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First Adsorbed Layer of Helium

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The discrepancy between the force constants for the adsorption of helium found by Bowers at high saturations using the Frenkel isotherm, and Strauss at medium saturations using the Brunauer-Emmet-Teller theory creates some doubts whether or not the amount v_m derived from the BET isotherm in the saturation range $P/P_0=0.02$–0.2 represents in the case of helium the amount adsorbed in the first layer. Adsorption measurements at very low saturations show a distinct plateau in the 2°K isotherm at $P/P_0\sim 10^{-7}$ for $\sim$0.5 cm^3/m^2 adsorbed suggesting the completion of the first layer already at these low saturations. At 4.2°K this plateau coalesces with the usual point B of sigmoid isotherms, where $\sim$0.8 cm^3/m$^2=v_m$ is adsorbed.

It is therefore proposed to interpret v_m as the amount adsorbed with $(\bar{E}_a-E_0)>RT$ ($\bar{E}_a$ being the differential energy of adsorption, E_0 the energy of vaporization of the bulk liquid), which coincides with the completion of the first layer only for (E_1-E_0) between about $2RT$ and $8RT$.

THE analysis of the data on the adsorption of helium at liquid helium temperatures using the Brunauer-Emmet-Teller (BET) theory[1–4] led to the result that the quantity v_m, supposed to be the amount of helium adsorbed in the first layer, exceeded several times the amount calculated for the first layer from the density of the liquid and the known surface area. One layer with the density of the liquid contains about 0.25 cm^3 at standard temperature and pressure per square meter, whereas values for v_m between 0.6 and 0.9 cm^3/m^2 were found. Since liquid helium is blown up by zero point energy to almost 4 times the volume of close-packed atoms, this seemed not impossible.

Strauss[5,6] performed a comprehensive study of the adsorption of helium on Jeweller's Rouge (used also by Frederikse[3] and Long and Meyer[4]) in the temperature range from 1.60 to 4.21°K. He evaluated his results in the range of saturation of 5–25% in the standard manner with the help of the BET-isotherm[7]:

$$\left(\frac{P}{P_0-P}\right)\frac{1}{v}=\frac{1}{v_mC}+\left(\frac{C-1}{Cv_m}\right)\frac{P}{P_0}, \tag{1}$$

where P is the equilibrium pressure for the amount v adsorbed, P_0 the vapor pressure of the bulk liquid at the temperature of the experiment. v_m is the amount of helium forming the first adsorbed layer in the BET model, and C is a constant representing the energy of adsorption. In the approximations of the BET model,

$$\ln C=(E_1-E_0)/RT, \tag{2}$$

E_1 being the energy (or heat) of adsorption for the first adsorbed layer, E_0 the energy (or heat) of vaporization of the bulk liquid. An abstract of Strauss' results is given in Table I.

Bowers[8] measured the adsorption of helium at high saturations ($P/P_0=0.7$–0.99) using a microbalance. He tested the isotherm derived by Frenkel,[9] Halsey,[10] and

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[1] W. H. Keesom and J. Schweers, Physica **8**, 1020, 1032 (1941).

[2] Schaeffer, Smith, and Wendell, J. Am. Chem. Soc. 71, 863 (1949).

[3] H. P. R. Frederikse, Physica **15**, 860 (1949); thesis, Leiden, 1950 (unpublished).

[4] E. Long and L. Meyer, Phys. Rev. **76**, 440 (1949).

[5] A. Strauss, thesis, Chicago, 1956 (unpublished); reviewed in reference 6.

[6] E. Long and L. Meyer, Advances in Phys. **2**, 1 (1953).

[7] Brunauer, Emmet, and Teller, J. Am. Chem. Soc. **60**, 309 (1938). See also S. Brunauer, *The Adsorption of Gases and Vapours* (Oxford University Press, New York, 1945); P. H. Emmet, *Advances in Catalysis*, edited by Frankenburg, Komarewski, and Rideal (Academic Press, Inc., New York, 1948), Vol. I, p. 65.

[8] R. Bowers, Phil. Mag. 44, 485 (1953).

[9] J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, New York, 1946), p. 332.

[10] G. D. Halsey, J. Chem. Phys. **16**, 931 (1948); *Advances in*

TABLE I. Strauss' results for the adsorption of helium on Jeweller's Rouge in terms of the BET isotherm, Eq. (1).

T	v_m	$(P/P_0)_{vm}$	$1/\sqrt{C}$	$\log_{10}C$	$\left(\frac{E_1-E_0}{RT}\right)$	E_1-E_0
1.60	0.79	0.051	0.052	2.57	5.9	18.7
1.80	0.77	0.052	0.055	2.52	5.8	20.7
2.01	0.74	0.052	0.050	2.60	6.0	23.9
2.14	0.74	0.052	0.053	2.56	5.9	25.1
2.25	0.72	0.053	0.054	2.54	5.8	26.2
2.42	0.71	0.059	0.060	2.43	5.6	26.9
3.02	0.66	0.054	0.055	2.52	5.8	34.7
4.21	0.60	0.059	0.064	2.38	5.4	45.8

Hill[11] from the assumption that the Van der Waals energy of the wall decreasing with the third power of the distance is simply superimposed on the heat of vaporization:

$$-\ln(P/P_0)=k/\nu^3. \qquad (3)$$

(ν is the number of statistical layers adsorbed: $\nu=v/v_m$.) He found that Eq. (3) is obeyed within experimental errors. According to McMillan and Teller,[12,13]

$$k=\tfrac{1}{6}\pi(E_1-E_0)/RT\sim\tfrac{1}{2}\ln C. \qquad (4)$$

The value of k that Bowers derived from his data is ~ 25 near the λ point of helium (2°K). Since relation (4) is only a zeroth approximation, not more than an order-of-magnitude agreement should be expected. However, the discrepancy between $\frac{1}{2}\ln C\cong 2.8$ derived by Strauss from a BET plot and given in column 5 of Table I and Bowers' value of 25 is far too great to be accounted for by approximations in the theory or by experimental errors.[14] The question therefore arises what causes this striking difference.

Table I shows $(P/P_0)_{vm}\sim 0.05$. Bowers' value of $k\sim 25$ would lead for $\nu=1$ to $(P/P_0)_{vm}\sim 10^{-10}$. It is true that extrapolating Eq. (3) into this region exceeds its range of validity; still it should provide an order-of-magnitude estimate. The value $(P/P_0)_{\nu=1}\sim 10^{-10}$ indicates that the first layer of helium might be completed at saturations much lower than hitherto investigated, even if one takes into account that the energy necessary to produce an eventual abnormally high density in the first layer consumes a considerable part of the energy provided by the Van der Waals forces of the wall, increasing thereby the value of $(P/P_0)_{\nu=1}$ tremendously. An attempt was therefore made to extend adsorption measurements to the range of extremely low saturations.

In principle standard adsorption technique was used as described in detail, e.g., by Frederikse[3] or Strauss,[5] or Inghram, Long, and Meyer[15] and Keesom and Schweers.[1] The lowest pressures were measured with a liquid nitrogen trapped RCA 1949 ion gauge empirically calibrated for helium.[16] Higher pressures were measured with a 2 in. long Octoil-S oil manometer of 5-mm o.d. Pyrex tubing which had only few cm^3 dead space, and could be read with a traveling microscope to 0.001 mm. The main deviation from standard procedure consisted in the possibility of moving the adsorption bulb inside the cryostat. The 1-mm i.d. stainless steel capillary which connected the bulb in the cryostat with the measuring line left the top of the cryostat through a rubber disk between Teflon washers which ensured a perfectly tight cryostat and allowed easy gliding of the Apiezon-greased capillary through the seal.

Every time before gas was added to the system during a run, the adsorption bulb was pulled up out of the liquid helium into a region of the cryostat where the temperature was known to range between 10–20°K in order to prevent added gas from being condensed in the capillary or at the entrance of the bulb. After adding a pipette of gas, the bulb was lowered back into the liquid until its upper end was flush with the liquid level. It was hoped that in this way all the gas present in the system would have a somewhat equal chance to reach all parts of the adsorbing surface. Equilibrium was reached with this method within 1 hour or less. In a first series of experiments the small adsorption bulb with Jeweller's Rouge of 1.7 m^2 surface used previously by Long and Meyer[4] and Inghram, Long, and Meyer[15] was employed. The values measured were quite reproducible; however, a too small temperature dependency at the lowest pressures ($P<10^{-5}$ mm) suggested incomplete equilibrium, probably because some inner parts of the surface of the powder were not always reached by the condensing gas.

The experiments were therefore repeated with a loosely coiled gold foil of thickness 5×10^{-4} in. and surface area 0.090 m^2 as adsorbent. In order to procure a surface as homogeneous as possible, the foil was transformed into cube texture[17] by first casting a small strip of gold on a cold steel plate in order to guarantee fine-grained material, then rolling to 3–5 $\times 10^{-4}$ in. thickness causing a reduction of more than 99%, and finally annealing at 1000°C for 2 hours. X-ray Laue patterns as well as etch pictures showed

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Catalysis, edited by Frankenburg, Komarewski, and Rideal (Academic Press, Inc., New York, 1952), Vol. IV, p. 259.

[11] T. L. Hill, *Advances of Catalysis*, edited by Frankenburg, Komarewski, and Rideal (Academic Press, Inc., New York, 1952), Vol. IV, p. 225.

[12] W. G. McMillan and E. Teller, J. Chem. Phys. **19**, 25 (1951); J. Phys. & Colloid Chem. **55**, 17 (1951).

[13] If Eq. (4) is valid, isotherms (3) and (1) yield essentially the same value of P/P_0 for $\nu=1$. In this case, Eq. (1) reduces to $1/C=P^2/(P_0-P)P_0\approx(P/P_0)^2$ as long as $(C-1)/C\approx 1$, or $(P/P_0)_{\nu=1}\approx 1/\sqrt{C}$ and $\ln(P/P_0)=-\frac{1}{2}\ln C$; whereas (3) yields $\ln(P/P_0)_{\nu=1}=-k$.

[14] The fact that Strauss used Jeweller's Rouge whereas Bowers used Al foil as adsorbent cannot cause this discrepancy. Frederikse[3] found no major difference between the adsorption of helium on Jeweller's Rouge and steel. As the metals used were covered with an oxide layer, the adsorption takes place on the surface of an oxide lattice in all these cases.

[15] Inghram, Long, and Meyer, Phys. Rev. **97**, 1453 (1955).

[16] Because of the high ionization potential of helium, the sensitivity of these gauges is only about 0.1 of the standard calibration when used for helium. The clean-up effect caused by ions being absorbed by the walls was corrected for by measuring the change of reading with time when the gauge was closed off.

[17] See C. S. Barrett, *The Structure of Metals* (McGraw-Hill Book Company, Inc., New York, 1952), p. 494.

that the foil consisted of more than 98% cube texture, the whole surface showing practically only the 100 face.

The accuracy of these measurements was only about ±5%. At the lowest pressures the pressure measurements themselves are uncertain to this amount, whereas at the higher pressure the dead space corrections contribute mostly to the inaccuracy. The correction for thermomolecular pressure differences were applied in the manner described by Keesom.[18] The geometrical surface of the gold was used in the evaluation since the results were, within the errors, equivalent to those obtained with the powder of known surface area and also to those of Schweers.[1] The results are given in Figs. 1 and 2. The ordinate in both figures is the amount adsorbed in cm³ at standard temperature and pressure per square meter of surface. In Fig. 1 the abscissa is the saturation P/P_0 in units of 10^{-4}. Figure 1 looks rather similar to the Fig. 2 of Keesom and Schweers[1] and deviates from the usual isotherms for physical adsorption only insofar as the point B where the isotherm flattens out, lies at very low values of P/P_0.

The same data are plotted in Fig. 2 with $\log(P/P_0)$ as abscissa in order to show also the low-pressure range in detail. The striking feature of this plot is the clear indication of a plateau, especially in the 2°K isotherm, starting at an adsorption of about 0.5 cm³/m². This effect appears in a much more pronounced form in the original data—the semilogarithmic representation of Fig. 2 tends to smear out the effect—because adding 0.13 cm³/m² changed P/P_0 in this range by a factor of more than 200, whereas otherwise this amount of gas would cause a change by a factor of at most 5–8. This result seems to indicate that the isotherm is step-wise and actually consists of two superimposed Langmuir type isotherms. If the first plateau is interpreted as the completion of the first layer, the second one—which is smeared out in the semilog plot of Fig. 2 but appears very clearly in Fig. 1—should then be the completion of the second layer. The v_m determined by Strauss in the usual way by plotting $P/(P_0-P)v$ against P/P_0 in the range of 2–20% saturation, yielding values equivalent to the second plateau, should then be considered as being due to the completion of the second layer, at about 0.8 cm³/m².

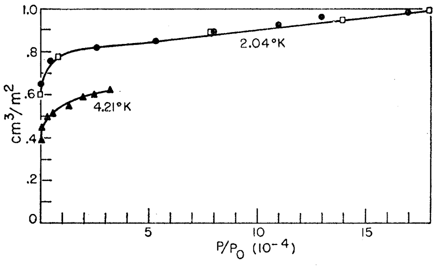

FIG. 1. Amount of helium adsorbed on gold foil of cube texture in cm³ at standard temperature and pressure per square meter, as a function of the saturation P/P_0 at 2.04°K and 4.21°K.

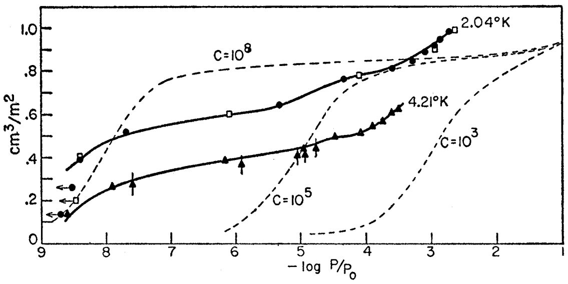

FIG. 2. Amount of helium adsorbed on gold foil in cm³ at standard temperature and pressure per square meter, as a function of $\log(P/P_0)$. Points with dashes: Keesom and Schweers. Dotted curves: BET isotherms with $v_m=0.85$ cm³/m² and $C=10^8$, 10^5, and 10^3 respectively.

The energy of adsorption decreases with the third power of the distance from the wall. Taking this distance proportional to the number of layers—even if such a procedure is somewhat doubtful just for the first layers—it is not surprising that the energy of adsorption derived by Strauss is an order of magnitude less than that found by Bowers. Using the BET theory in the range $P/P_0=0.02$–0.20 leads, in the case of helium, to results where not the wall itself but the wall already covered by the first layer is acting as adsorbent.[19,20]

In order to give comparative values, some BET isotherms are plotted in Fig. 2 as dotted curves for $v_m=0.85$ cm³/m² and $C=10^8$, 10^5, and 10^3 respectively and also Schweers' data for 4.21°K.[21] All BET isotherms being in this region identical with Langmuir isotherms show distinctly different forms than the experimental values. The lowest experimental values are near the points of a BET-isotherm with $C=10^8$ which, according to Eq. (4), is not too different from the force constant found by Bowers.[22]

The 4.2°K isotherm shows equally little resemblance to a BET isotherm; however, the indication of a first plateau became rather weak. Since

$$\frac{d\ln(P/P_0)}{d(1/T)}=\frac{(\Delta\bar{H}_a-\Delta H_0)}{R}, \tag{5}$$

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[18] W. H. Keesom, *Helium* (Elsevier Publishing Company, Amsterdam, 1942), p. 122.

[19] Mastrangelo and Aston[20] had already suggested that the amount v_m derived via the BET theory consists of several layers, probably 3, because by dividing v_m by the amount of helium that a monatomic layer with the density of solid helium would have, they obtained a figure near 3. No direct experimental proof for this hypothesis was given.

[20] S. V. R. Mastrangelo and J. Aston, J. Chem. Phys. **19**, 1370 (1951).

[21] Schweers' data for the lower temperatures are consistently somewhat lower than the values found in this investigation, the difference being about 10–15% which can be due to the combined experimental uncertainties.

[22] The quantity 0.5 cm³/m² adsorbed for the first plateau in the isotherm is still twice the amount one layer with liquid density would contain. If it is identified with the first layer, a considerable part of the Van der Waals energy must have been used for compression.

$\Delta\bar{H}_a$ being the differential heat of adsorption at a certain amount adsorbed, ΔH_0 the heat of vaporization of the bulk liquid, P/P_0 for the first plateau changes much faster with temperature than does $(P/P_0)_{v_m}$, because $\Delta\bar{H}_a$ is considerably greater. The two steps of the 2° isotherm therefore coalesce at higher temperatures.[23]

The data are not accurate enough to derive more than qualitative heats of adsorption. $\Delta\bar{H}_a$ ranges from about 100 cal/mole at 0.5 cm^3/m^2 to 40 cal/mole at 0.8 cm^3/m^2, in qualitative agreement with Fig. 6 of Keesom and Schweers.[1] Equation (4) yields, for 100 cal/mole, $k\sim 10$ and $C\sim 10^8$, which, considering the high density of the first layer, are consistent within the McMillan-Teller approximation with Bowers' value $k\sim 25$ and the dotted BET isotherm in Fig. 2 with $C=10^8$. The value 40 cal/mole at 0.8 cm^3/m^2 is in good agreement with Strauss' data, column 7 of Table I.

These results suggest a reinterpretation of the quantity v_m of the BET theory. It is not the amount adsorbed in the first layer, determined only by geometrical factors, but the amount adsorbed for $(\Delta\bar{H}_a-\Delta H_0)>RT$, or $(\bar{E}_a-E_0)>RT$. The BET theory assumes $(\bar{E}_a-E_0=0)$ for all but the first layer, making both definitions identical. In the famous test case confirming the BET theory, the adsorption of nitrogen near its boiling point (compare reference 7), k equals approximately 3 (compare Bowers, reference 8). By virtue of Eqs. (3) and (4), (E_2-E_0) is about 8 times smaller than (E_1-E_0) and $(\bar{E}_a-E_0)$ becomes smaller than RT just with the completion of the first layer.

In the case of helium, (E_2-E_0) is still considerably greater than RT and therefore v_m is not directly related any more to the completion of the first layer.[24]

Columns 6 and 7 of Table I contain an additional indication that v_m is related to the amount adsorbed for $(\Delta\bar{H}_a-\Delta H_0)>RT$ rather than to the first layer. E_1 is a measure of the Van der Waals attraction of the wall, and should therefore be essentially independent of temperature; consequently E_1-E_0 should vary only very little with temperature. The experimentally determined values of E_1-E_0 are, however, practically proportional to T, and $(E_1-E_0)/RT$ is essentially unaffected by the temperature in the wide range 1.60–4.21°K. Furthermore, if $(\Delta\bar{H}_a-\Delta H_0)$ decreases with d^3 or ν^3 according to Eqs. (3) and (4) and if v_m depends on a certain value of $(\Delta\bar{H}_a-\Delta H_0)/RT$, then v_m should decrease approximately inversely proportional to $T^{\frac{1}{3}}$, which it does.

Stepwise isotherms, as found in these experiments for helium, have been predicted as a consequence of the physical picture underlying the isotherm equation (3).[25] The fact that such steps were not found has been considered as an insufficiency of Eq. (3) and the heterogeneity of the surface has been invoked to explain the absence of steps.[26] Discrete steps are possible only if $(\Delta\bar{H}_\nu-\Delta H_0)-(\Delta\bar{H}_{\nu+1}-\Delta H_0)>RT$. With the exception of helium—and possibly hydrogen—in all cases of simple physical adsorption (A, N_2, O_2) the difference in binding of consecutive layers is a small fraction of RT for all but the first two layers, and steps are bound to be smeared out by fluctuations, even for homogeneous surfaces.

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[23] Attempts to get a still more pronounced step in the isotherm at lower temperatures failed because the pressure of the first step dropped below 10^{-7} mm, the lower limit of somewhat reliable measurements.

[24] The possibility that the BET theory might not be valid for all values of C has already been discussed from a different point of view; compare the review articles by Hill,[11] Emmet,[7] or Brunauer.[7]

[25] Compare Halsey, reference 10.

[26] The experiments with Jeweller's Rouge as adsorbent yielded besides the points at very low pressures essentially the same isotherms, including the step in the 2°K isotherm, showing that the step is not contingent on the more homogeneous surface of the foil.