
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

(Registered in U. S. Patent Office)

VOLUME 71

AUGUST 16, 1949

NUMBER 8

[CONTRIBUTION FROM THE SOUTHERN RESEARCH INSTITUTE]

Physical Adsorption from Mixtures of Gases. I. Oxygen-Nitrogen and Oxygen-Argon on Chromic Oxide Gel at -185.6°C ¹

BY LOCKE WHITE, JR., AND CHARLES H. SCHNEIDER

In recent years, several attempts have been made to improve the B.E.T. theory of multimolecular adsorption² so that it will be accurate over a wider range of pressures. Most of these attempts³ have refined some one of the postulates of the B.E.T. theory and have then examined the implications of the refinements. A somewhat different approach was adopted by Hill,⁴ who proposed to test an implication of what he considered to be the most important postulate of the B.E.T. theory, that the adsorbate in all layers after the first has the same evaporation-condensation properties as it has in bulk. If this is true, he reasoned, the isotherms for adsorption from mixtures of gases can be predicted from a knowledge of the individual isotherms and of the vapor pressures of condensed mixtures of the gases. Hill developed the mathematical form of the isotherms for mixtures and proposed that experimental data be compared with the predictions, in the hope of learning something of the validity of the fundamental B.E.T. postulate.

Suitable experimental data were not available for the comparison, and the present study was undertaken to provide them.

Hill suggested that the comparison between theory and experiment be made in the form of isotherms in which the partial pressure of one gas is held constant while the partial pressure of the other gas is varied. On account of the difficulty of

holding constant one partial pressure while varying the other, it is impracticable to obtain such isotherms by direct measurement. Instead, the procedure actually employed was to measure isotherms in which the *quantity* of one gas in the adsorption system was held constant, while the quantity of the other gas was progressively increased. From a set of isotherms measured under these conditions, there could be read the data needed to construct isotherms of the type desired for the comparison. Thus each point on any single isotherm in Figs. 3-10 is taken from a different day's measurement, but a single day's measurement contributes points to several of the isotherms. The conversion of direct experimental data into the form desired for comparison is explained more fully in the next section.

Experimental Details

Apparatus.—Figure 1 is a schematic diagram of the apparatus. The two gas burets were of conventional design⁵ and had a capacity of nearly 200 ml. One buret was calibrated by weighing the mercury required to fill its various bulbs; the other was used in a manner which did not require calibration. The temperature of their jackets was not controlled, but the jacket of the calibrated buret was filled with water to minimize temperature fluctuations. The mercury in the manometer was always brought to a constant level, as indicated by the "magic eye" device of Mills.⁶ In order to ensure that the gas throughout the system was in equilibrium with that adsorbed on the surface, an all-glass circulating pump was used, similar to that of Porter, Bardwell and Lind.⁷ Analysis of the gas in the system was by means of Pauling's oxygen analyzer,⁸ which gave the partial pressure of oxygen directly; the partial

(1) This research was supported jointly by the Office of Naval Research and the Institute-Sponsored Research Fund of Southern Research Institute.

(2) S. Brunauer, P. H. Emmett and E. Teller, *THIS JOURNAL*, **60**, 309 (1938).

(3) See, for example, R. B. Anderson, *ibid.*, **68**, 686 (1946); M. A. Cook, *ibid.*, **70**, 2925 (1948); W. C. Walker and A. C. Zettlemoyer, *J. Phys. Coll. Chem.*, **52**, 47 (1948).

(4) T. L. Hill, *J. Chem. Phys.*, **14**, 286 (1946).

(5) See, for example, W. E. Barr and V. J. Anhorn, *Instruments*, **20**, 454, 542 and 716 (1947).

(6) B. Mills, *Rev. Sci. Inst.*, **12**, 105 (1941).

(7) F. Porter, D. C. Bardwell and S. C. Lind, *Ind. Eng. Chem.*, **18**, 1086 (1926).

(8) L. Pauling, R. E. Wood and J. H. Sturdivant, *THIS JOURNAL*, **68**, 795 (1946).

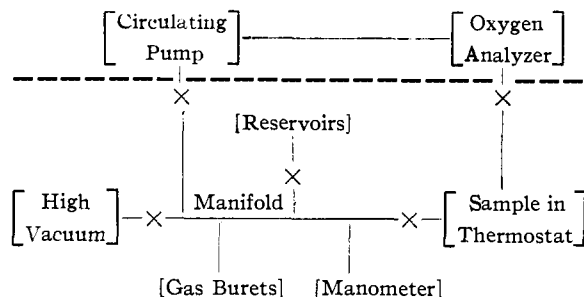


Fig. 1.—Schematic diagram of apparatus.

pressure of nitrogen was obtained by subtraction from the total pressure. A commercial model of the analyzer⁹ was used, with a nominal range of 0-200 mm. For reasons unknown, the commercial calibration was in error by some 10%, but a corrected calibration remained both linear and constant during more than a year of use. It was demonstrated that, after almost negligible corrections for the paramagnetism of nitrogen or argon, the analyzer gave accurate readings for the partial pressure of oxygen, independent of the total pressure, over the range of pressures used in this investigation. The nipples and rubber tubing supplied in the analyzer were discarded, so that the system included only metal and glass (plus stopcock grease and Apiezon "W" wax, which was used for metal-to-glass joints). In spite of generous applications of glyptal to all exposed surfaces of the analyzer, there remained leaks totalling about 0.04 ml. at S.T.P. per twenty-four hours. However, the procedure used made this leak negligible.

The sample holder, diagrammed in Fig. 2, was designed to permit circulation through the sample without unnecessary increase in dead space. A rod filled most of the otherwise dead space between the sample and the ring seal at the top. The clearances between the concentric tubes and between the inner tube and the rod were not over a few tenths of a millimeter.

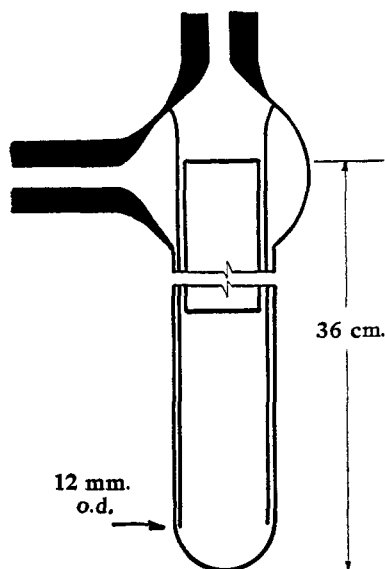


Fig. 2.—Sample Holder.

For temperature control, the sample holder was placed in a copper block which was separated from a surrounding bath of liquid nitrogen by a layer of hydrogen. Cooling by the liquid nitrogen was partially compensated by heat

supplied to the block, so that the desired temperature of -185.6° was maintained. The details of the arrangement were as follows: the sample holder fitted closely in a hole 6 inches deep in the center of the cylindrical copper block, $1\frac{1}{2}$ inches in diameter and 8 inches long, supported by three wires from a clamp about a foot above. On a layer of asbestos paper around the block for electrical insulation, there were wrapped 12 feet of No. 20 Nichrome wire, and the whole was covered with another layer of asbestos paper. Three copper-constantan thermocouples were placed in radial holes in the block, situated at the top, middle, and bottom of the region occupied by the sample. By means of a large rubber stopper fitted closely under the side-arm shown in Fig. 2, the sample holder and the block were sealed into a large "test-tube," 2.5 inches in diameter and 14.5 inches long, with a $\frac{1}{8}$ -inch hole in the bottom. The necessary electrical leads and the wires supporting the block passed through notches between the stopper and the tube; the notches were caulked with cotton and the whole joint was sealed with glyptal. Screws projecting radially from the block located it in the center of the "test-tube." Surrounding the "test-tube" was a Dewar flask, 5 inches in diameter and 12 inches deep, containing liquid nitrogen. A slow stream of hydrogen was passed into the top of the "test-tube" through a 2-inch length of 8-mm. glass tubing mounted in the rubber stopper. The hydrogen bubbled out of the "test-tube" through the hole in the bottom and so kept liquid nitrogen from contact with the copper block.

The three thermocouples were connected separately to a potentiometer to show that the maximum temperature differential over the region of the sample was less than 0.05° . Then the middle one, calibrated against a liquid-oxygen thermometer, was used both to measure and to control the temperature of the sample. The e. m. f. of the thermocouple was applied to a potentiometer. The light reflected from the mirror of the galvanometer shone on a phototube in a thyatron phase-shift circuit.¹⁰ One hundred and ten volt a.c. was applied to the plate circuit of the thyatron, and a 110-to-30 volt stepdown transformer in the plate circuit supplied the power to the heating coil on the block. Slow drifts in the zero point of the galvanometer were compensated by slight movement of the phototube. The operation of the control circuit was such that deviations from the null point did not exceed 1 mm., corresponding to about 0.08° . How much deviation from -185.6° may have been caused by stray e. m. f.'s in the thermocouple circuit is not known directly, but the close agreement of measurements taken many months apart seems to indicate that the strays were nearly negligible.

For heating the sample to clean the surface, the liquid nitrogen bath was removed and replaced with a Dewar flask fitting closely around the large "test-tube." The desired temperature (150°) was controlled by a Micromax, using the heating coil and stepdown transformer mentioned previously but now connected to the Micromax instead of the thyatron circuit.

Five-liter reservoirs were provided for oxygen, helium and either nitrogen or argon. Most of the tubing connecting the elements of Fig. 1 was 2 mm. capillary. The volume of the manifold to which the gas burets and manometer were attached was 8.7 ml.; the volume of the circulating pump and oxygen analyzer was 12.7 ml.; and the dead volume in the region of the sample was about 12 ml. The burets and manometer were connected to the manifold in such a way as to minimize the volume through which gas was not directly circulated by the pump; in other words, dead ends were avoided as much as possible.

Materials.—In order to adhere strictly to the conditions assumed by Hill's treatment, the surface of the adsorbent should preferably be plane. Because the adsorption of plane surfaces is small and difficult to measure, chromic oxide gel, which is not plane but which, when properly prepared, is known to be relatively free of fine capillaries, was adopted. It was prepared by the procedure of Em-

(9) Model "C," A. O. Beckman, 11 West State Street, Pasadena 2, California.

(10) See, for example, C. E. Waring and G. Robison, *Rev. Sci. Inst.*, **14**, 143 (1943).

mett and Cines.¹¹ A sample of 2.15 g. was used for these studies. To minimize the formation of capillaries, it was never heated over 180°, and over 150° only rarely and unintentionally. The reproducibility of isotherms obtained indicates that the surface was unchanged over the period of the measurements.

Oxygen was prepared by the thermal decomposition of potassium permanganate, in a slight modification of a procedure used at the National Bureau of Standards to prepare oxygen of sufficient purity for primary-standard vapor-pressure thermometers.¹² Tank nitrogen was purified by passing it slowly over reduced copper at 350° to remove oxygen and then through a bead-filled trap in liquid air to remove moisture. Tank helium was purified by passing it slowly over activated carbon at about -195°. The carbon was outgassed by heating under vacuum for sixteen hours at 300°. The procedures for both nitrogen and helium are those of Barr and Anhorn.⁵ Tank argon of 99.9% purity was used without further purification.

Procedure.—The surface of the sample was cleaned by evacuation to less than 10⁻³ mm. of mercury pressure at about 150°. It was established that evacuation for an hour under these conditions produced a reproducibly clean surface, but the treatment was usually continued overnight. While the sample was being cooled down in preparation for a measurement, the stream of hydrogen was not passed into the large "test-tube" of the thermostat. This permitted liquid nitrogen to come into contact with the copper block and to cool it very rapidly. The stream of hydrogen was connected only when the operating temperature was approached.

When an isotherm was to be determined with only one gas in the system, the conventional procedure was employed and the circulating pump and oxygen analyzer were not used. When an isotherm from a mixture was desired, slight modifications were required. The general procedure will be clear from consideration of a specific case. A quantity of nitrogen was measured in the buret and manifold and was then allowed to contact the adsorbent. All equilibrium adsorption readings with mixtures were taken with the burets filled with mercury, principally to avoid uncertainty as to the composition of the gas which would otherwise have remained in the burets without direct circulation into the rest of the system. When the equilibrium pressure was attained, the stopcocks connecting the manifold to the sample and the circulating pump were closed and most of the nitrogen left in the manifold was drawn into the uncalibrated buret, which was then closed off from the manifold. A quantity of oxygen, corrected for the residual nitrogen in the manifold, was then drawn into the calibrated buret and manifold. The adsorbent was then exposed to the gas in the manifold, the gas in both burets being forced into the system. In this procedure, no gas was lost from the system during the addition of further gas. Additional portions of oxygen were added to the system and adsorbed according to this procedure until the total pressure reached 900 mm. or the oxygen partial pressure reached 225 mm. At each equilibrium point, manometer and analyzer readings were recorded. Sometimes one gas was added first and sometimes the other, but the general procedure was the same in all cases.

For all the nitrogen-oxygen runs and for about half of the argon-oxygen runs, the sample was maintained at -185.6° throughout an entire run. For reasons to be explained later, during the latter half of the argon-oxygen runs the sample was allowed to warm up after each addition of gas until essentially all the gas was desorbed into the system; then the sample was cooled again to -185.6° and adsorption occurred.

From the data of the specific case described above there were prepared two graphs, each bearing two curves. On one graph, the volume of oxygen and nitrogen adsorbed were plotted against the pressure of oxygen. On the other

graph, the same volumes were plotted against the pressure of nitrogen. Similarly, from the data of each experimental run, two graphs, each containing two curves, were prepared.

It should be emphasized that, although any point on these four curves represents a perfectly general equilibrium condition between the partial pressures and the adsorbed volumes for the sample and temperature used, it would be possible to reproduce the identical curves only with an apparatus having the same ratio as ours between the weight of the sample and the volume of the system. This is true on account of the fact that the variable held constant in these measurements was the *quantity* of one of the gases in the system, in this case nitrogen.

For comparison with Hill's predictions, isotherms were required in which the *partial pressure* of one of the components is held constant. The data for these isotherms were obtained from the graphs described above. For example, suppose there is desired a point for an isotherm relating volume of oxygen adsorbed to partial pressure of nitrogen, at constant partial pressure P of oxygen. One of the graphs described above showed that in one run V_1 of oxygen was adsorbed at oxygen partial pressure P . From the other graph of the same run, it was found that, when V_1 of oxygen was adsorbed, the partial pressure of nitrogen was P_1 . Thus the desired point (P_1, V_1) was obtained. The rest of the points for the desired isotherms at constant partial pressures were obtained from the graphs of the directly measured data in a similar fashion.

Results

The comparison between Hill's predictions and these experiments is shown in Figs. 3-10. The individual circles are experimental observations, and the solid and dashed lines are theoretical predictions. The solid lines were calculated from Hill's equation (14), which is the extension to mixtures of the B.E.T. equation for unrestricted adsorption. The dashed lines of Figs. 5, 6, 9 and 10 were calculated from his equation (51), which allows for capillary condensation; whenever in these four figures no dashed line is shown, it is because the dashed and the solid lines coincide. The dashed lines have not been added to Figs. 3, 4, 7 and 8 because of the confusion which would have arisen from the frequent overlapping. Also to avoid confusion, fewer comparisons are included in some graphs than in others, although none were omitted which led to significantly different conclusions from those included.¹³

For all the experimental points of Figs. 3-10, a horizontal line in the circle indicates that oxygen was added first in the run from which the point was taken; a vertical line indicates that nitrogen or argon was added first. Open circles represent equilibria with only one constituent present. The fact that halves of some of the circles are blackened is of no significance, except to indicate which points go together.

In all the figures, V_m and P_0 are the values characteristic of the individual pure adsorbates.

To make the calculations for the solid curves, it was necessary to use two constants, C of the B.E.-

(13) Comparisons have been made for all combinations with the partial relative pressure of either component held constant at 0.05, 0.1, 0.2 and 0.3. A limited number of sets of photostats of the comparisons not included in this paper is available and, as long as the supply lasts, a set will be included with reprints requested from the authors.

(11) P. H. Emmett and M. Cines, *THIS JOURNAL*, **68**, 2536 (1946).

(12) R. B. Scott, in "Temperature," Reinhold Publishing Corp., New York, N. Y., 1941, p. 213.

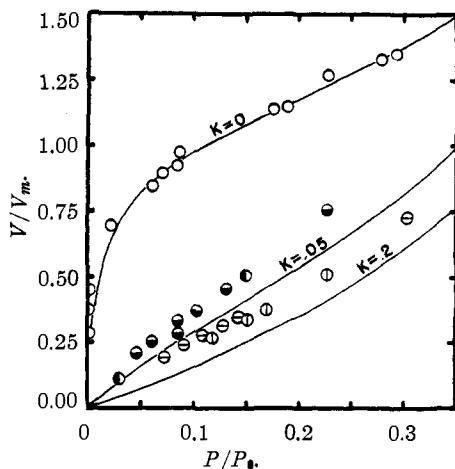


Fig. 3.—Oxygen adsorbed as function of oxygen pressure, nitrogen pressure being constant: $K = P/P_0$ of nitrogen.

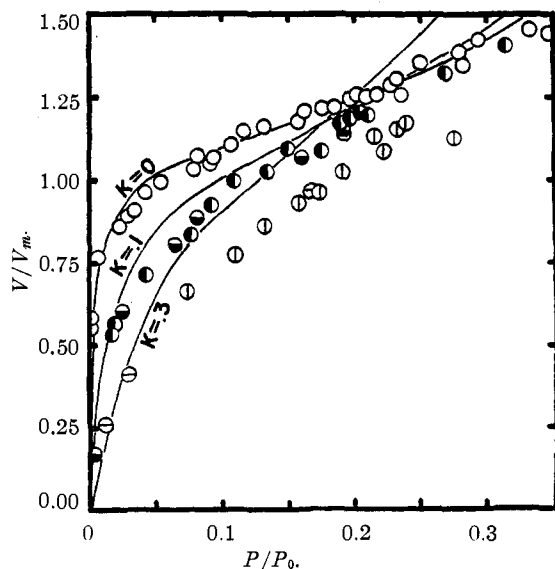


Fig. 4.—Nitrogen adsorbed as function of nitrogen pressure, oxygen pressure being constant: $K = P/P_0$ of oxygen.

T. equation and the volume equivalent to a monolayer, as determined from the isotherms of the individual pure components. The values used, which were calculated from the straight line of the usual B.E.T. plots, fitted by the method of least squares, were as follows:

	C	V_m^*
Argon	64.5	103.4
Nitrogen	462.6	90.1
Oxygen	68.1	111.6

* In ml. at S. T. P.

It was also necessary to know the vapor pressures of the binary mixtures involved. For nitrogen-oxygen, the data of the "International Critical Tables" were used; for argon-oxygen, those of

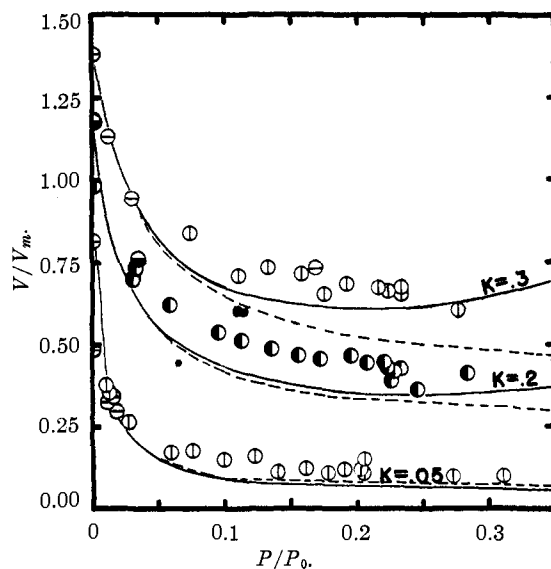


Fig. 5.—Oxygen adsorbed as function of nitrogen pressure, oxygen pressure being constant: $K = P/P_0$ of oxygen.

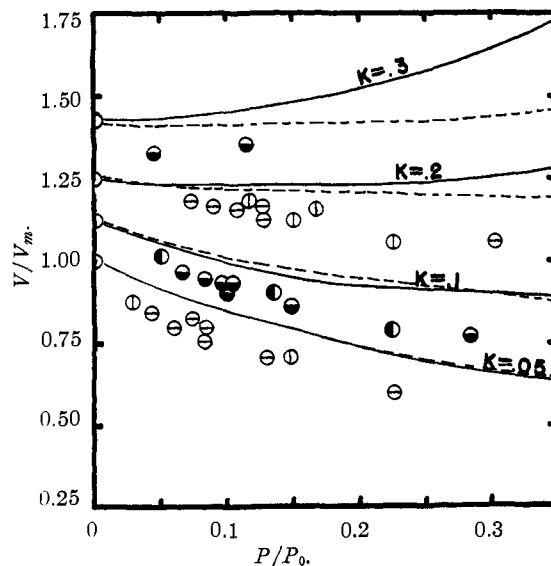


Fig. 6.—Nitrogen adsorbed as function of oxygen pressure, nitrogen pressure being constant: $K = P/P_0$ of nitrogen.

Bourbo and Ischkin.¹⁴ In both cases interpolation to -185.6° was required, but the interval was small enough that the method of interpolation was not very important.

For the dashed curves, it was necessary to use two other constants, n and g of Hill's equations (42 and 44), and these were obtained by fitting the oxygen isotherm of Fig. 11 as closely as possible with one of these equations. Although no combination of n and g predicted exactly the long, straight portion, the use of 4 and 1.5 for n and g

(14) P. Bourbo and I. Ischkin, *Physica*, **3**, 1067 (1936).

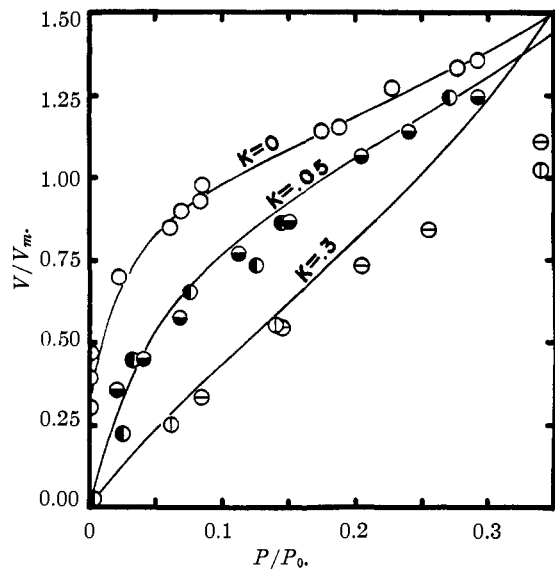


Fig. 7.—Argon adsorbed as function of argon pressure, oxygen pressure being constant: $K = P/P_0$ of oxygen.

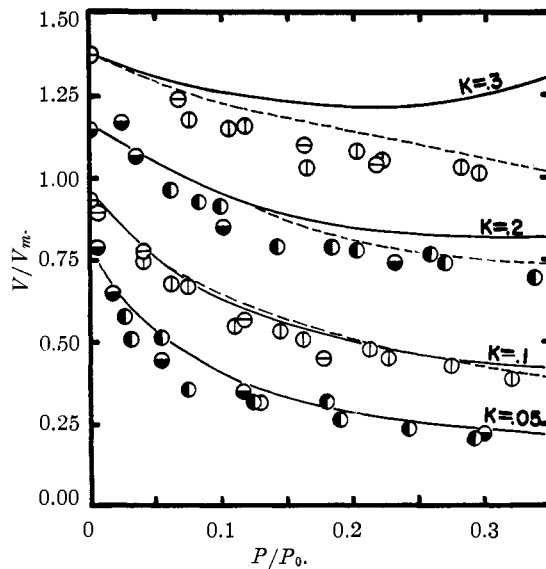


Fig. 9.—Oxygen adsorbed as function of argon pressure, oxygen pressure being constant: $K = P/P_0$ of oxygen.

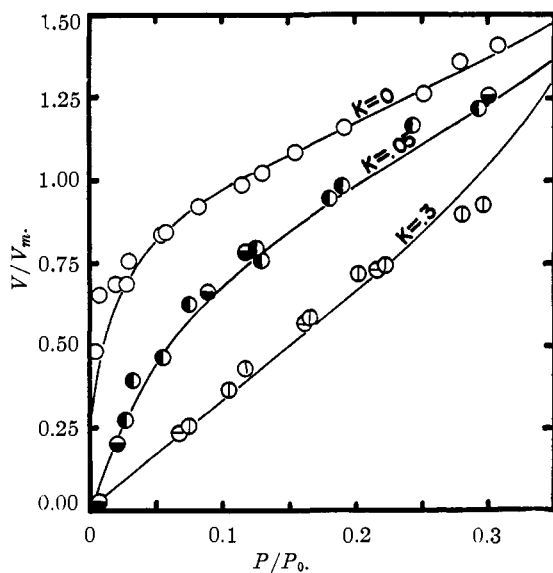


Fig. 8.—Oxygen adsorbed as function of oxygen pressure, argon pressure being constant: $K = P/P_0$ of argon.

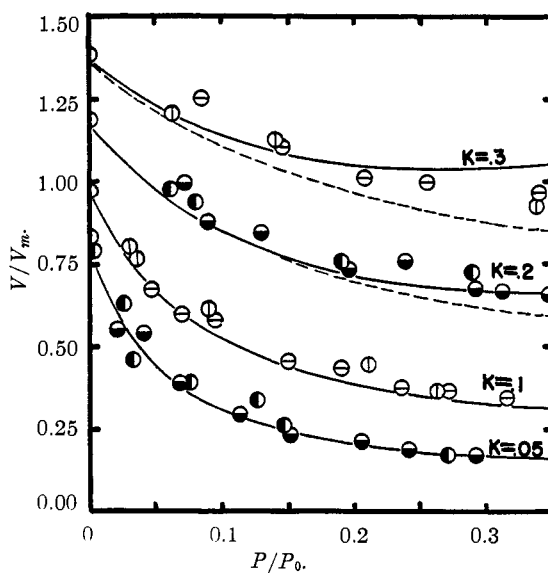


Fig. 10.—Argon adsorbed as function of oxygen pressure, argon pressure being constant: $K = P/P_0$ of argon.

gave an isotherm which never deviated by more than 3% from the observed adsorption isotherm for $0.05 \leq P/P_0 \leq 0.6$. In using Hill's equation (51), the g 's for argon and nitrogen were calculated from that for oxygen by his equation (54), assuming that $k_A = k_B$ and that the surface tension of the mixtures is a linear function of composition. Isotherms for pure argon and nitrogen, calculated from equation (44) on the basis of these assumptions, agreed with the experimental data as well as was the case with oxygen.

Figure 11 includes three isotherms of oxygen with desorption, which afford an indication of the

extent of capillary condensation. Adsorption-desorption isotherms for argon over a comparable range of relative pressure were very similar.

In appraising these data, it is important to know how well true equilibrium was approximated. Before the regular runs were started, a series of four test runs was made. The quantity of nitrogen used in each test run was approximately the same, and so was the quantity of oxygen (although the quantity of nitrogen was not equal to the quantity of oxygen). However, in two of the runs, the oxygen was adsorbed first and in two of the runs, nitrogen. In all four cases, the

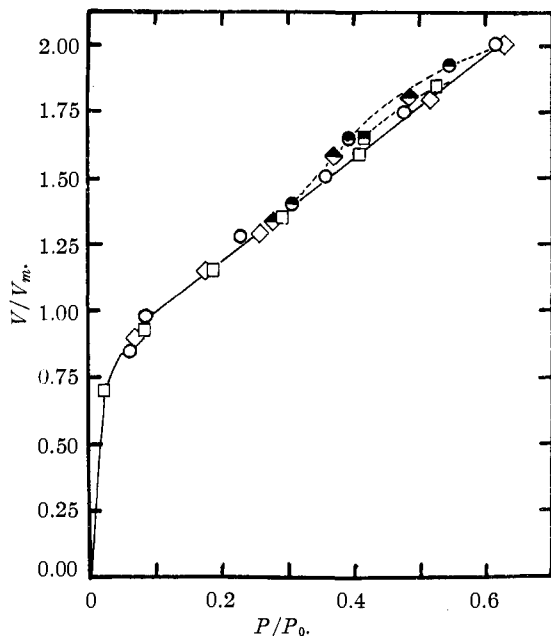


Fig. 11.—Adsorption-desorption isotherm for oxygen: open symbols and solid lines indicate adsorption; blackened symbols and dashed lines indicate desorption.

total pressure and the partial pressure of oxygen had reached values in forty-five minutes (usually in thirty minutes) which did not change for the next hour. With an agreement which was judged to be within the experimental error, the pressures reached were independent of which gas was adsorbed first. Therefore, it was assumed that a combination of total pressure and partial pressure of oxygen which was stable for about fifteen minutes represented a very close approximation to true equilibrium. All data reported here for oxygen-nitrogen were based upon that assumption.

About the middle of the argon-oxygen runs, it was necessary to interrupt a run, let the sample warm up, and cool it again for continuation of the run. It was noticed that the pressures obtained immediately after re-cooling did not agree with those before warming. Therefore, several experiments were performed in which the gases were added separately and allowed to come to apparent equilibrium, after which the sample was heated to room temperature and cooled again. The final partial pressures which resulted were invariably lower for both constituents, although the differences were nearly always less than 10%. In view of this finding, in the remaining oxygen-argon runs it was the practice at each point to desorb all the gas from the sample by heating and to adsorb again from the mixture, in order to obtain results more nearly indicative of true equilibrium. All the data for oxygen-argon in this paper were taken using this latter procedure. However, the previous data for oxygen-argon, obtained by the procedure used for oxygen-nitrogen, are indistinguishable from the later data. This seems to indi-

cate that, at least for oxygen-argon, the difference between the experimental procedures is either overshadowed by other experimental errors or compensated in some unknown way.

In the former procedure, when the total pressure and the partial pressure of oxygen had reached values which were constant for about fifteen minutes, these values did not change during several hours of observation. Whether the rate-limiting step in the approach to equilibrium was due to gaseous diffusion in the capillaries or to some phenomenon in the adsorbed layer was not determined; the former seems more plausible, since the average thickness of the adsorbed layer was almost never over two molecular diameters.

Whether a similar phenomenon really occurs with oxygen-nitrogen mixtures, contrary to the indications of the preliminary experiments quoted, was not determined, largely because of the fact that there was no consistent difference in the results obtained by the former procedure, regardless of which gas was adsorbed first. It can be seen in Figs. 3-6 that the differences due to which gas was adsorbed first are less than those due to other, undetermined causes.

In considering those isotherms of Figs. 3, 4, 7, and 8 in which only one component was present, it should be realized that most of the experimental points were not obtained in sequence. On the contrary, they were single, isolated observations, the first points of run with mixtures.

Discussion

Comparison of the experimental data with the solid lines (predictions of the basic B.E.T. equation extended to mixtures) permits the following generalizations:

(1) The total gas adsorbed from the mixture at any set of conditions tends to agree with Hill's equation (14) as well as the same quantity adsorbed of a pure gas agrees with the B.E.T. equation. For example, when oxygen alone is present and the volume adsorbed is twice V/V_m , the volume adsorbed is about 20% below that predicted by the B.E.T. theory for the corresponding value of P/P_0 , which is about 0.6; correspondingly, when P/P_0 for both oxygen and argon is 0.3, the combined volume adsorbed is nearly twice V/V_m and the individual adsorbed volumes of oxygen and argon are approximately 20% and 10% below the calculated.

(2) In oxygen-argon mixtures, at lower pressures there seems to be a tendency for slightly less oxygen to be adsorbed than theory predicts, and slightly more argon. At higher pressures, the adsorption of oxygen falls further below theory than does that of argon.

(3) In oxygen-nitrogen mixtures, at lower pressures oxygen is adsorbed more strongly than theory predicts, and nitrogen, less strongly. In fact, there is a tendency for the oxygen adsorbed to be as far above theory as nitrogen is below it, or, in other words, for the theory to predict the correct

TABLE I
COMPARISON OF MEASURED ADSORPTIONS WITH^a SELECTED CALCULATED ADSORPTION

	Oxygen-nitrogen				Oxygen-argon			
	Measured	Most probable	Calculated Comb. 1	Comb. 2	Measured	Most probable	Calculated Comb. 1	Comb. 2
	$(P/P_0)_1 = (P/P_0)_2 = 0.1$							
Oxygen	0.29	0.200	0.267	0.167	0.58	0.637	0.667	0.608
Nitrogen or argon	.95	1.006	.933	1.042	.55	.526	.497	.553
Total	1.24	1.206	1.200	1.209	1.13	1.163	1.164	1.161
	$(P/P_0)_1 = (P/P_0)_2 = 0.3$							
Oxygen	0.62	0.647	0.733	0.623	1.01	1.249	1.281	1.215
Nitrogen or argon	1.08	1.640	1.554	1.679	0.98	1.047	1.013	1.082
Total	1.70	2.287	2.287	2.302	1.99	2.296	2.294	2.297

^a In units of volumes equivalent to monolayers (V_m).

total adsorption but the wrong distribution between the adsorbates. At higher pressures, both measured adsorptions are lower than theory predicts, oxygen only slightly so, but nitrogen by as much as a third.

The first of these generalizations was to be expected, of course, since the extension of the theory to mixtures is hardly likely to be free of the limitations of the parent theory.

The third generalization especially (and to some extent the second) points to some feature not properly allowed for in the parent theory, probably horizontal interactions in the first layer.

By analogy with the situation when only one adsorbate is present, it might be expected that allowing for capillary condensation in the theory would minimize the discrepancies in total adsorption at high pressures. On the other hand, it is hardly to be expected that this allowance would affect very strongly the distribution between the adsorbates, especially at low pressures.

Examination of the dashed lines in Figs. 5, 6, 9, and 10 shows that allowing for capillary condensation very noticeably reduces the discrepancy between theory and experiment for the total adsorbed volume of oxygen-argon, although the experimental distribution between the adsorbates is still higher in argon than the theory predicts. In the case of oxygen-nitrogen, however, any improvement in the predicted total adsorption is gained at the expense of aggravating the discrepancy in the distribution between the adsorbates.

The accuracy of the calculations is dependent upon the accuracy of the constants previously quoted, especially C and V_m . These two constants are calculated from the slopes and intercepts of the usual B.E.T. plots.² The slopes and intercepts, with their probable errors as computed by established procedures,¹⁵ are as follows:

	Slope	Intercept
Argon	9.52 ± 0.034	0.15 ± 0.006
Nitrogen	11.08 ± .005	.024 ± .010
Oxygen	8.85 ± .021	.13 ± .012

(Units of both slopes and intercepts are 10^{-3} ml. -1 at S.T.P.) The volume equivalent to a monolayer

(15) H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry." D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 498 ff.

(V_m) is calculated as the reciprocal of the sum of the slope and the intercept. It is obvious that the probable errors of all the sums are quite small and, correspondingly, the probable errors of the V_m 's were only 0.4, 0.1 and 0.3% for argon, nitrogen and oxygen, respectively. But the constant C is calculated as unity plus the ratio of the slope to the intercept. Here the uncertainties in the intercepts, even though they are small on an absolute basis, are proportionately large and produce large uncertainties in the C 's. The probable errors of the C 's are 4.2, 38 and 7.7% for argon, nitrogen and oxygen, respectively.

Fortunately the fact that C cannot be determined very accurately from the isotherm has as a corollary the fact that the isotherm is not very sensitive to uncertainties in C of the magnitude just quoted. To demonstrate this fact, there have been calculated for selected pressures the volumes of gases which would have been adsorbed according to theory, had different values of the C 's been used. The partial relative pressures chosen were the same for both constituents in every case calculated, and the calculations were made for $P/P_0 = 0.1$ and 0.3. For both combinations of gases at each pressure, two extreme combinations of C 's were used:

$$\begin{aligned} \text{Combination 1: } & (C_1' = C_1 + (P. E.)_1 \text{ and } \\ & C_2' = C_2 - (P. E.)_2 \\ \text{Combination 2: } & C_1' = C_1 - (P. E.)_1 \text{ and } \\ & C_2' = C_2 + (P. E.)_2 \end{aligned}$$

A prime with a C denotes the value used in these latter calculations; the lack of a prime signifies the value used in calculating the continuous curves of Figs. 3-10; and the subscript identifies the gas with which the constants are associated. The results are shown in Table I. Oxygen is always component 1 in the combinations.

At first glance, these calculations seem to indicate that at the lower pressures the uncertainties in the C 's offer a fairly plausible explanation of the discrepancies between the predicted and measured adsorptions for mixtures of oxygen with both nitrogen and argon. However, the high value of C for oxygen is required to obtain agreement in the oxygen-nitrogen mixtures, while the low value is required for agreement with oxygen-argon. Since C for oxygen should be independent of the nature

of the mixture, it is doubtful that the uncertainties in the C 's offer a satisfactory explanation of the discrepancies at lower pressures. But the fact that variations in the C 's improve the agreement lends some support to the tentative hypothesis that horizontal interactions in the first layer account for the wrong distribution between the adsorbates, since such interactions would make the C 's variable.

However naive it may be to consider that closer fitting of Fig. 11 by equation (42 or 44) establishes the validity of the refinement of the B.E.T. model to allow for capillary effects, it seems considerably more significant that the parameters obtained by fitting the oxygen isotherm can so much improve the predicted adsorption from the mixtures. On the other hand, the validity of using 1.5 for g seems questionable, in view of the fact that the value calculated from Hill's equation (54), with $k = 1$ and S calculated from the cross-section of the oxygen molecule,¹⁶ is 18. In other words, the observed value of kS was only one seventh of the value to be expected for smooth, liquid packing of the top layer. That such a discrepancy can really be due to irregularities of packing seems unlikely.

Arnold¹⁷ has recently measured adsorption

(16) P. H. Emmett, in E. O. Kraemer's "Advances in Colloid Science," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942, p. 8.

(17) J. R. Arnold, *THIS JOURNAL*, **71**, 104 (1949). For comparing Arnold's results with ours, it must be emphasized that V_m and P_0 have different meanings in his paper than in ours.

from mixtures of oxygen and nitrogen on anatase. His results and ours agree in that the total adsorption conforms as well to Hill's theory as do the pure isotherms. But on anatase, nitrogen is adsorbed more strongly than theory predicts and oxygen, less strongly; this is just the reverse of the situation on chromic oxide gel. In fact, Arnold's results differ from Hill's theory much further than ours do in the pressure range we investigated. The differences between his results and ours at the lower pressure can hardly be attributed to capillary condensation and must rather be due to differing degrees of horizontal interactions on the two adsorbents.

Further experiments with other temperatures, adsorbents, and mixtures of adsorbates are being undertaken in the hope of obtaining more definite evidence as to the ultimate cause of such discrepancies between theory and experiment as those in the low-pressure region with oxygen-nitrogen mixtures.

Summary

1. Adsorption isotherms of binary mixtures of oxygen and nitrogen on chromic oxide gel at -185.6° have been measured and compared with Hill's⁴ extension of the B.E.T. theory.

2. With allowance for capillary condensation, the theoretical and experimental isotherms agree semi-quantitatively for both mixtures over the pressure range investigated.

SOUTHERN RESEARCH INSTITUTE

BIRMINGHAM, ALABAMA

RECEIVED JANUARY 24, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF CALIFORNIA]

The Complex Ions Formed by Iron and Thorium with Fluoride in Acid Solution^{1a}

BY H. W. DODGEN^{1b} AND G. K. ROLLEFSON

It has long been known that ferric fluoride is a weak electrolyte. Measurements^{1c} of the freezing point lowering, electrical conductivity, and the absence or very great inhibition of reactions characteristic of ferric ions and fluoride ions in solutions of ferric fluoride demonstrate this fact quite clearly. Peters² found that the electrical conductivity of a solution containing sodium fluoride and ferric fluoride was less than that of the separate solutions and that in a solution of Na_3FeF_6 the iron moved with fluoride toward the anode. This and other evidence^{1c} shows that a ferric fluoride anion does exist in solution; however, none of the above work yields the formulas of the complex ions or their degree of stability.

(1a) This work was performed under the auspices of the Manhattan District at the University of California during 1945 and 1946.

(1b) Present address: Department of Chemistry and Chemical Engineering, The State College of Washington, Pullman, Washington.

(1c) Abegg "Handbuch der anorganischen Chemie," 4 Band, 3 Abt. 2 Teil, p. B158, Verlag von S. Hirzel, Leipzig, 1935.

(2) Peters, *Z. physik. Chem.*, **26**, 195, 219 (1898).

It has become customary to write FeF_6^{3-} as the formula of the ferric fluoride complex ion, but Low and Pryde³ showed that this could not be the formula in acid solutions by studying the potential of the ferrous-ferric half cell as a function of hydrogen fluoride concentration. Their data can be interpreted quantitatively by assuming the equilibrium $\text{Fe}^{+3} + \text{HF} \rightleftharpoons \text{FeF}^{++} + \text{H}^+$. More recently Brosset and Gustaver⁴ interpreted potentiometric measurements on the ferrous-ferric half cell by assuming the existence of the ions FeF^{++} and FeF_2^+ , and Babko and Kleiner⁵ obtained equilibrium constants for the formation of the ions FeF^{++} , FeF_2^+ , FeF_3 , FeF_4^- , and FeF_5^{2-} from measurements on the decolorization of the ferric thiocyanate complexes with fluoride.

The first part of this paper presents the results of measuring the potential of the ferrous-ferric

(3) Low and Pryde, *THIS JOURNAL*, **61**, 2237 (1939).

(4) Brosset and Gustaver, *Sv. Kem. Tidskr.*, **54**, 185 (1942).

(5) Babko and Kleiner, *J. Gen. Chem. (U. S. S. R.)*, **17**, 1259 (1947).