have higher values for small pores. Should the adsorbent offer considerable convex surface to adsorption in the first several layers, the value of k may be expected to be less than 1. This is shown in the data of Table I. It is difficult to explain the values of $k = 1$ observed for isotherms approaching Type I. There is no objection to $k = 1$ for isotherms that are strictly of Type I in which all of the adsorption occurs in the first layer. However, for the isotherms of the two PCI-1042 charcoals the values of k might be expected to be considerably larger than 1, since the isotherms indicate multilayer adsorption and since the average pore diameters are smaller than those of the Type IV isotherms of Table I. It is possible that these charcoals are composed of small pores plus a fraction of larger pores that cause the adsorption at higher relative pressures. In this case equation (4) may be regarded as somewhat empirical; however, V_m from this equation and the values of j probably have their usual significance.

With most isotherms the simple B.E.T. equation usually predicts larger adsorption above relative pressures of 0.35 than the actual isotherm, and deviation in this direction is usually considered to occur with all isotherms. It is interesting to note that the isotherms in Table I for which jk is greater than 1 deviate from the simple B.E.T. equation in the opposite direction.

In a previous section adsorption was postulated to occur in the same manner as multilayer adsorption with the decreased free energy of adsorption due to capillary forces causing the pores to fill at a lower relative pressure than 1. Equation (4) was found to satisfactorily fit the data for the adsorption branch of the isotherms, but could not be fitted to the desorption branch. This may indicate that desorption occurs in a different manner. In the authors' opinion desorption occurs from menisci of filled pores to leave the pores covered with the number of layers predicted by equation (4) remaining on the surface. This is similar to the picture of adsorption and desorption given by Cohan[17] except that he postulated that the pore will empty completely on capillary evaporation.

Equation (4) provides a systematic method of determining V_m for isotherms to which the simple B.E.T. equation cannot be fitted. This is also true of isotherms which appear to be a composite of several types of simple isotherms such as those of the porous carbon blacks previously described,[8] and some of the isotherms of active magnesia of Zettlemoyer and Walker.[18] In the latter case equation (4) can be applied satisfactorily to relative pressures of 0.4 by taking jk greater than 1.

Acknowledgment.—The authors wish to thank Dr. P. H. Emmett for his constructive criticisms of the manuscript and for permission to use the isotherms of porous glasses and silica aerogel.

Summary

1. A modified B.E.T. equation similar to that of Anderson[8] has been derived and applied to physical adsorption isotherms of Types I and IV.[4]

2. With Type I isotherms satisfactory fit of this equation can be obtained if the free energy of adsorption in the second and subsequent layers is taken to be equal to the heat of liquefaction.

3. For isotherms of Type IV which flatten below relative pressures of 0.85, the equation satisfactorily fits the data, if the free energy of adsorption was taken less than that of liquefaction. For this kind of Type IV isotherm the equation was used to integrate the equation of Kistler,[9] and the resulting expression gave surface areas of the same order of magnitude as the B.E.T. areas.

4. The equation is believed to be a simple method of characterizing isotherms with four constants.

[17] Cohan, *ibid.*, **66**, 98 (1944).

[18] Zettlemoyer and Walker, *Ind. Eng. Chem.*, **39**, 69 (1947).

PITTSBURGH, PA. RECEIVED JULY 23, 1947

[CONTRIBUTION FROM THE RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION]

The Sorption of Gases on a Plane Surface of Two Stainless Iron–Chromium–Nickel Alloys at 20, −78 and −183°[1]

BY MARION H. ARMBRUSTER

The resistance to corrosion and other properties of the stainless iron alloy containing approximately 18% chromium and 8% nickel suggest that the surface of the alloy may differ considerably from that of ordinary steels. As it seemed likely that the sorption of gases on such an alloy might yield a clue to the character of the surface and, by comparison with data for steels, might indicate differences in the nature of the surface, the sorption of hydrogen, neon, argon, nitrogen, carbon monoxide and oxygen has been measured at 20, −78 and −183° and at pressures up to 0.1 cm. mercury. The sorption of carbon dioxide has been determined at −78 and −183°.

The apparatus used, its calibration and method of operation have previously been described.[2] The gases were likewise those used in an earlier study of sorption on mild carbon steel.[3]

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[1] Presented in part before the Chemical Research Conference on Catalysis sponsored by the American Association for the Advancement of Science, at New London, N. H., June 23–28, 1947.

[2] Armbruster and Austin, THIS JOURNAL, **60**, 467 (1938); **61**, 1117 (1939).

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

Samples.—Two samples of the alloy were used. The first (no. 25262), hereafter referred to as Alloy A, is the same sample used in an earlier determination of the solubility of hydrogen[4]; its composition was: C, 0.07; Mn, 0.37; P, 0.006; S, 0.005; Si, 0.47; Ni, 9.92; Cr, 18.30. After measurements with carbon monoxide and carbon dioxide at 400° on this alloy, the surface showed a very faint straw color which the usual reduction procedure with pure hydrogen at 450° did not appear to alter. The second sample (no. 25276), hereafter called Alloy B, is the same sample used in earlier measurements of the sorption of water vapor[5]; its composition was: C, 0.12; Mn, 0.37; P, 0.016; S, 0.005; Si, 0.44; Ni, 9.48; Cr, 18.48. Data collated by Maier[6] indicate that an alloy of this type is covered by an invisible yet protective oxide film not reducible by pure hydrogen. Both samples were commercial materials and are considered representative of this class of alloy within the regular tolerances. The sorbing surface in each case was a bundle of thin strips, each strip approximately 11.0 × 1.9 × 0.009 cm., with a geometric area, determined by summing the areas of the individual strips, of 11,130 sq. cm., the same as that of mild steel samples 1 (no. 25261) and 2 (no. 25277).[3]

Treatment of Samples.—The surface was degreased with absolute alcohol and anhydrous ether distilled over sodium, care being taken not to touch the surface with the fingers. Before each run the sample was reduced in place for about eight hours at 450° in a stream of hydrogen freed from traces of oxygen or water vapor; it was then outgassed for sixteen hours at 450° under a pressure of less than 10^{-6} mm., and finally was brought to the temperature at which the measurement was to be made in an atmosphere of hydrogen, which direct measurement has shown is not measurably adsorbed on this surface. The hydrogen was then pumped off and the pressure reduced to 10^{-6} mm. before the start of the run. In one series of measurements with Alloy A, the hydrogen reduction was omitted.

Orientation of Grains.—Microscopic examination showed that the grains are practically equiaxed. The X-ray pole figures of the two samples showed that there may be a slight preferred orientation of the grains with the (112) planes in the rolling plane.[7]

Microscopic Examination of Samples.—Examination of a polished but unetched section of each sample under the microscope showed that the amount of non-metallic inclusions was very small, less than 0.1%, these being of the same rounded type. Photomicrographs of the samples in the etched condition showed a shower precipitation of carbides mostly at the grain boundaries and to a lesser degree within the grains, mostly at crystallographic planes. The type of precipitation and sub-microscopic size of the individual particles make it impossible to specify the amount of carbides, or possibly nitrides, or to state positively that there is more carbide precipitate in Alloy B. The remainder of the surface is metallic, a solid solution of iron, chromium and nickel.

Results

The sorption of each gas was determined by building up the pressure in several increments, allowing sufficient time at each step for equilibrium to be attained. Several independent runs were made with each gas, the result being reproducible within the limit of measurement; moreover, the results for the two samples showed satisfactory agreement. Neon and hydrogen are not sorbed at any temperature, that is, the sorption, if any, is less than 3×10^{-4} cc. or less than 1% surface coverage.

Reduced Surface −183°.—Typical isotherms selected from concordant runs are shown for the several gases in Fig. 1, in which the amount of sorbed gas, expressed as a volume at 20° and 76 cm., is plotted for various pressures. Argon is sorbed very slightly and the gas taken up cannot be removed by pumping at this temperature. The rate of sorption of argon is virtually instantaneous. Nitrogen is sorbed in appreciable quantity and the sorption is completely reversible. The rate of adsorption is practically instantaneous, 99.7% being taken up within the time of measurement, two minutes, and the final increment slowly. Carbon monoxide is sorbed to a much greater extent. Approximately two-thirds of the sorbed carbon monoxide can be removed by evacuating the system at temperature, but the remaining one-third cannot be so removed. The rate of sorption is almost instantaneous, 99% being sorbed in a minute or two, the remainder very slowly, a drift being observed. Typical isotherms at all temperatures for oxygen are shown separately in Fig. 4: about one-tenth of the total oxygen can be removed by evacuating the system, the remainder is strongly held. The initial sorption is very rapid but is followed by a slow process of measurable rate.

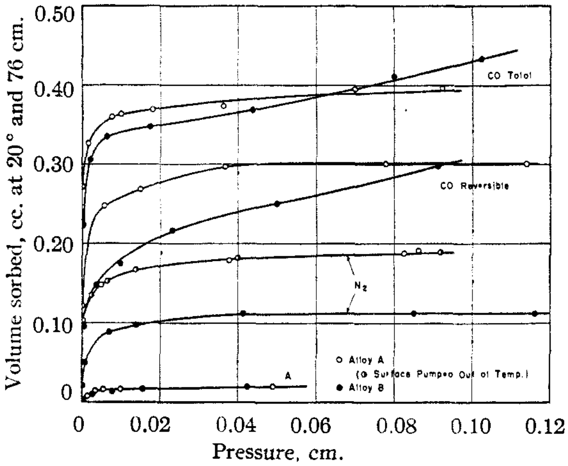

Fig. 1.—Typical adsorption isotherms of the several gases on reduced surface of stainless alloys at −183°.

Reduced Surface, −78°.—Argon and nitrogen are not measurably sorbed on either surface at this temperature. Typical isotherms for carbon monoxide and carbon dioxide are shown in Fig. 2. Carbon monoxide is slightly sorbed and cannot be removed by pumping at −78°; this chemisorption is appreciably less than that at −183°. The amount of carbon dioxide sorbed is relatively large and not completely reversible so that it is possible to differentiate two kinds: one

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(4) Armbruster, *ibid.*, **65**, 1043 (1943).

(5) Armbruster, *ibid.*, **68**, 1342 (1946).

(6) C. G. Maier, U. S. Bur. Mines, Bulletin 436, 1942, p. 17.

(7) The density of packing is believed less for the (112) plane than the average of that calculated for the other crystallographic planes. On the basis that in these alloys the iron is of the face centered cubic form, and that the distance between the centers of two iron atoms is a_0 = 3.55 Å, the areas per iron atom for the several planes are:

plane	(100)	(111)	(110)	(112)
area (sq. Å./iron atom)	6.3	5.5	8.9	15.4

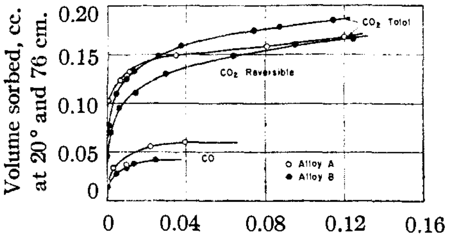

Fig. 2.—Typical isotherms for CO and CO_2 on reduced surface of stainless alloys at −78°.

in which 6% of the surface is covered by strongly held molecules; the other in which one-half of the surface is covered by weakly-held molecules. The sorption of oxygen (Fig. 4) is 30% greater than at −183°, apparently independent of pressure and too strongly held to be removed except by reducing with hydrogen and evacuating at 450°.

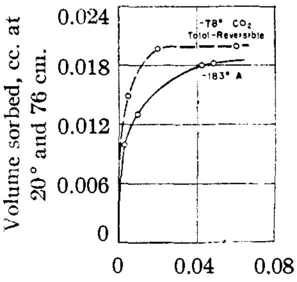

Fig. 3.—Sorption of argon at −183° and irreversible carbon dioxide at −78° on reduced surface of stainless alloy B.

Reduced Surface, 20°.—At room temperature the only gas sorbed to greater extent than the limit of error of measurement is oxygen, as is shown in Fig. 4. The amount of oxygen, which, as at −78°, appears to be independent of pressure, is almost twice as great as that sorbed at −183° and about 50% greater than at −78°.

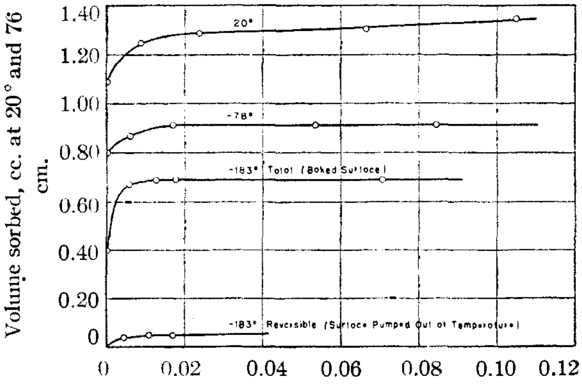

Fig. 4.—Typical isotherms for oxygen on reduced surface of stainless alloy A.

Unreduced Surface, −78°.—Measurements on the unreduced surface were limited to Alloy A at −78°, and typical isotherms are given in Fig. 5. The sorption of carbon monoxide is appreciable and, contrary to usual observation with this gas at −78° on steel, all of the sorbed gas is not strongly held. Only about 25% of the sorbed molecules are strongly held and the remainder can be pumped off at temperature. The total sorption of carbon dioxide is made up of a reversible sorption which corresponds to about 75% and a strongly held sorption which corresponds to about 25%.

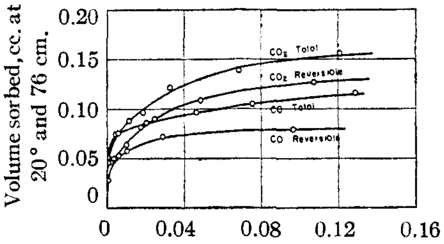

Fig. 5.—Typical isotherms for CO and CO_2 on unreduced surface of stainless alloy A at −78°.

Calculations and Discussion

Form of Isotherms.—The isotherms in Figs. 1, 2, 4 and 5 so greatly resemble in form those obtained for the same gases on mild steel as to suggest application of the Freundlich and Langmuir isotherms.

Freundlich Isotherm.—For initial comparison the data are expressed in the form of the exponential relation of Freundlich, $v = ap^{1/n}$, in which v is the volume sorbed at pressure p; a and n are constants. At lowest pressures this purely empirical expression had more satisfactorily represented the data for mild steels[3] than did the Langmuir equation. Typical Freundlich isotherms for several reversibly sorbed gases on these alloys are given in Fig. 6 in which the sorbed volume is plotted against pressure on double logarithmic coördinates and a straight line is obtained over a pressure range of a hundred fold or more.

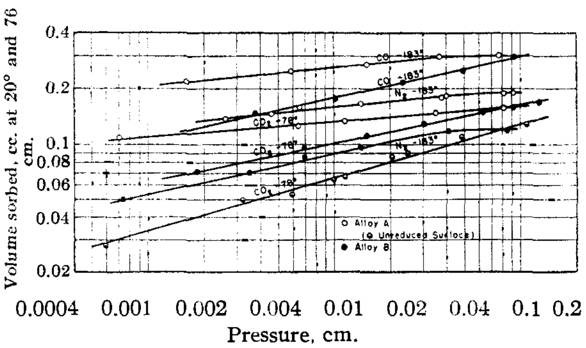

Fig. 6.—Reversible sorption of several gases on stainless alloys plotted on double logarithmic coördinates to illustrate application of parabolic or Freundlich relation.

The slope of the line corresponds to the exponent $1/n$ in the above equation. On the reduced Alloy B these slopes yield values of n which correspond with those for the same gases on mild steel surfaces.[3,5] For example nitrogen is 3, carbon monoxide 4 to 5 at −183°, and water is 3 at 20°. It is of interest to note that for carbon dioxide at −78° on Alloy B (reduced) n is 5. Generally in the case of Alloy A the slopes are less and the values of n are about twice as great as those for Alloy B. This point deserves further consideration in light of the interpretation of n as a measure of the departure of the sorbed film from that of an ideal two dimensional gas.

Langmuir Isotherm.—The Langmuir equation more satisfactorily represents the data over the whole range except at lowest pressures where the deviation is in the direction of greater volume sorbed than that required by the relation. This is shown in Fig. 7 in which typical isotherms are plotted as p/v against p and a linear relation is obtained down to about 0.01 cm. pressure. It is of significant interest to note that for the particular gas carbon monoxide on Alloy A this deviation at lowest pressure is least marked but for the same gas on Alloy B very marked deviation is evident below about 0.015 cm. as shown in a separate p/v against p plot given in Fig. 8. More marked deviation in this pressure range has generally been observed as characteristic of a reduced and not of an unreduced surface in the study of mild steels.[5] Possibly this may be interpreted as indicating more free metal or less oxide on alloy B than on Alloy A. If the Langmuir isotherms for carbon monoxide at −183° shown in Fig. 8 are considered further, the curves for Alloys B and A seem analogous in form to those for ethyl iodide on a reduced and unreduced surface of iron, respectively,[8] where there is evidence of a second layer forming on the reduced surface. The curve for Alloy B not only shows more marked deviation at lowest pressures but at higher pressures intersects the curve for Alloy A at about 0.095 cm. indicating that above this pressure the concentration of adsorbed carbon monoxide is greater on Alloy B than on Alloy A. In the intermediate pressure range the two curves are linear and have the same slope which shows that the same amount of gas is required as the limiting volume sorbed to complete a monolayer on the two surfaces. Then the increased adsorption at highest pressure for Alloy B may represent the beginning of a second layer and this behavior, by analogy with the increased adsorption of ethyl iodide on reduced but not on unreduced iron, suggests that the surface of Alloy B may be reduced to a higher degree than that of Alloy A. This deduction supports the earlier conclusion drawn from the adsorption behavior at lowest pressure that there may be less oxide or a lower oxide on Alloy B than on Alloy A.

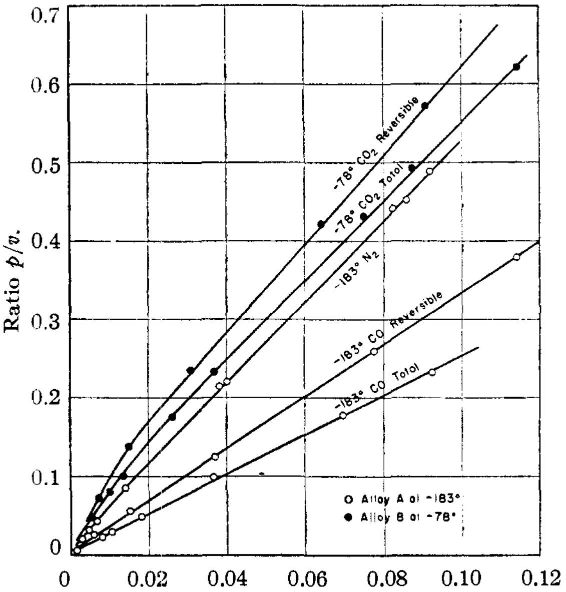

Fig. 7.—Typical isotherms for several gases on stainless alloys plotted as p/v against p.

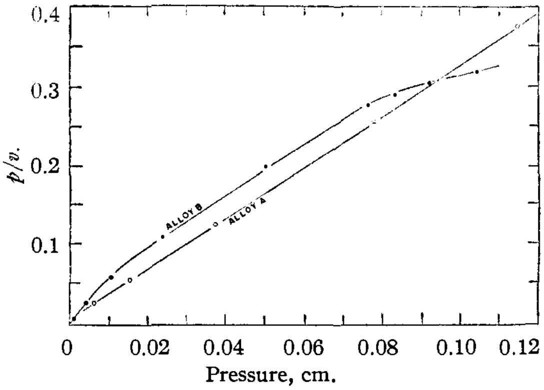

Fig. 8.—Isotherms for reversible sorption of CO at −183° plotted to show deviation from Langmuir relation.

Combined Form of Equation.—The isotherms may be represented over the entire range by a combined form of the Freundlich and Langmuir equations, namely,

$$v = v_s\sqrt[n]{ap}/(1 + ap)$$

in which a and n are constants, n corresponding to the value determined from the slope of the Freundlich plot for a particular temperature and system.

Comparison of Data

Reduced Surface.—The applicability of the Langmuir equation makes it possible to compare the results in terms of v_s, the so-called limiting volume sorbed, as obtained from such a plot. This comparison is made in Table I which contains: (a) the values of v_s derived from the Langmuir plot; (b) the per cent. surface coverage

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(8) Armbruster and Austin, THIS JOURNAL, **61**, 1119 (1939), Fig. 3.

TABLE I

VALUES OF THE LIMITING VOLUME SORBED (v_s), OF THE RATIO OF v_s TO THAT FOR REVERSIBLE CARBON MONOXIDE AT −183°, AND OF THE APPARENT COVERAGE OF THE REDUCED SURFACE

Temp., °C.	Gas	Type of sorption	v_s (cc. at 20°, 76 cm.) Alloy		Apparent surface coverage, % Alloy		$\frac{v_s \text{ (gas at temp.)}^a}{v_s \text{ (rev. CO } -183°)}$ Alloy	
			A	B	A	B	A	B
−183	A	Strongly held	0.020	0.017	6	4	0.07	0.05
	N_2	Total (reversible)	.197	.122	68	42	.65	.40
	CO	Total	.394	.455	135	155	1.30	1.43
	CO	Reversible	.304	.315	104	108	1.00	1.00
	CO	Chemisorbed	.090	.136	31	47	0.30	0.43
− 78	CO	Total (chemisorbed)	.070	.045	24	15	.23	.14
	CO_2	Total	.165	.199	61	74	.54	.63
	CO_2	Reversible	.146	.178	54	66	.48	.57
	CO_2	Strongly held	.019	.021	7	8	.06	.06

[a] Corresponding ratios with nitrogen at −183° as standard for comparison may be obtained by multiplying the factor for Alloy A and B by 1.54 and 2.58, respectively.

derived from v_s, the known geometric area and cross sectional area of the molecule[9]; and (c) the ratio v_s/v_s (reversible CO −183°), the relative number of molecules sorbed per unit area, a ratio in which it may be assumed that v_s is a measure of the concentration of molecules in a close packed monolayer and that v_s (reversible CO −183°) is a measure of the specific area of the surface. Whereas the per cent. coverage in the middle two columns is merely an apparent coverage, the ratio in the last two columns shows, on the basis of these assumptions, the extent to which the surface is covered by a monolayer and reduces the data to constant specific area.

Several deductions are possible from this comparison, together with our experience with mild steels at low pressure and the investigations of Emmett and Brunauer of iron catalysts, pure and promoted[10,11] at considerably higher pressure: (1) Argon is very slightly sorbed and so strongly held that it cannot be removed by pumping at temperature. Furthermore the amount of argon sorbed at −183° is practically the same as that of the chemisorbed carbon dioxide at −78°, namely, 5–7 and 6% surface coverage, respectively, for the two alloys. This is shown in Fig. 3 in which the chemisorbed carbon dioxide curve is the difference between the total and the reversible sorption data. These gases may, therefore, be sorbed on the same places, such as cracks, grain boundaries and virtual depressions on the surface. Similar strong adsorption has been reported in earlier study: for example, of argon and carbon monoxide on mica[12] in which the sorbed molecules appeared to be held in positions vacated by potassium ions during cleavage. Likewise argon, carbon monoxide and nitrogen strongly held on unreduced iron surfaces may be held on certain positions on the surface, resulting from the structure of the oxide film, on which the sorbed gas comes so close to oxygen atoms that the van der Waals forces are stronger. The existence of such sites on stainless alloy surface could explain the constant fraction (about 6 per cent.) of the surface covered by argon at −183° and chemisorbed carbon dioxide at −78°.

(2) All sorption, except for carbon monoxide, is less than a monolayer, even that of argon and nitrogen. Argon does not give a measure of surface area and one cannot be sure of nitrogen, since the limiting volume of nitrogen sorbed is only one-half that of reversibly sorbed carbon monoxide. If nitrogen were taken as a standard, as can readily be done by multiplying the values in the last two columns of Table I by the factor 1.54 and 2.58, respectively, and the limiting volume be assumed to correspond to a monolayer, it yields a true surface area only one-half that of the known geometric area, which is not reasonable. Also, reversible carbon dioxide at −78° as a measure of surface area is certainly in question. Hence the significant result follows that for a stainless alloy only the reversible sorption of carbon monoxide at −183° is a reliable measure of the surface area in the low pressure range studied. In contrast, Emmett and Brunauer[10] find for pure iron catalysts the same surface area is given by nitrogen −183°, carbon monoxide reversible −183° and carbon dioxide reversible −78°. Their work is at considerably higher pressure and applies an equation derived for multimolecular adsorption which, at low pressure, is formally identical to the Langmuir equation. Our experience with mild steels, reduced and unreduced, shows that nitrogen (−183°), carbon monoxide reversible (−183°) and argon reversible (−183°) may form a complete monolayer but that carbon dioxide reversible (−78°) is certainly in question.

(3) The following points deal with the sorption of carbon monoxide: (a) In all the reduced samples studied the total sorption of carbon monoxide at −78° is strongly held; there is no reversible sorption of this gas at −78° although this occurs at −183°. (b) Comparing carbon monoxide chemisorbed at −183° and at −78°, it is seen that

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[9] The values for the cross sectional areas of the molecules are the same as cited previously in reference 3.

[10] Emmett and Brunauer, THIS JOURNAL, 59, 1553 (1937).

[11] Emmett and Brunauer, *ibid.*, 59, 310 (1937).

[12] Armbruster and Austin, *ibid.*, 60, 467 (1938).

for Alloy A, carbon monoxide chemisorbed (−183°) is only slightly greater than at −78°, whereas for Alloy B, the chemisorption at −183° is three times greater than at −78°. In the work with mild steels, reduced, the chemisorbed carbon monoxide at −78° varied in amount from none to the same as that at −183°. Emmett and Brunauer[10] state that the chemisorption of this gas at the two temperatures is the same, though Brunauer[13] later mentions that with strongly sintered iron surfaces this chemisorption of carbon monoxide may be decreased and the binding forces of gas to iron may be weakened. (c) On Alloy B, carbon monoxide is chemisorbed at −183° in greater amount than on Alloy A. If carbon monoxide is considered sorbed on free metal, the fact that this corresponds to 30% and 43% for Alloys A and B, respectively, indicates that there is proportionally more free metal on Alloy B. Evidence afforded by the form of the isotherms supports further this conclusion. (d) It has been suggested that carbon monoxide chemisorbed at −183° may be not only a direct measure of the free metal present but also an indirect measure of the amount of oxide. Emmett and Brunauer[10] concluded that carbon monoxide chemisorbed at −183° is equivalent to van der Waals adsorption (a monolayer) if no oxide exists, but that if oxide is present chemisorbed carbon monoxide at −183° is less than a monolayer by an amount corresponding to the oxide. On this basis, if the chemisorbed carbon monoxide at −183° on Alloys A and B is 30 and 43%, respectively, which is less than a monolayer and indicates oxide exists, the corresponding oxide is 70 and 57%.

(4) Nitrogen may perhaps be sorbed on the non-metallic part of the surface of these alloys. The fact that sorption of nitrogen appears to be unreliable at the low pressures used in the present work as a measure of total surface area on these alloys, suggests that it is sorbed on some definite portion of the surface. For Alloys A and B the coverage is 65 and 40%, respectively, so that possibly the nitrogen-sorbing portion of the surface of Alloy B is less. Direct comparison of the ratio of nitrogen sorbed on Alloy A to that on Alloy B at definite pressure over the range studied can be made from the data presented in Fig. 1. This ratio varies from 1.76 to 1.64 over the pressure range 0.005 to 0.1 cm. which suggests, by its constancy, that the difference in nitrogen sorption on the two alloys is due to a difference in area of the nitrogen-sorbing portion of the surface and, by its value, that this portion of the surface is 60% greater for Alloy A. Lastly, if for Alloys A and B it is assumed that nitrogen is sorbed on metal, one would expect (*cf.* 3c and d) 30 and 43% coverage, respectively; but, if it is assumed that nitrogen is not sorbed on metal, one would expect 70 and 57% coverage, respectively, which is in better agreement with observation.

Sorption of Oxygen, −183°.—Typical data for the sorption of oxygen at the several temperatures are shown graphically in Fig. 4 to facilitate separate consideration. The surface of Alloy A in the reduced condition chemisorbs oxygen equivalent to a film two molecules thick; it also sorbs physically about one-fifth of a monolayer of oxygen. The concentration of oxygen sorbed reversibly is less than that of the other gases sorbed physically at this temperature: 80% less than reversible carbon monoxide which is considered as corresponding to a monolayer; 70% less than nitrogen which corresponds to one-half monolayer. In the case of a reduced mild steel the concentration of oxygen sorbed reversibly is the same as nitrogen and is equivalent to a monolayer. The relatively larger amount of chemisorption as compared to physical sorption is characteristic of a reduced rather than an unreduced steel surface.

Of this sorption a large amount is taken up instantaneously and the remainder over a period of hours. For instance, when the freshly reduced surface of Alloy A was exposed to oxygen at a pressure of 0.0325 cm. a volume of 0.394 cc. was sorbed instantaneously followed by a slower sorption in which 0.397 cc. had been sorbed at the end of an hour and the oxygen pressure had fallen to 3×10^{-5} cm. The instantaneous sorption is equivalent to a concentration of 0.892×10^{-15} molecules/sq.cm. which corresponds to a complete monolayer of sorbed oxygen atoms upon which the slower sorption may take place.

The rate of adsorption is initially very rapid and subsequently falls off gradually. The rate of the slow sorption which follows the instantaneous one obeys the equation for a first order reaction, expressed as

$$\log v_e/(v_e - v) = kt$$

v being the volume sorbed at time t, v_e that sorbed at equilibrium and k the rate constant. Values of k thus calculated are given in Table II and approximate 8.1×10^{-5} sec.$^{-1}$, that is, about 0.008% of the oxygen present is sorbed per second.

TABLE II

REACTION VELOCITY CONSTANT FOR SORPTION OF OXYGEN AT −183° ON REDUCED ALLOY A

(v_e = 0.273 cc.)

t, sec.	v, cc.	$v_e - v$, cc.	$k = \log(v_e/v_e - v)/$
90	0.008	0.265	14.2×10^{-5}
300	.020	.253	11.0
600	.029	.244	8.12
1200	.055	.218	8.13
2100	.089	.184	8.17
3660	.135	.138	8.09
4800	.161	.112	8.13
7200	.201	.072	8.04
9600	.227	.046	8.05
12300	.245	.028	8.03
15300	.256	.017	7.98
23520	.269	.004	7.70

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(13) Brunauer, private communication to Beebe and Stevens, THIS JOURNAL, 62, 2134 (1940), footnote 14.

This is not appreciably greater than the rate observed with mild steel where $k = 1.4 \times 10^{-5}$ sec.$^{-1}$ for the reduced and the unreduced surface.

The energy of activation, E, has been estimated from the rate data by means of the relation

$$\frac{\text{no. of molecules sorbed/sq. cm./sec.}}{\text{no. of molecules striking/unit surface/sec.}} = e^{-E/RT}$$

in which $R = 1.987$ cal./deg./mole and T is the absolute temperature; it is also assumed that the adsorbed gas behaves ideally and forms a mobile layer.[14] For example, at about 0.1 mm. pressure the numerator and denominator become 1.23×10^{11} and 6.54×10^{19} molecules/sq. cm./sec., respectively, so that E is 3600 cal.

Sorption of Oxygen, −78° and 20°.—At −78° the oxygen chemisorbed on reduced Alloy A corresponds to about three layers and at 20° to about five layers. In each case, a large sorption, too rapid for measurement of its rate, occurs. The amount of oxygen instantly sorbed varies with the initial oxygen pressure: if this is less than about 0.001 cm., the sorption is instantaneous; if greater, part of the sorption is instantaneous and part slow. As illustration, 0.80 cc. was instantly sorbed at −78° and 1.0 cc. at 20°, which represents a sorbed layer two and three molecules thick if the specific area of the surface is considered unity. At these temperatures the rate of the slow reaction, after making correction for the instantaneous one, does not follow the first order reaction equation but is a logarithmic function of time as shown in Fig. 9 for oxygen at 20°.

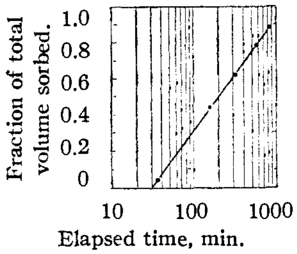

Fig. 9.—Logarithmic rate of formation of oxide film at 20° on reduced surface of alloy A.

All of these observations are quite similar to those reported for mild steel[15] and support the conclusion that the mechanism of the oxidation process of the stainless alloy as well as of iron is determined by the temperature.

The relative number of molecular layers of oxygen sorbed on stainless Alloy A and mild steel #1[3] are arbitrarily compared in Table III. For each sample, the coverage was estimated in the two ways used to obtain the middle two and last two columns of Table I, namely (a) from the limiting volume of nitrogen sorbed, the cross sectional area of the oxygen molecule, and the geometric area of the surface, and (b) from the ratio of the limiting volume of oxygen sorbed at a given temperature to that of carbon monoxide reversibly sorbed at −183°, the latter being assumed to correspond to a close packed monolayer. These two ways of estimating the coverage or thickness of the sorbed oxygen layer show good agreement. The samples are similar in that the total sorption at all temperatures is large, and the chemisorption is relatively much larger than the physical sorption at −183°. The sorption on the stainless alloy, however, is always less than on the mild steel; at −183° the reversible and chemisorption are one-third and two-thirds, respectively, of that on the mild steel and at −78 and 20° about one-half. This difference is one of degree and may well be attributed to the replacement of iron atoms by chromium and nickel, the presence and distribution of which on the surface of a crystal of solid solution may alter the structure, and nature of the oxygen film.

TABLE III

COMPARISON OF NUMBER OF LAYERS OF OXYGEN SORBED ON STAINLESS ALLOY A AND MILD STEEL 1[a]

		Stainless alloy A number of layers		Mild steel 1 number of layers	
Temp., °C.	Type of sorption	Comparison with CO rev.	From known area	Comparison with CO rev.	From known area
−183	Total	2.3	2.1	3.1	3.8
	Reversible	0.18	0.16	0.9	1.1
	Strongly held	2.1	1.9	2.2	2.7
− 78	Total (chemisorbed)	2.8	3.1	5.1	6.0
20	Total (chemisorbed)	4.0	4.5	8.6	10

[a] Complete data for this steel are reported in previous papers.[3,5]

Unreduced Surface −78°.—The data for the sorption of carbon monoxide and carbon dioxide at −78° on reduced Alloy A are compared with the results for the same alloy in the unreduced condition in Table IV. The chemisorption of carbon monoxide at −78° is more than twice as great on the reduced surface as the ratio shows, a fact which supports the assumption that carbon monoxide is chemisorbed on free metal. A noticeable difference in the case of the unreduced surface is that a large part of the sorption of carbon monoxide is reversible. As to carbon dioxide, the

TABLE IV

RATIO OF LIMITING VOLUME v_s (RELATIVE NUMBER OF MOLECULES) OF THE GASES SORBED AT −78° ON REDUCED SURFACE TO THAT ON UNREDUCED SURFACE OF ALLOY A

Gas	Type of sorption	v_s red.	v_s unred.	Ratio, red./unred.
CO_2	Reversible	0.146	0.138	1.04
CO_2	Total	.165	.170	0.97
CO_2	Chemisorbed	.019	.032	.59
CO	Reversible	0	.094	..
CO	Total	.070	.124	.56
CO	Chemisorbed	.070	.030	2.33

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(14) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, ref. 16, p. 351.

(15) Armbruster and Austin, THIS JOURNAL, 68, 1347 (1946).

ratio of 1.04 for the reversibly sorbed gas indicates that the concentration of molecules in this layer is the same for reduced and unreduced alloy. The number of strongly held molecules of carbon dioxide is about twice as great for the unreduced surface. The greater chemisorption for the unreduced surface, which should be rougher, is in agreement with the earlier supposition that this gas may be held on cracks and grain boundaries.

Heat of Adsorption.—The "average heat of adsorption" on the less active part of the surface has been calculated for gases which are reversibly sorbed at −183° and −78° by the method of Brunauer, Emmett and Teller[16] from the linear, higher pressure, region of the isotherms plotted in Fig. 7. Although this method is usually applied to a higher range of relative pressure (p/p_0, p_0 being the saturation pressure of the gas) the results derived by it are given in Table V for comparison. The heat effects at −183° are 3.2 (±0.2) kcal. per mole for the several gases on these surfaces which is in close agreement with those for the same gases on other metals.[3,5] Such correspondence within the error of calculation for the same gases at a given temperature on surfaces as chemically different in nature as a mild carbon steel and a stainless chromium nickel alloy points to a greater dependence of this heat on the physical state of the surface than its chemical composition or on that of the gas. The heat of sorption for oxygen agrees with that calculated by an independent method from rate data. At −78° this heat quantity for carbon dioxide is about 8 kcal. and is twice as great as the heat of liquefaction of the gas at the same temperature obtained from extrapolation of data.

TABLE V

AVERAGE HEAT OF REVERSIBLE ADSORPTION OF GASES ON STAINLESS ALLOYS AS DERIVED BY THE METHOD OF BRUNAUER, EMMETT AND TELLER

Gas	Temp., °C.	Heat of liquefaction at temp., kcal./mole	Heat of adsorption, kcal./mole Alloy A	B
N_2	−183	1.33	3.3	3.4
CO	−183	1.41	3.6	3.2
O_2	−183	1.63	3.5	...
CO_2[a]	− 78	3.94	8.3	7.6
CO_2[b]	− 78	3.94	7.5	...
CO_2	− 78	3.94	...	7.4

[a] This adsorption is on the unreduced surface of Alloy A whereas all other data are for the reduced surface. [b] The heat effect on a reduced mild steel (no. 3)[3] is included for comparison of the same gas at the same temperature on a chemically different surface.

Force–Area Curves.—Force–area curves for the sorption of the several gases have been derived by the method of Innes and Rowley[17] and in general are smooth over the whole range of measurement and are displaced from the curve for an ideal two-dimensional gas to an extent characterized by the exponent n of the Freundlich or parabolic equation which represents the isotherm. The force–area curve for the reversible sorption of carbon monoxide at −183° on the reduced surface of Alloy B is shown in Fig. 10. The curve lies well above that for an ideal two-dimensional gas and close to the curve represented by $FA = 4kT$, as might be expected since its isotherm follows the Freundlich relation $v = ap^{1/4}$. In this instance the curve is not smooth but shows a suggestion of a plateau. This behavior was previously observed to be characteristic of a film on a surface which already holds strongly, either physically or chemically, some molecules attached to definite sites; for example, reversible carbon monoxide on reduced mild steel at −183 and −195°, also nitrogen on unreduced mild steel at −195°.[3] In the reversible sorption of carbon monoxide on this stainless alloy the surface already has on it chemisorbed molecules of carbon monoxide; in the adsorption of nitrogen on the same surface no molecules are already strongly held and the curve is smooth. The discontinuity may represent a phase change of the first order resulting from the influence of the strongly held molecules on the more mobile molecules of the reversibly adsorbed layer, showing close resemblance of the phase formed by the condensation of the reversibly sorbed monolayer on a metal or solid to the expanded phase of an insoluble liquid film on water.[18]

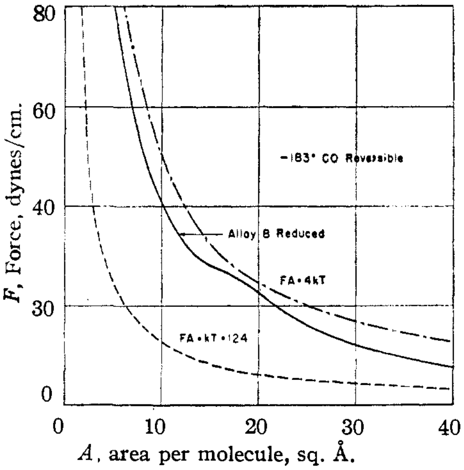

Fig. 10.—Typical force–area curves for film of carbon monoxide sorbed reversibly at −183° on reduced surface of stainless alloy B derived from data plotted as ln (p/v) *versus* v by method of Innes and Rowley.

Summary and Conclusions

The sorption of argon, neon, hydrogen, nitrogen, carbon monoxide, oxygen and carbon dioxide on two stainless iron–chromium–nickel alloys has been measured at −183, −78 and 20° and at pressures up to 0.1 cm. These determinations were made on a surface which had been degreased,

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

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

(18) Harkins, *et al.*, *J. Chem. Phys.*, **10**, 272 (1942); **13**, 535 (1945); **14**, 117 (1946).

outgassed and reduced by hydrogen, and subsequently outgassed; a few measurements were made on the degreased, outgassed surface. The surface was more readily conditioned to reproducibility of the sorption within the error of measurement than for mild steel.

Neon and hydrogen are not measurably sorbed in the range of temperature and pressure studied. Argon is very slightly sorbed at −183° and cannot be removed by pumping at temperature; the magnitude of the sorption is about the same as that of strongly held carbon dioxide at −78°. Nitrogen is sorbed to a greater extent at −183°, sufficient at apparent saturation to cover about one-half of the measured geometric surface and the sorption is completely reversible.

Carbon monoxide is the only gas which is physically adsorbed to as great an extent as a complete monolayer; furthermore the reversible sorption of this gas confirms the measured geometric area of the surface. Hence, it is concluded that at the low pressures used in this work only the reversible sorption of carbon monoxide at −183° is a reasonably reliable criterion of surface area in the case of stainless alloys whereas on mild steels nitrogen and argon are also satisfactory.

The agreement of the sorption data for the two alloys indicates that the surfaces are of the same specific area and this appears to approximate unity.

There is evidence of a tendency to form a second adsorbed layer in the case of Alloy B. Sorption data for Alloy B also show more marked deviation from the Langmuir equation in the lowest pressure region. These observations suggest that the surface of Alloy B is in a more reduced condition than that of Alloy A. Furthermore the proportionally greater chemisorption of carbon monoxide at −183° on Alloy B leads to the conclusion that there is more free metal on this surface.

The sorption of oxygen at −183° consists of a fraction of a monolayer reversibly held and about two monolayers which are chemisorbed. At −78 and 20° three and four layers, respectively, of oxygen are chemisorbed.

KEARNEY, NEW JERSEY RECEIVED NOVEMBER 29, 1947

[CONTRIBUTION FROM THE IPATIEFF HIGH PRESSURE AND CATALYTIC LABORATORY, DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

Isomerization of Saturated Hydrocarbons. V.[1] The Effect of Cyclohexene upon the Isomerization of Methylcyclopentane and Cyclohexane

BY HERMAN PINES, B. M. ABRAHAM[2] AND V. N. IPATIEFF

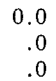
It was shown previously[1,3] that under certain carefully controlled conditions aluminum bromide–hydrogen bromide or aluminum chloride–hydrogen chloride did not cause the isomerization of *n*-butane to isobutane unless traces of olefins were present. This study has now been extended to the investigation of the reversible isomerization of methylcyclopentane to cyclohexane using aluminum bromide–hydrogen bromide as the catalyst. A high vacuum technique was used for the purification of materials, and for charging and discharging of the products.

It was found that methylcyclopentane did not undergo isomerization when shaken in a sealed tube for nineteen hours at 25° in the presence of as much as 9 mole per cent. of aluminum bromide[4] and 1 mole per cent. of hydrogen bromide. When the hydrogen bromide concentration was increased to 3.2 mole per cent., the yield of cyclohexane produced was 2%. However, when 0.05 mole per cent. of olefin such as cyclohexene was added to the reaction mixture, 28 mole per cent. of the methylcyclopentane was converted to cyclohexane. By increasing the molal ratio of the cyclohexene from 0.05 to 0.07 and to 0.1 mole per cent. the amount of cyclohexane formed increased to 30 to 38 mole per cent., respectively. The results are summarized in Table I. The amount of methylcyclopentane listed in the above table and in subsequent experiments was 8.00 to 10.00 g. ± 0.001 g.

TABLE I

THE EFFECT OF OLEFINS ON ISOMERIZATION

Reaction time 19 hrs. The amount of methylcyclopentane used in the various experiments varied from 8–10 g.

	Reagents: moles/100 moles methylcyclopentane			
No.	$AlBr_3$	HBr		Analysis mole % cyclohexane
1	1.0	1.0	0.0	0
2	9.0	1.0	.0	0
3	9.0	3.2	.0	2
4	9.0	1.0	.05	28
5	9.0	1.1	.07	30
6	9.0	1.0	.10	38
7	1.0	1.0	.20	58

A 58% yield of cyclohexane was obtained when the concentration of cyclohexene added was 0.2 mole per cent.; in this particular experiment the

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[1] The previous paper of this series was marked as "Isomerization of Alkanes. IV," see H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 2518 (1946).

[2] Universal Oil Products Company Postdoctoral Fellow 1946–1947. Present address Argonne National Laboratory, Chicago, Illinois.

[3] H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595 (1946).

[4] Throughout this paper for the purpose of calculation the aluminum bromide was considered to be monomeric.