

shaken up with water, allowed to settle and a drop of the top of the aqueous suspension applied to the collodion film and dried. The remarkable dispersion of particles is shown in Fig. 2 (magnification 62,000 X). A fairly uniform distribution of single primary particles some of which are only 100 Å. in diameter, appears in the background. These particles are narrower in one dimension than the other and probably lie flat as still thinner flakes. As might be expected otherwise, these are too small to show definite crystalline faces. Some small flocs representing the first stages of agglomeration of the individual particles appear in the center of the photograph. Finally, there is a distribution of larger, darker and more nearly spherical particles which must represent larger primary particles of the order of several hundred Ångström units in size.

This proof of a typical colloidal structure, therefore, confirms the interpretation of the broad X-ray interferences by means of which calculations can be made of a particle size of the order of 100 Å., or somewhat less. It is not necessary to claim absolute crystalline perfections of these extremely small particles. That some lattice organization is present is indicated by the number of diffraction halos on the patterns—several more than for carbon black which is known to be built up into particles from crystalline layers which are stacked at random like a twisted deck of cards.

#### Summary

Molybdenum blue has been prepared by a number of new methods and purified carefully.

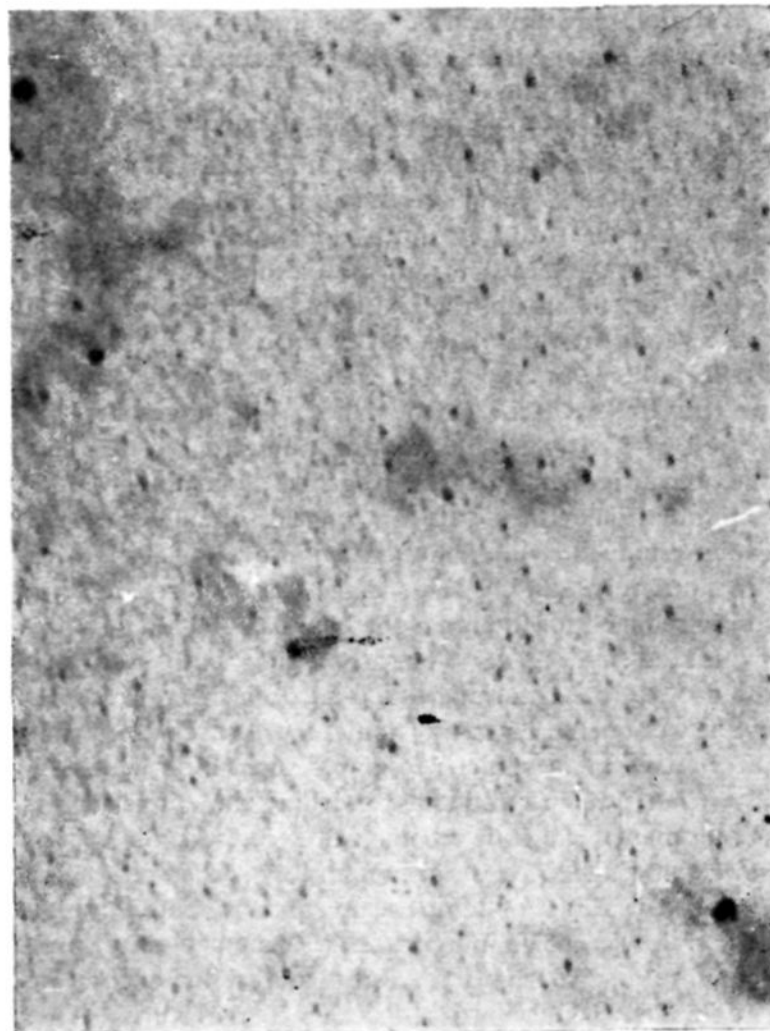


Fig. 2.—Electron photomicrograph of molybdenum blue (62,000 X).

Its composition may be represented by the empirical formula,  $\text{Mo}_8\text{O}_{23}\cdot x\text{H}_2\text{O}$ . Samples prepared under the prescribed conditions yield identical and characteristic diffraction patterns. Electron photomicrographs confirm the colloidal nature of molybdenum blue.

URBANA, ILLINOIS

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

## The Adsorption of Gases at Low Temperature and Pressure on Smooth Silver

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This paper reports the results of measurements of the adsorption of hydrogen, nitrogen, argon, carbon monoxide, carbon dioxide and oxygen at pressures up to 0.1 cm. on a substantially plane, reduced surface of silver over the temperature range  $-195$  to  $20^\circ$ . The investigation was undertaken to determine the nature and properties of the smooth surface of a typical, pure, homogeneous metal as a first step toward a better understanding of the characteristics of the surface of a

less pure or less homogeneous metal, such as steel. Silver was selected chiefly because it is readily obtainable in a high degree of purity in the form of foil, a form which provides a large, smooth and reproducible surface; it is also relatively inert so that, aside from the sorption of oxygen, there should, in the range of experimental conditions covered, be no complex chemisorption which might confuse interpretation of the results.

**Materials and Apparatus.**—The quality of the several gases used, the apparatus, and the experimental procedure already have been described.<sup>1</sup>

**Silver Surface.**—The silver used (99.98+ % Ag) was foil 0.021 cm. thick, cut into strips,  $1.8 \times 11.0$  cm. to form a bundle weighing 846.5 g. and having a total geometric area of 8002 sq. cm. X-Ray diffraction patterns of the foil, obtained by D. S. Miller, indicated a fairly high degree of preferred orientation of the grains on the surface of the foil. The crystallographic plane in the surface was not one of simple indices, but appeared to be one which made an angle of  $15^\circ$  with the (110) plane. The strips were degreased with absolute alcohol and anhydrous ether, suitable precautions being taken to guard against subsequent contamination. Since oxygen sorbed on silver is not readily removed by baking in vacuum even at a temperature as high as  $300^\circ$ ,<sup>2,3</sup> the surface was, before each run, freshly reduced for four to eight hours at  $400^\circ$  in a stream of purified hydrogen. The adsorption bulb was then sealed off in an atmosphere of hydrogen after which the sample was outgassed at  $450^\circ$  under a pressure of  $10^{-6}$  mm. This pretreatment sufficed to give a surface on which the adsorption was reproducible within the precision of measurement, which is about 0.001 cc. As direct test showed that hydrogen is not measurably sorbed on smooth silver in the range of temperature and pressure covered, the sample was cooled in hydrogen to hasten equalization of temperature. At least two, and usually four, check runs were made with each gas at each temperature. After

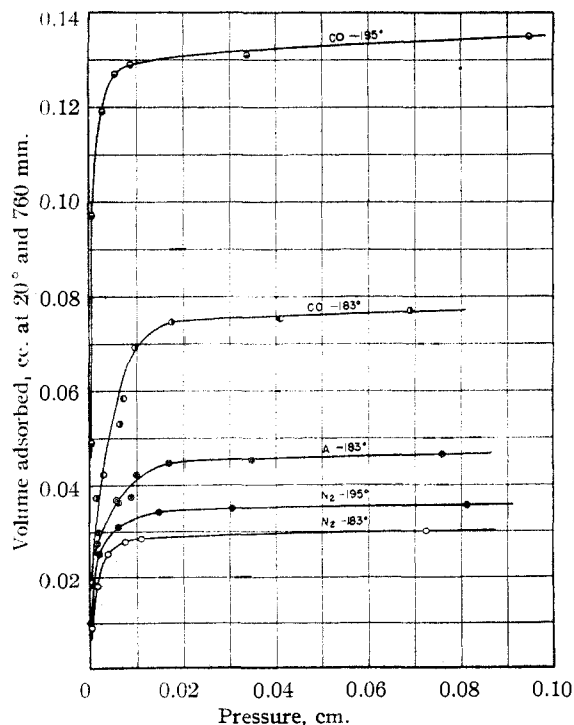


Fig. 1.—Isotherms for CO, A and  $N_2$  at  $-183$  and  $-195^\circ$ .

- (1) Armbruster and Austin, *THIS JOURNAL*, **60**, 467 (1938); **61**, 1117 (1939).
- (2) Benton and Elgin, *ibid.*, **48**, 3027 (1926).
- (3) Benton and Drake, *ibid.*, **56**, 255 (1934).

several measurements the surface of the silver developed an etched appearance, probably as a result of evaporation but this was not accompanied by any appreciable increase of surface area since the sorption was not measurably altered. The Pyrex bulb containing the silver also developed a slight brown discoloration, indicating probable contamination by silver.

**Results.**—Hydrogen was not measurably sorbed at any temperature investigated; argon, nitrogen and carbon monoxide were sorbed at  $-195^\circ$  and  $-183^\circ$  but not at  $-78^\circ$  or  $20^\circ$ . Carbon dioxide was not sorbed at  $20^\circ$ , but at  $-78^\circ$  was sorbed to the slight extent of 6 cu. mm. at a pressure of 0.02 cm. Typical isotherms for nitrogen, argon and carbon monoxide at  $-195^\circ$  and  $-183^\circ$ , selected as representative from among the several concordant runs made with each gas, are given in Fig. 1. For each gas, adsorption was instantaneous and completely reversible in the sense that measurements on desorption agreed with those for adsorption, and a surface pumped out at temperature gave results identical with those obtained on a baked out surface.

The sorption of oxygen is illustrated by the typical isotherms presented in Fig. 2. At  $-195^\circ$  and  $-183^\circ$  the adsorption was fairly rapid, being substantially complete within a few minutes.

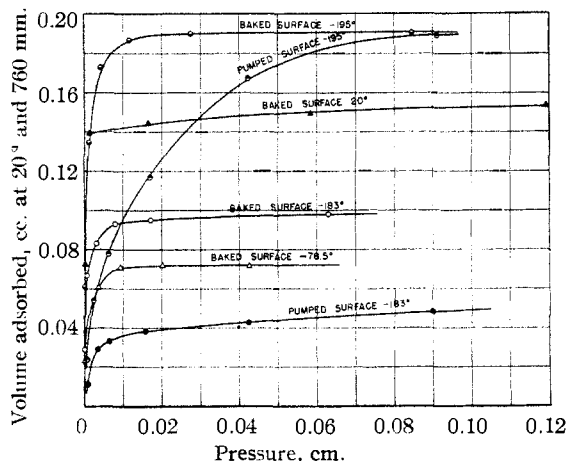


Fig. 2.—Isotherms for oxygen at  $-195$ ,  $-183$ ,  $-78.5$  and  $20^\circ$ .

The adsorption was not, however, entirely reversible since the amount of gas sorbed was not the same on a surface which had been pumped out at temperature as on one which had been freshly reduced and baked out. Thus, at  $-183^\circ$ , the sorption on the pumped out surface was markedly less than on the surface which had been reduced and baked, whereas at  $-195^\circ$  it was less in the lower range of pressure but probably was greater

at higher pressures. At  $-78^\circ$  and  $20^\circ$ , on the other hand, the rate of adsorption was relatively slow; the first portion of oxygen admitted came to equilibrium only after an hour or more, as is illustrated by the typical rate curves shown in Fig. 3; subsequent additions attained equilibrium more rapidly. At these higher temperatures, the volume of oxygen sorbed was, over most of the range investigated, virtually independent of pressure. Moreover, at  $-78^\circ$  and above, the sorbed oxygen could not be removed by pumping at temperature but was taken off by reduction and baking in vacuum at  $400^\circ$  or higher.

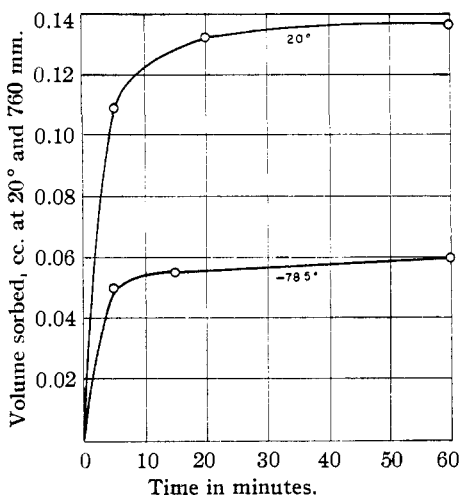


Fig. 3.—Rate of initial adsorption of oxygen at  $-78.5$  and  $20^\circ$ .

Discussion of Results

**Nature of the Adsorption.**—The fact that nitrogen, argon, and carbon monoxide are adsorbed instantaneously and reversibly, together with the fact that the volume sorbed at a given pressure increases with decreasing temperature, indicates that the adsorption is of the van der Waals type. The sorption of oxygen at  $-195^\circ$  and  $-183^\circ$  is, in part, likewise of the van der Waals type but at least some portion of the sorbed film appears to be held to the surface more tightly than would be expected from the action of purely physical forces. Thus, at  $-183^\circ$ , the sorption on the pumped out surface is less than on the freshly reduced and baked surface, which suggests that all the sorbed oxygen was not removed by evacuation. At  $-78^\circ$  and  $20^\circ$ , the rate of adsorption of oxygen is slow and the sorbed gas is not removed from the surface by evacuation of the system, indicating that the sorption is of the activated type, a conclusion which is confirmed by the

fact that the volume of gas sorbed at a given pressure increases with increasing temperature, as is illustrated by the typical isobar shown in Fig. 4.

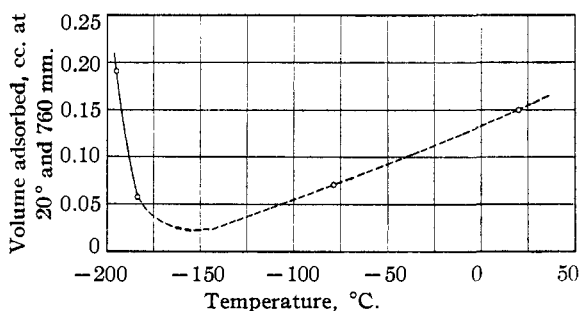


Fig. 4.—Isobar for oxygen at  $P = 0.05$  cm.

**Form of the Isotherms.**—Since the curves in Figs. 1 and 2 appear to be of the Langmuir type, representative isotherms for the several gases have been replotted in Fig. 5 as  $p/v$  against  $p$ , a method which yields a straight line if the observations conform to either the Langmuir equation<sup>4</sup> or to the formally identical equation for monomolecular adsorption developed by Bru-

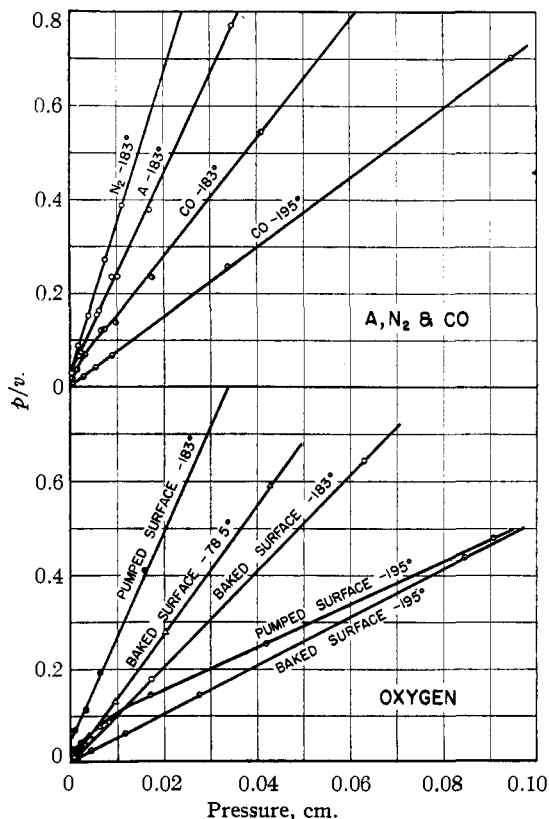


Fig. 5.—Isotherms plotted as  $p/v$  against  $p$ . Upper section shows data for  $N_2$ , A and CO; lower section shows data for  $O_2$ .

(4) Langmuir, THIS JOURNAL, 40, 1361 (1918).

nauer, Emmett and Teller.<sup>5</sup> It is evident from this diagram that a linear relation is obtained except at the lowest pressures, hence, over virtually the entire range of pressure covered, the data are represented with satisfactory accuracy by either of these relations.<sup>6</sup> The greatest deviation from a straight line is in the isotherm for oxygen at  $-195^\circ$  at pressures up to 0.010 cm.; another, less marked, departure occurs in the same range of pressure in the isotherm for carbon monoxide at  $-183^\circ$ .

In Fig. 6 the isotherms for  $-183^\circ$  are plotted in the form of  $v$ , the volume (reduced to 1 atm. and  $20^\circ$ ) sorbed at pressure  $p$ , against the logarithm of the adsorption potential  $\phi$ ,<sup>7</sup> as suggested by Palmer and Clark.<sup>8</sup> This method of plotting is of interest in connection with the calculation of the force-area curve, since, if a straight line is obtained, as it frequently is,<sup>8,9</sup> the spreading force can be calculated by means of an equation derived by Palmer.<sup>10</sup>

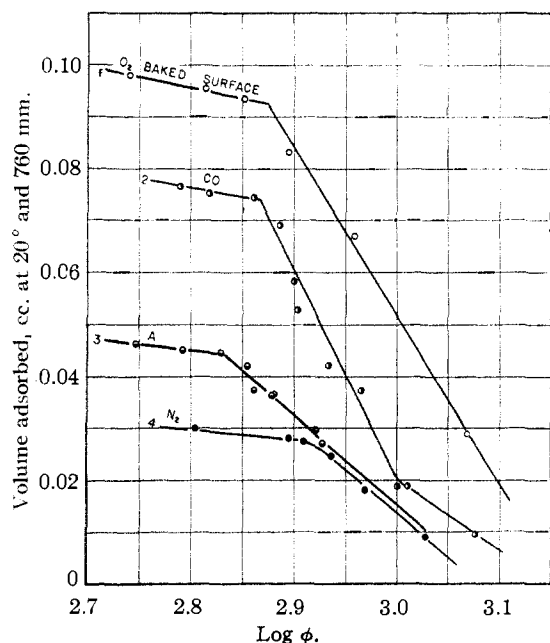


Fig. 6.—Isotherms at  $-183^\circ$  plotted as volume sorbed against  $\log \phi$ .

All the isotherms in Fig. 6, except that for car-

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

(6) This does not preclude the possibility that at higher pressures the isotherms might curve upwards to become convex to the pressure axis.

(7) The adsorption potential  $\phi$  is equal to  $RT \log p_0/p$ , where  $p_0$  is the vapor pressure of the adsorbate in the liquid phase at temperature  $T$ .

(8) Palmer and Clark, *Proc. Roy. Soc. (London)*, **A149**, 360 (1935).

(9) Armbruster and Austin, *THIS JOURNAL*, **60**, 474 (1938).

(10) Palmer, *Proc. Roy. Soc. (London)*, **A160**, 254 (1937).

bon monoxide, consist of two straight lines which intersect at a value of  $v$  approximately equal to that at which the corresponding curve in Figure 1 flattens off. The isotherm for carbon monoxide consists of three sections, two of which intersect at a value of  $v$  which, just as with the other gases, corresponds approximately to the value at which the isotherm in Fig. 1 flattens off; the other intersection occurs in the range of higher adsorption potentials, that is, at lower pressure, at a value of  $v$  which corresponds fairly well with the pressure at which deviation from linearity becomes evident in the isotherm shown in Fig. 5. The isotherms for the several gases at  $-195^\circ$  fall so close to the corresponding curves for  $-183^\circ$  that they have not been included in Fig. 6.

**Fraction of Surface Covered.**—The limiting volume,  $V_s$ ,<sup>11</sup> for each gas at each temperature, as derived from the slope of the  $p/v-p$  isotherm, is given in Table I. On the assumptions that the geometric area of the foil represents the true area of the surface, and that the mean cross-section of a sorbed molecule is the same as that of a molecule in the liquid, the fraction of the surface covered, in the pressure range in which the isotherm is virtually horizontal, can be estimated from the value of  $V_s$ . The coverage derived on this basis is shown in the last column of Table I. In only one instance, the sorption of oxygen on a pumped out surface at  $-195^\circ$ , is the coverage substantially complete; in every other, only from

TABLE I  
 $V_s$ , VOLUME OF GAS SORBED AND FRACTION OF SURFACE COVERED AT SATURATION AS CALCULATED BY MEANS OF THE LANGMUIR EQUATION

Gas (surface)	Temp., $^\circ\text{C}.$	$V_s$ , cc. at $20^\circ$ and 760 mm.	Molecules sorbed per sq. cm. as derived from $V_s$	Fraction of surface covered
A	-183	0.0486	$0.153 \times 10^{15}$	0.20
$\text{N}_2$	-183	.0305	.096	.15
$\text{N}_2$	-195	.0355	.112	.17
CO	-183	.0769	.242	.37
CO	-195	.1360	.428	.65
$\text{O}_2$ (Baked)	-78.5	.0729	.230	.29
$\text{O}_2$ (Baked)	-183	.0980	.309	.40
$\text{O}_2$ (Pumped)	-183	.0450	.142	.18
$\text{O}_2$ (Baked)	-195	.1904	.560	.78
$\text{O}_2$ (Pumped)	-195	.2295	.722	.94

(11) This is the volume which investigators of adsorption at low pressure on plane surfaces have commonly called the maximum volume sorbed, or the saturation maximum, and have designated  $b$ ,  $c_1$ ,  $x_s$ , or  $v_m$ . (cf. Langmuir, ref. 4; Bawn, *THIS JOURNAL*, **54**, 81 (1932); Wilkins, *Proc. Roy. Soc. (London)*, **A164**, 510 (1938)). It is to be distinguished from the volume  $v_m$  defined by Brunauer, Emmett and Teller (ref. 5) as the volume required to form a close-packed monolayer.

one-third to two-thirds of the surface is covered. Although it is customary to calculate coverage of the surface in this manner, it is entirely permissible, and in some ways preferable, to interpret the apparent saturation of the surface in terms of effective cross-section of the sorbed molecules, that is, in terms of the density of packing in the sorbed film. On this basis, the effective cross-section derived from  $V_s$  (Table I) is considerably greater than that of a molecule in a three-dimensional condensed phase.

Apparent saturation of the surface, as indicated by the flattening of the isotherm, at such a relatively low pressure is in marked contrast to the behavior of metal powders for which there is no comparable flattening even at a much higher pressure. Moreover, the relatively small estimated coverage of the smooth surface in the range of apparent saturation appears to be characteristic of a number of metals. For example, Langmuir<sup>4</sup> reports saturation of a surface of platinum foil with hydrogen, carbon monoxide and oxygen at a coverage not exceeding a few per cent. More recently, Wilkins<sup>12</sup> in more extensive measurements on platinum foil, observed saturation at  $-183^\circ$  by argon, nitrogen and oxygen with a coverage of 34, 30 and 42%, respectively. With argon at  $-195^\circ$  the surface appeared to be completely covered at saturation by a monomolecular layer. Wilkins found further that when his data were plotted as  $p/v$  against  $p$ , there were marked deviations from linearity at low pressures, the departures becoming more marked the lower the temperature. Finally, Smittenberg<sup>13</sup> reports that on a smooth surface of nickel at  $-183^\circ$  the greatest adsorption of hydrogen or argon corresponded to a coverage which does not exceed 2 and 8%, respectively. It is evident, therefore, that the observed adsorption on the silver surface is typical of that on a smooth metallic surface.

The sorption of oxygen at  $-195^\circ$  has another feature worthy of special mention in that  $V_s$  is greater for the pumped out surface than for a surface which has been freshly reduced and baked. This difference is reflected in a difference in the form of the isotherms (Figs. 2 and 5) which was confirmed by repeated measurements. The cause of the difference is not apparent for it is difficult to visualize a mechanism by which merely pumping the gas from the system should so con-

dition the surface that it can subsequently adsorb a significantly greater volume of oxygen. The observations suggest, however, that at  $-195^\circ$ , as at  $-183^\circ$ , all the sorbed oxygen is not removed by pumping, and that the molecules remaining so alter the surface that it becomes virtually an oxide surface capable of forming a complete monolayer of the van der Waals type of adsorption. In line with this difference it should be noted that the calculated heat of sorption, as derived in a later section, is 2800 cal. for the pumped out surface, which is significantly less than the value 3400 cal. for the surface which has been reduced and baked.

**Variation of  $V_s$  with Temperature.**—As indicated in Table I,  $V_s$  increases markedly with decreasing temperature, a variation seemingly characteristic of adsorption in which there is an apparent saturation of the surface. Wilkins and Ward<sup>14</sup> have suggested that this temperature coefficient is due to some factor which alters the number of molecules which can be packed into the adsorbed phase, the volume of which is independent of temperature; that is, the temperature coefficient of  $V_s$  corresponds to the expansion coefficient of a gas at constant pressure. On this basis,  $dV_s/V_s dT$  should have about the same value as  $dV/V dT$  for an ideal gas, which is equal to  $1/T$ . The value of  $dV_s/V_s dT$  derived from the present measurements (Table II) is, for nitrogen, approximately that of an ideal gas but for carbon monoxide and oxygen it is very much greater, which suggests that the molecular interactions in the sorbed film are much greater for carbon monoxide and oxygen than for nitrogen. The value derived for nitrogen also agrees fairly well with that derived from Langmuir's measurements on mica. Thus, if the value of  $dV_s/V_s dT$  is taken as 0.0145 at  $-150^\circ$  and varies about 2% per degree, as given by Langmuir, the difference in  $V_s$  for nitrogen at  $-183^\circ$  and  $-195^\circ$  should be 7 cu. mm., which is in excellent agreement with the observed value of 6 cu. mm.

TABLE II  
VALUES OF  $-dV_s/V_s dT$

Gas	$-dV_s/V_s dT$
N <sub>2</sub>	0.0130
CO	.034
O <sub>2</sub> (total)	.040
Ideal gas (1/T)	.012

**Heat of Sorption.**—Of the several methods for calculating heat of sorption, that described by

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

(13) Smittenberg, *Rec. trav. chim.*, **53**, 1065 (1934).

(14) Wilkins and Ward, *Z. physik. Chem.*, **144**, 259 (1929).

Brunauer, Emmett and Teller<sup>5</sup> appears to be the most reliable. This method, which yields the average heat of sorption, when applied to the present data for  $-195^{\circ}$  and  $-183^{\circ}$ , yields the heat effects shown in Table III, which includes, for comparison, the heat of liquefaction of each gas. In every case, the heat of adsorption lies in the range 2800 to 3600 calories and is about twice the heat of liquefaction, again indicating that the sorption is chiefly of the van der Waals type. The heats of sorption on silver are also virtually identical with those for adsorption of the same gases on platinum foil at  $-183^{\circ}$  (last column Table III) as calculated by the same method from Wilkins' measurements.<sup>12</sup>

TABLE III

COMPARISON OF THE CALCULATED HEAT OF SORPTION ON SILVER FOIL WITH THE HEAT OF LIQUEFACTION AND WITH THE CALCULATED HEAT OF SORPTION ON PLATINUM FOIL

Gas (surface)	Temp., °C.	Heat of adsorption, (cal./mole)		Heat of liquefaction at nominal boiling point, cal./mole
		Silver	Platinum <sup>b</sup>	
A	-183	3500	3280	1505
N <sub>2</sub>	-183	3600	3385	1330
N <sub>2</sub>	-195	3050	3244 <sup>a</sup>	1330
CO	-183	3600		1410
CO	-195	3270		1410
O <sub>2</sub> (Baked)	-183	3700	4302	1630
O <sub>2</sub> (Pumped)	-183	3530		1630
O <sub>2</sub> (Baked)	-195	3400		1630
O <sub>2</sub> (Pumped)	-195	2800		1630

<sup>a</sup> Temperature  $-189.5^{\circ}$ . <sup>b</sup> Calculated from data of Wilkins.

**Force-Area Curves.**—Two methods, both based upon the Gibbs adsorption equation, are available for deriving the force-area curve of a sorbed film. The first was devised by Palmer,<sup>15</sup> who suggests that if the observations yield a straight line when  $\log \phi$  is plotted against  $v$  (Fig. 6), that is, if the potential can be represented as a function of  $v$  by the relation  $\phi = \phi_0 e^{-sv}$ , then the spreading force,  $F$ , of the film when volume  $v$  is adsorbed is given by

$$F = f\phi_0 e^{-sv}(v + 1/s) + I$$

where  $f$  is a constant for adjusting units,  $\phi_0$  is the extrapolated value of the adsorption potential at zero volume adsorbed,  $s$  is the slope of the  $\log \phi - v$  line, ( $d \log \phi / dv$ ), and  $I$  is an integration constant which is evaluated on the assumption that  $F$  is zero when  $v$  is zero. In applying this equation to adsorption data which yield a plot with two linear portions (Fig. 6), the value of the

integration constant of the section covering the range of higher volume sorbed has been adjusted so that the value of  $F$  agrees with that of the other linear section at the intersection. The value of  $A$ , the area occupied per molecule, corresponding to a given value of  $F$  is calculated by dividing the geometric area of the surface by the number of molecules contained in the volume of gas sorbed.

The force-area curves for the several gases at  $-183^{\circ}$ , derived on this basis, are shown in Figs. 7 and 8, which also include the force-area curve for an ideal two-dimensional gas at the same temperature, calculated by means of the relation  $FA = 1.372T$ . In every case the spreading force calculated by Palmer's method is less than that for an ideal gas in the range of relatively large values of  $A$  but is greater in the range of small values of  $A$ . The curves for argon and nitrogen are, as might be expected, very similar (Fig. 7). The curve for carbon monoxide falls very close to the ideal curve over the major part of the range covered. In the case of oxygen the deviation from ideality in the region of the larger values of  $A$  is more marked than in the case of any other gas at  $-183^{\circ}$ . The curve for oxygen on a pumped out surface has not been given since it lies very close to that for total oxygen.

The corresponding force-area curves for the several gases at  $-195^{\circ}$  have not been included. However, it may be said that these bear similar relation to the ideal curve at  $-195^{\circ}$  with two exceptions. The curve for carbon monoxide at  $-195^{\circ}$  falls more markedly below the ideal curve in the region of the larger values of  $A$ ; the curves for oxygen lie closer to the ideal curve, that for oxygen on a pumped out surface practically coinciding with it.

The resemblance of these curves to the corresponding  $P-V$  curve of a three-dimensional gas is striking, yet the data are not adequately represented by a two dimensional analog of van der Waals' equation of the form  $(F + C/A^2)(A - A_0) = kT$ , where  $C$  and  $A_0$  are constants. The deviations from this relation are, however, of the same kind as are obtained when the van der Waals' equation is applied to a three dimensional gas.

The force-area curves bear an even stronger resemblance to those for certain insoluble films on water. Thus, in a number of them there is a rather sudden break in the curve in the range of lower values of  $A$ , indicating a much more marked

(15) Palmer, *Proc. Roy. Soc. (London)*, **A160**, 254 (1937).

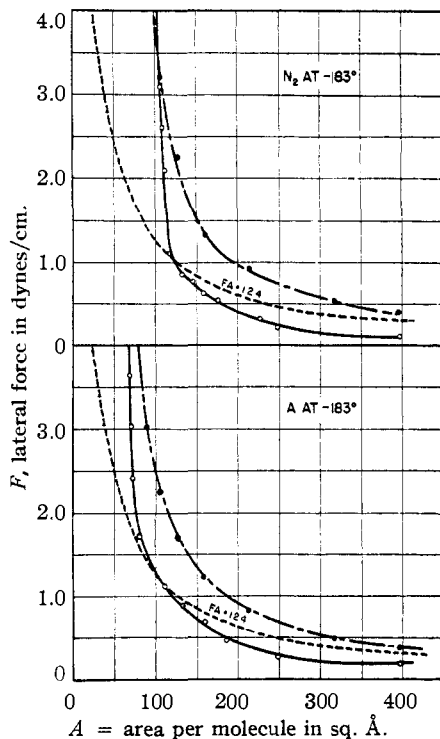


Fig. 7.—Variation of lateral force with surface area per molecule for  $N_2$  and A sorbed at  $-183^\circ$ . Full lines calculated by Palmer's method, dot-dash lines by method of Innes and Rowley. Dotted curve for an ideal two dimensional gas ( $FA = 1.372T$ ).

increase in spreading force with decrease in area. Too much emphasis should not be placed upon the significance of this break, however, since the occurrence of the break is in part probably a consequence of the assumption that the Palmer isotherm consists of two linear branches, that is, that there is, in effect a discontinuity on the isotherm. It is, nevertheless, interesting to compare the value of  $A$  obtained by extrapolating the steep part of the curve to  $F = 0$  with the area per molecule as calculated from  $v_s$ . This comparison is made in Table IV. For argon and nitrogen at  $-183^\circ$  and for carbon monoxide at  $-183$  and  $-195^\circ$ , the agreement is fairly good, but in the other cases the value of  $A$  obtained from the force-area curve is of the order of twice that calculated from  $v_s$ . This is the deviation which is to be expected, however, since the force-area curve indicates the area at which the virtual compressibility of the film becomes markedly less, whereas the other method gives the value in a much more highly compressed film. It should be noted that in every case the area per molecule is many times greater than the mean cross section of the molecule in liquid phase

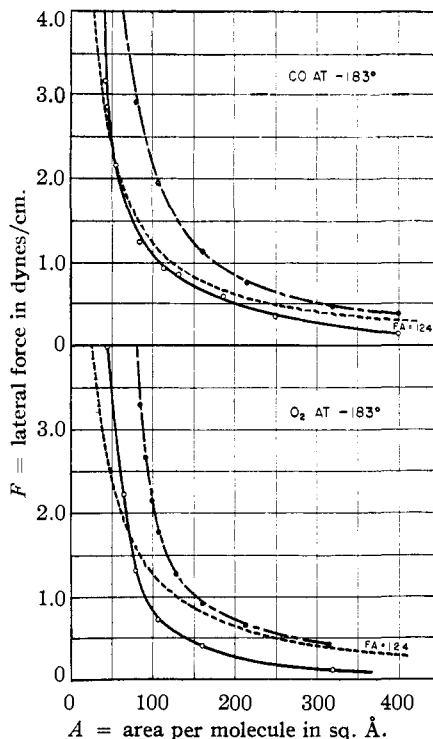


Fig. 8.—Variation of lateral force with surface area per molecule for CO and  $O_2$  (baked surface) at  $-183^\circ$ . (Curve for  $O_2$  on pumped out surface lies close to that for the baked surface.) Full lines calculated by Palmer's method, dot-dash curves by method of Innes and Rowley. Dotted curve is for an ideal two dimensional gas ( $FA = 1.372T$ ).

at this temperature; moreover, the area per molecule at saturation is less at  $-195^\circ$  than at  $-183^\circ$ .

TABLE IV  
COMPARISON OF CROSS-SECTIONAL AREA/MOLECULE FROM FORCE-AREA CURVE AND LANGMUIR'S ISOTHERM

Gas (surface)	Temp., $^\circ\text{C.}$	Area/molecule in sq. $\text{\AA.}$ at break in force-area curve	Area/molecule in sq. $\text{\AA.}$ at Langmuir saturation
A	$-183$	70	65.3
$N_2$	$-183$	128	104.1
$N_2$	$-195$	120	89.2
CO (Baked and pumped)	$-183$	44	41.3
	$-195$	27	23.4
$O_2$ (Baked)	$-183$	52	33.0
$O_2$ (Pumped)	$-183$	113	70.4
$O_2$ (Baked)	$-195$	37	17.9
$O_2$ (Pumped)	$-195$	25	13.9

The second method of calculating the force-area curve is a graphical one based on the following equation reported by Innes and Rowley<sup>16</sup>

$$FA = v_1 RT + RT \int_{p/v \text{ as } v \rightarrow 0}^{p_1/v_1} v \, d \ln \left( \frac{p}{v} \right)$$

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

in which  $F$  is the spreading force in dynes/cm., and  $v$  and  $v_1$  are the volumes of gas adsorbed at pressures  $p$  and  $p_1$ , respectively.<sup>17</sup> Hence, by plotting  $v$  against  $\ln(p/v)$  and measuring the area under the curve between the desired limits, the value of  $FA$  may be readily computed. The extrapolation involved in this method introduces some uncertainty since reliable values of  $v$  and of  $p/v$  are difficult to obtain experimentally as  $v$  approaches zero. The several force-area curves derived by this method are shown by the dash-dot lines in Figs. 7 and 8. Without exception they lie above the curve for an ideal two-dimensional gas and they do not show the sharp break evident in the curves derived by Palmer's method.

The curves derived by the Innes-Rowley method indicate the existence of large repulsive forces acting between the sorbed molecules over the entire range of sorption covered, whereas, the curves derived by the Palmer method indicate that attractive forces predominate in the range of small volume sorbed but that repulsive forces predominate when the volume sorbed approaches saturation. This difference in the two methods is not easy to explain but is probably due in part to the extrapolations necessary in each case.

**Comparison of Sorption of Oxygen on Foil and on Powder.**—The sorption of oxygen on two samples of finely-divided silver at  $-183^\circ$  and  $-78.5^\circ$ , and at pressures up to one atmosphere, has been measured by Benton and Drake<sup>18</sup> with results which, though in many respects similar to those obtained with silver foil, are in others significantly different. Thus, on the powder, as on the foil, the sorption at  $-183^\circ$  is chiefly of the van der Waals type with, however, an indication of a small amount of a somewhat stronger sorption characterized by a relatively slow rate of sorption for the initial additions of oxygen. At  $-78.5^\circ$ , the sorption is in each case chiefly of the activated type; moreover, at this temperature the isotherm is in each case of the saturation type in which the amount of oxygen adsorbed is substantially independent of pressure over virtually the entire range of pressure studied, that is, up to 0.1 cm. on the

foil and on the powder up to the dissociation pressure of silver oxide.

The chief point of difference is in the isotherms at  $-183^\circ$ . On the foil there is a flattening of the curve at a pressure of less than 0.01 cm. and at a volume of gas sorbed corresponding to only a fraction of a close-packed monolayer, with no appreciable further sorption up to a pressure of about 0.15 cm. In contrast, the isotherm for the powder gives no indication of flattening of the curve at low pressures, although the data for this range are not very satisfactory, but has the S-shape characteristic of adsorption which is multi-molecular at the higher pressures. On the basis that the beginning of the linear portion of the isotherm for the powder corresponds to the first appearance of a second layer, an assumption used to estimate the surface area of powders,<sup>19</sup> the first layer on the powder is complete at a pressure of approximately 10 cm. which is 1000 times greater than the pressure at which the surface of the foil appears to be saturated. It should also be noted that on the pumped out foil at  $-195^\circ$  the sorbed oxygen forms a substantially complete monolayer, and that this apparent saturation is very nearly achieved at a pressure of the order of 0.1 cm. These facts indicate that although the forces involved may be basically the same they differ in degree between the surface of a powder and that of foil. This difference is further illustrated by a comparison of the heat of adsorption on the different surfaces. Thus the heat derived by means of the Brunauer-Emmett-Teller equation for powder II, used by Benton and Drake, is 2390 cal. which is significantly lower than the heat of 3560 cal. calculated for the foil by the same method. A difference such as this between the surfaces, also the fact that the range of pressure studied is considerably lower than is used for powders, may account for the apparent flattening of the curve at relatively lower pressures in the case of the foil.

Another interesting comparison is that the surface concentration of oxygen in the activated adsorption at  $-78.5^\circ$  is the same on the foil as it is on the powder. Thus, on the foil, the concentration is  $0.22 \times 10^{15}$  molecules per sq. cm., as calculated from the value of  $V_s$  and the geometric surface area. The surface area of the powders used by Benton and Drake, as estimated by means of the Brunauer-Emmett-Teller equation, is 13 and

(17) The relation given by Innes and Rowley is

$$FA = RT \int_{v=0}^{v=v_1} \ln \frac{p_1}{p} dv$$

but in a personal communication they have suggested the alternative form above because it requires a less difficult extrapolation.

(18) Benton and Drake, *THIS JOURNAL*, **56**, 255 (1934).

(19) Emmett and Brunauer, *ibid.*, **59**, 1558 (1937).



26 sq. m., respectively,<sup>20</sup> for powders I and II. On the basis of these areas, the surface concentration of oxygen at  $-78.5^\circ$  is  $0.21 \times 10^{15}$  and  $0.16 \times 10^{15}$  molecules per sq. cm. which is virtually identical with that on the foil. The fact that the oxygen held on the foil so strongly at  $-183^\circ$  that it could not be pumped off at temperature was also present on the surface at a concentration of  $0.16 \times 10^{15}$  molecules per sq. cm. suggests, though it does not prove, that the sites which hold oxygen so strongly at  $-183^\circ$  are the same upon which activated adsorption occurs at  $-78.5^\circ$ .

It is interesting to note that if one assumes that the activated adsorption at  $-78^\circ$  represents the formation of a silver oxide complex on the surface, the number of sites is about equal to the observed number of molecules sorbed. Thus, on this basis, each oxygen molecule would be associated with 4 atoms of the silver on the surface. The X-ray diffraction patterns indicate that as a first approximation the silver grains are so arranged that the (110) planes lie on the surface, and since, on this plane, four silver atoms occupy an area of about 46 sq. Å., the concentration of groups of sites of four silver atoms is about  $0.22 \times 10^{15}$  per sq. cm., which corresponds very well with the observed concentration of oxygen sorbed at  $-78^\circ$ , and to the concentration of oxygen held so tightly at  $-183^\circ$  that it cannot be removed by pumping at temperature.

(20) Assuming that the cross section of an oxygen molecule in a complete monolayer is 12 sq. Å.

### Summary

The adsorption of hydrogen, nitrogen, argon, carbon monoxide, carbon dioxide and oxygen at pressures up to 0.1 cm. on a substantially plane, reduced surface of silver has been measured over the temperature range  $-195$  to  $20^\circ$ . Hydrogen is not measurably sorbed at any temperature; argon, nitrogen and carbon monoxide are sorbed at  $-195$  and  $-183^\circ$  but not at  $-78$  or  $20^\circ$ . Carbon dioxide is not sorbed at  $20^\circ$  but at  $-78^\circ$  is sorbed to the slight extent of 6 cu. mm. at a pressure of 0.02 cm. The adsorption is in each case instantaneous and reversible. Oxygen is sorbed at  $-195$  and  $-183^\circ$  and although most of the gas appears to be held by van der Waals forces some part of it cannot be removed by pumping at temperature. At  $-78$  and  $20^\circ$  there is activated adsorption of oxygen. All the isotherms are of the type observed in a plane surface of other metals, and are satisfactorily represented by the Langmuir equation. The values of  $V_s$  as derived from the slope of the  $p/v - p$  isotherm, correspond to a surface only partially covered, the coverage varying from about 20 to 90% of a close-packed monolayer.

Force-area curves are derived by two different methods, with results which differ significantly. The adsorption of oxygen on smooth silver is compared with the adsorption of oxygen on finely-divided silver as reported by Benton and Drake.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

## The Attachment and Detachment of Dropping Mercury under Various Conditions

BY I. M. KOLTHOFF AND G. J. KAHAN

Although the mercury-water interfacial tension is little affected by dissolved non-capillary active electrolytes in the aqueous phase, it has been found by several workers that the drop time of mercury from a glass capillary into air-saturated water can be quite different from that into electrolyte solutions. For example, J. Heyrovský reports<sup>1</sup> that his capillary had a drop time of six to eight seconds in distilled water and of three seconds in electrolyte solutions. On the other

(1) J. Heyrovský, in W. Böttger, "Physikalische Methoden der analytischen Chemie," Vol. 11, Akadem. Verlagsges. Leipzig, 1936, p. 276.

hand, Kolthoff and Lingane<sup>2</sup> mention that with their capillary the drop times in water and in 0.1 *M* potassium chloride were hardly different. It is not stated whether the water used was air-free.

In our experiments we found that the drop time of an electrically disconnected capillary in air-containing water was badly reproducible and, as a rule, much larger than in 0.1 *M* salt solutions. Slight deviations from the vertical in the position of the capillary resulted in large variations of the drop time, whereas no such effect was found in not

(2) I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 26 (1939).