

determining step, equation (7), whereas experimentally no salt effect was observed. On the other hand, it is the only mechanism which has been found to explain the order of the reaction with respect to the various reactants.

Acknowledgment.—The author is indebted for helpful discussions to Dr. J. J. Katz, Dr. D. W. Osborne and Dr. Martin Kilpatrick, and to Dr. Bruce Longtin for suggestions for the mechanism.

Summary

Exchange reactions between U(IV) and U(VI)

in hydrochloric acid solutions have been studied. It was found that the reaction is of the first order with respect to the U(VI), second order with respect to the U(IV), and minus third order with respect to the hydrogen ion concentration. The rates of exchange did not change with added inert salt, with chloride ion concentration, nor with illumination. The apparent heat of activation was found to be $33,400 \pm 800$ cal. per mole.

A mechanism is proposed for the exchange.

RECEIVED DECEMBER 12, 1949

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

Studies of Copper Surfaces by Low Temperature Adsorption Isotherms

BY T. N. RHODIN, JR.

Introduction

Much of the research that has been done in the past on the corrosion of metals and on the reactions between gases and metals has been handicapped by a lack of knowledge of the surface structure in general and of the true surface area in particular. It is now recognized that the physical adsorption of gases near their boiling points provides a method for determining true surface area under certain circumstances using the Brunauer-Emmett-Teller interpretation.¹ The absolute method of Harkins and Jura² for the determination of surface areas makes it possible to evaluate the effective cross-sectional area of some adsorbate molecules without making questionable assumptions.

The methods using gases such as nitrogen near their boiling points as adsorbates are ordinarily capable of giving a reproducible surface area if the sample has an area of one square meter and a bulk volume of only a few cubic centimeters. When the particles are large and the adsorptions are small the common technique of following the adsorption by measuring the change in pressure of the gas at constant volume in the presence of the adsorbent becomes inaccurate. This difficulty can be avoided by using a gas having a low vapor pressure at the temperature of the run. Using ethylene, for example, at 78.1°K. and very sensitive pressure gages, the sensitivity of the method can be extended to permit the measuring of surfaces as low as one hundred square centimeters.³ It is evident that this method is still not sufficiently sensitive for the surface chemistry study of metal specimens of small enough area to be conveniently prepared. Very sensitive

beam microbalances have sufficient sensitivity to measure adsorptions as small as one ten thousandth of a cubic centimeter (STP) but their use in adsorption studies has been relatively limited.⁴ The main sources of error in their application have been the large buoyancy corrections required and the presence of thermal eddy currents which obscure the rest-point determination. It is the purpose of this paper to show how surfaces of copper samples, ten square centimeters in area, subject to various oxidation-reduction treatments, can be studied by microbalance measurements of gas adsorptions at low temperatures.

Procedure

Technique.—The system used for measuring the adsorption is schematically indicated in Fig. 1. Gas pressures were measured over the range 10^{-6} to 760 mm. with the usual combination of McLeod gage, ionization gage, and mercury manometer. The gages had been cross-calibrated. The tank nitrogen and tank argon were passed over copper at 500°, a phosphorus pentoxide drying column, a liquid nitrogen trap and a cotton filter to remove oxygen and any condensable gases. The tank oxygen and tank hydrogen were dried in the same system by-passing the copper furnace. The metal sample, hanging in place at one end of the microbalance beam, was outgassed at 400° to a vacuum of 10^{-7} mm. in the presence of a 50/50 barium-aluminum getter. The sample was then cooled to a low temperature. Introduction of spurious vapors to the sample after cooling was minimized by separating the microbalance and getter from the rest of the system by mercury cut-offs and a liquid nitrogen trap. The microbalance case was outgassed at 300° prior to a run. It was also suitably shock-mounted, electrically grounded and thermostated at $40 \pm 0.02^\circ$.

The vacuum microbalance developed by Gulbransen⁵ and modified by the author is suited to the study of surface effect involving small weight changes. Its high sensitivity and reasonable stability are its most important merits. It is also important that it can be adequately baked out and vacuum up to 10^{-7} mm. may be obtained with it using suitable getter material. The operation of the balance is presented elsewhere.⁵ It was possible to observe

(1) P. H. Emmett, S. J. Brunauer and E. Teller, *THIS JOURNAL*, **60**, 309 (1938); P. H. Emmett, "Advances in Catalysis," Academic Press, New York, N. Y., 1948, pp. 65.

(2) W. D. Harkins and G. Jura, *THIS JOURNAL*, **66**, 1366 (1944); **66**, 1362 (1944).

(3) Wooten and Brown, *ibid.*, **65**, 113 (1943).

(4) H. M. Barrett, A. W. Birnie and M. J. Cohen, *ibid.*, **62**, 2839 (1940).

(5) E. A. Gulbransen, *Rec. Sci. Inst.*, **15**, 201 (1944).

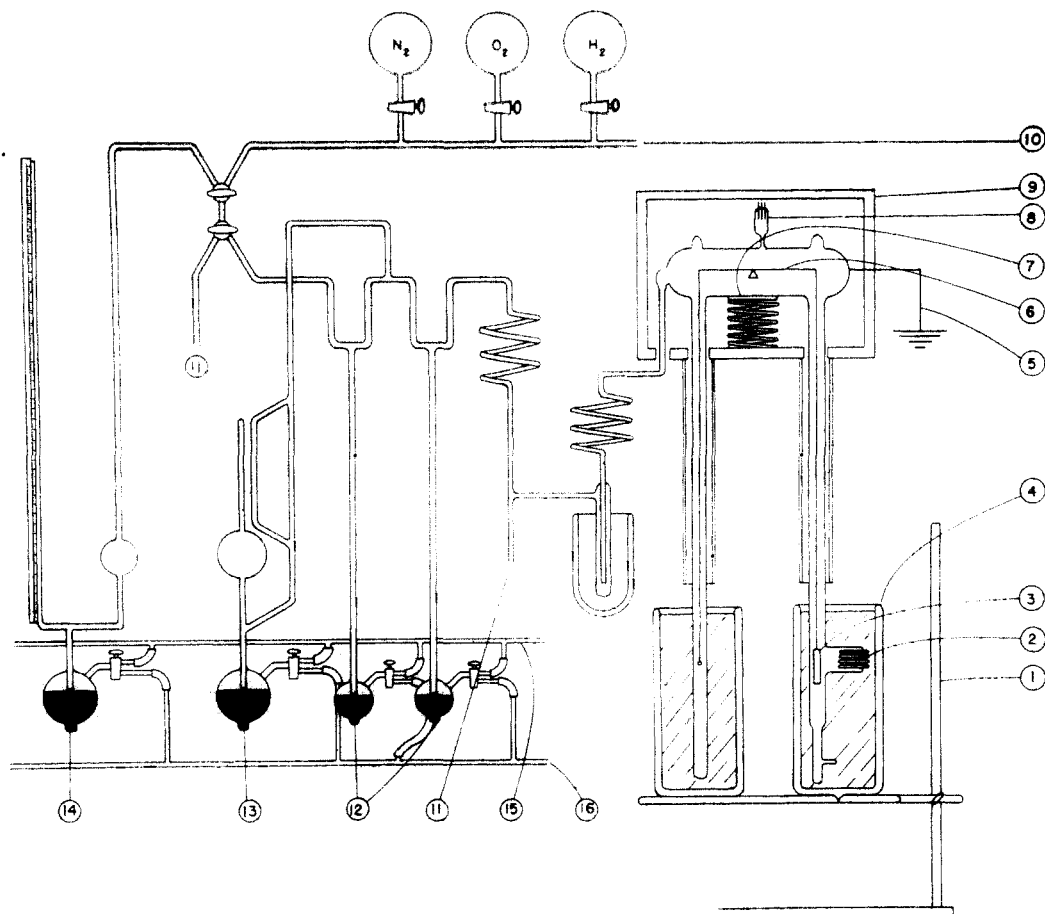


Fig. 1.—Vacuum microbalance assembly for measuring low temperature adsorption; assembly details: 1, elevator platform; 2, evaporator (not used); 3, single crystal plate; 4, dewar; 5, electrical ground; 6, microbalance beam; 7, shock mounting; 8, ionization gage; 9, air thermostat; 10, purified gases; 11, high vacuum manifold; 12, mercury cut-offs; 13, McLeod gage; 14, gas buret; 15, air line; 16, vacuum line.

reproducibly the weight change caused by the physical adsorption of a monolayer of nitrogen or by the formation of a monolayer of oxide on a single crystal metal plate with a surface area of ten square centimeters or more. This required a sensitivity of one microgram per tenth millimeter vertical displacement of the beam. This sensitivity is about six times greater than that of the original instrument. It was achieved by raising the center of gravity of the beam 0.15 mm. and decreasing the diameter of the tungsten cross-wire to 0.01 mm. This change impaired the stability of the balance but did not interfere with its usefulness. Using a Bausch and Lomb filar micrometer eyepiece mounted on a Geneva cathetometer, a precision of better than a hundredth of a mm. could be obtained over a vertical displacement of a cm. The horizontal swing of the cathetometer was checked against the two levels of a mercury U-tube, the menisci of which were located at approximately the same position as the two ends of the beam. Sights were taken of 0.001" tungsten wire pointers mounted at each end of the beam, the beam deflection was obtained from the difference of the two readings, and the weight change was calculated from the sensitivity value. It was possible to observe weight changes of 10^{-7} g. \pm 20% in a reproducible manner. This corresponds to 10^{-4} cc. (STP) of nitrogen.

Another innovation in the design was also added to make the instrument suitable for adsorption measurements. It was introduced to minimize thermal eddy current effects and to eliminate buoyancy corrections. It consisted of

making the balance and its envelop as symmetrical as possible. The beam itself, as well as the hang-down wires and the tubes in which they were hanging, was made and assembled with that in mind. Most important of all, both sample and counterweight were maintained at the same temperature during the run. The ends of the tubes containing them were immersed in dewars containing suitable liquid gases for temperature control. Both sample and counterweight were immersed 20 cm. below the surface of the liquid and the temperature of the coolant was measured at that point, before, during and after the run, with an oxygen gas thermometer. When the liquid level was kept constant during a run, the temperature varied less than 0.1°K . The sample was in the form of a plate ($0.75" \times 1.0" \times 0.010"$), approximately 0.5 g. in weight and balanced by a counterweight of identical material and matched within 10^{-6} g. in weight. Hence the volumes displaced by each were essentially the same, although the surface of the sample was ten to one hundred times that of the counterweight. The spherical surface of the counterweight was highly polished. Weight changes caused by surface reactions were magnified in this manner. A positive correction of one to ten per cent. had to be made to the observed weight change to compensate for the increase in weight of the counterweight at each measurement. The error in the correction was less than that of the experimental error and hence it was possible to obtain reproducible points for the smallest adsorptions measured.

Material.—Single crystal cylinders of copper ($6'' \times 1\frac{1}{4}''$) were prepared by the standard Bridgman method. The original oxygen-free high-conductivity copper was refined by vacuum casting to yield material 99.995% pure with traces of iron, silicon and carbon. Sections $\frac{1}{8}''$ thick with the desired orientation were cut with an alundum cutting-off wheel and mounted in lucite to prevent distortion. The samples were then reduced in thickness to 0.040'' by a long and careful process of mechanical polishing. The samples were then floated off the mount in benzene and reduced to plates 0.010'' in thickness by an extended standard electropolishing treatment. The distortion and orientation of the plates were checked by back-reflection X-rays using the Laue technique.⁶ Single crystal samples showing a lattice distortion of three degrees or less were retained for adsorption and oxidation studies. There is evidence to believe that the surfaces were essentially planar and the surface atoms existed in an orientation corresponding to a considerable extent to that characteristic of parallel crystallographic planes in the matrix of the crystal.⁷ A polycrystalline cylinder with no casting or drawing textures was used to obtain polycrystalline sections in a similar manner.

Results and Discussion

1. Adsorption Isotherms of Nitrogen and Argon on the Same Copper Sample.—The adsorption isotherms of nitrogen and argon at 78.1 and 89.2°K. on the same surface of freshly reduced polycrystalline copper are plotted in Fig. 2. The smooth curves obtained from different runs using adsorption and desorption points indicate the reproducibility of the data. It is observed that they are of the typical sigmoidal shape characteristic of adsorption on iron catalysts and various metallic oxides where the amounts adsorbed are, however, ten thousand times greater.⁸ Multilayer adsorption at high saturation is clearly indicated. Although the roughness factor is 2.5 for this sample, multilayer adsorption is also indicated in subsequent isotherms on surfaces with roughness factors close to unity. The roughness factor (R) of the surface can be defined as the ratio of the true surface area, obtained from the adsorption isotherms, to the geometric surface area apparent on a macroscopic scale. It has been established that if the amount adsorbed (x) is plotted as a function of the pressure of the adsorbate (p), and the saturation pressure (p_0), a straight line indicates the applicability of the Brunauer-Emmett-Teller multilayer adsorption interpretation, according to

$$\frac{p/p_0}{x(1-p/p_0)} = \frac{1}{x_{mc}} + \frac{c-1}{x_{mc}} p/p_0 \quad (1)$$

where

$$c = e^{(E_1 - E_L)/RT} \quad (2)$$

and E_1 = heat of adsorption first layer; E_L = heat of liquefaction. The applicability of Eq. (1) in the pressure range p/p_0 from 0.05 to 0.40 was observed by this test for all the adsorption isotherms considered in this study. The surface

(6) A. B. Greniger, *Trans. A. I. M. E.*, **117**, 75 (1935); **122**, 74 (1936).

(7) T. N. Rhodin, *J. App. Phys.*, to be published.

(8) S. J. Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, p. 162.

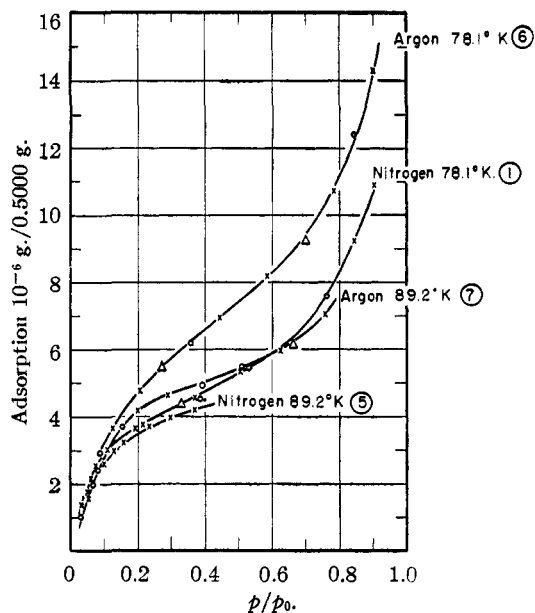


Fig. 2.—Adsorption isotherms of nitrogen and argon on the same sample of reduced polycrystalline copper: curve 1, adsorption of nitrogen at 78.1°K.; curve 5, adsorption of nitrogen at 89.2°K.; curve 6, adsorption of argon at 78.1°K.; curve 7, adsorption of argon at 89.2°K.; \times and \circ are for two different runs; Δ and \blacktriangle are for desorption points.

areas were calculated in the usual manner from these plots. In addition, the isosteric heats (ΔH) of adsorption were calculated from Eq. (3)

$$\log_e p_1/p_2 = \frac{\Delta H}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (3)$$

where p_1 and p_2 are the pressures required to obtain an adsorption corresponding to one monolayer at the two temperatures T_1 (78.1°K.) and T_2 (89.2°K.). It was felt that this value of the heat of adsorption would be the most significant one for comparison. Other values could also be calculated from the isotherms corresponding to adsorptions of more or less than a monolayer at the two temperatures by the same method. These values are collected in Table I under columns 4, 5, 7 and 8, for Runs No. 1, 5, 6 and 7. The heats of adsorption calculated from Eq. (2) are all too small by about 30% and are not included.

It is seen that the values obtained for the surface area from Eq. (1) from four different adsorption isotherms on the same sample agree with an average deviation of $\pm 6\%$. The cross-sectional areas for the nitrogen and argon molecules were taken to be 16.1 and 15.2 sq. Å., respectively. These values are known to yield the most reliable surface areas for non-porous adsorbents of this type. The isosteric heats of adsorption for one monolayer calculated from the same data averaged 2600 ± 60 calories per mole. This is in agreement with the corresponding value

TABLE I

| (1) | (2) | (3) | (4) | (5) | (6) | (7) | (8) |
|-----|---------------------------------------|------------------------|--------------------------------------|---|---|---------------------------|------|
| No. | Sample | Iso-therm | $\frac{A_m}{10^{-6}}$ (g./0.5 g.) | $\frac{A}{10^{-6}}$ (sq. cm./0.5 g.) | $\frac{A}{10^{-6}}$ (sq. cm./0.5 g.) | ΔH (cal./mole) | R |
| 1 | Polycrystal reduced Cu | N ₂ 78.1°K. | 3.5 | 120 | 103 | 2500 | 2.46 |
| 2 | Polycrystal 75Å. Cu ₂ O | N ₂ 78.1°K. | 1.3 | 45 | 50 | 3000 | 1.03 |
| 3 | Single crystal reduced Cu | N ₂ 78.1°K. | 0.7 | 26 | 19 | 3500 | 2.10 |
| 4 | Single crystal 10Å. Cu ₂ O | N ₂ 78.1°K. | 0.4 | 13 | 11 | 3650 | 1.20 |
| 5 | Polycrystal, reduced Cu | N ₂ 89.2°K. | 3.3 | 117 | ... | 2500 | 2.40 |
| 6 | Polycrystal, reduced Cu | A 78.1°K. | 4.6 | 110 | ... | 2650 | 2.32 |
| 7 | Polycrystal, reduced Cu | A 89.2°K. | 4.5 | 107 | ... | 2600 | 2.27 |

obtained for monolayer adsorption calorimetrically established by others.⁹ Since it was not the point of this paper to consider the variation of heat of adsorption with the extent of surface covered, the isosteric heats of adsorption were calculated only for the coverage of the surface corresponding to a monolayer in each case. It was felt that comparison of this value for different surfaces would be significant.

2. Oxidation-Reduction of Copper.—A sample of freshly electropolished polycrystalline copper with an initial roughness factor of unity was treated to an oxidation-reduction cycle in

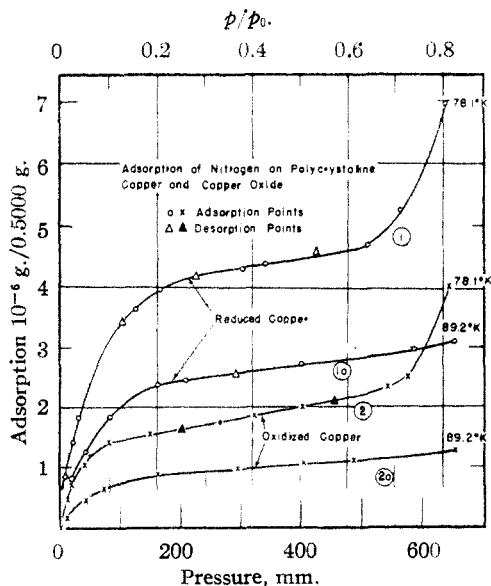


Fig. 3.—Adsorption of nitrogen on polycrystalline copper and on cuprous oxide: curve 1, adsorption on reduced copper at 78.1°K.; curve 1a, adsorption on reduced copper at 89.2°K.; curve 2, adsorption on oxidized copper at 78.1°K.; curve 2a, adsorption on oxidized copper at 89.2°K.; O and X are adsorption points; Δ and ▲ are desorption points. Saturation pressure units on ordinate axis apply only to curves 1 and 2.

(9) S. J. Brunauer, ref. 8, pp. 230-247.

which an oxide film with an effective thickness of 200 Å. was added and removed. This study was done, (1) to illustrate the usefulness of the adsorption technique for defining roughness factor and surface area changes of samples with small areas, and (2) to characterize the surface itself prior to oxidation studies. The thickness of the oxide film corresponding to a given weight change was calculated for a determined surface area assuming the oxide film to be as flat as the substrate and continuous. The film density was also assumed to be comparable to the density of the bulk oxide. The calculated oxide film thickness was based on the average of the surface areas measured before and after oxidation or reduction in each case. The oxide film does not always follow the contours of the original substrate but the deviation is not critical in this particular case. The effect will be discussed in more detail in the following section. The surface of a single crystal plate of copper with the cubic face exposed was also treated in the same manner except that the average thickness of the oxide film added and removed was about 10 Å. The values of the surface areas, roughness factors and isosteric heats of adsorption for the two samples are listed under Runs 1, 2, 3 and 4 in columns 5, 7 and 8 of Table I for comparison. Nitrogen adsorption isotherms at two temperatures for the reduced and oxidized polycrystal are plotted in Fig. 3 and the corresponding four isotherms for the single crystal surface in Fig. 4.

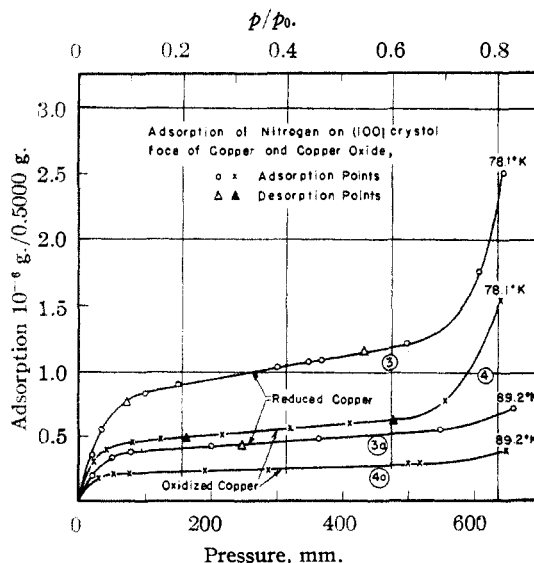


Fig. 4.—Adsorption of nitrogen on the (100) crystal face of copper and of cuprous oxide: curve 3, adsorption on reduced crystal at 78.1°K.; curve 3a, adsorption on reduced crystal at 89.2°K.; curve 4, adsorption on oxidized crystal at 78.1°K.; curve 4a, adsorption on oxidized crystal at 89.2°K.; O and X are adsorption points; Δ and ▲ are desorption points. Saturation pressure units on ordinate axis apply only to curves 3 and 4.

In both cases it is significant that the roughness factors that had increased about two-fold upon reduction, decreased to unity for the thick oxide film and approached unity for the thin oxide film. In other words, the effect of oxidation in this particular case was to make the surface more smooth. It is not unreasonable that an oxide film of 200 Å. average film thickness might tend to obscure the irregularities of the substrate. It is surprising that an oxide film with an average film thickness corresponding to three monolayers was almost sufficient to mask the surface irregularities. Detailed consideration as to the manner in which such thin oxide films form on the surface must be postponed for another study.

It is observed that the heats of adsorption (Col. 7) are higher for the oxide surfaces than for the reduced metal surface in both cases. It is felt that the values of the isosteric heats of adsorption listed in Table I are significant in spite of the fact that it was not possible to compare the adsorptions at more than two temperatures. The actual values obtained lie in the range of similar values obtained by others on much larger surfaces.⁹ It is interesting to note that the heat of adsorption on the single crystal metal surface is approximately one-third higher than that for the polycrystal. This is in accord with the general opinion that the heat of adsorption depends on the crystallographic arrangement of the surface atoms. Although the heat of adsorption is far from constant over the surface one might expect that it would tend to vary less for surfaces prepared in the manner of this study than those formed by reduction at comparatively high temperatures. It is planned to extend the technique to measure experimentally the variation of heat of adsorption with different crystallographic arrangements of the surface atoms.

Some doubt has been indicated in a previous section as to the proper choice of a value for the cross-sectional area of the nitrogen molecule involved in the calculation of the surface area from the BET plot. The data were replotted according to the following equation derived from an analysis of Harkins and Jura.²

$$\log_e p/p_0 = B - A/v^2 \tag{4}$$

where (v) is the volume adsorbed at pressure (p) and (A) is a constant, the square root of which is directly proportional to the absolute surface area (Σ). Plotting $\log_e p/p_0$ against $1/v^2$ yielded a series of unbroken straight lines. The values of the surface areas were readily calculated from the slopes of the straight lines by the Harkins-Jura method and found to be in good agreement with those calculated from the Brunauer-Emmett-Teller equation (Col. 5 and 6 in Table I). A comparison of the two methods has been adequately described elsewhere.¹⁰ It is sufficient to observe that the agreement confirms

(10) J. F. Duncan, *Trans. Faraday Soc.*, **45**, 879 (1949).

the value for the cross-section area of the nitrogen molecule previously used.

3. Effect of Progressive Oxidation on Surface Area.—It has already been observed that the effect of oxidation of a roughened copper surface was to decrease the true area until it approached that of a planar surface. This effect was systematically studied for a polycrystalline copper surface with an original roughness factor of 2.45. The originally smooth surface was roughened by an oxidation-reduction cycle at 400° in which an oxide film about 300 Å. average thickness was added and removed. Subsequent stepwise oxidation at 100° of the reduced surface showed a progressive decrease in surface area as the oxidation progressed. This is indicated in Fig. 5, in which the true surface area is plotted against the total average oxide film thickness. It is noteworthy

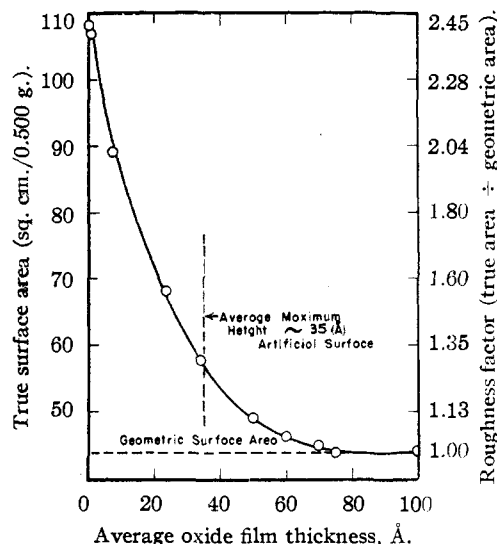


Fig. 5.—Effect of oxidation on surface area of polycrystalline reduced copper.

that a considerable decrease in the surface area occurred in the first stages of oxidation. For this sample the surface was approaching flatness at an average oxide film thickness of 100 Å. When the oxidation-reduction treatment was less severe the surface resumed its initial flatness at a thinner average oxide film thickness. A number of such experiments indicated this effect to be a typical one for the surfaces studied. It may be recalled that all surfaces studied were initially flat and even for the most severe treatment the average oxide film thickness involved was about 300 Å. It is possible that the oxidation-reduction treatment developed protuberances on the surface; the more severe the treatment, the greater the maximum size of the protuberances. Pyramidal protuberances have been actually observed in this laboratory on oxidized copper surfaces annealed in an atmosphere of hydrogen for four hours at 400°. The size was about that of the wave

length of light but smaller ones may occur for the milder treatment used in this study. In the initial stages of oxidation the metal surface is only partly covered with oxide. It is generally considered that the oxidation starts out at a limited number of points and spreads out laterally. It is possible that the oxidation selectively attacks the edges and points of the protuberances in such a manner as to smooth out the surface. A satisfactory analysis of the mechanism by which the surface structure changed during oxidation is beyond the scope of this paper. It seems experimentally true, however, for the surfaces considered that the smaller irregularities were the first to disappear during oxidation. If this be true, the rapid initial decrease of surface during oxidation may suggest that the smallest irregularities contribute the most to the area of the roughened surface. A rough clue as to their dimensions may be had by constructing a hypothetical surface of a suitable distribution of regular pyramidal protuberances. Their size would vary from 5 to 100 Å. for the surface of Fig. 5 and their distribution would be chosen so as to reproduce the observed surface area effect, assuming the effect of oxidation is to smooth out larger and larger protuberances. This particular hypothetical surface would suffer a decrease in surface area of 82% when all the protuberances 35 Å. in height or less disappeared. Since each model surface was unique to the corresponding real surface, it is possible that the value of the average maximum protuberance size calculated for the artificial surface had some real significance for the actual surface at least as an order of magnitude. The analysis is a very

simple illustration of a possible technique for systematically defining relative surface irregularities on a molecular scale using controlled oxidation data together with surface area data.

Acknowledgments.—The writer is indebted to C. S. Smith, C. S. Barrett and E. A. Gulbransen for discussions and also to J. Cerny, W. Bergmann and J. Hess for the preparation of samples. The microbalance was built by W. Mankowich, J. Getzholz and T. O'Donnell and their craftsmanship is also acknowledged. The research was done under U. S. Army Air Force Contract AF-33 (038)-6534.

Conclusions

1. The true surface areas of metal surfaces as small as 10 cm.² have been measured with an error of 6% from low temperature adsorption isotherms using a specially designed vacuum microbalance technique. This method is of special value in determining the average thickness of corrosion films formed by the reactions of gases or liquids with solids.

2. The isosteric heats of adsorption corresponding to an adsorption of one monolayer of nitrogen are found to be 3500 cal./mole on the (100) face of copper and 2500 cal./mole on the polycrystal face for the particular surfaces studied.

3. The effect of the progressive oxidation of a rough polycrystalline surface of copper was to decrease the surface area to a point where the roughness factor approached unity. The analogous effect on a very simple hypothetical surface was considered.

RECEIVED JANUARY 19, 1950

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

Solubility of Perfluoro-*n*-heptane with Benzene, Carbon Tetrachloride, Chloroform, *n*-Heptane and 2,2,4-Trimethylpentane

BY J. H. HILDEBRAND, B. B. FISHER AND H. A. BENESI

The work reported in this paper is a further contribution to the general investigation of the solubility relations of fluorocarbons that has been going on in this laboratory for several years,¹ and is a sequel, in particular, to the similar determinations with perfluoromethylcyclohexane.^{1f} The extremely low internal pressures of the fluorocarbons makes it possible to study miscibilities of these liquids with other non-polar liquids in a convenient temperature range. Since perfluoro-*n*-heptane has even a lower internal pressure than

perfluoromethylcyclohexane it was to be expected that perfluoroheptane would show slightly higher critical mixing temperatures with any other liquid.

Experimental Section.—Spectrophotometric measurements revealed that commercial perfluoro-*n*-heptane (C₇F₁₆) strongly absorbed at 210 mμ, this absorption presumably arising from unsaturated impurities. After passing the fluoroheptane through a 2 meter long, 1 cm. diameter, silica gel column, the absorption at 210 mμ was negligible. The product was then distilled twice through a 30-plate fractionating column at a 30:1 reflux ratio, the course of the fractionation being followed by density measurements at 25°. The densities of the fractions making up the final product ranged from 1.72062 to 1.72101 g./ml. at 25°. A mass spectrometric analysis of this product, kindly made by the Shell Development Company at Emeryville, California, revealed the presence of impurities to which were assigned the empirical formulas, C₇F₁₄, C₇F₁₂H₂, and C₇F₁₄H₂. Since these impurities did not total

(1) (a) H. A. Benesi and J. H. Hildebrand, *THIS JOURNAL*, **70**, 3978 (1948); (b) R. L. Scott, *ibid.*, **70**, 4090 (1948); (c) J. C. Gjaldback and J. H. Hildebrand, *ibid.*, **71**, 3147 (1949); (d) J. H. Hildebrand, *J. Phys. Coll. Chem.*, **53**, 944 (1949); (e) J. H. Hildebrand, H. A. Benesi and L. M. Mower, *THIS JOURNAL*, **72**, 670 (1950); (f) J. H. Hildebrand and D. R. F. Cochran, *ibid.*, **71**, 22 (1949).