

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF BRISTOL]

THE ADSORPTION OF GASES AND VAPORS ON PLANE SURFACES

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The adsorption of gases on solid surfaces has been the subject of numerous investigations. Most of the work, however, is concerned with the adsorption on non-uniform or amorphous surfaces, the accessible area of which is unknown. This has led to an uncertainty as to the thickness of the adsorbed layer, which is found to vary from a monomolecular layer¹ to a layer many molecules in thickness.² The decision on this point is complicated by the difficulty of obtaining a molecularly plane surface of large enough area upon which to measure the adsorption. The most suitable plane surface is that of a crystal. The present work, in which a large crystalline surface of mica has been employed, arose out of an investigation of the nature of the adsorbed film of vapors on mica surfaces.³ These investigations were extended to confirm the important work of Langmuir¹ on the adsorption of gases on plane surfaces, and to throw further light on the nature of the monomolecular adsorbed film.

Part I. The Adsorption of Carbon Monoxide, Argon and Oxygen on Mica at $P = 1 \times 10^{-4}$ cm. to $P = 2 \times 10^{-2}$ cm. at $T = 90^\circ$ Abs. and $T = 193^\circ$ Abs.

Materials.—The sheets of mica were obtained by splitting a specially selected piece of muscovite. The mica was cut into strips of definite size (11.3×1.8 cm.) by means of a very sharp razor, only pieces which showed no cracks and were uniform in thickness being selected. The strips were loosely held in the adsorption vessel in a thin silver wire frame, a similar frame being placed in the blank adsorption vessel. The total area of the mica was 6239 sq. cm.

Oxygen was obtained by heating pure potassium permanganate and was dried by passage through phosphoric oxide.

Carbon monoxide was prepared by dropping 100% formic acid onto concentrated sulfuric acid. It was passed through caustic potash to remove carbon dioxide and dried over phosphoric oxide.

Hydrogen.—This gas was carefully purified by the use of palladium and upon analysis was found to be 99.9% pure.

Argon was freed from other gases by passing through tubes containing (a) heated calcium oxide-magnesium, (b) heated copper oxide, the process being repeated until the gases showed that nitrogen and hydrogen were absent when the purity of the gas was tested in a discharge tube.

¹ Langmuir, *THIS JOURNAL*, 40, 1361 (1918); Zeise, *Z. physik. Chem.*, 136, 385 (1928).

² McHaffie and Lenher, *J. Chem. Soc.*, 1559 (1925); 1785 (1926); Lenher, *ibid.*, 272 (1927).

³ To be published.

Experimental

The adsorption was measured in the usual way by observing the decrease in the amount of gas, measured by change of pressure, which occurred when a known volume was admitted to the vessel containing the adsorbing surface.¹ The method possessed an advantage over that used by Langmuir in that the adsorption over a range of pressures could be measured in a single experiment by admitting successive amounts of gas. The pressures were measured by two McLeod gages, the capillary lengths of which had been calibrated and the volumes accurately determined. The first McLeod gage was used for pressures from 10^{-6} to 2×10^{-2} cm. and the other from 10^{-2} to 2.5×10^{-1} cm. The complete apparatus is shown in Fig. 1. The glass connections were constructed wholly of wide tubing 2 cm. in diameter, all joints being sealed glass and mercury U-seals used instead of stopcocks. The level of the mercury in the U-seals,

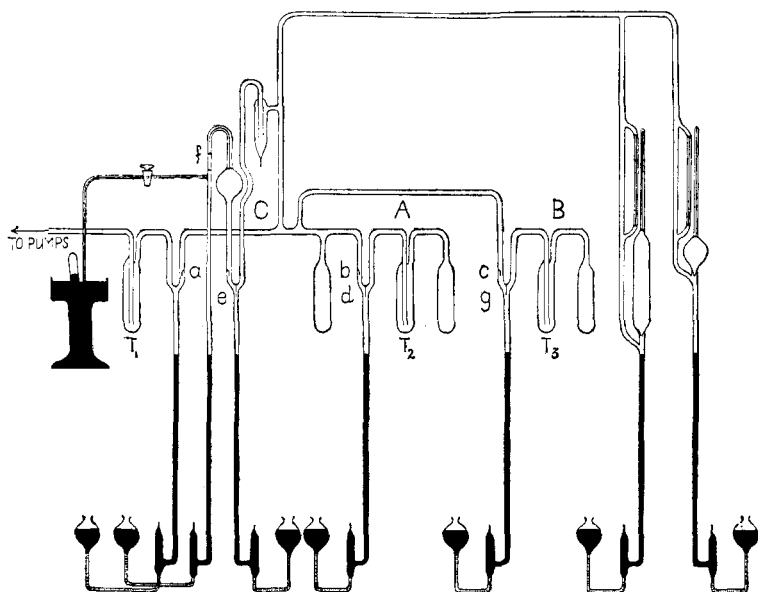


Fig. 1.

when either opened or closed, could be adjusted to the tips of pointers a, b, c, etc., sealed into the glass. The tap used to admit the gas was always cut off by a mercury seal during an experiment. T_1 , T_2 and T_3 are traps which could be cooled in liquid air. The pumping system consisted of a glass mercury diffusion pump backed by a Hyvac oil pump. Two adsorption systems, A containing the mica, and B the blank were used. Each consisted of a mercury seal (bd or cg), liquid-air trap (T_2 or T_3) and adsorption vessel. The total volume and total glass surface were approximately the same in the two cases. The gas buret C was used both for calibration purposes and for admitting the gas during adsorption experiments.

Calibrations.—The volumes of the parts of the apparatus were determined by admitting a measured amount of hydrogen gas to the evacuated apparatus, measuring the pressure by the McLeod gage and applying Boyle's Law. Hydrogen gas was employed because no measurable adsorption of this gas on mica or glass occurred, as was shown by the fact that at all pressures of hydrogen the measured volumes agreed within

less than 1%. The volumes of the systems A and B were 962.3 and 965.1 cc., respectively.

As the adsorption experiments were conducted at 90°A. (liquid air) and 193°A. (solid carbon dioxide and alcohol), it was necessary to correct for the pressure change which occurs on cooling. Account has also to be taken of the "thermal molecular flow" discovered by Knudsen⁴ which occurs at low pressures and in tubes of small diameter, when the mean free path is of the order of the diameter of the tube. The corrections were determined by the method of Langmuir, hydrogen gas being used. In Fig. 2, a typical calibration curve is given. The curve shows the variation with pressure of the ratio R, that of the pressure at room temperature to that of the pressure with the adsorption vessel containing the mica and trap (System A) cooled to liquid-air temperatures. The ratios for other gases were obtained from the hydrogen curve on the assumption that they would be the same at pressures at which the mean free paths were equal.

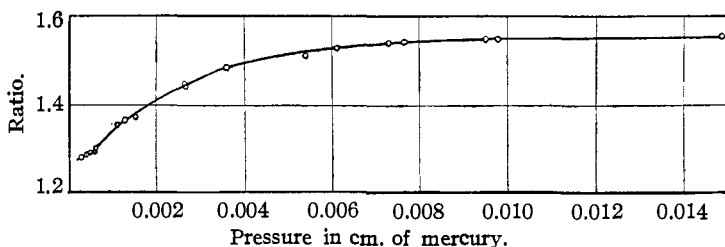


Fig. 2.—Calibration curve.

Outgassing of the Surface.—Langmuir⁵ and Sherwood⁶ concluded from an extensive series of investigations on the gases evolved from glass on heat treatment that the products below 300° were adsorbed gases, while at higher temperatures diffusion from the deeper layers and probably an actual decomposition of the glass occurred. The gases evolved from mica on heating are probably of a similar nature, the heating below 300° causing the removal of the adsorbed layers,⁷ while above this temperature diffusion from the interior layers may occur, accompanied by a splitting of the crystal lattice. For these reasons, the temperature during the baking out process was maintained at 300°.

Method of Experiment.—This can best be understood by reference to Fig. 1. The mica was baked out for three hours, the system B being cut off by the U-seal *cg*. The trap T_1 was cooled in liquid air during this period and, for reasons discussed later, the trap T_2 was also cooled during the latter part of the baking out. The final pressure in the apparatus after baking out was always less than 10^{-6} cm. With the system A cut off by the U-seal *bd*, a quantity of gas was measured approximately in the gas buret C in order to obtain the necessary working pressure. The seal *e* was opened, the mercury surfaces leveled to *a*, *f*, *e* and *b*, and the pressure in this part of the system (say volume v_1) measured. The gas was now expanded to A (volume v_2), the mercury leveled to the pointer *d* and the equilibrium pressure measured. From this pressure, after application of the low temperature-pressure correction, the amount of gas in V_1 and V_2 together was found; the difference between this amount and the amount previously measured in V_1

⁴ Knudsen, *Ann. Physik*, **31**, 305 (1910); **33**, 1435 (1910).

⁵ Langmuir, *THIS JOURNAL*, **38**, 2283 (1916).

⁶ Sherwood, *ibid.*, **40**, 1645 (1918).

⁷ Langmuir found that the gases given off by mica at 300° corresponded to a double layer of water molecules and a single layer of carbon dioxide.

gives the amount of gas adsorbed by the mica and glass in A. The U-seal bd was now closed, and the mercury leveled to b. From a knowledge of the residual pressure in V_1 and V_2 , and the volumes of the parts of the U-seal bd, and assuming that the gas in bd is divided proportionally between V_1 and V_2 on closing the seal, the total amount of gas left in V_2 was known. A second amount of gas was admitted to V_1 and the pressure measured. This was expanded to V_2 as before, the measurement of the total pressure giving the amount of gas now in V_1 and V_2 . The difference between this amount and the amount of gas in V_1 and V_2 previously, gives the amount adsorbed due to the first increase in gas pressure. The addition of this amount to the former amount of adsorption is the total amount adsorbed at the second pressure. This process was repeated. With increase in pressure, the accuracy of the measurement of the small decrease in volume of gas became less and the series was usually discontinued at a pressure of 2×10^{-2} cm. Values for higher pressures were obtained by admitting the gas at the required pressure and measuring the total adsorption. It was found that the amount of the adsorption at any pressure was independent of the number of increments by which the pressure was built up or whether the adsorption was measured directly at that pressure.

The procedure for the determination of the amount of gas adsorbed by the glass blank was exactly the same as described above, the adsorption vessel containing the mica being cut off during these experiments.

Rate of Adsorption.—In view of a recent publication by H. S. Taylor⁸ the time required for adsorption equilibrium to be reached is of interest. At 193°A . equilibrium was reached very rapidly, in fact, no change of pressure was observed three minutes after admitting the gases. Owing to the time taken in reading the pressure by means of the McLeod gage, it was impossible to investigate the pressure change during this period. Table I shows two series of results for carbon monoxide at 193°A . At 90°A ., however, the time taken to reach equilibrium was much longer. A typical series of results for carbon monoxide is as given in Table II and shown graphically in Fig. 3. It is observed that equilibrium is reached after forty-five minutes. These results are in agreement with the work of Taylor, who postulates the existence of an activation energy for adsorption

TABLE I

RESULTS FOR CARBON MONOXIDE AT 193°A .

Time after admitting gas, min.	Pressure, cm.	Amt. adsorbed, cc.
3	0.00293	0.00136
35	.00291	
55	.00292	
3	.000654
13	.000648	

TABLE II

RESULTS FOR CARBON MONOXIDE AT 90°A .

Time after admitting gas, min.	Pressure, cm.	Amt. adsorbed, cc.
2	0.00532	0.0132
7	.00439	.0317
13	.00302	.0595
18	.00218	.0763
23	.00163	.0874
32	.00110	.0984
47	.000801	.1039
53	.000653	.1057
67	.000606	.1075
78	.000566	.1082

⁸ Taylor, THIS JOURNAL, 53, 578 (1931).

processes, and therefore a slow rate of adsorption. The observed rate of adsorption could not be attributed to "slow diffusion of the gas through spaces between the mica strips," as Langmuir⁹ had assumed, otherwise the effect would have been noticed at 193°A. The data were insufficient to allow a calculation of the energy of activation to be made.

In all the experiments described below, the pressure was recorded fifteen minutes after admitting the gas to the mica at 193°A. and after sixty-five minutes at 90°A.

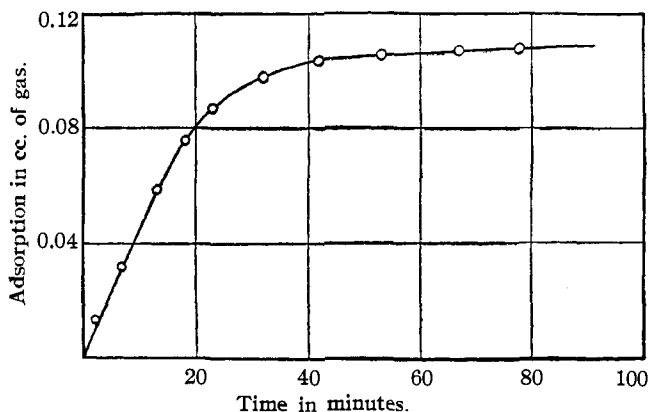


Fig. 3.—Curve showing the rate of adsorption of carbon monoxide at 90°A.

Summary of Experimental Results.—The results for the adsorption of three gases on mica at temperatures 90°A. and 193°A. are given in Tables III–VIII. In the first two columns, the pressure and the amount of gas adsorbed on the mica and glass together are given; columns III

TABLE III

CARBON MONOXIDE AT 193°A.

Expt.	Adsorption on mica and glass		Adsorption on glass blank		Corrected results for adsorption on mica	
	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.
17	0.00121	0.00075	0.00252	0.00080	0.002	0.00200
	.00326	.00315	.00534	.00283	.004	.00400
	.00597	.00624	.00829	.00434	.006	.00630
	.00932	.0104	.0120	.00553	.008	.00825
	.0138	.0150			.010	.01038
	.0225	.0229			.012	.01250
18	.00274	.00278	.00387	.00113	.014	.01438
	.00871	.00981	.00587	.00242	.016	.01653
	.0139	.0146	.00983	.00309	.018	.01838
	.0205	.0213	.0145	.00351	.020	.02013
					.022	.02163

⁹ Ref. 1, p. 1381.

TABLE IV
CARBON MONOXIDE AT 90°A.

Expt.	Adsorption on mica and glass		Adsorption on glass blank		Corrected results for adsorption on mica	
	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.
22	0.000566	0.1082	0.00132	0.00498	0.00025	0.070
	.00105	.1339	.00205	.00698	.0005	.101
	.00453	.1717	.00344	.00797	.001	.130
	.00545	.1769	.00465	.00820	.0015	.141
	.00791	.1889	.00852	.01114	.002	.147
	.01059	.1960			.003	.156
23	.000123	.0544			.004	.160
	.000197	.0893			.005	.165
	.00756	.1230			.006	.169
	.00228	.1490			.007	.173
	.00713	.1785			.008	.177
					.009	.181
				.010	.182	

and IV contain the corresponding results for the blank adsorption vessel and columns V and VI the pressure-adsorption values for the mica surface only. The latter results were obtained from the plots of the figures in columns I and II, and III and IV, and subtraction of the two curves. These results were read off from the final curve. This was simplified by the fact that the adsorption on the blank was so small that the isotherm was usually linear. The adsorption isotherms are shown in Figs. 4, 5 and 6. In the case of the adsorption of argon the three curves, total adsorption on mica and glass, blank adsorption and the final corrected curve, are given as an illustration of the method. Curve II, Fig. 4, also shows the plots of two series of results for the adsorption of carbon monoxide by the blank adsorption vessel.

The two series of results obtained in Experiments 17 and 18 and Experiments 22 and 23 for the adsorption of carbon monoxide at 193 and 90°A., respectively, agreed so well that the corrected results given in columns V and VI are the mean of the two series in each case. The same procedure applies to Experiments 33 and 34, Table VIII, for the adsorption of argon at 90°A.

TABLE V
OXYGEN AT 193°A.

Expt.	Adsorption on mica and glass	
	Press., cm.	Adsorption, cc.
43	0.002318	0.00200
	.00479	.00490
	.00625	.00641
	.00989	.01025
	.01391	.01328
	.01665	.01483

TABLE VI
OXYGEN AT 90°A.

Expt.	Adsorption on mica and glass	
	Press., cm.	Adsorption, cc.
41	0.00232	0.00619
	.00356	.00952
	.00560	.0126
	.00755	.0156
	.01186	.0204
	.01295	.0208

The adsorption of oxygen at 193°A. on the glass blank was so small that it was impossible to measure the small decrease in volume of gas which occurred on admitting successive quantities of gas. The amount adsorbed on the glass was not greater than 8×10^{-4} cc. or less than 5% of the adsorption on the mica surface. No correction was made for this either at 193°A. or 90°A.

TABLE VII
ARGON AT 193°A.

Expt.	Adsorption on mica and glass		Adsorption on glass blank		Corrected results for adsorption on mica	
	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.
37	0.00180	0.00162	0.00409	0.0006	0.001	0.0010
	.00344	.00358	.00601	.00110	.0025	.0019
	.00561	.00585	.00844	.00125	.0035	.0028
	.00833	.00841	.01480	.00165	.005	.00425
	.01140	.01165			.007	.00590
	.01460	.0150			.0095	.00825
					.0115	.0100
					.013	.01125
					.0145	.01270

TABLE VIII
ARGON AT 90°A.

Expt.	Adsorption on mica and glass		Adsorption on glass blank		Corrected results for adsorption on mica	
	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.
33	0.00103	0.00257	0.00088	0.00158	0.001	0.00252
	.00162	.00630	.00386	.00296	.003	.00550
	.00319	.0115	.00489	.00374	.005	.01375
	.00500	.0173	.00734	.00606	.007	.01875
	.00815	.0280	.00988	.00751	.009	.0230
	.0113	.0344			.010	.0245
34	.00164	.00559			.011	.02575
	.00340	.0112			.0115	.0265
	.00507	.0170				

In the preliminary experiments with carbon monoxide, in which the traps T_1 and T_2 were not cooled, the adsorption was very slight and varied greatly with the time of beginning the run after the baking process. At this time, the surface was baked out overnight and allowed to cool during the night. The slight adsorption was thought to be due to the long period of cooling, mercury vapor having diffused into the adsorption vessel and in some way "blocking" the surface. It has been suggested since that this effect may have resulted from the occurrence of a different kind of adsorption with a high activation energy, such as that observed by Garner and Kingman¹⁰ and fully discussed by Taylor.⁸ This takes place at the higher temperature during the process of baking out. The difficulty was over-

¹⁰ Garner and Kingman, *Nature*, 126, 352 (1930); Kingman, *ibid.*, 127, 742 (1931).

come by cooling the trap T_1 in liquid air during the baking out and also T_2 during the latter part of the baking out process. T_2 was maintained in

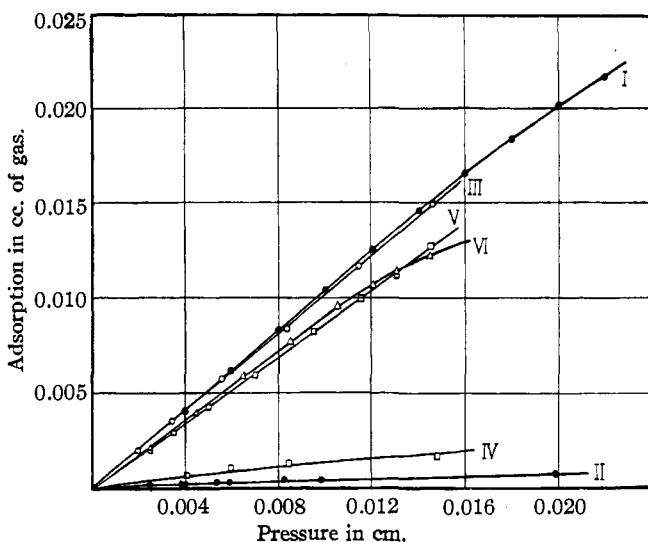


Fig. 4.—Adsorption of gases at 193°A.: Curve I, carbon monoxide on mica; curve II, carbon monoxide on glass blank; curve III, argon on glass and mica; curve IV, argon on glass blank; curve V, argon on mica; curve VI, oxygen on mica.

liquid air to constant level throughout the investigations, both for results at 90°A. and at 193°A. In the experiments described, the mica was baked out on the same day as the experiment was made, being allowed

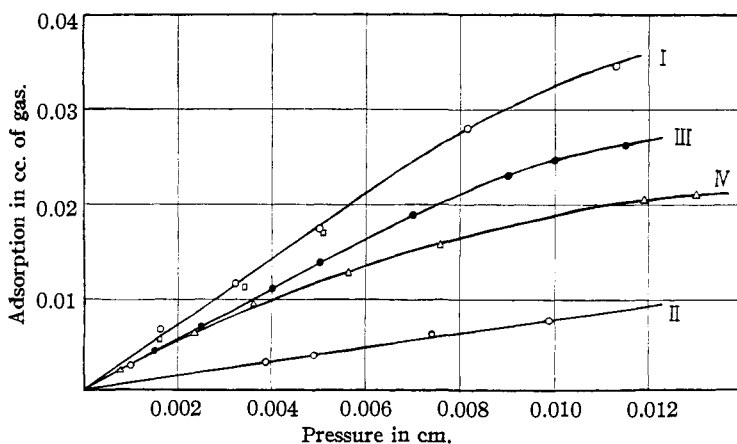


Fig. 5.—Adsorption of gases at 90°A.: Curve I, argon on glass and mica; curve II, argon on glass blank; curve III, argon on mica; curve IV, oxygen on mica.

to cool for two hours before the commencement of the experiment. With this standard procedure, the isotherms were quite reproducible, especially after the cooled surface had been treated with the gas to be adsorbed several times and baked out each time. It was generally found that lower values of the adsorption were obtained in the earlier experiments although the same form of isotherm was always obtained.

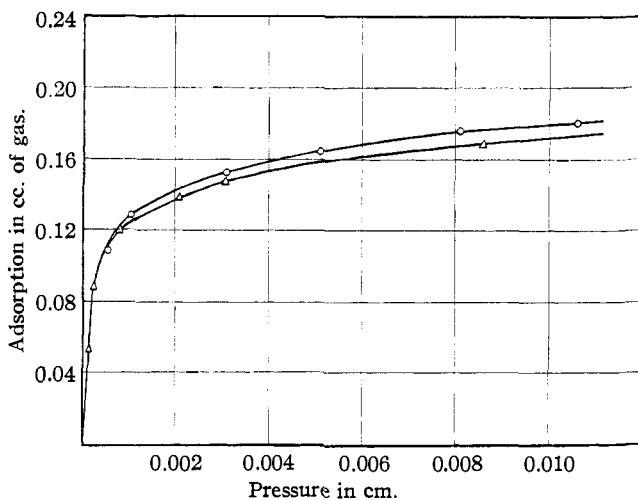


Fig. 6.—Adsorption of carbon monoxide on mica at 90°A. (two series).

Adsorption at Room Temperature.—An attempt was made to measure the adsorption of carbon monoxide at room temperature. The amount adsorbed, however, was so very little that up to a pressure of 0.016 cm. the loss of gas was of the order of ≈ 0.00005 cc. to 0.0001 cc. The area of surface covered was therefore never more than 0.5% at room temperature. These values also indicate the order of accuracy of the measurements, as at low pressures the amount of gas could always be checked up to ≈ 0.0001 cc.

Discussion

The adsorption equation deduced by Langmuir¹ and Hückel¹¹ may be expressed in the form

$$x = \frac{c_1 c_2 p}{1 + c_2 p} \quad (1)$$

c_1 and c_2 are constants at any given temperature; c_1 is adsorption maximum for the surface, c_2 is average time of stay of molecule on the surface.

Two important facts follow from this equation. (1) At low pressures, $c_2 p$ is negligible compared to unity and the equation reduces to

$$x = c_1 c_2 p \quad (2)$$

¹¹ Hückel, "Adsorption and Kapillar-Kondensation," Leipzig, 1928.

that is, the adsorption is directly proportional to the pressure. (2) At high pressures, c_2p is large compared to unity so that the amount adsorbed reaches a limiting value c_1 .

Adsorption at 90°A.—The results for the adsorption of carbon monoxide at liquid-air temperature (Fig. 5) show clearly the existence of the saturation value for the surface. The Langmuir equation is obeyed very closely. The data for oxygen (Fig. 5, curve IV) are also in agreement with the Langmuir equation, although this gas is adsorbed to a far less extent than carbon monoxide. In the case of argon (Fig. 5, curve II), however, the equation is not followed over the whole pressure range studied. The isotherm is nearly linear up to pressures 5×10^{-3} cm., but the Langmuir equation holds above a pressure of 8×10^{-3} cm. Langmuir¹² found that in the case of the adsorption of carbon monoxide on glass the simple equation (1) had to be modified in order to take into account the existence of two distinct stages of adsorption. In a similar manner the adsorption of argon on mica can be explained if we assume that the adsorption occurs on more than one kind of "elementary space." The adsorption equation may then be written

$$x = k_1 \frac{c_1 c_2 p}{1 + c_2 p} + k_2 \frac{c_1' c_2' p}{1 + c_2' p} + \text{etc.} \quad (3)$$

where k_1 and k_2 , etc., represent the fraction of the various surfaces. The actual form of the resulting isotherm depends on the magnitude of the terms in this equation. No other simple equation has been found to cover the adsorption of argon from pressures 1×10^{-4} cm. to pressure 1.2×10^{-2} cm.¹³

Writing equation (1) in the form

$$\frac{p}{x} = \frac{1}{c_1 c_2} + \frac{p}{c_1} \quad (4)$$

it will be seen that the plot of p/x against p should be a straight line, the slope of which is $1/c_1$. The values of c_1 , the saturation for the surface in molecules adsorbed per sq. cm., are given in Table IX.

TABLE IX

Gas	c_1 (moles/sq. cm.)	β % surface covered at saturation	Heat of adsorption, cal.
O ₂	0.180×10^{16}	23	186
A	$.233 \times 10^{16}$	30	334
CO	$.745 \times 10^{16}$	113	1048

The values of β , percentage surface covered at saturation, are also given, the number of molecules required to form a monomolecular layer being estimated from the diameter of the molecules in the liquid state. The

¹² Langmuir, Ref. 1, p. 1388.

¹³ Langmuir gives the results for the adsorption of argon at two pressures only; hence, no comparison with the complete form of the isotherm can be made.

surface is completely covered in the case of carbon monoxide,¹⁴ but with argon and oxygen only about one-fourth of the surface is covered. Comparison with the adsorption values obtained by Langmuir for these gases shows that the order of the amounts necessary to saturate the surface, namely, carbon monoxide, argon, oxygen—carbon monoxide being the most and oxygen the least adsorbed—is the same in both cases. The saturation value of the adsorption is, however, two to three times greater than for the mica used by Langmuir.

In order to account for the variation in β for different gases, Langmuir assumed that the surface was not homogeneous, but was composed of different kinds of elementary spaces, each possessing a different adsorptive power. The surface of muscovite consists of a complex distribution of K, Al, Si, and O and H atoms, the layers of mica according to Pauling¹⁵ being held together by potassium atoms. Several kinds of adsorption would therefore be expected. The low saturation value for oxygen may result from the oxygen being adsorbed only on the metallic atoms in the surface while carbon monoxide, being unsaturated, is adsorbed on all types of surface atoms, giving a complete layer. In the case of argon, the adsorption on more than one kind of elementary space has already been discussed.

Adsorption at 193°A.—It is evident from Fig. 4 that for small amounts adsorbed corresponding to less than one-tenth of the measured area of the surface covered, the amount adsorbed is directly proportional to the pressure. For small amounts adsorbed, Hückel¹⁶ deduces the equation

$$\frac{Na}{Ng} = \Delta e^{\varphi/RT} \quad (5)$$

Na being number of g. moles adsorbed per sq. cm., Ng being number of g. moles per cc. in gas phase, Δ , thickness of adsorbed layer and φ , heat of adsorption.

The amount adsorbed is therefore directly proportional to the pressure if the surface is homogeneous, and thus φ is constant, and if the area does not alter during adsorption. The variation of the heat of adsorption for different amounts adsorbed has been demonstrated by Garner and his co-workers,¹⁷ Taylor,¹⁸ *et al.*, but in such cases the measurements were made on active surfaces, for which the heat of adsorption is high. In this case it may be assumed that φ remains constant for small amounts adsorbed, as is indicated both by the linear variation of the amounts adsorbed with pressure and the low value obtained for the heat of adsorption.

¹⁴ This value is calculated from the measured surface, which is probably an under-estimation of the true surface area.

¹⁵ Pauling, *Proc. Nat. Acad. Sci.*, **16**, 123 (1930).

¹⁶ Ref. 11, p. 58.

¹⁷ Garner, Bull and Hall, *J. Chem. Soc.*, 837 (1931).

¹⁸ Taylor and Kistiakowsky, *Z. physik. Chem.*, **A125**, 341 (1927).

From the logarithmic form of equation (5)

$$\log \frac{Na}{N_g} = \log \Delta + \frac{\varphi}{RT}$$

the plot of $\log Na/N_g$ against $1/T$ gives a straight line, the slope of which is φ/R . The values of φ determined in this manner from the results at two temperatures are given in Table IX.

Above pressures 8×10^{-3} cm., the isotherms for oxygen and carbon monoxide show a marked curvature and in this region the data are in agreement with Langmuir's equation. Extrapolation as before to the saturation value gives the approximate values for the percentage surface covered at saturation as CO 82%, O₂ 16%. The isotherm for argon (Fig. 5, curve III), is linear up to the highest pressure measured.

The saturation value on Langmuir's theory is attained with the formation of a monomolecular layer and should therefore be independent of temperature except in so far as the number of elementary spaces per unit area (N_0) does not vary with temperature. The results at 90 and 193°A. for carbon monoxide and oxygen confirm the observations of Langmuir at 90 and 155°A. in that the saturation value is largely dependent on temperature. The temperature variation of the values of the constants c_1 and c_2 in the Langmuir equation have recently been examined theoretically by Zeise,¹⁹ Polanyi²⁰ and Wilkins and Ward.²¹ The latter authors, following the work of Volmer²² and his collaborators, assume that the adsorbed molecules possess lateral motion over the surface and show that the temperature coefficient of the saturation maximum is that of the coefficient of expansion of a gas at constant pressure. This motion of the adsorbed molecules may occur when the oscillatory motion of the molecules tangential to the surface is large enough to allow the molecules to jump from one elementary space to another. The present author has obtained some direct evidence that this occurs in the case of acetone vapor adsorbed on mica at room temperatures.²³

Part II. The Adsorption of Acetone Vapor on Mica at Pressures 2×10^{-6} cm. to $1-2 \times 10^{-2}$ cm. and at 292°A.

The apparatus described in Part I, with slight modifications, was employed. Although the McLeod gage is not the most suitable for use with vapor, the gage can be used to measure the pressures of vapors accurately if the mercury levels in the two capillaries of the McLeod gage are nearly level when taking a pressure reading. The pressures measured on two

¹⁹ Zeise, *Z. Elektrochem.*, **35**, 426 (1929).

²⁰ Polanyi, *Z. physik. Chem.*, **A138**, 439 (1929).

²¹ Wilkins and Ward, *ibid.*, **A144**, 259 (1929).

²² Volmer and Adhikari, *ibid.*, **119**, 46 (1926).

²³ To be published.

McLeod gages of different volumes agreed closely. The system for admitting the acetone consisted of a U-tube with small bulb in series. The acetone was contained in the evacuated bulb in a small sealed tube which was easily broken by gentle heating. The vapor liberated was frozen out in the U-tube by means of liquid air and the system again evacuated to remove any air which may have been dissolved in the acetone. The experimental procedure for measuring the adsorption was as described previously, the adsorption vessel being maintained at constant temperature by immersion in a Dewar vessel containing water.

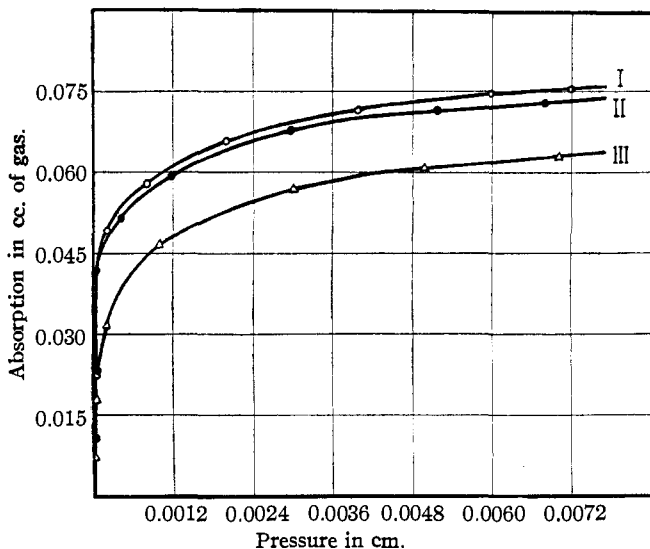


Fig. 7.—Adsorption of acetone on mica at 290°A.

In order to obtain concordant results for a series of adsorptions, it was necessary to keep the trap T_1 cooled by liquid air during the whole period of baking out. Without this trap, the pressure in the apparatus after baking out was still 10^{-4} cm., but as soon as T_1 was cooled, the pressure fell within ten minutes to 4×10^{-6} cm. The isotherms obtained are given in Fig. 7. Curve III shows the decrease in the amount of adsorption resulting through cooling the trap T_1 during the last half hour of the baking-out only. With no trap, the saturation value was reached when 0.035 cc. of acetone had been adsorbed. Increased periods of baking out produced no further increase in the final saturation value than that reached in Experiments 27 and 28, Table X, and plotted in Fig. 7, curves I and II.

No measurements of the rate of adsorption were made other than to ascertain the time taken to attain equilibrium. This was reached in less than fifteen minutes after the vapor had been admitted to the adsorption vessel.

TABLE X
ACETONE ON MICA AT 292°A.

Expt.	Adsorption on mica,		Adsorption on glass, blank		Corrected results for adsorption on mica	
	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.	Press., cm.	Adsorption, cc.
27	2.3×10^{-6}	0.0109	0.00051	0.00181	2.3×10^{-6}	0.0109
	1.4×10^{-5}	.0231	.00110	.00204	1.4×10^{-5}	.0231
	0.000135	.0418	.00202	.00267	0.000135	.0418
	.000634	.0561	.00381	.00345	.00040	.0515
	.00281	.0694	.00703	.00445	.00080	.0561
	.00450	.0731			.0012	.0593
					.0030	.0676
				.0052	.0710	
				.0068	.0725	
28	1.7×10^{-5}	0.0226			1.7×10^{-5}	.0226
	0.00104	.0625			0.0008	.0576
	.00257	.0707			.0012	.0609
	.00508	.0765			.0020	.0655
	.00751	.0800			.0040	.0720
				.0072	.0750	
25	.000015	.00746			.000015	.00746
	.000037	.0181			.000037	.0181
	.000333	.0376			.0002	.0315
	.000898	.0477			.0004	.0380
	.00160	.0528			.001	.0465
	.00460	.0629			.002	.0525
					.004	.0585
				.006	.0612	
				.007	.0625	

Discussion

The data in the foregoing tables can be represented accurately by the simple Langmuir equation (1). The saturation value for the adsorption corresponds to 33% of the surface covered. This was calculated from the number of molecules required to form a complete monomolecular film as estimated from the diameter of the acetone molecule.²⁴ The adsorbed layer is therefore not greater than one molecule in thickness, in agreement with the work of Carver,²⁵ Frazer, Patrick and Smith,²⁶ Latham,²⁷ *et al.*, for the adsorption of vapors on plane surfaces. Up to pressures of one-thousandth of the saturation pressure of acetone, no evidence for capillary condensation was obtained.

In conclusion, the author wishes to express his appreciation to Professor W. E. Garner, who suggested this study and under whose direction it was

²⁴ Landolt-Börnstein, Vol. I, pp. 120, 122.

²⁵ Carver, THIS JOURNAL, 45, 63 (1923).

²⁶ Frazer, Patrick and Smith, *J. Phys. Chem.*, 31, 847 (1927).

²⁷ Latham, THIS JOURNAL, 50, 2996 (1928).

carried out, and to the Imperial Chemical Industries, Limited, for a personal grant.

Summary

1. The adsorption of carbon monoxide, oxygen and argon by mica surfaces has been measured from pressures 1×10^{-4} cm. to 2×10^{-2} cm., and at temperatures 90°A . and 193°A .

2. The data for the adsorption of carbon monoxide and oxygen at 90°A . are adequately represented by the Langmuir formula. No simple equation expresses the results for argon.

3. The isotherms at 193°A . are linear for small amounts adsorbed and up to pressure 8×10^{-3} cm. The Langmuir equation is followed at higher pressures.

4. The magnitude of the adsorption has been shown to be dependent upon the conditions of the outgassing of the surface. A suggested explanation is based on the concept of the activation energy for adsorption processes as postulated by Taylor.

5. The thickness of the adsorbed film of carbon monoxide, oxygen and argon, is not greater than unimolecular.

6. The adsorption of acetone vapor on mica at room temperature has also been measured. The data are accurately represented by the Langmuir equation. The adsorbed layer is not greater than one molecule in thickness.

BRISTOL, ENGLAND

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE
UNIVERSITY OF PENNSYLVANIA]

THE QUANTITATIVE SEPARATION OF GERMANIUM AND ARSENIC¹

BY HAROLD J. ABRAHAMS AND JOHN HUGHES MÜLLER

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The quantitative separation of germanium from arsenic is attended by considerable difficulty, a fact which is not surprising in view of their relative positions in the periodic arrangement of the elements. As these two elements are so universally associated in germanium bearing minerals, this separation has been made the subject of several investigations in the past. As early as 1886 Winkler² suggested a means of effecting this separation through the mixed sulfides. According to this method, both elements are taken into alkaline solution as thio compounds, and the

¹ From the thesis presented by Harold J. Abrahams to the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Winkler, *J. prakt. Chem.*, **142**, 194 (1886).