

[CONTRIBUTION FROM THE STEELE CHEMICAL LABORATORY, DARTMOUTH COLLEGE]

## THE ADSORPTION OF MIXED GASES BY CHARCOAL. I. CARBON DIOXIDE AND NITROUS OXIDE

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While the adsorption of single gases by charcoal has been the subject of extensive investigation, similar studies for mixtures of gases have been much less abundant. Bancroft<sup>1</sup> states that such work as has been done "indicates that the more readily adsorbed gas displaces the other to some extent, and is adsorbed to a greater relative amount than one would have predicted from experiments on the single gases." The experiments which led to this deduction were, however, largely qualitative; or where quantitative, were carried on at low pressures. Thus Bergter<sup>2</sup> investigated the adsorption of nitrogen and oxygen mixtures at very low pressures and Hunter,<sup>3</sup> that of a number of easily condensable gases which probably dissolved in one another; Lemon and Blodgett,<sup>4</sup> working at the temperature of liquid air, studied the rate of adsorption of nitrogen-oxygen mixtures; and Miss Homfray<sup>5</sup> worked with mixtures of carbon monoxide and nitrogen at  $-79^{\circ}$ . In all these cases, however, the pressures were low and extended through a very limited range; the temperatures were also low; nor was any attempt made to determine the adsorption of the separate gases in the mixture at a number of pressure points. It seemed worth while, therefore, to investigate the total adsorption of gaseous mixtures at  $0^{\circ}$  through pressures ranging from very low values to a maximum of 3.5 atmospheres, and also to determine at numerous pressure points, by methods of analysis, the adsorption of each gas separately. Carbon dioxide and nitrous oxide were selected as materials for the first study. It is hoped that other pairs of gases will form material for subsequent papers from this Laboratory upon the same general problem.

### Materials and Apparatus

**Charcoal.**—As an adsorbent, steam-activated charcoal<sup>6</sup> was used. Its density determined in a vacuum in the usual way gave results 1.809 and 1.806. The ash content was 1.87%. The pieces were 8–10 mesh size, and the same sample, weighing 4.5332 g., was used throughout the determinations. The material was highly adsorbent, and took up each time, even after extensive use, nearly the same amount of a given gas.

**Gases.**—In the selection of gases the following conditions were considered desirable.

(1) The gases should not react upon each other or upon the charcoal. (2) They

<sup>1</sup> Bancroft, "Applied Colloid Chemistry," McGraw-Hill Book Co., 1921, p. 16.

<sup>2</sup> Bergter, *Ann. Physik.*, **37**, 472 (1912).

<sup>3</sup> Hunter, *J. Chem. Soc.*, **23**, 73 (1878).

<sup>4</sup> Lemon and Blodgett, *Phys. Rev.*, **14**, 394 (1919).

<sup>5</sup> Homfray, *Z. physik. Chem.*, **74**, 129 (1910).

<sup>6</sup> Procured from the Barneby-Chaney Company.

should not, when liquefied, dissolve appreciably in each other. (3) They should be adsorbed to a large extent at 0°. (4) They should be of nearly equal density, to insure quick and easy mixing. These requirements seemed to be met by the selection of carbon dioxide and nitrous oxide. The adsorption of the first has been widely studied; its isotherms have been repeatedly determined. Very little work has been done on the second, but from its physical constants and from the results of Hempel and Vater<sup>7</sup> it is apparent that its degree of adsorption is comparable to that of carbon dioxide. The only point that caused apprehension was that at the temperature required for out-gassing (425°) the charcoal might be oxidized by the nitrous oxide. Consequently, an analysis of the gas subjected to the action of the charcoal during the out-gassing process was made in each determination of the nitrous oxide isotherm. In no case was the slightest amount of carbon dioxide detected in the gas withdrawn from the cell; nor in the runs of mixed gases was any excess of carbon dioxide over that introduced into the system ever obtained.

The carbon dioxide used was 99.7–99.9% absorbable in potassium hydroxide solution. The nitrous oxide was a commercial product which by analysis was shown to be 98.4–99.1% pure, the sole impurity appearing to be nitrogen. It is difficult to prepare nitrous oxide in sufficient quantities by the ordinary processes of the laboratory of as high purity as this. As the influence of the small quantities of contaminating nitrogen was slight, and as its precise effect on the isotherms could be determined, the gas as procured was deemed sufficiently good for the purpose of these experiments.

**Method of Determining Isotherms.**—The adsorption isotherms of the mixture were made by running known quantities of the gases into a cell containing the adsorbent. When the maximum pressure was reached the points on the isotherm were determined by withdrawing successive portions of the mixture and analyzing each portion withdrawn. The system was allowed to come to equilibrium and the pressure read after each withdrawal. The apparatus having been carefully calibrated, the volume of the gaseous phase could be determined from the pressure reading, while the volume of each of its components could be obtained by the analysis of the gas withdrawn. The total volume of each gas admitted to the apparatus being known, the volume adsorbed, both total gas and each component, could be determined by difference.

**Apparatus.**—The apparatus used in the determinations was of the type employed by one of us<sup>8</sup> in the determinations of the individual isotherms of carbon dioxide and ammonia. It was modified in such details as became necessary through the use of more than one gas, and of their withdrawal for analysis. A diagram of the essential parts is given in Fig. 1. Cell C contains the charcoal, and is connected on one side with the manometer M capable of registering pressures to 3000 mm., and on the other, through the 3-way stopcock A to the 100cc. water-jacketed buret B. To the right, the gas buret is joined through the 3-way stopcock D to the gas supply tubes E and E'. All connecting tubing is of 1 mm. bore, and all connections are made by fusing the glass together.

Carbon dioxide, dried by being passed through a calcium chloride tube and two Friedrichs wash bottles filled with sulfuric acid, was introduced through E. Nitrous oxide, first bubbled through two large Winkler bulbs filled with sulfuric acid, was brought in at E'. This tube also served for the withdrawal of gas and its transfer to the analysis apparatus. If the gas was not required for analysis it was run out through the mercury trap F. By the manipulation of the stopcock A and the mercury-filled leveling bulb L, gas could be pumped into the cell up to high pressures, or out of it through F until a vacuum was obtained. The leveling bulb could be raised by a wire running through a pulley in

<sup>7</sup> Hempel and Vater, *Z. Elektrochem.*, **18**, 724 (1912).

<sup>8</sup> Richardson, *THIS JOURNAL*, **39**, 1829 (1917).

the ceiling so that the maximum pressure could be easily secured. After exhausting the cell, gas could be drawn in through E or E', measured under known conditions of pressure and temperature in the buret, and then forced into the cell.

The buret was calibrated in duplicate by weighing its water content. The volume of gas in the manometer at various mercury levels was determined by sealing off the capillary tube connecting the cell with the apparatus and passing in successive volumes of carbon dioxide measured in the buret. Three calibrations were made, the maximum divergence being 0.4%.

The cell was constructed as shown in Fig. 1. Tube a has an internal diameter of 9 mm.; Tube b, 4 mm.; Tube c, 1 mm. The capacity of the cell to the point f was determined thrice with a maximum variation of 0.13%. The volume from e to f was also obtained. The weighed sample of charcoal was introduced through b, and the cell was then sealed off between e and f, care being taken to make a very flat end, thus avoiding any uncertainty of measurement caused by a conical tip. By measurement from e to the end, the fraction of the known volume (e to f) then in the cell could be calculated. The small free space in the capillary above the level f was ascertained by calibration of

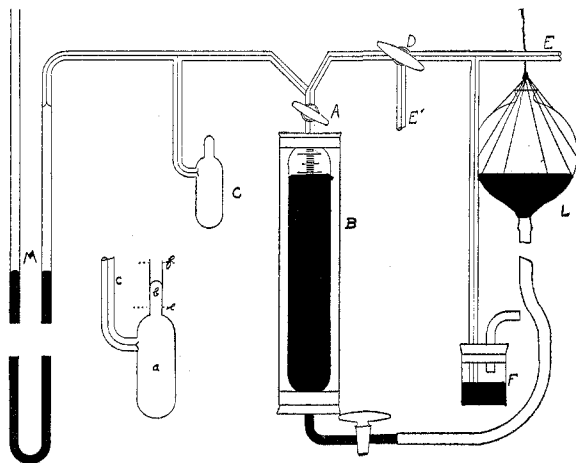


Fig. 1

other pieces of the same tubing. The total volume of the cell thus obtained was 8.45 cc. The volume of the charcoal in the cell, determined from its weight and density, was 2.51 cc. The free space in the cell was thus 5.94 cc. The tubing of the apparatus was cut off at a measured distance above the point at which it was sealed during the manometer calibration, and the volume thus removed was subtracted from that calibration. The volume of capillary tubing from point e to the point at which the fused joint was made was also calculated and added to the cell volume. The volume of the gas in the cell at various pressures (corrected in accordance with the data of Regnault) and at a temperature of  $0^\circ$  was added to the volume of gas in the manometer at the same pressures and at the temperature of the manometer calibration ( $20^\circ \pm 1^\circ$ ). These total volume results were plotted, and from the curve obtained the volume of the gaseous phase could be read at any pressure registered by the manometer.

As all determinations were made at  $0^\circ$ , temperature regulation was effected by a bath of finely divided ice and water. The variation was less than  $0.1^\circ$ . The thermometers used in determining the temperatures of the bath, the manometer, and the buret were checked against one another and against a standard thermometer graduated to  $0.1^\circ$ .

### Analysis

The successful prosecution of the work required an accurate method for the analysis of mixtures of carbon dioxide and nitrous oxide. The ordinary methods, namely, absorption of carbon dioxide in potassium hydroxide, and the explosion of nitrous oxide after mixture with a measured volume of hydrogen, are accurate enough for each gas separately but require modification when the gases are mixed. The difficulty lies in the solubility of nitrous oxide in the potassium hydroxide, which is sufficiently great under ordinary circumstances to vitiate the process. It was necessary, therefore, to determine just how much nitrous oxide is dissolved in solutions of potassium hydroxide of various concentrations. It was found that although solutions of the alkali of concentrations usual in gas analysis (30–40%) do dissolve sufficient amounts of nitrous oxide to make the separation inaccurate, a 55% solution, after the first exposure of nitrous oxide to it, takes up only inappreciable amounts of the gas. Fresh solution of this concentration placed in contact with 100 cc. of nitrous oxide for three hours dissolved only 1.4 cc.; a much smaller amount than is taken up by alkali solutions of lower concentrations. After this exposure of the fresh potassium hydroxide solution, nitrous oxide was again placed over the solution for the period of 10 minutes or so customary in gas analysis, and also for longer periods, both alone and mixed in various proportions with carbon dioxide. In no case was any nitrous oxide given off from the liquid or any more dissolved by it. This decrease of solubility is in accord with the results of Geffcken<sup>9</sup> although his work was not carried to such high concentrations of alkali. Extrapolation of his figures gives solubilities of nitrous oxide in potassium hydroxide solutions very close to those here obtained.

Attention should be called to two precautions necessary in the ignition of mixtures of nitrous oxide and hydrogen which are not mentioned in the texts on gas analysis. Incomplete mixing of the two gases not infrequently causes feeble explosions. The gases should be passed from the buret to the pipet and back several times. Even more important is the necessity for the presence of a small amount of water (0.5–1 cc.) in the explosion pipet. Again and again, in cases in which it had been found impossible to initiate an explosion when the gases were dry, the spark became thoroughly effective after the addition of this small quantity of water. Consequently, assurance of the presence of water was finally made a matter of routine practice in the analysis.

Variations in the volume of gaseous mixtures from the sum of the volumes of the component gases before mixing may also have an effect upon the results. Fuchs<sup>10</sup> presents data covering various mixtures; among others,

<sup>9</sup> Geffcken, *Z. physik. Chem.*, **42**, 257 (1904).

<sup>10</sup> Fuchs, *ibid.*, **92**, 641 (1918).

carbon dioxide and nitrous oxide. His results seem to show that a 50-50 mixture of these gases occupies a volume 1.42% greater than the sum of the volumes of the individual gases. Investigations of our own showed that the expansion, in this case at least, is approximately that indicated by Fuchs. From his data, therefore, a graph was drawn which indicated what this variation should be for all proportions of mixtures of the gases in question, and what corrections should be made in each analysis. It should be said, however, that this correction exercises so slight an influence upon the final result as to make its effect almost negligible.

### Experimental Procedure

The amount of gas adsorbed by charcoal is dependent upon many seemingly unimportant factors. Slight variations in conditions produce relatively great variations in results. If values are to be duplicated, the process must be standardized and, when thus standardized, accurately followed. This done, as described below, no difficulty was found in obtaining close duplicates of the isotherms, both of single gases and of each mixture with which experiments were made.

To prepare the charcoal for the adsorption, the cell was heated to 425° by an electric furnace, gas being pumped out at frequent intervals as it escaped. In the course of four hours the pressure was reduced to not more than 1 mm., even at the high temperature. The cell was then cooled slowly (20 minutes) to 0°, and allowed to remain for 10 minutes at this point before any gas was run in. In the meantime gas, carbon dioxide or nitrous oxide, as might be desired, was being passed in through E or E' and out through F, so that residual gas might be removed from that part of the apparatus. The two gases were then admitted to the buret in such proportions as might be desired, and mixed by raising and lowering L, several times. The amounts run in were such that their total volume would equal the capacity of the buret, and in the proportions which were desired in the final mixture. The contents of the buret as a whole were then admitted to the cell. It was found especially important for the duplication of results that the volume of each portion admitted should be uniform. When equilibrium was attained, as shown by the constancy of the level in the manometer, a fresh portion, which in the meantime had been prepared in the buret, was run in. This process was continued until no more gas could be forced in at the maximum pressure attainable by the apparatus. The capillary from A to the cell was then sealed with a thread of mercury to prevent any possible chance of leakage, and the gas left at 0° overnight.

Inasmuch as the gaseous phase was to be analyzed and the composition of the adsorbed phase determined thereby, measurement of the adsorption isotherms had to be made during withdrawal of the gas. Such isotherms

are subject to a lag of gas leaving charcoal as compared with those determined from data obtained by measuring equilibrium pressures of gases "going in." This lag has been previously observed and is confirmed in this work. The results here obtained, however, are comparable with each other, for the lag is a relatively constant factor in them all. The question of lag will be discussed in detail in the theoretical section following.

The withdrawal of gas was made in 50cc. fractions. After measurement in the buret the gas was driven through E' to a Hempel gas buret and analyzed, correction being made for the expansion due to the mixing of gases and to the tension of aqueous vapor in the pipets. This withdrawal was continued in successive portions until the pressure was not more than 75 mm. As numerous points low in the curve were not especially important in this work, and as the amounts of gas which could be withdrawn by evacuation alone from this point on were extremely small, the cell was heated and all the rest of the gas was driven out. The final result gave about 14 readings for each isotherm.

The total volume of gas withdrawn agreed very closely with that admitted, the average variation being about 2 cc. in 750 cc. The same can be said of the component gases measured "going in" and analyzed "coming out."

The carbon dioxide was to all intents pure, and no difficulty was experienced in accounting for all the gas introduced; the deviations in the nitrous oxide were almost exactly equal to the nitrogen contained in the original gas (1-1.5%). Practically all of this impurity was found in the first fraction withdrawn.

As a result of this standardization of the manipulation, a surprisingly close duplication of results was obtained, both with the gases unmixed and with each of the mixtures studied, a condition not always reached in studies of adsorption by charcoal. This duplication was true of the total amount adsorbed, of the general shape of the curves, and of the amounts of the individual gases adsorbed from mixtures and their adsorption curves. In the case of each curve, duplicates were obtained in which the variation was not more than 0.5%, a smaller difference than could be shown in any plotting of the curve on an ordinary scale.

As the nitrous oxide was slightly impure, an individual run was made to see whether increased purity changed the shape of the isotherm. It has been stated above that practically all of the impurity remained unadsorbed and was removed in the first portion of the gas withdrawn, the succeeding portions analyzing over 99.7%. For this reason an isotherm run was started in the usual way, with 99% nitrous oxide from the cylinder. When the maximum pressure was reached, the system was left for four hours; then 100 cc. of gas was withdrawn and replaced by fresh nitrous oxide, thus raising the purity of all the gas in the system to 99.8%. After

the mixture had stood overnight the isotherm was determined in the usual manner. Its deviation from the isotherms previously produced without this special care was negligible. The two were identical below 2200 mm., and the variation at the highest pressure was only 1%.

### Experimental Data

Table I gives the essential data for the individual adsorptions of carbon dioxide and nitrous oxide unmixed. The figures show the volume of each gas in cc. adsorbed per gram of charcoal at the pressures stated.

TABLE I  
ADSORPTION OF EACH GAS SEPARATELY

CO <sub>2</sub>	Gas in system, Meas. in, 677.1 cc.; meas. out, 672.7 cc. Adsorb. Cc.	N <sub>2</sub> O	In, 671.8 cc.; out, 673.0 cc. Adsorb. Cc.
Pressure Mm.		Pressure Mm.	
90.4	24.6	61.5	26.0
176.2	34.0	110.4	35.8
271.9	45.7	178.8	45.7
399.4	55.3	262.6	55.1
552.6	64.7	369.2	64.4
734.0	73.8	504.3	73.5
950.2	82.4	674.4	82.7
1207.1	91.6	881.4	90.5
1478.2	97.9	1138.4	99.3
1829.1	104.1	1447.8	106.1
2155.9	110.1	1666.8	109.9
2506.0	114.9	2041.5	113.3
2864.8	119.1	2396.0	115.8
		2842.3	118.6

These results are given in graphical form in Fig. 2.

TABLE II  
ADSORPTION OF A MIXTURE OF 49.2 PER CENT. OF CARBON DIOXIDE AND  
50.8 PER CENT. OF NITROUS OXIDE  
Gas in, 672.3 cc. Gas out, 670.8 cc. Temperature 0°

Pressure Mm.	Total ads.	CO <sub>2</sub> ads.	N <sub>2</sub> O ads.
72.8	26.0	8.6	17.4
127.6	35.1	12.7	22.4
206.7	44.9	17.4	27.4
316.8	54.8	22.5	32.3
420.4	62.4	26.5	35.9
572.7	72.0	31.7	40.3
773.1	80.5	36.4	44.1
1010.4	89.1	41.1	48.0
1298.3	97.1	45.5	51.6
1625.6	103.6	49.1	54.5
1983.2	109.3	52.3	57.0
2366.1	113.6	54.7	58.9
2870.5	117.5	57.3	60.2

Three mixtures of the gases were investigated. These contained approximately 50% CO<sub>2</sub>-50% N<sub>2</sub>O, 75% CO<sub>2</sub>-25% N<sub>2</sub>O, and 25% CO<sub>2</sub>-75% N<sub>2</sub>O, respectively.

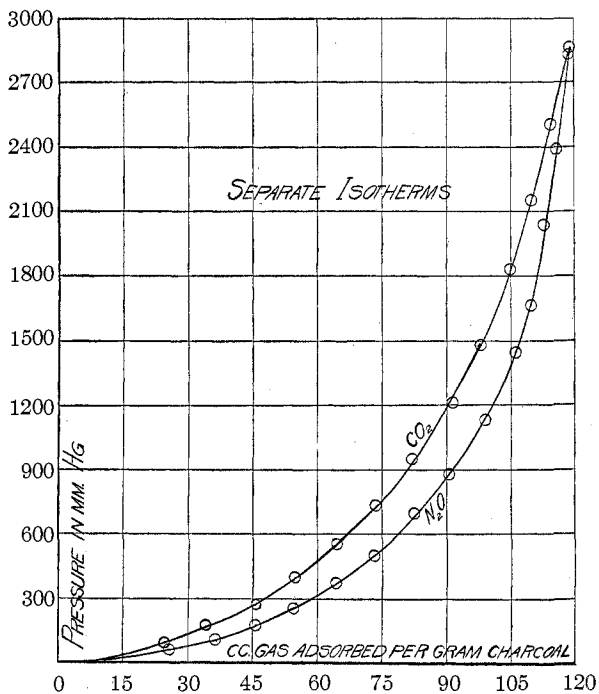


Fig. 2

N<sub>2</sub>O, respectively. The results are given in Tables II, III and IV. The first column records the pressures in millimeters; the second, the total vol-

TABLE III

ADSORPTION OF A MIXTURE OF 73.9 PER CENT. OF CARBON DIOXIDE AND 26.3 PER CENT. OF NITROUS OXIDE

Gas in, 666.7 cc. Gas out, 665.8 cc. Temperature 0°

Pressure Mm.	Total ads.	CO <sub>2</sub> ads.	N <sub>2</sub> O ads.
58.3	22.2	13.0	9.2
113.9	31.1	19.3	11.8
187.8	40.6	26.2	14.4
286.5	50.2	33.4	16.8
416.1	59.8	40.8	19.0
567.6	68.8	47.8	20.9
748.0	77.9	55.0	22.9
984.2	86.4	61.8	24.6
1251.3	94.2	68.0	26.2
1556.2	101.4	73.7	27.7
1899.0	107.4	78.4	29.0
2263.8	112.1	82.1	30.0
2781.0	118.0	87.1	30.9



ume of the mixture adsorbed; the third, the volume of carbon dioxide adsorbed; and the fourth, the volume of nitrous oxide adsorbed, in each case per gram of charcoal. Col. 2 gives results obtained by measurement of the residual gas; Cols. 3 and 4 from the analytical figures in each case (not by difference).

TABLE IV  
ADSORPTION OF A MIXTURE OF 23.4 PER CENT. OF CARBON DIOXIDE AND 76.6 PER CENT.  
OF NITROUS OXIDE

Pressure Mm.	Gas in, 674.2 cc.	Gas out, 675.6 cc.	Temperature, 0°
	Total ads.	CO <sub>2</sub> ads.	N <sub>2</sub> O ads.
77.3	28.9	3.9	25.0
137.4	38.9	5.8	33.1
220.1	48.9	8.1	40.8
322.6	58.3	10.4	47.9
431.0	66.2	12.2	54.0
607.4	75.3	14.7	60.6
1011.6	92.4	19.7	72.7
1287.3	99.5	21.9	77.6
1610.4	106.0	23.7	82.3
1988.0	111.4	25.3	86.1
2404.0	115.4	26.7	88.7
2858.0	118.9	27.8	91.1

Figs. 3, 4 and 5 give these results in graphical form.

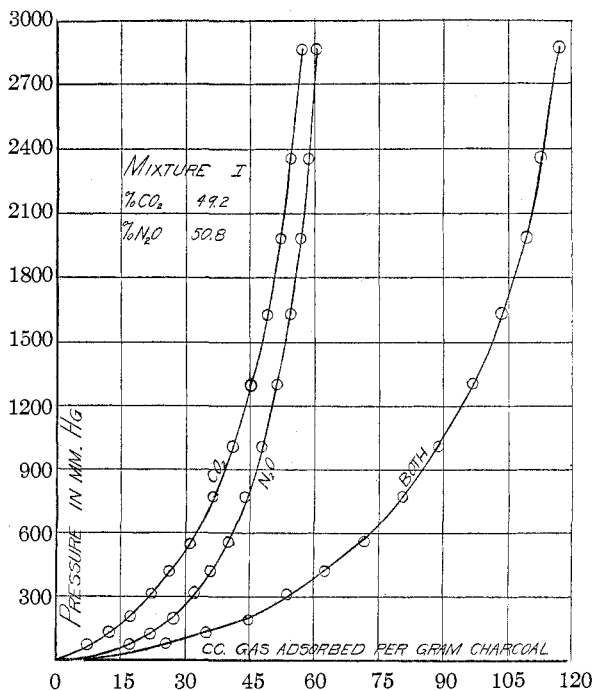


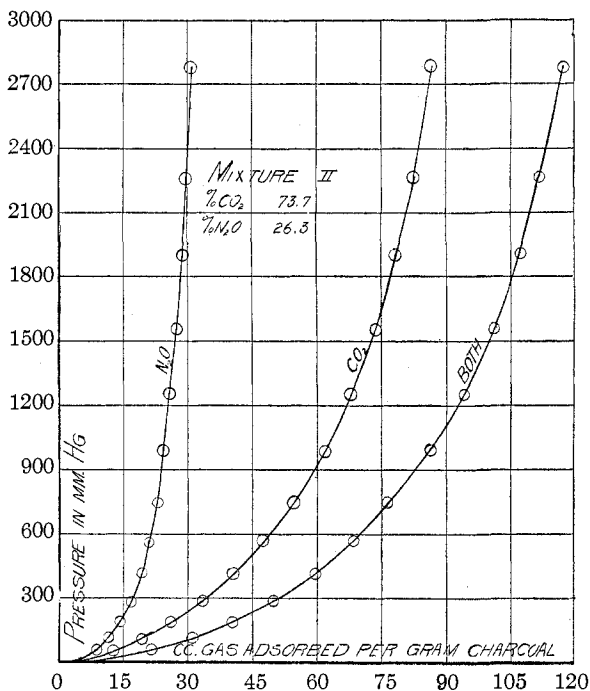
Fig. 3

Discussion

From the data given above it seems possible to deduce the total amount of any mixture of carbon dioxide and nitrous oxide adsorbed by charcoal, if the isotherms of the independent adsorption of the individual gases are known. The formula

$$V_{\text{mixt.}} = \frac{V_{\text{N}_2\text{O}} a_1 + V_{\text{CO}_2} a_2}{100}$$

in which  $V_{\text{N}_2\text{O}}$  and  $V_{\text{CO}_2}$  represent the volumes of those gases separately adsorbed at the total pressure of the mixture, and  $a_1$  and  $a_2$  stand for the

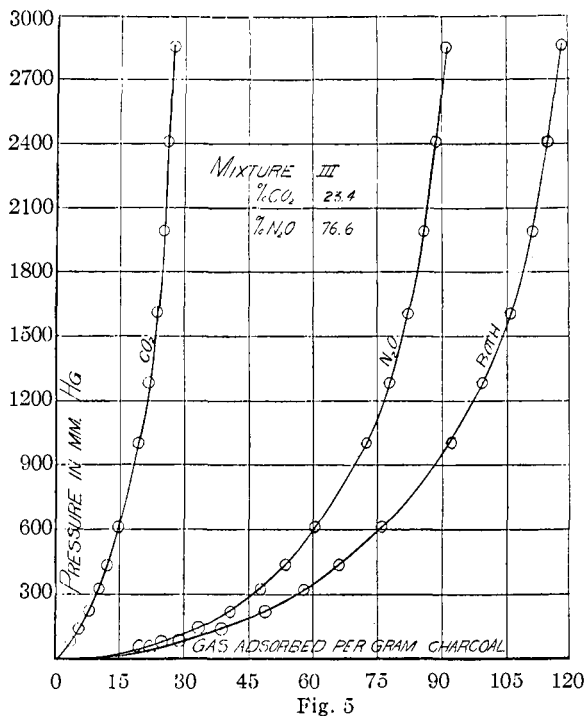


percentages of the respective gases in the mixture, holds within reasonable limits, as shown in Table V.

TABLE V  
 VOLUME OF MIXTURE ADSORBED, CALCULATED FROM SEPARATE ADSORPTION CURVES, COMPARED WITH VALUES EXPERIMENTALLY DETERMINED

Pressure Mm.	"50-50 mixt."		"75-25 mixt."		"25-75 mixt."	
	Calc.	Obt.	Calc.	Obt.	Calc.	Obt.
2800	118.3	117.1	118.4	118.4	118.3	118.5
1600	104.2	102.4	102.2	102.3	106.4	105.8
1000	89.7	88.7	87.3	87.0	92.3	91.9
600	73.4	73.2	70.6	70.2	76.5	75.1
200	44.1	43.7	41.7	41.4	46.7	47.1

When we consider that under the best of conditions the amount of gas adsorbed by a given specimen of charcoal varies several cubic centimeters in duplicate determinations, this agreement seems remarkably close. It should be said, however, that the relative nearness to each other of the



isotherms of the two gases under consideration is particularly favorable to the application of the above formula. It might not work so well with other pairs of gases.

TABLE VI  
RATIO OF ADSORPTION:  $N_2O/CO_2$

Pressure Mm.	Ind. ads.	"50-50"	"75-25"	"25-75"
2800	1.00	1.02	1.00	1.00
2400	1.018	1.05	1.02	1.02
2000	1.03	1.06	1.03	1.05
1600	1.084	1.07	1.05	1.06
1400	1.09	1.08	1.06	1.08
1200	1.102	1.10	1.08	1.10
1000	1.114	1.12	1.11	1.14
800	1.146	1.17	1.15	1.19
600	1.173	1.23	1.20	1.26
400	1.204	1.32	1.34	1.35
200	1.256	1.54	1.53	1.56

On the other hand, there seems to be no possibility of calculating the volume of each of the component gases adsorbed in the charcoal from the total volume of the gaseous mixture. In other words the ratio of the amounts of the two gases adsorbed varies with the pressure, whether we are dealing with them as separately in contact with the charcoal, or whether they are mixed. This fact is shown by the data given in Table VI. Col. 1 gives the pressure, Col. 2 the ratio  $N_2O/CO_2$  in independent adsorption, Cols. 3, 4 and 5 similar ratios (the volume of each gas being multiplied by the percentage of the other in the mixture) for the three mixtures studied. It will be seen that at the lower pressures there is a continually increasing proportion of nitrous oxide adsorbed.

This point has been touched upon, in connection with other gases, by a number of other investigators. Bergter, working at pressures of not over 10 mm. with mixtures of nitrogen and oxygen, concluded that while the relationship in which the two gases are adsorbed depends very considerably upon the pressure, under conditions with which he worked oxygen is adsorbed 30 to 40 times as much as nitrogen. He also came to the curious decision that the presence of adsorbed nitrogen more than doubles the capacity of charcoal to take up oxygen. Lemon and Blodgett, working with the same gases at low pressures and at the temperature of liquid air, believe, on the contrary, that there is a nearly linear relation between the logarithm of the equilibrium pressure and the percentage of oxygen in the mixture; and that gases are not adsorbed "independently"—that the presence of one gas reduces the capacity of the charcoal to take up another. Miss Homfray, as a result of a series of single determinations of mixtures of carbon monoxide and nitrogen at pressures up to one atmosphere and at  $-79^\circ$ , comes to the conclusion that the relative volumes of these gases adsorbed under the conditions stated is constant within an error of 2%. She made, however, no determination of a complete isotherm for any mixture, nor did she analyze the unadsorbed gases, but based her deductions on the fact that the total volume adsorbed was what it should be to satisfy a formula similar to that given above. Her conclusion, therefore, while probably valid for the total adsorption of the mixture, cannot be considered as indicating anything quantitatively definite as to the adsorption of the individual gases of the mixture.

### Molecular Volumes and Adsorption

Recently suggestions have been made that a proportionality exists between degree of adsorption and the molecular volumes of the adsorbed gases. Thus Wilson,<sup>11</sup> using the data of Lemon and Blodgett, calls attention to the fact that in their work the ratio of moles of nitrogen adsorbed

<sup>11</sup> Wilson, *Phys. Rev.*, **16**, 8 (1920).

to moles of oxygen is very nearly 1 to 1.3, which is the inverse ratio to their molecular volumes. Lamb and Coolidge,<sup>12</sup> in researches on the adsorption of the vapors of carbon tetrachloride, ether, methyl alcohol, etc., find that a similar relationship holds. They further point out that the figures of Titoff<sup>13</sup> on the adsorption of ammonia and carbon dioxide (as single gases) permit a similar conclusion. It is to be noted, however, that the pressure points at which this last relation was found to hold were selected, apparently by chance, at 20 mm.

It is obvious from an inspection of the figures in Table VI that in our work, either with single gases or with mixtures, such a relationship holds only within a limited pressure range. For the single gases the ratio varies from 1 at 2800 mm. to 1.256 at 200 mm. For the mixtures there is a similar but greater variation, reaching a maximum of 1.56 at 200 mm. The ratio of the molecular volumes of carbon dioxide and nitrous oxide is 1 to 1.025.<sup>14</sup> It may then be stated that, within the experimental error, the gases herein studied are adsorbed inversely as their molecular volumes at pressures ranging from 1800–2800 mm. only; and that, below this, the lower the pressure, so far as the results of this investigation can be brought to bear upon the problem, the greater the divergence from this rule. It should be noted, however, that the apparatus used in this investigation was not adapted for the determination of equilibrium points at very low pressures, and such values are not given.

As all comparisons between adsorption and molecular volumes have been made at low pressures, except those discussed in this paper, it is of interest to apply the method to previously obtained isotherms of gases over as wide a pressure range as possible, and thereby to determine whether these ratios vary as they seem to do in the present work. The comparison must, of course, be made upon the basis of data obtained from the isotherms of single gases, as mixtures have not been studied. Ammonia and carbon dioxide have been investigated through a wider pressure range than other gases: at pressures up to one atmosphere by Titoff, and at higher points by one of us.

TABLE VII  
RATIO OF ADSORPTION: CO<sub>2</sub>/NH<sub>3</sub>, AT VARIOUS PRESSURES

Pressure Mm.	Ratio Richardson	Titoff Ratio	Pressure Mm.	Ratio Richardson	Ratio Titoff
1600	2.00	..	200	2.28	2.28
1200	2.07	..	100	..	2.30
800	2.15	2.05	50	2.10	2.09
600	2.21	2.12	25	..	1.80
400	2.28	2.26	2	..	1.75

<sup>12</sup> Lamb and Coolidge, *THIS JOURNAL*, **42**, 1146 (1920).

<sup>13</sup> Titoff, *Z. physik. Chem.*, **74**, 641 (1910).

<sup>14</sup> Cailletet and Mathias, *Compt. rend.*, **102**, 1202 (1886).

The results of the comparison are given in Table VII; temperature 0°. The ratio of the molecular volumes is 1.81. Apparently, then, at 0° for very low pressures with these gases, the inverse proportionality of the adsorption to the molecular volume holds; at higher pressures the deviation increases, reaching a maximum at 100 mm. From that point, as far as these results go, it decreases. Extrapolation of Richardson's results indicate that at a pressure of 3.5–4 atmospheres the adsorption of carbon dioxide and ammonia again approaches a ratio which is inversely proportional to the molecular volumes, as it was found to be in the case of carbon dioxide and nitrous oxide in the present work.

### Replaceability of One Gas by Another

In all the experiments described above, the gases were mixed before being admitted to the charcoal. It seemed worth while to compare the result thus obtained with that gained by adding one gas (nitrous oxide) to the other, already adsorbed by the charcoal. After a certain time interval the unadsorbed gas was withdrawn and analyzed, and the composition of the gaseous phase was determined. This was compared with the composition of the gaseous phase obtained from a mixture of the same composition, admitted to the charcoal subsequent to mixing, and showing approximately the same pressure (data obtained in the course of the work previously described). The experiment was then repeated at longer time intervals until the general course of the reaction could be determined. The findings are given in percentages of unadsorbed gas: the upper value (gases mixed before adsorption) being, of course, the limit to which the others should approach.

Pressure Mm.	Time Hrs.	%N <sub>2</sub> O	%CO <sub>2</sub>
1403.5	..	21.1	78.9
1488.0	3	47.3	52.7
1428.0	18	35.6	64.4
1400.8	39	33.9	66.1

These figures indicate that although replacement goes on rapidly at first, it proceeds at a much slower rate when about half the gas that one would expect to be replaced has been thus driven out. The speed of the action then becomes so small that it is doubtful whether an equilibrium close to that obtained with the previously mixed gases would ever be reached.

### Lag

As all measurements in these determinations were made on gas withdrawn from the charcoal, they are subject to the lag of gas thus leaving, compared with the amounts entering at the same pressure. A study of the exact effect of this lag seemed desirable. It was found to be sufficiently

uniform, both with the separate gases and with the mixtures, so that the results as obtained could be considered as strictly comparable. The two isotherms of carbon dioxide "going in" and "coming out" are given in Fig. 6. It will be seen that the lag reaches a maximum of about 5% at pressures from 1000 to 1600 mm., and decreases continuously toward either pressure extreme.

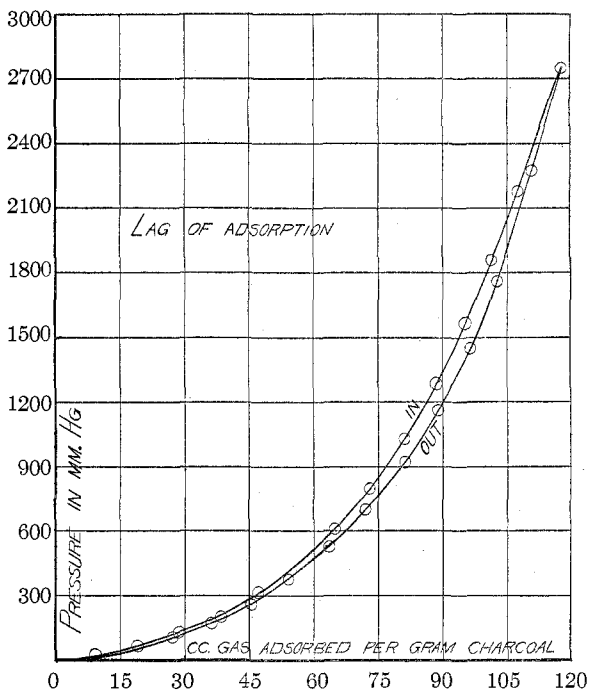


Fig. 6

### Summary

1. The adsorption isotherms of carbon dioxide and nitrous oxide independently, and in mixtures of the approximate proportions 50%  $\text{CO}_2$ -50%  $\text{N}_2\text{O}$ , 75%  $\text{CO}_2$ -25%  $\text{N}_2\text{O}$ , and 25%  $\text{CO}_2$ -75%  $\text{N}_2\text{O}$  have been determined at  $0^\circ$ , and through pressure ranges up to 2800 mm.

2. At each reference point of the three isotherms of the mixtures the amounts of the carbon dioxide and nitrous oxide adsorbed have been determined by analysis.

3. The total amount of the mixture adsorbed can be calculated from the independent adsorption isotherms of the individual gases.

4. The ratio of the degree of adsorption of the two gases varies with the pressure. Only at the highest pressure is it found to be in inverse ratio to the molecular volumes of the adsorbed substances in the liquid form.

Calculations from other work make it probable that a similar ratio holds at very low pressures.

5. It was shown that a gas admitted to another already adsorbed by charcoal replaces it rapidly at first, then with increasing slowness, and that replacement never goes so far as to give an amount of the second gas adsorbed equal to that which would be adsorbed from a mixture of the same composition mixed before being admitted to the charcoal.

6. A considerable lag in the adsorption isotherm obtained from carbon dioxide leaving charcoal compared with that obtained when the gas was entering it was detected; the lag amounted at its maximum to 5%.

7. The problem of the analysis of mixtures of carbon dioxide and nitrous oxide was satisfactorily worked out.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY OF THE CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 34]

## THE SOLUBILITY OF POTASSIUM PERCHLORATE IN SALT SOLUTIONS AND THE CORRESPONDING ACTIVITY RELATIONS

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### Introduction

Activity values may be derived, as is well known, from the solubilities of salts in solutions of other salts through the following considerations. In any solution saturated at a definite temperature with a uni-univalent salt such as AB the product of the activities  $a_A \times a_B$  of the ion constituents A and B has a constant value whatever other salts may be in the solution. Expressing the concentration of the ion constituents by  $c$  with appropriate subscripts and putting the activity coefficient  $\alpha = a/c$ , we may write for any such solution

$$c_A \alpha_A c_B \alpha_B = \text{a constant, or } \frac{\alpha_A \alpha_B}{\alpha_{A_0} \alpha_{B_0}} = \frac{c_{A_0} c_{B_0}}{c_A c_B}$$

where the subscripts zero refer to the solution in pure water. Hence from solubility data the change can be determined of the activity-coefficient product with the nature and concentration of an added salt, or with the total concentration of the solution.

The purpose of the work described in this paper was to determine to what extent the activity-coefficient product for potassium perchlorate is dependent on the nature of the ions added to the solution. The ions for which the effect has been determined are:  $K^+$ ,  $Na^+$ ,  $Ba^{++}$ ,  $Cl^-$ ,  $NO_3^-$ ,  $ClO_4^-$ ,  $SO_4^{--}$ , the added salts producing these ions being  $KCl$ ,  $KNO_3$ ,  $K_2SO_4$ ,  $NaCl$ ,  $NaNO_3$ ,  $NaClO_4$ ,  $Na_2SO_4$ ,  $BaCl_2$ , and  $Ba(NO_3)_2$ . The total