption decreases with increasing coverage. At low coverages, a 1% decrease in the absolute value of the differential entropy of adsorption ($\Delta\bar{S}_\Gamma$) causes an increase of approximately 20% in the value of $N$, all other terms constant. The per cent increase in $N$ drops rapidly with increasing coverage to approximately 6%.

As a good first approximation, these results indicate behavior according to the Langmuir isotherm in each infinitesimally small region of constant adsorption energy.

We recognize that an isotherm equation, even though it contains no arbitrary constants, may not be unique. There may be other equations which fit the data within the limits of experimental accuracy. Yet the agreement obtained in the present case gives considerable confidence in the Langmuir model.

So far we have considered the case of fixed adsorption with no rotation. Actually, all states are allowable that are consistent with the total differential surface entropy, $\bar{S}_\Gamma$, since basically the Langmuir equation is dependent only on this quantity, as pointed out in Section IV. Even states that are not physically realistic, such as one having three degrees of rotation and no translation, fit the data through the Langmuir equation at coverages where $\bar{S}_\Gamma$ is not exceeded by the sum of $\bar{S}_{v'}$ (1.5 eu at 400°C) and $\bar{S}_{R_3}$, the entropy (13.93 eu at 400°C) of three degrees of rotational freedom. Changes in $U_0$ are compensated by changes in the partition function, $q_a$. In Fig. 1, $U_0$ is plotted against surface coverage for this case, and is seen to be different from the case of no rotation.

Below approximately $0.36 \times 10^{14}$ molecules/cm², it is seen in Table 1 that the total differential surface entropy, $\bar{S}_\Gamma$, is less than the sum of $\bar{S}_{v'}$ and $\bar{S}_{R_1}$, the entropy (4.15 eu at 400°C) of one degree of rotational freedom. We conclude that below this coverage the adsorbed ammonia molecules are fixed and in addition have lost all rotation. They possess only vibration.

Above $0.36 \times 10^{14}$ molecules/cm², still in the region of fixed adsorption, the adsorbed ammonia molecules may have regained one

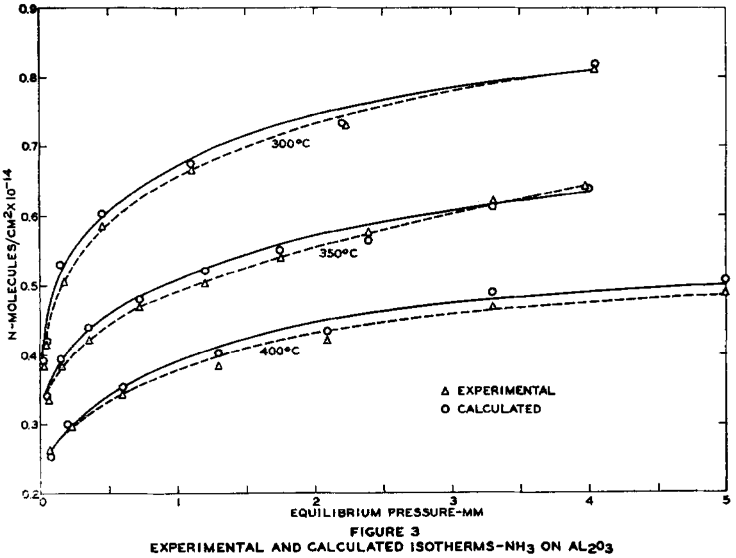

FIG. 3. Experimental and calculated isotherms—$NH_3$ on $Al_2O_3$.

degree of rotational freedom. Our data are not sufficiently accurate to distinguish between the values of $U_0$ for this case and that for no rotation, as may be seen from Fig. 1, where the separation between the curves for three degrees of rotation and no rotation is already small. It does not seem physically realistic to consider more than one degree of rotational freedom for fixed adsorption.

If Eq. (2) is integrated from $-\infty$ to $+\infty$ with $q_a$ independent of $U_0$ (*14*), the Freundlich isotherm is obtained: $N = A(T)p^{c(T)}$, where $A$ and $c$ are constants dependent only on temperature. But Eq. (2) in its correct form (*15*), with integration limits 0 to $\infty$ and $q_a$ a function of $U_0$, leads to no such simple expression. Yet the over-all isothermal plots of ln $N$ versus ln $p$ give reasonably straight lines (*1*). It must be presumed that there is no necessity for theoretically justifying the Freundlich equation in the present case.

### *Configurational Entropies*

Configurational entropies are independent of the assumed state of adsorbed ammonia molecules so long as fixed adsorption is assumed and the differential surface entropies of the various possible modes of freedom assumed are consistent with the total differential surface entropy, $\bar{S}_T$. We have calculated configurational entropies on the basis of fixed adsorption and no rotation, using Eq. (5).

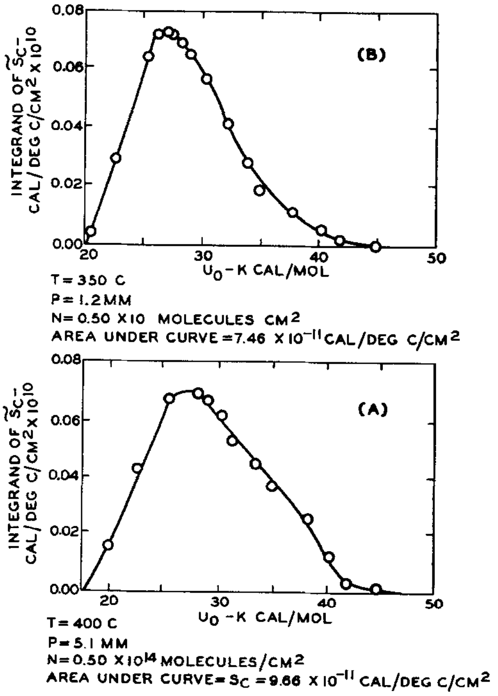

FIG. 4. Configurational entropy of $NH_3$ on $Al_2O_3$.

The integrand of Eq. (5) was plotted against $U_0$ for each pressure and temperature, using the appropriate values of $q_v$. The area under each curve gives one point on the curve of total configurational entropy ($\tilde{S}_c$) versus surface coverage. Typical curves are shown in Figs. 4A and 4B for 400° and 350°C at an experimental coverage of $0.50 \times 10^{14}$ molecules/cm². The configurational entropy is zero down to some adsorption energy dependent on coverage and then rises sharply. From the entropy equation, $\tilde{S}_c = k ln W$, zero entropy indicates only one possible arrangement ($W$) of the adsorbed molecules on the adsorption sites, so that $W = 1$, which indicates all sites occupied in the order of decreasing energies down to that point. Most of the adsorbed molecules are adsorbed in the region of zero configurational entropy. A small percentage of them scatter over a range of sites, not filling them exactly in order of decreasing adsorption energy. This range is narrow, and with further decrease in adsorption energy, the configurational entropy drops to zero again. From this point on, the sites are completely empty, where $W$, again, is equal to 1.

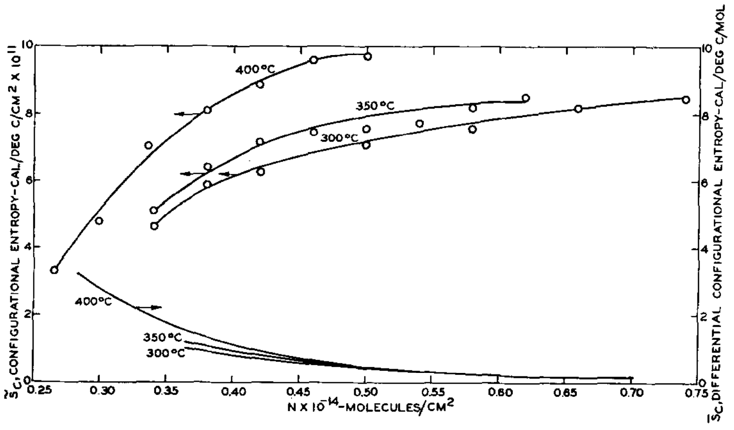

FIG. 5. Configurational entropy $\tilde{S}_c$ and $\bar{S}_c$ as a function of surface coverage ($NH_3$ on $Al_3O_2$).

In Fig. 5, $\tilde{S}_c$ (eu/cm²) is plotted against surface coverage $N$ (molceules/cm²), for the three temperatures. Each point on these curves corresponds to an equilibrium pressure which determines the coverage. It will be noted that at low coverages the entropy is low and is rising. This is the region of steepest descent of the adsorption site energies, where the adsorbing molecules would be expected to have the least choice of adsorption sites. With increasing coverage, configurational entropies increase and finally tend to level out as would be expected from the physical picture for an exponential distribution of site energies. As the temperature is decreased, at constant coverage, the configurational entropy decreases as a result of less scattering by thermal agitation.

Also shown in Fig. 5 are the partial molal configurational entropies, $\bar{S}_c = \partial\tilde{S}_c/\partial n$, where $n$ is the number of moles adsorbed per cm². These curves were obtained by graphical differentiation of $\tilde{S}_c$. The partial molal configurational entropies are small, never exceeding approximately 3 eu/mole. If they were not, the values calculated could be used in Eq. (4) and the entire procedure of Section III repeated until final calculated values showed no further change. As explained previously, the deviations of the calculated from the experimental isotherms were not considered sufficient to warrant going through this process of iteration.

In Fig. 6, the molal configurational entropies, $\tilde{S}_c/n$, are plotted against surface coverage. As would be expected from the physical picture, these entropies rise to a maximum from low coverages and then decline slowly.

Also shown in Fig. 6 are the molal con-

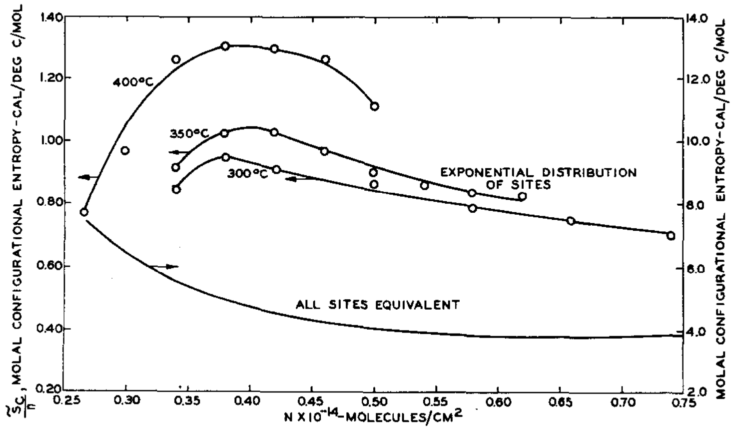

FIG. 6. Molal configurational entropy—$NH_3$ on $Al_2O_3$—as a function of surface coverage.

figurational entropies that would have been obtained if all adsorption sites had possessed the same adsorption energy. They are plotted on a scale ten times that of the curves for an exponential distribution of adsorption energies, and are four- to tenfold greater than those for an exponential distribution. The value of $N_0$, the total number of adsorption sites, was estimated roughly for this calculation by expressing the distribution function in the form:

$$\int_0^\infty \frac{dN}{N_0} = \int_0^\infty \left(\frac{0.1425}{N_0}\right) \exp\left(-0.0544U_0\right) dU_0 = 1$$

where $\int_0^\infty dN/N_0$ has been normalized.

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