

### Summary

A method is presented of studying the rate of loss of oxygen from an adsorbed film on tungsten, as well as of detecting its presence in a gas. This consists in observing its effect on the electron emission of a tungsten filament, sensitized by the presence of minute traces of cesium vapor ( $10^{-6}$  mm.). Under properly chosen conditions a monatomic oxygen film makes its presence known by increasing the emission a millionfold.

Using this method, the heat of evaporation of oxygen from the adsorbed layer was found to be 162 kg. cal. (7.0 v.) per gram atom.

SCHENECTADY, NEW YORK

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, No. 69]

## THE ADSORPTION OF GAS MIXTURES BY SILICA

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### Introduction

Studies of the adsorption of gases by catalytically active solids, particularly in the last decade, have contributed greatly to a qualitative understanding of the kinetics and mechanism of contact catalysis. Frequently, however, more than one of the reactants or products are simultaneously adsorbed, and in such cases it is obviously necessary to have information concerning the adsorption of one gas in the presence of a second. Such data should also be useful in connection with the practical problem of separating the components of a mixture of gases or vapors. In addition, the behavior of mixtures may be expected to furnish a deeper insight into the nature of adsorption.

Comparatively little is known about the adsorption of the individual constituents of gas mixtures. Richardson and Woodhouse<sup>1</sup> studied the adsorption of carbon dioxide-nitrous oxide mixtures on charcoal. With their static method, however, the composition of the gas phase and of the adsorbed layer can be estimated only approximately. Klosky and Woo,<sup>2</sup> employing the flow method, have studied the adsorption of sulfur dioxide-butane and sulfur dioxide-methyl chloride mixtures on titania gel. Their results indicate that the presence of a second gas decreases the amount of the first gas adsorbed. Other recent studies on the adsorption of gaseous mixtures are those of Putnoky and Szélényi<sup>3</sup> on ethanol-ether-air mixtures with various silica gels, and of Frolich and White<sup>4</sup> on mixtures of methane and hydrogen at elevated pressures in contact with charcoal.

<sup>1</sup> Richardson and Woodhouse, *THIS JOURNAL*, **45**, 2638 (1923).

<sup>2</sup> Klosky and Woo, *J. Phys. Chem.*, **32**, 1387 (1928).

<sup>3</sup> Putnoky and Szélényi, *Z. Elektrochem.*, **34**, 805 (1928); **36**, 10 (1930).

<sup>4</sup> Frolich and White, *Ind. Eng. Chem.*, **22**, 1058 (1930).

From the standpoint of contact catalysis it would be more interesting to study the adsorption of mixtures by catalytically active adsorbents than by such materials as charcoal and titania gel. Griffin<sup>5</sup> has shown that the presence of a small amount of carbon monoxide, less than 0.05 cc., upon a sample of catalytically active copper, increases the amount of hydrogen adsorbed at low pressures but decreases the amount adsorbed at higher pressures. This is an indication of the complexity of adsorption of gas mixtures by active catalysts.

As a preliminary investigation to the study of mixture adsorption by active catalysts it seemed advisable to investigate first the behavior of a solid which normally shows adsorptions of the "secondary," or non-selective, type. Silica was chosen as a suitable material, since previous work<sup>6</sup> has shown that its behavior with a number of gases is of the type in question.

Carbon monoxide, carbon dioxide and oxygen were selected because silica does not induce interaction between any of these at the temperatures used, yet it adsorbs convenient amounts of each, a small amount of oxygen, a large amount of carbon dioxide and an intermediate amount of carbon monoxide.

### Experimental Procedure

The apparatus used in this investigation is illustrated in Fig. 1. The entire apparatus up to G and H, including the gas generators and purifying lines, was constructed of pyrex glass, all joints being fused. The pyrex-to-soft glass seals (G, H) were effected by surrounding the ends of the tubing by glass cups which were filled with deKhotinsky cement. The adsorbent was contained in bulb B, which could be maintained at either 0 or 100° by an ice- or steam-bath. The pressure in bulb B was determined by the mercury manometer M. A Töpler pump, T, was connected as indicated to bulb B and to the calibrated gas buret A, the latter being connected to the buret of a modified Orsat gas analysis apparatus (not shown).

The individual gases from the generators and purifying lines (not shown in Fig. 1), entering at C, D, E, could be passed directly over the adsorbent in B, or into any of the three mixture reservoirs, only one of which is shown in the figure (1, 2). From these reservoirs the mixtures passed over calcium chloride and phosphorus pentoxide, respectively, in X and Y, and thence through bulb B, or to buret A for analysis. Freshly boiled water was used as the confining liquid in the reservoirs, except for mixtures containing carbon dioxide, for which a concentrated solution of magnesium sulfate was preferable on account of the diminished solubility of carbon dioxide.

The mixtures were passed over the adsorbent in bulb B for about two hours, the pressure in the bulb being maintained at exactly 760 mm. by regulation of the head of concentrated sulfuric acid in N. The failure of the manometer M to denote any change of pressure within the bulb after standing for an hour or more after it was closed off by stopcocks indicated that equilibrium had been reached. As a further check on the establishment of equilibrium, mixtures were passed over the adsorbent in one case for fifteen minutes and in a second case for two hours, the same adsorption being obtained

<sup>5</sup> Griffin, *THIS JOURNAL*, 49, 2136 (1927).

<sup>6</sup> Benton, *ibid.*, 45, 887 (1923).

in each instance. After equilibrium was reached the gas was removed from the bulb by means of the Töpler pump and forced into the gas buret A, where its volume was determined. From this buret it was passed into the gas analysis apparatus.

The isotherms of the individual gases were determined by streaming the pure gas over the adsorbent until equilibrium was reached. Successive small amounts of gas were pumped out of the bulb by means of the Töpler pump and the volumes read in the buret. After each removal of gas the pressure in the bulb was determined by means of the mercury manometer after it had become constant, thus indicating that equilibrium had been reached.

All adsorptions were repeated and the results duplicated to within an average of about 0.05 cc., with the exception of mixtures containing carbon dioxide. In such mixtures the solution of carbon dioxide in the confining liquid in the reservoir caused a progressive change which made it impossible to carry out duplicate runs with mixtures of identical composition. All gas analyses were run in duplicate and checked to within one-tenth of one per cent., and in most cases to within a few hundredths of one per cent.

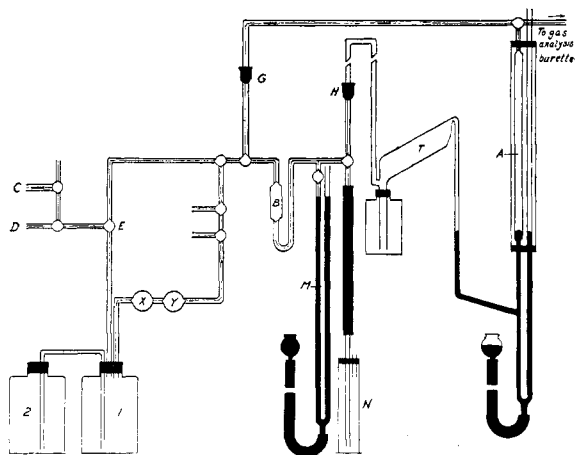


Fig. 1.—Apparatus.

The free space in the bulb was determined by measuring the amount of helium necessary to fill it at a pressure of 760 mm. and at temperatures of 0 and 100°. It is assumed that helium was not adsorbed by the silica.

The adsorptions of the separate gases are calculated by taking the difference between the volumes of the gas in question and of helium required to fill the bulb containing the adsorbent at a given temperature and pressure. In the case of mixtures the amount of each component adsorbed is obtained as follows. From the total volume of gas pumped out of the bulb, and its analysis, the total volume of each component present (that is, gas adsorbed plus gas in free space) is known. The amount of each component in the free space is obtained from the analysis of the mixture which is passed over the adsorbent, together with the volume of the free space as determined with helium. By subtraction of the amount of each gas in the free space from the total amount of that gas present, the quantity adsorbed may be calculated. All pressures have been expressed in mm. of mercury at 0°, and volumes in cc. at 0°, 760 mm.

Oxygen was prepared by electrolysis of a solution of sodium hydroxide between nickel electrodes. Carbon monoxide was generated by dropping concentrated sulfuric acid on hot 85% formic acid solution. Carbon dioxide was obtained by dropping

sulfuric acid into a concentrated solution of chemically pure sodium bicarbonate. To each generator were attached the usual devices for removing spray and for purifying and drying the gases.

The adsorbent was prepared by prolonged washing of *c. p.* precipitated silicic acid and subsequent heating to 250° for a period of several days. The sample of adsorbent weighed 19.6 g.

### Experimental Results

**Isotherms for Individual Gases.**—The isotherms of oxygen and of carbon monoxide have been determined at 0 and at 100°. Since inconveniently large amounts of carbon dioxide are adsorbed at 0° the isotherm for this gas has been determined only at 100°. The experimental data are recorded in Tables I and II. Pressures are expressed in mm. of mercury at 0°, and volumes are in cc. at 0° and 760 mm. The calculated values recorded in these tables will be discussed in a later section.

All the measurements with carbon monoxide and oxygen, both singly and in mixtures of the two, were completed before any carbon dioxide was used. All the values so obtained were found to be accurately reproducible, regardless of the order of the experiments. On first employing carbon dioxide, however, the adsorptive capacity of the silica for this gas underwent a gradual increase of about 6 cc. during nine successive runs, after which it remained constant for three additional runs. It was then found that the adsorptive capacity for oxygen had been slightly increased, while it had remained unchanged for carbon monoxide. From this point on, the new values were accurately reproducible. Because of the above effects it is necessary in comparing adsorptions in mixtures with those of the separate gases, to use the data headed "100° (before CO<sub>2</sub>)" in Table I for comparison with oxygen-carbon monoxide mixtures, and those headed "100° (after CO<sub>2</sub>)" for comparison with oxygen-carbon dioxide mixtures.

It is not known whether or not the increase in adsorptive capacity produced by repeated treatments with carbon dioxide is due to a displacement of water from the silica.

TABLE I  
ADSORPTION OF OXYGEN BY SILICA (19.6 G.)

Press., mm.	0°		100° (before CO <sub>2</sub> )			100° (after CO <sub>2</sub> )		
	Volume adsorbed Obs., cc.	Calcd., cc.	Press., mm.	Volume adsorbed Obs., cc.	Calcd., cc.	Press., mm.	Volume adsorbed Obs., cc.	Calcd., cc.
83.0	3.32	3.27	17.9	0.08	0.12	40.4	0.37	0.29
142.4	5.57	5.57	88.6	.54	.60	139.1	1.00	.99
224.3	8.73	8.71	133.9	.90	.91	204.1	1.40	1.45
329.6	12.68	12.67	221.9	1.52	1.51	260.9	1.77	1.85
405.1	15.48	15.48	329.0	2.19	2.22	361.7	2.53	2.55
544.1	20.42	20.49	417.1	2.87	2.81	428.7	3.04	3.01
602.5	22.48	22.56	471.4	3.18	3.17	527.3	3.69	3.69
667.5	24.86	24.84	570.5	3.92	3.82	608.4	4.25	4.24
760.0	28.03	28.04	653.2	4.38	4.36	760.0	5.26	5.26
			760.0	5.01	5.05			

TABLE II

## ADSORPTIONS OF CARBON MONOXIDE AND DIOXIDE BY SILICA (19.6 G.)

Press., mm.	CO at 0°		Press., mm.	CO at 100°		Press., mm.	CO <sub>2</sub> at 100°	
	Obs., cc.	Calcd., cc.		Obs., cc.	Calcd., cc.		Obs., cc.	Calcd., cc.
95.5	7.09	7.08	26.3	0.26	0.29	26.3	3.37	3.46
127.4	9.48	9.38	127.9	1.37	1.38	77.6	10.07	10.05
199.7	14.37	14.46	224.4	2.36	2.38	114.9	14.73	14.71
272.4	19.41	19.41	321.0	3.37	3.34	141.1	17.94	17.92
367.4	25.54	25.64	434.5	4.42	4.44	190.8	23.93	23.88
463.7	31.70	31.70	537.2	5.30	5.39	239.9	29.61	29.60
549.7	37.01	36.91	639.4	6.33	6.31	289.0	35.18	35.16
647.9	42.65	42.63	760.0	7.40	7.35	332.8	40.02	39.99
760.0	48.89	48.88				378.4	44.82	44.89
						434.8	50.76	50.79
						477.3	55.05	55.11
						536.8	61.01	61.00
						593.1	66.40	66.40
						689.1	75.47	75.25
						760.0	81.78	81.51

**Adsorption of Mixtures.**—The adsorption of each gas in mixtures of carbon monoxide and oxygen has been determined at 0 and at 100°. The adsorption of each gas in mixtures of carbon dioxide and carbon monoxide and in mixtures of carbon dioxide and oxygen has been determined only at 100°.

The results obtained are recorded in Tables III to VI. The pressures of each gas in the various mixtures are given in the first and second columns. The values recorded in the third and sixth columns are the volumes which would be adsorbed at the pressures given if the second gas were not present, as determined by interpolation from the isotherms for the individual gases.

TABLE III

CO-O<sub>2</sub> MIXTURES AT 0°

p <sub>O</sub>	p <sub>CO</sub>	Volume of oxygen adsorbed			Volume of carbon monoxide adsorbed		
		Iso-therm	Obs.	Calcd.	Iso-therm	Obs.	Calcd.
230.2	529.8	8.98	8.31	7.96	35.90	35.02	35.00
391.1	368.9	15.05	14.10	13.79	25.82	24.69	24.84
585.1	174.9	21.93	21.73	21.12	12.80	11.63	12.06

TABLE IV

CO-O<sub>2</sub> MIXTURES AT 100°

p <sub>O</sub>	p <sub>CO</sub>	Volume of oxygen adsorbed			Volume of carbon monoxide adsorbed		
		Iso-therm	Obs.	Calcd.	Iso-therm	Obs.	Calcd.
210.3	549.7	1.45	1.56	1.30	5.50	5.27	5.46
286.4	473.6	1.95	1.96	1.79	4.80	4.40	4.75
335.7	424.3	2.30	2.33	2.11	4.34	4.05	4.29
548.9	211.1	3.73	3.72	3.55	2.24	2.16	2.19

TABLE V  
CO<sub>2</sub>-O<sub>2</sub> MIXTURES AT 100°

pO	pCO <sub>2</sub>	Volume of oxygen adsorbed			Volume of carbon dioxide adsorbed		
		Iso-therm	Obs.	Calcd.	Iso-therm	Obs.	Calcd.
182.5	577.5	1.30	1.81	1.10	64.90	65.14	64.45
199.0	561.0	1.42	1.78	1.21	63.40	63.89	62.84
438.6	321.4	3.08	2.90	2.81	38.70	38.82	38.04
614.1	145.9	4.30	4.25	4.10	18.70	18.65	18.02
618.0	142.0	4.32	4.21	4.13	18.20	18.45	17.55

TABLE VI  
CO<sub>2</sub>-CO MIXTURES AT 100°

pCO	pCO <sub>2</sub>	Volume of carbon monoxide adsorbed			Volume of carbon dioxide adsorbed		
		Iso-therm	Obs.	Calcd.	Iso-therm	Obs.	Calcd.
211.6	548.4	2.34	2.98	1.93	62.10	61.51	60.13
259.5	500.5	2.73	3.21	2.38	57.50	57.30	55.16
377.0	383.0	3.89	3.77	3.50	45.40	45.42	42.75
384.9	375.1	3.97	3.70	3.57	44.50	44.68	41.90
555.0	205.0	5.55	5.53	5.25	25.60	25.93	23.32

The volumes actually adsorbed in the mixtures are given in the fourth and seventh columns headed "observed." The fifth and eighth columns headed "calculated" will be discussed in a later section.

### Discussion

**Adsorption of Single Gases.**—Langmuir,<sup>7</sup> assuming adsorption in a unimolecular layer on a plane surface, has derived an equation of the general form

$$V = V^{\circ} \frac{ap}{1 + ap} \quad (1)$$

where  $V$  is the volume of gas adsorbed at pressure  $p$ ,  $a$  is a constant at a given temperature, and  $V^{\circ}$  is the saturation value, or the amount of gas adsorbed when the surface is entirely covered. This equation may be written in the form

$$1/V = (1/aV^{\circ})(1/p) + (1/V^{\circ})$$

If this equation holds, a plot of  $1/V$  against  $1/p$  should yield a straight line whose slope and intercept should permit a calculation of  $a$  and  $V^{\circ}$ .

In Figs. 2 and 3 are shown the plots of  $1/V$  against  $1/p$  for the various gases at the two temperatures. It is evident that Equation 1 is satisfactory. The values of  $V^{\circ}$  and  $a$  thus obtained are given in Table VII.

The values calculated from Equation 1, with the constants of Table VII, are given in Tables I and II under the columns headed "calculated."

Although Equation 1 agrees with the experimental data within the estimated limits of error at almost every point, it must nevertheless be

<sup>7</sup> Langmuir, THIS JOURNAL, 40, 1361 (1918).

TABLE VII  
CONSTANTS IN ADSORPTION EQUATION

Gas and temperature	$V^\circ$ , cc.	$a$ , mm. <sup>-1</sup>
O <sub>2</sub> at 0°	397.0	0.000100
CO at 0°	322.6	.000235
O <sub>2</sub> at 100°, before CO <sub>2</sub>	171.3	.000040
O <sub>2</sub> at 100°, after CO <sub>2</sub>	153.9	.0000466
CO at 100°	60.2	.000183
CO <sub>2</sub> at 100°	426.4	.000311

regarded as purely empirical, since  $V^\circ$ , the saturation value, is widely different not only for different gases but for the same gas at different temperatures. Owing to the fact that in these experiments  $ap$  is small compared to unity, that is, that the volume adsorbed is so nearly proportional to the pressure, only the product  $aV^\circ$  can be estimated accurately,

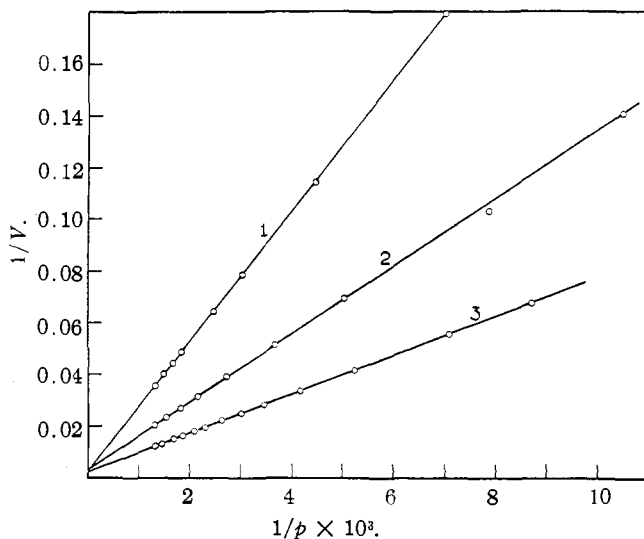


Fig. 2.—Variation of  $1/V$  with  $1/p$  for the adsorption of oxygen at 0° (Curve 1), carbon monoxide at 0° (Curve 2), carbon dioxide at 100° (Curve 3).

while  $a$  and  $V^\circ$  are each subject to considerable uncertainty. The errors in the values of  $V^\circ$  thus introduced are enormously less than the differences shown in Table VII. It is obvious, however, that the equation could be more adequately tested by extending the measurements to higher pressures.

**Adsorption in Binary Mixtures.**—If it is assumed that the surface of the adsorbent is uniform and capable of adsorbing only a single layer of gas, and, furthermore, that there is no interaction between the adsorbed gases, an equation can be derived which relates the amount of one gas adsorbed to its pressure and to the pressure of the second gas.

Let  $\sigma_1$  and  $\sigma_2$  represent the fractions of the surface covered by Gases 1 and 2, respectively. The rate of condensation of Gas 1,  $\mu_1$ , is equal to  $k_1 p_1 (1 - \sigma_1 - \sigma_2)$ , where  $(1 - \sigma_1 - \sigma_2)$  is the fraction of the surface free from gas,  $p_1$  is the pressure of Gas 1, and  $k_1$  is a constant at a given temperature. The rate of evaporation,  $\nu_1$ , can be expressed by the equation  $\nu_1 = k'_1 \sigma_1$ .

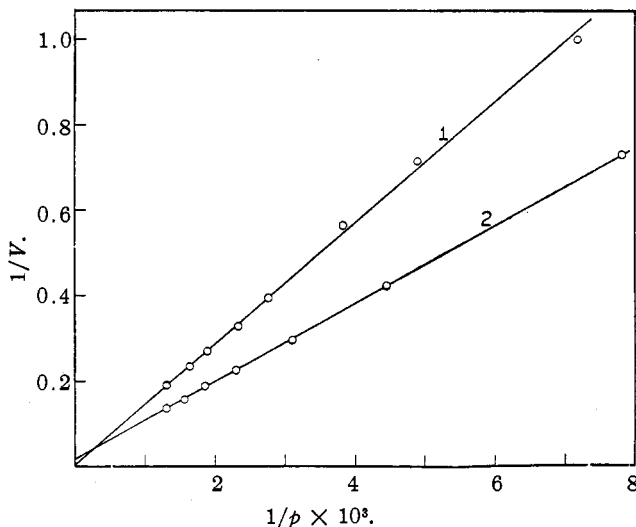


Fig. 3.—Variation of  $1/V$  with  $1/p$  for the adsorption of oxygen at  $100^\circ$  (Curve 1), and of carbon monoxide at  $100^\circ$  (Curve 2).

Similarly for Gas 2,  $\mu_2 = k_2 p_2 (1 - \sigma_1 - \sigma_2)$  and  $\nu_2 = k'_2 \sigma_2$ . At equilibrium, where the rates of condensation and evaporation are equal

$$k_1 p_1 (1 - \sigma_1 - \sigma_2) = k'_1 \sigma_1$$

Substitution of  $a$  for  $k_1/k'_1$  and simplification gives

$$\sigma_1 = \frac{a p_1 (1 - \sigma_2)}{1 + a p_1} \quad (2)$$

Similarly for Gas 2

$$\sigma_2 = \frac{b p_2 (1 - \sigma_1)}{1 + b p_2} \quad (3)$$

Substitution in (2) of the value of  $\sigma_2$  from (3) gives

$$\sigma_1 = \frac{a p_1}{1 + a p_1 + b p_2} \quad (4)$$

and for  $\sigma_2$

$$\sigma_2 = \frac{b p_2}{1 + a p_1 + b p_2} \quad (5)$$

The fraction of the surface,  $\sigma$ , covered by a gas may be expressed by the equation,  $\sigma = V/V^\circ$ , where  $V$  and  $V^\circ$  have the same significance as before. Making the substitutions for  $\sigma_1$  and  $\sigma_2$  in Equations 4 and 5, we arrive at the final equations



$$V_1 = \frac{a V_1^{\circ} p_1}{1 + a p_1 + b p_2} \quad (6)$$

$$V_2 = \frac{b V_2^{\circ} p_2}{1 + a p_1 + b p_2} \quad (7)$$

Equations 6 and 7 involving constants previously determined from the isotherms for the separate gases indicate that the presence of a second gas should diminish the amount of the first gas adsorbed, particularly at high pressures of the second gas. From these equations and the constants recorded in Table VII, the adsorbed volumes have been calculated and recorded in the fifth and eighth columns of Tables III, IV, V, VI.

The values recorded in Table III show that in mixtures of carbon monoxide and oxygen at 0° the adsorption of each gas at given pressure is materially diminished by the presence of the other gas. The amount of oxygen adsorbed, however, is more than the amount calculated from Equations 6 and 7, while the reverse is, in general, the case for carbon monoxide. Table IV shows essentially similar relations for these gases at 100°.

In mixtures of carbon dioxide with oxygen or with carbon monoxide, the adsorption of the dioxide is many times greater than that of the second component. Tables V and VI show that at the higher pressures of carbon dioxide the adsorbed volumes of either oxygen or carbon monoxide are not only greater than the calculated volumes but even exceed the amounts which would be adsorbed in absence of the carbon dioxide. At the lower pressures of the dioxide the adsorbed volumes of oxygen and carbon monoxide are less than the isotherm volumes but greater than the calculated. It is seen that the corresponding comparison is, in general, true with respect to the amount of carbon dioxide adsorbed in these mixtures.

Equations 6 and 7 require that the ratio of the adsorbed volumes should be proportional to the ratio of the pressures of the two gases. Division of (7) by (6) gives the expression

$$\frac{V_2}{V_1} = \frac{b V_2^{\circ} p_2}{a V_1^{\circ} p_1}$$

or, since in these experiments  $p_2 = 760 - p_1$

$$\frac{V_2}{V_1} = \frac{760 b V_2^{\circ}}{a V_1^{\circ} p_1} - \frac{b V_2^{\circ}}{a V_1^{\circ}} \quad (8)$$

Thus, if  $V_2/V_1$  is plotted against  $1/p_1$ , the experimental points should lie on a straight line whose slope is  $760 b V_2^{\circ}/a V_1^{\circ}$ . When plotted in this manner the observed adsorptions in mixtures of carbon monoxide and oxygen at 0 and at 100° agree fairly well with Equation 8. In the case of mixtures containing carbon dioxide, however, the plotted points lie on a distinct curve, which approaches the theoretical straight line at the lower pressures of the dioxide.

The applicability of Equation 7 (or 6) may be tested without employing the constants obtained from the isotherms of the separate gases, by putting it in the form

$$\frac{1}{V_2} = \frac{1 + 760a}{bV_2^0 p_2} + \frac{b - a}{bV_2^0}$$

By plotting  $1/V$  against  $1/p$  for each gas in each mixture, it was found that the points yield satisfactory straight lines for both components of the carbon monoxide-oxygen mixtures, and for carbon dioxide in mixtures containing this gas. The points for either oxygen or carbon monoxide in mixtures with the dioxide yield distinct curves.

### Conclusions

The results of this study show that the assumptions underlying Equations 6 and 7 are fairly satisfactory for mixtures of carbon monoxide and oxygen, but prove inadequate when applied to mixtures containing carbon dioxide. It is apparent that the failure of the equations in the latter case cannot be attributed entirely to the assumptions of unimolecular adsorption and uniformity of surface, since these assumptions are also necessary in deriving Equation 1 for the individual gases, and this equation has been shown to give satisfactory results over the range in question.

It is concluded, therefore, that the failure of Equations 6 and 7 in the case of mixtures containing carbon dioxide is to be attributed mainly to interaction between the adsorbed molecules in the sense that the rate of evaporation of a given molecule may be decreased by the presence in an adjacent space of a molecule of a second gas. Elaboration of this idea may be postponed until further data have been accumulated.

### Summary

1. The adsorption of each gas in binary mixtures of carbon monoxide and oxygen has been measured at one atmosphere and temperatures of 0 and 100°, and in mixtures of carbon dioxide with carbon monoxide and with oxygen at 100°. The isotherms of the separate gases have been determined at the same temperatures.

2. The results have been interpreted on the basis of a simple extension of Langmuir's theory of adsorption to the case of gas mixtures. The equations so derived permit the adsorption of each gas in the mixture to be calculated for any given partial pressures without the employment of constants other than those obtainable from the isotherms of the separate gases. The equations indicate that each gas in the mixture should be adsorbed to a smaller extent than if it were present alone at the same partial pressure.

3. With mixtures of carbon monoxide and oxygen there is rough agreement between the calculated and observed adsorptions. On the other

hand, in mixtures containing carbon dioxide the observed values are not only greater than the calculated, but in many cases even exceed the adsorptions found in the absence of the second gas. Pending the accumulation of further data, it is suggested that this anomaly may be due to some kind of mutual interaction between the two kinds of adsorbed molecules.

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

## NUCLEAR SPIN AND THE THIRD LAW OF THERMODYNAMICS. THE ENTROPY OF IODINE

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Much interest is attached to the problem of determining the manner in which nuclear spin is concerned in the application of the third law of thermodynamics. The somewhat complicated but well-established situation which exists in hydrogen has recently been discussed.<sup>1</sup> In this case nuclear spin results in ortho and para forms which establish equilibrium with each other so slowly that it is impractical to use heat capacity measurements to obtain the entropy. However, it was suggested that hydrogen might be the only substance in which nuclear spin would appreciably affect the calorimetric properties at temperatures above a few degrees absolute. If this proves to be true, it will be convenient to ignore the effect of nuclear spin on the absolute entropy except for hydrogen. This would be possible since, as first pointed out by Gibson and Heitler,<sup>2</sup> for certain gas reactions, the limiting contribution which nuclear spin makes to the entropy cancels in obtaining the entropy change which occurs during a reaction.

The diatomic elements offer a suitable opportunity for obtaining information concerning the above problem and of these the ones consisting primarily of one isotope present the most favorable cases. Diatomic gas molecules which consist of two isotopes of the same element do not have the division of such molecules into ortho and para states. This is the situation most open to suspicion in connection with the possibility of anomalous calorimetric effects. For example, in chlorine the 35-37 molecules would be expected to establish their limiting spin entropy below the lowest attained temperature. The 35-35 and 37-37 molecules are of the type in which we are more interested. Since these latter two would behave differently if the nuclear spins of the two isotopes are different, we believe it best to confine the initial investigation to simpler substances. Of these nitrogen is at present under experimental investigation and existing data on iodine are sufficient for our purpose. In this paper we shall consider the case of iodine.

<sup>1</sup> Giauque, THIS JOURNAL, 52, 4816 (1930).

<sup>2</sup> Gibson and Heitler, *Z. Physik*, 49, 465 (1928).