

Fig. 1.—Activity ratio of cadmium iodide in heavy and light water at 25° as a function of concentration.

is transferred isothermally and reversibly from pure deuterium oxide solution to pure protium oxide solution is  $-398$  cal. This may be compared with about  $-225$  cal. for a similar transfer of potassium chloride.<sup>2</sup>

#### Correction for Differences in Molar Volume.—

Because a mole of  $D_2O$  occupies 0.36% more volume than a mole of  $H_2O$  at 25° a correction should be applied for the electrical work obtained on isothermally and reversibly expanding the ionic assembly in light water to the volume it would occupy in heavy water. Using the ap-

propriate e.m.f. equation for a cadmium iodide concentration cell, and assuming that the density and activity coefficients of the solutions do not change over a range of 0.36% variation in molality, it will be found that the value is 0.00014 volt. This correction should be added to the difference,  $E_H - E_D$ . It is about the order of the experimental error in measuring the most concentrated solutions and was neglected in treating the results.

#### Summary and Conclusions

1. The e.m.f. of cell (C) has been determined (C) Cd-Hg(2 phase)/CdI<sub>2</sub>( $m'$  in H<sub>2</sub>O, D<sub>2</sub>O)/AgI-Ag at 25° as a function of concentration,  $m'$ , of cadmium iodide in terms of moles of salt per 55.507 moles of total water species. By combining the results with light water data, relative stoichiometric mean ionic activity coefficients,  $\gamma_D$ , in deuterium oxide have been computed. The value of this activity coefficient is not unity at infinite dilution, but it affords a comparison of the activity behavior of cadmium iodide in the isotopic solvents.
2. At 0.1  $m'$  the e.m.f. of cell (C) was found to be nearly a linear function of the deuterium content of the solvent.

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## Adsorption of Gas Mixtures. Nitrogen-Oxygen on Anatase

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The data on multilayer adsorption of gas mixtures<sup>2</sup> are limited in quantity compared to those available on single gases. Moreover, the studies which have been made have employed chiefly charcoal and silica gel as adsorbents. These substances, while industrially important, are not suitable for fundamental studies, since the phenomena of multilayer adsorption and capillary condensation occur simultaneously on their surfaces. A further limitation of some of the studies<sup>3</sup> is the choice of pairs of adsorbates for which large deviations from additive properties, *e. g.*, Raoult's law, are to be expected. Such data are peculiar to the system studied, and cannot yield generally useful information.

Hill<sup>4</sup> has recently generalized the Brunauer-Emmett-Teller (BET) theory<sup>2,5</sup> to mixtures of gases, for which no or moderate deviations from

Raoult's law occur. This extension brings out the important fact that any statistical theory of adsorption can be generalized to give adsorption isotherms for such mixtures. Since the added assumption involved in the generalization will not introduce a large error, for a well-chosen pair of gases, the degree of agreement obtained between gas mixture data and the extended theory will provide evidence for or against the original theory. It will be shown below that the present study provides strong evidence against at least one of the postulates of the BET theory, and indications in favor of a quite different model.

The system chosen for this study was the gas pair nitrogen-oxygen on the adsorbent anatase (TiO<sub>2</sub>). The two gases have convenient vapor pressures at liquid nitrogen temperature, and their phase diagrams at this temperature show small deviations from Raoult's law. The analysis can be made readily by a direct method. The adsorbent is one which has been extensively studied,<sup>6,7</sup> and consists of single crystals, free from

(1) Present address: Institute for Nuclear Studies, University of Chicago, Chicago 37, Illinois.

(2) Brunauer, "The Adsorption of Gases and Vapors," Princeton University Press, Princeton, N. J., 1943, pp. 474-497.

(3) Rao, *J. Phys. Chem.*, **36**, 616 (1932); Tryhorn and Wyatt, *Trans. Far. Soc.*, **22**, 139 (1926).

(4) Hill, *J. Chem. Phys.*, **14**, 268 (1946).

(5) Hill, *ibid.*, **14**, 263 (1946).

(6) Jura and Harkins, *THIS JOURNAL*, **66**, 1356 (1944); Harkins and Jura, *ibid.*, **66**, 1362, 1366 (1944).

(7) Beebe, Beckwith and Honig, *ibid.*, **67**, 1557 (1945).

microscopic flaws and fissures, so that capillary condensation is minimized.

The usual technique for taking mixture adsorption data consists of varying gas composition at constant pressure in a static system. A flow method, in which data are taken over a range of pressures for a few definite gas compositions, has a double advantage. First, the time taken to reach equilibrium is greatly reduced by the elimination of diffusion block and, second, the isotherm equations come out in particularly simple form. This method was used in the present work.

### Experimental

**Materials.**—The anatase used in this study was supplied through the kindness of Professor W. D. Harkins. It was degassed under high vacuum at 300° before each run, and as frequently as necessary during the course of a run. Measurement of the area of a 3-g. sample, using nitrogen as adsorbate, in a multibulb apparatus of standard type<sup>9</sup> gave a value of 13.73 sq. meters/gram for its specific area, in good agreement with values obtained elsewhere.<sup>6,7</sup> The area of a 1.294-g. sample measured with the flow apparatus described below was 13.81 sq. meters/gram.

Five tanks of nitrogen-oxygen mixtures, containing 14.9, 29.8, 50.2, 70.2 and 85.3% oxygen, respectively, were obtained from the Linde Air Products Co. They were certified to contain less than 0.1% argon, and only traces of other non-condensable impurities. The nitrogen and oxygen used for the single gas isotherms were Air Reduction Co. Prepurified and Electrolytic grades, respectively.

The gases were passed over "Dehydrite" (magnesium perchlorate) to remove water, and used without further purification.

**Apparatus and Procedure.**—The measurements were made in the flow apparatus shown in Fig. 1. The detachable sample cell F has 2-mm. capillary leads to cut down dead space; the sample itself is about six inches below the surface of a liquid nitrogen bath. The anatase powder is prevented from blowing over by a loose-fitting glass ball-socket valve at the base of the bulb. The pretrap C consists of an identical sample of anatase in a liquid nitrogen bath, and serves to remove condensible impurities.

In operation, gas flows at the rate of 20 cc./min. through the capillary flowmeter A (maintained at slightly above atmospheric pressure), through the Hoke needle valve B, the pretrap C, the cell F, the Hoke needle valve H, and finally through the stopcock P to a Nelson roughing pump. The needle valves B and H allow the pressure in the cell system to be set at any desired value (as read on the manometer D). The time necessary for the adsorbed gas to come into equilibrium with the given mixture at a given pressure was tested in a series of preliminary experiments. A running time of eight to ten minutes was found to be sufficient, except at very low pressures, where the flow rate had to be decreased to prevent excessive pressure drops in the line, and at pressures near the condensation pressure, where especially large volumes of gas were taken up. The running time used in the actual measurements was approximately thirty minutes.

At the end of this period valves B and H are closed simultaneously, and the pressure read on manometer D. The temperature was read on a nitrogen vapor pressure thermometer<sup>8</sup> with bulb immersed in the bath surrounding F. Data used for calibration were those of Dodge and Dunbar.<sup>10</sup> Stopcocks E and G are then closed, valve H opened, and the system evacuated through stopcock N. The analytical train, consisting of Toepler pump K, measuring bulb L, and reaction bulb M, is also evacuated.

(8) See, for example, Deitz and Gleysteen, *J. Research Natl. Bur. Standards*, **29**, 191 (1942).

(9) Farkas and Melville, "Experimental Methods in Gas Reactions," Macmillan and Co., London, 1939, p. 194.

(10) Dodge and Dunbar, *THIS JOURNAL*, **49**, 610 (1927).

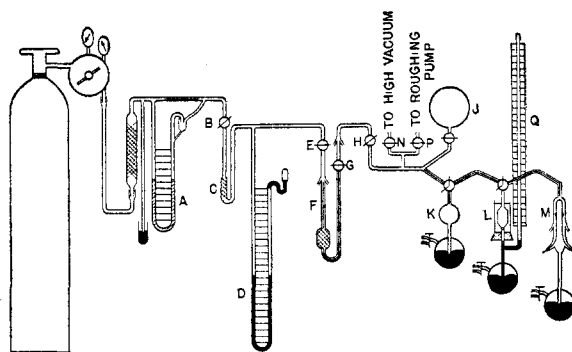


Fig. 1.—Diagram of flow apparatus.

Stopcock N is then closed, G opened, the liquid nitrogen bath removed, and the gas in the cell transferred with the Toepler pump to the measuring bulb L. The gas pressure, measured with manometer Q, the known volume of bulb L, and dead space of the cell F, permit the calculation of the total amount adsorbed at the given pressure and gas composition. After mixing to insure homogeneity, an aliquot of the gas is measured in L and transferred to the analytical bulb M. Smaller samples of gas are used entire.

The reactive element in M is an iron-plated platinum wire (after Lambert and Peel<sup>11</sup>), heated electrically to bright red heat. Two one-minute passes usually suffice for complete reaction, after which the gas is transferred back to bulb L, the residual pressure representing the nitrogen content of the sample. From this value the amount of each gas adsorbed can be calculated. After several analyses the wire is restored to activity by reduction with hydrogen. This method of analysis is quite satisfactory in practice, though a small correction (a few tenths per cent.) was necessary for residual gases in the electrolytically plated iron. The method is reproducible to 0.1%. It is necessary to replace the plated wire occasionally, as it burns out after prolonged use.

To begin a new point, stopcock G is closed, and the liquid nitrogen bath placed around cell F. Stopcock E is then opened. As points on an isotherm of a given gas composition are taken in more or less random order, the pressure in the cell might now be either greater or less than the final running pressure. Thus the points on the isotherm include indiscriminately "adsorption" and "desorption" points. The fact that the isotherm points showed no scatter due to this effect was a further check that the points represent equilibrium. Valves B and H are then roughly adjusted, stopcock P opened, followed by stopcock G, and the valves adjusted until the desired pressure is reached.

Each mixture isotherm consists of 40 to 50 points taken as described above. The pure gas isotherms were determined in the same way, omitting the analysis. The lowest pressure at which the apparatus gave reliable results was 2-3 mm.

The points on the pure gas isotherms below 1 mm. pressure were measured in a static system, using a three-range calibrated McLeod gage in place of the usual gas buret, with the sample contained in the detachable cell F. Thermal transpiration causes an error in pressure readings at these low pressures; the maximum possible error is a factor of  $\sqrt{T_1/T_2} = \sqrt{298/78} = 1.95$ . Correction for this effect was made according to Loeb.<sup>12</sup> The theory given is not exact, so that residual errors in pressure of 10-20% may be expected. The resulting errors in amount adsorbed are negligible.

### Results and Discussion

The isotherms obtained for the two pure gases and the five mixtures are shown in Figs. 2-8. The

(11) Lambert and Peel, *Proc. Roy. Soc. (London)*, **A144**, 205 (1934).

(12) Loeb, "Kinetic Theory of Gases," McGraw-Hill Book Co., New York, N. Y., 1934, pp. 352-363.

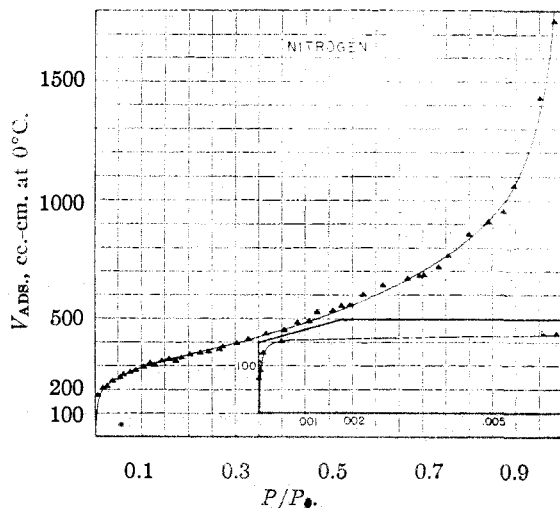


Fig. 2.—Pure nitrogen isotherm.

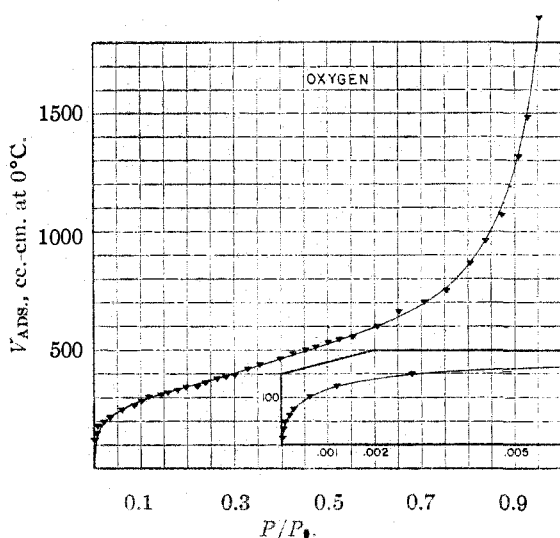


Fig. 3.—Pure oxygen isotherm.

pressure  $p_0$  is the saturation vapor pressure of the liquid phase in equilibrium with gas of the given composition at 78.2°K. The composition and vapor pressure of these liquid phases are given in Table I. It may be seen that Raoult's law is obeyed in this system within a few per cent.

In examining the pure gas isotherms, we note that in the region of moderate to high  $p/p_0$ , the two curves are nearly superimposable. In the low pressure region, however (inserts, Figs. 2 and 3), the adsorption of nitrogen greatly exceeds that of oxygen.

The mixed adsorption isotherms show a number of striking features. First, we note the close resemblance between the total gas isotherms and those for the pure gases. In fact, except for a small difference in scale, all seven total gas isotherms can be nearly superposed (except below  $p/p_0 = 0.01$ , where there are no mixture data). At the highest pressures, the adsorbed phase is much

TABLE I  
GAS-LIQUID EQUILIBRIUM AT 78.2°K.<sup>a</sup>

$y_2$ , %	$r_2$ , %	$p_0$ , mm.	$r_2'$ , %	$p_0'$ , mm.
0	0	840	0	840
14.9	43.4	581	45.1	543
29.8	67.7	418	66.5	401
50.2	84.6	296	82.5	295
70.2	93.1	232.4	91.7	234.6
85.3	97.1	202.1	96.4	203.2
100	100	179.7	100	179.7

$y_2$  = mole per cent. O<sub>2</sub> in gas phase.

$r_2$  = mole per cent. O<sub>2</sub> in liquid phase.

$r_2'$  = mole per cent. O<sub>2</sub> in liquid phase in Raoult's law.

$p_0$  = vapor pressure of liquid of composition  $r_2$

$p_0'$  = vapor pressure of liquid of composition  $r_2'$ , from Raoult's law.

<sup>a</sup> Dodge and Davis, THIS JOURNAL, 49, 591 (1927).

richer in oxygen, the more condensable gas, than is the gas phase, its composition approaching that of the bulk liquid asymptotically as  $p$  approaches  $p_0$ . This behavior is to be expected unless there is a first order phase transition at  $p_0$  between the adsorbed and liquid phases. At low pressures, corresponding to low surface coverage, the adsorbed phase becomes poorer in oxygen than the gas phase. This characteristic may be seen most readily in Fig. 6. At the lowest pressure measured, the adsorbed phase contains 23% nitrogen, compared to 77% at the highest pressure. Considering the generally parallel features of the two pure gas isotherms, the specificity of the surface for nitrogen adsorption is an apparent anomaly.

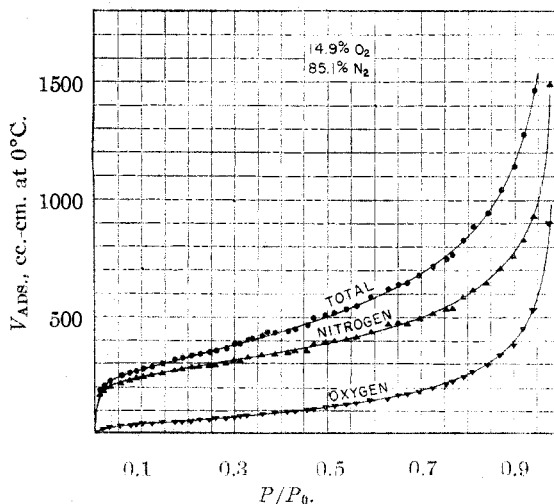


Fig. 4.—14.9% oxygen, 85.1% nitrogen isotherms. ▲, nitrogen; ▼, oxygen; ●, total gas adsorbed. The designations are the same in succeeding figures.

Another qualitative feature may be noted in the oxygen-rich mixtures, Figs. 7 and 8. In these isotherms the adsorption of nitrogen is almost independent of pressure over a considerable range of pressure.

**Comparison with Extended BET Theory. The Total Gas Isotherms.**—We shall use

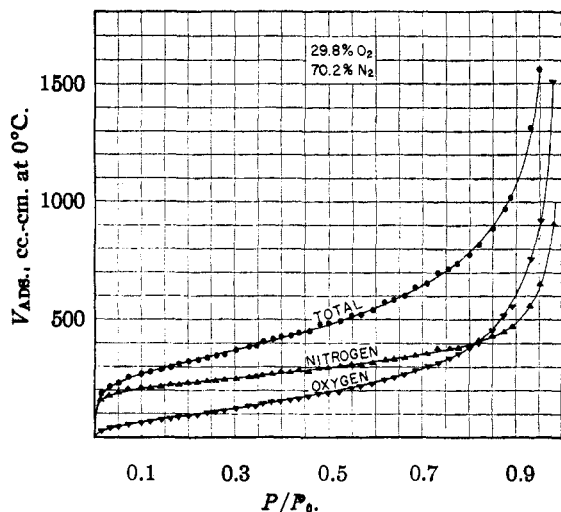


Fig. 5.—29.8% Oxygen, 70.2% nitrogen isotherm.

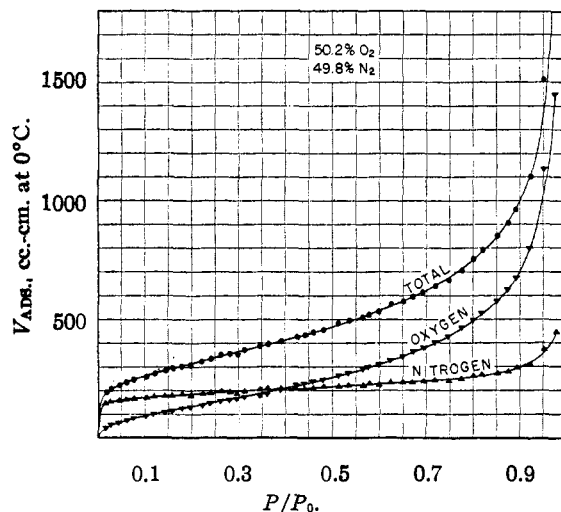


Fig. 6.—50.2% Oxygen, 49.8% nitrogen isotherm.

Hill's<sup>4</sup> eqn. (38), under the condition that Raoult's law is obeyed. Raoult's law, it may be noted, can be derived rigorously from statistical mechanics only on the assumption that the molecular area (or volume) is the same.<sup>13</sup> The error introduced by moderate differences in molecular size is small, however. We shall restate the equation in the form

$$\frac{v_1}{v_m} = \frac{cxX}{1 + cxY} \quad (1)$$

letting

$$c = \frac{x_1c_1 + x_2c_2}{x_1 + x_2}, \quad x = x_1 + x_2, \quad x_1 = y_1p/p_{10}$$

where

- $p$  = gas pressure
- $y_1$  = mole fraction of component 1 in gas phase
- $p_{10}$  = vapor pressure of (pure) component 1

(13) Fowler. "Statistical Mechanics," Cambridge Univ. Press, Cambridge, England, 1936, p. 532.

$c_1 = c$  (after Brunauer, Emmett and Teller) for component 1, as determined from the pure gas isotherm  
 $v_1$  = volume of component 1 adsorbed from the mixture  
 $v_m$  = volume adsorbed corresponding to one monolayer  
 with similar definitions for component 2.

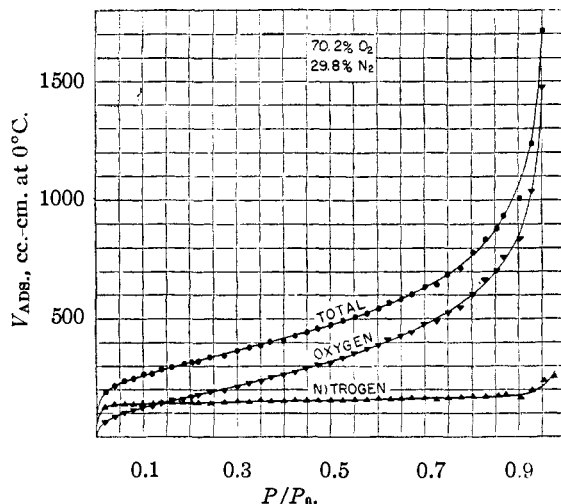


Fig. 7.—70.2% Oxygen, 29.8% nitrogen isotherm.

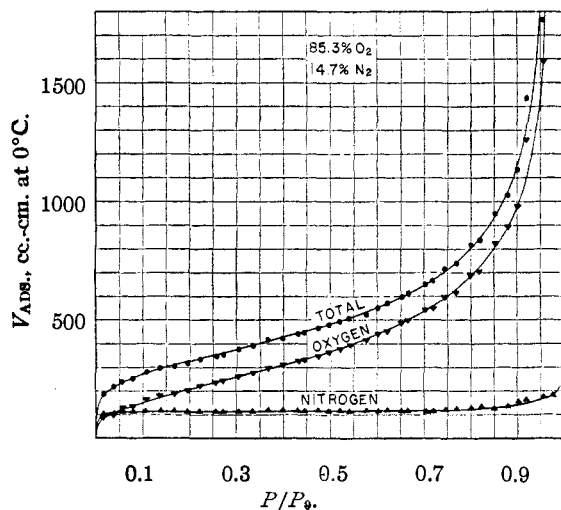


Fig. 8.—85.3% Oxygen, 14.7% nitrogen isotherm.

The two functions  $X$  and  $Y$  are given by Hill's eqns. (29) and (30), which we can restate as

$$X = \left[ \frac{c_1x_1}{cx} + \frac{x_1}{(1-x)} \right] \frac{1}{(1-x)} \quad (2)$$

$$Y = 1/(1-x) \quad (3)$$

Combining and simplifying

$$\frac{v_1}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \left[ \frac{c_1x_1(1-x)}{cx} + x_1 \right] \quad (4a)$$

Likewise for component 2

$$\frac{v_2}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \left[ \frac{c_2x_2(1-x)}{cx} + x_2 \right] \quad (4b)$$

The total gas adsorbed will then be

$$\frac{v_1 + v_2}{v_m} = \frac{cx}{(1-x)(1-x+cx)} \quad (5)$$

This equation has the same form as the BET isotherm for a single gas.<sup>5</sup> That the terms have substantially the same significance may be seen by the following transformations. If the gas composition  $y_1$  is held constant, the condensation pressure of the gas mixture will be given by

$$1/p_0 = y_1/p_{10} + y_2/p_{20} \quad (6)$$

and

$$x = y_1 p/p_{10} + y_2 p/p_{20} = p/p_0 \quad (7)$$

while  $c$ , the weighted mean of the  $c$  values for the pure components, is likewise a constant over the whole pressure range.

It is apparent from Figs. 2 to 8 that the total gas isotherms for the various mixtures fit the BET eqn. (5) about as well as those for the pure gases. The BET constants, calculated from the isotherms by least squares, are given in Table II.

TABLE II  
BET CONSTANTS FOR ISOTHERMS

yt. %	$v_m$ , cc.-cm.	Mol. area, sq. Å.	$c$	$c$ (from eqn. 1)
0	312 <sup>a</sup>	16.2	143	143
14.9	273	18.5	94	112
29.8	266	19.0	92	95
50.2	261	19.4	86	83
70.2	261	19.4	90	77
85.3	267	18.9	83	74
100	288	17.5	72	72

<sup>a</sup> This value is somewhat uncertain due to non-linearity of the BET plot for this isotherm.  $V_m$  may be as low as 288 cc.-cm.

The  $p_0$ 's used in calculating the constants, and in plotting Figs. 4 to 8, are the actual saturation pressures, not those calculated from Raoult's law. The difference in  $c$  values by the two methods of

calculation is at most 6%; the difference in molecular areas is negligible. The last column lists the  $c$  values calculated from eqn. (1).

The range over which eqn. (5) holds for the mixtures is the same as that for the pure gases, namely, from  $p/p_0 = 0.05$  to 0.30. The difference between the two sets of  $c$  values is probably outside experimental error; it is too small, however, to cause more than minute deviations in the observed isotherms.

The  $v_m$  values show strikingly the effect of molecular environment on molecular area in films of moderate thickness. We note that the observed value of the molecular area of oxygen on anatase (taking 16.2 sq. Å. for nitrogen as a reference value) is 17.5 sq. Å., compared with 13.2 sq. Å. calculated for liquid packing. This greater apparent area is common when other adsorbates are compared to nitrogen.<sup>6,7</sup> It has the fortunate effect, from our point of view, of bringing the two molecular areas into closer agreement. The areas for the mixtures are average areas per molecule of whatever species, it being impossible to treat the average molecular areas of nitrogen and oxygen separately. These areas turn out to be greater in every case than the molecular areas of either pure gas, and to pass through a smooth maximum between the 50.2 and 70.2% oxygen mixtures. The effect is far outside the experimental error, estimated at 0.5 to 1%. Moreover, it is independent of the correctness of the extended BET theory, since, as pointed out above, the isotherms are nearly superimposable except for a scale factor. Thus whatever point on the isotherm represents complete coverage of a monolayer, the relative values of  $v_m$  in Table II will be preserved.

This effect is presumably associated with other signs of non-ideal behavior in these systems (see below).

**Component Isotherms.**—Figure 9 gives a comparison between the 50.2% oxygen isotherm (Fig. 6) and the isotherm predicted by the extended BET theory. Between  $p/p_0 = 0.05$  and 0.30 the observed and calculated total gas isotherms run parallel, differing only by the scale factor discussed above. Above  $p/p_0 = 0.30$  the predicted isotherm diverges increasingly in the direction of increased adsorption. This behavior exactly parallels that for the pure gas isotherms. When we compare the isotherms of the component gases in the moderate pressure region, however, we find a sharp discrepancy between theory and experiment. The observed isotherms for the individual components, oxygen and nitrogen, differ from those calculated from the extended BET theory by more than a factor of two. Instead of the observed highly selective adsorption of nitrogen at low pressures, the theory predicts only a small difference between the composition of the adsorbed phase below one monolayer surface coverage, and that of the bulk liquid. This discrepancy is equally apparent in all five mixture isotherms.

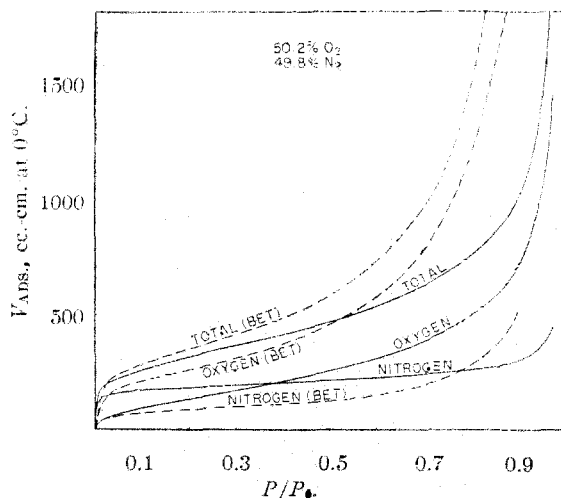


Fig. 9.—50.2% Oxygen isotherm: —, observed; - - - -, calculated from extended BET theory.

Returning to equations (4a) and (4b), we note that in the special case  $c_1 = c_2 = c$

$$v_1/(v_1 + v_2) = x_1/(x_1 + x_2) = \frac{(y_1/p_{10})}{(y_1/p_{10} + (y_2/p_{20}))} \quad (8)$$

That is, the composition of the adsorbed phase is equal to that of the bulk liquid, and is independent of  $c$  and  $x$ . We can see from Table II that the difference between  $c_1$  and  $c_2$  is small, although in the right direction. In fact, the theory predicts a minimum oxygen concentration of 71% in the adsorbed phase, compared with 85% in the bulk liquid and 23% actually observed at  $p/p_0 = 0.017$ .

**Theoretical Discussion. The "Liquid Entropy" Model.**—Since the adsorbed phase is in equilibrium with gas at a lower pressure than the vapor pressure, we have from elementary thermodynamics

$$(\mu_A - \mu_L) = RT \ln (p/p_0) \quad (9)$$

that is, the partial molal free energy of the adsorbed phase is always less than that for the bulk liquid. This free energy difference (henceforth written  $\Delta\mu_A$ ) can be considered as the sum of two terms

$$\Delta\mu_A = \overline{\Delta H_A} - T\overline{\Delta S_A} \quad (10)$$

In the simplest possible case of the BET theory, where  $c = 1$ , and  $\Delta H_1 = 0$ ,  $\overline{\Delta H_A} = 0$  over the whole isotherm and equation (10) reduces to

$$\Delta\mu_A = -T\overline{\Delta S_A} \quad (11)$$

That is, the partial molal entropy of the adsorbed phase is greater than that of the bulk liquid. In the usual type II BET isotherm  $H_1 < H_L$  (these are negative quantities; the heat content of the adsorbed phase decreases with increasing heat of adsorption).  $\overline{\Delta H_A}$  has its minimum value  $\Delta H_1$  at zero pressure and coverage, and increases to zero at high coverage. Thus both heat and entropy contribute to adsorption in this case, but at least at high coverage, where the family of BET isotherms approach one another, the entropy term is the major contributor to the decreased free energy of the adsorbed phase, according to this theory. This entropy term may be loosely spoken of as "configurational entropy," thought of as arising from the large number of possible states for a BET adsorbed phase (see Hill's eqn. (4)), or the large amount of "disorder" in such a phase.

One of the basic assumptions of the BET theory is that a molecule may be adsorbed on another molecule with equal probability whether or not the lower or upper molecules have any nearest neighbors, *i. e.*, horizontal interactions are neglected. Thus the physical picture of the BET adsorbed phase at high coverage is of columns of molecules of various heights scattered at random, so that occasional columns of many molecules arise out of nearly bare areas. It has been pointed out, for example by Cassel,<sup>14</sup> that the van der

Waals forces, which produce surface tension in liquids, will tend to draw these columns down and produce a smooth, ordered film. Hill's<sup>15</sup> calculations have shown the importance of this effect. This assumption, of the BET theory, together with the assumption of a constant  $E_1$  which stands or falls with it, is its most obvious weakness.

The recent accurate heat measurements of Beebe and Kington<sup>16</sup> have permitted the calculation of the partial molal entropies of adsorption in a number of gas-solid systems, including the systems nitrogen-anatase and oxygen-anatase. In the systems studied the partial molal entropy of the adsorbed phase is uniformly *less* than that of the bulk liquid, approaching it closely at about  $v/v_m = 1$  and above. The observed entropies have a minimum value about 4-5 e. u. less than that of the bulk liquid.

In light of these observations, a model is proposed based on the following assumptions: (1) the partial molal entropy of the adsorbed phase is constant and equal to that of the bulk liquid, for the pure gas isotherms; (2) if the sites for adsorption are arranged in order of decreasing heat of adsorption for component 1, they will also be in decreasing order for component 2; (3) for sites of a given heat of adsorption Raoult's law is obeyed. Assumption (1) is an approximation to the observed entropies of Beebe and Kington. Assumption (2) is a pure assumption in the region of low coverage, so long as the reason for the varying heat of adsorption is not known. In the region of multilayer adsorption, it must be approximately valid on purely geometrical grounds, since here the concept of "sites" gives way to that of "layers," the order of filling of which must be the same. The physical picture here, one frequently proposed before,<sup>2</sup> is of a smooth liquid-like film, the van der Waals field of the solid being superimposed on the liquid forces, and falling off fairly slowly with distance from the surface. Halsey, in a fundamental paper on the theory of adsorption,<sup>17</sup> has discussed this assumption extensively. As a consequence of assumptions (1) and (2), all sites of heat of adsorption  $\Delta H_A$  fill at the pressure given by  $\Delta H_A = RT \ln (p/p_0)$ . If the first two assumptions are granted, the third becomes subject to experimental test. We shall refer to this set of assumptions as the "liquid entropy" (LE) model.

Calculation of a mixed adsorption isotherm then proceeds as follows. For any given set of sites, let the heats of adsorption for the two components be  $\Delta H_{A1}$  and  $\Delta H_{A2}$ , and let the equilibrium pressures on the two pure gas isotherms be  $p'_1$  and  $p'_2$ . Then the composition of the gas adsorbed on these sites is

$$r_1(v) = \frac{(y_1/p'_1)}{(y_1/p'_1 + (y_2/p'_2))} \quad (12)$$

(15) Hill, *J. Chem. Phys.*, **15**, 767 (1944).

(16) Beebe and Kington, *THIS JOURNAL* (in press). The author is greatly indebted to Drs. Beebe and Kington for making their data available to him before publication.

(17) Halsey, *J. Chem. Phys.*, **16**, 931 (1948).

(14) Cassel, *J. Phys. Chem.*, **48**, 195 (1944).

The equilibrium pressure is determined by

$$1/p = y_1/p_1' + y_2/p_2' \quad (13)$$

The composition of the whole film at volume adsorbed  $v$  and pressure  $p$  is given by

$$R_1(v) = \frac{1}{v} \int_0^v r_1(v) dv \quad (14)$$

$r_1(v)$  and  $p(v)$  may be determined from the pure gas isotherms. These isotherms must be determined down to very low surface coverage. The integration of eqn. (14) is performed numerically.

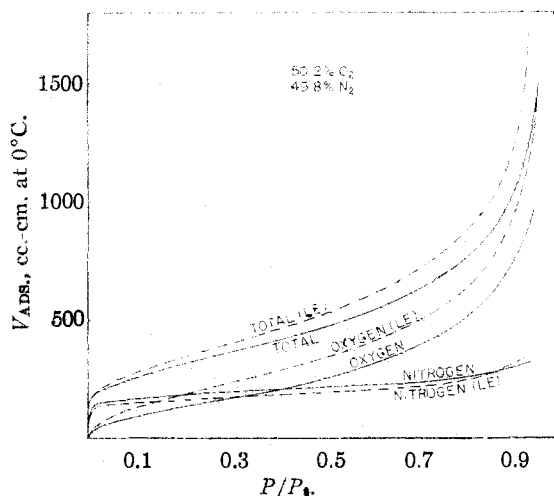


Fig. 10.—50.2% Oxygen isotherm: —, observed; ----, calculated from "liquid entropy" (LE) model.

The result of such a calculation for the 50.2% oxygen isotherm is shown in Fig. 10. The agreement is seen to be much better than that in Fig. 9. That this is so for the total gas isotherm reflects no credit on our model since the functions  $p'(v)$  and  $p_2'(v)$  are the observed isotherms (Figs. 2 and 3), while the pure gas isotherms used in eqns. (4) and (5) are the BET isotherms, which fit the experimental data only between  $p/p_0 = 0.05$  and 0.30. For the component isotherms a real improvement is apparent. The composition of the adsorbed phase at  $p/p_0 = 0.017$  is now 29% oxygen, compared to 71% on the BET model, and 23% actually observed. The discrepancy between calculated and observed isotherm is greater for oxygen than for nitrogen, the scale factor of the total gas isotherm tending to increase the discrepancy in the oxygen case, and reduce it in the nitrogen case.

Semi-quantitative agreement is likewise obtained with the isotherms for the other four gas mixtures.

In testing assumption (3) of our model, given the other two, we again encounter the scale factor of the total gas isotherm, as a positive deviation from Raoult's law, *i. e.*, greater pressure corresponding to a given surface coverage. The assumption of "regular solution" behavior, and the introduction of the scale factor as a measure

of departure from ideality, would undoubtedly improve the calculations somewhat, bringing the total gas isotherms closely into line with predictions.

The use of the measured entropies of Beebe and Kingston, instead of assumption (1), is also possible. The calculations become tedious, and assumption (3) can no longer hold at more than one temperature, or even at one temperature except by fortuitous cancellation of effects. Rough approximate calculations show improved agreement; more accurate entropy data, especially at low coverage, would probably be necessary for a real test of this method.

We may conclude that in this system, and probably in others where small deviations from Raoult's law are to be expected, the "liquid entropy" model gives semi-quantitative agreement with experiment. The data required for this model are simply the pure gas isotherms, over the whole range from low coverage to many-layer coverage. Determination of the total gas isotherms at constant gas composition will improve the agreement by allowing for "regular solution" behavior. Measurement of heats of adsorption, and use of observed rather than liquid entropies, will give further improvements. Since determination of the two pure gas isotherms is much less difficult and time-consuming than measurement of a series of gas mixture isotherms, the "liquid entropy" model will be a practical tool for predicting mixed adsorption behavior. The more exact methods, requiring data more difficult to determine, probably will not.

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### Summary

Adsorption isotherms at constant gas composition have been determined at 78.2°K. for five nitrogen-oxygen mixtures on Harkins' anatase. Isotherms for the two pure gases have also been determined. The isotherms show selective adsorption of nitrogen by this surface at low coverage.

Comparison with the extended BET theory shows qualitative disagreement, and provides evidence against at least one of the assumptions of the BET theory.

Use of a "liquid entropy" model gives semi-quantitative agreement with experiment.

This model allows the prediction of mixed adsorption behavior from the pure gas isotherms, for pairs of gases for which Raoult's law holds approximately.