JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

VOLUME 66 FEBRUARY 10, 1944 NUMBER 2

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

The Adsorption of Gases on Smooth Surfaces of Steel[1]

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This paper reports the results of measurements of the adsorption of hydrogen, argon, neon, nitrogen, carbon monoxide and carbon dioxide at pressures up to 0.1 cm. and at 20, −78, −183 and −195° on three surfaces of cold-rolled steel of the same nominal composition. The sorption on each surface was determined first after degreasing and degassing and subsequently on the identical surface after reduction in carefully purified hydrogen. In some cases it was necessary to condition the surface many times before adsorption was reproducible within the experimental error.

Apparatus and Materials.—The apparatus is described in an earlier paper.[2] The fixed temperatures were: (1) that of a mixture of solid carbon dioxide and alcohol (−78°); (2) the boiling point of oxygen (−183°); and (3) the boiling point of nitrogen (−195°). All temperatures were checked by means of a copper–constantan thermocouple immersed in the bath. Proper corrections, as described in the earlier paper, were made for the difference in temperature between the several parts of the system, a correction which also took account of the effect of thermal diffusion.

Argon, neon, nitrogen and carbon dioxide of the Air Reduction Company's "spectroscopically pure" grade were obtained in glass flasks which were sealed to the gas manifold of the adsorption system before being opened.

Carbon monoxide, prepared by the reaction of formic acid with sulfuric acid, was freed of carbon dioxide by passage through a solution of potassium hydroxide and was then dried over phosphorus pentoxide.

Hydrogen used in the measurement of sorption was of the Air Reduction Company's "spectroscopically pure" grade; that used for reducing the surface 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.

Steel Surfaces.—These were all cold-rolled flat wire whose chemical composition is given in Table I. Sample 1 (no. 25261), the surface used in our measurements of the sorption of ethyl iodide,[3] was a bundle of strips 0.08 mm. in thickness, 110 mm. in length and 19 mm. in width; it weighed 357.1 g. The total surface area, determined by measuring the dimensions of each strip, was 11130 sq. cm. Examination of a polished section under the microscope showed that this sample contained an unusually large number of non-metallic inclusions which appeared on the surface as small ellipsoids elongated in the direction of rolling; there were also a number of spheroidized carbide particles. The portion of the surface covered by each of the several phases, as estimated by cutting up photomicrographs and weighing the bits of paper representing each phase, was: inclusions about 5%, carbides about 30%, and iron about 65%.

TABLE I

CHEMICAL COMPOSITION OF THE STEELS

Sample	C	Mn	S	P	Si
1	0.39	0.70	0.049	0.016	0.128
2	.31	.58	.024	.011	.115
3	.12	.47	.041	.016	.003

Sample 2 (no. 25277) was a similar bundle of strips 0.07 mm. in thickness; it weighed 308.4 g. The total area was again 11130 sq. cm. This sample contained very few non-metallic inclusions; the carbides, which were spheroidized, covered about 25% of the surface, the rest of which was iron.

Sample 3 (no. 25278), was a bundle of strips 0.04 mm. thick; it weighed 366.7 g. The total measured area was 24680 sq. cm. or 2.22 times that of the other samples. This sample contained few inclusions, which covered not more than 2% of the surface; the carbides, which were spheroidized, covered about 15% of the surface, the remainder of which was iron.

Orientation of Grains.—Photomicrographs showed that initially the grains of each sample were elongated in the direction of rolling, the elongation being greatest on Sample 3 which had been rolled thinner than the others. The X-ray pole figure of each sample showed, as expected, a marked preferred orientation of the grains with the (100) planes in the rolling plane. Examination of a strip from each sample after the sorption measurements had been completed showed that the grains had become equiaxed but that preferred orientation persisted.

Treatment of Surfaces.—Before use, each piece of metal was degreased with absolute alcohol and anhydrous

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(1) Presented in part before the Division of Physical and Inorganic Chemistry at the meeting of the American Chemical Society, Atlantic City, N. J., September 8–12, 1941.

(2) Armbruster and Austin, THIS JOURNAL, 61, 1117 (1939).

(3) Armbruster and Austin, *ibid.*, 61, 1117 (1939).

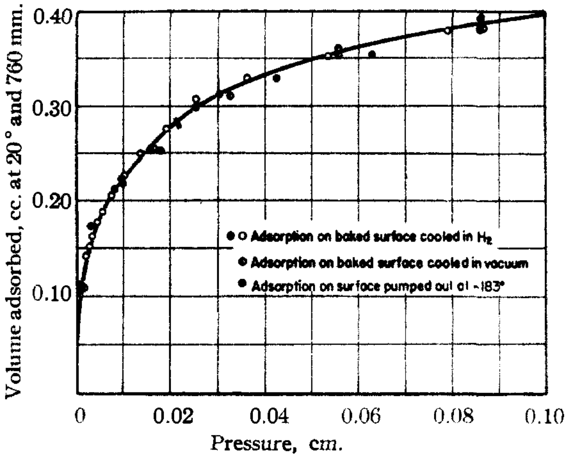

Fig. 1.—Sorption of argon at −183° on reduced surface of Sample 1: ●, surface outgassed and cooled in hydrogen, measurements made by increasing pressure; ○, surface outgassed, cooled in hydrogen (decreasing pressure); ◐, sample outgassed and cooled in vacuum (increasing pressure); ⊖, surface pumped out at temperature (increasing pressure).

ether, care being taken to avoid touching the strips with the fingers. The first set of measurements was made on the degreased surface after it had been baked for two hours at 300° at a pressure of less than 10^{-6} mm. In the first few runs on each surface the results were not satisfactorily reproducible, the amount of adsorption increasing slightly on successive runs, but this increase became successively smaller and was negligible after about 20 measurements so that the volume of gas sorbed at a given pressure was reproducible within 5%. Although the magnitude of the adsorption of a specific gas changed during this initial period, the relative adsorption of different gases remained substantially the same, indicating that the increasing adsorption was due to an effective increase in surface area rather than to a change in the nature of the surface. Since tests using longer time of baking or higher temperature failed to show any significant deviation from the results obtained by baking for two hours at 300°, this latter procedure was adopted as standard. In the first set of measurements no attempt was made to reduce the invisible "oxide" always present on iron which has been exposed to oxygen, hence, the degreased and outgassed surface is referred to as "unreduced."

A second set of measurements was made after the surface had been reduced at 450° in a stream of purified tank hydrogen introduced at the bottom of the adsorption bulb, the surface being freshly reduced before each run. The period of reduction ranged in general from twenty-four to forty-eight hours, although in a few cases it was as much as sixty hours. After reduction of the surface the hydrogen inlet tube was sealed off and the sample was given the standard degassing treatment at 300° which yielded a surface, apparently free of oxide, on which adsorption was satisfactorily reproducible. The absence of an oxide film on the reduced surface was demonstrated by an accident which occurred during one of the runs. In replenishing the liquid air around one of the traps, the trap cracked and mercury was blown into the adsorption bulb, where it wet the iron wherever there was contact, a reaction which is observed only when an iron surface is substantially oxide-free. There was a tendency for the amount of adsorption on the reduced surface to decrease slightly on successive runs, the change being relatively the same for all gases, indicating a slight decrease in effective surface area. This change usually became negligible after a number of check runs had been made. The purified hydrogen used in reducing the surface tends to decarburize as well as to deoxidize, but the rate of decarburization with the carefully dried gas employed is so small that no significant loss of carbon from the surface was observed.

The adsorbent was cooled either in vacuum or in hydrogen, which direct measurement shows is not measurably sorbed on a smooth surface of steel in the temperature range studied. Direct comparison showed that the amount of adsorption was independent of the method of cooling, as is evident from Fig. 1 which shows the sorption of argon on the reduced surface of Sample 1 as determined by different procedures. Since cooling was most rapid in hydrogen, this gas was used in most runs. The trap between the adsorption train and the diffusion pump was immersed in liquid air from about half way through the baking period to the end of a run. A number of check runs, up to as many as 25, were made for each combination of gas, surface and temperature.

Procedure.—After the surface of the sample had been suitably prepared and brought to equilibrium at the temperature of test, adsorption was determined by admitting successive increments of gas; this is the procedure of building up to the pressure in steps described in our earlier paper.[4] The pressure was then diminished by steps to determine the amount of gas desorbed as the pressure decreased. A difference between the results on adsorption and on desorption at a given pressure was taken to indicate the existence of some irreversible sorption which was checked by measuring the adsorption a second time after the system had been pumped down to a pressure of less than 10^{-6} mm. at the temperature of test. A typical example of the agreement obtained when the adsorption was completely reversible[5] is shown in Fig. 1.

Results

Neither neon nor hydrogen was measurably sorbed on any of the surfaces within the temperature range investigated. Likewise none of the gases investigated was measurably sorbed at room temperature (20°). The sorption of the several gases on the three reduced surfaces at −78, −183 and −195° is shown by typical isotherms in Figs. 2, 3 and 4; representative iso-

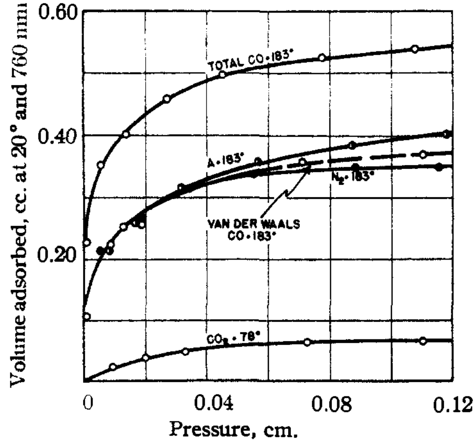

Fig. 2.—Adsorption isotherms for the several gases on reduced surface of Sample 1.

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[4] Armbruster and Austin, THIS JOURNAL, 61, 1117 (1939).

[5] The term reversible adsorption is used to describe that part of the total sorption which can be removed by evacuation at temperature. It is used without any connotation as to the forces involved and implies nothing more than the observation that the sorbed gas can be removed by reducing the pressure to the order of 10^{-6} mm. at the temperature of test. Adsorption which cannot be removed by evacuation at temperature is designated as irreversible.

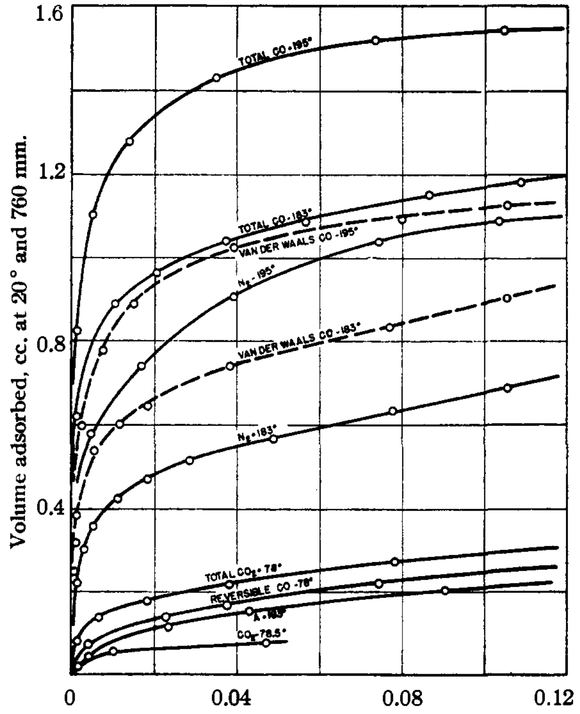

Fig. 3.—Adsorption isotherms for the several gases on reduced surface of Sample 2.

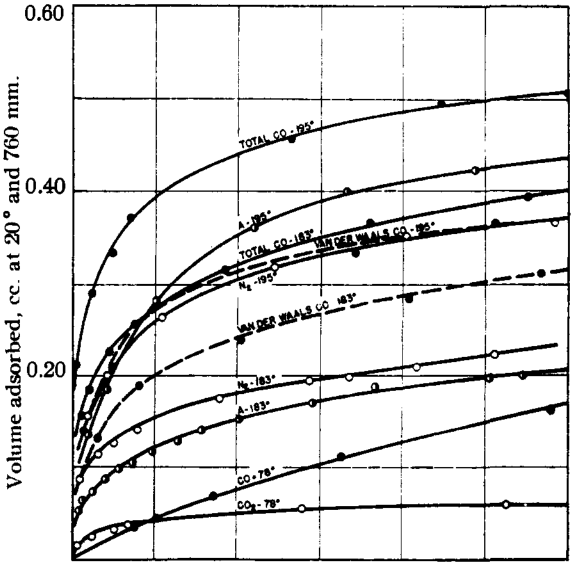

Fig. 4.—Adsorption isotherms for the several gases on reduced surface of Sample 3.

therms for the unreduced surfaces are shown in Figs. 5 and 6. For ease of comparison the data for Sample 3 are corrected to correspond to the surface area of the other two samples. The limiting volume sorbed (v_s) as derived by means of the Langmuir equation, the ratio of this volume to that of nitrogen at −183°, and the apparent

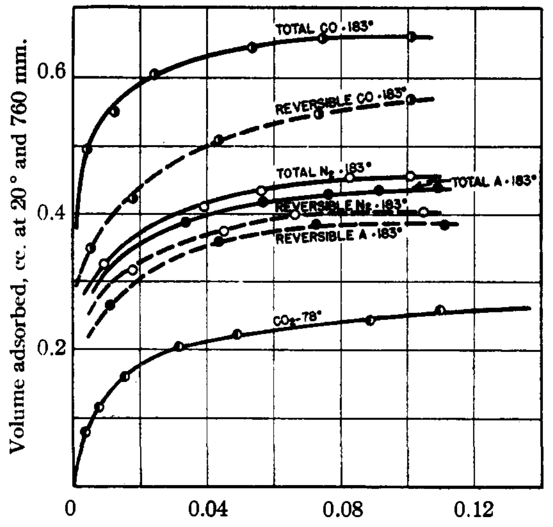

Fig. 5.—Adsorption isotherms for the several gases on unreduced surface of Sample 1.

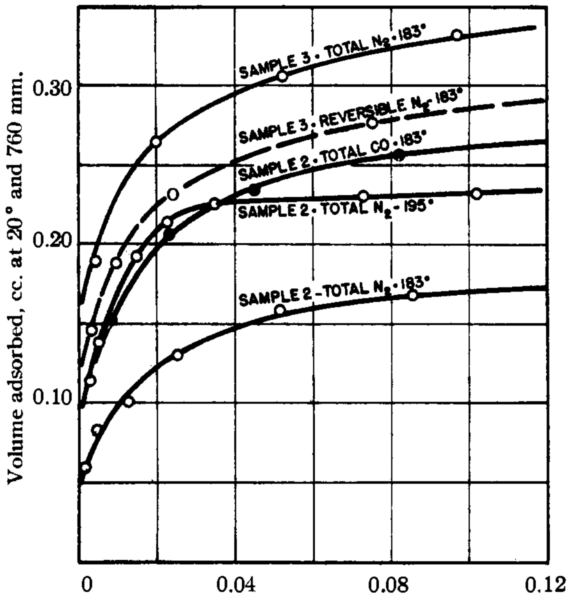

Fig. 6.—Adsorption isotherms for the several gases on unreduced surface of Samples 2 and 3.

coverage of the surface by a close-packed monolayer as derived from the corresponding value of v_s, the nominal or geometric area of the surface, and the cross-section[6] of the adsorbed molecule are given in Table III.

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[6] The apparent coverage is calculated from the relation: $v_s \times 2.5 \times 10^{19} \times$ cross section per molecule/geometric area of surface. The exact value to be taken for the cross-sectional area is not as yet well established; in fact, data reported by Harkins and Jura (*J. Chem. Physics*, **11** 431 (1943)) suggest that it may not be constant for all surfaces. We have selected the areas used by Langmuir, namely, A 12.9, N_2 15.2, CO 15.2, CO_2 16.4 sq. Å. which lie between the two sets calculated by Brunauer, Emmett and Teller from the density of the respective liquid and solid phases. They are believed to be a reasonable compromise and in any case are sufficiently accurate for the present purpose.

Adsorption on a freshly outgassed surface, either reduced or unreduced, was always slow when the sample had cooled in vacuum; more specifically, there was initially a fairly rapid adsorption which slowed down markedly as equilibrium was approached. On the other hand, when an outgassed sample had cooled in hydrogen or argon, or when the surface had merely been pumped out at temperature, sorption was practically instantaneous. This suggests that the slow adsorption on a surface cooled in vacuum may have been due to failure to attain temperature equilibrium, yet holding in vacuum at temperature for as long as fifty hours did not suffice to make the sorption instantaneous.

Discussion

Sorption of Neon and Hydrogen.—The sorption of these gases was less than the error of measurement, that is, less than 3×10^{-4} cc., which corresponds to less than 1% of the surface covered.

Adsorption at −183° on Unreduced Surfaces.—The characteristics of the unreduced surface were studied most extensively on Sample 1, measurements on the other samples being made chiefly to confirm certain specific observations on the first. The unreduced surfaces were without question covered with a thin film of oxygen or oxide, as is demonstrated directly by the observation that the sorption of oxygen on the unreduced surface was always less than that on a reduced surface by an amount equivalent to a film about three molecules thick. The behavior of these surfaces must therefore be interpreted in terms of the presence of this film.

The most significant result obtained for this type of surface is that at −183° some of the sorbed nitrogen, argon or carbon monoxide is held so strongly that it cannot be removed by reducing the pressure at temperature, in marked contrast to the behavior of a reduced surface on which the sorption of argon and nitrogen is entirely reversible. Moreover, the percentage of the total gas which is thus strongly held is in every case substantially the same, as is illustrated by the data in Table II, which indicate that about one-seventh of the total amount adsorbed was not removed by reducing the pressure to 10^{-6} mm.

TABLE II

Difference between amount of gas sorbed at −183° on a baked out surface and that on a surface pumped out at temperature, expressed as a percentage of the former.

Gas	Sample	
	1	3
N_2	14.5	11.0
A	16.1	..
CO	11.8	..

The exact nature of this strong adsorption is not clear; but the instantaneous rate of sorption and the improbability that argon is held to the surface by anything other than physical forces indicates that it is basically van der Waals adsorption. It might be a process of the sort described by Beebe and Dowden,[7] who found that at low temperature nitrogen and certain other gases are instantaneously adsorbed on chromic oxide by what appears to be van der Waals adsorption, but later go over to another type of sorption for which the heat effect is much greater; against this view, however, is the fact that they did not find such an effect with argon. An alternative view is that this gas is held in cracks and fissures in the surface, since van der Waals forces are much stronger in such crevices than on a plane surface; yet it seems unlikely that the volume of gas thus sorbed would be so nearly the same for different gases or on different surfaces. A third possibility is that because of the structure of the film there are on the surface certain sites which are virtual depressions in which a sorbed molecule can come in very close contact with a number of oxygen atoms so that the strength of the van der Waals attraction is greatly increased. We incline to this last view because a similar strong adsorption of nitrogen and argon has already been observed on mica[8] in which case the sorbed molecules appeared to be held in positions vacated by potassium ions during cleavage; moreover, if these sites are a result of the structure of the film, the constant fraction of the surface so covered is easily explained.

Adsorption at −78° on Unreduced Surfaces.—Carbon dioxide was measurably sorbed on the unreduced surface of Sample 1, the only surface on which measurements were made. The rate of sorption was virtually instantaneous and the isotherm for a surface pumped out at temperature agreed with that for a baked surface, indicating that carbon dioxide is physically sorbed on this surface.

Carbon monoxide was not measurably sorbed on any of the unreduced surfaces at this temperature.

Adsorption at −78° on Reduced Surfaces.—Carbon dioxide was measurably sorbed on all three samples, the amount being from one-fourth to one-half that of nitrogen on the same surface at −183°. The rate of sorption was instantaneous and on Samples 1 and 3 the isotherm for a surface evacuated at temperature agreed with that for a baked out surface, indicating that the adsorption is entirely physical. On Sample 2, however, adsorption on a pumped surface was slightly less than on a baked surface (Fig. 3), indicating some chemisorption. In view of the observation of Emmett and Brunauer,[9] that on a promoted iron catalyst at −78° carbon dioxide is chemisorbed on the alkali promoter but not on iron, it is likely that this chemisorption on the smooth surface occurs on some non-metallic phase.

The amount of carbon monoxide sorbed at −78° differed widely, ranging from none on

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(7) Beebe and Dowden, THIS JOURNAL, 60, 2912 (1938).

(8) Armbruster and Austin, *ibid.*, 60, 467 (1938).

(9) Emmett and Brunauer, *ibid.*, 59, 310 (1937).

TABLE III

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

Temp., °C.	Gas	v_s, limiting volume derived by means of Langmuir equation, cc. at 20° and 760 mm.[a] Sample no. 1	2	3[b]	Ratio of v_s to that for N_2 at −183° Sample no. 1	2	3[b]	Apparent coverage of surface by monolayer, % Sample no. 1	2	3[b]
		Surface Reduced in Hydrogen								
−195	N_2		1.154	0.416		1.60	1.72		396	143
	A			.483			2.00			142
	CO (reversible)		1.158	.384		1.60	1.59		397	131
	CO (chemisorbed)		0.377	.180		0.52	0.74		130	62
	CO (total)		1.535	.564		2.12	2.33		527	194
−183	N_2	0.381	0.722	.243	1.00	1.00	1.00	131	248	83
	A	.440	0.272	.238	1.15	0.38	0.98	129	80	70
	CO (reversible)	.410	0.966	.363	1.07	1.34	1.49	141	331	125
	CO (chemisorbed)	.252	0.290	.088	0.65	0.40	0.36	86	100	30
	CO (total)	.662	1.256	.451	1.72	1.74	1.85	227	431	155
− 78	CO (total)	0	0.083	.384		0.15	1.59	>1	29	132
	CO_2 (total)	.083	0.329	.067	0.22	0.46	0.28	31	122	25
	CO_2 (reversible)	...	0.315	...	..	0.44	..	...	117	...
		Degreased (Unreduced) Surface								
−195	N_2 (total)		0.250			1.30			85	
−183	N_2 (reversible)	0.410		0.300	0.85		0.88	141		104
	N_2 (total)	.480	0.191	.337	1.00	1.00	1.00	165	65	116
	A (reversible)	.390			0.80			115		
	A (total)	.465			0.97			137		
	CO (reversible)	.600			1.25			205		
	CO (total)	.680	0.280	...	1.41	1.45		233	147	
− 78	CO_2	.290	...	...	0.60			108		
	CO	0	0	0						

[a] 1 cc. = 41.6 micromoles = 2.5×10^{19} molecules. [b] The observations for Sample 3 have been divided by 2.2 to reduce them to the same geometric surface area as for the other samples.

Sample 1 to something approaching a complete layer on Sample 3, as estimated by comparison of the values of v_s (Table III) with that for nitrogen sorbed at −183°. The gas was adsorbed instantaneously but could not be desorbed by pumping at temperature. Brunauer and Emmett report that a complete layer of carbon monoxide is chemisorbed at −78° on iron catalysts, a result confirmed, insofar as strength of binding is concerned, by the calorimetric measurements of Beebe and Stevens.[10] On this basis one would expect a similar layer to be sorbed on a smooth surface, as it was on Sample 3, though not on the other two surfaces. Again the explanation for this difference is uncertain. Brunauer[11] has stated, however, that in his experiments if the iron surface was strongly sintered, not only did the quantity of chemisorbed carbon monoxide decrease but also the binding of the adsorbed gas to the iron was weakened as is evident from the fact that it was possible to pump off a part of the carbon monoxide at −78° from a strongly sintered catalyst. These observations, together with the fact that the surface of Sample 1, on which there was no measurable adsorption, had been baked out a great many times, whereas that of Sample 3, on which a complete layer of carbon monoxide was sorbed, had been baked out only a few times, suggest that the different behavior of the several samples was due to an effective difference in the smoothness of the surface. Thus, if the reduction of the oxide film were to leave a relatively rough skin on the iron which then sintered during subsequent bakings, there might be variations of the sort described by Brunauer.

It should be noted that on Sample 3, all the carbon monoxide was chemisorbed at −78° whereas at −183° only a small fraction of it was chemisorbed, a result in accord with the observation of Beebe and Stevens,[10] that the heat of adsorption is greater at −78° than at −183°.

Adsorption at −183 and −195° on Reduced Surfaces.—Since most of the isotherms are represented reasonably well, especially at the higher pressures, by the Langmuir equation, the results for −183 and −195° are most conveniently discussed in terms of the limiting volume sorbed (v_s), as derived by means of this equation. The value of this limiting volume is given in Table III along with the ratio of this value to that for nitrogen at −183°, which in effect reduces the observations to a common effective surface area.

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(10) Beebe and Stevens, THIS JOURNAL, 62, 2134 (1940).

(11) See footnote 14, Beebe and Stevens, ref. 10.

This ratio for carbon monoxide (total) at −183° is approximately constant; moreover, the fraction of the surface covered by chemisorbed carbon monoxide is substantially constant and is roughly 0.4 times the coverage by nitrogen. This is less than half that reported by Emmett and Brunauer,[12] who observed a complete layer of chemisorbed carbon monoxide as well as a complete layer of van der Waals adsorption. The reason for this difference is not clear.

Specific Surface Area.—The coverage, shown in Table III, indicates that the layer of sorbed gas does not exceed one molecule in thickness, and the close agreement in coverage by the several gases at the same temperature is presumptive, though not conclusive, evidence that the monolayer covers substantially the whole surface. Emmett and his colleagues[13] have had considerable success in estimating the surface area of a powder from the observed adsorption of nitrogen or argon at low temperature by assuming that the volume, corresponding to the point at which the isotherm ceases to be concave to the pressure axis and becomes substantially linear (the point they call B, which corresponds to v_m calculated by means of their equation for multimolecular adsorption) represents the volume of gas required for complete coverage by a close-packed monolayer. Since, as is shown later, our isotherms are very probably of the same type as theirs, the coverage by nitrogen and argon, as derived from the value of v_s, should likewise represent the completion of a monolayer on the cold-rolled steel. Investigations of adsorption on the smooth surface of other metals, notably silver and platinum,[14] have demonstrated, however, that under certain conditions substantial saturation of the surface may be achieved by a monolayer in which the effective cross-sectional area of the sorbed molecules is much greater than that commonly assumed, which indicates that the Emmett–Brunauer–Teller method may not always be reliable when applied to a smooth metallic surface; this makes necessary some reservation on the above conclusions.

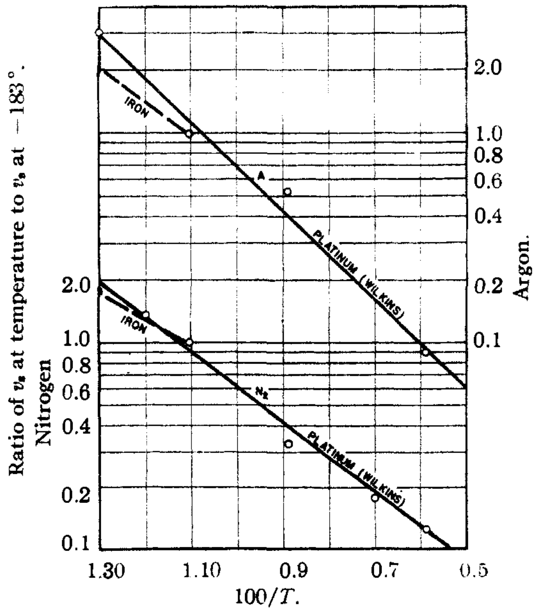

Fig. 7.—Variation with temperature of the limiting volume (v_s), as derived by means of the Langmuir equation, plotted as the ratio v_s at temperature to v_s at −183°. Solid lines and circles represent Wilkins' data for nitrogen and argon on smooth platinum; dashed lines, our data for smooth iron.

On the basis that the limiting volume (v_s) corresponds to the completion of a relatively close-packed monolayer, the specific surface of the steel, relative to the geometric area of the strips, is approximately 1.5 for Sample 1, 3 to 4 for Sample 2 and about 1 to 1.5 for Sample 3, which indicates that these surfaces are remarkably flat.

Variation of v_s with Temperature.—The value of v_s increases markedly with decreasing temperature, as is common in systems of this type. Although the exact form of the variation cannot be determined from observations at only two temperatures, it appears to be consistent with that reported by Wilkins for the sorption of argon and nitrogen on platinum foil. He found that for the range −100 to −195° v_s is satisfactorily represented by the relation

$$v_s = v_0 e^{\beta/T} \qquad (1)$$

where v_0 and β are constants. His more extensive data are plotted along with ours in Fig. 7 in which, to eliminate the effect of the difference in surface area and to permit direct comparison of the two sets of observations, log (v_t/v_{-183}) is plotted against $1/T$. The agreement between the two sets of data is as close as could be expected, indicating that in this temperature range the variation of v_s for nitrogen and argon is substantially the same on both platinum and iron foil.

Heat of adsorption can be calculated by means of an analog of the Clausius–Clapeyron equation or by means of an equation developed by Brunauer, Emmett and Teller.[15] The former method, based upon the adsorption isostere, is commonly assumed to give the heat of sorption corresponding to a given volume of gas sorbed; the second method, which requires but a single isotherm, yields the average heat of sorption in the less active portion of the first layer. In several instances the results of application of these two methods to our data differ significantly; moreover, the heat calculated by means of the Clausius–Clapeyron equation in a number of cases increases as the fraction of the surface covered increases, a result which is hardly acceptable in view of the great body of evidence, including di-

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[12] Emmett and Brunauer, THIS JOURNAL, 59, 310 (1937).

[13] *Cf.* Emmett and DeWitt, *Ind. Eng. Chem., Anal. Ed.*, 13, 28 (1941).

[14] Armbruster, THIS JOURNAL, 64, 2545 (1942); Wilkins, *Proc. Roy. Soc.* (London), A164, 510 (1938).

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

rect calorimetric measurement, that on iron the heat of adsorption decreases with increasing coverage. For example, the heat of adsorption for nitrogen on the reduced surface of Sample 2 as derived by means of the Clausius–Clapeyron equation varies from 1370 cal. per mole at 200 cu. mm. sorbed to 2800 cal. at 600 cu. mm.; the corresponding heat calculated by means of the Brunauer–Emmett–Teller relation is 2750 cal. at −195° and 3160 cal. at −183°. The values derived by means of the Clausius–Clapeyron equation are, therefore, significantly lower in the range of small fraction of the surface covered, which is, however, just the range in which they should be higher. These discrepancies led us to suspect that the heat of sorption derived by means of the Clausius–Clapeyron equation may not be reliable under all circumstances and resulted in a critical examination of its accuracy and precision as compared to those of the Brunauer–Emmett–Teller method.

For monomolecular adsorption, the Brunauer–Emmett–Teller relation is

$$p/v = \frac{p_0}{v_m c} + \frac{p}{v_m} \qquad (2)$$

where v is the volume sorbed at pressure p, v_m is the volume of gas required to complete a close-packed monolayer, p_0 is the saturation pressure of the liquid adsorbate at the given temperature, and c is a quantity defined by the relation

$$c = fe^{-(\Delta H_a - \Delta H_L)/RT} \qquad (3)$$

where ΔH_a is the average heat of adsorption, ΔH_L is the heat of liquefaction of the gas and f is a coefficient whose value is close to unity.

The most convenient form of this relation for ordinary use, and the one best fitted to show the accuracy and precision of the calculation, is

$$\Delta H_a = A - 2.303\ RT \log v_m I \qquad (4)$$

in which v_m and I are, respectively, the numerical value of the reciprocal of the slope and the intercept derived from the linear plot of p/v against p, and

$$A = \Delta H_L + 2.303\ RT \log p_0 \qquad (5)$$

Inspection of equation (4) shows that the use of this method tends greatly to reduce the effect of any observational error. The only term containing a factor derived from the adsorption data is log $(v_m I)$, whose value is commonly smaller, and frequently is very much smaller, than that of A, so that this term is in essence merely a correction to A, whose value can in most cases be determined with considerable accuracy. Furthermore, the value of this correction is, because of the logarithmic form of the term, relatively insensitive to an error in the value of v_m or I. For example, if the value of the product $(v_m I)$ is in error by a factor of 2, the change in the logarithm is only 0.301 unit, corresponding to an error of (4.57 T × 0.301) calories in the heat effect; for T = 100°K., this is about 150 calories.

The analog of the Clausius–Clapeyron equation is

$$\left(\frac{\partial \ln p}{\partial (1/T)}\right)_v = \frac{\Delta H_a}{R} \qquad (6)$$

in which p is the pressure required at absolute temperature T to cause the sorption of volume v.

Its accuracy appears to be open to serious question. The limitations of the Clausius–Clapeyron equation when applied to vaporization are well recognized but no corresponding evaluation of equation (6) as applied to adsorption appears to have been reported, although we have not exhaustively searched the early literature. On the other hand, the use of the equation has been criticized on several different grounds. The primary objection is a practical one, namely, that if the isotherms indicate saturation of the surface at the higher pressures, as they do in monomolecular adsorption, and if the maximum volume sorbed increases with decreasing temperature, as it commonly does, then the isostere can be constructed for a limited range of volume only.

Wilkins,[16] from statistical calculations, has concluded that equation (6) should be used not at constant volume but at constant concentration on the surface, that is, at constant fraction of the surface covered, a procedure which removes the primary difficulty in constructing the isostere. Wilkins has shown further that, if equation (1) is valid, then the heat of adsorption calculated by means of equation (6) is in error by the amount $R\beta$,[17] where R is the gas constant.

Since it is clear that the use of equation (6) may yield a result significantly in error, it is instructive to compare it with the Brunauer–Emmett–Teller equation, which may be written

$$p = p_0 e^{-\Delta H_a - \Delta H_L/RT} \left(\frac{v}{v_m - v}\right) \qquad (7)$$

whence

$$\left(\frac{\partial \ln p}{\partial (1/T)}\right)_v = \left(\frac{\partial \ln p_0}{\partial (1/T)}\right)_v + \frac{\Delta H_a}{R} - \frac{\Delta H_L}{R} - \left(\frac{\partial \ln (v_m - v)}{\partial (1/T)}\right)_v \qquad (8)$$

but

$$\left(\frac{\partial \ln p_0}{\partial (1/T)}\right) = \frac{\Delta H_L}{R} \qquad (9)$$

hence

$$\Delta H_a = R\left[\left(\frac{\partial \ln p}{\partial (1/T)}\right)_v + \left(\frac{\partial \ln (v_m - v)}{\partial (1/T)}\right)_v\right] \qquad (10)$$

On this basis, the ordinary analog of the Clausius–Clapeyron equation yields a value of ΔH_a which is in error by the amount $R(\partial \ln (v_m - v)/\partial (1/T))_v$. Under optimum conditions, as for example a very small variation of v_m with temperature, this error is negligible, but under less favorable circumstances it may be appreciable.

If v_m can be represented as a function of $(1/T)$,

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(16) Wilkins, *Proc. Roy. Soc.* (London), **A164**, 496 (1938).

(17) Wilkins' paper gives this difference as β, but this is clearly a typographical error and should be $R\beta$.

equation (10) can be simplified. Thus, on the basis of Wilkins' suggestion that $v_m = v_0e^{\beta/T}$

$$\left(\frac{\partial \ln (v_m - v)}{\partial(1/T)}\right)_v = \frac{\beta v_0 e^{\beta/T}}{v_0e^{\beta/T} - v} = \frac{\beta v_m}{v_m - v} \qquad (11)$$

For $v \ll v_m$, this correction reduces to β, whence

$$\Delta H_a = R\left(\frac{\partial \ln p}{\partial(1/T)}\right) + R\beta \qquad (12)$$

which is the same relation as was obtained by Wilkins.

Equation (10) is clearly limited in use to the range of v in which the isostere can be constructed, a restriction which, however, is inherent in any calculation based on constant volume. This difficulty can be avoided, as suggested by Wilkins, by the use of constant concentration, a procedure which gives the true heat of adsorption. Thus, if the ratio v/v_m be represented by θ, equation (7) leads to the relation

$$\left(\frac{\partial \ln p}{\partial(1/T)}\right)_\theta = \frac{\mathrm{d} \ln p_0}{\mathrm{d}(1/T)} + \frac{\Delta H_a}{R} - \frac{\Delta H_L}{R} \qquad (13)$$

whence

$$\Delta H_a = R\left(\frac{\partial \ln p}{\partial(1/T)}\right)_\theta \qquad (14)$$

In contrast to the Brunauer–Emmett–Teller method, in which the adsorption data yield a relatively small correction to be applied to a quantity which is known precisely, the Clausius–Clapeyron relation and its several modifications tend to magnify experimental error and are, in consequence, less likely to give satisfactory results. In view of this conclusion, we report only the average heat as derived by the method of Brunauer, Emmett and Teller.

The average heat of reversible adsorption of the several gases is given in Table IV, which includes for comparison the heat of liquefaction of each gas at its normal boiling point. In each case the heat effect is 2 to 3 times the heat of liquefaction which indicates that the sorbed molecules are held to the surface by fairly strong physical forces. These data show further that, except for the sorption of carbon dioxide at −78°, the heat is substantially the same for all the gases on all the surfaces; moreover, these heats are virtually identical with those for the sorption of the same gases at the same temperature on smooth surfaces of silver or platinum, as is illustrated in Table V. They are, however, significantly higher than the heat effect of 2170 ± 70 cal. reported by Brunauer, Emmett and Teller[18] for the sorption of both argon and nitrogen at −183° on porous iron catalysts. A similar difference in the heat of adsorption of oxygen on silver at −183° has already been described.[19]

TABLE IV

AVERAGE HEAT OF REVERSIBLE ABSORPTION (ΔH_a) OF THE SEVERAL GASES ON SMOOTH IRON AS DERIVED BY MEANS OF THE EQUATION OF BRUNAUER, EMMETT AND TELLER

Gas	Temp., °C.	Surface	Sample	Value of c	ΔH_a, cal./mole	Heat of liquefaction of gas at normal boiling point
N_2	−183	Unreduced	1	52480	3280	
		Unreduced	2	225900	3577	
		Reduced	1	33110	3205	
		Reduced	2	251200	3568	1330
		Reduced	3	245500	3560	
	−195	Unreduced	2	438	2276	
		Reduced	2	6918	2705	
		Reduced	3	69180	3073	
A	−183	Unreduced	1	19500	3280	
		Reduced	1	7943	3120	
		Reduced	3	4217	3007	1505
	−195	Reduced	3	13650	2984	
CO	−183	Unreduced	1	67610	3400	
		Reduced	1	17780	3170	
		Reduced	2	305500	3680	1410
		Reduced	3	245500	3642	
	−195	Reduced	2	20420	3306	
		Reduced	3	263200	3350	

TABLE V

COMPARISON OF MOLAR HEAT OF ADSORPTION ON A SMOOTH SURFACE OF IRON, SILVER OR PLATINUM

	Fe			
	Unreduced, cal.	Reduced, cal.	Ag.[a] cal.	Pt.[b] cal.
A	3280	3200	3500	3280
N_2	3280	3120	3600	3385
CO		3400	3170	3600

[a] Derived from data of Armbruster. [b] Derived from data of Wilkins.

The difference between the heat effect on the two kinds of iron surface appears, moreover, to be characteristic of the physical condition of the surface rather than of its chemical nature; since Brunauer, Emmett and Teller found that the heat of sorption of nitrogen at −183° on twelve different catalysts, including iron, copper, silica gel, and chromic oxide is always 2170 ± 70 cal., whereas the data in Table V indicate that on a smooth metallic surface, whether it be iron, silver, or platinum, the heat is always close to 3000 cal. Moreover, since both argon and nitrogen have the same heat of sorption on the same surface, it is concluded that at a given temperature the heat of sorption is chiefly a function of the physical state of the surface and relatively independent of the chemical nature of either adsorbent or adsorbate.

The difference between the heat of adsorption on smooth iron and that on an iron catalyst provides a possible explanation for the seemingly different form of the isotherm for the two kinds of surface, and makes it possible to show that the isotherm for sorption on a smooth surface, though apparently of the saturation type, is probably of the sigmoid type characteristic of sorption on a catalyst. Thus the Brunauer–Emmett–Teller relation for multimolecular adsorption may be written

$$v/v_m = \frac{p/p_0\Big/\left(1 - \frac{p}{p_0}\right)}{\left(\frac{1}{c} + \frac{c-1}{c}\frac{p}{p_0}\right)} \qquad (15)$$

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

(19) Armbruster, *ibid.*, 64, 2545 (1942).

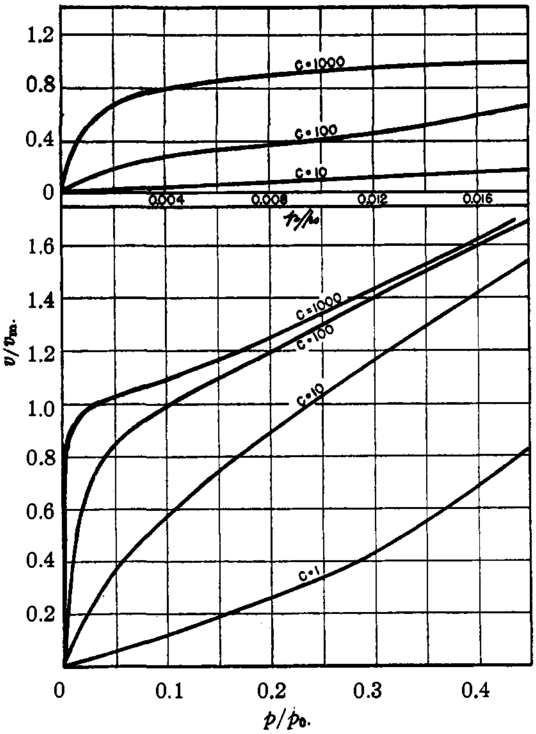

Fig. 8.—Variation of ratio v/v_m with p/p_0 for different values of c as derived by means of the equation of Emmett, Brunauer and Teller.

where the symbols have the significance explained earlier. Since the difference $\Delta H_a - \Delta H_L$ enters exponentially into the quantity c, this quantity, hence, the shape of the isotherm, is very sensitive to a change in ΔH_a, as is illustrated in Fig. 8 which shows v/v_m plotted against p/p_0 for different values of c. As c increases, v/v_m approaches unity at a much lower value of p/p_0, and tends to remain virtually constant at unity over an appreciable range of p/p_0, as is illustrated in the upper part of Fig. 8 which shows the low-pressure portion of the several curves on a greatly enlarged scale. For sorption on iron catalysts at −183°, the value of c is between 10 and 100, whereas for the smooth surface it is well over 1000 (see Table IV). On this basis, the isotherms in Figs. 2 to 6 are probably of the same type as those described by Brunauer, Emmett and Teller, and had our measurements been carried to a higher pressure, the isotherms would have become convex to the pressure axis.

Form of Isotherms.—The isotherms in Figs. 2 to 6 are of the form apparently typical of sorption at a relatively low pressure on a smooth metallic surface, which has generally been considered by investigators in this specific field to be of the saturation type. There is reason to doubt the justification for this classification, as has been pointed out earlier, yet it is instructive to consider our results from the standpoint of two common adsorption equations

$$v = ap^{1/n} \tag{16}$$

$$v = \frac{av_sp}{1 + ap} \tag{17}$$

where v is the volume of gas sorbed at pressure p, v_s is the maximum volume of gas sorbed at apparent saturation of the surface, and a and n are constants.

The first of these is the parabolic isotherm, variously and inaccurately called the classic, Freundlich or exponential isotherm, in which the value of n is almost always positive and greater than unity. Applied to our data, it fits very well over the low pressure range, as is illustrated in Fig. 9 by typical data for nitrogen plotted on double logarithmic coördinates to yield a straight line. These data yield a straight line over the 200 fold pressure range 0.0001 to 0.020 cm.; moreover, the several lines are substantially parallel, with a slope corresponding to a value of n of about 4. A similar plot of the data for argon yields an analogous set of parallel straight lines with a slope corresponding to a value of n of about 3. The equation fails, as it must, as the surface approaches saturation.

Equation (7) is the relation originally derived by Langmuir,[20] which yields a straight line when the ratio p/v is plotted against p. When this test is applied to our results, the equation holds over a considerable range of pressure, yet there are marked deviations in the low pressure range as is well illustrated by the typical isotherms for nitrogen shown in Fig. 10. These deviations are all of the same kind—the volume adsorbed at a given pressure in the low range being greater than that calculated by extrapolation of the data in the high

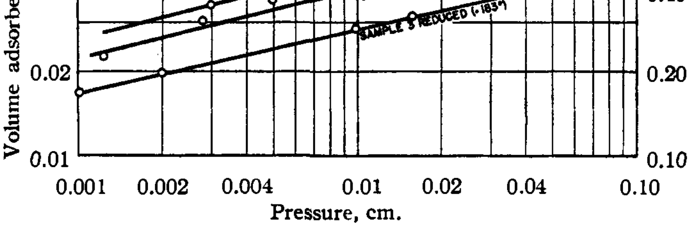

Fig. 9.—Adsorption of nitrogen on different surfaces plotted on double logarithmic coördinates on which data following the parabolic isotherm yield a straight line.

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[20] Langmuir, THIS JOURNAL, 40, 1361 (1918).

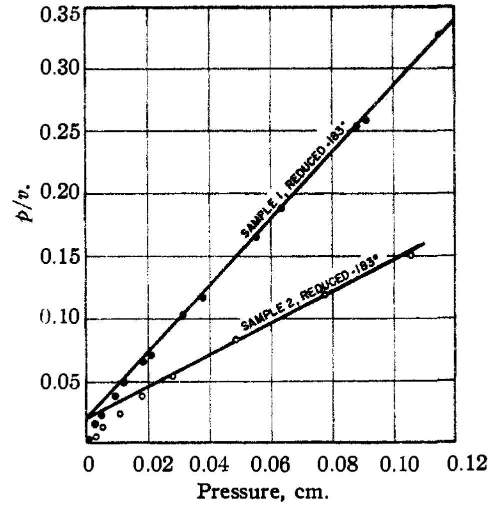

Fig. 10.—Isotherm at −183° for nitrogen adsorbed on reduced surface of Samples 1 and 2 plotted as p/v against p.

pressure range. Such deviations, which seem to be quite common, have been discussed at some length by Barrer,[21] who cites a number of examples in addition to those in his own measurements of adsorption of gases in graphite; similar behavior has been noted by Wilkins in his studies of adsorption on platinum foil.[22] These deviations from the Langmuir equation occur in the range of low pressure, precisely that in which the parabolic isotherm fits, which suggests that a combination of the two equations might hold over the whole range. Such a combination can be made in two ways

$$v = \frac{av_s p^{1/n}}{1 + ap^{1/n}} \tag{18}$$

$$v = v_s \sqrt[n]{\frac{ap}{1 + ap}} \tag{19}$$

each of which reduces to the form of equation (16) for low pressures, that is, when the product ap becomes small compared to unity, and to the form of equation (17) when ap is very large compared to unity.

The first equation (18), is analogous to Langmuir's expression for adsorption of a gas which occupies n elementary spaces. It fails, however, to yield a satisfactory fit for our measurements. Equation (19) is a generalized form of the equation

$$v = \sqrt{\frac{k_1k_2p}{1 + k_1p}} \tag{20}$$

proposed by Zeise which describes the adsorption of gases and vapors on glass,[23] and the adsorption of hydrogen on nickel.[24] Our results do not conform to equation (20) but the data for argon and nitrogen are represented satisfactorily by equation (19), if n is taken as 3 and 4, respectively, as is illustrated by the typical isotherm for nitrogen shown in Fig. 11. The equation also fits our measurements of the adsorption of carbon monoxide, although in this case the value of n varies between 4 and 5 for different isotherms. It is believed, therefore, that equation (19) holds over a very much wider range of pressure than equation (16) or (17).

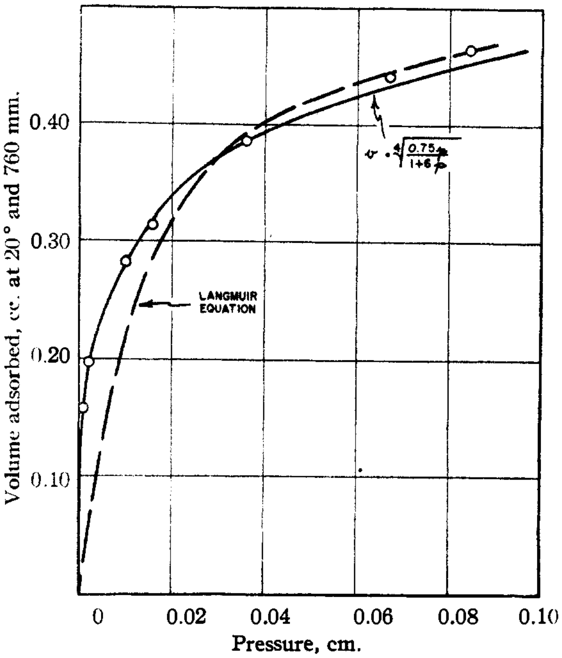

Fig. 11.—Adsorption of nitrogen on reduced surface of Sample 3. Circles represent the observations; the dashed line is derived by means of the Langmuir equation, fitted to the data over the higher range of pressure; the solid line represents equation (19) fitted to the observations.

Significance of Exponent n.—The exponent n in these several equations can be demonstrated to be a measure of the departure of the behavior of the sorbed film from that of an ideal two-dimensional gas. Thus, Innes and Rowley[25] have shown that, if the adsorption equation is known, the equation of state of the sorbed gas can be calculated by a modified form of the Gibbs adsorption equation, specifically

$$m_1 \frac{d(RT \ln p_1)}{dm_1} = A_s \frac{dF}{dm_1} \tag{21}$$

in which F is the spreading force (more strictly the two dimensional pressure exerted against a theoretical barrier) of the film, A_s is the total surface area, and m_1 is the number of moles of gas sorbed at pressure p_1. By means of this relation they have also demonstrated that if the adsorption isotherm is linear, that is, if $v = ap$ (or $n = 1$), the sorbed film is an ideal two-dimensional gas, in which case the equation of state may be written $FA = kT$, where A is the cross-sectional area occupied by a single molecule and k is the

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(21) Barrer, *Proc. Roy. Soc.* (London), **A161**, 476 (1937).

(22) Wilkins, *ibid.*, **A164**, 510 (1938).

(23) Zeise, *Z. physik. Chem.*, **136**, 385 (1928).

(24) Müller and Schwabe, *Z. Elektrochem.*, **35**, 165 (1929).

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

Boltzmann constant. If instead of a linear isotherm, one uses equation (16), expressed in terms of moles, that is

$$p_1 = bm_1^n \qquad (22)$$

where b is a constant, then

$$\mathrm{d} \ln p_1/\mathrm{d}m_1 = n/m_1 \qquad (23)$$

and

$$A_s \mathrm{d}F/\mathrm{d}m_1 = nRT \qquad (24)$$

or

$$FA_s = nm_1RT \qquad (25)$$

Expressing equation (25) in terms of area occupied per molecule

$$FA = nkT\ \text{[26]} \qquad (26)$$

which shows that if the adsorption isotherm is represented by equation (16), the two-dimensional pressure for a given value of A is n times as great as for an ideal two-dimensional gas.

This interpretation of the significance of n makes it possible, in some special cases, to estimate the value of n, or to predict how it may vary. For example, since the value of n characterizes the departure of the behavior of the sorbed film from that of an ideal two-dimensional gas, it should, as a first approximation, be the same for a given gas at a given temperature on surfaces of the same type, as for instance smooth metallic surfaces. This conclusion is supported by Wilkins'[27] data for the sorption of argon and nitrogen at low pressures on platinum foil at −183° which fit equation (16) satisfactorily and which at the same temperature yield a value of n of approximately 3 and 4, respectively, in agreement with the value of n derived from our measurements on the sorption of these gases on smooth iron. Moreover, since the deviation from ideality in the sorbed film should decrease as the temperature is increased, the value of n should for all systems approach unity at the higher temperatures; stated in other terms, deviation from the Langmuir equation should be most marked for a gas or vapor which deviates widely from ideal behavior and should, therefore, become more evident as the temperature of the system is decreased toward the critical temperature of the adsorbate. That this is in fact the case is amply confirmed by evidence available in the literature. To mention but two examples, Wilkins' measurements on the sorption of argon on platinum[27] show that the lower the temperature, the greater the deviation from the Langmuir isotherm, and Titoff's[28] measurements of the sorption of vapors on charcoal show clearly that the value of n approaches unity at the higher temperature, Table VI.

On the basis of this interpretation of the significance of n, it is possible to derive equation (19) by a reasonable modification of the postulates which Langmuir used to derive equation (17). Specifically, he assumed: (1) that the rate of condensation of atoms on the surface is equal $\alpha\mu\theta$, where μ is the number of molecules striking the surface in unit time, θ is the fraction of the surface still uncovered; and (2) that the rate of evaporation of adsorbed molecules is equal to $\nu\theta_1$, where ν is the rate of evaporation when the surface is covered by a complete monolayer and θ_1 is the fraction of the surface covered. The fact that at low pressures, that is, when θ is small, the observed adsorption is greater than that derived by extrapolation of the data at higher pressures indicates that the Langmuir postulates yield a rate of condensation which is too small, or a rate of evaporation which is too large, or, more probably, both. The general validity of the postulate that the rate of evaporation is a linear function of θ_1 is extremely doubtful in view of Becker's measurements of the rate of evaporation of cesium atoms from tungsten, which show that the rate varies exponentially[29] with θ_1; hence, if ν is the rate where $\theta_1 = 1$, the rate when $\theta_1 = 0.5$ should be much less than the value of 0.5 ν calculated on the basis of the Langmuir postulate, and this is in the direction of the observed deviations.

TABLE VI

Values of the exponent n in the parabolic isotherm for the sorption of different gases on charcoal at different temperatures (derived from the data of Titoff).

Temp., °C.	Gas		
	N_2	CO_2	NH
151.5	1.0	1.1	...
80	1.1	1.4	1.3
30	1.1	2.0	1.7
0	1.2	2.7	3.3
−79	2.2	11.6	...

In place of Langmuir's postulate that the rate of evaporation varies linearly with θ_1, it is assumed, as a second approximation, that the rate varies as θ_1^n, where n is the exponent in equation (19), that is, the rate is assumed to be a function not only of the fraction of the surface covered but also of the strength of the intermolecular forces within the film. On this basis, if ν be the rate of evaporation where $\theta_1 = 1$, the rate for a lesser coverage is $\nu\theta_1^n$, a variation which for $n = 1$, that is, for an ideal two-dimensional film, reduces to the linear variation assumed by Langmuir, but which, for a value of n greater than unity, approximates the type of variation observed experimentally by Becker.

The rate of condensation is taken as proportional to the rate at which molecules strike the surface and to the fraction of those impinging which condense. The rate at which molecules strike the surface is proportional to the pressure and it is assumed that the fraction which condenses varies with the fraction of the surface covered and with the value of n, specifically, it is taken as proportional to $(1 - \theta_1^n)$, on which basis the rate of condensation is equal to $\alpha p(1 - \theta_1^n)$ where α is a proportionality constant. This result is admittedly somewhat arbitrary but never-

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(26) If A is expressed in sq. Å. and F in dynes/cm. $FA = 1.372\ nT$.

(27) Wilkins, *Proc. Roy. Soc.* (London), **A164**, 510 (1938).

(28) Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

(29) J. A. Becker, *Trans. Am. Electrochem. Soc.*, **55**, 153 (1929).

theless meets two of the ends desired: namely, for a film which is an ideal two-dimensional gas, that is, one for which $n = 1$, this rate reduces to $\alpha p\theta$, where θ is the fraction of the surface not covered, which is the rate of condensation postulated by Langmuir; for a value of n greater than unity this variation is in accord with the general principle that the rate of condensation is initially high but falls off rapidly with increasing fraction of the surface covered.

Since at equilibrium the rate of condensation must equal the rate of evaporation

$$\alpha p(1 - \theta_1{}^n) = \nu\theta_1{}^n \qquad (27)$$

whence

$$\theta_1 = \frac{v}{v_s} = \sqrt[n]{\frac{\alpha p/\nu}{1 + \alpha p\nu}} \qquad (28)$$

which is identical with equation (19).

Force–Area Curves.—Two methods, both based on Gibbs' adsorption equation, have been considered for deriving the force–area curve of a sorbed film from the adsorption isotherms. The first, that of Innes and Rowley,[30] depends upon the relation

$$FA = v_1RT + RT\int_{p/v \text{ as } v \to 0}^{p_1/v_1} v\mathrm{d}\ln(p/v) \qquad (29)$$

in which F is the surface pressure in dyne/cm., A is the area of the absorbing surface and v and v_1 are, respectively, the volume of gas adsorbed at pressure p and p_1. The integration can be carried out mathematically if the variation of v with p can be represented satisfactorily, or it can be carried out graphically, which is in general more convenient. The second method was devised by Palmer[31] on the assumption that the logarithm of φ, the adsorption potential, varies linearly with the volume sorbed, a postulate which in many instances is valid over a fairly wide range of pressure.

These two methods yield significantly different results, as has been pointed out in an earlier paper.[32] The cause of this difference is not certain but is probably the extrapolation to $v = 0$ which must be made with either method and, on this basis, the Innes and Rowley method is to be preferred. For the Palmer method assumes that log φ is linear with v down to $v = 0$, which cannot be so if the behavior of the sorbed film is to approach that of an ideal film, as it should. Moreover, it has already been demonstrated that if the isotherm is represented by equation (19) the force–area curve should lie above that for the ideal two-dimensional gas. For these several reasons we report here only force–area curves derived by the method of Innes and Rowley.

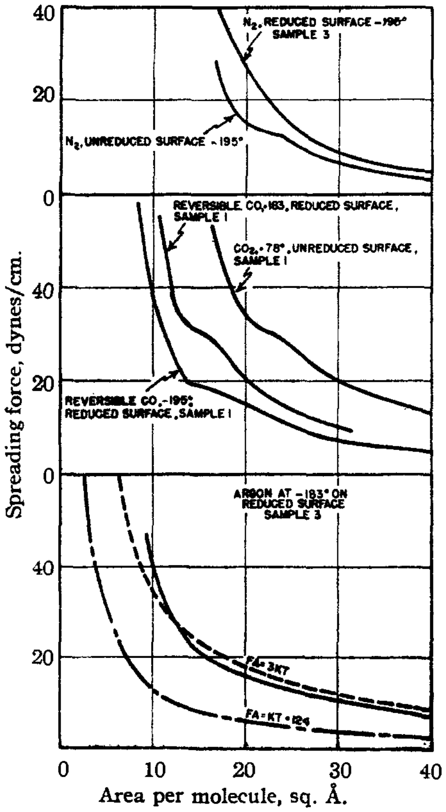

Fig. 12.—Force–area curves for sorbed films derived by the method of Innes and Rowley: (a) argon at −183° on reduced surface of Sample 3; (b) CO and CO_2 on Sample 1; N_2 at −195° on Sample 3.

Typical force–area curves are shown in Fig. 12, the lowest section of which shows the curve for argon sorbed at −183° on a reduced surface of Sample 3. These data were selected because the specific surface of this sample appears to be very nearly unity and because the isotherm is closely represented, over most of the range studied, by the relation $v = ap^{1/n}$. It is evident that over the whole range the curve derived by means of equation (29) lies close to that representing the equation $FA = 3\,kt$, as it should, on the basis of equation (26). The curve is also smooth over the whole range of measurement. Similar smooth curves were obtained for the sorption of argon or nitrogen on all the reduced surfaces at both −183 and −195°, another example being the curve for nitrogen sorbed at −195° on a reduced surface of Sample 3, shown in the top section of Fig. 12.

In a number of instances, however, the force–area curve was not smooth but showed a plateau, as is illustrated by several typical curves shown in the middle and upper sections of Fig. 12. These curves are derived from a curve of ln (p/v) *vs.* v based on the experimental observations, not on the smooth isotherms shown in Figs. 2 to 6. These curves are entirely analogous to those for an insoluble liquid film on water,[33] and indicate the existence of phase transformations in the sorbed film. The two curves in the middle sec-

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

[31] Palmer, *Proc. Roy. Soc.* (London), **A160**, 254 (1941).

[32] Innes and Rowley, *loc. cit.*; Armbruster, This Journal, **64**, 2545 (1942).

[33] See, for example, the curves for octadecanol given by Harkins and Copeland, *J. Chem. Physics*, **10**, 272 (1942).

tion of Fig. 12 for carbon monoxide sorbed at −183 and −195° also show that with increasing temperature the plateau appears at a higher surface pressure and at a slightly lower value of *A*, as is usually observed for a monomolecular film on water.

These plateaus appear only when some molecules are held to the surface very strongly, either by physical or chemical forces; for instance, in the physical sorption of carbon monoxide, the surface already has on it some molecules which are chemisorbed. Another illustration is given in the top section of Fig. 12, which shows the sorption of nitrogen at −195° on the unreduced and reduced surface of Sample 3. The curve for the reduced surface, in which adsorption is completely reversible, is smooth whereas the curve for the unreduced surface, from which some nitrogen molecules cannot be removed by pumping at temperature, shows a plateau, which suggests that the molecules which are strongly held are attached to definite sites whereas those which can be desorbed by reducing the pressure are not. As the concentration of mobile molecules increases their mobility is diminished because of the interference by what is equivalent to a lattice of rigidly held molecules so that the film condenses to a less fluid structure and undergoes a phase transformation.

Summary

The adsorption on cold-rolled steel of argon, neon, hydrogen, nitrogen, carbon monoxide and carbon dioxide has been determined at 20, −78, −183 and −195° and at pressures up to 0.1 cm. Measurements were made first on a degreased and outgassed surface and subsequently on the same surface after reduction by hydrogen. In some cases the surface had to be conditioned a number of times before adsorption was reproducible within the error of measurement. Neither hydrogen nor neon was measurably adsorbed on either surface within the range of temperature or pressure investigated. A monomolecular layer of physically-held nitrogen, argon or carbon monoxide was sorbed on the unreduced surface at −183° but in each case approximately 15% of the total volume of gas sorbed was held so strongly that it could not be desorbed by reducing the pressure at temperature. A similar monolayer of physically-held nitrogen and argon was adsorbed on the reduced surface but could be entirely desorbed by evacuation of the system at temperature. On this same surface a complete monolayer of physically-held carbon monoxide was adsorbed along with a partial layer of chemisorbed molecules.

The isotherms appear to be of the saturation type but it is believed that they are in fact merely the low pressure section of an isotherm of the sigmoid type characteristic of adsorption on iron catalysts.

The ordinary analog of the Clausius–Clapeyron equation does not in principle yield a correct value for the heat of adsorption. The Emmett–Brunauer–Teller equation appears to be preferable. The heat of adsorption calculated by this method is, for all the physically-held sorption, approximately 3000 cal./mole. The heat of adsorption is influenced more by the physical nature of the surface than by the chemical nature of the gas.

The isotherms are represented in the low pressure range by the parabolic or Freundlich, equation and in the high pressure range by the Langmuir relation. A combination of these equations

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

represents most of our results over the whole range of pressure. The exponent *n* is interpreted as a measure of the departure of the behavior of sorbed film from that of an ideal two-dimensional gas. The value of *n* decreases with increasing temperature; when it is unity, the film is ideal and the isotherm equation reduces to the Langmuir relation.

Force–area curves for the sorbed films show that when some of the gas is held to the surface very strongly phase-transformations similar to those occurring in monomolecular films on water may take place.

The surface of cold-rolled steel is remarkably flat, the specific surface being not more than 4 times the geometric area of the steel.

KEARNY, N. J. RECEIVED JULY 15, 1943