

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HOWARD UNIVERSITY]

## Adsorption of Vapors on Glass Spheres. I. The Adsorption of Nitrogen

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## Introduction

In a previous investigation<sup>1</sup> of the adsorption of oxygen by glass spheres, it was observed that the amount of adsorption at corresponding pressures increased with the number of contacts per sphere. As this effect could also be due to differences in the degree of activation of the surface resulting from unequal periods of the degassing process, it was considered essential to obtain reproducible isotherms under the same conditions of treatment and packing before any definite conclusions as to the effect of the number of contacts on the adsorption could be reached.

Inasmuch as every oxygen isotherm exhibited a peculiar pressure reversal apparently connected with a discontinuity or break in the isotherm it was considered desirable to use nitrogen in place of oxygen in order to ascertain whether the peculiarity was characteristic of oxygen or was more general in nature. Nitrogen has the added advantage of being more strongly adsorbed while very similar to oxygen in its physical properties. The experiments were carried out at the temperature of liquid air where the nitrogen, as well as the oxygen previously investigated, may be classed as a vapor.

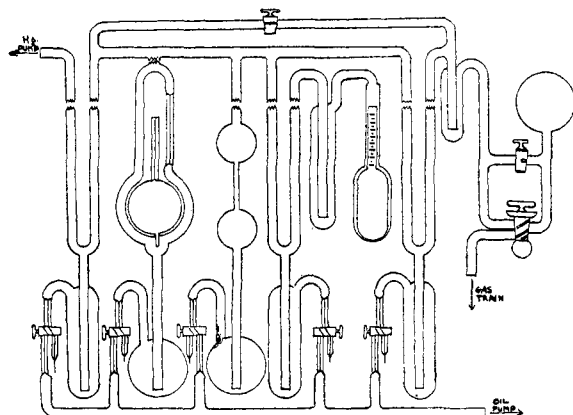


Fig. 1.—Apparatus.

## Apparatus

A schematic representation of the apparatus is shown in Fig. 1. As may be seen the adsorption system proper is the conventional arrangement used when adsorption is to be calculated from pressure measurements. The McLeod

gage was calibrated in three ranges, from  $1 \times 10^{-6}$  to  $1 \times 10^{-4}$ , from  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$ , and from  $1 \times 10^{-4}$  to  $5 \times 10^{-2}$  cm. of mercury. F is a gas reservoir, D is a dosing stopcock, and C<sub>1</sub> and C<sub>2</sub> are auxiliary stopcocks. By varying the pressure in F, or by repetitive use of stopcock D, any desired quantity of gas could be introduced into the adsorption system by filling the bore of the dosing stopcock from the reservoir and then discharging this gas into the adsorption apparatus through mercury stop S<sub>2</sub>.

The volumes of the various parts of the apparatus were determined with hydrogen at pressures ranging from 2 to 20 cm. of mercury. In these determinations we made use of the calibrated bulbs B<sub>1</sub> and B<sub>2</sub>. All pressures were read on the mercury stop S<sub>3</sub> with a cathetometer reading to 0.01 mm. The pre-expansion volume extending from X<sub>2</sub> to X<sub>3</sub> was found to be 981 cc.; the total volume consisting of the pre-expansion volume and the adsorption chamber and extending from X<sub>2</sub> to A was 1599 cc.

## Preparation of Materials

Tank hydrogen containing water and oxygen as possible impurities was purified by passage through activated charcoal at liquid air temperature.

Commercial helium containing hydrocarbons as possible impurities was likewise purified<sup>2</sup> by passage through activated charcoal at liquid air temperature.

Nitrogen was prepared from pure ammonium hydroxide and bromine water in a manner described by Waran.<sup>3</sup> The nitrogen was stored over phosphorus pentoxide for forty-eight hours before being used.

The spheres 3 mm. in diameter and of soft glass were cleaned with chromic and nitric acids and washed with distilled water. The actual surface was obtained by measuring the adsorption of methylene blue in accordance with the method of Paneth.<sup>4</sup> The isotherms thus obtained showed a well-defined maximum at about 1.53 mg. of the dye. Using the value given by Paneth of 1 mg. of methylene blue per square meter, the actual surface of 1000 spheres was found to be 15,380 sq. cm. as compared with the 283 sq. cm. of apparent surface calculated from the dimensions of the spheres.

## Results and Discussion

**Thermal Flow.**—In view of the phenomenon of thermal flow observed by Knudsen<sup>5</sup> at low temperatures and pressures, it was necessary to establish a correction curve relating the equilibrium pressure in the apparatus at room temperature with the equilibrium pressure in the cooled portion of the system. Using a gas which is not

(2) Lang, *Trans. Roy. Soc., Can.*, **17**, III, 181 (1923).(3) Waran, *Phil. Mag.*, **42**, 246 (1921).(4) Paneth and Radu, *Ber.*, **57B**, 1221 (1924).(5) Knudsen, *Ann. Physik*, **31**, 205, 633 (1910).

(1) Unpublished.

adsorbed, the pressure in the cooled portion can be calculated from the equation

$$P_1 V_1 / RT_1 = P_2 V_2 / RT_1 + P_3 V_3 / RT_3 \quad (1)$$

where  $P_1$  is the calculated pressure obtained from a knowledge of the total gas in the system and the total volume  $V_1$  at temperature  $T_1$ ,  $P_2$  is the equilibrium pressure measured with the McLeod gage in the volume  $V_2$  at temperature  $T_1$ , and  $P_3$  is the equilibrium pressure in the volume  $V_3$  kept at temperature  $T_3$ . In this equation all quantities except  $P_3$  are measured.

Four runs were carried out, two using helium and two using hydrogen. One of the hydrogen runs was made with an empty vessel having the same volume as the voids in the chamber filled with spheres. The other runs were made with the spheres in the chamber. The results of these measurements are given in Tables I and II, and Fig. 2. The dotted line in Fig. 2 represents the values obtained from the relation

$$P_3 = P_2 \sqrt{T_3/T_1} \quad (2)$$

which is required by the theory<sup>6</sup> of thermal flow

TABLE I  
THERMAL FLOW OF HELIUM

Run 1 Temperature of liquid air 93° A.		Run 2 Temperature of liquid air 94° A.	
$P_2$ , cm.	$P_3$ , cm.	$P_2$ , cm.	$P_3$ , cm.
$0.72 \times 10^{-5}$	$0.17 \times 10^{-5}$	$0.60 \times 10^{-5}$	$0.17 \times 10^{-5}$
2.08	.89	.95	.69
3.30	1.77	2.25	1.31
4.84	2.56	3.35	2.47
6.59	3.87	5.03	3.29
7.95	4.72	6.40	3.99
13.5	7.96	8.95	6.88
22.5	12.37	14.7	9.64
35.5	21.84	20.1	14.89
52.5	32.10	26.1	19.38
79.7	50.20	43.4	29.3
103.3	71.50	61.3	44.2
		82.7	60.2
		102.2	76.9
		121.8	103.5

TABLE II  
THERMAL FLOW OF HYDROGEN

Run 1 In presence of glass spheres Temperature of liquid air 95° A.		Run 2 In blank chamber Temperature of liquid air 94° A.	
$P_2$ , cm.	$P_3$ , cm.	$P_2$ , cm.	$P_3$ , cm.
$0.90 \times 10^{-5}$	$0.50 \times 10^{-5}$	$0.64 \times 10^{-5}$	$0.42 \times 10^{-5}$
2.14	1.18	1.85	1.88
3.33	2.07	3.21	2.45
4.79	2.74	5.24	3.11
7.00	3.85	6.40	4.25
8.00	4.65	9.12	5.94
9.83	7.91	20.5	16.9
15.60	12.78	27.6	20.1
23.00	18.23	40.3	29.3
37.2	27.4	55.5	43.7
53.7	42.4	69.0	62.9
66.7	53.1	86.0	77.0
87.0	69.3		
101.1	70.3		

(6) Reynolds, *Phil. Trans.*, P127 (1879).

under conditions where the mean free path of the gas is large compared to the diameter of the tubing. It is to be observed that the experimental values approach the theoretical at low pressures, but in the region of  $1 \times 10^{-5}$  to  $1 \times 10^{-3}$  cm. of mercury the deviation is large.

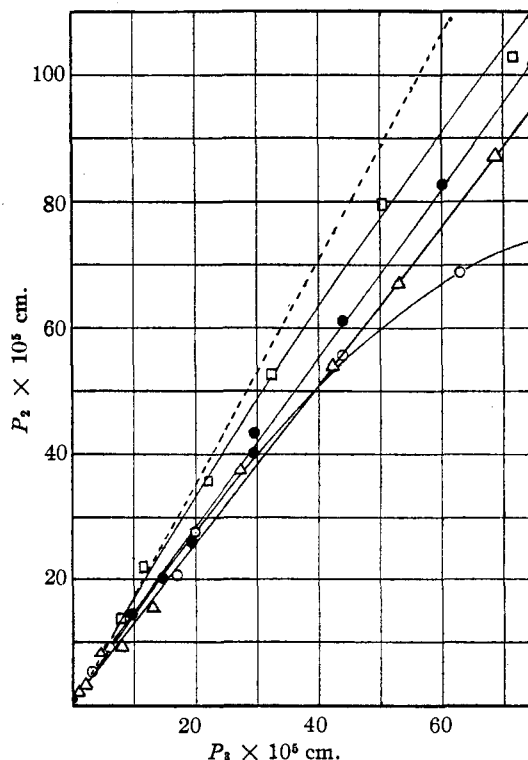


Fig. 2.—Thermal flow: □, helium Run 1; ●, helium Run 2; ○, hydrogen in blank; △, hydrogen with spheres in chamber; ---, theoretical.

The lack of agreement between the hydrogen curves can be explained by the large adsorbing surface due to the presence of the spheres in one of the two runs. Even though the adsorption of hydrogen is negligible, the disparity in the surfaces of the two experiments is great enough to account for the difference. In the case of the helium no such explanation can be offered. However, it is in accord with observations reported by many experimenters<sup>7</sup> who found that repeated treatment of adsorbing surfaces with a gas enhances the adsorption of the gas.

In comparing the ratios  $P_3/P_2$  for hydrogen in the blank chamber with corresponding ratios for the first helium run, we found them to agree with the assumption of Langmuir<sup>8</sup> that these ratios are

(7) Harned, *THIS JOURNAL*, 42, 372 (1920); McBain, *Nature*, 117, 550 (1926); Chaplin, *Proc. Roy. Soc. (London)*, A121, 344 (1925).

(8) Langmuir, *THIS JOURNAL*, 40, 1378 (1918).

equal at pressures corresponding to equal mean free paths. Slight differences in these ratios, those of hydrogen always being higher, most likely indicate the presence of adsorption for hydrogen. This correspondence was taken into consideration in the adsorption calculations of nitrogen described below.

**Nitrogen Adsorption.**—The results of the experiments on nitrogen are presented in Tables III-IV and Figs. 3 and 4. Column 1 of each table gives the pressures of the gas in the system previous to adsorption. They were calculated from the known amount of gas introduced and the total volume of the system. The values given are all reduced to 0°. In column 2 are given the corresponding pressures reduced to 0° after adsorption has taken place and equilibrium was established. These pressures were measured with the McLeod gage at room temperature. From the measured values of this column and the calibration curve, we obtained the equilibrium pressures in the adsorption chamber which are given in column 3. The adsorption values given in column 4 were calculated by means of the equation

$$A = P_1V_1/RT_1 - (P_2V_2/RT_1 + P_3V_3/RT_3) \quad (3)$$

where the terms have the same meaning as in equation (1).

To establish a procedure of treatment for the purpose of obtaining reproducible activation of the adsorbing surface, we first tried degassing at

TABLE III

## ADSORPTION OF NITROGEN ON GLASS SPHERES

No. of Spheres, 5000. Activated at Room Temperature

Run No. 1			
No. contact points per sphere—10.88			
Liquid air temperature 92° A.			
$P_1$ , cm.	$P_2$ , cm.	$P_3$ , cm.	A, moles
$0.77 \times 10^{-5}$	$0.71 \times 10^{-5}$	$0.48 \times 10^{-5}$	$0.00 \times 10^{-5}$
1.57	1.54	1.06	.07
3.04	2.78	1.90	.04
5.39	4.71	3.31	.23
9.38	0.89	0.61	6.74
10.80	.83	.55	7.94
12.29	.83	.56	9.12
14.89	1.11	.74	10.97
17.17	1.60	1.06	12.38
19.98	1.97	1.32	14.30
23.51	2.72	1.85	15.74
29.14	4.32	3.01	19.43
38.58	6.30	4.50	25.33
46.86	8.48	6.22	30.11
57.06	13.21	10.49	33.99
68.4	17.74	14.62	38.96
78.7	22.14	18.75	43.20
94.3	30.16	26.96	46.66
108.4	36.44	34.40	53.52
127.6	45.4	45.4	60.25
142.9	53.8	53.8	64.73
173.9	63.6	63.6	80.50
200.0	87.9	87.9	78.95

Run No. 2			
No. contact points per sphere—10.88			
Liquid air temperature 95° A.			
$1.03 \times 10^{-5}$	$0.86 \times 10^{-5}$	$0.58 \times 10^{-5}$	$0.09 \times 10^{-5}$
1.88	.45	.30	1.16
2.59	.34	.23	1.84
3.19	.34	.23	2.34
4.24	.45	.30	3.11
5.84	.55	.37	4.35
6.65	.62	.41	4.96
11.91	1.55	1.05	8.48
24.76	4.46	3.13	16.53
40.4	8.42	6.17	25.91
57.6	14.0	11.24	34.95

Run No. 3			
No. contact points per sphere—10.88			
Liquid air temperature 93° A.			
$0.77 \times 10^{-5}$	$0.30 \times 10^{-5}$	$0.20 \times 10^{-5}$	$0.37 \times 10^{-5}$
1.29	.24	.16	.85
1.98	.16	.09	1.50
4.21	.46	.31	3.07
9.47	.92	.62	7.02
34.5	7.16	5.15	22.16
55.2	13.6	10.88	33.35
89.4	32.6	29.76	43.79
109.5	43.3	43.3	49.37
143.9	60.4	60.4	62.11

Run No. 4			
No. contact points per sphere—10.92			
Liquid air temperature 93° A.			
$0.59 \times 10^{-5}$	$0.31 \times 10^{-5}$	$0.21 \times 10^{-5}$	$0.21 \times 10^{-5}$
1.15	.19	.12	.78
2.22	.19	.12	1.67
3.52	.30	.20	2.65
5.33	.42	.29	4.04
7.84	.65	.43	5.92
10.57	.88	.57	7.98
14.46	1.65	1.12	10.52
19.87	2.66	1.83	14.09
25.6	4.37	3.05	17.31
35.3	7.54	5.47	22.47
43.8	10.1	7.61	27.15
51.2	16.8	13.66	27.01
64.0	22.6	19.35	32.18
73.1	27.4	23.89	35.23
87.8	36.7	34.02	38.44
101.6	45.7	45.52	40.86
122.1	57.8	57.80	46.30
147.5	73.2	73.2	52.74
166.0	80.6	80.6	61.05

Run No. 5			
No. contact points per sphere—10.90			
Liquid air temperature 92° A.			
$1.21 \times 10^{-5}$	$0.84 \times 10^{-5}$	$0.58 \times 10^{-5}$	$0.21 \times 10^{-5}$
2.02	1.48	1.01	.28
2.96	0.85	0.58	1.60
3.73	.74	.50	2.32
5.28	.82	.56	3.48
8.81	1.61	1.10	5.59
12.09	2.21	1.52	7.66
15.33	3.23	2.22	9.32
18.57	4.62	3.24	10.65
21.52	5.19	3.65	12.50
27.61	7.38	5.54	15.27
37.57	10.7	8.15	21.00
52.40	17.1	14.02	25.72
65.46	23.8	20.37	29.59
83.56	32.5	29.70	35.11
104.3	42.6	41.87	40.95
128.1	57.4	57.40	44.95
142.3	63.9	63.90	49.74
160.2	74.7	74.7	53.37
179.5	87.5	87.5	55.40
199.1	98.0	98.0	60.88
221.8	110.6	110.6	66.35
249.3	124.6	124.6	73.73

TABLE IV  
 ADSORPTION OF NITROGEN ON GLASS SPHERES  
 No. of Spheres—5000. Activated at 250°C.

Run No. 9			
No. contact points per sphere—10.73			
Liquid air temperature 95°A.			
$P_1$ , cm.	$P_2$ , cm.	$P_3$ , cm.	A, moles
$0.68 \times 10^{-3}$	$0.48 \times 10^{-3}$	$0.33 \times 10^{-3}$	$0.09 \times 10^{-3}$
1.65	1.14	.76	.25
2.77	1.74	1.16	.62
4.35	0.63	0.42	3.39
5.35	.69	.46	4.26
6.77	.90	.61	5.36
9.19	1.28	.87	7.20
12.41	1.82	1.23	9.61
15.42	2.29	1.57	11.90
19.61	3.18	2.20	14.81
25.8	4.80	3.35	18.74
35.9	6.51	4.65	26.18
48.1	10.27	7.78	32.98
65.7	16.5	13.51	41.47
75.8	18.5	15.32	48.36
90.9	23.1	19.68	56.51
106.6	28.0	24.61	64.78
124.8	35.3	33.08	71.06
148.3	41.9	40.31	83.98
179.6	53.2	53.1	97.14
212.6	63.4	63.4	114.3
251.4	84.7	84.7	122.1

Run No. 10			
No. contact points per sphere—10.73			
Liquid air temperature 95°A.			
$P_1$ , cm.	$P_2$ , cm.	$P_3$ , cm.	A, moles
$1.23 \times 10^{-3}$	$0.37 \times 10^{-3}$	$0.58 \times 10^{-3}$	$0.16 \times 10^{-3}$
2.46	1.81	1.22	.24
3.05	0.36	0.23	2.47
4.33	.57	.38	3.43
6.37	.81	.54	5.07
9.59	1.10	.73	7.77
12.15	1.50	1.02	9.71
15.30	2.04	1.39	12.05
19.59	2.96	2.04	15.02
24.65	3.61	2.45	19.06
30.3	4.48	3.14	23.31
45.6	8.00	5.82	33.48
55.3	11.2	8.58	38.54
69.5	15.8	12.84	45.90
86.8	19.2	15.95	57.76
109.1	28.0	24.6	66.9
138.8	39.3	37.6	78.5
169.6	49.7	49.7	92.9
198.8	59.5	59.5	106.5
234.1	73.5	73.5	120.8

Run No. 11			
No. contact points per sphere—11.32			
Liquid air temperature 94°A.			
$P_1$ , cm.	$P_2$ , cm.	$P_3$ , cm.	A, moles
$1.27 \times 10^{-3}$	$0.96 \times 10^{-3}$	$0.64 \times 10^{-3}$	$0.09 \times 10^{-3}$
3.65	2.14	1.43	.97
6.12	0.82	0.55	4.82
9.52	1.72	1.16	6.98
14.7	2.94	2.01	10.43
20.6	4.39	3.07	14.27
29.6	6.72	4.82	19.94
37.8	9.22	6.83	24.62
51.6	11.6	8.95	34.45
67.6	18.1	14.95	41.0
85.5	23.1	19.66	51.2
108.5	31.7	28.7	60.8
134.6	40.4	38.9	72.7
164.2	49.5	49.5	87.1
190.5	58.6	58.6	99.5
218.9	69.2	69.2	112.2

obtained. This method did not prove successful as shown by the lack of agreement between the isotherms given in Table III and Fig. 3. We next studied adsorption on these spheres after they were degassed at 250° for two and one-half hours.

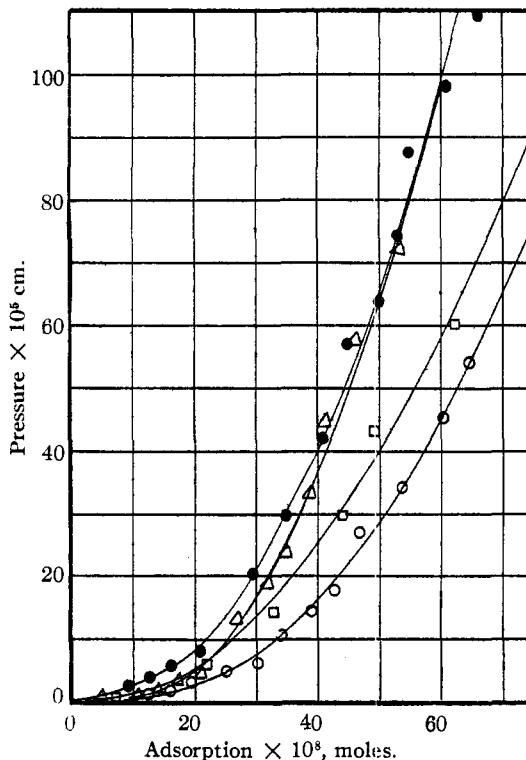


Fig. 3.—Adsorption of nitrogen on glass spheres activated at room temperature: O, Run 1; □, Run 3; △, Run 4; ●, Run 5.

The results of these runs are given in Table IV and Fig. 4. Curves 9 and 10 are practically identical. Curve 11 shows a slight negative deviation, and is most likely due to a decrease in the adsorbing surface resulting from the greater compactness of the spheres. This higher packing was purposely brought about in order to test for the effect of capillarity. If capillarity played any role, an increase in the number of contacts per sphere should result in an increased adsorption; but since the reverse was actually observed, we must conclude that in this pressure range capillarity seems not to have influenced the adsorption of nitrogen. The observed variations in the adsorption of oxygen of a previous investigation<sup>1</sup> were most likely due to differences in activation of the glass spheres.

**Pressure Reversal.**—Similar to the results obtained with oxygen we observed pressure reversals also in the isotherms of nitrogen. As

room temperature, to eliminate the bursting of the sphere chamber on heating, until an arbitrary but fixed rate of rise of pressure in a good vacuum was

shown in Figs. 5 and 6, all isotherms show an abrupt lowering of the equilibrium pressure and a corresponding rapid rise in adsorption. The pressure at which this phenomenon sets in and the lowest pressure reached, referred to here as the reversal point, vary slightly with the isotherm.

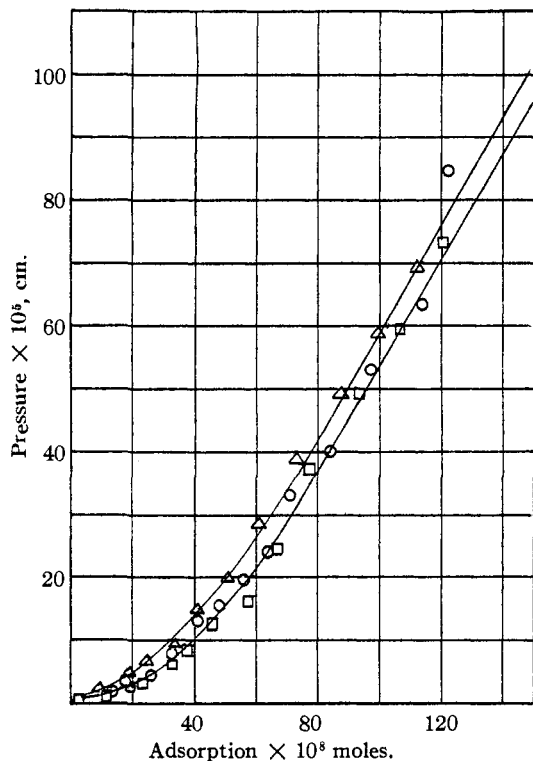


Fig. 4.—Adsorption of nitrogen on glass spheres activated at 250°: ○, Run 9; □, Run 10; △, Run 11.

It was also observed that the rates of adsorption before and after the break were at great variance. Along the linear portion of the isotherm equilibrium was established in the course of a few minutes, while in the receding portion it was established very slowly, sometimes requiring as long as forty-eight hours. It is due to this slowness of the process that curves 1, 2 and 3 show more than one equilibrium point in the receding portions of the isotherms. In all others there was observed only one equilibrium point, namely, the reversal point. Beyond this point equilibrium was attained again very rapidly, although somewhat more slowly than along the linear portion of the isotherm.

This made it evident that the rate of adsorption in the interval in which reversal took place was dependent upon some intermediate slow process which was responsible for the lowering of the equilibrium pressure.

To study the nature of this process the rates of sorption in this region of the isotherm were measured. The intervals of time over which the pressures were observed varied from ten to twenty hours, depending upon the initial pressure, *i. e.*, the quantity of gas introduced. The pressure-time curves so obtained on a number of isotherms were found to be identical in character. With the exception of the initial period of approximately five minutes where the pressure falls very rapidly and adsorption is apparently the dominating process, as shown by the typical curve in Fig. 7, each curve follows fairly closely the equation

$$\ln P/P_0 = kt \quad (4)$$

where  $P$  is the pressure at time  $t$ , and  $P_0$  is the initial pressure of the intermediate slow process at  $t = 0$ . The value of  $k$ , the specific reaction rate, was found to be the same for all isotherms studied.

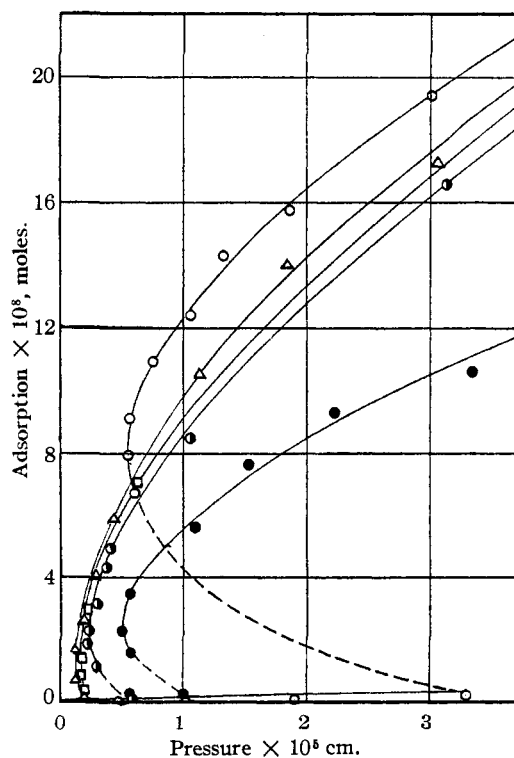


Fig. 5.—Adsorption of nitrogen at low pressures on glass spheres activated at room temperature: ○, Run 1; ○●, Run 2; □, Run 3; △, Run 4; ●, Run 5.

It might be assumed, in view of its being frequently associated with adsorption in porous bodies, that the intermediate slow process is due to adsorption and the slow diffusion of the gaseous molecules through the cracks and crevices in the spheres which may have been there or have

formed during the activation treatment to which the system was subjected numerous times. This seems to be supported by the consideration that theoretically absorption processes follow equation (4). However, because it was not observed after carefully testing for it at higher pressures both along the linear portion of the isotherm preceding

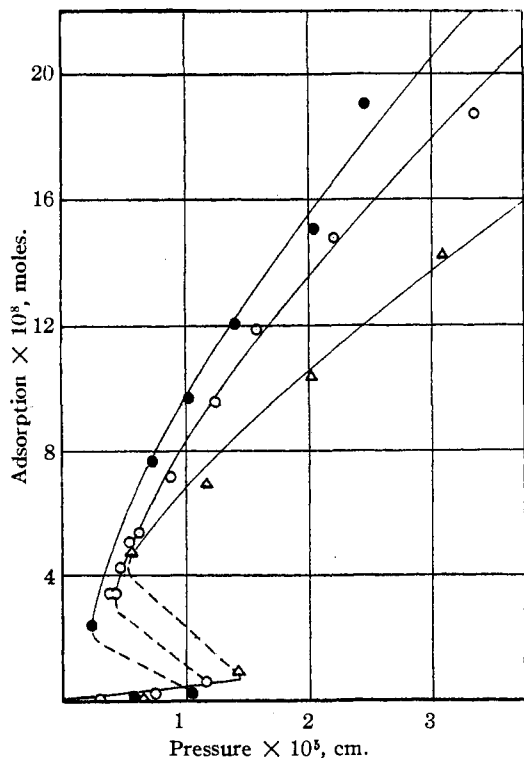


Fig. 6.—Adsorption of nitrogen at low pressures on glass spheres activated at 250°: ○, Run 9; ●, Run 10; △, Run 11.

and the portion of the isotherm following the point of reversal, absorption is most likely not the cause of the reversal phenomenon. The phenomenon is easily explained, if we assume that the adsorbed phase exists in two different states of aggregation. While there is no direct evidence to that effect, the behavior of films on liquid surfaces makes this assumption very plausible. On this basis the break in the isotherm represents the transition of the adsorbed phase from one state into the other; and the reversal in the equilibrium pressure is undoubtedly due to the tendency of the initial state toward supersaturation, as indicated by the abruptness or explosiveness of the first stage of the reversal process. The assumption is also in agreement with the measurements on the rate of the reversal process, as all transition processes follow the equation of first order reactions.

As to the nature of the states, only the most general observations can be made. The branch of the isotherm to the left of the break seems, in view of the low pressures and the linear relationship between it and the adsorption, to represent a state in which the adsorbed gas obeys Boyle's law. In this state the van der Waals constants are either ineffective or compensating, with the result that the gas is ideal in behavior, and the adsorption isotherm follows Henry's law. In the state of the adsorbed phase described by the branch of the isotherm extending to the right of the break, the gas due to the van der Waals forces is most likely liquefied, as evidenced by the increased rise of adsorption with pressure and the abruptness of the transition. The course of adsorption in this phase seems to depend also upon the heterogeneity of the surface, as will be shown in the discussion to follow.

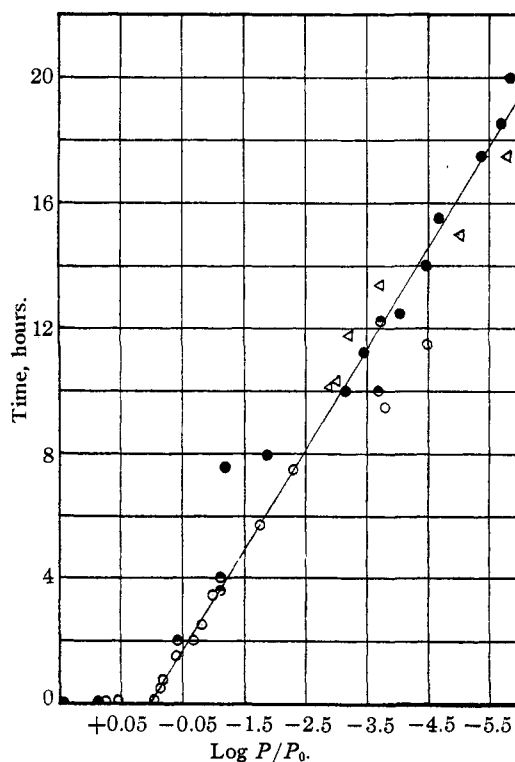


Fig. 7.—Rate of sorption at reversal point: ●, Run 1; ○, Run 5; ○, Run 9; △, Run 10.

**Adsorption Isotherm.**—It is clear that no present adsorption theory will apply to the complete isotherm obtained in these experiments, and consequently in subsequent discussions reference is made only to the regular branch shown in Figs. 3 and 4.

A graphical analysis of a typical adsorption isotherm in the manner described by Cunningham<sup>9</sup> yielded the information that two principal types of adsorption occurred in this region. It was therefore expected that Langmuir's simple equation<sup>10</sup>

$$A = abP/(1 + bP) \quad (5)$$

will not apply to these data. Such is actually the case, for graphs of  $P/A$  against  $P$  show consistently large deviations from linearity. However, an equation based on the assumption of two different elementary spaces,<sup>10</sup> namely

$$A = a_1b_1P/(1 + b_1P) + a_2b_2P/(1 + b_2P) \quad (6)$$

was also found not to apply. Attempts to fit this equation to several sets of data by a few different methods, including the method of least squares,

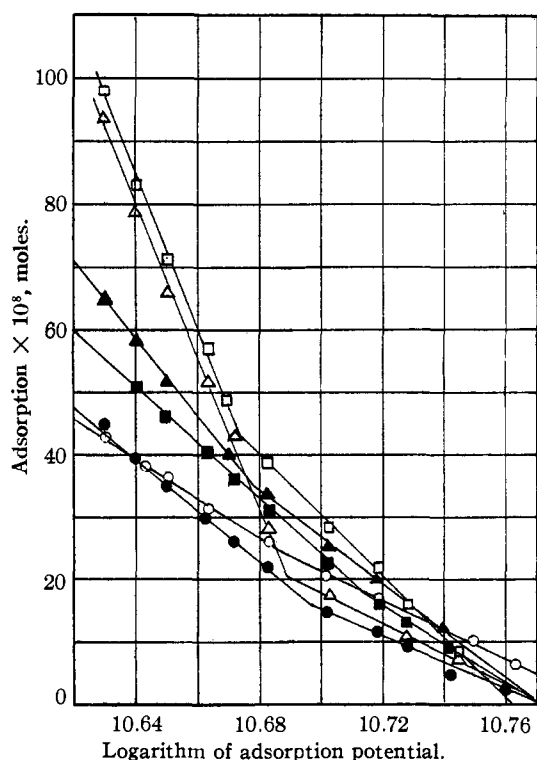


Fig. 8.—Application of equation of Palmer and Clark:  $\blacktriangle$ , Run 1;  $\blacksquare$ , Run 3;  $\circ$ , Run 4;  $\bullet$ , Run 5;  $\square$ , Runs 9 and 10;  $\triangle$ , Run 11.

produced results which were meaningless from the point of view of Langmuir's hypotheses. Similar attempts to apply to our results the equations of Zeise<sup>11</sup> and of Williams-Henry<sup>12</sup> proved unsuccessful. On the other hand, fitting our data to

(9) Cunningham, *J. Phys. Chem.*, **39**, 69 (1935).

(10) Langmuir, *THIS JOURNAL*, **40**, 1384 (1918).

(11) Zeise, *Z. physik. Chem.*, **136**, 397 (1928).

(12) Williams, *Proc. Roy. Soc. (London)*, **A96**, 287 (1919); Henry, *Phil. Mag.*, [6] **44**, 689 (1922).

the Freundlich equation<sup>13</sup> results in two straight lines for every isotherm, which seems to be in agreement with the two types of adsorption shown by Cunningham's method of analysis.<sup>9</sup>

We next attempted to apply the relationship recently suggested by Palmer and Clark,<sup>14</sup> who assumed direct proportionality between the logarithm of the adsorption potential and the adsorption, the potential being defined in accordance with Polanyi<sup>15</sup> by the equation

$$\epsilon = RT \ln (P_x/P_s) \quad (7)$$

where  $P_s$  is the saturation pressure, in this case 283 cm. of mercury,<sup>16</sup> and  $P_x$  is the equilibrium pressure. The plotting of our results in this manner produced two straight lines for each isotherm as shown in Fig. 8. Assuming that the two straight lines represent two different types of adsorption, we obtain by extrapolating each line to zero adsorption the maximum potential corresponding to each type. These maximum potentials correspond to the minimum pressures below which the corresponding types of adsorption cannot take place. This assumption seems to be verified by the fact that the calculated values of  $P_x$  corresponding to the maximum potentials of the upper straight line of each isotherm check fairly closely the pressures corresponding to the reversal points, which are most likely points of inflection marking the beginning of the condensed adsorption phase. This agreement is shown in Table V where the values of  $\epsilon_m$  obtained by extrapolation are given in column 1; the corresponding calculated equilibrium pressures are given in column 2 and the observed pressures in column 3.

TABLE V  
THE MINIMUM PRESSURES OF ADSORPTION OF NITROGEN ON GLASS

Run	$\epsilon_m$ , ergs	$P$ (calcd.), cm.	$P$ (meas.), cm.
9	$5.81 \times 10^{10}$	$0.45 \times 10^{-5}$	$0.42 \times 10^{-5}$
4	6.17	.18	.12
5	5.85	.43	.50
11	5.94	.32	.55
10	5.81	.45	.23
3	6.03	.22	.09
2	6.10	.20	.23

### Summary

1. The thermal flow effect of hydrogen and helium was determined and found to agree at

(13) Freundlich, *Z. physik. Chem.*, **57**, 385 (1906).

(14) Palmer and Clark, *Proc. Roy. Soc. (London)*, **A149**, 360 (1935).

(15) Polanyi, *Verhandl. deut. physik. Ges.*, **16**, 1012 (1914).

(16) "International Critical Tables," Vol. III, p. 204.

pressures corresponding to equal mean free paths.

2. The activation of glass surfaces was studied under different conditions.

3. The adsorption of nitrogen on glass spheres at liquid air temperatures was studied. Different degrees of packing of the spheres was found to have no effect on the adsorption.

4. Similar to oxygen the adsorption isotherm of nitrogen at low pressures shows the unusual phenomenon of recession of the equilibrium pressure. A possible explanation for this behavior is suggested.

5. The application of various adsorption theories to the data is discussed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF BRITISH COLUMBIA]

## The Mutual Solubilities of Hydrocarbons. I. The Freezing Point Curves of Dotriacontane (Dicetyl) in Propane and Butane

BY W. F. SEYER AND REID FORDYCE

A considerable amount of information exists concerning the mutual solubilities of hydrocarbons. Thus over thirty years ago Holde was familiar with the fact that light hydrocarbons when added to petroleum caused the asphalt portion to be precipitated. This idea was further extended by Kling<sup>1</sup> in 1922 and by S. V. Pilatt and M. Godlevicz<sup>2</sup> in 1932. This work established the fact that mutual solubility among hydrocarbons was governed largely by the molecular weights of solute and solvent. Already extensive use has been made of this knowledge to isolate and purify certain petroleum fractions by utilizing solvents of various selective powers. So far all the information which has been forthcoming has been of a qualitative nature; consequently before much more headway can be made along this line, quantitative measurements concerning the solubility relationships existing among simple systems of hydrocarbons must be made. The following pages deal with the results obtained from a study of the systems, dotriacontane (dicetyl,  $C_{32}H_{66}$ ) and propane and dotriacontane and butane.

**Materials.**—The propane and butane were purchased from The Ohio Chemical & Manufacturing Company, Cleveland. These gases were listed c. p. and the butane was claimed to be free of propane but to contain a trace of isobutane, while an analysis of the propane failed to reveal any traces of either of the two isomeric butanes. The hydrocarbon, dicetyl, was synthesized from Eastman c. p. cetyl alcohol by the method first used by Kraft.<sup>3</sup> The hydrocarbon was recrystallized five times from ether until no change in melting point could be detected. The final melting point was  $69.9^\circ$  as measured by a standardized mercury thermometer. This agrees with the findings of

Hildebrand and Wachter who have pointed out that the true melting point of the hydrocarbon must be in the neighborhood of  $70^\circ$ .<sup>4</sup>

### Experimental Procedure

The time honored bulb method was considered the most practical one for the determination of the freezing points. In the present case this method was susceptible of considerable accuracy because of the "cloud effect"; *i. e.*, whenever a solution of dicetyl in either propane or butane was cooled beyond the limits of solubility a white suspension immediately developed. The phenomenon is apparently due to the formation of tiny crystals of the high molecular weight hydrocarbon. The point of appearance and disappearance of these crystals was extremely sharp and did not vary more than  $\pm 0.02^\circ$  in any case. The difference between the two temperatures was never greater than  $0.05^\circ$ .

Thick-walled uniform bulbs, 2 cm. in diameter, were blown and to these were attached glass stems 9 cm. long and 2 mm. in diameter. Varying amounts of dotriacontane were introduced by first melting the hydrocarbon and then allowing it to run down a long stemmed funnel into the bulb proper. The bulbs, after weighing, were then sealed onto the apparatus outlined in Fig. 1, evacuated and the required amounts of butane or propane condensed in each. These gases were stored in two 5-liter flasks which served as gas holders and which were placed in an insulated box whose temperature could be controlled. Before allowing either of these two gases to diffuse into the systems, it was evacuated by means of a mercury vapor pump down to a pressure of the order of 0.001 mm. as measured by a McLeod gage. Knowing the volume of the apparatus and noting the pressure changes on the manometer, it was a simple matter to calculate the amounts of gases condensed in the bulbs before they were sealed and detached from the apparatus. The amounts of the hydrocarbons in each bulb were again measured by weighing the sealed bulb after the freezing point had been obtained, then breaking off the tip, allowing the gas to escape and then weighing again.

Besides the buoyancy correction one other one was con-

(1) Kling, German Patent 362,458.

(2) S. V. Pilatt and M. Godlevicz, *Oel und Kohle*, **11**, 655 (1935).

(3) Kraft, *Ber.*, **40**, 4783 (1907).

(4) Hildebrand and Wachter, *THIS JOURNAL*, **51**, 2487 (1929).