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).

[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).

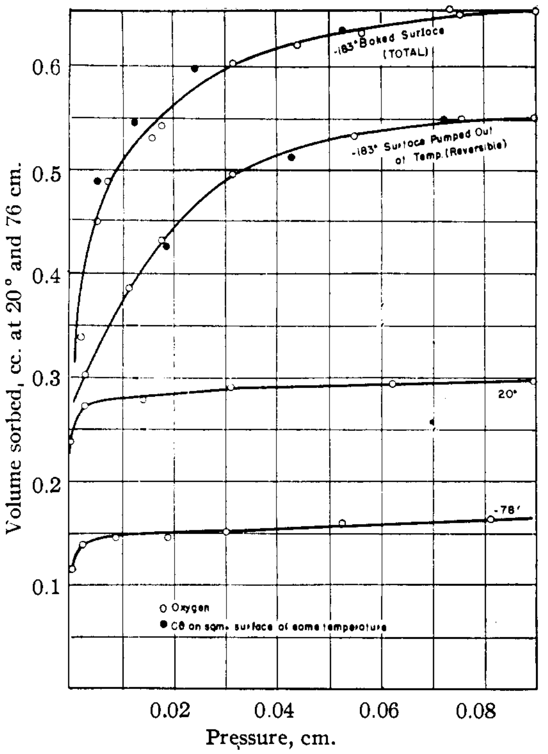

Fig. 1.—Typical isotherms for unreduced surface of Sample 1.

served on a surface cooled in argon as well as on one cooled in vacuum.

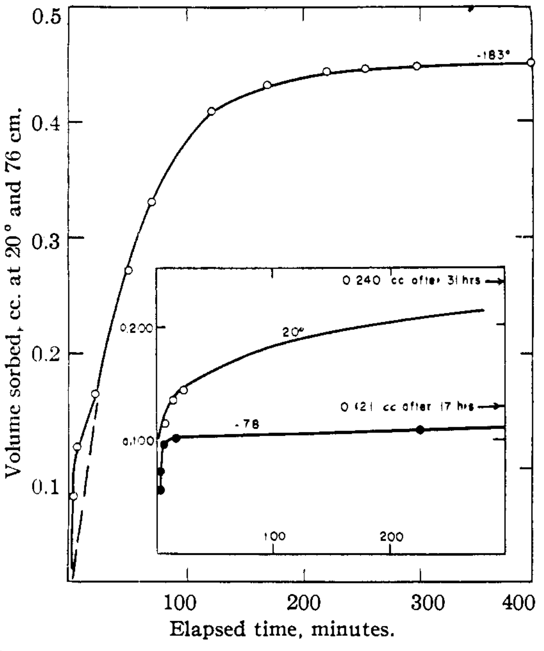

Fig. 2.—Curves illustrating rate of adsorption on unreduced surface of Sample 1.

At −78°, a surface baked out at 300° adsorbs oxygen in an amount which, over the range investigated, is virtually independent of pressure and is of the order of that held so strongly at −183° that it cannot be removed at temperature. The gas sorbed at −78° is likewise not removed by reducing the pressure in the system at temperature. A surface exposed to oxygen at −183°, then warmed to −78°, evacuated and again exposed to oxygen (at −78°) adsorbs no gas, although, as already noted, evacuation at −78° conditions the surface so that on subsequent cooling to −183° oxygen is adsorbed in the same amount as on a surface outgassed at 300°. The rate of adsorption at −78° is relatively slow, being most rapid immediately following exposure of the surface to oxygen but decreasing rapidly as pressure decreases; adsorption continues slowly, however, until substantially all the gas admitted is taken up. In one instance in which 0.122 cc. (at 20° and 76 cm.) was admitted to the adsorption bulb, 0.082 cc. was adsorbed after one minute, 0.095 after four minutes, 0.115 after fifteen minutes, and 0.121 cc. after seventeen hours. During this period the pressure decreased to 3×10^{-5} cm.; increasing the pressure to 0.10 cm. increased the adsorption only to 0.165 cc.

A surface conditioned at 300° adsorbed about twice as much oxygen at 20° as at −78°, the amount sorbed being virtually independent of pressure over most of the range investigated; moreover, the sorbed gas was not removable by reducing the pressure at temperature. At this temperature, as at −78°, the rate of adsorption was slow. In one instance in which 0.240 cc. of gas was admitted, 0.146 cc. was adsorbed within twenty minutes, 0.226 cc. after seventeen hours, and 0.240 cc. after thirty-one hours, at which time the pressure in the system had decreased to 4×10^{-5} cm.; when it was increased to 0.116 cm., the amount adsorbed increased only to 0.298 cc.

Surface Reduced by Hydrogen.—Typical isotherms for the reduced surface of Sample 1 are shown in Fig. 3; representative data illustrating the rate of adsorption on this type of surface are presented in Fig. 4.

At −183° approximately one-third of the sorbed oxygen can be removed by evacuating the system but the remaining two-thirds cannot be so removed. The amount of oxygen which can be pumped off is somewhat less than the amount adsorbed reversibly on the same surface before it is reduced (*cf.* Fig. 1); but since a corresponding decrease was observed with other gases, it is concluded that this change is associated with a change in the effective surface area during reduction and that the amount of oxygen held reversibly at −183° is the same on the reduced as on the unreduced surface. The rate of adsorption at this temperature is initially very rapid, an amount roughly equivalent to that sorbed reversibly being adsorbed very slowly (see Fig. 4).

At −78°, oxygen is adsorbed in an amount

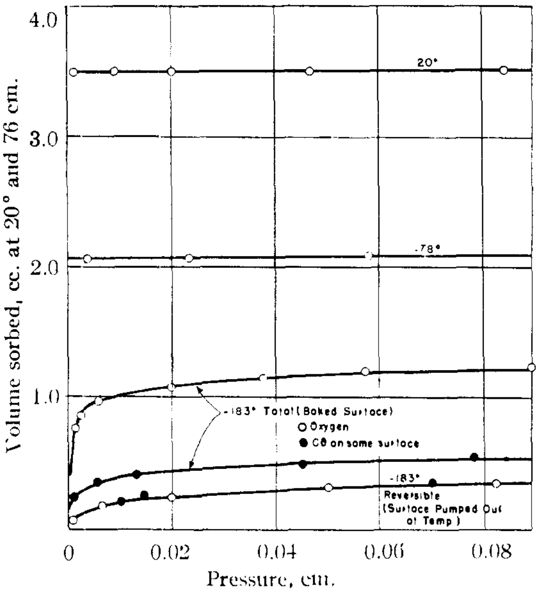

Fig. 3.—Typical isotherms for reduced surface of Sample 1.

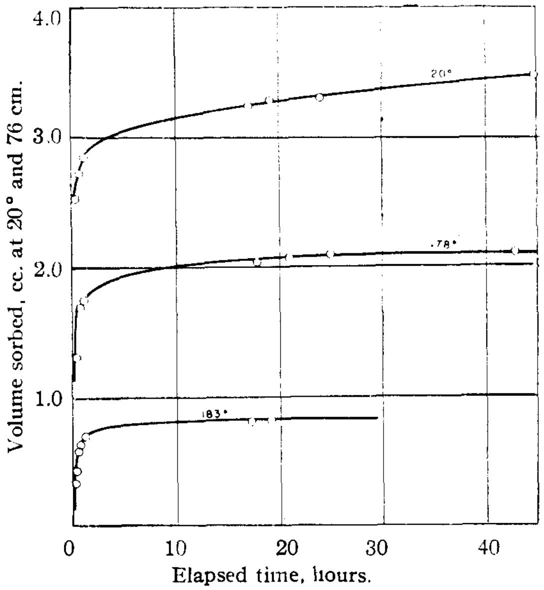

Fig. 4.—Curves illustrating rate of adsorption on reduced surface of Sample 1.

which, over the range investigated, is independent of pressure and nearly twice that adsorbed at −183°; moreover, the sorbed gas cannot be removed at temperature. As at −183°, there is an almost instantaneous initial adsorption, followed by a very slow process which continues for days.

At 20°, the amount of oxygen adsorbed, which, as at −78°, is independent of pressure, is about three times as great as that adsorbed at −183° and nearly twice as great as at −78°. Oxygen adsorbed on a reduced surface at 20° cannot be pumped off even at 300° but must be removed by hydrogen. Again the rate of adsorption is initially very rapid but soon slows down eventually to become exceedingly slow (see Fig. 4).

Calculations and Inferences Based on Observations

Form of Isotherms.—The isotherms at 20° and at −78°, which are essentially horizontal straight lines, are of little interest so far as form is concerned; those at −183° are of greater significance because they confirm the general pattern observed in the sorption of other gases on these identical samples in that they are satisfactorily represented by the Langmuir equation except at the lowest pressures[5] in which range they are better fitted by the Freundlich exponential relation. This is illustrated in Figs. 5 and 6, the former presenting two typical isotherms plotted as the ratio p/v against p, which yields a straight line for the Langmuir equation; the latter shows these same data plotted on double logarithmic coördinates on which the Freundlich relation is a straight line. The greater curvature of the isotherm for the reduced surface (Fig. 5) is typical of all the surfaces.

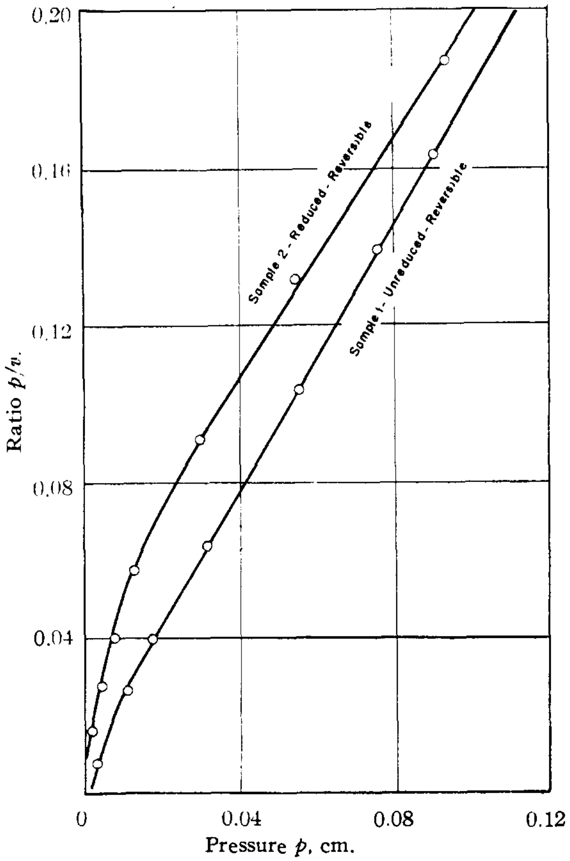

Fig. 5.—Two typical isotherms plotted as p/v against p to illustrate deviation from the Langmuir equation.

In Fig. 6, the slope of the line, which corresponds to the exponent in the Freundlich rela-

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(5) Armbruster and Austin, THIS JOURNAL, **66**, 159 (1944).

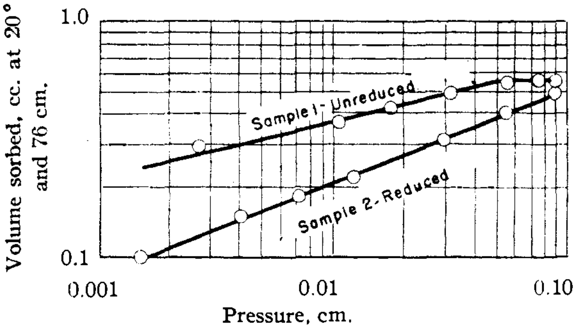

Fig. 6.—Typical isotherms of Fig. 5 plotted on double logarithmic coordinates to illustrate application of Freundlich exponential relation.

tion, also to the exponent of the combined expression given in an earlier paper,[6] is 3 for the measurements with Sample 1 and 5 for those with Sample 2; these are both relatively large, as would be expected for a gas sorbed at a temperature near its condensation point.

The several isotherms are satisfactorily represented over the whole range by the equation[5]

$$v = v_s \sqrt[n]{\frac{ap}{1 + ap}}$$

with the exponent n ranging from 3 to 5 for the different samples.

Relative Concentration of Sorbed Oxygen.—Comparison of data for different gases sorbed on surfaces differently conditioned is facilitated by having some objective measure of the relative number of molecules sorbed per unit area and by eliminating the influence of differences in true area among the several samples, or even for any one sample after different treatments. These ends can be attained by making two assumptions: (1) that the limiting volume (v_s) of the Langmuir equation provides an index of the concentration of sorbed molecules in a close-packed monolayer; (2) that for nitrogen sorbed at −183° this limiting volume is a measure of the specific surface of the sample. Neither of these assumptions is beyond question, yet each is believed to be sufficiently valid to permit its use as a basis of comparison.

The correspondence already noted between the isotherms for oxygen and for carbon monoxide on the unreduced surface of steel (*cf.* Fig. 1) is further illustrated by the data in Table I which presents the relative concentration of these gases derived on the above assumptions. The constancy of this ratio indicates that on these several surfaces the concentration of oxygen in a close-packed monolayer is the same in both total and reversible adsorption, and that it is the same as the concentration of carbon monoxide in a monolayer of carbon monoxide but approximately 50% greater than that of nitrogen in a monolayer of nitrogen. This suggests that on the unreduced surface the effective cross-section of sorbed oxygen is equal to that of carbon monoxide but may be significantly less than that of nitrogen, although the cross-section of these molecules as calculated from the density of the liquid or solid indicates that the effective area of oxygen is less than that of carbon monoxide and nitrogen which are about the same.

Table I includes ratios only for reversible and total sorption, the quantities directly measured. The amount of strongly-held oxygen is calculated by difference, a procedure which magnifies the experimental error so that the ratio of strongly-held oxygen (or carbon monoxide) to the strongly-held nitrogen varies from 1.15 to 1.35.

TABLE I

RATIO OF LIMITING VOLUME v_s (RELATIVE NUMBER OF MOLECULES) OF OXYGEN OR CARBON MONOXIDE ON AN UNREDUCED SURFACE AT −183° TO THAT OF NITROGEN ON THE SAME SAMPLE AT THE SAME TEMPERATURE

	Sample 1	Sample 2
Total O_2/Total N_2	1.43	1.42
Total CO/Total N_2	1.41	1.45
Reversible O_2/Reversible N_2	1.45	
Reversible CO/Reversible N_2	1.46	

Analogous ratios for the reduced surfaces, presented in Table II, indicate that on this type of surface: (1) the concentration of oxygen sorbed reversibly at −183° is the same as that of nitrogen. (Note difference from ratio of 1.4 observed on the unreduced type of surface.) (2) The concentration of carbon monoxide sorbed reversibly at −183° varies from virtually the same as that of oxygen and nitrogen (Sample 1) to about 50% greater (Sample 3) which is the ratio observed on the unreduced surfaces. (3) The amount of oxygen chemisorbed at −183° is 2 to 4 times as great as that of nitrogen or of chemisorbed carbon monoxide. (4) The amount of oxygen chemisorbed at −78° is 5 to 8 times, and that at 20° about 10 times, as great as that of nitrogen at −183°.

TABLE II

RATIO OF LIMITING VOLUME v_s (RELATIVE NUMBER OF MOLECULES) OF OXYGEN SORBED ON A REDUCED SURFACE TO THAT FOR OTHER GASES ON THE SAME SURFACE

	Sample 1	Sample 2	Sample 3
Reversible O_2 (−183°)/Reversible N_2 (−183°)	0.97	0.94	0.95
Reversible CO (−183°)/Reversible N_2 (−183°)	1.07	1.34	1.49
Reversible O_2 (−183°)/(Reversible CO (183°)	0.90	0.70	0.64
Chemisorbed O_2 (−183°)/Reversible N_2 (−183°)	2.3	2.0	4.3
Chemisorbed O_2 (−183°)/(Chemisorbed CO −183°)	3.6	2.6	2.3
Total O_2 (−78°)/Reversible N_2 (−183)	5.5	6.6	8.2
Total O_2 (20°)/Reversible N_2 (−183°)	9.2	...	11.0

Observation 3 substantiates the data of Brunauer and Emmett,[7] and of Beebe and Stevens,[8] who report that the amount of oxygen taken up

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[6] Armbruster and Austin, THIS JOURNAL, **66**, 159 (1944), eqs. (19) and (26).

[7] Brunauer and Emmett, *ibid.*, **62**, 1732 (1940).

[8] Beebe and Stevens, *ibid.*, **62**, 2134 (1940).

at −183° by iron catalysts varies with the rate at which the oxygen is admitted and that the volume of oxygen chemisorbed is 5 to 10 times as great as the volume of chemisorbed carbon monoxide.

The difference between observations 1 and 2 and the results for the unreduced surface is difficult to account for; but one possible interpretation is that the oxide film formed on exposure of reduced iron to oxygen at −183° may differ significantly in structure or in nature from that present on the unreduced surface, which presumably formed at room temperature or above. Another is that the effective cross-section of the molecules may vary because of orientation effects or interactions. Further evidence of this difference is presented in Table III which shows for Sample 1, the only sample for which complete data are available, the ratio of the limiting volume sorbed in the different types of sorption of oxygen and carbon monoxide on the reduced and unreduced surfaces. These ratios indicate that the amount of each gas sorbed reversibly on the reduced surface is only about two-thirds that on the unreduced surface; that the total amount of carbon monoxide sorbed is about the same on both types of surface, but that this proportion of reversible and chemisorbed changes; that, as might be expected, chemisorption and total sorption of oxygen is much greater on the reduced than on the unreduced surface.

TABLE III

RATIO OF LIMITING VOLUME v_s (RELATIVE NUMBER OF MOLECULES) OF OXYGEN AND OF CARBON MONOXIDE SORBED AT −183° ON REDUCED SURFACE TO THAT ON UNREDUCED SURFACE OF SAMPLE 1

Type sorption	Ratio red./unred. O_2	CO
Reversible	0.65	0.68
Total	1.85	0.97
Chemisorbed	7.9	3.1

Thickness of Films.—The relative thickness of the oxygen or oxide films on the several surfaces at the different temperatures can be estimated in two ways: (1) Since there is considerable evidence[5] to support the view that the limiting volume of nitrogen sorbed reversibly at −183° corresponds nearly to a close-packed monolayer, the relative thickness of other films can be derived directly by means of ratios such as are given in Table II; (2) from a nominal value for the effective cross-section of the oxygen molecule (13 sq. Å.)[9] and the geometric area of the surface one can derive the number of oxygen molecules required to form a monolayer, hence, the number of layers. Both these methods have been used with results presented in Table IV. The agreement is surprisingly good.

In interpreting these data it must be remembered that they are essentially an arbitrary mode of comparison and that they do not imply that oxygen is in fact sorbed in successive layers of the number indicated. The reversible sorption at −183° on both unreduced and reduced surfaces, which appears to be of the usual physical type, may well correspond to a complete monolayer. Oxygen strongly held on the unreduced surface is almost certainly likewise held physically since its amount agrees fairly well with that of the strongly-held argon and nitrogen already described.[5] The oxygen chemisorbed on the reduced surface at −183° may possibly exist as multilayers yet this seems unlikely in view of the evidence of penetration reported by Brunauer and Emmett[7] and the large heat effect reported by Beebe and Stevens.[8] The process is undoubtedly complex.

TABLE IV

COMPARISON OF NUMBER OF LAYERS SORBED ON SAMPLE 1 AS ESTIMATED: (1) BY COMPARISON WITH LIMITING VOLUME OF NITROGEN SORBED REVERSIBLY ON THE SAME SURFACE AT THE SAME TEMPERATURE; AND (2) FROM GEOMETRIC AREA OF SURFACE AND A NOMINAL CROSS-SECTIONAL AREA OF THE OXYGEN MOLECULE

Temp., °C.	Condition of surface	Type of sorption	Number of layers 1 Comparison with N_2	2 From known area
−183	Unreduced	Reversible	1.4	1.6
		Strongly-held	0.25	0.30
	Reduced	Reversible	1	1.1
		Chemisorbed	2.3	2.7
− 78	Unreduced		0.4	0.5
	Reduced		5.5	6
20	Unreduced		0.7	0.9
	Reduced		9.2	10

The relatively large amount of oxygen chemisorbed at −78 or 20° almost certainly represents the formation of some type of oxide film, a conclusion which is confirmed by the fact that the rate of sorption (see later section) is logarithmic as is characteristic of the growth of many thin oxide films on metals. With respect to this point, it is of interest to compare our results at room temperature with those of other investigators. Gulbransen[10] has measured the increase in weight of freshly reduced iron exposed to oxygen at 25° and at pressures ranging from 0.8 to 15 cm. with results which indicate that the increase is from 0.15 to 0.20 mg. per sq. cm. This compares favorably with our measurements which show a sorption of about 0.40 mg. per sq. cm. He has also calculated the thickness of these films on the assumption that their structure approximates that of the lattice of Fe_3O_4; on this basis he concludes that they range in thickness from about 5 to 15 Å. An analogous calculation based on our data yields a film thickness of 20 to 30 Å. These compare favorably with the thickness of 20 Å. reported by Winterbottom[11] for bright an-

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(9) This is a compromise between the two values calculated by Emmett and Brunauer, THIS JOURNAL, **59**, 1553 (1937).

(10) Gulbransen, *Trans. Electrochem. Soc.*, **81**, 327 (1942).

(11) Winterbottom, *Trans. Electro. Soc.*, **76**, 327 (1939), discussion.

nealed carbonyl iron exposed to air at room temperature, and of 15 to 40 Å. reported by Tronstad[12] for iron in dry air; both these estimates were based on polarimetric measurements.

Force–Area Curves.—A force–area curve, derived by the method of Innes and Rowley,[13] for oxygen sorbed reversibly on the reduced surface of Sample 1 is presented in Fig. 7. This curve, which is typical for reversible sorption on the reduced surfaces, is smooth and throughout its length lies very close to the curve representing the relation $FA = 3kT$, which, as has been shown, is the equation of state for a sorbed film for which the exponent in the Freundlich equation is 3, as it is for Sample 1.

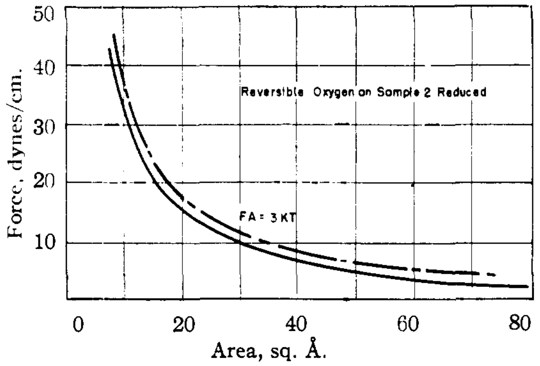

Fig. 7.—Typical force–area curve for oxygen sorbed reversibly on reduced surface of Sample 2.

The force–area curves for reversible sorption on the unreduced surfaces were, in general, not so smooth but show irregularities analogous to those previously reported for nitrogen and carbon monoxide on these same surfaces.[14] These irregularities are believed to result from the presence on the surfaces of molecules so strongly held that they cannot be pumped off at temperature, and are therefore presumably immobile, which give a certain rigidity to the film. This difference also supplies additional evidence that the oxide film formed on reduced iron by exposure to oxygen at −183° differs from that existing on the unreduced but outgassed surface.

Heat of Adsorption.—The "average heat of adsorption" of oxygen at −183° as calculated by the method of Brunauer, Emmett and Teller,[15] using the linear (higher pressure) portion of the isotherms, plotted as in Fig. 5, has been calculated for each pumped-out surface with results presented in Table V. This quantity, although its significance has been questioned, is included for the sake of comparison. It is, within the error of calculation, the same on all the surfaces, is very close to the heat effects similarly derived for other gases on these same surfaces,[5] is two to three times as great as the heat of liquefaction of oxygen at its normal boiling point, and is also about the same order of magnitude as the heat effect (4 kcal.) of van der Waals adsorption on an oxide-covered catalyst.[8] As noted later, it also agrees with the energy of activation (3.5 kcal.) calculated from the rate of adsorption.

TABLE V

"AVERAGE HEAT OF ADSORPTION" OF OXYGEN AT −183° ON A PUMPED-OUT SURFACE (REVERSIBLE OXYGEN)

As derived by the method of Brunauer, Emmett and Teller

	Kcal.	
Sample	Unreduced	Reduced
1	3.3	3.2
2	3.3	3.0
3	...	3.6

Rate of Adsorption on Unreduced Surface.—At −183° the rate of adsorption on the unreduced surface (*cf.* Fig. 2) is for a brief period at the beginning rapid, though gradually diminishing; after about twenty minutes it increases again, then once more decreases to zero as equilibrium is approached (400 minutes).[15a] Except for the brief initial period, the rate is that of a first order reaction, the data being accurately represented by the relation

$$\log \frac{V_e}{V_e - V} = kt \qquad (1)$$

where V is the volume sorbed up to time t, V_e that sorbed at equilibrium, and k is the rate constant. This is demonstrated by the values of k presented in the upper part of Table VI. The rate at any given time is also directly proportional to the residual oxygen pressure at that time, as is evident from Fig. 8 in which the rate, derived by differentiation of eq. (1), is plotted against the observed pressure. Since it is likely that the sorbed oxygen is dissociated, this relationship implies[16] that the rate of absorption is very much slower than the rate of dissociation or diffusion.

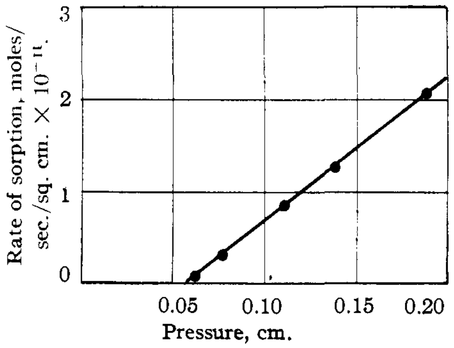

Fig. 8.—Chart showing linear variation with pressure of rate of sorption on unreduced surface of Sample 1 at −183°.

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(12) Tronstad, quoted by Evans, "Metallic Corrosion, Passivity and Protection," London, 1937, p. 76.

(13) Innes and Rowley, *J. Phys. Chem.*, **45**, 158 (1941).

(14) Armbruster and Austin, ref. 5, Fig. 12.

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

(15a) A somewhat analogous curve for the rate of oxidation of iron at 300° has been reported by Gulbransen, *Rev. Sci. Instruments*, **15**, 201 (1944).

(16) *Cf.* Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 856 ff.

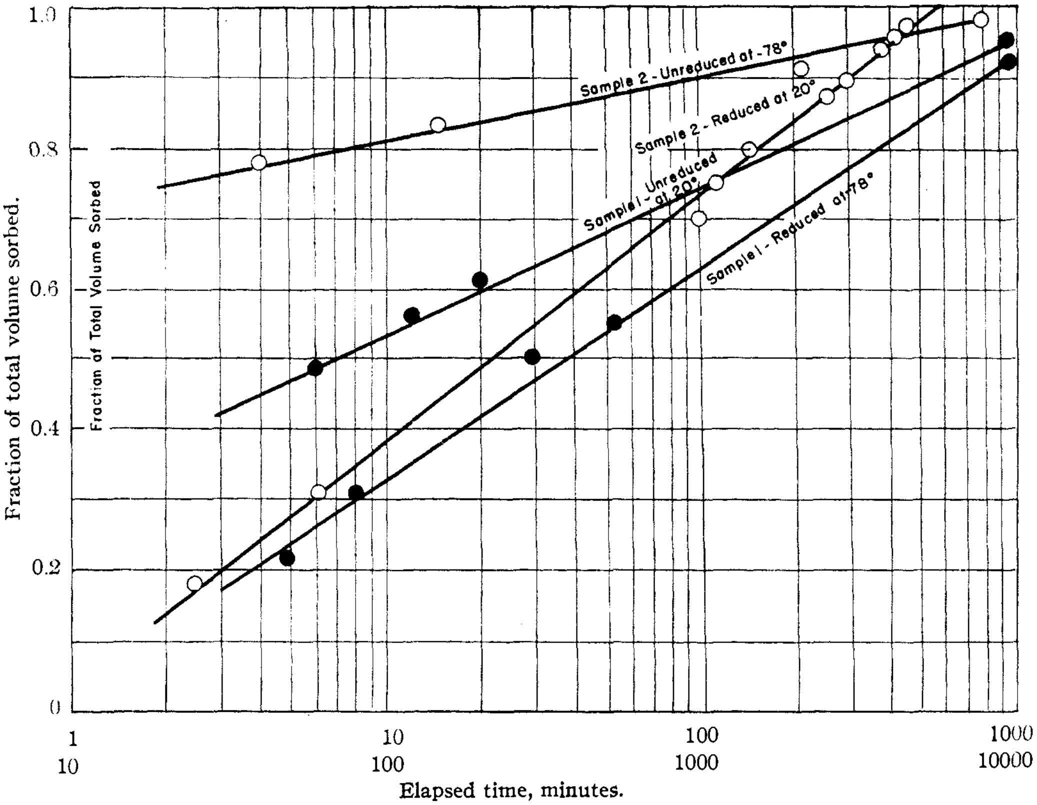

Fig. 9.—Chart illustrating logarithmic rate of formation of oxide film at −78° and at 20°. For ease of comparison, the volume sorbed at a given time is plotted as a fraction of the volume sorbed at equilibrium. Two time scales are also employed to facilitate comparison of the several curves.

TABLE VI

REACTION VELOCITY CONSTANT FOR SORPTION OF OXYGEN AT −183° ON SAMPLE 1

Unreduced Surface (V_e = 0.451 cc.)

t, sec.	V, cc.	$V_e - V$, cc.	$k = \log (V_e/V_e - V)/t$
120	0.057	0.394	47×10^{-5}
480	.120	.331	28
1380	.167	.284	1.45
3000	.272	.179	1.34
4260	.330	.121	1.34
7320	.408	.043	1.38
10020	.432	.019	1.37
13380	.444	.007	1.35
15240	.446	.005	1.28
18120	.449	.002	1.30
23820	.451	...	..
Reduced Surface (V_e = 0.411)[a]			
1380	0.171	0.240	1.57
1680	.190	.221	1.48
3480	.263	.148	1.22
4080	.274	.137	1.14

[a] Calculations are based on slow sorption following instantaneous sorption. Quantities V and V_e are the observed volume less the amount sorbed instantaneously.

The energy of "activation," as derived from the ratio of the number of molecules sorbed per sq. cm. per second to the number striking the surface, on the assumptions[17] that the gas is ideal and that the sorbed layer is mobile, is about 3.5 kcal. which agrees very well with the heat effect derived from the adsorption isotherms by means of the Brunauer–Emmett–Teller relation (*cf.* Table V).

At −78 and 20°, the rate is not that of a first-order reaction but is logarithmic with respect to time, as is evident from Fig. 9 in which, for ease of comparison, the fraction of the final volume sorbed at equilibrium (V_e) is plotted against time on a logarithmic scale.

Since an analogous logarithmic rate has been reported for the growth of a thin-oxide film on several different metals,[18] this result suggests that the rate-controlling process here is not adsorption, as at −183°, but formation of an oxide film. The possible significance of this logarithmic rate of growth has been discussed by Evans.[19]

Rate of Adsorption on Reduced Surface.—At −183° the freshly-reduced surface sorbs a large amount of oxygen instantaneously, after which there is a further slow sorption extending over

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(17) *Cf.* Glasstone, Laidler and Eyring, ref. 16, p. 351.

(18) *Cf.* Lustman and Mehl, *Trans. Am. Inst. Min. Met. Engineers*, **143**, 246 (1941); Vernon, Akeroyd and Stroud, *J. Inst. Metals*, **65**, 301 (1939); Gulbransen, *Trans. Electrochem. Soc.*, **81**, 327 (1942). It should be noted that in most of these investigations the oxygen pressure remained substantially constant whereas in our measurements it decreased markedly.

(19) U. R. Evans, *Trans. Electrochem. Soc.*, **83**, 335 (1943).

several hours. For example, the reduced surface of Sample 1, when exposed to oxygen at a pressure of 0.024 cm., sorbed about 0.04 cc. before the first measurement could be made (less than 1 minute); thereafter there was a further and slower adsorption until, after five hours, a total of 0.83 cc. had been taken up and the oxygen pressure had decreased to 0.00086 cm. The volume sorbed instantaneously corresponds to a concentration of 0.9×10^{15} molecules per sq. cm. which, even making allowance for some roughness, is sufficient to form a complete monolayer of sorbed oxygen atoms; this indicates that the slow sorption takes place on an oxide surface. The rate of this slow sorption, therefore, should be, and in fact is, the same as that on the unreduced surface; this is evident from the data presented in the lower portion of Table VI, which show that the rate after the initial instantaneous sorption is that of a first-order reaction with the constant the same as for the unreduced surface.

At −78 and at 20°, there is likewise a large amount of oxygen sorbed instantaneously with a further and much slower sorption thereafter. At these temperatures, however, the amount of gas sorbed initially varies significantly with the initial oxygen pressure to which the surface is exposed, a result in accord with the observations at −183° reported by Emmett and Brunauer.[7] When the oxygen pressure was less than about 0.02 cm., sorption was instantaneous; when it was much greater, only part of the oxygen was taken up immediately. For example, on Sample 1 about 1.3 cc. was sorbed instantaneously at −78° and about 2.5 cc. at 20°; assuming a specific surface of unity, these amounts correspond respectively to a sorbed layer 3 or 6 molecules thick, indicating again that after initial exposure to oxygen, one has to deal with an oxide rather than an iron surface. When correction is made for the amount of oxygen sorbed instantaneously, the rate of the subsequent slower sorption is logarithmic with respect to time (see Fig. 9), though not quantitatively the same as on the unreduced surface.

These results suggest that the mode of oxidation of iron, perhaps of other metals, varies with temperature. At very low temperature (−183°) it appears to be essentially an adsorption with some penetration for the few atomic layers beneath the surface; in the range −78 to 20° it is the growth, logarithmically with time, of a thin oxide film; at still higher temperatures the process probably proceeds by diffusion through a relatively thick scale.

Conclusions and Summary

The sorption of oxygen on three smooth surfaces of iron (cold-rolled steel), on which the sorption of other gases had also been determined, was measured at 20, −78 and −183° and at pressures up to 0.1 cm. Sorption on each surface was observed first after degreasing and outgassing, subsequently on the same sample after it had been reduced in purified hydrogen and again outgassed.

At −183° the unreduced surface sorbs a monolayer of oxygen physically, also a small amount held so strongly that it cannot be pumped off at temperature; the amount of this strongly-held oxygen is about that of argon, nitrogen or carbon monoxide likewise strongly sorbed. The isotherms for the sorption of oxygen lie very close to those for carbon monoxide on the same surface. The reduced surface at −183° chemisorbs oxygen equivalent to a film several molecules thick but there is evidence that this oxygen penetrates the surface; it also sorbs a monolayer of oxygen physically. There are many indications that the oxide film formed by exposing reduced iron to oxygen at −183° differs significantly from that which was present on the unreduced surface.

At −78° the oxygen chemisorbed on the unreduced surface is equivalent to less than half a monolayer; that on the reduced surface corresponds to about 5 layers. At 20° both unreduced and reduced surfaces chemisorb an amount almost twice that sorbed at −78°.

As was the case with other gases on these identical specimens of cold rolled steel the isotherms deviate from the Langmuir equation at the lowest pressures, but are there represented accurately by the Freundlich relation, the exponent ranging from 3 to 5. The combined relation $v = v_s \sqrt[n]{\frac{ap}{1 + ap}}$ represents the data satisfactorily over the whole pressure range.

The heat of adsorption of oxygen physically sorbed on the unreduced surfaces, as derived by the method of Brunauer, Emmett and Teller, is about 3.5 kcal., in agreement about 4 kcal. for oxygen physically sorbed on iron catalysts as determined calorimetrically; the activation energy calculated from the rate of adsorption is likewise about 3.5 kcal.

The rate of adsorption on the unreduced surface at −183° is that of a first order reaction, as is that on the reduced surface following the initial instantaneous sorption. The rate of adsorption on all surfaces at −78 and 20° is logarithmic.

Force–area curves indicate that the equation of state of the sorbed films is $FA = nkT$ where n is the exponent in the equation representing the isotherm.

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