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ABSOLUTE AREAS OF SOME METALLIC SURFACES

Thomas L. O'Connor* and Herbert H. Uhlig

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Knowledge of the absolute surface area is important to the interpretation of many measurements dealing with metal properties. This factor concerns, for example, studies of catalysis, adsorption, overvoltage, and reaction rates, including measurements of high temperature oxidation and corrosion. Common neglect of this factor does not mean it is of small consequence, or that it can be justifiably neglected. The presently reported results show, confirming limited information by other investigators, that surface preparation of bulk metals by one means or another may change the ratio of absolute to apparent area (roughness factor) by either a small percentage or by several hundred percent. Brown and Uhlig⁽¹⁾ showed that when deep fissures result from pickling a metal

⁽¹⁾ C. Brown and H. H. Uhlig, J.A.C.S., 69, 462 (1947)

like electrodeposited chromium, this ratio may increase to a value as high as 50.

METHOD OF MEASUREMENT

The method used for presently reported values was the well known

*Present Address:
American Cyanamid Company
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FC

BET method of gas adsorption^(2,3) which is concerned essentially with the

(2)

S. Brunauer, P. Emmett and E. Teller, J.A.C.S., 60, 309 (1938)

(3)

L. Wooten and C. Brown, J. A. C. S., 65, 113 (1943)

volume of gas v_m necessary to form a monolayer on the surface. From this volume of gas, the absolute surface area A_{ab} covered by the adsorbed gas can be calculated using the expression:

$$A_{ab} = \frac{v_m N \sigma}{V}$$

where N is Avogadro's number, V is the gaseous molar volume and σ is the cross sectional area of the adsorbate molecule. The quantity of gas v_m is obtained by measuring the volumes V of gas adsorbed at constant temperature and at various pressures p , and plotting $\frac{p}{V(p_0 - p)}$ vs $\frac{p}{p_0}$ where p_0 is the vapor pressure of adsorbate, in accord with the BET equation. From the slope of data so plotted and from the intercept at $\frac{p}{p_0} = 0$, the following relation holds:

$$v_m = \frac{1}{\text{slope} + \text{intercept}}$$

The BET equation is stated to satisfactorily describe physical adsorption within the range of pressures, measured in millimeters of mercury, up to approximately $(0.05 - 0.3)p_0$.

Ethane as adsorbate at liquid oxygen temperatures (-183°C) in accord with similar use of this gas previously.⁽¹⁾ Ethane has a low vapor pressure at -183°C , thereby permitting area measurements for a total surface no larger than 100 cm^2 or even less. The cross sectional area of

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The BET equation is stated to satisfactorily describe physical adsorption within the range of pressures, measured in millimeters of mercury, up to approximately $(0.05 - 0.3)p_0$.

We chose ethane as adsorbate at liquid oxygen temperatures (-183°C) in accord with similar use of this gas previously.⁽¹⁾ Ethane has a low vapor pressure at -183°C , thereby permitting area measurements for a total surface no larger than 100 cm^2 or even less. The cross sectional area of

the ethane molecule computed from x-ray data of solid ethane is equal to 20.5×10^{-16} cm². This value is in satisfactory accord with the area computed from adsorption of the gas on fused quartz beads⁽¹⁾, or on glass beads, as shown by the present data, assuming that quartz or glass are supercooled liquids having absolute surface areas identical with apparent areas. Research grade ethane obtained from the Phillips Petroleum Company was fractionated, the middle portion was dried with P₂O₅ and then stored in a five-liter glass flask. Tank helium was purified by passing it through a glass bead-packed liquid N₂ trap at -196°C and through activated charcoal also at liquid N₂ temperature, and was then stored in a glass flask.

The procedure was to seal the metal specimen in a glass adsorption cell (dead space = 16 cc), evacuate, and surround the cell with liquid oxygen. Helium, at a few millimeters of pressure, was introduced into the cell to accelerate cooling of the metal specimen to liquid O₂ temperature. Helium was then pumped out and ethane adsorbed at successively higher pressures, values for which were measured using a McLeod gauge. Helium, which does not adsorb at liquid oxygen temperature, was employed in the usual manner to calibrate the volume of the system. A glass U bend cold trap surrounded by solid CO₂-acetone mixture prevented condensation of mercury into the cell at -183°C. Separate measurements showed that ethane was not adsorbed in this trap.

The maximum pressures of ethane employed were sufficiently low (max. = 2×10^{-3} mm Hg) to make deviations from the perfect gas law negligible.

However, all pressure measurements involving a temperature gradient were corrected for thermal diffusion using the empirical equations outlined by Liang⁽⁴⁾. In accord with his method, the ratio of true to observed

(4)

S. Chu Liang, J. Applied Phys., 22, 148 (1951); J. Phys. and Colloid Chem., 56, 660 (1952)

pressure R is given by
$$\frac{\alpha(\frac{x}{f_1})^2 + \beta(\frac{x}{f_1}) + R_m}{\alpha(\frac{x}{f_1})^2 + \beta(\frac{x}{f_1}) + 1}$$
 where α and β are tem-

perature dependent constants equal to 27.6 and 11.0 respectively at -183°C ⁽⁵⁾;

(5)

S. Chu Liang, Private communication

X is the product of observed pressure (in mm Hg) and of tube diameter in mm (in the present instance 4 mm); $R_m = \sqrt{\frac{T_1}{T_2}}$ where T_1 equals absolute temperature of gas in the adsorption cell and T_2 is room temperature, hence, $R_m = \sqrt{\frac{90}{298}} = 0.55$; and f_1 is a function of the collision diameters for ethane (5.30 Å) and nitrogen (3.75 Å) equal to 0.382. Values of R so calculated are plotted as a function of observed pressure in Fig. 1. For example, the vapor pressure of ethane (p_0) at -183°C as measured by the McLeod gauge was 9.0 microns, but taking into account thermal diffusion ($R = 0.80$), the corrected vapor pressure became 7.2 microns. In general, the thermal diffusion corrections increase the BET area by about 10% over that calculated without applying the correction. This correction is less than the apparent variation of area

as determined through the use of various gases as adsorbates⁽⁶⁾.

(6)

R. Davis, T. deWitt and P. Emmett, J. Phys. and Colloid Chem., 51, 1232 (1947)

AREA OF IRON AND STAINLESS STEEL SPECIMENS

Areas were determined for rolled Armco iron sheets 0.003-inch thick, measuring 200 cm² geometric area and formed into spirals. Some of these were treated in a stream of purified dry hydrogen for 1/2 hour at 1000°C and cooled in hydrogen. They were then sealed individually in the adsorption cell which was cooled during glassblowing operations so as to avoid surface oxidation. The specimens within the cell were finally reduced in hydrogen at 400°C for 1/2 hour, followed by a two-hour baking in vacuum at 400°C.

Stainless steel sheet specimens (18-8 Type 304) were abraded, finished with 2/0 emery paper and coiled into spirals. They were degreased with benzene, pickled, washed, and then immersed successively into acetone and distilled benzene. Either of two pickles was employed, resulting in different surface areas. The first consisted of 25 vol. % concentrated HCl, 25 vol. % concentrated H₂SO₄ at 35°C for 10 minutes, (producing the larger surface), and the second consisted of 15 vol. % concentrated HNO₃, 10 vol. % concentrated HF at 90°C for 10 minutes.

One stainless steel and one Armco iron specimen, both abraded, were also measured. They were degreased in benzene before sealing within the adsorption cell.

Electropolished stainless steel specimens were prepared from rolled sheet using the glycerine-phosphoric acid electrolyte as described by Uhlig⁽⁷⁾.

⁽⁷⁾H. H. Uhlig, Trans. Electrochem. Soc., 78, 265 (1940)

Electropolishing was carried out at about 100°C at a current density of 0.3 amp./cm² for 60 minutes. The specimens were then washed, and immersed successively into acetone and benzene.

Areas determined from the amount of adsorbed ethane are listed in Table I. Order of reproducibility of the area determination itself can be estimated from single specimens whose areas were determined twice in succession. Maximum deviation is $\pm 1.5\%$ of the determined area. Various specimens of pickled 18-8 steel show this same order of reproducibility, indicating that surface area preparation by pickling can be repeated within close limits. Three hydrogen-reduced specimens show a maximum deviation of 4% from the average area.

Glass beads were also run in order to check the cross sectional area of the ethane molecule used for calculation of absolute area. The beads were new, not having been used for any purpose previously, and were cleaned with a synthetic detergent, washed in water, and dried. After sealing into the adsorption cell, they were baked out at 400°C for several hours. Their average diameter, as determined with a micrometer, was 0.407 cm² and their absolute area was within 4% of the apparent area.

AREA OF EVAPORATED IRON FILMS

Iron was evaporated in vacuum (less than 10^{-6} mm Hg) onto glass tubes measuring approximately 3.5 cm long by 0.4 cm in diameter. The

source of iron was either electrically heated "Puron" wire 0.04-inch diameter, or high purity Bureau of Standards wire 0.010-inch diameter wrapped around electrically heat tungsten wires of .025 inch diameter located at the center of an evacuated glass bulb. The procedure of evaporation has been described previously by Gatos and Uhlig⁽⁸⁾ who used similar iron

⁽⁸⁾ H. Gatos and H. H. Uhlig, J. Electrochem. Soc., 99, 250 (1952)

films in their studies of passivity. Eight glass tubes, each of which contained an iron wire sealed inside, were confined to a rotary track in vacuum by eight magnets moving slowly on a circular platform outside a 500 ml glass bulb. The glass tubes in this way acquired a uniform layer of iron from the evaporation source over a period of several minutes to one hour. The iron-coated tubes were then transferred through a larger size evacuated glass tube connecting to the gas adsorption cell. Accordingly the surface areas could be measured uncontaminated by previous contact with air and without correction for the metal filaments used as source of evaporated iron. The two sources of iron vapor differed in that the iron wires were electrically heated to only 1000-1100°C as determined by an optical pyrometer, whereas iron-wrapped tungsten wires were heated to about 1300°C. This difference produced a marked change in surface area as described later. The iron wires in both cases were previously cleaned by pickling in HCl, and were then reduced in purified dry H₂ at 1000°C for 1/2 hour. Thickness of the evaporated films was estimated by their dissolution in HCl and determination of total iron colorimetrically by the o-phenanthroline method. In the

calculation of thickness, the density of iron was assumed equal to that of bulk iron, namely, 7.86. Absolute areas are listed in Table II.

DISCUSSION OF RESULTS

Evaporation of iron from electrically heated wires at 1000-1100°C produces films having 3 to 6 times the area of films formed by evaporating iron on tungsten at 1300°C. This difference is thought to result primarily from differences in temperature of the condensed film during evaporation, the lower evaporation temperatures favoring growth of a porous film made up perhaps of individual crystals, whereas at higher evaporation temperatures the condensed film is heated sufficiently ^{by radiation} to sinter it to a pore-free layer. The effect presumably depends on the metal as well as temperature because Beeck et al⁽⁹⁾ reported that evaporated copper films characteristically

⁽⁹⁾ O. Beeck, A. Smith and A. Wheeler, Proc. Royal Soc. (London), A 177, 62 (1940)

sinter rapidly to a film having no measurable internal surface in contrast to nickel films which in their experiments were found to be porous.

Trapnell's⁽¹⁰⁾ results on evaporated Ni, Fe, Rh, Mo, Ta and W films showed

⁽¹⁰⁾ B. Trapnell, Trans. Faraday Soc., 51, 368 (1955)

greater adsorption on films deposited on glass at -183°C in contrast to films on glass maintained at 0°C during evaporation. This corresponds, as in our case, to greater surface area the lower the temperature of the film

during condensation. Porter and Tompkins⁽¹¹⁾ also report that available area

(11)

A. Porter and F. Tompkins, Proc. Royal Soc., A 217, 529 (1953)

for adsorption of H₂ on evaporated iron films decreases with increasing temperature used to presinter the film in vacuo.

When the films are porous, but probably not otherwise, the observed roughness factor depends on film thickness, increasing from 4.9 for a film 840 Å thick to about 10 for films 1800 Å or more thick. Baeck et al also found that the available surface of nickel films increased with thickness, as did Rideal and Trapnell⁽¹²⁾ for evaporated tungsten films, and Porter and Tompkins⁽¹³⁾

(12)

E. Rideal and B. Trapnell, Proc. Royal Soc. (London), A 205, 409 (1951)

(13)

A. Porter and F. Tompkins, Loc. Cit., p. 544

for iron films.

Roughness factors for abraded stainless steel and for iron equal to 3.1 and 3.4 respectively, agree reasonably well with the value 3.8 for abraded Armco iron reported by Powers and Hackerman⁽¹⁴⁾ using the BET method

(14)

R. Powers and N. Hackerman, J. Electrochem. Soc., 100, 314 (1953)

with krypton for adsorbate. Burstein, Shumilova and Golbert⁽¹⁵⁾ report

(15)

R. Burstein, N. Shumilova and K. Golbert, Acta Physicochimica, 21, 785 (1946)

a value of 2 for rolled iron using a method based on chemisorption of oxygen. Erbacher⁽¹⁶⁾ determined surface areas of metals by adsorption of radioactive

⁽¹⁶⁾O. Erbacher, Zeit. Physik. Chem., 163, 215 (1933); Chemiker Zeit., 62, 601 (1938)

monolayers of bismuth containing Th-C indicator, or of polonium, from their aqueous salt solutions. He and his coworkers also employed $\text{Pb}(\text{NO}_3)_2$ in methanol or pyridine⁽¹⁷⁾. Roughness factors were reported of 1.7 for polished

⁽¹⁷⁾O. Erbacher, G. Jensen-Hellmann and A. Mellin, Z. Metallkunde, 40, 249 (1949)

surfaces of Ni, and 2.5 for abraded surfaces of Ni, Au and Ag using either fine or coarse emery paper. Erbacher's value of 2.5 for abraded metals is in reasonable agreement with the values listed in Table I. Davis, Dewitt and Emmett⁽⁶⁾ using krypton, butane and "Freon" for adsorbates reported roughness factors of 1.10 to 1.37 for silver foil and 1.07 to 1.64 for Monel foil depending on the gas used. No direct comparison can be made with values listed in Table I because the authors did not state surface preparation, but it would appear reasonable that the surfaces were probably those resulting from rolling and would therefore be essentially smooth.

Electropolished stainless steel is relatively smooth having a roughness factor of only 1.12. In comparison, Rhodin⁽¹⁸⁾ reported that abraded

⁽¹⁸⁾T. N. Rhodin, J. A. C. S., 72, 4343, (1950)

and electropolished copper had a roughness factor of about unity.

Polarization capacity measurements have been used for surface area measurements^(19, 20), but the results appear to be much higher than those

(19)

F. Bowden and E. Rideal, Proc. Royal Soc. (London), 120A, 59 (1928)

(20)

F. Bowden and E. O'Connor, Ibid, 128A, 317 (1930)

reported above. Hackerman and Powers⁽¹⁴⁾, using this method, report a roughness factor of 20 for abraded iron. Impurities have been indicated as one source of error, causing as much as a three-fold change in measured surface capacitance⁽²¹⁾. Other possible sources of error are discussed by Wiebe

(21)

F. Bowden and K. Gre¹², "Electrode Processes", p. 91, Discussions Faraday Soc. (1947)

and Winkler⁽²²⁾. Surface area measurements in this laboratory using the

(22)

A. Wiebe and C. Winkler, Canadian Journal of Chem., 31, 306, 665, 1118, (1953)

current-time integral for a given change of potential, with the aid of a ballistic galvanometer, confirm that this method, without further refinements, does not lead to reproducible results, and that the values obtained of absolute areas are not in accord with values derived from gas adsorption. The fair correspondence of metal areas reported by several investigators, values of which were obtained by gas adsorption using more than one gas, and with radioactive ion deposition measurements by Erbacher et al suggests that the presently reported roughness factors are reliable and are the correct order of magnitude.

June 27, 1956

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TABLE I

ABSOLUTE AREAS OF IRON AND STAINLESS STEEL SURFACES

Spec. No.	Specimen	Surface Prep.	Area (cm ²)		Roughness Factor
			Geometric	Absolute	
1a.	Armco Iron Sheet	H ₂ -reduced 1000°C	200	244	1.22
b.	" " " (check on same spec.)		200	244	1.22
2.	Armco Iron Sheet	H ₂ -reduced 1000°C	200	257	1.29
3a.	18-8 Stainless Steel	Pickled 25 vol. % HCl-25 vol. % H ₂ SO ₄ , 35°C, 10 min.	40.5	164	4.05
b.	" " " (check " on same spec.)	" (10 min.)	40.5	169	4.17
c.	" " "	" (20 min.)	40.5	165	4.1
d.	" " "	" (50 min.)	40.5	149	3.7
4.	18-8 Stainless Steel	" (10 min.)	40.5	166	4.10
5.	18-8 Stainless Steel	" (10 min.)	69.6	292	4.20
6.	18-8 Stainless Steel	" (10 min.)	64.0	260	4.06
7.	18-8 Stainless Steel	Pickled 15 vol. % HNO ₃ , 10 vol. % HF 90°C, 10 min.	40.5	55	1.36
8.	18-8 Stainless Steel	Abraded 2/0 Emery, degreased in benzene	40.5	124	3.06
9.	Armco Iron Sheet	" "	41.1	138	3.4
10.	18-8 Stainless Steel	Electropolished	115	129	1.12
11.	Glass beads	washed, baked 400°C	137	142	1.04

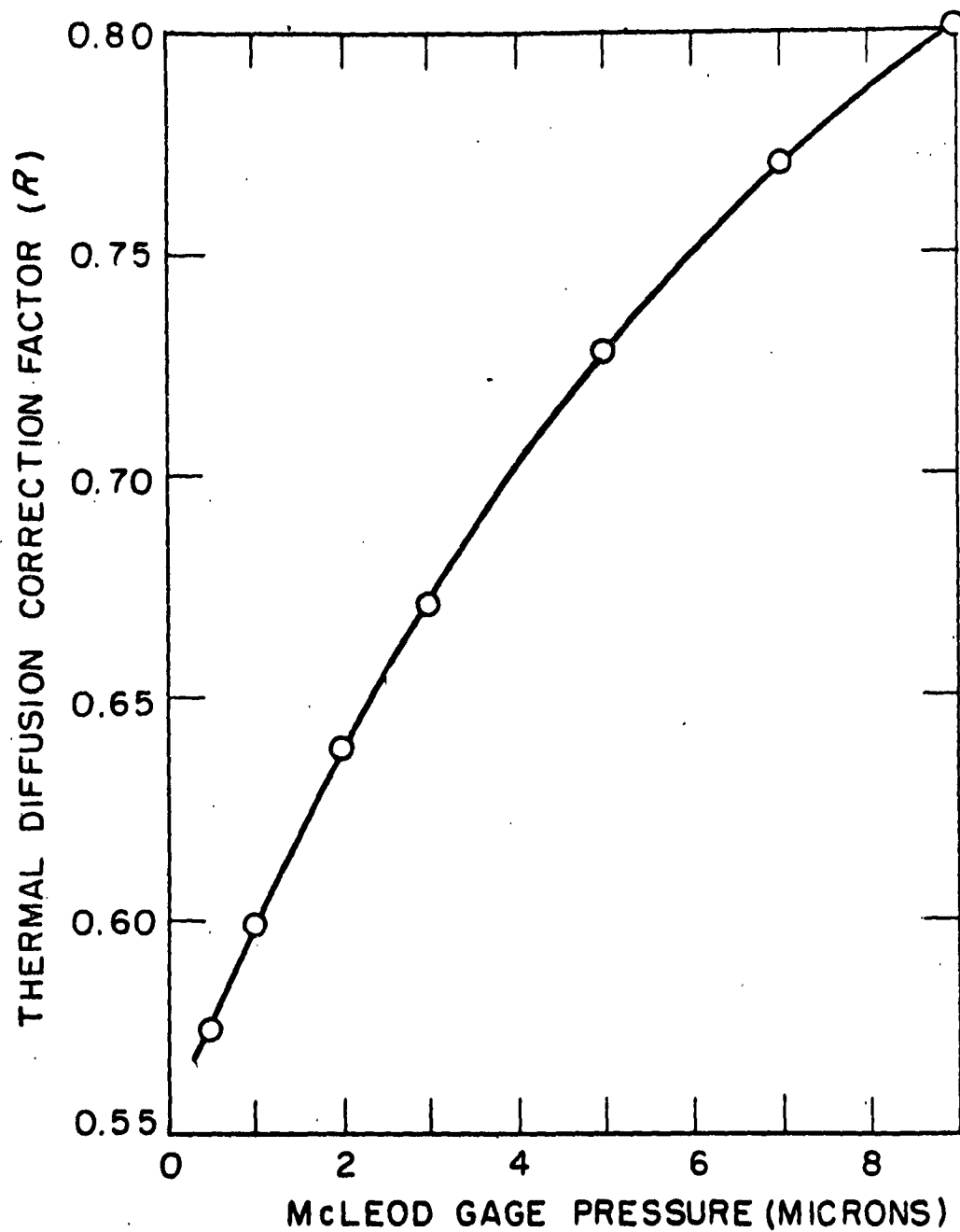
TABLE II

ABSOLUTE AREAS OF EVAPORATED IRON FILMS

Spec. No.	Source of Evaporated Iron	Thickness of Film, Å	Area (cm ²) Geometric Absolute	Roughness Factor
1.	Westinghouse "Puron" Wire	840	34.0	167
2.	"	"	"	4.9
3.	"	1720	29.6	312
4.	"	1860	34.0	10.5
5.	"	2000	17.3	317
6.	"	3250	17.2	9.3
	"	4150	16.5	10.7
	"	"	144	9.5
	"	"	"	8.7
7.	Bureau Stds Wire** (wrapped on Tungsten wire)	1500	17.7	31.6
8.	"	"	"	1.79
9.	Westinghouse "Puron" (wrapped on Tungsten wire)	1730	16.8	29.7
	"	1660	34.0	1.77
	"	"	"	1.74

*0.005% C, 0.003% S, <0.001% P, <0.001% Si, 0.001% Cu (proximate analysis by supplier).

**0.001%C, 0.001% S, 0.0005% P, 0.001% Si, 0.002% Cu (analysis supplied through courtesy of H. E. Cleaves, National Bureau of Standards)



Thermal Diffusion Correction Factor For Ethane

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