[CONTRIBUTION FROM THE INSTITUTE FOR THE STUDY OF METALS, UNIVERSITY OF CHICAGO]

The Anisotropy of Nitrogen Adsorption on Single Crystal Copper Surfaces[1]

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Introduction

It has been shown that certain metal crystal faces have higher catalytic activity than others.[1a] Similarly, one would expect the physical adsorption of gases on solids to depend on the distances and geometrical configurations characteristic of different crystal faces. The closest approximation to an ideal surface is probably a plane through a metal single crystal. Until now the heat of adsorption on a definite face of a crystal has not been measured experimentally because ideal plane surfaces large enough to test adsorption theories with available techniques were not available. Suitable single crystal copper surfaces which approach flatness on an atomic scale and are composed of a single species of atoms arranged in a well-ordered surface array have now been successfully prepared and characterized.[2]

Although non-specificity is generally considered characteristic of van der Waal adsorption, ordinarily heats of physical adsorption vary considerably with the amount of gas adsorbed in a manner characteristic of a given adsorbent.[3] Roberts has shown that interaction between adsorbed molecules can lead to a complex variation of heat of adsorption with coverage of the surface even when the adsorption takes place on a uniform plane surface. In addition, the variation of packing of adsorbed molecules, variation of surface electron distribution, and variation in the equilibrium distance of approach of the molecules to the surface, characteristic of different crystal faces may also be important in defining the adsorption potential on a plane uniform surface.

In order to define these effects for a simple gas-surface system, the adsorption isotherms of nitrogen at 78.1, 83.5 and 89.2°K. on single crystal and polycrystal surfaces of copper were determined with a sensitive quartz beam vacuum microbalance.

Experimental

Materials.—The samples were flat single crystal plates of copper carefully prepared by a laborious technique of sectioning and electropolishing. The procedure of preparation and the criteria used to evaluate the success of the preparation are the same as described elsewhere in detail.[2] Adsorption, as well as electron microscope and electron diffraction studies, indicate that (1) the surfaces are essentially flat on an atomic scale, and (2) the surface atoms are arranged in an approximately undistorted lattice characteristic of a given crystal face. It is believed that the experimentally determined values of this study yield heats of adsorption that are characteristic of a surface in which the atoms are arranged in a single known geometric array and where complications from cracks, edges, crevices, pores and grain boundaries are negligible.

Considerable effort was made to evaluate properly the cleanliness and purity of the surface. The latter was insured by starting with high purity copper and purifying it further to 99.996% by careful vacuum casting at 10^{-5} mm.; the chief impurities remaining were aluminum and iron. The aluminum and iron were observed by standard techniques of spectrochemical analysis. Most of the samples were electropolished, washed in water, alcohol and ammonium hydroxide, reduced in hydrogen at 400° and outgassed at 750° to 10^{-7} mm. using barium–aluminum getters. Outgassing the surfaces under these conditions is generally considered to free the surface of chemisorbed hydrogen. It is not unreasonable to disregard also the possibility of contamination of the surface by chemisorbed nitrogen at these temperatures. It should be pointed out that should a chemisorbed monolayer form, particularly of nitrogen, heat of adsorption effects unique for a particular surface structure will very likely persist. In studies of gas adsorption on the (100) face of a single crystal copper surface by low speed electron diffraction it has been reported for a well out-gassed crystal that the surface is covered with a monolayer of a double-spaced face-centered structure, the gas atoms being located directly above the copper atoms.[4]

It is particularly critical to preserve the surface free of contaminants particularly because of its relatively extremely small surface area. Elimination of oxygen contaminations was particularly important. This was accomplished by connecting the reaction volume by a short 20-mm. tube to a large bulb in which freshly formed surfaces of copper were formed periodically during the cooling down period of the sample by evaporating the copper from a small source. Contamination of the sample by evaporated copper was prevented by a suitable system of baffles. Previous to this stage the reactor tube had been baked out at 1000°, the connecting tubes at 550° and the Pyrex envelope containing the balance at 300°. A sealed-off system of this type would preserve a vacuum of 10^{-6} mm. for a week. Samples cooled from the outgassing temperatures to liquid nitrogen temperatures in this manner were tested by exposing to oxygen at 78°K. It has been shown that a stable monolayer of oxygen forms very rapidly on copper surfaces free of oxygen at this temperature.[5] The practically instantaneous and irreversible formation of a stable monolayer of oxide under these conditions was taken to indicate that the cleanliness of the surfaces prepared at 750° was preserved by cooling in this manner to the adsorption temperatures. Adsorption isotherms were also determined for two polycrystalline samples which had been outgassed at 1000° *in situ* in addition to the above treatment. Although the surface was somewhat roughened by this treatment, adsorption isotherms and the heat-coverage plots were essentially unchanged. Samples that were not cooled in the presence of freshly formed copper surfaces did not show any additional irreversible oxygen uptake in pure oxygen at 78°K. It may be noted that although the production and preservation of clean metal surfaces is extremely difficult, by the same token the presence of a clean surface can be rapidly evaluated from its high reactivity.

The gases used were purified in the usual manner except

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(1) Army Air Forces Contract AF-33(038)-6534.

(1a) "Advances in Catalysis," Vol. I, Academic Press, New York, N. Y., 1948, p. 91; H. Leidheiser and A. T. Gwathmey, THIS JOURNAL, **70**, 1200 (1948); **70**, 1206 (1948).

(2) T. N. Rhodin, *J. Appl. Phys.*, **21**, 971 (1950).

(3) H. R. Kruyt and J. G. Modderman, *Chem. Revs.*, **7**, 259 (1930); A. Titoff, *Z. physik. Chem.*, **74**, 641 (1910); J. K. Roberts, *Trans. Faraday Soc.*, **34**, 1342 (1938); J. K. Roberts and W. J. C. Orr, *ibid.*, **34**, 1436 (1938).

(4) E. Schlier and H. E. Farnsworth, *Bull. Am. Phys. Soc.*, **25**, No. 1, 8 (1950).

(5) T. N. Rhodin, THIS JOURNAL, **72**, 5102 (1950).

that considerable effort was made to remove traces of oxygen from the hydrogen and particularly the nitrogen by passing through extended tubes of freshly reduced copper at 500°. All gases were finally dried by passing through clean activated charcoal traps at liquid nitrogen temperatures.

Apparatus.—The adsorption apparatus was a modified version of a differential adsorption microbalance technique.[6] Gas pressures were measured over the range 10^{-6} to 760 mm. with the usual combination of McLeod gage, ionization gage and precision bore manometers containing either dibutyl phthalate or mercury depending on the pressure range. Pressures lower than 10 cm. were observed with a microscope cathetometer. The gages had been cross-calibrated and in the lowest range the pressures could be read with a precision of a 0.01 mm. The vapor pressure of the nitrogen was read continuously with a mercury manometer connected to a bulb containing purified nitrogen immersed in the bath in close proximity to the reactor. Liquid oxygen and nitrogen refrigerants were used to maintain the reactor temperature except at 83.5°K. where the temperature was maintained ±0.05° by controlled pumping on liquid oxygen in a closed system.

The differential adsorption microbalance technique has already been described in great detail by the author.[6] The balance itself has a sensitivity of 10^{-6} g./0.1 mm. vertical displacement of the beam. Making readings with great care it is possible to observe weight changes of 10^{-7} g. $\pm 0.02 \times 10^{-6}$ g. This corresponds to about 10^{-4} cc. (S. T. P.) of nitrogen. The samples of this study consisted of 2 plates (2 cm. × 1.2 cm. × 0.01 cm.) with a total weight of approximately 1 g. and an apparent surface area of approximately 13 cm.^{2}. In order to minimize thermal eddy current effects and to eliminate relatively large buoyancy corrections the balance and the envelope containing it and the hang-downs and samples were designed to preserve as perfect symmetry as possible. Most important of all, both sample and counterweight were maintained at the same temperature during the run. Volumes displaced by sample plate and counterweight were essentially the same, although weight effects occurring on the former were greatly magnified since its surface was 10 to 100 times greater than the highly polished surface of the spherical counterweight. The positive correction for the adsorption occurring on the counterweight was well defined and always much smaller than the observed weight change caused by adsorption on the sample plate itself. These considerations have been discussed at great length. The edge effects of the thin crystals contribute less than 0.6% to the total surface area and have been neglected.

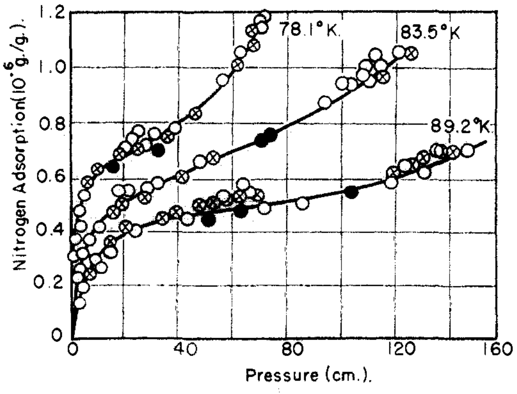

Fig. 1.—Adsorption of nitrogen on electropolished and hydrogen-reduced (110) crystal face of copper at 78.1, 83.5 and 89.2°K. Size of circles indicates error in microweighings. Scatter of points indicates typical distribution: O, sample 1; ⊗, sample 2; ●, desorption points.

All surface area values were obtained by a linear plot of the adsorption data according to the Brunauer–Emmett–Teller[7] equation

$$\frac{x}{V(1-x)} = \frac{1}{V_{m}c} + \frac{(c-1)x}{V_{m}c} \qquad (1)$$

where x is the relative pressure at which volume V(S.T.P.) of gas is adsorbed, V_m is the volume of gas required to form a monolayer, and c is a constant which together with V_m can be determined by substituting the experimental values of V and of x in Eq. (1). Actually in this study the adsorbed gas is weighed and hence V_m is expressed in micrograms. Using the most likely value for the cross-sectional area of the nitrogen molecule (16.1 Å.^{2})[8] the surface areas calculated in this manner were found to check reasonably well with a Harkins–Jura[9] analysis of the same data.

The differential or isosteric heat of adsorption (H) was determined in the usual manner by comparing the pressures of gas (P) in equilibrium with a given weight of gas (a) adsorbed on the surface at three different temperatures (T)

$$[\partial \ln P/\partial(1/T)]_{a} = -H/R \qquad (2)$$

Actually the treatment of Joyner and Emmett[10] was used to calculate the values of (H) for different amounts of adsorbed gas (a). The isotherms of Figs. 1–6 were replotted on a large scale with the logarithm of the pressure (p) as abcissa against the amount of adsorption (a) as ordinate. The ratio of the horizontal distances corresponding to the two pressures, P_2 and P_1, for a given adsorption (a) at two temperatures

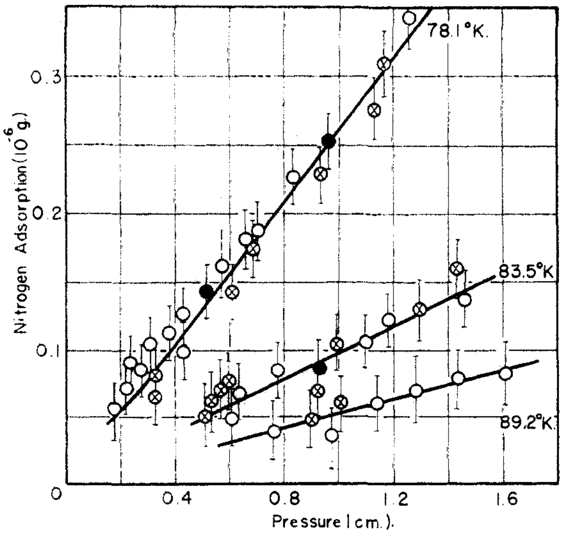

Fig. 2.—Insert from Fig. 1 in low pressure region (symbols as in Fig. 1).

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[6] T. N. Rhodin, This Journal, 72, 4343 (1950).

[7] S. Brunauer, P. H. Emmett and E. Teller, *ibid.*, 60, 309 (1938).

[8] "Advances in Catalysis," Vol. I, Academic Press, New York, N. Y., 1948, p. 77.

[9] W. Harkins and G. Jura, This Journal, 66, 1366 (1944).

[10] L. Joyner and P. H. Emmett, *ibid.*, 70, 2353 (1948).

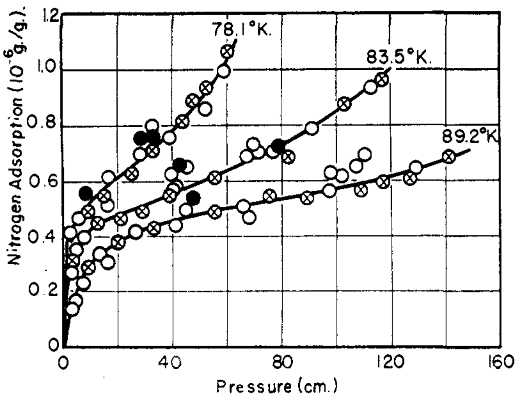

Fig. 3.—Adsorption of nitrogen on electropolished and hydrogen-reduced (100) crystal face of copper at 78.1, 83.5 and 89.2°K.: ○, sample 6; ⊗, sample 7; ●, desorption points.

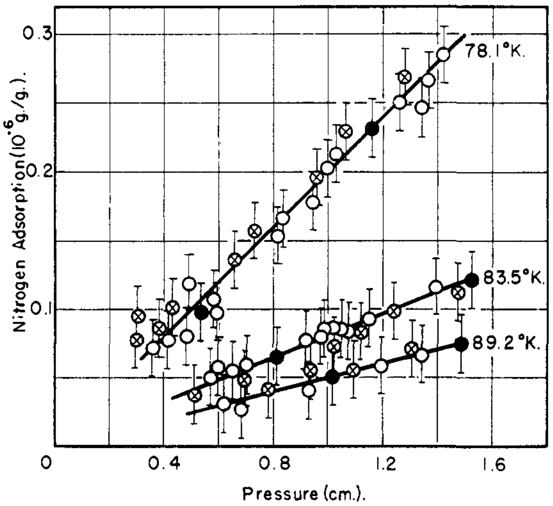

Fig. 4.—Insert from Fig. 3 in low pressure regions (symbols as in Fig. 3).

T_2 and T_1 was then substituted in the following integrated form of Eq. (2).

$$H = 2.303R\left(\frac{T_1T_2}{T_2 - T_1}\right)\log\frac{P_2}{P_1} \qquad (3)$$

The maximum variation in the heat values and the surface coverage values of Figs. 8 and 9 is indicated so as to avoid making the data look better than they really are. Adsorptions were measured and compared at pressures from 0.01 to 150 cm. at each of three temperatures in the range 78.1–89.2°K. for each of 2 samples of a given crystal face. The variation of heat of adsorption with coverage of the surface could be determined and plotted in typical heat (H) *vs.* coverage (θ) curves. The thermodynamic interpretation of the isosteric heats of adsorption is now generally believed to be on a sound basis. Hill[11] has recently demonstrated a direct relationship between the isothermal differential heat of adsorption and the isosteric heat. It is essential for the valid application of the Clausius-Clapeyron type equation that the adsorbate be in a strictly comparable state at the various temperatures of comparison. This point will be considered in more detail in the discussion of the experimental results. There is good reason to believe that a more strict application of Eq. (2) should involve comparisons at constant coverage[12] of the surface or constant spreading pressure[11] of the adsorbed film rather than at constant amounts of adsorbed gas. Interpretation of the data from the former type of basis is, however, full of uncertainties at the present time. It seems desirable to use the more classical basis to calculate the heats now although interpretation of the results should be made with this reservation in mind.

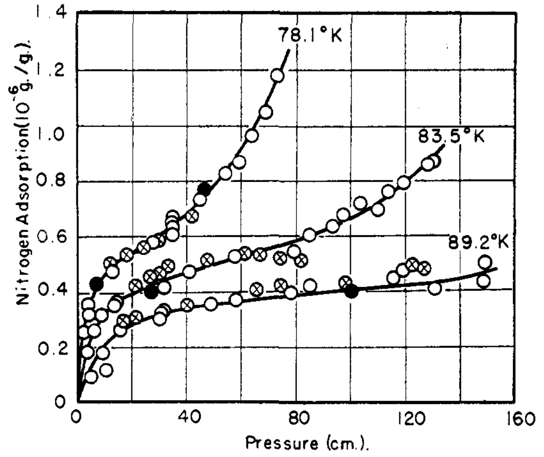

Fig. 5.—Adsorption of nitrogen on electropolished and hydrogen-reduced (111) crystal face of copper at 78.1, 83.5 and 89.2°K.: ○, sample 8; ⊗, sample 11; ●, desorption points.

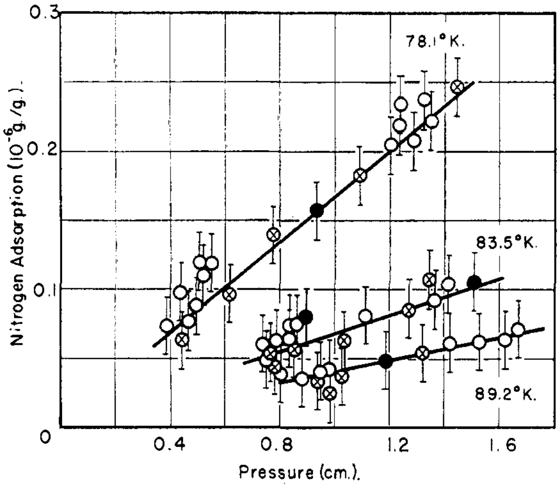

Fig. 6.—Insert from Fig. 5 in low pressure region (symbols as in Fig. 5).

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[11] T. Hill, *J. Chem. Phys.*, **17**, 520 (1949).

[12] Wilkins, *Proc. Roy. Soc.* (*London*), **A164**, 496 (1938).

Results

The adsorption isotherms on all the surfaces were of the sigmoidal shape characteristic of Type II isotherms. Typical isotherms for adsorption runs on two different sets of single crystal plates of the (110), (100) and (111) orientations at 78.1, 83.5 and 89.2°K. are plotted in Figs. 1, 3 and 5. Since Eq. (3) is very sensitive to small variations in the pressure in the low pressure region, enlarged plots of the isotherms in this region are replotted on an enlarged scale in Figs. 2, 4 and 6. These plots indicate the uncertainty in evaluating the adsorptions in the very low range particularly for the adsorption at 78.1°K. where, of course, the equilibrium pressures were particularly small. All values of (H) are, however, included in the heat-coverage plots although the variation in pressure readings for the very sparsely covered surface introduces some considerable uncertainty in the heat values as indicated.

Characteristic data for the three major crystal faces are summarized in Table I.

TABLE I

Crystal face	Temp., °K.	V_m × 10^{-6} g.	V_m' × 10^{-6} g.	Apparent roughness factor	Apparent number Cu/N_2 per unit area
(110)	78.1	0.54	0.54	1.42	1.8
(110)	83.5	.48	.49	1.29	2.0
(110)	89.2	.44	.45	1.19	2.2
(100)	78.1	.47	.47	1.35	2.7
(100)	83.5	.45	.46	1.32	2.8
(100)	89.2	.43	.45	1.29	2.8
(111)	78.1	.44	.44	1.20	3.3
(111)	83.5	.43	.44	1.20	3.3
(111)	89.2	.42	.44	1.20	3.3

The values of V_m in (3) were determined from BET plots which yielded good straight lines in the pressure range P/P_0 from 0.02 to 0.25. These values were corrected for the variation of the cross-sectional area of the nitrogen molecule with temperature from the equation of Emmett and Brunauer[13] using the data of Yost and Russell[14] for the density of liquid nitrogen. The corrected values (V_m') in column 4 show a dependence on the adsorption temperature and the crystal face, being highest for the lowest adsorption temperature and highest for the (110) face. This variation is clearly illustrated in Fig. 7. The variation of weight of adsorbed monolayer of nitrogen on the (110), (100) and (111) crystal faces of copper with temperature in the range 78–89°K. is plotted. The V_m' values for the (110) face are observed to decrease about 20% as the adsorption temperature increases from 78 to 89°K. This trend is greater than the uncertainty of the V_m' values indicated by the vertical arrows. The trend is much less distinct for adsorption on the (100) crystal face and is essentially nonexistent for adsorption on the (111) crystal face. This effect must be related to the unusually high heat of adsorption values observed especially on the (110) crystal face around monolayer coverage.

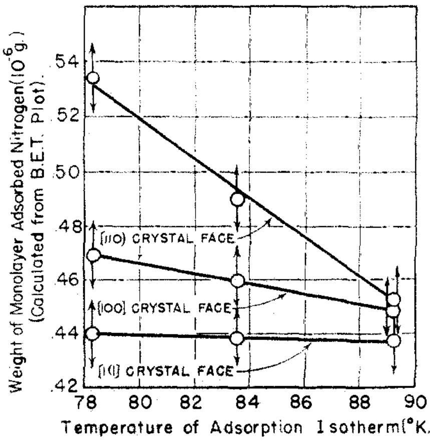

Fig. 7.—Variation of weight of adsorbed monolayer of nitrogen on (110), (100) and (111) crystal faces of copper with adsorption temperature in range 78–89°K. V_m values are corrected for variation of density of liquid nitrogen with temperature as described in text. Height of vertical arrows indicates experimental uncertainty.

All the samples had the same macroscopic surface area of 13.2 cm.^{2}. The apparent roughness factors calculated from the corresponding (V_m') values are listed in column 5. The apparent packing index of nitrogen molecules on various crystal faces and at various temperatures indicated in column 6, is the ratio of the number of copper atoms calculated from the atom planar density of a given crystal face of copper to the number of nitrogen molecules per unit area obtained from the corrected V_m' values. The values in columns 5 and 6 are apparent in the sense that the manner of packing of nitrogen molecules and hence their effective cross-sectional area is somewhat ambiguous.

The differential heats of adsorption for nitrogen on the (110) (100) and (111) single crystal faces of copper and on polycrystalline copper surfaces calculated from the adsorption isotherms by the author at 78.1–83.5, 78.1–89.2 and 83.5–89.2°K. are plotted in terms of surface coverage in Fig. 8. The horizontal and vertical lines indicate the maximum experimental uncertainties in the values of (H) and (θ), respectively. The average of the corrected V_m' values from Table I was used for each temperature pair to calculate values of (θ). Representative curves are drawn through a very large number of points. The latter are not indicated because of the complexity of the diagram. The heat-coverage curve for nitrogen on polycrystalline iron at 90°K. has been calculated from the calorimetric and adsorption data of Beebe and Stevens.[15] The limitation of their

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(13) P. H. Emmett and S. Brunauer, THIS JOURNAL, **59**, 1553 (1937).

(14) Yost and Russell, "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 5.

(15) R. Beebe and Stevens, THIS JOURNAL, **62**, 2134 (1940).

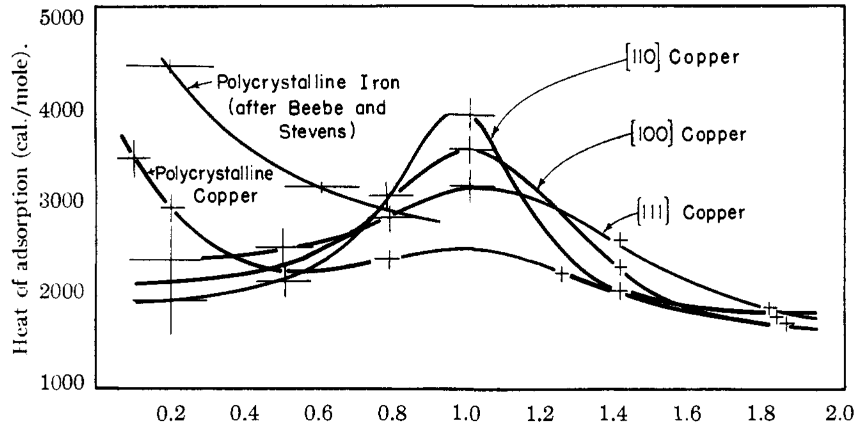

Fig. 8.—Differential heats of adsorption for nitrogen on (110), (100) and (111) single crystal faces of copper and on polycrystalline copper surfaces calculated from the adsorption isotherms by the author at 78.1–83.5, 78.1–89.2 and 83.5–89.2°K. (Vertical lines indicate total spread of the values calculated from the isosteric data. Horizontal lines indicate spread in values of θ introduced by the error in the microweighings.)

data presents an ambiguity as to the location of the curve with reference to the coverage axis but does not substantially affect the shape of the heat-coverage plot.

Large heat values for a sparsely covered surface occur for the polycrystalline surfaces but not for the single crystal surfaces indicating the apparent absence of an active heterogeneous part of the surface in the latter case. The heat values are about the same for all surfaces as the coverage increases. They tend to remain so for the polycrystalline surfaces except for a slight hump for polycrystalline copper. The heat values on the single crystal surfaces, however, go through distinct maxima which correspond to about monolayer coverage within the experimental error for all three orientations. The height and the sharpness of the maxima vary with the crystal face in such a manner as to be greatest for the least dense crystal face (110) and smallest for the most dense crystal face (111). Careful examination of the heat values for single crystal surfaces around surface coverage corresponding to 2 monolayers provides no indication of a distinct second maximum similar to that reported on graphitized carbon.[10] The heat of adsorption plots for all surfaces for surface coverage exceeding a monolayer have a descending portion that approaches the value corresponding to the heat of liquefaction of nitrogen characteristic of normal multilayer adsorption.

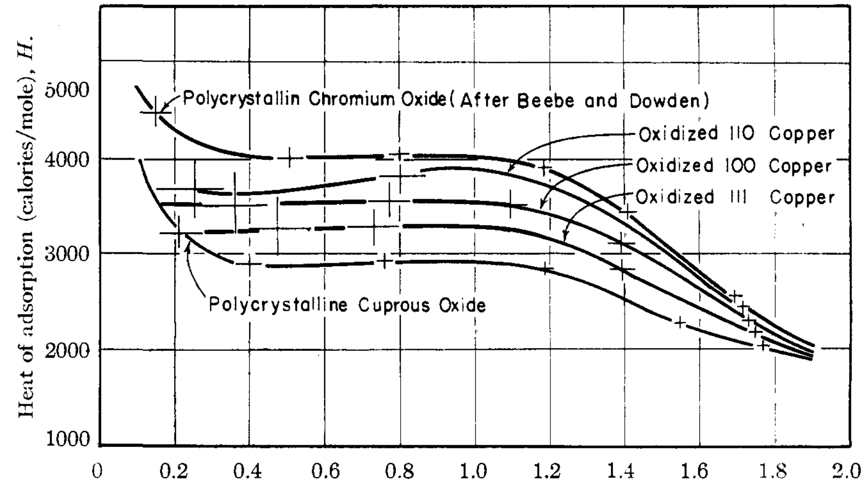

Fig. 9.—Differential heats of adsorption for nitrogen on the oxidized (110), (100) and (111) single crystal faces and the polycrystalline surface of copper calculated from the adsorption isotherms by the author at 78.1–83.5, 78.1–89.2 and 83.5–89.2°K. The heat-coverage curve for nitrogen adsorption on polycrystalline chromic oxide at 90°K. has been calculated from the calorimetric and adsorption data of Beebe and Dowden. The experimental errors are indicated as in Fig. 8.

The heats of adsorption were also determined for the oxidized surfaces and the corresponding data are plotted in a similar manner in Fig. 9. For the sake of brevity the corresponding adsorption isotherms are omitted. The oxidation treatment was such as to form a thin coherent oxide film with an average oxide film thickness of about ten monolayers of cuprous oxide. Electron diffraction studies of thin oxide films of this type indicate that they tend to be composed of small oxide crystallites oriented in a preferred manner depending on the orientation of the metal surface from which the oxide forms. The heat-coverage curves are very similar for the oxidized single and polycrystal copper surfaces as well as for a chromic oxide surface. The heat-coverage curve for nitrogen adsorption on polycrystalline chromic oxide at 90°K. has been included for comparison. It was calculated by the author from calorimetric and adsorption data of Beebe and

Dowden.[16] The experimental errors are indicated as in Fig. 8. The differences in the orientation of the oxide overgrowths appear to result in a small but distinctive effect on the heat values although they are essentially insensitive to surface coverage and substrate geometry. The heat values on the oxides are much more nearly constant with surface coverage than those for the metal as well as being somewhat higher. High values for a sparsely covered surface are observed only on the oxidized polycrystalline surfaces. Grain boundaries, edges and other irregularities more characteristic of polycrystal than single crystal surfaces may be contributing to the heat of adsorption in this case.

The heats of adsorption of nitrogen on evaporated metal films of nickel and iron have been reported[17] to decrease from 10 to 5 kcal./mole as the surface coverage increased from about 0.1 to 1.0 monolayer. Beeck states that nitrogen is unsuitable for evaluation of surface areas of evaporated iron and nickel films by the Brunauer–Emmett–Teller method because of its high heat of adsorption at 78°K. which would yield a value for monolayer adsorption too high by 50%. This effect is believed not to be characteristic of the nitrogen adsorption on reduced electro-polished planar copper plates for the following reasons.

1. Outgassing of the surfaces of 750 or 1000° is believed to free the surface of chemisorbed hydrogen and nitrogen. No preadsorption of nitrogen at low pressures was observed by the micro-weighings.
2. The isosteric heats of adsorption in this study are shown to vary from 2–4 kcal./mole. Nitrogen may be considered to be a well-behaved gas for area measurements of relatively planar non-porous copper surfaces.
3. The observed roughness factors (ratio of true to geometric surface) of the surfaces of this study varied from 1.2 to 1.4 (Table I). This degree of flatness checked with electron microscope pictures of alumina replicas from electropolished single crystal copper surfaces.[18] It is unlikely that the surface areas determined from the Brunauer–Emmett–Teller analysis are too high by 50% or even 25% in some cases for a fictitious roughness factor of less than unity would result.
4. Although iron and to a lesser extent nickel tend to form nitrides in nitrogen atmospheres at elevated temperatures, copper does not show this effect.

In spite of these reasons the possibility that a chemisorbed nitrogen monolayer may form cannot be completely excluded. Should this occur, it is not unreasonable to expect the nitrogen monolayer to form a strongly oriented structure which would tend to reflect the structure of the underlying metal face in a unique manner.

Discussion

There exist insufficient data on the physical adsorption of gases on single crystal metal surfaces to justify a generalized or quantitative treatment. It seems appropriate, however, to make some brief qualitative remarks in the frame of well-known theoretical treatments on related systems.

1. **Variation of the Differential Heat of Adsorption with the Amount of Gas Adsorbed.**—Since surfaces are almost always non-uniform, it is generally believed that adsorption occurs first on the most active parts of the surface. Subsequently less active areas are covered. Continuation of the process yields statistical monolayers although their physical interpretation is not often well-defined. It is believed that the single crystal surfaces of this study are sufficiently uniform to justify considering the adsorption layers in a geometric sense to a first approximation. Coöperative adsorption occurs when horizontal interactions between adsorbed molecules are involved as well as vertical interactions between adsorbed molecules and the surface. The Brunauer–Emmett–Teller theory ignores horizontal interactions. They have been considered in the early theory on monolayer adsorption[19]; their contribution to multimolecular adsorption[20] on uniform surfaces was treated later. However, the latter treatment does not yield an explicit expression for the heat of adsorption in terms of any usable quantity, such as surface coverage, and hence could not be applied by the author to the present study. The physical significance of coöperative adsorption is more obvious from Halsey's[21] treatment but, unfortunately, his conclusions are essentially limited to physical adsorption on non-uniform surfaces. It is proper, however, from his viewpoint to assume that horizontal interactions are negligible on a strongly non-uniform surface although coöperative adsorption would occur were the surface sufficiently uniform. If one associates the maxima in the heat coverage curves of Fig. 8 with a strong contribution from horizontal interaction, the lack of maxima observed for the reduced and oxidized polycrystalline copper surfaces is in accord with this approach. It may also explain in a rough manner the lack of distinct maxima in the heat coverage curves of Fig. 9 for the oxidized single crystal copper surfaces if one assumes sufficient non-uniformity is introduced by the formation of the oxide crystals. It is not likely, however, that this explanation can be pushed one step further to explain the differences in the coöperative effect observed on the three major single crystal faces of this study. Although the roughness factors of the 6 separate single crystal sam-

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(16) R. Beebe and Dowden, This Journal, **60**, 2912 (1938).

(17) O. Beeck, "Advances in Catalysis," Vol. II, Academic Press, New York, N. Y., 1950, p. 155.

(18) H. Raether, *Optik*, **1**, 69 (1946).

(19) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics," Cambridge University Press, London, 1939, Chap. X.

(20) T. L. Hill, *J. Chem. Phys.*, **15**, 767 (1949).

(21) G. Halsey, *ibid.*, **16**, 931 (1948).

ples studied varied from 1.2–1.4 there was no correlation between observed maxima and the precise roughness factor. Secondly, the reproducibility of the heat-coverage relationship for each crystal face would indicate that the preparative technique employed always yielded a more uniform surface for the least dense face and so on. It is not obvious why this should be true. For these reasons it is believed that the distinct differences in the heat-coverage curves observed for the three major single crystal surfaces are distinctly related to the surface crystallography in each case. This relationship will be considered in more detail in the next section.

On the other hand, a flat uniform single crystal surface is unlikely to possess a very active fraction of the surface. Horizontal interactions may be expected to make a considerable contribution to the heat of adsorption for neighboring non-polar molecules. In the case of nitrogen the horizontal interactions are attractive and this contribution will tend to cause the heat of adsorption to pass through a maximum at approximately monolayer coverage in a manner similar to that observed in this study. Orr[22] has shown by both theoretical and experimental considerations of nitrogen and argon adsorption on alkali halides that this effect can contribute about 0.5 kc./m. to the heat of adsorption. The differential heats of adsorption of nitrogen on a partially graphitized carbon black at liquid nitrogen temperatures have been carefully studied calorimetrically by Beebe, Biscoe, Smith and Wendell.[23] Their results were systematically confirmed from isosteric heats calculated from adsorption isotherms in the temperature range 68.4–90.0°K. on the same material by Joyner and Emmett.[10] In both cases a maximum was also observed in the heat of adsorption when the surface was covered with approximately 0.75 monolayer. It must be noted, however, that the apparent contribution to the maximum for the heat of adsorption on graphitized carbon appears to be about 0.5 kcal./mole at most, whereas the corresponding apparent contribution to the heats of adsorption on single crystal copper faces varies from 0.6 to 1.8 kcal./mole. It is possible that the maximum for the heat-coverage plots for the former case would be considerably more accentuated were the physical structure of the graphitized carbon much more uniform. The greater increase of the heat of adsorption around monolayer coverage observed for the single crystal surfaces of this study may be caused by the fact that they are relatively more uniform and planar. It is not unlikely, however, that other effects in addition to that of attractive horizontal interactions must be contributing to the observed maxima for single crystal copper surfaces. It is possible that a rearrangement of the adsorbed nitrogen occurs to a more stable structure somewhere between the temperatures at which the adsorption isotherms were measured. The non-symmetrical nitrogen molecules may, for example, tend to form an adsorbed film with the long axis normal instead of horizontal to the substrate as generally expected at sufficiently low temperatures. These geometric considerations will be considered in somewhat more detail in the subsequent section. It should be remarked, however, that when such a condition holds the adsorption isotherm will be affected accordingly, and hence a simple application of the Clausius–Clapeyron equation is not valid since the two states are not thermodynamically comparable.

First-order phase changes have been reported[24] for *n*-heptane on various solids and nitrogen on alumina–silica cracking catalysts at very low pressures. Although the coöperative contribution on single crystal surfaces of copper at monolayer coverage is unusually high, no obvious distortion of the adsorption isotherm was observed at the lowest temperature studied (78.1°K.). In like manner, no obvious distortion of the adsorption isotherms of nitrogen on graphitized carbon was reported at the lowest temperature studied (68.4°K.). Lowering the adsorption temperature sufficiently in the former case may induce a first-order phase transition on single crystal surfaces of a metal in a pressure range much higher than heretofore reported because of the relatively large contribution from cooperative effects.

2. Variation of Heats of Adsorption on Different Major Crystal Faces of Copper.—The effect of crystal face on physical adsorption has been treated theoretically by Barrer[25] for covalent surfaces and by Orr[26] and by Lenel[27] for dielectric surfaces. The vertical interactions between a non-polar molecule and a polycrystalline metal surface have been independently treated by Lennard-Jones,[28] by Bardeen[29] and by Margenau and Pollard.[30] The theoretical limitations involved in the last development are such that the observed agreement in order of magnitude with experiment is acceptable. At present no explicit theoretical treatment of the physical adsorption of a non-polar gas molecule on a single crystal metal surface in terms of the crystal parameter and geometry of the latter is available.

According to Hill[31] a non-symmetrical molecule will tend to be oriented on the surface in such a manner as to give a large "contact" between the surface and the adsorbed molecule. This will lead clearly to a different intermolecular potential

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[22] W. J. Orr, *Trans. Faraday Soc.*, **35**, 1247 (1939); *Proc. Roy. Soc.* (*London*), **A173**, 349 (1939).

[23] R. Beebe, J. Biscoe, R. Smith and C. B. Wendell, THIS JOURNAL, **69**, 95 (1947).

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[25] Barrer, *Proc. Roy. Soc.* (*London*), **A161**, 476 (1937).

[26] Reference 22.

[27] Lenel, *Z. physik. Chem.*, **B23**, 379 (1933).

[28] J. Lennard-Jones, *Trans. Faraday Soc.*, **28**, 333 (1932).

[29] J. Bardeen, *Phys. Rev.*, **58**, 727 (1940).

[30] H. Margenau and W. Pollard, *ibid.*, **60**, 128 (1941).

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

function for adsorbed molecules as compared to molecules in the gas phase. Also the extent to which a molecule is flattened by the surface will be a function of the nature of the surface even if the latter is non-polar. Hence not only will the intermolecular potential be different between adsorbed and evaporated molecules but the adsorption potential will also be different for adsorbed molecules on different crystal faces of the same solid because of varying degrees of flattening. In this manner the packing of the adsorbate and hence the compressibility of the adsorbed film will be expected to depend on the crystal face of the adsorbent. In this study it is not possible to resolve the factors contributing to the maxima observed in the heat-coverage curves of Fig. 8 but the observed variation of the height and shape of the maxima with crystal face must be influenced in part by this type of consideration.

A geometric consideration of the arrangements in which a nitrogen molecule may sit on the various major crystal faces of copper indicates that the packing may be most effective on the least dense (110) face as a rough approximation. The dimensions of the nitrogen molecule may be roughly approximate as that of a dumbbell with an internuclear distance of 1.09 Å.[32] and an effective cross-sectional area of 16.1 Å.^{2} Top and side views of the manner in which such a molecule may sit on the various major crystal faces of copper are drawn to scale in Fig. 10. The positions are those that give the lowest molecule to surface distance for each face using the very crude models described. Examination of this type of model indicates the effective cross-sectional area for a nitrogen molecule would be approximately 16.1 Å.^{2} if it lay flat and 12.2 Å.^{2} if it lay with its long axis normal to the substrate. If the former orientation holds, then the greatest packing occurs for the least dense (110) crystal face and the poorest packing for the most dense (111) crystal face. This is an agreement with the data summarized in Fig. 7 where the V_m' values are observed to vary with crystal face in a corresponding manner. The large values of V_m' observed especially at low temperatures for the (110) crystal face suggest that an even more efficient packing of the nitrogen molecules may be occurring on that crystal face as the temperature decreased, namely, a tendency for the adsorbed nitrogen to be oriented normal to the substrate. A reorientation of this type would not only account for the increase of V_m' values with decreasing temperature but would also distort the lower temperature isotherms sufficiently to account for the unusually high maximum observed in the heat-coverage plot. This trend is in agreement with the apparent number of copper atoms per nitrogen molecule calculated for each face (Table I). By the same token the observed roughness factors indicated in Table I seem to be highest for the least dense (110) face. If one considers the roughnesses of the various crystal faces to be about the same, this trend again may mean that the packing is more efficient on the least dense face and the higher observed roughness factors are only apparent. Actually, it does not seem desirable to speculate further until more is known about the size factor in adsorption on single crystal surfaces.

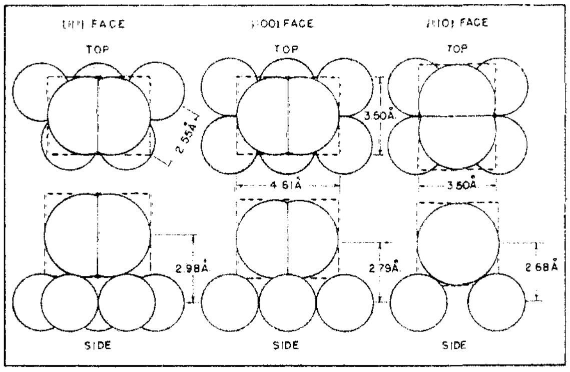

Fig. 10.—Some possible positions of a nitrogen molecule physically adsorbed on single crystal copper surfaces. (Projections are constructed to scale in directions normal and parallel to the substrate. Copper atoms are schematically indicated as rigid close packed spheres and nitrogen molecules as rigid dumbbells.)

The heat of adsorption on all single crystal faces for low values of θ in Fig. 8 should be considered from a different viewpoint. Contributions from horizontal interactions are likely to be small on a sparsely covered surface. The variation of heat of adsorption may be reasonably considered to be determined mainly by the vertical interaction between a single adsorbed molecule and a relatively large and uniform surface. It is under these conditions that the theoretical treatment of Margenau and Pollard is most applicable and the agreement between the calculated value (1800 cal./mole) and the average experimental value (2200 cal./mole) furnishes some additional, if fragmentary, evidence as to the validity of their treatment.

The vertical interactions are known to depend on the surface density of atoms and electrons as well as the equilibrium molecule to surface distance. The dependence of the heat of adsorption of nitrogen upon the crystal face of the copper for all values of $\theta > 1$ probably depends on the variation of one or more of these variables to some extent with the surface crystallography.

Acknowledgments.—The author is grateful to Professors L. Meyer and J. Arnold for helpful discussions. The copper samples were prepared by J. Cerny and K. Ikeuye.

Summary

1. The isosteric heats of physical adsorption of nitrogen near its boiling point on reduced and

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(32) A. Rasetti, *Phys. Rev.*, **34**, 367 (1929).

oxidized electropolished single crystal copper surfaces have been studied.

2. The adsorption isotherms were determined with a quartz beam vacuum microbalance of high sensitivity. The surfaces studied are believed to be good approximations to flat, clean, undistorted single crystals.

3. The heats of adsorption were found to vary in a unique manner with the coverage, uniformity and crystallography of the surfaces.

4. The physical significance of these studies has been evaluated qualitatively within the frame of established theoretical understanding of adsorption phenomena on single crystal metal surfaces. The approximations and assumptions inherent in such treatments now available considerably limit their quantitative application.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MARYLAND]

Kinetics of the Alkaline Hydrolysis of Monoethyl Malonate Ion[1]

BY W. J. SVIRBELY AND IRVING L. MADOR

The alkaline hydrolysis of monoethyl malonate ion has been studied previously.[2,3] Ritchie's studies were carried out over a temperature range of 0 to 25° in water, ethanol and a 50% ethanol–water mixture. The reaction was found to be of the second order. Ritchie, however, neglected salt effects. Westheimer, Jones and Lad investigated the reaction at 0° in water and in an 80% ethanol–water mixture. They observed a positive salt effect. Neither of the above investigations provides sufficient data for testing the various theories dealing with ionic reaction rates.

The purpose of this research was to reinvestigate the reaction

$$C_2H_5O_2CCH_2CO_2^{-1} + OH^{-1} \longrightarrow CH_2(CO_2)_2^{-2} + C_2H_5OH \quad (1)$$

in order: (1) to determine systematically the influence of the dielectric constant of the solvent upon the rate; (2) to obtain the various thermodynamic quantities of activation; (3) to test the applicability of the theories dealing with electrostatic effects on ionic reaction rates. Accordingly, the above reaction has been studied over a temperature range of 5 to 35° in two isocomposition media, water and 27.57 wt. % dioxane in water; and in three isodielectric dioxane–water media corresponding to dielectric constants of 50, 55 and 60; and at 25° in three isodielectric mixtures of *t*-butyl alcohol–water also corresponding to the dielectric constants of 50, 55 and 60.

Materials and Apparatus

Potassium Ethyl Malonate.—A technical grade of diethyl malonate was fractionally distilled under reduced pressure and the middle cut was collected. One mole of the distilled diethyl ester was dissolved in three times its volume of ethanol. Four-tenths of a mole of potassium hydroxide, also in alcoholic solution, was added slowly with stirring to the diethyl ester solution. The resulting semi-solid mass, which consisted mainly of potassium ethyl malonate and dipotassium malonate, was digested for 24 hours at 70°, cooled and filtered. The salts were washed with ether, dissolved in absolute ethanol and fractionally precipitated with ether. The first 10% of material to crystallize was discarded. The next 80% proved to be potassium ethyl malonate. Saponification analysis indicated a purity of 100 ± 0.1%.

Dioxane.—Commercial dioxane was purified by a standard procedure.[4]

***t*-Butyl Alcohol.**—Eastman Kodak Co. best-grade *t*-butyl alcohol was dried over anhydrous calcium sulfate and fractionally distilled. The center portion, boiling at 82.2°, was collected.

Water.—Boiled, distilled water was used in preparing all solutions.

Sodium Hydroxide.—Carbonate-free sodium hydroxide was used in the preparation of the standard alkali solutions. The solutions were standardized against a National Bureau of Standards standard sample of potassium acid phthalate.

The rate measurements were carried out in a thermostat held within ±0.02°. The thermometer was calibrated against a similar one which had been certified by the National Bureau of Standards.

A stopwatch, which had been calibrated against the National Bureau of Standards time signals, was used to observe the times of sampling.

A 20-ml., jacketed pipet was used for withdrawing samples. Water was circulated from the bath through the jacket. All pipets and burets were calibrated.

The reactions were carried out in glass-stoppered, alkali resistant flasks. Titrations were carried out in glass-stoppered, Pyrex flasks. All flasks were provided with a side arm through which nitrogen was passed. An atmosphere of nitrogen was thus kept over all solutions to prevent absorption of carbon dioxide.

Standard alkali solutions in stock bottles and in burets were protected from atmospheric carbon dioxide by Ascarite tubes. An automatic delivery arrangement permitted direct transfer from stock bottle to buret.

Experimental Method

In preparing a reaction mixture, the following procedure was used: (1) a sample of potassium ethyl malonate was weighed in a small vial; (2) the volume of standard sodium hydroxide (0.04253 *N*) calculated to contain an amount of alkali equivalent to the malonate sample was run into the reaction flask from a buret; (3) if a high ionic strength was required, a weighed sample of sodium chloride was added to the reaction flask; (4) when a mixed

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[1] (a) Abstracted from a thesis submitted by Irving L. Mador to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Presented in part at the Atlantic City Meeting of the American Chemical Society, September, 1949.

[2] M. Ritchie, *J. Chem. Soc.*, **139**, 3112 (1931).

[3] F. H. Westheimer, W. A. Jones and R. A. Lad, *J. Chem. Phys.*, **10**, 478 (1942).

[4] L. F. Fieser, "Experiments in Organic Chemistry," 2nd edition, D. C. Heath and Co., New York, N. Y., 1941, p. 368.