[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA.]

# THE VELOCITY OF ADSORPTION OF CHLOROPICRIN AND CARBON TETRACHLORIDE BY CHARCOAL.[1]

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This investigation has been pursued with the purpose, first, of obtaining reproducible results in the measurements of the velocity of adsorption of gases on a relatively gas-free solid surface, and, second, of determining the effect of the presence of a foreign gas on this velocity of adsorption. The method of weighing the gas adsorbed at selected time intervals of exposure of the surface to the gas has been employed throughout. The advantage of this method lies in its directness and simplicity, but is limited to the cases where relatively large weights of gases are adsorbed. For this reason, the present investigation has been confined to the study of two gases of relatively high molecular weight on a solid which, for unit weight, affords an exceedingly large surface.

## Apparatus and Method of Measurement.

The apparatus employed was designed to accomplish 3 operations: (1) To purify the liquid used as the source of gas by 2 distillations in vacuum, accompanied by a special operation which assured the efficient removal of all gases dissolved in the liquid; (2) to permit the heating of the charcoal to temperatures up to 1100° in a vacuum produced by mercury vapor pumps; (3) to permit exposures of the charcoals for definite and selected time intervals to the constant pressure of the gas.

Fig. 1 shows a sketch of the essential part of the apparatus. The tubes A, B, and C were evacuated, and a dried sample of the liquid of high purity was sucked in through a capillary tube at *b*, which was then sealed off. The tubes A, B, C were again evacuated and the liquid was slowly distilled from A to B by immersing B in liquid ammonia contained in a Dewar bulb or in a suitable salt-ice mixture. The stopcock 1 was kept closed during this operation. The tube B contains a device, *a*, which serves both as a stirrer and a means of indicating with great delicacy whether or not the liquid is air-free.[2] The bottom part of *a* is a small inverted cup; the center portion is a glass tube, sealed on to the cup, which contains an iron bar, indicated by the cross hatching. The

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[1] A part of the work here presented was started at the suggestion of Major Frederick G. Keyes, Director of the Chemical Warfare Service Laboratory in Paris. Initially it was merely intended to determine by direct experiment the influence of air and moisture already adsorbed by charcoal on the rate of adsorption of chloropicrin. The study has been continued and extended at the John Harrison Laboratory of Chemistry of the University of Pennsylvania.

[2] Young, *Phil. Mag.*, 20, 793 (1910); see also Keyes and Felsing, THIS JOURNAL, 41, 604 (1919).

upper part is a closed glass tube slightly less in diameter than the inside diameter of B. By means of a solenoid around the tube B, *a* can be raised and lowered at will. When the liquid is free from dissolved gas vapor entrapped in the inverted cup will quickly and completely condense under the hydrostatic pressure when the cup is lowered. A very small quantity of gas dissolved in the liquid will prevent this. By repeatedly stirring the liquid in B under suction it was completely freed from dissolved air. C was then heated to 250° in a vacuum in order to remove any gases adsorbed on the glass wool contained in it until the pressure was reduced to $10^{-6}$ mm. of mercury, cooled to room temperature and immersed

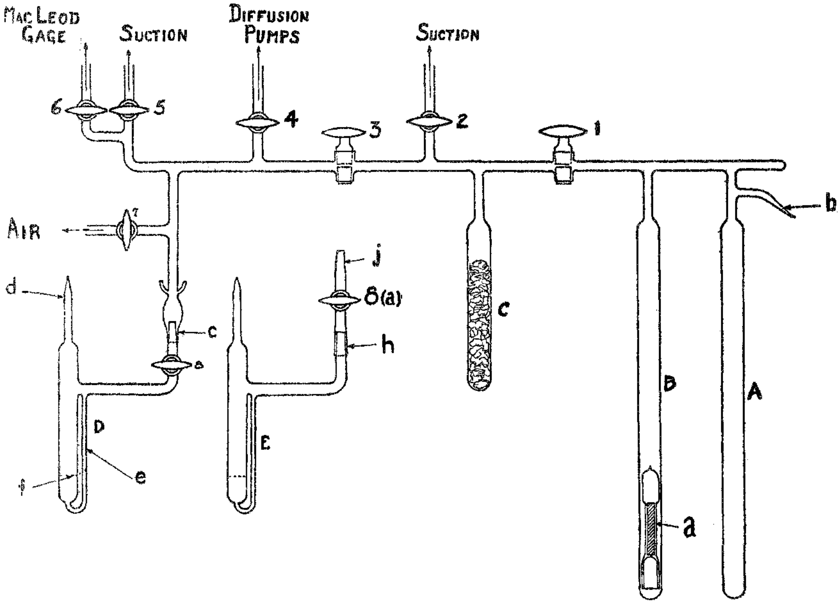

Fig 1.

in an ice and salt mixture or liquid ammonia. Stopcocks 2 and 3 were closed, 1 was opened and a fraction of the liquid in B was distilled into C after which the stopcock 1 was again closed. The distillation was carried on slowly so that no liquid came into contact with the grease used to lubricate the stopcocks. The tubes containing the liquid were always maintained below room temperature so that only vapor could come in contact with the grease. By exercising sufficient care, it was found that a properly lubricated stopcock could be used for at least one month without further attention. The glass wool was put in C in order to afford a large liquid surface available for evaporation.

Two types of weighing tubes containing the charcoal were employed, one made of Pyrex glass, the other of quartz, shown in Fig. 1 by D and E, respectively. D is all Pyrex glass ground into soft glass at *c*. E is of quartz, ground into Pyrex at *h*, which in turn is ground into soft glass at *j*. 8 and 8(*a*) are Pyrex stopcocks. The inside diameter of these cocks at the narrowest point was 2 mm. The charcoal was introduced through *d* or through *h*, respectively, and rested on the diaphrams *f*. *d* was sealed off. The tube *e* serves the purpose of introducing the gas from both sides of the charcoal. The weighing tubes could be connected to suction (geared oil vacuum pump), to the mercury-vapor pump, to a MacLeod gage or to air, by operating Cocks 4, 5, 6, 7, and 8. The mercury-vapor pumps were made of Pyrex glass and were similar in design to those described by Kraus.[1] For a time an oil pump which produced an average vacuum of 0.001 mm. of mercury was connected to a mercury-vapor pump; later, a Cenco-Nelson pump averaging 0.05 mm. of mercury was connected to two mercury-vapor pumps of the proper design in series. Both these systems would give a pressure of 0.01 bar. The tubes D and E were weighed against a suitable counterpoise. They were heated by a small electric resistance furnace. Dewar tubes containing suitable liquids or ice mixtures were used to maintain D or E and C at the desired constant temperatures.

After the preliminary purification of the liquid, the tube C was immersed in a thermostat and maintained at constant temperature. This will give a constant pressure of vapor from the liquid. The charcoal was then heated in a vacuum for some hours and then Stopcock 8 or 8(*a*) was closed. The apparatus was then evacuated with the cocks 3, 5, 7 closed until a vacuum of $10^{-6}$ mm. was reached. Stopcocks 4 and 6 were closed and 3 was opened; then 8 was opened for a definite time interval. The velocity of diffusion of a gas into a high vacuum is very high, approaching the mean average velocity of molecules, and, hence, practically instantaneous contact of the gas with the charcoal was obtained. After the exposure, the cocks 4, 8, 6 and 3 were closed, 7 was opened and the weighing Tube D or E was withdrawn and weighed, after which the same operation was repeated. Correction was made for the volume of the weighing tube (approximately 10 cc.). The principal source of error in these measurements results from the difficulty and time taken to turn the cocks 8 or 8(*a*). With practice, this operation can be carried out successfully to within ±0.1 of a second. When low pressures of gas are employed, the adsorption takes place so slowly that this error becomes negligible.

## Results.[2]

### I. Chloropicrin Adsorption.

A. The first series of results was obtained by using a wood charcoal

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[1] THIS JOURNAL, 39, 2183 (1917).

[2] Series A and C and No. 4 Series B were obtained in Paris, all other results in Philadelphia.

(French canister charcoal of 14 to 16 mesh) which contained 6.0% non-volatile material. The Pyrex glass weighing tube D (Fig. 1) was used.

(1) Wt. of charcoal equalled 0.842 g. Heated to 350° for 2 hours in a high vacuum, cooled and maintained at 20° ± 1°. The tube C (Fig. 1) containing chloropicrin was kept in ice water contained in a Dewar bulb. By keeping the liquid reservoir at a temperature lower than the charcoal, distillation was avoided. Vapor pressure of chloropicrin at 0° = 5.90 mm. of mercury.

(2) Same charcoal, same weight as in (1). No air or moisture was permitted to come into contact with the charcoal between measurements (1) and (2). Reheated to 350° for 2.5 hours in a high vacuum. Gain in weight of charcoal equalled 10 mg. Same temperature conditions during velocity measurements as in (1).

(3) Same charcoal. Reheated to 350° for 7 hours in a high vacuum. No foreign gas admitted. Gain in weight of charcoal equalled 1.5 mg. Same temperature conditions as in (1) and (2).

Table I contains the results of Series A.

TABLE I.

Chloropicrin. $p = 5.90$ min. $t$ = Time of Exposure in Seconds. $K$ = Wt. of Gas adsorbed per g. of Charcoal in Time $t$.

| 1. | | 2. | | 3. | |
|---|---|---|---|---|---|
| $t$. | $K$. | $t$. | $K$. | $t$. | $K$. |
| 1.6 | 0.0030 | 1.6 | 0.0056 | 2.2 | 0.0091 |
| 3.2 | 0.0070 | 2.8 | 0.0082 | 5.4 | 0.0221 |
| 5.7 | 0.0116 | 5.1 | 0.0159 | 8.6 | 0.0374 |
| 9.1 | 0.0241 | 7.4 | 0.0234 | 13.8 | 0.0568 |
| 14.4 | 0.0418 | 9.7 | 0.0305 | 24.3 | 0.0753 |
| 25.1 | 0.0636 | 15.0 | 0.0479 | 6600.0 | 0.1854 |
| 463.0 | 0.1578 | 25.4 | 0.0728 | .... | .... |
| ... | .... | 503.0 | 0.1406 | .... | .... |

The $t$, $K$ plots of these results are given in Fig. 2.

B. Since there was an increase in weight of the charcoal with each successive determination, it was decided to use much higher temperatures in the further investigations, in order to drive off any chloropicrin remaining on the surface. To this end a transparent quartz weighing Tube E (Fig. 1) was employed. In the second place, since the non-volatile matter in the charcoal was so high, it was considerably reduced by a process of extraction.

(4) Another portion of the same sample of charcoal used in Series A was extracted in a Soxhlet extractor with constant boiling hydrochloric acid for 16 hours, then with water for 8 hours. It was finally heated in a muffle furnace for 15 minutes at 900°. The ash from two samples of this material was 1.0% and 1.3% respectively.

Wt. of charcoal used equalled to 0.5253 g. This was heated in a high vacuum to 700° for 2.5 hours. Charcoal at 20.0 ± 1°, chloropicrin at 0° during the velocity measurement.

(5) Another sample of charcoal extracted and ignited as in (4).

Wt. charcoal used equalled 0.5146 g. This was heated to 750° for 4 hours. Charcoal at 20°; chloropicrin at 0° during the measurement.

(6) Same charcoal as in (5). Reheated to 800° for 8 hours in a high vacuum. No foreign gas was permitted to come into contact with the charcoal between measure-

ments (5) and (6). Gain in weight of charcoal equalled 0.4 mg. Charcoal at 20 ± 1°, chloropicrin at 0° C.

(7) Same charcoal as in (6). Reheated to 800° for 2 hours in a high vacuum. Charcoal unexposed to foreign gases between measurements (6) and (7). Charcoal at 20°, chloropicrin at 0°.

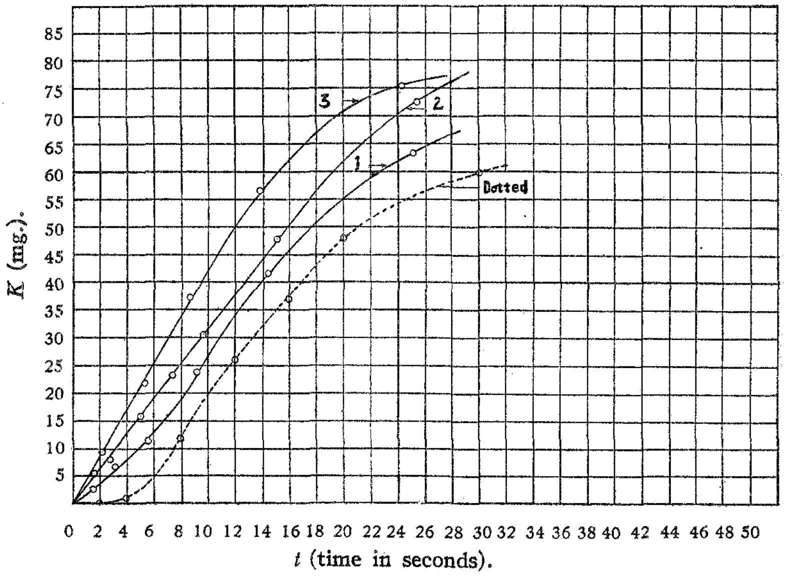

Fig. 2,

The results of Series B are given in Table II.

TABLE II.

Chloropicrin. $p = 5.90$ mm.

| 4. | | 5. | | 6. | | 7. | |
|---|---|---|---|---|---|---|---|
| $t$. | $K$. | $t$. | $K$. | $t$. | $K$. | $t$. | $K$. |
| 1.9 | 0.0138 | 10.0 | 0.0743 | 10.0 | 0.0901 | 10.0 | 0.0875 |
| 4.9 | 0.0340 | 21.0 | 0.1345 | 21.0 | 0.1520 | 21.0 | 0.1493 |
| 10.0 | 0.0671 | 32.0 | 0.1800 | 32.0 | 0.1963 | 32.0 | 0.1930 |
| 20.0 | 0.1284 | 44.0 | 0.2168 | 44.0 | 0.2340 | 44.0 | 0.2328 |
| 30.0 | 0.1666 | 57.0 | 0.2343 | 57.0 | 0.2556 | 57.0 | 0.2580 |
| 45.0 | 0.2300 | 80.0 | 0.2485 | 80.0 | 0.2820 | 80.0 | 0.2862 |
| 65.0 | 0.2560 | 137.0 | 0.2702 | 500.0 | 0.3083 | .. | .... |
| 85.0 | 0.2695 | 20.0 (min.) | 0.3085 | ... | .... | .. | .... |
| 125.0 | 0.2724 | ... | .... | ... | .... | ... | .... |
| 1625.0 | 0.2972 | ... | .... | ... | .... | .. | .... |

The $K$, $t$ plots of these results are given in Fig. 3.

In this series of measurements, the pressure of the chloropicrin was reduced by immersing the Tube C (Fig. 1) in liquid ammonia contained in a Dewar bulb. This reduced the gas pressure to a magnitude of approximately 0.61 mm. of mercury of $^1/_{10}$ of the pressure employed in Series

A and B. This value for the vapor pressure of chloropicrin at —33.3° was obtained by extrapolation from the plot of the log of the vapor pressure against $1/T$, where $T$ is the absolute temperature, which is a straight line for temperatures from 0–70° and is, therefore provisional.

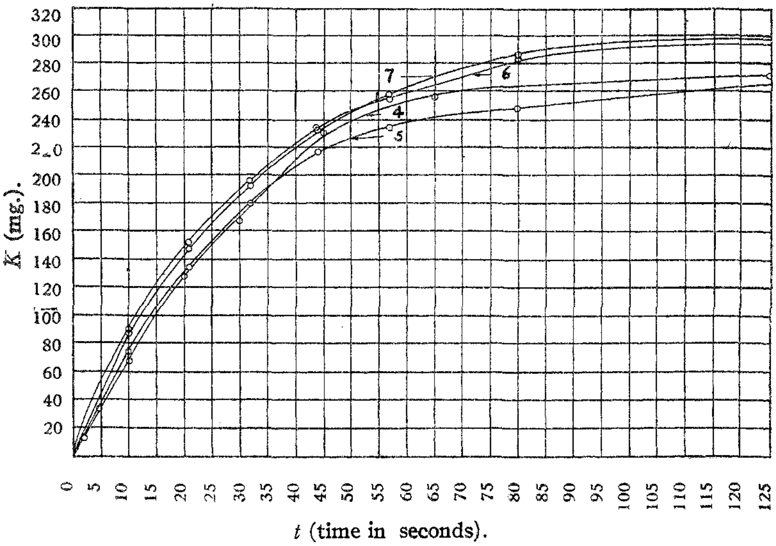

Fig. 3.

(8) The charcoal used in B (4), which has been extracted with hydrochloric acid, was covered with a hydrofluoric acid solution which was then evaporated to dryness. The charcoal was again extracted with hydrochloric acid and water, and finally heated to 900° for 15 minutes in a muffle furnace.

Wt. charcoal equalled 0.4294 g. Heated to 700° in a quartz weighing tube for 3 hours in a high vacuum. Chloropicrin at 33.3°, charcoal at 20° during the velocity measurement. Vapor pressure of chloropicrin equals 0.61 mm.

(9) Same sample of charcoal as in (8). Reheated to 700° in a high vacuum fo 2 hours. No foreign gas was permitted to reach charcoal between (8) and (9). Charcoal at 20°, chloropicrin at 33.3°.

(10) Same charcoal as in (9). Reheated at 700° in high vacuum. No foreign gas admitted.

(11) Same charcoal as in (10). Heated in vacuum for 2 hours to 700°, then cooled to room temperature, then exposed to air at one atm. pressure for one minute, again heated for $^1/_2$ hour at 700° in a vacuum, and again exposed to air for one minute. This process was repeated 5 times. After this rinsing out process, the charcoal was cooled to room temperature, exposed to air for one minute, and then evacuated at room temperature for 20 minutes.

The results of Series C are contained in Table III.

These results are plotted in Fig. 4 along with a result obtained on the sample used in B (4) and denoted (*a*).

TABLE III.

Chloropicrin. $p$ = 0.61 Mm. $t$ is Given in Minutes.

| 8. | | 9. | | 10. | | 11. | |
|---|---|---|---|---|---|---|---|
| *t.* | *K.* | *t.* | *K.* | *t.* | *K.* | *t.* | *K.* |
| 5.0 | 0.0002 | 5.0 | 0.0532 | 5.0 | 0.0571 | 5.0 | 0.0036 |
| 10.0 | 0.0012 | 10.0 | 0.0948 | 10.0 | 0.1034 | 10.0 | 0.0054 |
| 15.0 | 0.0037 | 15.0 | 0.1250 | 15.0 | 0.1385 | 15.0 | 0.0065 |
| 20.0 | 0.0051 | 20.0 | 0.1574 | 20.0 | 0.1683 | 25.0 | 0.0107 |
| 25.0 | 0.0077 | 30.0 | 0.1972 | 30.0 | 0.2089 | 40.0 | 0.0193 |
| 35.0 | 0.0149 | 40.0 | 0.2265 | 40.0 | 0.2329 | 60.0 | 0.0234 |
| 45.0 | 0.0237 | 50.0 | 0.2430 | 50.0 | 0.2351 | 80.0 | 0.0356 |
| 55.0 | 0.0347 | 70.0 | 0.2610 | 60.0 | 0.2378 | 100.0 | 0.0431 |
| 65.0 | 0.0470 | .. | .... | 90.0 | 0.2468 | ... | .... |
| 85.0 | 0.0640 | .. | .... | 120.0 | 0.2541 | ... | .... |
| 105.0 | 0.0771 | .. | .... | ... | .... | ... | .... |
| 135.0 | 0.0941 | .. | .... | ... | .... | ... | .... |

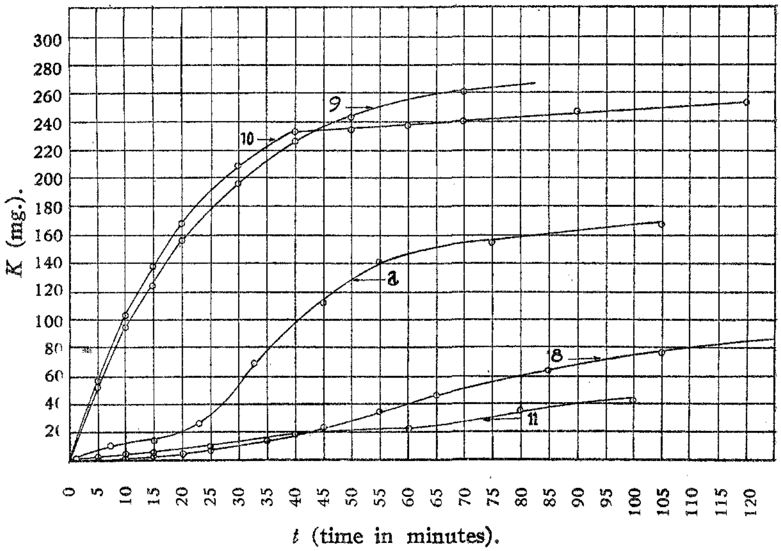

Fig. 4.

## II. Carbon Tetrachloride Adsorption.

In the following 3 series of measurements, the charcoal was exposed to the vapors of carbon tetrachloride maintained at a pressure of 32.8 mm. and 18.8 mm. of mercury.

D. (1) The charcoal used in this experiment was a sample of wood charcoal (French 14–16 mesh) which had been extracted with constant boiling hydrochloric acid, water and then heated to 900° for 15 minutes in a muffle furnace.

Wt. charcoal equalled 0.5447 g. Heated for 4 hours at 750° in a high vacuum. Charcoal at 20°, carbon tetrachloride at 0° during measurement. The vapor pressure of carbon tetrachloride at 0° is 32.8 mm. (Reference, "Landoltu Börnstein Tabellen.")

(2) Same charcoal as in D (1). Reheated in vacuum to 750° for 2.5 hours. There was a gain in weight of 0.0109 g. No foreign gases came in contact with charcoal between measurements D (1) and (2). Charcoal at 20°, carbon tetrachloride at 0°.

(3) Same charcoal as in D (2). Exhausted for $^1/_2$ hour at 30°. Then reheated in a high vacuum for 8 hours at 750°. Then again reheated for 1.5 hours to 800° in a high vacuum. The pressure over the charcoal with the pumps on the line equalled $4 \times 10^{-4}$ mm. of mercury. There was a gain in weight of the charcoal of 0.0213 g. over D (2). Charcoal was maintained at 20°, carbon tetrachloride at 0°.

(4) Same charcoal as in D (3) was heated for 4 hours to 800° in a high vacuum. Exposed to air at atmospheric pressure for 10 minutes. Reheated for $^1/_2$ hour to 800° in a high vacuum. Cooled to 30°, exposed to air for one minute at atmospheric pressure. Gain in weight of charcoal over D (3) equalled 0.0037 g. Charcoal at 20°, carbon tetrachloride at 0°.

The results of Series D are given in Table IV.

TABLE IV.

Carbon Tetrachloride. $p$ = 32.8 Mm. $t$ = Time of Exposure in Seconds.

| 1. | | 2. | | 3. | | 4. | |
|---|---|---|---|---|---|---|---|
| $t$. | $K$. | $t$. | $K$. | $t$. | $K$. | $t$. | $K$. |
| 5.0 | 0.0187 | 5.0 | 0.0211 | 10.0 | 0.0280 | 20.0 | 0.0165 |
| 14.5 | 0.0341 | 15.0 | 0.0328 | 33.1 | 0.0860 | 50.0 | 0.0405 |
| 35.0 | 0.0499 | 35.0 | 0.0413 | 67.2 | 0.1607 | 80.0 | 0.0700 |
| 100.0 | 0.0717 | 100.0 | 0.0536 | 74.8 | 0.1962 | 110.0 | 0.0993 |
| 200.0 | 0.0814 | 180.0 | 0.0631 | 100.0 | 0.2011 | 150.0 | 0.1247 |
| 300.0 | 0.0881 | 420.0 | 0.0845 | 240.0 | 0.2024 | 230.0 | 0.1389 |
| 600.0 | 0.1029 | 1020.0 | 0.1123 | ... | .... | 470.0 | 0.1418 |
| 1200.0 | 0.1209 | 2420.0 | 0.1438 | ... | .... | ... | .... |

The plots of these results are shown in Fig. 5.

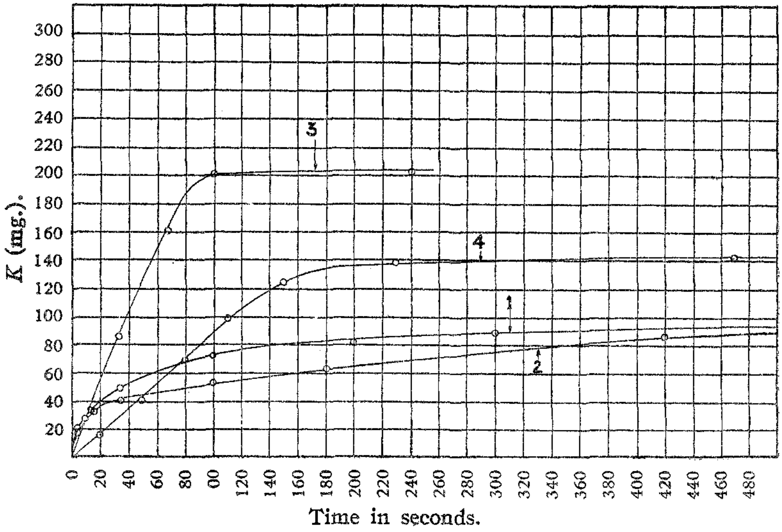

Fig. 5.

Another series of results with a fresh sample of charcoal was made under similar conditions to Series D but no greater reproducibility than given in the above table was obtained. Because of this discordancy and because of the fact that even after prolonged heating of the charcoal, constant weight was not obtained, it was decided to increase the preliminary heating of the charcoal to above 1000°.

E. (5) A fresh sample of charcoal, which had been extracted and treated in an identical manner as that employed in Series D was used.

Non-volatile matter equalled 0.9%. Heated in a high vacuum to 1040–1060° for 6.5 hours. Pressure in the system above the charcoal was finally reduced to $5 \times 10^{-3}$ mm. of mercury with the pumps on. Wt. charcoal equalled 0.5391 g. Charcoal at 20°, carbon tetrachloride at 0°.

(6) Same charcoal as in E (5). Reheated to 1060–1080° for 16 hours. The pressure above the charcoal was reduced to $8 \times 10^{-4}$ mm. with the pumps on. Gain in weight of charcoal equalled to 0.0153 g. or 28 mg. per g. of charcoal. Charcoal at 20°, carbon tetrachloride at 0°.

(7) Same charcoal as in E (6). Reheated to 1100° for 4 hours. Pressure above charcoal was reduced to $5 \times 10^{-3}$ mm. Gain in weight of charcoal equalled 0.0100 g. or 19 mg. per g. of charcoal. Charcoal at 20°, carbon tetrachloride at 0°.

The results of Series E are given in Table V.

TABLE V.

Carbon Tetrachloride. $p$ = 32.8 Mm. $t$ = Time of Exposure in Seconds.

| 5. | | 6. | | 7. | |
|---|---|---|---|---|---|
| *t.* | *K.* | *t.* | *K.* | *t.* | *K.* |
| 10.0 | 0.0966 | 5.0 | 0.0872 | 5.0 | 0.0805 |
| 21.0 | 0.1383 | 10.0 | 0.1413 | 10.0 | 0.1284 |
| 43.0 | 0.1704 | 21.0 | 0.1858 | 21.0 | 0.1637 |
| 78.0 | 0.1949 | 42.0 | 0.2043 | 40.0 | 0.1826 |
| 136.0 | 0.2135 | 80.0 | 0.2060 | 80.0 | 0.1872 |
| 235.0 | 0.2239 | 250.0 | 0.2075 | 1000.0 | 0.1878 |
| 500.0 | 0.2337 | 1000.0 | 0.2082 | .... | .... |

The plots of these results are shown in Fig. 6.

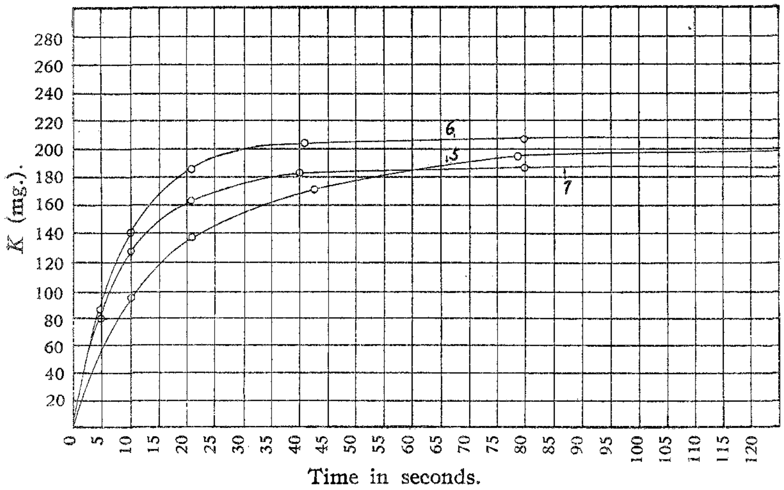

Fig. 6.

F. In this series of results the gas pressure was reduced to 18.8 mm. by immersing the tube containing carbon tetrachloride in a salt-ice mixture contained in a Dewar bulb.

(8) Fresh sample of charcoal similarly treated to that used in E. Heated to 1060–1080° for 7 hours in a high vacuum. Cooled to room temperature in vacuum, then exposed to carbon tetrachloride (32.8 mm.) for 2 minutes. Reheated for 6 hours to 1060–1080° in high vacuum. Charcoal at 20°, carbon tetrachloride at —10°.

(9) Same samples of charcoal as in F (8). Reheated to 1080–1100° for 3.5 hours in high vacuum. Gain in weight of charcoal equalled 14 mg. per g. charcoal. Charcoal at 20°, carbon tetrachloride at —10°.

The results of Series F are given in Table VI.

TABLE VI.

Carbon Tetrachloride. $p$ = 18.8 Mm.

| 8. | | 9. | |
|---|---|---|---|
| *t*. | *K*. | *t*. | *K*. |
| 5.0 | 0.0583 | 5.0 | 0.0495 |
| 10.0 | 0.0941 | 10.0 | 0.0892 |
| 21.0 | 0.1460 | 21.0 | 0.1400 |
| 33.0 | 0.1782 | 33.0 | 0.1683 |
| 47.0 | 0.1915 | 48.0 | 0.1799 |
| 64.0 | 0.1963 | 66.0 | 0.1831 |
| 90.0 | 0.1975 | 92.0 | 0.1858 |
| 120.0 | 0.1980 | 120.0 | 0.1887 |
| 240.0 | 0.1998 | 240.0 | 0.1890 |

The plots of the results of Series F are shown in Fig. 7.

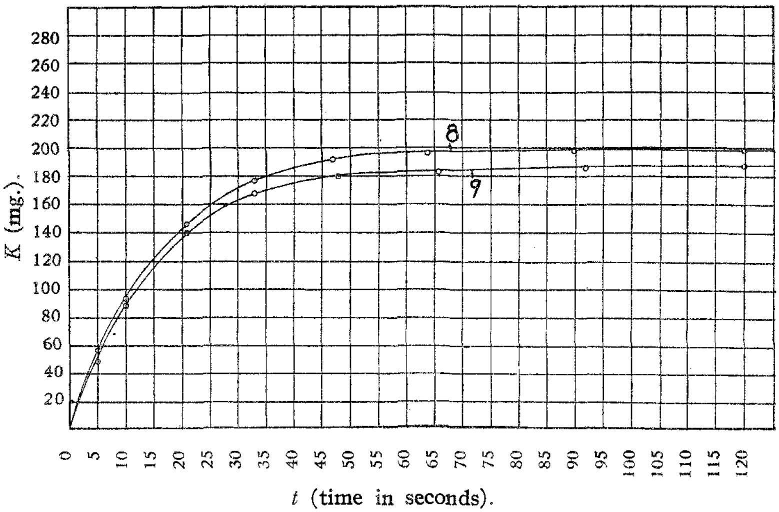

Fig. 7.

## Discussion of Results.

1. **The Initial Lag.**—From measurements of the velocity of adsorption of various canister charcoals containing air, moisture, oxides of carbon and other gases, by passing a war-gas and air mixture over them, Keyes and Finklestein (A. E. F. reports) found that the plot of log $K$ against $1/t$ was a straight line, where $K$ is the amount of war-gas in grams per g. of charcoal adsorbed in a time, $t$. Analytically, this expression becomes

$$K = Ae^{-B/t} \text{ or } \log K = \log A - B/t \qquad (1)$$

where $A$ and $B$ are constants. $A$ is the number of g. adsorbed per g. of charcoal when $t$ is infinity, or the capacity constant; $B$ is the rate constant. By differentiating (1), the equation,

$$\frac{dK}{dt} = \frac{AB/t^2}{e^{B/t}}$$

for the rate of adsorption is obtained. This equation has one interesting peculiarity. At first, the rate is slow, then it increases to a maximum, and finally decreases until equilibrium is reached. When $t = B/2$, $dK/dt$ is a maximum.

A $K$, $t$ plot using Equation 1 is shown by the dotted line in Fig. 2 where $A = 120$ (mg.), $B = 7$, $t$ is in seconds and $K$ in mg. This equation is purely empirical, and furthermore, the lag predicted by it had not been proved or disproved by direct experiment prior to the present work because the experimental method used by Keyes and Finklestein did not permit measurements to be made for small enough values of $t$.

A lag somewhat similar to this has been realized experimentally many times in this investigation. Curves A-1, A-2, A-3, C-8, C-11, and C-*a*, and D-8 are good examples, but do not, however, fit the above equation. It should be observed, however, that in the measurements here presented the charcoal has been probably deprived of a considerable portion of its adsorbed air by a preliminary heating in high vacuum and the charcoal surface probably uncovered considerably, whereas in the Keyes and Finklestein work charcoals completely saturated with air or air and moisture were employed. The behavior in both cases was thought to be due to the presence of foreign gases on the charcoal at the beginning and throughout the experiment; a considerable time delay being caused during their displacement.

2. **The Effects of Foreign Gases.**—The method of heating the charcoal to as high a temperature as was permissible in the apparatus employed in a high vacuum was well calculated to remove most of the foreign gases and eliminate this lag. There is much evidence, *e. g.*, as here presented and also by other investigators, that simply heating charcoal up to 1200° in a vacuum will not suffice to produce an absolutely gas-free

surface. For example, Chaney[1] reports that a hydrocarbon resembling anthracene, the boiling point of which is 360°, has been isolated from a cedar charcoal which had been previously calcined to 850°. However, relatively free surfaces may be obtained this way. In no case yet observed were anything like reproducible velocity results obtained until the charcoal had been heated to over 700° in a vacuum, cooled in a vacuum, exposed to the gas until considerable quantities were adsorbed, and then again reheated to above 700° in a high vacuum. This process of "washing out" the charcoal with the gas whose adsorption velocity was being measured seemed to be necessary under the temperature conditions employed before reproducibility could be obtained. The presence on the surface of molecules of the gas whose velocity of adsorption is being determined, and this gas alone, will not affect the form of the plots. In order to bring out more clearly the significance of the adsorption behavior, it will be necessary to consider each of the series of results obtained.

*Series A, Fig. 2.*—These curves show the successive effect of "washing out" and heating in vacuum to 350°. Curve 1 has a decided lag, Curve 2 less, Curve 3 still less but reaching a maximum rate only after the expiration of 7 minutes. These curves lie somewhere between those obtained by the equation of Keyes and Finklestein for completely air saturated charcoal of the same kind and the curves which will be obtained after a more effective removal of foreign gases from the surfaces. No regularity in the experimental results was observed at values of $t$ above 30 seconds (results not tabulated), and even after exposures of 110 minutes, the full capacity of the charcoal was by no means obtained. These curves are valuable for illustrating the gradual elimination of the lag by successive heating and washing out of foreign molecules.

*Series B, Fig. 3.*—In these results, the more effective cleansing of the surface at higher temperatures (700° as compared to 350°) is to be observed. Curve 4 (obtained in Paris) was the first obtained in which the initial lag was entirely eliminated. The maximum rate occurs at the very beginning of the process. Curves 5, 6 and 7 give the history of a charcoal which was reheated and "washed out" twice. Curves 6 and 7 are regarded as reproducible because they are easily rectified by a simple equation. In Fig. 8, $\log A/A - K$ is plotted against $t$, where $K$ the amount adsorbed in time $t$ and $A$ is the amount adsorbed when $t$ is infinite or the capacity factor. The plot is a straight line, B-6 and -7.

In addition, no faster adsorption was caused by further repetition of the above successive heating and pumping treatment. Curve 5 represents a slower adsorption, because it has only been heated and not "washed out" with chloropicrin. It is very interesting at this juncture to compare the rapidity with which the total capacity is reached in Experiments B-4,

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[1] *Trans. Am. Electrochem. Soc.*, Paper 13, Sept. 26, 1919.

6, 7 and those described in Series A. In Series B, the charcoal was filled in practically 100 seconds, in Series A3 only 0.1854 g. was adsorbed in 6600 seconds, corresponding to only 60% of the capacity in $^1/_{66}$ of the time.

*Series C, Fig. 4.*—In these measurements, a pressure of 0.61 mm. of chloropicrin was employed. This pressure, 10 times less than that employed above, was used to magnify any effect due to foreign gases on the surface. Curve *a* has been introduced solely for the purpose of showing the initial lag. It is best to observe Plots 8, 9, 10 and 11 in order, which give the history of one sample of charcoal. Curve 8 is extremely slow; there is no doubt from this of the existence of the initial lag. The maximum rate occurs in about 60 minutes from the start. When this charcoal was rinsed out with chloropicrin by reheating in a high vacuum, Curve 9 was obtained. In the first 5 minutes, the charcoal had taken up 250 times the quantity of gas; in the first 10 minutes, 90 times the quantity and so forth. This shows the great efficiency of the "washing out" process.[1] Furthermore, Plot 9 is rectified by the same equation which rectified Series B, 6 and 7. The plots of log $A/A - K$ against $t$ are given in Fig. 9. The same is true of Curve 10 which varies only slightly from 9; with the exception of a sharp break occurring when $t$ equals 40, which was probably caused by a slight inrush of air into the apparatus. As further proof that these abnormal effects are due to the presence of foreign gases, the charcoal used in Expt. 10 was rinsed out as described and some air was allowed to remain on the surface. The original slow process was nearly reproduced. The amount of foreign gases necessary to cause this remarkable change cannot be given. The charcoal was 0.0002 g. heavier in Expt. 11 than in 10. However, repeated heating in the presence of air must have caused the burning off of some of the charcoal.[2] Further investigations of these phenomena will be made.

At this point it may be said that whenever the curves can be closely reproduced as with B-6 and -7, C-9 and -10, they all conform to the same equation. All other curves which do not fit the form of this equation vary in a most erratic manner as illustrated by Curves *a*, 8 and 11 (Fig. 4) and D-1, -2, -3 and -4 (Fig. 5).

*Series D, Fig. 5.*—These results were obtained with carbon tetrachloride at a pressure of 32.8 mm. of mercury. Curve 1 shows results obtained after heating the charcoal to 750° in a vacuum. Curve 2, after a first reheating to 750° and rinsing with carbon tetrachloride; and Curve 3

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[1] To offer a crude analogy, it is similar to soaking up gasoline with a sponge which is already covered with a film of water. Practically no gasoline will be taken up until the sponge is washed out a number of times with gasoline.

[2] Langmuir, THIS JOURNAL, 40, 1400 (1918), has observed a similar behavior in studying the velocity of the reaction between oxygen and carbon monoxide on platinum foil. In the latter instance erratic slow and fast reactions were observable when no foreign gas was present in sufficient quantities to form a film one molecule thick.

after a second reheating to 750° in a vacuum and a second rinsing. The effects of the presence of foreign gases on the surface were very noticeable. Although Curve 3 shows a large increase in velocity over 1 and 2, it does not conform to the form of curve found for B-6 and -7, C-9 and -10. The experiments in 4 were carried out in the presence of air and exhibit a lag. Another series of 5 results, not included in the data, was carried out in the same manner, and the results were as discordant and as unpredictable as the above. Even after a continued exhaustion at 750°, a considerable gain in weight of charcoal was observed.

*Series E, Fig. 6.*—The exhaustion of the charcoal in the 3 experiments in this series was carried out at from 1050–1100°. This made a notable difference in reaction velocity. Curve 5 was obtained after the first heating, 6 after reheating and rinsing out with the gas, and 7 after a second reheating and rinsing out process. Curves 6 and 7 are identical in form and are rectified by the same equations as B-6 and -7, C-9 and -10. The plots of log $A/A - K$ against $t$ are given in Fig. 8. There is a difference, however, in final capacities between E-5, -6 and -7 which corresponds closely to the gain in weight of the charcoal between the measurements. Even a continuous exhaustion for 16 hours at 1060–1100° failed to reduce the weight of the charcoal to the original weight. In fact, between Expts. 5 and 6, the charcoal had gained 28 mg. per g. The decrease in final capacity between Expts. 5 and 6 was 25 mg. per g. Again, the gain in weight of charcoal between Expts. 6 and 7 was 19 mg. per g. The decrease in final capacity was 21 mg. per g. This is proof that a considerable quantity of carbon tetrachloride is held by the surface at temperatures from 1060 to 1100°. Others have reported that hydrocarbons are held by charcoal at these temperatures.[1]

*Series F, Fig. 7.*—What has been said of Expts. E-6 and -7 may be said of F-8 and -9. The only difference in behavior is due to the fact that the gas pressure has been lowered from 32.8 mm. to 18.8 mm. The plots of log $A/A - K$ against $t$ are also given in Fig. 8.

## General Considerations.

Langmuir[2] has developed a general theory of adsorption of gases on solids. From consideration of the unsymmetrical arrangement of the atoms of the surface of a solid, it is assumed that they are "unsaturated chemically and thus are surrounded by an intense field of force." Further, "when gas molecules impinge against any solid or liquid surface they do not, in general, rebound elastically, but condense on the surface, being held there by the field of force (residual valence) of the surface atoms. These molecules may subsequently evaporate from the surface. The length of time that elapses between the condensation of a molecule and its subse-

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[1] Chaney, *loc. cit.*

[2] THIS JOURNAL, 40, 1361 (1918).

quent evaporation depends on the intensity of the surface forces. Adsorption is the direct result of this time lag. If the surface forces are relatively intense, evaporation will take place at only a negligible rate, so that the surface of the solid becomes completely covered with a layer of molcules. In cases of true adsorption this layer will usually be not more than one molecule deep, for as soon as the surface becomes covered by a single layer, the surface forces become chemically saturated. Where, on the other hand, the surface forces are weak the evaporation may occur so soon after condensation that only a small fraction of the surface becomes coated with a single layer of adsorbed molecules. In agreement with the chemical nature of the surface forces, the range of these forces has been found to be extremely small, of the order of $10^{-8}$ cm. That is, the effective range of the forces is less than the diameter of a molecule."

Case 1.—In the present investigation, the pressure of the gases has been kept sufficiently low to eliminate any "capillary effects," so that the phenomena are cases of true adsorption. In accordance with the above scheme, let it be assumed that we have to do with a film one molecule thick. Let it also be assumed that the ratio of the number of molecules condensing on unit surface in unit time to the number evaporating from the surface is a constant throughout the process. Furthermore, let it be assumed that all molecules of the gas which impinge on the layer of molecules already on the surface, rebound and do not condense. With such conditions, the velocity will then be proportional to the bare surface, which, expressed in the quantities measured, becomes

$$\frac{dK}{dt} = m(A - K), \text{ or } m = \frac{1}{t} \, ln \, \frac{A}{A - K} \qquad (3)$$

where $A$ is the total weight capacity per g. of charcoal, $K$ is the weight absorbed per g. of charcoal in time $t$, and $m$ is a constant. Langmuir's Equation[1] 15 which takes into consideration the factors of surface, condensation and evaporation involved is

$$\frac{N}{N_0} v_1 \left(1 + \frac{\alpha}{v_1} \mu\right) = \frac{1}{t} \, ln \, \frac{\theta_1}{\theta_1 - \theta'}$$

where $N_0$ represents the number of the elementary spaces per sq. cm. of surface, $N$ is Avogadro's number, $\alpha$ the fraction of the number of molecules which condense on the surface, $\mu$ is the number of gram molecules of gas striking each sq. cm. surface per second, $v_1$ is the rate at which the gas would evaporate if the surface were completely covered, $\theta_1$ is the fraction of the surface covered at equilibrium and $\theta'$ the fraction covered in a time $t$. The left-hand member of the foregoing equation corresponds to $m$ in Formula 3 and should be a constant at constant gas pressure and temperature.

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[1] An error in printing in Langmuir's paper gives the right-hand member of this equation, $1/t \log \theta'/\theta_1 - \theta'$.

**Case 2.**—Assume that the force of attraction between the surface and the molecules is active through a distance greater than one molecule thick, and that a fraction of a second layer is adsorbed. Second, let it be assumed that the ratio of the number of molecules condensing on the first layer to the number evaporating from the first layer is a constant. This will produce a second reaction of the first layer and proceeding with a different velocity. Such a condition is expressed by the equations

$$\left.\begin{aligned} dx/dt &= m_1(a - x) \\ dy/dt &= m_2(xF - y) \end{aligned}\right\} \qquad (4)$$

where $x$ is the amount on first layer in time $t$, $a$ is the amount on first layer when $t$ is infinite, $m_1$ is the constant of the first reaction, $y$ is the amount on second layer in time $t$, $m_2$ is the constant of the second reaction, and $F$ is a coefficient such that $aF$ equals the amount on the second layer when $t$ is infinite. Furthermore, $x + y = K$ and $a + aF = A$, the capacity factor. The solution of these equations give

$$(x + y) = a + aF + a\left[\frac{F(m_1e^{-m_2t} - m_2e^{-m_1t})}{m_2 - m_1} - e^{-m_1t}\right] \qquad (5)$$

The form of the $(x + y)$, $t$ plot of this equation will be the same as the $K$, $t$ plots of Equation 3 when $F$ equals unity and $m_1$ equals $m_2$. These conditions appear improbable, however, since a fast and a slow reaction is

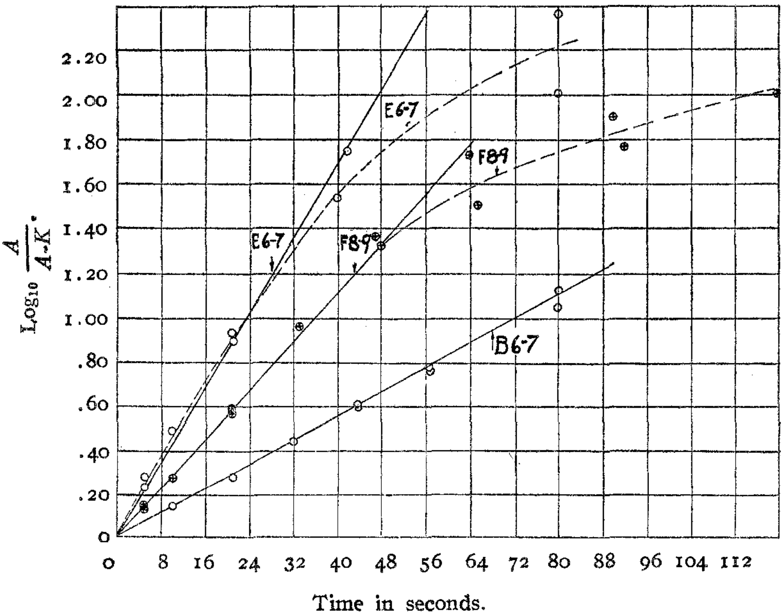

Fig. 8.

to be expected owing to the variation of the surface forces due to the successive layers. The form of the $(x + y)$ against $t$ plot of Equation 5 will approach the form of the $K$, $t$ plot of Equation 3 when $F$ is small compared to unity and hence $m_1$ has many times the value of $m_2$. To test these later conditions, accurate results must be obtained, especially near the end of the reaction.

## Final Considerations.

To summarize one aspect of the results obtained in this investigation, it may be said that in all cases discordant and unreproducible values were always obtained except when the reaction was proceeding at the maximum velocity obtainable under a given set of temperature and pressure conditions. When the maximum velocity was obtained, the reaction proceeded according to Equation 1 as shown by the figures in Table VII, and the plots in Figs. 8 and 9.

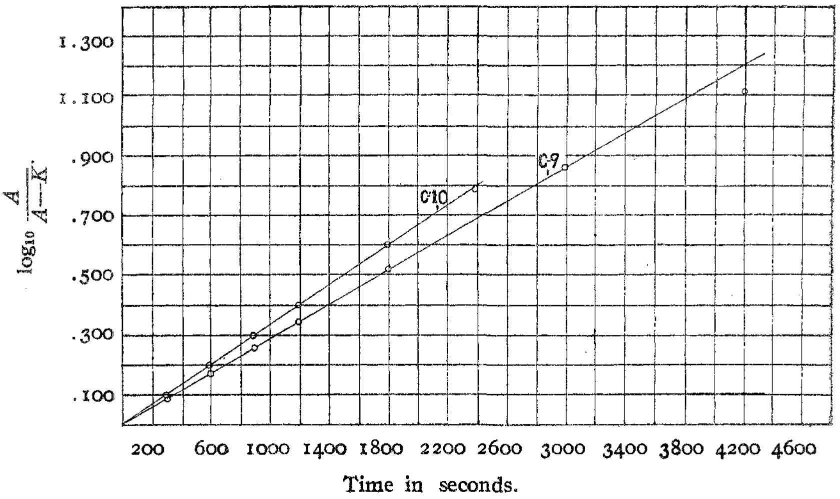

Fig 9.

TABLE VII.

$CCl_3NO_2$. B 6. $p = 5.9$ mm.

| $t$ (secs.). | $K$. | $m \times 10^2$. |
|---|---|---|
| 10 | 0.0901 | 1.49 |
| 21 | 0.1520 | 1.39 |
| 32 | 0.1963 | 1.36 |
| 44 | 0.2340 | 1.39 |
| 57 | 0.2556 | 1.33 |
| 80 | 0.2820 | 1.33 |
| 500 | 0.3083 | .... |
| A | 0.3100 | .... |
| | | Mean, 1.38 |

$CCl_3NO_2$. B 7.

| $t$ (secs.). | $K$. | $m \times 10^2$. |
|---|---|---|
| 10 | 0.0875 | 1.44 |
| 21 | 0.1473 | 1.33 |
| 32 | 0.1930 | 1.32 |
| 44 | 0.2328 | 1.37 |
| 57 | 0.2580 | 1.36 |
| 80 | 0.2862 | 1.40 |
| A | 0.3100 | .... |
| .. | .... | .... |
| | | Mean, 1.37 |

TABLE VII (*continued*).

$CCl_3NO_2$. C 9. $p = 0.61$ mm.

| $t$ (secs.). | $K$. | $m \times 10^4$. |
|---|---|---|
| 300.0 | 0.0532 | 3.00 |
| 600.0 | 0.0948 | 3.00 |
| 900.0 | 0.1250 | 2.87 |
| 1200.0 | 0.1574 | 2.98 |
| 1800.0 | 0.1972 | 2.90 |
| 2400.0 | 0.2265 | 3.00 |
| 3000.0 | 0.2430 | 2.94 |
| 4200.0 | 0.2585 | 2.65 |
| A | 0.2800 | .... |

Mean, 2.90

$CCl_3NO_2$. C 10.

| $t$ (secs.). | $K$. | $m \times 10^4$. |
|---|---|---|
| 300.0 | 0.0571 | 3.27 |
| 600.0 | 0.1034 | 3.33 |
| 900.0 | 0.1385 | 3.30 |
| 1200.0 | 0.1683 | 3.32 |
| 1800.0 | 0.2089 | 3.29 |
| 2400.0 | 0.2329 | 3.24 |
| A | 0.2800 | .... |
| .. | .... | .... |
| .. | .... | .... |

Mean, 3.29

$CCl_4$. E 6. $p = 32.8$ mm.

| $t$ (secs.). | $K$. | $m \times 10^2$. |
|---|---|---|
| 5 | 0.0872 | 4.71 |
| 10 | 0.1413 | 4.94 |
| 21 | 0.1858 | 4.74 |
| 42 | 0.2043 | 4.18[a] |
| A | 0.2080 | .... |

Mean, 4.83

$CCl_4$. E 7.

| $t$ (secs.). | $K$. | $m \times 10^2$. |
|---|---|---|
| 5 | 0.0805 | 4.88 |
| 10 | 0.1284 | 5.03 |
| 21 | 0.1637 | 4.31 |
| 40 | 0.1826 | 4.07[a] |
| A | 0.1870 | .... |

Mean, 4.74

$CCl_4$. F 8. $p = 18.8$ mm.

| $t$ (secs.). | $K$. | $m \times 10^2$. |
|---|---|---|
| 5 | 0.0583 | 2.97 |
| 10 | 0.0941 | 2.76 |
| 21 | 0.1460 | 2.72 |
| 33 | 0.1782 | 2.90 |
| A | 0.2000 | .... |

Mean, 2.84

$CCl_4$. F 9.

| $t$ (secs.). | $K$. | $m \times 10^2$. |
|---|---|---|
| 5 | 0.0495 | 2.61 |
| 10 | 0.0892 | 2.76 |
| 21 | 0.1400 | 2.78 |
| 33 | 0.1683 | 2.87 |
| A | 0.1890 | .... |

Mean, 2.75

[a] Values determined near the end of the reaction are subject to considerable variation from the general mean. These values will be neglected in computing a mean value.

Referring now to plots in Figs. 8 and 9, it is seen that at pressures of 0.61 mm. and 5.90 mm. of chloropicrin, the log $A/A-K)$, $t$ plots are straight lines, thus conforming to Equation 3.[1] F-8 and -9 conform to the same equation up to very nearly the final capacity and then fall off in accordance with the slow secondary reaction of Equation 5. This is true to a greater extent with the results E-6 and -7 at a gas pressure of 32.8 mm. of carbon tetrachloride, as shown by the dotted line in Fig. 8 which is drawn through the points obtained. Although this deviation is not due to experimental error, sufficient data near the end-point have not been

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[1] Others have pointed out that this reaction was probably monomolecular. Valentiner (*Beibl. Ann. Physik.*, 40, 489 (1916)). Lamb and Finklestein were the first to study these adsorption velocities in the Chemical Warfare Service work. They found that the reaction followed closely the monomolecular form.

obtained to decide the matter. For the present, the slopes of the straight lines will be taken as the values of $m$. This may be regarded as an approximation and thus far all the above velocity data are, in general, in agreement with Langmuir's theory.

However, if only very minute quantities of gases retard the velocity of adsorption to the extent observed in this investigation, the above theory will have to be modified or further assumptions added. A further investigation of the quantity of foreign gas necessary to cause such lags is of great importance and is about to be undertaken.

## The Pressure Effect.

(1) *On Velocity.*—Langmuir[1] has employed the formula

$$\mu = \frac{p}{\sqrt{2\pi MRT}} \qquad (6)$$

for calculating the rate of bombardment of the gas molecules on a solid surface. $\mu$ is the number of gram molecules striking unit surface per second, $m$ the molecular weight, $T$ the absolute temperature, $p$ the pressure, and $R$ the gas constant in ergs per degree. Thus, for an ideal gas the rate of bombardment is proportional to the pressure.

Langmuir's equations give, where $m$ is the constant of Equation 3

$$m = \frac{N_0}{N} v_1(1 + \frac{\alpha}{v_1}\mu),$$

an expression which, combined with (6) will make $m$ a linear function of the pressure. A sufficient number of reliable results have not yet been obtained to test this relation adequately. The 2 carbon tetrachloride measurements at pressures of 18.8 mm. and 32.8 mm., however, indicate that at these high pressures the velocity constant $m$ is directly proportional to the pressure. The result on the other hand is quite different for chloropicrin since the pressure decrease from 5.9 mm. to 0.61 mm. or a 10-fold decrease, causes a 42-fold decrease in $m$.

(2) *On Capacity.*—Langmuir's Equation 9 gives

$$q = \frac{abp}{1 + ap}$$

for the relation between $q$, the total capacity, and $p$, the pressure where $a$ and $b$ are constants. This agrees with the large amount of evidence obtained by Langmuir on the adsorption of various gases at low pressures (2 to 100 bars) on glass and mica. Differentiation of the above gives

$$\frac{dq}{dp} = \frac{ab}{(1 + ap)^2} = 0, \text{ for } p = \infty$$

and hence $dq/dp$ becomes smaller as $p$ increases. At higher pressures

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[1] *Phys. Rev.*, **2**, 331 (1913); THIS JOURNAL, **37**, 1135 (1915); also *loc. cit.*

the capacity should vary little with the pressure. This conclusion is confirmed by the result with chloropicrin reported in this investigation. The capacity per g. of charcoal was 0.2800 g. at a pressure of approximately $5 \times 10^3$ bars and 0.3100 g. at $5 \times 10^4$ bars, an increase of only 10% in capacity with a 10-fold increase in pressure. The present data are, therefore, qualitatively in accordance with the one layer theory as regards the capacity.

The author wishes to express his appreciation to Professor Frederick G. Keyes of the Massachusetts Institute of Technology for criticisms and suggestions in connection with this work.

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# SOME PROPERTIES OF CHARCOALS.

BY H. E. CUDE AND G. A. HULETT.

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In a study of the moisture and gas content of various types of charcoals used in gas warfare we incidently determined the densities of these charcoals.[1] It soon developed that it was by no means an easy matter to determine the true density of a charcoal for we soon discovered that there was a "drift" or increase in weight when it was immersed in a liquid. This drift decreased with time but was noticeable after weeks, and in some cases it was detectable after months. Furthermore, its magnitude was such that the first suggested explanations proved quite inadequate.

In determining the moisture and gas content of the activated chars, 5 to 10 cc. of the material was inclosed in a thin-walled glass tube with a capillary outlet, and the moisture and gases pumped out and determined. The charcoal was finally heated to 445° (sulfur b. p.), and the system was thoroughly out-gassed and the capillary sealed off. After the tube and charcoal were weighed, the capillary was broken under the liquid, a fine platinum suspension wire was attached to the tube, which was then immersed in the liquid and the whole was thereupon weighed. Finally the glass tube was weighed in air and also in the liquid, so that many corrections were eliminated in the density calculations. Temperature effects due to wetting the charcoal were found to disappear in some 10 to 15 minutes and weighings were then made at intervals. The weighings were made in a constant-temperature room, but the temperature of the liquid was also carefully followed. It was found that the weight increased markedly at first, then fell off with time. The following table will give an idea of the observations:

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[1] War Gas Investigations, G. A. Hulett, C. W. S., Reports, September–December, 1918.