If a completely anhydrous solution is desired solid potassium hydroxide may be used after the preliminary drying with the anhydrous magnesium sulfate.

α-Methyl-β-hydroxyphenethylamines.— The amines were demethylated by heating the amine with 36% hydrochloric acid solution for two hours at 160° in a sealed tube. The solution was evaporated to dryness and the residue taken up in absolute alcohol and boiled with decolorizing charcoal. After filtration the alcoholic solution was concentrated and absolute ether added to cloudiness. The pure amine hydrochloride precipitated on cooling. The yield of the crude product, which was nearly pure, was the theoretical. Losses in crystallization were out of proportion with the amount of impurity present as shown by change in melting point. The α-methyl-β-*m*-hydroxyphenethylamine hydrochloride was particularly difficult to obtain in a crystalline condition. It finally was obtained by allowing a toluene–alcohol solution of the hydrochloride to stand at room temperature until crystals formed.

The authors are indebted to Mr. C. H. Emerson for the micro analyses given and to Mr. Earl Pierson for assistance in the demethylation of the methoxy amines. The pharmacological results will appear elsewhere.

Summary

1. The method of Bogert and Davidson for the preparation of α-alkyl cinnamic acids has been extended to their monomethoxy derivatives.

2. Four new and three previously known α-methyl-β-phenethylamines have been prepared for the purpose of pharmacological study.

KALAMAZOO, MICH. RECEIVED DECEMBER 20, 1937

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

The Adsorption of Gases on Plane Surfaces of Mica

BY MARION H. ARMBRUSTER AND J. B. AUSTIN

As a preliminary to a general study of the adsorption of gases on plane surfaces of iron, it seemed advisable to check the reliability of the apparatus and to develop the technique of using it by making a few measurements of adsorption on mica, which has been investigated by Langmuir,[1] by Bawn[2] and by Zickermann.[3]

The adsorption of argon and of carbon monoxide on mica at −183° has therefore been determined with the following results. The data for carbon monoxide are in excellent agreement with those of Bawn but are not in accord with those reported by Langmuir, whereas the results for argon show better agreement with Langmuir's data than with Bawn's. At saturation the mica surface appears to be completely covered with carbon monoxide but is only 17% covered with argon. Two kinds of adsorption of carbon monoxide were observed. The first which occurs on approximately a quarter of the surface is a chemisorption, the second, which covers the rest of the surface is physical adsorption. It is concluded that adsorbed argon atoms and the chemisorbed carbon monoxide are held on active centers which are probably the points on the surface from which a potassium ion is removed on cleavage. The adsorbed carbon monoxide behaves as if it were a two-dimensional gas, and obeys a two-dimensional analog of the van der Waals equation.

Materials

Hydrogen for Calibration.—Three different samples were used: (1) hydrogen from a Bunsen flame, collected by diffusion through palladium; (2) tank hydrogen freed from traces of water and oxygen by passing it through sulfuric acid and calcium chloride, then over hot platinized asbestos and phosphorus pentoxide; (3) a commercial sample of spectroscopically pure hydrogen. All three samples gave the same results within the error of measurement.

Carbon monoxide was prepared by dropping formic acid into concentrated sulfuric acid. It was passed through a solution of potassium hydroxide to remove carbon dioxide and was dried over phosphorus pentoxide.

Argon.—A commercial sample of spectroscopically pure gas was used.

Mica.—Sheets of mica split from a specially selected piece of muscovite were cut into strips 9.0 × 1.7 cm., care being taken to avoid touching the surface with the fingers and to discard pieces with cracks. The geometrical area of the surface was 7200 sq. cm. and the sample weighed 34.0 g.

Apparatus

Adsorption was determined by observing the decrease in the amount of gas, as measured by the change in pressure, when a known volume of gas was admitted to a bulb of known volume containing the absorbing surface. The apparatus used, shown schematically in Fig. 1, was in principle the same as that used by Bawn[2] and need be described but briefly here. It consists of three parts: an adsorption system, A, comprising a bulb containing the

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(1) Langmuir, THIS JOURNAL, **40**, 1361 (1918).

(2) Bawn, *ibid.*, **54**, 72 (1932).

(3) Zickermann, *Z. Physik*, **88**, 43–54 (1934).

adsorbent, a liquid air trap and a mercury U seal; a blank system, B, identical with A, of approximately the same volume and surface area; the main part of the train, C, containing the McLeod gage G. The third part, C, is connected to a diffusion pump through a liquid air trap at one end and to the gas buret, D, and gas reservoir, R, at the other. The entire system was of Pyrex-brand glass; all connections were made with tubing of 2 cm. diameter, and all stopcocks were eliminated by the use of mercury seals.

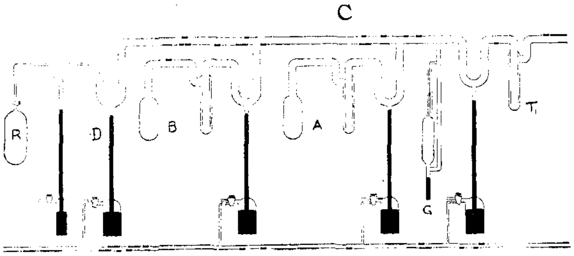

Fig. 1.—Diagram of adsorption apparatus.

Calibration.—The volume of each part was determined before inserting it in the system by filling it with water or mercury. After assembly, the calibration was checked by measuring the change in pressure when a known volume of hydrogen was expanded from one part of the system to another. This check also indicated that hydrogen is not adsorbed appreciably on Pyrex at room temperature.

Corrections.—As the temperature of the adsorption bulbs and liquid air traps differs from that of the rest of the system it is necessary to correct for the pressure change on cooling and, at the lowest pressures, for the effect of thermal effusion as well. These corrections were determined by filling the system with hydrogen and measuring the change in pressure when the traps and bulbs were cooled to the temperature of liquid air. The ratio of the pressure when the system was at room temperature to that when the traps and bulbs were cooled was constant at the higher pressures, and its value agreed with that calculated by the perfect-gas laws, indicating that hydrogen is not appreciably adsorbed on Pyrex even at −183°. The use of hydrogen for calibration is therefore justified.

In principle, a separate calibration curve should be determined for each gas in the range in which the thermal effusion effect is measurable, but calculations based on the assumption that the correction is the same for all gases at the pressures at which the mean free path of the molecules is equal, showed that at a given pressure the difference between the correction for hydrogen and that for argon and carbon monoxide is of the same order of magnitude as the error of measurement; consequently, the correction curve determined with hydrogen was used for other gases as well. This procedure is further justified by the fact that a direct determination of the correction for argon gave results which differed from the curve for hydrogen by less than the limit of error.

Procedure.—At first an attempt was made to check the adsorption isotherms by making measurements with decreasing pressure as well as with increasing pressure. In the method of increasing pressure, gas was introduced into C, and its pressure measured, after which it was expanded into the adsorption system and the pressure again measured. The adsorption system was then trapped off, more gas was added to C and the expansion process repeated. By this method the amount of gas adsorbed at each increase in pressure was determined. The other procedure was to introduce a large quantity of gas into C, to expand it into A and determine the amount adsorbed; part A was then trapped off and part C was evacuated, after which the gas was allowed to expand from A into C. By repeating this process the amount of gas given up on each decrease in pressure was determined.

In general results by the two methods do not agree, the apparent adsorption on decreasing pressure being greater and less reproducible than that determined on increasing pressure. This difference is due in part to the fact, discussed in detail later, that some of the adsorbed molecules are much more strongly held than others. The method of increasing pressure was therefore adopted as standard and was used in obtaining the data reported in the tables.

Adsorption by Blank.—The amount of gas adsorbed at −183° by the glass walls of system B was determined for each gas. With argon this correction was so small as to be insignificant, but with carbon monoxide it was large enough to be measurable and was applied to the observed adsorption on mica.

Outgassing Treatment.—The mica surface was outgassed before each run by baking the adsorption bulb for at least two hours at 300° under a pressure of 10^{-6} mm. with the trap (T_1) between the system and the pumps cooled in liquid air throughout the baking. The other traps were cooled during the last hour of baking out and were kept cold for the remainder of the run. The glass tubing was flamed at the same pressure. The bulb containing the sample was cooled one to two hours at room temperature and at least two hours in liquid air before gas was admitted to it.

Results

The results with argon are given in Table I and are shown by the lowest curve in Fig. 2. The rate of adsorption is relatively slow, the time required to reach equilibrium being about an hour. Desorption by pumping is also difficult as shown by the fact that it was impossible to attain a vacuum of 10^{-6} mm. even after pumping for a period of many hours. This is due in part to the fact that some gas is held so strongly that it is not released on lowering the pressure and, indeed, cannot be removed by pumping alone. For this reason, isotherms were determined only on a surface which had been baked out to remove all the gas adsorbed in the previous measurement.

Typical data for carbon monoxide are given in Tables II and III and are shown by the upper two curves in Fig. 2. As with argon, the rate of adsorption is slow, equilibrium being attained only after about an hour. There appear to be two kinds of adsorption. When a baked-out surface has been saturated, or nearly saturated, the

TABLE I

ADSORPTION OF ARGON ON MICA AT −183° (90°K.)

Pressure, cm.	Gas, cc. adsorbed at 20° and 760 mm.	Pressure, cm.	Gas, cc. adsorbed at 20° and 760 mm.
0.00042	0.0056	0.00403	0.0218
.00075	.0089	.00408	.0208
.00170	.0130	.00485	.0229
.00205	.0160	.00495	.0232
.00235	.0151	.00540	.0217
.00305	.0165	.00588	.0233
.00355	.0194	.00595	.0251
.00390	.0209		

system may be evacuated to a pressure of 10^{-6} mm. by pumping, but the subsequent adsorption on the pumped-out surface, though reproducible, is much less than that on the initial baked surface.

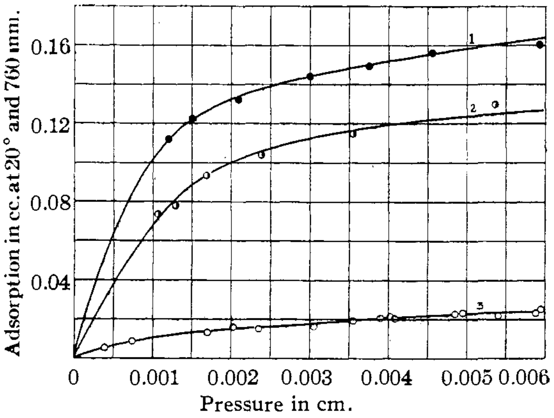

Fig. 2.—Adsorption isotherms for carbon monoxide and argon corrected for adsorption on blank: curve 1, CO on baked surface; 2, CO on pumped-out surface; 3, argon on baked surface.

Curve 1 in Fig. 2 represents the total adsorption on a baked-out surface, curve 2 is a typical isotherm after long pumping of a surface previously saturated with carbon monoxide. The difference between the isotherms is approximately constant, indicating that approximately 0.040 cc. of gas is so strongly held that it is not removed by pumping alone.

TABLE II

TYPICAL ADSORPTION OF CARBON MONOXIDE ON BAKED-OUT SURFACE OF MICA AT −183° (90°K.)

Pressure, cm.	Total adsorption in cc. at 20° and 760 mm.	Adsorption on blank in cc. at 20° and 760 mm.	Adsorption on mica in cc. at 20° and 760 mm.
0.0012	0.1167	0.0046	0.112
.0015	.1273	.0048	.122
.0021	.1370	.0052	.132
.0030	.1497	.0059	.144
.00375	.1552	.0064	.149
.00455	.1631	.0071	.156
.00596	.1684	.0080	.160

TABLE III

TYPICAL ADSORPTION OF CARBON MONOXIDE ON A PUMPED-OUT SURFACE OF MICA AT −183° (90°K.)

Pressure, cm.	Total adsorption in cc. at 20° and 760 mm.	Adsorption on blank in cc. at 20° and 760 mm.	Adsorption on mica in cc. at 20° and 760 mm.
0.00105	0.0790	0.0045	0.0745
.00128	.0830	.0047	.078
.00168	.0989	.0050	.094
.00238	.1093	.0054	.104
.00355	.1218	.0063	.115
.00535	.1390	.0076	.131

Discussion of Results

Comparison with Data of Previous Investigators.—The simplest way of comparing our results with those of previous investigators is through the amount of gas adsorbed at saturation as calculated by means of the Langmuir equation in the form

$$p/x = p/c_1 + 1/c_2 \qquad (1)$$

where x is the amount of gas adsorbed at pressure p and c_1 and c_2 are constants, c_1 being the amount adsorbed at saturation. The data for the adsorption of carbon monoxide in Tables II and III fit this equation closely (see Fig. 3); the saturation adsorption c_1 thus calculated, and corrected to 0°, is compared in Table IV with the saturation adsorption measured by Langmuir and by Bawn. Our value for the total adsorption is in good agreement with that of Bawn, whose procedure was such that he did not differentiate be-

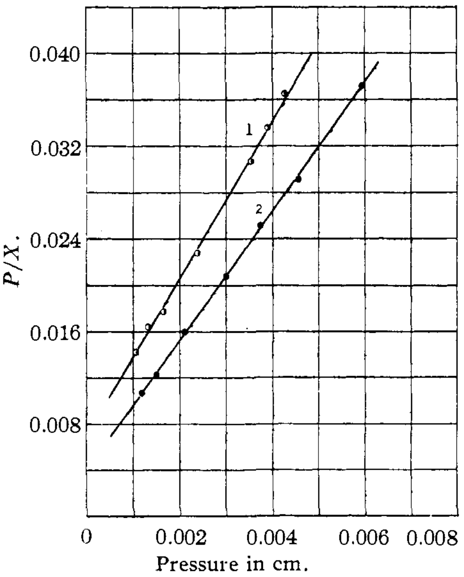

Fig. 3.—Isotherms for CO plotted according to Langmuir's equation: curve 1 for pumped-out surface; curve 2 for baked-out surface.

tween the two kinds of adsorption. His data also fit the Langmuir equation closely. Langmuir's saturation value is much lower than the other two but as it is based on only two observations it cannot be given the same weight. Assuming that the geometric surface is also the true surface area, the amount of gas adsorbed at saturation corresponds to the completion of a monomolecular layer of carbon monoxide on the mica surface. In fact, the calculated amount of coverage comes so near to 100% that there is little doubt that the geometric surface area is nearly the true area.

TABLE IV

COMPARISON OF SATURATION ADSORPTION OF CARBON MONOXIDE ON MICA AT −183° AS OBSERVED BY DIFFERENT INVESTIGATORS

Investigator	Type of adsorption	c_1, molecules per sq. cm.	Percentage of surface covered[a]
Langmuir	Total	0.252×10^{15}	38
Bawn	Total	.745	113
Armbruster and Austin	Total	.715	108
Armbruster and Austin	Weakly held	.557	84
Armbruster and Austin	Strongly held	.164	24

[a] Assuming complete coverage to be 0.66×10^{15} molecules per sq. cm.

The slow rate of adsorption of carbon monoxide has been reported by both Langmuir and Bawn. Langmuir ascribed it to slow diffusion of the gas through the small spaces separating the plates of mica, but Bawn construed it to be evidence of "activated" adsorption, which seems a more plausible explanation.

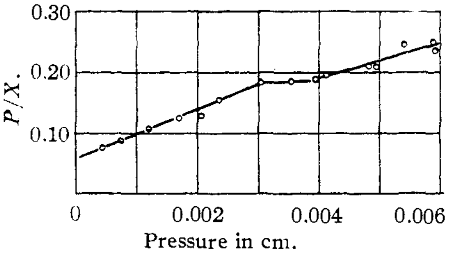

Fig. 4.—Isotherm for argon plotted according to Langmuir's equation.

The adsorption of argon (Table I) cannot be represented over the whole range of pressure by the simple Langmuir equation. Instead, it appears to take place in two steps, each of which follows the equation fairly closely (see Fig. 4). The amount adsorbed at saturation, calculated from the slope of the second step, is compared in Table V with the values obtained by Langmuir and by Bawn. In contrast to the adsorption of carbon monoxide, our datum for argon is apparently in much better agreement with Langmuir's than with Bawn's, but as Langmuir's value is based on only two observations, and as there is some scatter to the points in Fig. 4, which allows a small choice on the slope of the line, the exact agreement appears to be purely fortuitous and should not be given too much weight. Moreover, as the data of Table I and Fig. 4 stop at a much lower pressure than Bawn's it is possible that there might have been another step had they been carried to a higher pressure range.

TABLE V

COMPARISON OF SATURATION ADSORPTION OF ARGON ON MICA AT −183° OBSERVED BY DIFFERENT INVESTIGATORS

Investigator	c_1 molecules per sq. cm.	Percentage of surface covered[a]
Langmuir	0.131×10^{15}	17
Bawn	.233	30
Armbruster and Austin	.134	17

[a] Assuming complete coverage to be 0.66×10^{15} molecules per sq. cm.

It is clear, however, that whereas the isotherm for total adsorption of carbon monoxide (Fig. 2) follows that determined by Bawn quite closely, but differs markedly from Langmuir's, the isotherm for argon is much nearer to Langmuir's than to Bawn's, at least over the pressure range investigated.

The adsorption of argon on mica at pressures below 3×10^{-4} mm. also has been measured by Zickermann,[3] who used a method radically different from that used by any of the authors included in Table V, whose methods were substantially identical. Zickermann determined the rate of change of pressure in an empty vessel and in the same vessel containing the adsorbing surface when gas was admitted at a known rate, and calculated adsorption from the difference, a rather involved method about which relatively little is known. With this method it is necessary to assume that adsorption is instantaneous, hence the accuracy of the results obtained with it depends entirely upon the extent to which this assumption is justified. Zickermann believes that he has established the validity of the assumption, which may be true for the pressure range in which he worked, but the fact that three independent observers have found the rate of adsorption at higher pressures to be slow casts some doubt upon the accuracy of his results. Certainly, it would be desirable to have more evidence for the validity of the basic assumption than has yet been advanced. With this in mind it should be noted that Zickermann found the amount of adsorption of argon on mica at liquid air temperature to be much less than that found by others. Judging from the curves given in his paper, an apparent saturation was reached at a concentration of about 0.15×10^{13} molecules per sq. cm. which is 100 times less than the concentrations given in Table V.

His data at very low pressures do not follow Langmuir's equation, there being a marked deviation from a linear isotherm, and he concludes from this that the initial adsorption takes place on active centers which hold about 0.4×10^{12} molecules per sq. cm. It is entirely reasonable to suppose that there are active centers on the surface of mica, as will be shown in a later section, but it is difficult to subscribe to Zickermann's quantitative estimate in view of the uncertainties involved.

All available data indicate that at saturation not more than one-third of the mica surface is covered with argon atoms, so that the adsorbed layer is less than a complete monomolecular film.

Active Centers.—The data for carbon monoxide (Table IV) show that only about three-fourths of the gas on a saturated surface can be removed by pumping at −183°; the remainder can be taken off only at a higher temperature, which indicates that although most of the gas is held to the surface by a relatively weak physical adsorption, about one-fourth is held much more strongly.

That these strongly-held molecules are carbon monoxide and not some impurity in the gas is indicated by the following evidence. Condensable gases, such as water or carbon dioxide, are removed by the liquid air trap, consequently, the only impurity able to get into the adsorption bulb would be a non-condensable gas—and the only likely one is air. Strong adsorption of an inert gas such as nitrogen is not to be expected on principle, nor is any indication of it found in Langmuir's measurements, hence, the only gas which might be present and at the same time be strongly adsorbed on mica is oxygen. But oxygen is not present, because the same preparation of carbon monoxide shows no measurable adsorption on a reduced iron surface at room temperature—and direct experiment shows that under these conditions any oxygen present would be strongly adsorbed.

The amount of strongly-held carbon monoxide is difficult to determine exactly because it is calculated by taking the difference between two large numbers, each of which is subject to some variability, but the best estimate, based on what appear to be the most reliable isotherms, is 1.6×10^{14} molecules per sq. cm. assuming that the geometric area of the surface is the true area.

The existence of two kinds of adsorption implies a non-homogeneous surface containing spaces or points which are more active than others, and it is of interest to see what evidence there is as to their nature. It is possible that they are submicroscopic cracks or fissures into which the gas condenses, but this seems unlikely for several reasons: (1) gas adsorbed in this manner would not be expected to be so strongly held or so reproducible in amount; (2) a precisely similar behavior on certain types of iron surface in which the active points are removed by reduction with hydrogen. A more probable explanation is that there are certain atoms or ions exposed on the mica surface to which a carbon monoxide molecule becomes strongly attached.

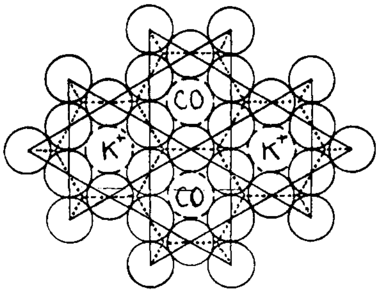

Fig. 5.—Diagram after Pauling showing suggested position of active centers for adsorption of CO on mica surface.

Pauling[4] states that when mica is cleaved the bonds of the univalent potassium ions are broken and separation takes place on the plane of these ions. He also believes[5] that on cleavage the potassium ions divide themselves equally between the two new surfaces, leaving spaces upon which strong adsorption might occur. The position of these spaces is shown in Fig. 5 which is based upon Fig. 3 of his paper on the structure of mica.[4] On this basis there is one such space for every rectangle 5.19×8.99 Å., which means one space for each area of 46.67 Å.^{2} or 2.1×10^{14} molecules per

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[4] Pauling, *Proc. Nat. Acad. Sci.*, **16**, 123 (1930).

[5] Pauling, personal communication.

sq. cm. The agreement with the observed number of active points, *i. e.*, 1.6×10^{14} molecules per sq. cm. is not exact; nevertheless, it is close enough to lend strong support to the view that carbon monoxide is held more strongly on the places left vacant by these ions than it is on the remainder of the surface.

In addition to the error of observation which is involved in the value 1.6×10^{14} molecules per sq. cm., there may also be present a systematic error which would tend to make this value low. If, for example, the baking-out process does not remove all the strongly held carbon monoxide molecules, the total adsorption observed in subsequent measurements, and hence the calculated number of active spaces, will be lower than it is in fact. The data in the tables represent measurements made after a number of heatings when the adsorption appeared to have attained a constant and reproducible value, but it was noted, both in the present investigation and in Bawn's, that in the first two or three sets of measurements the total adsorption tended to increase after each baking. It may well be, therefore, that the fact that no further adsorption occurred in later measurements does not mean that the surface is completely clean but merely that it is as clean as it is ever likely to become with the outgassing treatment adopted. Although this possibility cannot be dismissed, the agreement between the amount of carbon monoxide adsorbed at saturation as found in the present investigation with that reported by Bawn (Table IV) would seem to preclude any large error from this source.

If the conclusion as to the nature of the active spaces is correct, it might be supposed that these would be the spaces upon which inert gases such as argon or nitrogen are adsorbed, on which basis the amount of these gases adsorbed at saturation would be 2×10^{14} molecules per sq. cm. The experimental evidence shows that this is approximately true, as can be seen from Table VI, which gives the saturation concentration for different gases as reported by different investigators. With the exception of Langmuir's datum for oxygen and Bawn's for argon the several values lie so closely within the range 1.3 to 1.8×10^{14} molecules per sq. cm. that one is justified in concluding that these gases are all adsorbed on the same active spaces. Moreover, the fact that the observed number of these spaces approaches the number of spaces left vacant by potassium ions, namely, 2×10^{14} molecules per sq. cm. makes it probable that these spaces are indeed those upon which adsorption occurs. One possible weakness in this line of reasoning is that argon appears to be adsorbed in steps—as if there were more than one kind of elementary space, a behavior for which no convincing explanation has been found.

TABLE VI

COMPARISON OF CONCENTRATION OF MOLECULES OF DIFFERENT GASES AT SATURATION AT −183° (90°K.) WITH NUMBER OF SPACES LEFT BY POTASSIUM IONS

Gas	Concn. in molecules per sq. cm.	Investigator
CO (strongly-held)	1.6×10^{14}	Armbruster and Austin
A	1.4	Armbruster and Austin
A	2.3	Bawn
A	1.3	Langmuir
N_2	1.4 to 1.70	Langmuir
O_2	1.80	Bawn
O_2	0.88	Langmuir
Spaces from structure data	2.1	Pauling

Form of the Isotherm.—The fact that the results for carbon monoxide can be represented accurately by the simple Langmuir isotherm and fall nicely on a straight line when plotted as in Fig. 3, is surprising because Langmuir's derivation of this isotherm assumes a homogeneous adsorbing surface whereas the mica surface is clearly not homogeneous. One would expect to find that the adsorption followed equation 33 of Langmuir's original paper[1] which he found applied to the adsorption of carbon monoxide on glass, yet our values, and Bawn's as well, fit the simpler equation over a wide range of pressure. It may be that after the active spaces are filled the remainder of the surface is virtually homogeneous so far as adsorption of carbon monoxide is concerned, which would account for the observed result for the gas that can be removed by pumping at −183°, but there seems to be no satisfactory way of explaining why this relation holds for the total adsorption of carbon monoxide on the basis of the mechanism postulated by Langmuir. It might be argued that the observations do not extend to a low enough pressure to observe a deviation from the simple isotherm but Bawn's measurements were carried to pressures of only a few microns, and if any deviation does occur, at least some indication of it should be observed in this range. The difficulty appears, therefore, to be a real one, and its existence implies that Langmuir's postulates are sufficient but not necessary conditions for the simple adsorption isotherm.

This failure of the Langmuir mechanism recalls another one, which has been recognized for many years, namely, that his postulates do not account for the observed variation of the saturation adsorption with temperature. Each of these difficulties arises from a too minute specification of the adsorption process and both may be avoided by using a more general thermodynamic view. Thus, an isotherm which has the Langmuir form, at least in the range of moderate pressures, has been derived by Volmer[6] starting from a two-dimensional gas law analogous to van der Waals' equation, and it has been shown by Wilkins and Ward[7] that the temperature variaton of the amount adsorbed at saturation is of the same order of magnitude as the thermal expansion coefficient of an ideal gas. If, therefore, it is assumed that the adsorbed carbon monoxide is a mobile two-dimensional gas, an assumption which is supported by evidence given in the next section, then the linear relation between p/x and p is to be expected from Volmer's line of reasoning.

The adsorption of argon is quite different. The data fit neither Volmer's equation nor Langmuir's isotherm for a homogeneous surface, but are represented by Langmuir's equation for a surface with two kinds of elementary spaces. The fact that Volmer's equation is not obeyed may be taken as further evidence that the adsorbed argon is not mobile but is held on active centers. The exact interpretation to be placed upon the fact that Langmuir's equation for a non-homogeneous surface holds is not clear. In view of the evidence that argon is adsorbed only on certain active spaces, it implies the existence of two kinds of spaces but it is difficult to determine from adsorption measurements alone what these two types may be. It is not impossible, however, that the more complex equation fits merely because it has more arbitrary constants and that too fine conclusions as to mechanism are not warranted.

Most of the many equations for the isotherm which have been proposed from time to time are substantially equivalent to Langmuir's, but there is one recently proposed by Palmer[8] and shown by him to hold for the adsorption of vapors of organic compounds on fused silica, which is quite different and which appears to have a special usefulness because it provides an easy method of calculating the spreading force of the adsorbed film. Palmer found that over a considerable range of pressure the logarithm of the adsorption potential $\phi(\phi = RT \ln P_s/P)$, where P_s is the condensation pressure of the gas at that temperature and P is the observed pressure, is a linear function of a, the amount of gas adsorbed at pressure P; hence the potential is given by

$$\phi = \phi_0 e^{-sa} \qquad (2)$$

where e is the base of natural logs and s is a constant.

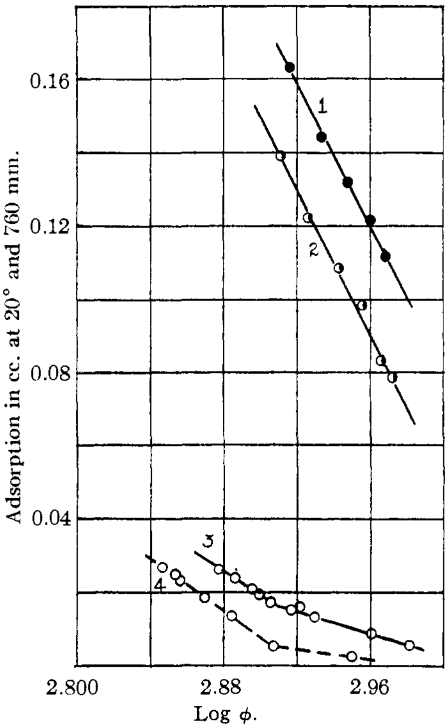

Fig. 6.—Isotherms for CO and A plotted according to Palmer's equation: curve 1, CO on baked-out surface; 2, CO on pumped-out surface; 3, argon on baked surface; 4, Bawn's data for argon.

This relation accurately represents the adsorption of carbon monoxide on mica as can be seen from the upper curves in Fig. 6, which show typical data for each type of adsorption plotted in this form. The constant difference between the two kinds of adsorption, which corresponds to the amount strongly held on active centers, is clearly revealed in the diagram. This figure also reveals a disadvantage of the Palmer isotherm relative to Langmuir's, namely, that it is not possible to extrapolate to the amount adsorbed at saturation.

The results with argon, shown by curve 3 of

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[6] Volmer, *Z. physik. Chem.*, **115**, 252 (1925).

[7] Wilkins and Ward, *ibid.*, **144A**, 259 (1929).

[8] Palmer, *Proc. Roy. Soc.* (London), **A160**, 254 (1937).

Fig. 6, do not fit on a single straight line as do those with carbon monoxide, but can be fairly well represented by two straight lines. Bawn's data for argon on mica are also included (curve 4) and show the same general behavior for which we have no completely satisfactory explanation. The course of curve 4 at low pressures is, however, very similar to the isotherm obtained by Palmer and Clark[9] for the adsorption of cyclopentane on vitreous silica, and, as they have pointed out, this general form agrees with the predictions of Polanyi's theory. It may well be, therefore, that this behavior is characteristic of adsorption at low pressure.

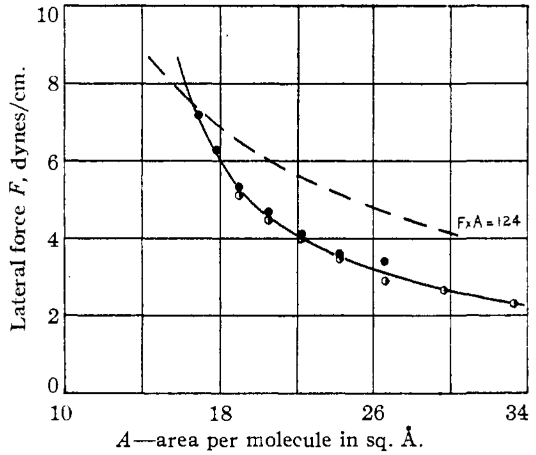

Fig. 7.—Diagram showing calculated variation of lateral force in the film with surface area per molecule.

Equation of State for Adsorbed Films.—The Gibbs adsorption equation may be written

$$A\mathrm{d}F = \mathrm{d}\phi_T \qquad (3)$$

where A is the area per molecule, F is the spreading force and ϕ_T is the adsorption potential at temperature T. By the use of his relation $\phi_T = \phi_0 e^{-sa}$, Palmer[8] has integrated this equation to obtain

$$F = f\phi_0 e^{-sa}\,(a + 1/s) + I \qquad (4)$$

where f is a numerical factor for reducing the result to the desired units and I is the constant of integration. In applying this relation to his data, Palmer adjusted I to take care of some departure from his isotherm at low pressures, but as the curves for carbon monoxide on mica (Fig. 6) are linear over the whole range of pressure investigated, the value of I obtained by extrapolating these lines to zero adsorption has been used in the present case. This may introduce a slight, but not serious, uncertainty into F.

The spreading force of the adsorbed carbon monoxide calculated by means of equation (4) is of the same order of magnitude as the spreading force of surface films on liquids and its variation with the surface area per molecule, shown by the solid curve in Fig. 7, is very similar to corresponding curves for surface films on water. Moreover, this curve lies not far from the curve representing the perfect gas law for a two-dimensional gas, *i. e.*, $FA = kT = 1.372T$, shown by the dashed line in the figure, and the deviation from ideality is very much like the deviation of an imperfect gas from the perfect gas law for three dimensions. The correspondence is further demonstrated by the fact that the data for the adsorbed film are represented by the following analog of the van der Waals equation.

$$\left(F + \frac{3090}{A^2}\right)(A - 10) = 124 \qquad (5)$$

There seems little room to doubt, therefore, that the adsorbed carbon monoxide behaves as a mobile two-dimensional gas and shows the same behavior as many insoluble films on water. It should be noted that the spreading force goes up rapidly as the area per molecule approaches 15.1 Å.^{2}, the area per molecule calculated from the molecular volume in the liquid, indicating that the monomolecular layer is approaching completion.

The spreading force of the adsorbed argon is very small over the whole range of pressure investigated, being never more than a small fraction of a dyne per cm., which implies that the adsorbed argon does not behave as a mobile gas but appears to be held on active centers, although the possibility of jumping from one such space to another is not excluded.

The accumulated evidence gives ample reason for concluding that there are at least two kinds of adsorption on the mica surface: (1) adsorption on active centers, such as is observed with argon and the strongly-held carbon monoxide, in which the adsorbed molecules occupy fixed positions; (2) a general surface adsorption, due to physical forces of the van der Waals type or to dipole interaction, in which the molecules are free to migrate over the surface, and show the characteristic behavior of an imperfect two-dimensional gas.

Acknowledgments.—The authors are greatly indebted to Professor Linus Pauling for his suggestions and discussion on the nature of the active centers.

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[9] Palmer and Clark, *Proc. Roy. Soc.* (London), **A149**, 360–384 (1925), *cf.* Fig. 10.

Summary

1. The adsorption of carbon monoxide and of argon on mica has been determined at −183°. The data for carbon monoxide are in excellent agreement with those of Bawn but are not in accord with those reported by Langmuir, whereas the results with argon show better agreement with Langmuir's data than with Bawn's. At saturation the mica surface is completely covered with a monomolecular layer of carbon monoxide but is only 17% covered with argon.

2. The rate of adsorption is certainly not instantaneous with either gas, indicating that the process is not physical adsorption alone.

3. Two types of adsorption of carbon monoxide were observed. The first, which covers approximately a quarter of the surface, cannot be removed by pumping at −183° but can be taken off only at a higher temperature. The second, which covers the rest of the surface, can be removed by pumping at −183°. It is concluded that argon and the strongly-held molecules of carbon monoxide are adsorbed on active centers and it is suggested that these centers are the points on the mica surface from which a potassium atom is removed on cleavage. Support for this view is obtained from X-ray data.

4. The adsorption of carbon monoxide follows the simple Langmuir isotherm even though the surface is not homogeneous. The adsorption of argon follows the Langmuir equation for two kinds of elementary spaces. Palmer's isotherm represents the results with carbon monoxide but does not fit those for argon.

5. The spreading force of adsorbed carbon monoxide is calculated. It varies with the surface area per molecule in the same way as the spreading force of insoluble films on water. The adsorbed gas follows a two-dimensional van der Waals equation and shows the general behavior characteristic of a two-dimensional gas. The spreading force of adsorbed argon is very small over the entire pressure range investigated.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Electron Diffraction Investigation of the Molecular Structures of Isobutane, *t*-Butyl Chloride and *t*-Butyl Bromide[1]

BY J. Y. BEACH[2] AND D. P. STEVENSON

The concept of the tetrahedral carbon atom has been an indispensable part of chemistry for many years. For much of that time, however, it remained a hypothesis necessary to account for the number and properties of the isomers of carbon compounds that could be prepared. It was not until the advent of X-ray and electron diffraction methods that the concept was put on a direct quantitative basis. The X-ray investigations of diamond and carborundum afforded the first direct evidence for the tetrahedral carbon atom. More recently electron diffraction methods have been used to prove the tetrahedral form for the gas molecules of carbon tetrafluoride, carbon tetrachloride, carbon tetrabromide, tetramethylmethane and other group IV compounds. Many other molecules, methylene chloride, chloroform, etc., have been shown to be only slightly distorted from tetrahedral symmetry. It is with this question of distortion of tetrahedral angles that we are concerned in the present investigation.

Because of the electrostatic and steric repulsions of the methyl groups it is to be expected that the C–C–C angle in isobutane is greater than the tetrahedral angle (109° 28′). In discussing *t*-butyl chloride and *t*-butyl bromide it is not immediately clear what effect the substitution of a halogen atom for a hydrogen atom will have on the C–C–C angle. The charge on the hydrogen atom, because of the direction of the C–H moment, is positive.[3] The electrostatic attraction of the negative halogen atom for the positive hydrogen atoms would tend to spread the C–C–C angle more than in isobutane. But, on the other hand, the increased steric repulsion between halogen and hydrogen atoms would tend to decrease the C–C–C angle below that in isobutane and possibly below the tetrahedral angle.

Assuming that the charges giving rise to the di-

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[1] These results were presented to the American Chemical Society at Rochester, N. Y., September, 1937.

[2] National Research Fellow in Chemistry.

[3] C. P. Smyth, *J. Phys. Chem.*, **41**, 209 (1937).