about 85°. Dispersion is faint. The optic axial angle for blue light is slightly greater than for red light judging from the optic axis that most nearly coincides with the crystal axis *a*. The other optic axis was not observed.

**X-Ray Powder Diffraction.**—As an aid to the study of calcium oxalate and its double salts with calcium chloride, the X-ray diffraction lines obtained from powdered samples of calcium oxalate monohydrate and the two double salts described in this paper are listed in Table III.

## Discussion

The formation of these characteristic crystals by reaction of calcium oxalate with hydrochloric acid can be used to aid in the identification of calcium oxalate in many cases where the unknown does not contain crystals large enough to be identified by optical methods.

No special attempt was made to prepare other double salts of calcium oxalate-chloride, but when conditions of preparation were similar to those described by Souchay and Lensen[5] we did not obtain the compound $4CaC_2O_4 \cdot CaCl_2 \cdot 24H_2O$ that they reported. Consequently it seems possible that their double salt was actually a mixture. In fact they mention the presence of oxalic acid crystals in some of their preparations. Microscopic examination, including a determination of optical properties, would have revealed such a lack of homogeneity in the sample taken for analysis. It is possible that a complete phase study of this system would reveal other double salts.

**Acknowledgment.**—Acknowledgment is due Merle B. Hartzog for taking the X-ray powder diffraction photographs and for making the measurements given in Table III.

## Summary

A microscopical study of the reaction of calcium oxalate with hydrochloric acid has been reported. The composition, optical and crystallographic properties, and X-ray lines of a new double salt, $CaC_2O_4 \cdot CaCl_2 \cdot 2H_2O$, and those of the previously reported double salt, $CaC_2O_4 \cdot CaCl_2 \cdot 7H_2O$, have been determined.

The formation of these crystalline materials can be used as an aid in the microscopical identification of calcium oxalate, and to aid the phase study of this system.

ALBANY, CALIF. RECEIVED MARCH 4, 1946

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[CONTRIBUTION FROM RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

# The Sorption of Water Vapor at Low Pressure on the Surface of Some Cold-Rolled Steels at 20°

BY MARION H. ARMBRUSTER[1]

Because there are few unexceptionable data relative to the sorption of water vapor on a plane surface, especially of a metal, and because of the possible practical utility of a better knowledge of this matter, several series of careful measurements have been made at 20° at pressures up to 0.15 cm. on some of the identical samples of steel used in earlier measurements of the sorption of other gases.[2] These samples were three cold-rolled surfaces, two of low-carbon steel, the third a stainless alloy containing 18% chromium and 8% nickel, all of which had been carefully preheated to ensure reproducible results comparable with those for the sorption of other gases. At the highest pressures investigated mild steel sorbs what appears to be a complete monolayer physically and a partial layer by chemisorption, the completeness of coverage being estimated by comparison with data for carbon monoxide sorbed reversibly at −183° on the identical sample. On the same basis, the total volume of gas sorbed on the stainless alloy, which is presumably covered by an invisible yet protective oxide film, not reducible by hydrogen at 600°, is three to four times as great as on the mild steel, and of this amount about one-third is chemisorbed. The calculated heat of physical adsorption is about 25% greater than the heat of liquefaction of water vapor.

**Apparatus and Procedure.**—These were the same as previously described[3] except that the double McLeod gage,[4] which with water vapor could be used only up to $2 \times 10^{-3}$ cm. was supplemented by a second similar gage such that a higher pressure range could be covered without danger of condensation in the gage during a measurement. This danger was avoided, at the higher pressures, by warming the capillary of the second gage to about 30° during a reading. The correction for this difference in temperature was calculated and checked experimentally by means of hydrogen; it proved to be small. The supplementary gage was calibrated by comparison with the double gage, by use of "spectroscopically

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[1] Present address, Department of Chemistry, Barnard College, New York, N. Y.

[2] Armbruster and Austin, THIS JOURNAL, **66**, 159 (1944); also unpublished data for stainless alloys.

(3) Armbruster and Austin, *ibid.*, **60**, 467 (1938); **61**, 1117 (1939).

(4) It is of interest to note that in some preliminary measurements condensation of water vapor at 20° in the capillary of this gage was observed at a pressure of about 1.3 cm., whereas 1.7 cm. is the saturation pressure of water at this temperature. Similar condensation at a pressure lower than the saturation pressure of water has been observed by Frazer, Patrick and Smith, *J. Phys. Chem.*, **31**, 897 (1927), using the pressure-temperature curve method of determining adsorption; by Frazer, *Phys. Rev.*, (2) **33**, 97 (1929), using the optical method of Drude and Rayleigh modified for greater accuracy; and by Coolidge, THIS JOURNAL, **49**, 708 (1927).

TABLE I

CHEMICAL COMPOSITION AND OTHER DATA FOR THE SEVERAL SAMPLES

| Sample | Chemical composition,[a] % C | Mn | Si | Ni | Cr | Weight, g. | Thickness, mm. | Geometric area, sq. cm. |
|---|---|---|---|---|---|---|---|---|
| 1 (no. 25276) | 0.12 | 0.37 | 0.44 | 9.48 | 18.48 | 411.4 | 0.09 | 11,130 |
| 2 (no. 25277) | .31 | .58 | .115 | | | 308.4 | .07 | 11,130 |
| 3 (no. 25278) | .12 | .47 | .003 | | | 366.7 | .04 | 24,680 |

[a] Percentages of S and P omitted because small, therefore immaterial.

pure" hydrogen. The amount of gas sorbed at a given pressure was, under favorable circumstances, reproducible within 1.5% and always reproducible within 5%, which is considered satisfactory.

A blank experiment, made to determine the correction for water adsorbed on the walls of the system (Pyrex brand glass which had been chemically cleaned) which had a geometric area only 1-2% of that of the steel surfaces, showed this correction to be about 2 × $10^{-3}$ cc., corresponding to a coverage of less than 1%, which is within the experimental error of the measurements recorded.

The rate of total sorption of water vapor on the metal was slow. In general, the amount adsorbed reversibly is taken up in a few minutes with attainment of "equilibrium" in half an hour; about 90% of the total sorption occurs in three or four hours, the remainder in about fifteen more hours, with no further observed change over a period of ninety-six hours. Accordingly, the usual procedure was to allow a period of twenty hours for the attainment of equilibrium.

**Materials.**—Water was purified by repeated distillation from alkaline permanganate and from chromic acid, the final distillate being collected in a bulb which was later connected to the gas manifold of the train through a U-tube and vacuum stopcock. In order to remove any foreign gas, the water was distilled from this bulb at 35° into the U-tube at −78° with the vacuum pump operating; by alternating the temperature of bulb and tube the water was distilled back and forth until the pressure on the gage was down to $10^{-5}$ cm., the vapor pressure of water at −78°.

The two mild-carbon steels are described in an earlier paper[2]; the stainless alloy was that used in measurements as yet unpublished.[5] For convenience, the main characteristics of these samples are listed in Table I. Examination under the microscope of polished sections of each specimen showed that the surface of the stainless steel comprised less than 0.1% of non-metallic inclusions, and that on the carbon steels this area was less than 1% on no. 2 and less than 2% on no. 3; further, that on these two about 15 and 25%, respectively, of the area was covered by spheroidized carbide particles.

The pretreatment of each surface included degreasing, reduction in hydrogen at 600°, outgassing at 450° and $10^{-6}$ mm., bringing down to 20°, either in vacuum or in hydrogen, and conditioning by repeated exposure to various gases; all as described previously.[2]

**Results.**—Typical results, selected from a large number of concordant runs, covering the pressure range up to 0.15 cm. are plotted directly in Fig. 1, the volumes absorbed being all corrected so as to refer to the same geometric area (11,130 sq. cm.). The total adsorption is that taken up by the reduced, outgassed surface as the pressure is increased; the reversible is that part of the total which is removed by evacuation at 20°. The amount chemisorbed is taken as the difference between total and reversible.

It is to be noted that there is at least a possibility of some reaction between water and iron

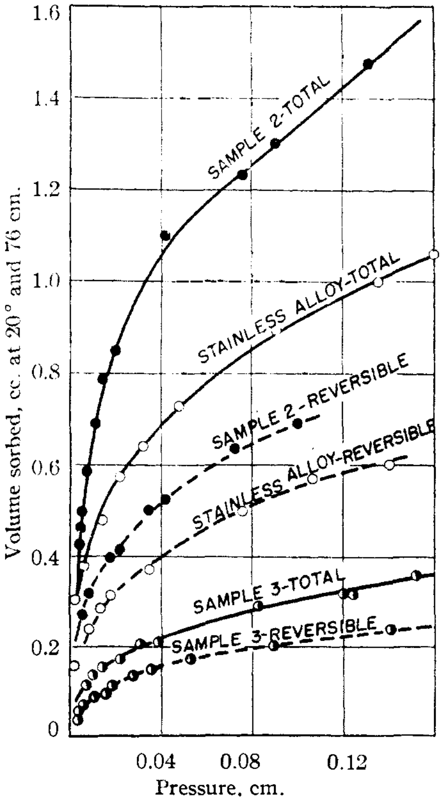

Fig. 1.—Representative isotherms for water vapor sorbed on the several samples corrected to same nominal surface area.

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(5) This is, however, not the sample used in determining the solubility of hydrogen in austenitic steel, *cf.* Armbruster, THIS JOURNAL, **65**, 1043-1054 (1943).

of the carbon steels, with formation of two-dimensional "oxide" over some part of the surface; the stainless alloy is already covered with such a film which cannot be removed by hydrogen even at temperatures considerably above 600°, the maximum feasible in this apparatus. This possibility may require some modification of interpretation of the results in terms of the processes operating to produce them; for simplicity, however, the usual terms have been retained in the subsequent discussion.

## General Discussion and Inferences

In order to learn whether the difference in volume of gas sorbed by these samples is due to a difference in nature of the surface or merely in true surface area, the ratio at a given pressure of the volume sorbed on the stainless alloy or on sample 2 to that on sample 3 has been calculated, with results presented in Table II. These ratios prove to be substantially constant over the whole range of pressure except for the stainless alloy below about 0.005 cm., indicating that the observed differences arise chiefly from a difference in effective surface area. The deviation in the case of the stainless steel is considered later. An analogous comparison of the volume of nitrogen sorbed at −183° on the two carbon steels[2] yields a ratio of 4.62 which is in fair agreement with that for these samples in Table II. Corresponding data for the reversible sorption of carbon monoxide at −183° on these steels yields a somewhat less constant ratio which varies from 4.31 at 0.005 cm. to 2.86 at 0.11 cm. All these comparisons indicate, however, that the specific area of sample 2 is about three to four times that of sample 3.

TABLE II

VOLUME OF WATER VAPOR SORBED ON SAMPLES 1 AND 2 RELATIVE TO THAT ON SAMPLE 3 (CARBON STEEL) AT THE SAME PRESSURE

| | Ratio of volume sorbed on | | | |
|---|---|---|---|---|
| | Stainless alloy to that on 3 | | Carbon steel 2 to that on 3 | |
| $p$, cm. | Total | Reversible | Total | Reversible |
| 0.001 | 3.43 | 3.48 | 4.53 | 3.12 |
| .005 | 3.39 | 2.77 | 4.58 | 3.23 |
| .01 | 3.23 | 2.64 | 4.82 | 2.88 |
| .02 | 3.17 | 2.55 | 4.84 | 3.19 |
| .03 | 3.17 | 2.33 | 4.84 | 3.19 |
| .04 | 3.15 | 2.60 | 4.80 | 3.24 |
| .05 | 3.08 | 2.75 | 4.72 | 3.28 |
| .06 | 3.08 | 2.68 | 4.66 | 3.30 |
| .07 | 3.02 | 2.66 | 4.56 | 3.28 |
| .08 | 2.97 | 2.64 | 4.49 | 3.26 |
| .09 | 2.93 | 2.64 | 4.44 | 3.28 |
| .10 | 2.95 | 2.64 | 4.44 | 3.30 |
| .11 | 3.00 | 2.64 | 4.46 | 3.30 |
| .12 | 3.07 | 2.64 | 4.60 | 3.30 |

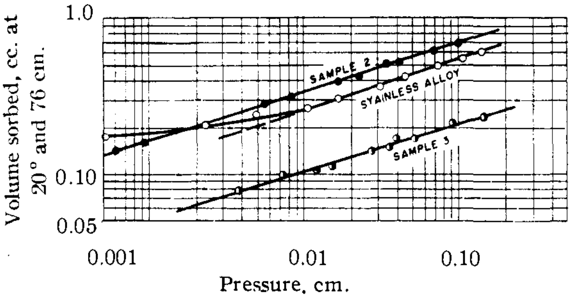

Fig. 2.—Typical isotherms for reversible sorption on the three samples plotted to illustrate degree of validity of Freundlich relation.

When the data for reversible adsorption are plotted as log $v$ *versus* log $p$ (Fig. 2), which is a method of testing the applicability of the relation $v = ap^{1/n}$, the results for steels 2 and 3 yield a straight line with slope corresponding to $n = 3$. This value of $n$ is relatively high, as would be expected in view of the significance of this index as discussed in an earlier paper.[2] For the stainless alloy in the range above 0.01 cm. the graph is likewise linear and has about the same slope; at lower pressures it deviates in the direction corresponding to higher values of $n$. The total sorption when plotted in this way shows analogous deviations for the steels at pressures of 0.001 cm. or less.

Data for both reversible and total adsorption are also plotted in Fig. 3 in terms of $p/v$ against $p$, which is a means of testing the applicability of the Langmuir equation

$$v = \frac{a\,v_s p}{1 + ap}$$

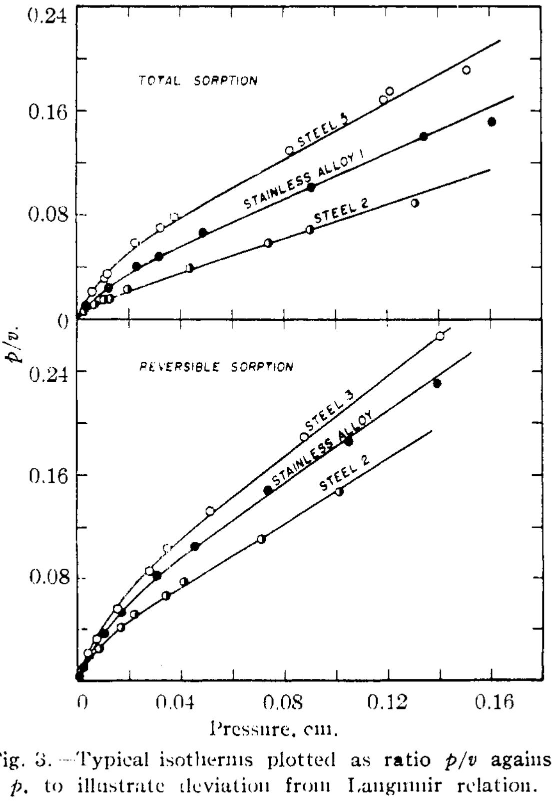

Fig. 3.—Typical isotherms plotted as ratio $p/v$ against $p$, to illustrate deviation from Langmuir relation.

TABLE III

LIMITING VOLUME ($v_s$) OF WATER VAPOR SORBED AT 20° AS DERIVED FROM LANGMUIR ISOTHERMS

| Sample | Type of sorption | $v_s$ (cc. at 20° and 76 cm.) | Molecules/sq. cm. derived from $v_s$ | Apparent surface coverage (per cent.)[a] | $\frac{v_s(20°\text{-}H_2O)}{v_s(-183°\text{-}CO)}$[b] |
|---|---|---|---|---|---|
| #1 (Stainless) | Total | 1.116 | $2.527 \times 10^{15}$ | 265 | 3.67 |
| #1 (Stainless) | Reversible | 0.715 | 1.620 | 170 | 2.35 |
| #1 (Stainless) | Chemisorbed | 0.401 | 0.907 | 95 | 1.32 |
| #2 (Mild Steel) | Total | 1.375 | 3.113 | 327 | 1.42 |
| #2 (Mild Steel) | Reversible | 0.775 | 1.755 | 184 | 0.80 |
| #2 (Mild Steel) | Chemisorbed | 0.600 | 1.358 | 143 | 0.62 |
| #3[c] (Mild Steel) | Total | 0.370 | 0.839 | 88 | 1.02 |
| #3[c] (Mild Steel) | Reversible | 0.293 | 0.664 | 70 | 0.81 |
| #3[c] (Mild Steel) | Chemisorbed | 0.077 | 0.175 | 18 | 0.21 |

[a] Assuming complete coverage to be $0.95 \times 10^{15}$ molecules/sq. cm. [b] Corresponding ratios with nitrogen at −183° as standard for comparison may be obtained by multiplying the factor for samples #1, #2 and #3, respectively, by 2.58, 1.34 and 1.49. [c] Since geometric area of sample #3 was 2.22 fold that of #1 and #2, the data have been corrected for comparison of adsorption on the same geometric area.

where $v_s$ is interpreted as a maximum or limiting value. The linearity of the graphs at the higher pressures shows that this equation holds in that region, but it fails at lower pressures in the direction that the observed volume is greater than the amount required by extrapolation of the linear portion. Analogous deviations observed with other gases are discussed in an earlier paper. The quantity $v_s$, although there is some question as to its precise significance, affords a convenient means of comparing the sorption on different samples. Values of $v_s$ derived from the linear portion of each of the several curves in Fig. 3 are presented in Table III. Comparison of the first two columns of this Table shows, as did the more direct comparison in Table II, that the effective surface area of Sample 2 is several times as great as that of Sample 3.

The column headed "apparent percentage of surface covered" gives the coverage of the surface calculated on the assumptions: (a) that the specific surface is the same in each case; and (b) that the cross-sectional area of the water molecule is 10.5 *A*,[6] on which basis there are $0.95 \times 10^{15}$ molecules per sq. cm. in a complete monolayer. The extent to which the surface is in fact covered by a monolayer cannot be derived from such a comparison but can be estimated by comparison with the volume of some other gas sorbed under conditions which appear to yield a complete monolayer. Experience with these samples indicates that whereas on mild steel the reversible sorption at −183° of either nitrogen or carbon monoxide is a reasonably reliable criterion, on stainless steels only carbon monoxide should be used for this purpose.[7]

Accordingly, carbon monoxide was chosen as reference, and the last column in Table III presents the ratio of $v_s$ for water vapor at 20° to that for reversible carbon monoxide at −183° on the same sample, which in effect eliminates any difference arising from a difference in specific area. These ratios are the same for the reversible sorption of water vapor on the steels and are so close to unity that, on the basis of carbon monoxide as a criterion, it seems justifiable to conclude that the steel surfaces are similar in nature; both take up a monolayer reversibly; the amount of strongly held water vapor varies somewhat, that for mild steel 2 being greater and corresponding to about a half of a monolayer. Furthermore, the nature of the surface of the stainless alloy differs markedly from that of the steels: the stainless alloy sorbs reversibly three times as much water vapor as mild steel; about one and a half monolayers are held strongly. The water chemisorbed on mild steel only partially covers the surface and so closely approximates the observed concentration of chemisorbed carbon monoxide at −183° that it seems reasonable to believe it is also sorbed on iron atoms, which constitute 75% of the surface according to microscopic analysis, rather than on carbide particles or inclusions, possibly with one water molecule to four iron atoms. In the case of the stainless alloy the reversible and chemisorbed water may be sorbed on the whole surface and on the free metal atoms, respectively, but to a greater degree. The reversibly adsorbed water at 20° is two to three times as great as the physically adsorbed carbon monoxide at −183°. Both water and carbon monoxide are polar molecules but the dipole moment of water is very large compared to that of carbon monoxide ($0.12 \times 10^{-18}$ esu) and its orientation energy, which

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(6) This cross-section is derived by means of the equation given by Emmett and Brunauer [THIS JOURNAL, **59**, 1558 (1937)] taking the density of liquid water at 20° as 0.998 g. per cc. It lies between the value 12.65 sq. Å. obtained from the same equation by using the density of ice (as 0.917 g. per cc. at 4°), and that of 9.60 sq. Å. estimated by Langmuir from the molecular volume of liquid water.

(7) Unpublished data on the adsorption of gases on the stainless alloy show that the limiting volume of nitrogen is only half that for reversibly sorbed carbon monoxide; moreover the true area derived from the sorption of nitrogen is but one-half the geometric area. This is in marked contrast to mild steel on which these two gases are reversibly sorbed to substantially the same extent. Measurements on silver (Armbruster, THIS JOURNAL, **64**, 2545 (1942)), and unpublished data for tin, both of which have a face-centered cubic lattice of the same type as the stainless alloy, show that the sorption of nitrogen is but half that of the reversible carbon monoxide.

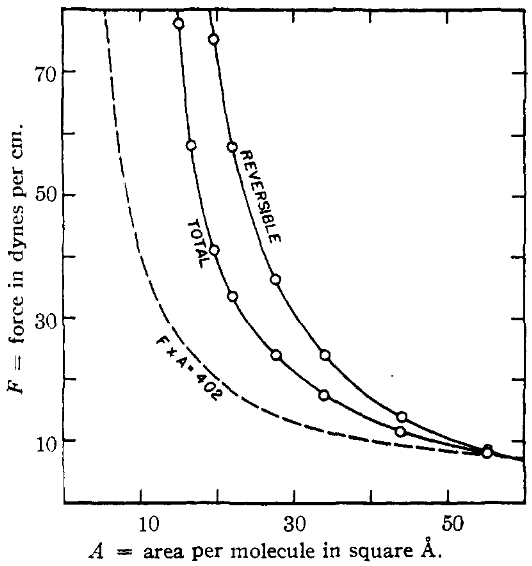

Fig. 4.—Typical force–area curve for water sorbed on the stainless alloy.

is the largest constituent of the van der Waals forces involved in its adsorption, is about 50,000 fold greater than for carbon monoxide. Accordingly on this surface of greater activity the water molecule may be oriented on end so that the density of packing is greater. The chemisorbed water at 20° is about three times as great as the strongly held carbon monoxide at −183°.

Several factors may contribute to the greater adsorptive capacity of the stainless alloy. First, there appears to be more metal on the surface of the stainless alloy than on that of the mild steel as indicated by a relatively greater ratio of chemisorbed carbon monoxide to reversible carbon monoxide. This greater amount of metal may lead to an increased tendency to form a second layer as was observed on iron but not on oxide in our measurements with ethyl iodide vapor. Secondly, in the case of the stainless alloy, in contrast to the mild steel, both argon at −183° and carbon dioxide at −78° are held irreversibly to the same extent corresponding to 5 to 10% of the surface; undoubtedly these gases are strongly held to the same places, such as cracks and grain boundaries, which may enhance condensation. Furthermore, the fact that slight preferred orientation of the metal crystals with the (112) plane in the rolling plane, that is a plane other than a principal one, further supports this view. Finally, and most likely, the greatest contributing factor is the character imparted to the stainless alloy surface by its chromium content. Whereas the metal phase in the case of the mild steel consists of iron atoms and has the body-centered cubic lattice of $\alpha$-iron, that of the stainless alloy is a solid solution containing 18% chromium, 8% nickel and the remainder iron and is austenitic, that is, it has the face-centered cubic lattice of $\gamma$-iron. Chromium is more active than iron and is known to impart to certain of its alloys with iron some of its own properties, such as a strong or effective film forming tendency.

**Heat of Adsorption.**—The "average heat of adsorption" on the less active part of the surface has been calculated by the method of Brunauer, Emmett and Teller[8] with results presented in Table IV. It is substantially the same for all three samples and about 25% greater than the heat of liquefaction of water (10520 cal./mole). Unpublished measurements of the sorption of water vapor on tin plate and on tin foil yield a value which is close to 13000 cal./mole, indicating that the heat of sorption is virtually the same on a number of metallic surfaces regardless of chemical composition and is, in every case, greater than the heat of liquefaction of water. In this connection, the heat of sorption of water vapor on gold[9] determined calorimetrically is likewise greater than the heat of liquefaction.

TABLE IV

COMPARISON OF HEAT OF ADSORPTION OF WATER VAPOR ON PLANE SURFACES AT 20°

| Surface | Type of adsorption | $E_1 - E$ Net heat of adsorption cal./mole | $E_1$ Heat of adsorption, cal./mole |
|---|---|---|---|
| #1 Stainless Alloy | Total | 2540 | 13,060 |
| #1 Stainless Alloy | Reversible | 2410 | 12,930 |
| #2 Mild Steel | Total | 2980 | 13,500 |
| #2 Mild Steel | Reversible | 2700 | 13,510 |
| #2 Mild Steel | Total | 2440 | 12,960 |
| #3 Mild Steel | Reversible | 2320 | 12,840 |
| Tin Plate (a) | Total | 2210 | 12,730 |
| Tin Plate (a) | Reversible | 2430 | 12,950 |
| Tin Foil (a) | Total | 2160 | 12,680 |
| Tin Foil (a) | Reversible | 2120 | 12,640 |

[a] Derived from unpublished data of Armbruster.

On the other hand, the heat of sorption of water vapor on sugar charcoal (calculated)[10a] or gas mask charcoal (directly measured),[10b] or silica gel,[11] or freshly blown or fractured glass,[12] is approximately equal to, or slightly less than, the heat of liquefaction. These results imply that the attraction between molecules of water and the surface is greater than the cohesive force between water molecules, if the surface is metallic but not if the surface is non-metallic, a conclusion which is to be expected since the metal surface is ionic and the water molecule has a large dipole moment ($1.84 \times 10^{-18}$ e.s.u) which leads to large orientation effects. This positive net heat of adsorption for these dipolar molecules on iron determines the shape of the adsorption isotherm in the pressure range investigated, up to a relative pressure of

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(8) Brunauer, Emmett and Teller, THIS JOURNAL, **60**, 309 (1938).

(9) Barry and Barrett, *ibid.*, **55**, 3088 (1933).

(10) (a) A. S. Coolidge, *ibid.* **48**, 1795 (1926); (b) Keyes and Marshall, *ibid.*, **49**, 156 (1927).

(11) Reyerson and Cameron, *J. Phys. Chem.*, **39**, 181 (1935); "International Critical Tables." Vol. V, 1941.

(12) Frazer, Patrick and Smith, *J. Phys. Chem.*, **31**, 897 (1927).

$p/p_0$ = 0.06, which is concave to the pressure axis; the isotherms are most likely of the sigmoid type if the pressure is sufficiently extended, as the data for ethyl iodide indicate, and resemble the isotherm for water vapor on silica gel. In contrast, the net heat of adsorption of water on charcoal is negative; accordingly the isotherm at low pressure is convex to the pressure axis and extended to higher pressure is believed to be type V according to the classification of Brunauer, *et al.*[13]

**Force-Area Curves.**—Figure 4 presents the force-area curve, derived graphically by the method of Innes and Rowley,[14] for the film sorbed on the surface of the stainless alloy; the analogous curves for the carbod steels are substantially the same.

## Summary

The sorption of water vapor at 20° and pressures up to 0.15 cm. has been measured on two surfaces of cold-rolled, mild carbon steel on which the sorption of other gases had previously been measured; also on a stainless alloy containing 18% chromium and 8% nickel. At the highest pressures investigated the carbon steels sorb what is interpreted, by comparison with the amount of carbon monoxide sorbed reversibly at −183° on the identical surface, as a complete layer held physically and a partial layer by chemisorption. The stainless alloy adsorbed three to four times as much as the carbon steel and of this amount one-third was chemisorbed. The effective surface area of the two carbon steels was significantly different, though the surfaces were nominally the same.

The rate of sorption is slow. An amount corresponding approximately to that held physically is taken up within a few minutes, with attainment of equilibrium in half an hour; about 90% of the total sorption occurs within three to four hours, the remainder in an additional fifteen hours.

KEARNY, N. J. RECEIVED MARCH 15, 1946

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[13] Brunauer, L. Deming, W. Deming and Teller, THIS JOURNAL, **62**, 1723 (1940).

[14] Innes and Rowley, *J. Phys. Chem.*, **45**, 158 (1941).

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, U. S. STEEL CORPORATION]

# The Adsorption of Oxygen at Low Temperature and Pressure on Smooth Iron

BY MARION H. ARMBRUSTER[1] AND J. B. AUSTIN

This paper reports the results of measurements of the sorption of oxygen at 20°, −78° and at −183°, and at pressures up to 0.1 cm. of mercury on three smooth surfaces of iron (cold-rolled steel) on which the sorption of other gases had already been determined. The sorption on each surface was determined first after it had been degreased and outgassed, and subsequently after it had been reduced in purified hydrogen at 450° for a period up to sixty hours and again outgassed. Surfaces given these treatments are designated unreduced and reduced, respectively.

**Apparatus and procedure** were identical with those described in earlier papers.[2]

**Oxygen** of "spectroscopic" grade was obtained in glass flasks which were sealed to the gas manifold of the adsorption train before being opened.

**Hydrogen** used for reducing the surfaces, was tank hydrogen freed from traces of water vapor and oxygen by passage through sulfuric acid, then successively over calcium chloride, hot-platinized asbestos, activated alumina, and phosphorus pentoxide.

**Iron Surfaces.**—These were the identical samples used in earlier measurements of the sorption of other gases on smooth iron. Their characteristics, and the general treatment given them, are already described. The identifying number is in each case the same as in the earlier paper.[3] Before each run the surface was conditioned by baking it for 2 hours at 300° at a pressure of less than $10^{-6}$ mm.

## Observations

**Degreased (Unreduced) Surface.**—Typical isotherms for Sample 1, selected from a large number of concordant runs, showing the amount of gas, expressed as a volume at 20° and 76 cm. adsorbed at 20°, −78° and −183°, are given in Fig. 1. Typical data illustrating the rate of adsorption at each of these temperatures are presented in Fig. 2.

At −183° the amount of gas sorbed on a surface which had been exposed to oxygen and then pumped out, all at temperatures, is about 15% less than that sorbed on the same surface after it had been outgassed at −78, 20 or 300°. In each case the isotherms lie very close to those for the sorption of CO (black disks in Fig. 1) on the identical sample.[4] Moreover, on a surface pumped out at temperature the rate of adsorption was virtually instantaneous, whereas on one outgassed at −78, 20 or 300° it was slow for the initial increment of gas, occasionally for the second, but was virtually instantaneous for all subsequent additions. The slow rate was ob-

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[2] Armbruster and Austin, THIS JOURNAL, **60**, 467 (1938); **61**, 1117 (1939); **66**, 159 (1944); Armbruster, *ibid.*, **64**, 2545 (1942).

[3] Armbruster and Austin, *ibid.*, **66**, 159 (1944).

[4] *Cf.* Armbruster and Austin, *ibid.*, **66**, 159 (1944).