aromatic nucleus and the acceptor molecule.[8,18] Although the points for the hexaethylbenzene complex do not lie close to the straight lines of Figs. 1 and 2, it is obvious that the general relationship concerning the variations in ΔF, ΔH and ΔS probably can be extended to include the hexaethylbenzene case. The relatively small negative value of ΔF for this complex is matched by those for ΔH and ΔS. In other words it would appear, in the light of the small magnitude of the value for ΔS, that in this complex the iodine component has not penetrated the steric barrier. Rather it must interact feebly with the π-electrons of the ring at a distance away from them which is sufficiently great to provide for smaller heat and entropy differences between the complex and its components than is observed for a similarly constituted non-hindered donor.

One point concerning the hexaethylbenzene complex which remains unexplained is the fact that its ultraviolet absorption maximum appears at about the same wave length as that for hexamethylbenzene.[8,18] In general the position of the maximum shifts toward the visible as the complex becomes more stable. On this basis the $\lambda_{\text{max.}}$ value for the hexaethylbenzene complex should appear much further toward the ultraviolet region than it actually ($\lambda_{\text{max.}}$ 375 mμ) does. It is obvious from the present work that this anomaly cannot be explained through consideration of heat or entropy effects.[19]

The thermodynamic data for the *sym*-tri-*t*-butylbenzene complex fit the linear plots of Figs. 1 and 2 quite well. However the ΔF value in this case is much less than those for the mesitylene and *sym*-triethylbenzene complexes. Since toluene, ethylbenzene and *t*-butylbenzene all show the same tendency for halogen interaction,[8] it seems that the rather low stability of the *sym*-tri-*t*-butylbenzene complex must be accounted for in terms of unfavorable steric effects of the three bulky alkyl groups in the donor molecule. This effect is even more apparent in the case of the iodine monochloride–*sym*-tri-*t*-butylbenzene complex.[17]

While it is impossible to assert with certainty that small-sized alkyl substituents offer no steric inhibition to complex formation, a consideration of molecular models for the polymethylbenzenes suggests that no marked steric barrier toward interaction exists even when the acceptor molecule is as large as iodine. This conclusion is based on the assumption that in the complex the acceptor lies above the ring plane of the donor.[4] It is interesting that there are indications of a linear variation in the ΔF values for complexes of polymethylbenzenes and halogen acceptors with those for a variety of other types of acceptors.[4] These facts suggest that the ΔF values (except in the most unfavorable steric situations in which the closeness of approach of donors and acceptors is not controlled primarily by electronic factors) are reasonable standards for the comparison of electronic influences of alkyl substituents on the π-electron density of the aromatic nucleus.

Acknowledgment.—The authors are indebted to Research Corporation for a grant in support of this research.

DAVIS, CALIFORNIA

[18] M. Tamres, D. R. Virzi and S. Searles, THIS JOURNAL, **75**, 4358 (1953).

[19] Recently J. S. Ham, *ibid.*, **76**, 3875 (1954), has studied the spectra of the hexaethylbenzene–iodine complexes at room temperature and liquid nitrogen temperatures and has found that temperature reduction causes a marked shift of $\lambda_{\text{max.}}$ to the ultraviolet. He has suggested that different types of complexes exist at the two temperatures. It is not yet clear how the steric effects of the ethyl groups might be manifested in the formation of the two types of complex.

CONTRIBUTION FROM THE COLLEGE OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE UNIVERSITY]

Thermodynamic Properties of Neon Adsorbed on Titanium Dioxide[1]

BY R. J. TYKODI,[2] J. G. ASTON AND G. D. L. SCHREINER[3]

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The heat capacity of neon adsorbed on TiO_2 has been determined, in the region below the monolayer, for three surface concentrations, in the temperature range 16 to 30°K. Isotherms have been determined at 30.00 and 45.93°K. Isosteric heats of adsorption have been determined calorimetrically, and differential and integral entropies of adsorbed neon have been calculated at 30°K. The zero-point entropy calculated for the three coverages was found to be essentially zero, within experimental error.

Calorimetric studies of simple gases adsorbed on non-porous media yield basic facts about adsorption systems which any serious theory of adsorption must take into account. The number of such studies is still relatively small.[4–7] The present paper deals with neon adsorbed on titanium dioxide (rutile).

Experimental

Materials.—The neon was from a cylinder of reagent neon purchased from the Air Reduction Sales Company,

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

[5] J. G. Aston, G. Szasz and G. Kington, THIS JOURNAL, **73**, 1937 (1951).

[6] J. Morrison, J. Los and L. Drain, *Trans. Faraday Soc.*, **47**, 1023 (1951).

[7] L. Drain and J. Morrison, *ibid.*, **48**, 1 (1952).

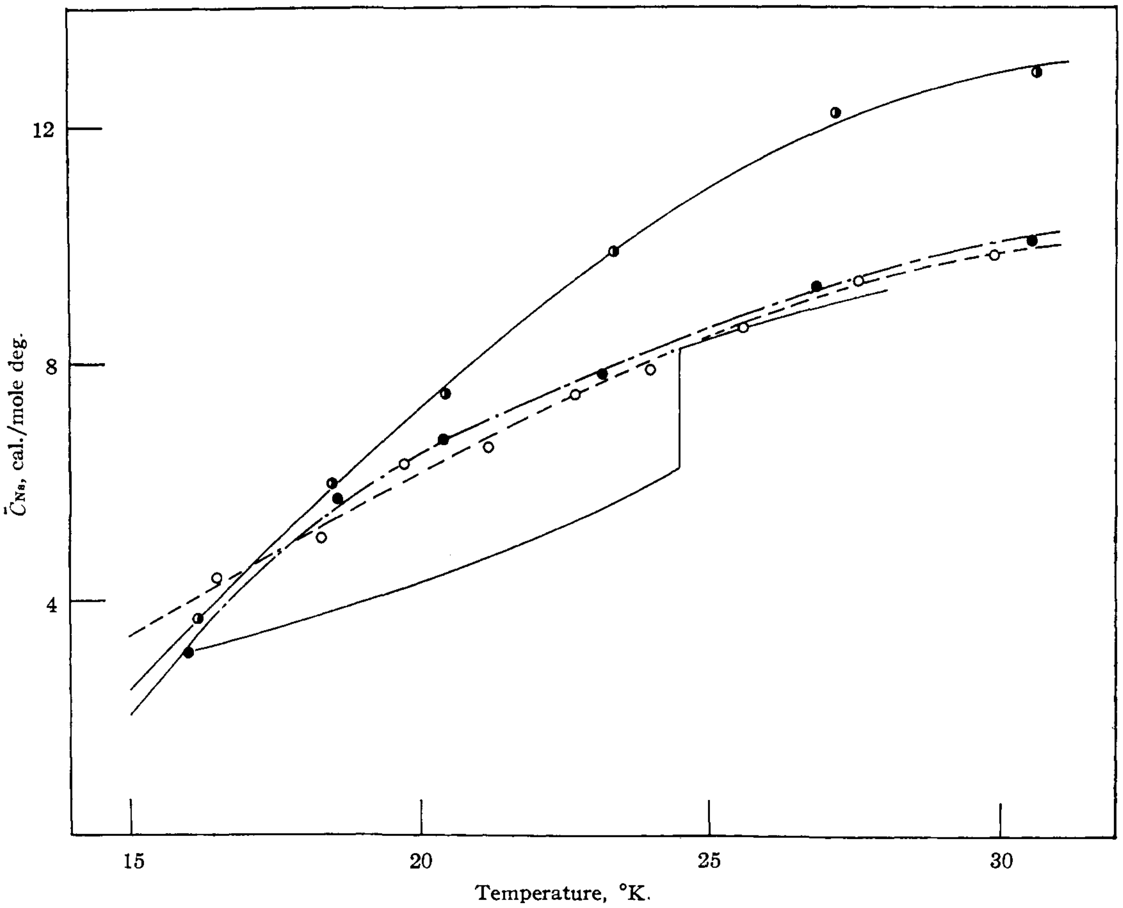

Fig. 1.—Molar heat capacity of adsorbed neon: ◑, 0.101; ●, 0.192; ○, 0.332 cm.^{3}/m.^{2}-STP; bulk neon, —.

Jersey City, N. J. A mass spectrometric analysis furnished with the cylinder indicated the presence of 0.02 ± 0.015 mole % helium as a trace impurity; no other impurities were revealed by the analysis. Prior to entering the adsorption calorimeter the neon was passed over charcoal cooled in liquid nitrogen.

The titanium dioxide used in the calorimeter was part of a sample—code MP 812—of rutile donated by the National Lead Company, South Amboy, N. J., through the courtesy of Dr. W. K. Nelson. The surface area of the rutile as determined by the BET nitrogen adsorption method was 64.0 m.^{2}/g.

The calorimeter used in the present study was the adiabatic adsorption calorimeter described by Morrison and Szasz[4] and used recently by Aston and co-workers.[5,8] The calorimeter was charged with 72.0 g. of the TiO_2 mentioned previously (64 m.^{2}/g.). Prior to beginning the adsorption measurements the adsorbent was outgassed at room temperature until the residual pressure in the calorimeter was less than 1×10^{-6} mm.

Pressure measurements were made in a 12.5 mm. diameter mercury manometer using the Société Génévoise comparison cathetometer described in a previous publication.[9]

Measurement of the Heat Capacity.—For the heat capacity of the total system C_{tot} the following form was assumed

$$C_{tot} = \Delta Q/\Delta T = C_{cal} + C_{pG} + C_{N_s} - (q_{st}/22414)\Delta V/\Delta T - V_{cal}(\Delta P/\Delta T) \quad (1)$$

where

Q = heat supplied

C_{cal} = heat capacity of the calorimeter filled with adsorbent but with no adsorbed gas

C_{pG} = heat capacity at constant pressure of the gas in the dead space of the calorimeter

C_{N_s} = heat capacity of the adsorbed material at constant amount adsorbed

V = amount adsorbed in cm.^{3} at S.T.P.

V_{cal} = volume of the dead space in the calorimeter

P and T = the pressure and temperature, respectively

The desorption correction to the heat capacity amounted to 14% of C_{tot} for the highest coverage (0.332 cm.^{3}/m.^{2}-S.T.P.) at 30°K. and was known to 0.6% (±4 cal./mole), the isosteric heat of adsorption q_{st} being calculated from measured heats of adsorption. The expected uncertainty in C_{N_s}, from all causes, for the lowest and highest coverages at 16°, 30°K. was 5.2, 1.6% and 1.4, 0.8%, respectively. It was found that when the pressure in the calorimeter was less than approximately 1 mm. the time for equilibrium after a heating period was quite long—a matter of hours. No serious difficulty was encountered in the measurements for the coverages reported; however, in the course of measurements at lower coverages, where the pressures were much less than 1 mm., it was found that small warm drifts persisted for more than two hours. A formal calculation of the heat capacity of the adsorbed neon yielded extremely high, non-reproducible values (15–30 cal./mole). The interpretation adopted was that, due to local overheating, molecules were being distilled from high energy (absolute value) sites to sites of lower energy—the change in pressure during the heating period was very small, indicating that but few molecules were being driven off into the gas phase. Because of the very low pressure in the calorimeter the route back to an equilibrium configuration via the gas phase (after a heating period) was seriously impaired. The net consequence of such a situation was that the system, on a short time basis, behaved as a heat sponge, soaking up inordinate amounts of energy. Of course, if one waited a sufficient length of time, the excess heat absorbed would gradually be liberated as the system found its way back to an equilibrium configuration, and the heat capacity calculated for the system would have a smaller, more reasonable value.

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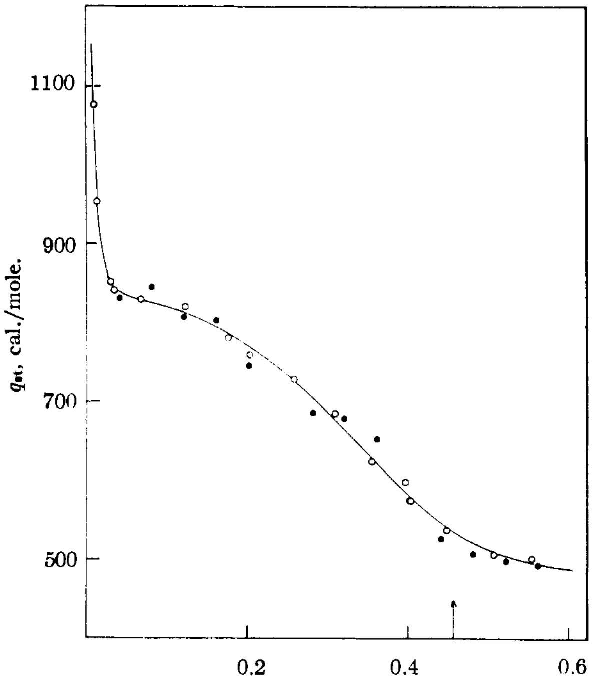
(8) G. L. Kington and J. G. Aston, THIS JOURNAL, **73**, 1929 (1951).

(9) S. V. R. Mastrangelo and J. G. Aston, *J. Chem. Phys.*, **19**, 1370 (1951).



V, cm.^{3}/m.^{2}-STP.

Fig. 2.—Isosteric heats of adsorption: ○, calorimetric, ●, calculated; 30°K.; q_{st}(liq.) = 400 cal./mole.

In fact, corresponding warm drifts were always observed in such cases.

In an attempt to arrive at an estimate of the requirements for equilibrium, an equilibrium index dependent on the time that the system was drifting between heating periods, on the number of gas molecules striking unit area in unit time, and on the fractional rise in temperature was constructed, *i.e.*, $I \equiv t(P/T^{1/2})\,(T/\Delta T)$, where t is time in minutes, P is pressure in mm., T is temperature in degrees Kelvin, and ΔT is the temperature rise. The variables were evaluated at the end of each heating period-drift. It was found that for the data reported the values of I were all greater than 75, whereas for the very low coverage, non-reproducible data the values of I were as low as 1–10, there being a very crude correlation between the excess heat capacity over the expected and the smallness of the index I. Experimentally determined values of the molar heat capacity of adsorbed neon are shown in Fig. 1; heat capacity data for bulk neon taken from the measurements of K. Clusius[10] are included for comparison.

Heat of Adsorption Measurements.—For the heat of adsorption measurements increments of gas ranging from 60 to 250 cm.^{3} at S.T.P. were admitted to the calorimeter, and the temperature rise under adiabatic conditions was measured. The appropriate form for calculating the isosteric heat of adsorption q_{st} was assumed to be

$$q_{st}/22414 = (C_{cal} + C_{pG} + C_{\mathrm{Ne}})(\Delta T/\Delta V) - V_{cal}(\Delta P/\Delta V) \qquad (2)$$

The calorimeter was cooled between increments so that the mean temperature for each rise was approximately 30°K.

Figure 2 is a plot of q_{st} *vs.* amount adsorbed. The estimated accuracy is ±4 cal./mole. From pressure measurements made during the heat capacity and heat of adsorption measurements isotherms were deduced at 29.00 and 31.50°K. by means of a Clausius–Clapeyron type of relationship, *i.e.* $(\partial \ln P/\partial T) = q_{st}/RT.^2$ Since the experimentally determined points were seldom as much as a few tenths of a degree from the chosen isotherm temperatures and the difference in temperature of the two isotherms is 2.50°, a calculation of the heat of adsorption from the isotherms, using an integral form of the Clausius–Clapeyron type relation, should serve as a useful check on the consistency of the heat of adsorption and pressure measurements. The calculated values of the isosteric heat of adsorption are included in Fig. 2; they agree satisfactorily with the calorimetrically measured heats, however, we hasten to add that the latter have by far the greater accuracy.

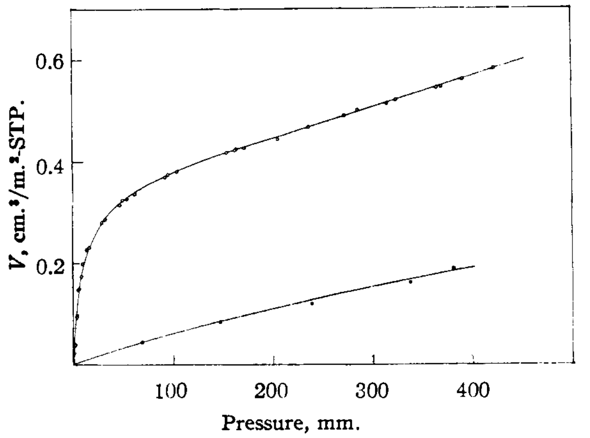


Fig. 3.—Isotherms: ○ (top curve, 30.00°K.; ● (bottom curve), 45.93°K.

Isotherms.—From pressure measurements made during the heat capacity and heat of adsorption measurements an isotherm was deduced at 30.00°K. An additional isotherm at 45.93°K. was measured directly. The two isotherms are shown in Fig. 3. A BET plot of the 30.00°K. data (P_0 = 1640 mm.)[11,12] yielded a value for the monolayer capacity of V_m = 0.456 cm.^{3}/m^2. – S.T.P.

Calculation of the Zero-point Entropy.—For adsorption systems the following relations hold for molar $\tilde{S}$ and differential molar $\bar{S}$ entropy of the adsorbed material[7,13]

$$\tilde{S} = \tilde{S}_0 + \int_0^T (\tilde{C}_{\mathrm{Ne}}/T)\,\mathrm{d}T \qquad (3)$$

$$\tilde{S} = \tilde{S}_{\mathrm{G}}(T,P) - (1/TV)\int_0^V q_{st}\mathrm{d}V - (R/V)\left[\int_0^V \ln p\,\mathrm{d}V - V\ln P\right] - (\alpha/V)\int_0^V P\,\mathrm{d}V \qquad (4)$$

$$\bar{S} = \tilde{S}_{\mathrm{G}}(T,P) - q_{st}/T - \alpha P \qquad (5)$$

$$\tilde{S} = (1/V)\int_0^V \bar{S}\,\mathrm{d}V \qquad (6)$$

$$\tilde{S}(V_2) = \frac{1}{V_2}\left\{ V_1\tilde{S}(V_1) + \int_{V_1}^{V_2} \bar{S}\,\mathrm{d}V \right. \qquad (6')$$

and

$$\tilde{S} = -R[\ln\theta + (1-\theta/\theta)\ln(1-\theta)] \qquad (7)$$

where $\tilde{S}_{\mathrm{G}}\,(T, P)$ is the molar entropy of an ideal gas at temperature T and pressure P, $\tilde{S}_0$ is the molar zero-point entropy, and $\alpha = 27RT_c^3/32P_cT^3$ (modified Berthelot equation of state). Equation 7 is an expression for the configurational entropy of N indistinguishable molecules distributed on Z indistinguishable sites with no interactions between the adsorbed molecules; $\theta \equiv N/Z = V/V_m$.

Equation 4 is readily obtained by substituting from eq. 5 into eq. 6; it is not necessary or desirable to introduce the concepts of spreading pressure and area into the derivation of eq. 4.

By using eq. 3, 4 and 6′ it is possible to evaluate the zero-point entropy. In the integration of $\tilde{C}_{\mathrm{Ne}}/T$ it is assumed that below 16°K. the heat capacity of the adsorbed neon was that appropriate to an isotropic three-dimensional oscillator; thus the form actually used was

$$\tilde{S} = \tilde{S}_0 + \int_0^{16} [\tilde{C}(\mathrm{osc})/T]\,\mathrm{d}T + \int_{16}^{T} (\tilde{C}_{\mathrm{Ne}}/T)\mathrm{d}T \qquad (8)$$

The isosteric heat of adsorption was assumed to have the following limiting value at zero coverage: $q_{st}(0)$ = 1530 cal./mole; the 30°K. isotherm was taken as linear over the

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(10) K. Clusius, *Z. physik. Chem.*, **B31**, 459 (1936).

(11) F. Henning and J. Otto, *Physik. Z.*, **37**, 633 (1936).

(12) J. Verschaffelt, *Comm. Leiden*, *Suppl.* 64d (1928).

(13) T. L. Hill, *J. Chem. Phys.*, **17**, 520 (1949).

range 0.00–0.04 cm.^{3}/m.^{2} – S.T.P. The entropy calculations, based upon eq. 3, 4 and 6′, are summarized in Table I along with the estimated errors. Within experimental error there appears to be no zero-point entropy.

Figure 4 is a plot of differential and integral entropy *vs.* amount adsorbed at 30.00° K.

TABLE I

ZERO-POINT ENTROPY CALCULATIONS (UNITS, CAL./MOLE DEG.)

V, cm.^{3}/m.^{2}-S.T.P.	0.101	0.192	0.332
$\int_{16}^{30} (\bar{C}_{N_s}/T)\,dT$	5.44 ± 0.104	4.53 ± 0.058	4.41 ± 0.034
$\int_{0}^{16} [\bar{C}(\text{osc})/T]dT$	1.62 ± .083	1.52 ± .048	1.81 ± .022
$\tilde{S}$ (30°K.)	6.72 ± .42	6.66 ± .29	6.62 ± .24
$\tilde{S}_0$	−0.34 ± .61	0.61 ± .40	0.40 ± .30
$\tilde{S}_0$ [eq. (5)]	4.56	3.36	1.80

Discussion

The results of the heat capacity measurements and zero-point entropy calculations are qualitatively in accord with the findings of Morrison and co-workers[6,7] for argon adsorbed on TiO_2. The heat capacity of adsorbed neon at low coverage is considerably in excess of the heat capacity of bulk neon. Above 20°K. the heat capacity of adsorbed neon exceeds the maximum heat capacity of a three-dimensional oscillator; the conjecture of Morrison, *et al.*,[6] that the high heat capacities of adsorbed argon at low coverage are related in some way to a transition from localized adsorption to non-localized adsorption seems to be the best available explanation for the similar behavior of adsorbed neon (however, see the above discussion of the effect of lack of equilibrium). Also, the heat capacity curves at various coverages appear to cross in the neighborhood of 18°K. as is the case for argon on TiO_2.

The zero-point entropy calculations yield results similar to those for the systems nitrogen–TiO_2[5] and argon–TiO_2,[7] *i.e.*, essentially no zero-point entropy. Heterogeneity of the adsorbent surface together with attractive nearest neighbor interactions between the adsorbed molecules would be expected to reduce the value of the zero-point entropy somewhat below that calculated from eq. 7. However, one should carefully note that failure to obtain equilibrium in the heat capacity measurements would lead to high apparent heat capacities and, thus, to extrapolations which would imply lower zero-point entropies than the true ones.

An interesting feature of the present study is the sharp fall off of the differential and integral entropy at low coverage (Fig. 4). One of the referees of this paper pointed out that it is thermodynamically necessary that both integral and differential entropy (molar) go to + ∞ at zero coverage.[13] The differential and integral entropy curves will therefore intersect at some very low coverage; eventually, as zero coverage is approached, both curves will proceed toward + ∞.[14] For monolayer adsorption on a surface composed of sets of sites characterized by different energies of adsorption the expression analogous to eq. 7 for the entropy of the system is

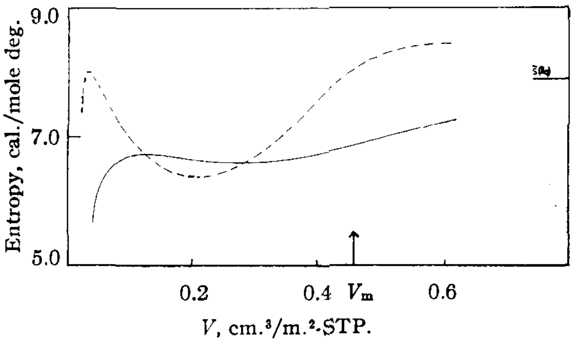

Fig. 4.—Differential and integral entropy of adsorbed neon: $\tilde{S}$, —; $\bar{S}$, - - -; 30°K.

$$\tilde{S} = -(R/\theta)\Sigma F_i\{\theta_i \ln \theta_i + (1 - \theta_i) \ln (1 - \theta_i)\} \quad (9)$$

where F_i is the fraction of the surface covered by sites of the i-th kind, θ_i is the fractional occupation of the i-th kind of sites, and $\theta \equiv \Sigma F_i\theta_i$. If the various sets of sites are filled one at a time, eq. 9 yields an entropy which oscillates with coverage. The behavior of the neon–TiO_2 system at low coverage may be partly attributable to some such cause; the steep portion, at low coverage, of the heat of adsorption plot (Fig. 2) indicates strong heterogeneity of the adsorbent surface.

Finally, it has become customary to identify the minimum in the plot of integral entropy *versus* coverage with V_m, since, for strong surface binding, $V_m(\tilde{S})$ has been found to agree closely with V_m(BET).[7,15] In the present case the two values differ considerably, *i.e.*, $V_m(\tilde{S})$ = 0.28 cm.^{3}/m.^{2}-S.T.P. and V_m(BET) = 0.46 cm.^{3}/m.^{2}-S.T.P. The monolayer capacity to be expected from the BET area (determined with nitrogen) and liquid density (30°K.) is V_m(liq) = 0.36 cm.^{3}/m.^{2}-S.T.P.

STATE COLLEGE, PA.

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[14] Needless to add the entropy must be zero at 0°K. if there is *true equilibrium.*

[15] T. L. Hill, P. H. Emmett and L. Joyner, THIS JOURNAL, **73**, 5102 (1951).