

OCCLUSION OF WATER BY GAS-MASK CHARCOAL

BY

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The following work was begun with the object of determining the effect of temperature upon the amount of water occluded by charcoal. Some preliminary experiments showed that charcoal, which had been stored in an open tube, gave off steam in unusually large quantities when heated to several degrees above the boiling point of water.

The first part of the work was to determine the relation between amount of water in the charcoal and temperature, at atmospheric pressure. The second part was to determine the relation between pressure and temperature, keeping the water content constant. This relation was determined for various amounts of water. Equilibrium conditions were obtained for all the determinations.

Several methods were tried before satisfactory results could be obtained. The first problem was to maintain the sample of charcoal at various temperatures above  $100^{\circ}$  C. This was accomplished at first by means of a steam bath. The temperature was determined by measuring the pressure of the saturated water vapor and by using steam tables. A gas flame supplied the heat. The temperature could be controlled by regulating the flame and by changing the flow of cold water through a condenser by means of which the water vapor was condensed rapidly enough to insure boiling conditions. This method failed because it required con-

stant attention to keep the temperature regulated, and it was soon discovered that several hours did not suffice for equilibrium. The method finally adopted was to use a mercury bath, electrically heated, and controlled by means of a thermostat. The mercury bath was about 5 cm. in diameter and 20 cm. in height, and was made from fibre. A heating coil of German Silver wire with double cotton insulation was wound about a thin cylinder of copper of such size as to fit snugly inside the fibre cylinder. The heating coil was lowered into the mercury bath and fastened down. The whole bath was packed in cotton to minimize heat losses and therefore to lessen temperature gradients in the bath. The thermostat which controlled the heating current was actuated by steam pressure. It is shown diagrammatically in fig. 3.

Another difficulty was to measure the pressure of the vapor in the space above the sample of charcoal. The chief difficulty here was to get rid of all the gases and vapors except water vapor. At first an attempt was made to flood the charcoal with water and then drive off large quantities of steam which would carry the air along with it. The steam was allowed to bubble through a U tube partially filled with mercury until equilibrium was reached at some fixed temperature. The charcoal might then be weighed, and if it were subjected to a high temperature and most of the re-

maining water driven off, the loss of weight would give the weight of the water that had remained in the charcoal when equilibrium conditions prevailed. There were two chief causes of failure in this method. In the first place the sample of charcoal must be removed from the bath for each single determination, and when the steam bath was used this caused a great deal of delay. Also the effect of the mercury in the U tube upon the pressure could not be accurately determined. The splashing of mercury back into the charcoal had to be guarded against very carefully.

The final results were obtained by the following method.

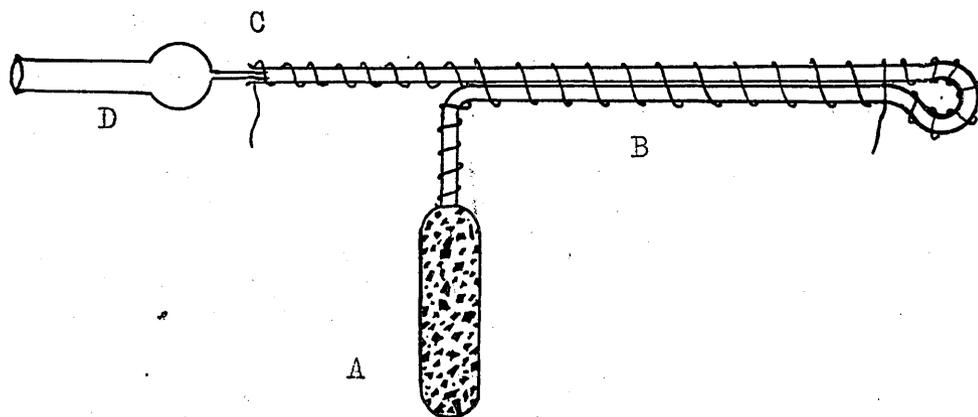
A test tube containing 8.5 grams of gas-mask charcoal, which was obtained through the courtesy of Mr. Van H. Manning, Director of the Bureau of Mines, was flooded with distilled water. It was then placed in a mercury bath and maintained at a temperature of from 101° to 104° C until no more water vapor was driven off. The temperature was then raised a few degrees and again kept constant until equilibrium was obtained. The amount of water driven off was measured by collecting it in a drying tube and weighing. To prevent air from diffusing back into the charcoal a capillary tube of about  $\frac{3}{4}$  mm. bore and 30 cm. in length was sealed to the test tube. The

INDEX TO APPARATUS FOR MEASURING TEMPERATURE-  
CONCENTRATION RELATION.

- A Charcoal tube containing 8.5 grams of gas-mask charcoal.
- B Capillary tube to prevent air from diffusing into the charcoal.
- C Ground glass joint.
- D Drying tube by means of which the water driven off was collected and weighed.

The heating coil wound around the capillary tube prevented the water vapor from condensing before it reached the drying tube.

Fig. 1



APPARATUS USED FOR MEASURING TEMPERATURE-  
CONCENTRATION RELATION.

INDEX TO MANOMETER AND APPARATUS USED TO DETERMINE  
TEMPERATURE-PRESSURE RELATION.

- A Charcoal tube
- B Glass tube forming one side of the manometer. It was made long enough so that there was always an outward pressure at the rubber connection at the bottom of the tube.
- C Rubber connection
- D Small bore glass tube
- E Heating device to fit over the end of the tube at F
- F End of one branch of the T tube which was sealed off when sufficient water had been driven off
- S Slit in heating coil. The top of the mercury column on this side of the manometer was made to coincide with S by raising or lowering the opposite side.

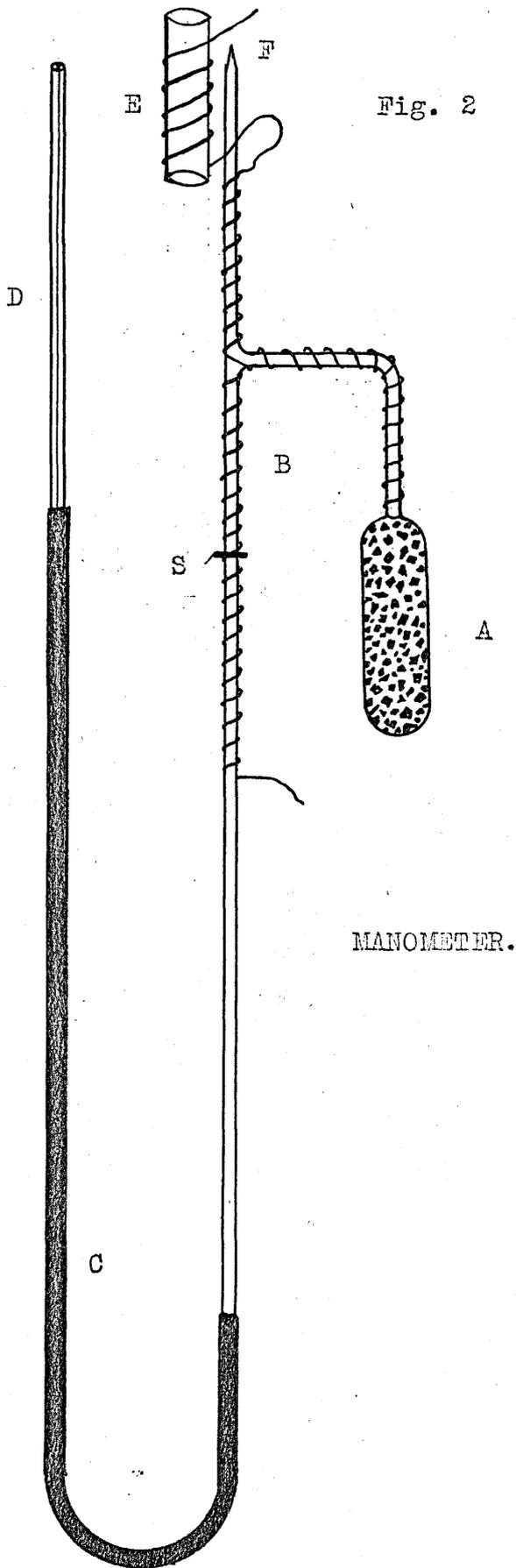


Fig. 2

MANOMETER.

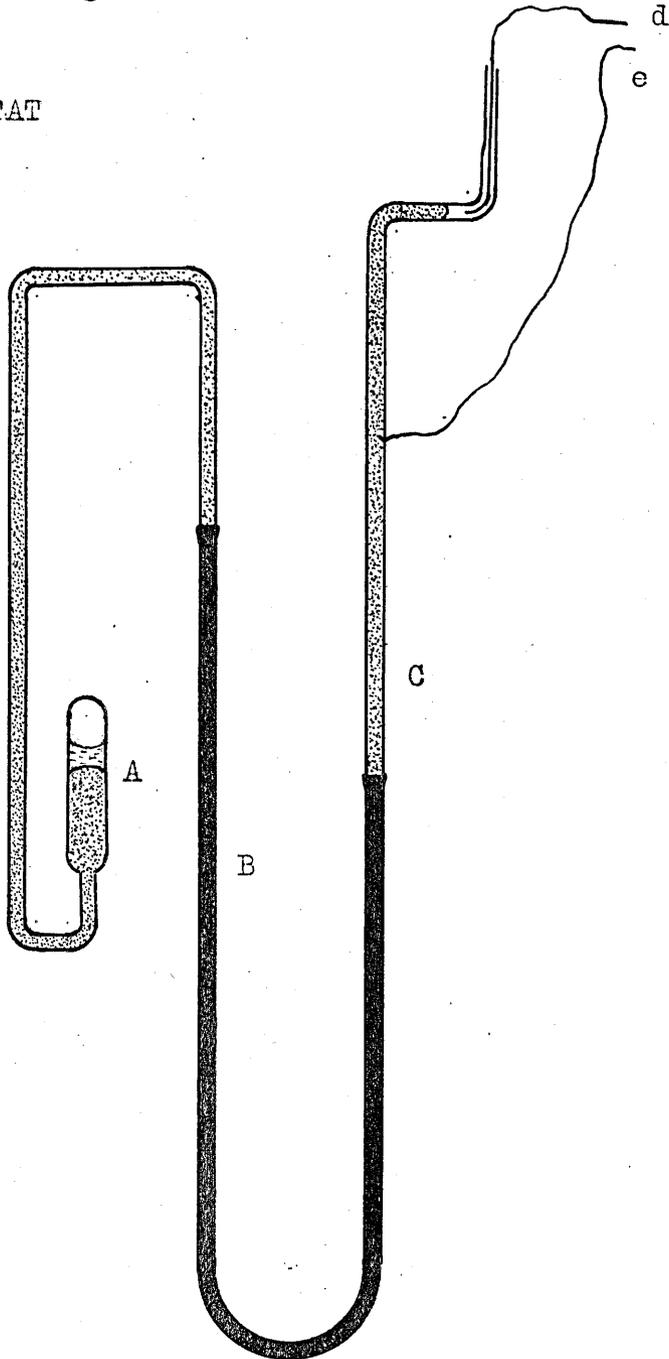
## INDEX TO THERMOSTAT

- A Inverted test tube containing water above mercury.
- B Rubber connection
- C Glass tube
- d & e Wires leading to a relay

The tube A Was lowered into the mercury bath and the pressure of the water vapor forced mercury into the tube C until contact was made by the mercury with the wire e . When contact was made the relay controlling the heating coil in the mercury bath shut off the heating current. The bend in the upper part of C was such as to give a maximum movement to the end of the mercury column with a small change of pressure in the tube A .

Fig. 3

THERMOSTAT



drying tube was connected by means of a ground glass joint, one part of which was sealed to the capillary tube. To prevent water vapor from condensing in the capillary tube a heating coil of German Silver wire was wound along its entire length. Moisture from the air was prevented from entering the open end of the drying tube by means of a cotton plug.

A temperature range of about  $40^{\circ}$  was covered in four or five steps. Equilibrium was sometimes difficult to obtain, as much as 6 hours being required for points on the steep part of the curve. The charcoal was then baked in an electric oven for more than  $1/2$  hour at a temperature of about  $220^{\circ}$  C. The amount of water in the charcoal when the drying tube was first connected was taken as the sum of all the amounts driven off. The amount at the second temperature was this same sum minus the water driven off during the first step, etc.

The results of four complete runs are shown in the curve. The variation of the barometric pressure from 74 cm. of Hg., which was taken as the average barometer reading, was taken into account after the relation between temperature and pressure had been determined. The temperature correction, corresponding to the greatest variation in pressure from 74 cm. was 0.35 of one degree. The amount of water in the charcoal is calculated upon the assumption that all the water was driven off when the charcoal was baked. This is, of course, not accurately true since more water vapor would be obtained if the char-

coal was thoroughly outgased. This small amount of water must be added to all the values given in the tables and curves in order to give the actual amount.

For determining the pressure temperature relation a T-tube was sealed to the charcoal tube. To one branch of the T was sealed a glass tube about 80 cm. in length which was bent to form one side of an ordinary open tube mercury manometer. The remainder of the manometer consisted of a rubber tube and a second glass tube of small bore. The mercury on the side of the manometer next the charcoal was kept at a constant level by raising or lowering the other side of the manometer. By reason of the extra length of the first glass tube the pressure on the rubber connection was always outward even if the pressure above the charcoal approached zero. This prevented air from leaking into the system through the rubber connection. A heating coil was wound from the charcoal tube to a point well below the top of the mercury column in the manometer. The top of the mercury column was made to coincide with a slit in the heating coil and the height of the opposite column, above a fixed point, was measured when the second arm of the T was open. The variation of the height of this column when the system was sealed off, together with the barometric reading, gave the pressure of the vapor above the charcoal.

To make a determination, the charcoal was flooded with water through the second branch of the T. The tem-

perature was maintained fixed at some point well above the boiling point of water. The open tube through which the water was introduced was sealed off before equilibrium had been obtained to make sure that no air diffused into the system. The temperature was then maintained at various points and the pressures measured. The amount of water present was found by noting the temperature which gave a pressure of 74 cm. of Hg. and by taking the corresponding point on the first curve.

For another determination the pressure was raised to something greater than atmospheric pressure. A flame applied to the end of the glass tube allowed it to open up and let out more water. The system was again sealed off and data taken for another curve. Curves 1, 4, 5, were all determined from one initial charge of water. Curves 2 and 3 were each determined by separate initial charges. These two curves happened to be so close together that they are plotted as one curve. (The points are shown as dots for one curve and as circles for the other).

#### SOURCES OF ERROR

To make certain that the pressure measured was due in measurable extent, at least, to water vapor only, the whole system was allowed to cool to room temperature. If the pressure did not fall to a value less than the saturated vapor pressure of water at that temperature a fresh start was made. For curves where the amount of water was small the pressure fell to a lower value than when the

amount of water was large. For curve (5) the value of the pressure was about half of the saturated vapor pressure at room temperature. These small pressures could not be measured with sufficient accuracy to insure a small percent error. Therefore the values obtained were not put into the tables.

The temperature was read on a mercury thermometer calibrated to tenths of degrees. Owing to temperature gradients in the bath and other causes the error in reading the temperature may be as great as  $1/2$  degree.

A small amount of mercury distilled from the manometer over into the charcoal on account of the effects of the heating coil. Since some of the runs extended over two and three days with no noticeable change in pressure at any given temperature, it seems evident that this mercury had no appreciable effect on the results obtained.

No estimate can be made of the effect upon the data that would be obtained if the charcoal were subjected to an out-gasing process, which is the usual procedure when working with charcoal.

Since charcoal is of a porous nature it seems reasonable to expect that capillarity might play an important part in the occlusion of water. In the third edition of "Properties of Matter" by Poynting and Thomson, page 168, is given a discussion upon the pressure of a vapor in equilibrium with a curved surface of its liquid. If a liquid rises to a height  $h$  in a capillary tube and the temperature is uniform throughout the system the pressure of the vapor in equilibrium with the top of the thread of liquid must differ from the pressure at the surface of the liquid by an amount equal to the product of the density of the vapor and  $h$  or  $\Delta P = - \Delta h d = - K h P$ , assuming that the vapor obeys Boyles Law. Here  $d$  is the density of the vapor and  $P$  its pressure. Solving this equation we get  $- h = \frac{\log p/p_0}{K}$   $P$  is the pressure of the vapor at the top of the thread of liquid and  $P_0$  is the saturated vapor pressure at the given temperature. If a short capillary tube is only partly filled with liquid the curvature at each end of the thread of liquid will be the same as it would be at the top of a long capillary in which the liquid rises to its maximum height, and the pressure of vapor in equilibrium with it would be  $P$ . If  $h$  is calculated from measurements of  $P$ , and  $P_0$  is known, the radius  $r$  of the capillary may be calculated in terms of the surface tension  $T$  and the density of the liquid  $D$ .  $r = \frac{2T}{hD} = \frac{2TK}{-\log p/p_0}$  which is essentially the formula used by Lowry and

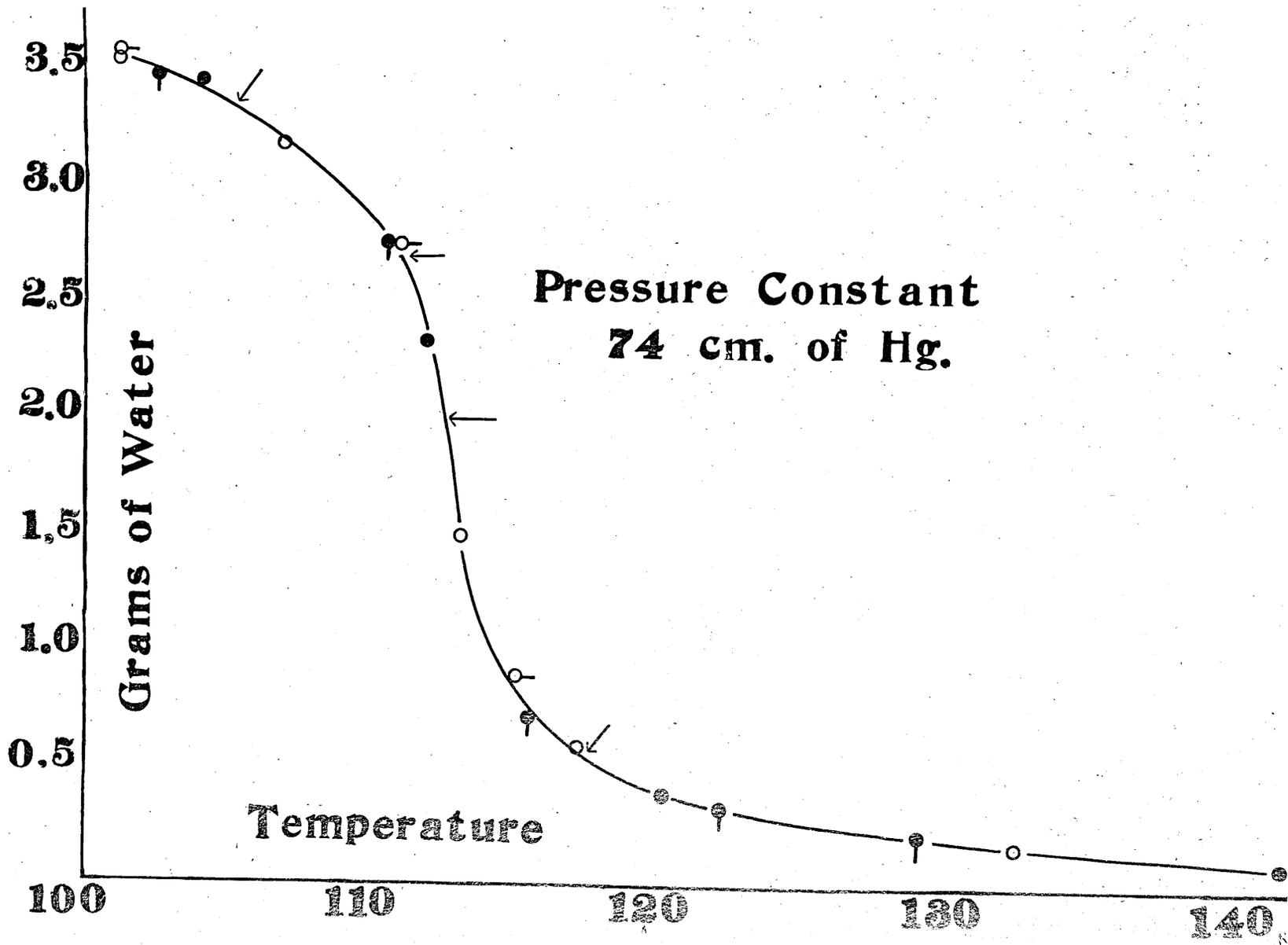
Hulett<sup>1</sup> in calculating the radius of the pores in charcoal.  
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 1. Studies in Adsorption of Charcoal. H.H. Lowry and G.A. Hulett, Journal Chem. Soc., July 1920.

coal upon the assumption that it is a capillary effect which causes water vapor to be absorbed.

In table III are given values of  $h$  at various temperatures, with different amounts of water in the charcoal. With rise in temperature, the value of  $h$  should decrease if the surface tension decreases as it does under ordinary circumstances. In all but the first curve it is seen that the value of  $h$  increases, with rise in temperature, instead of decreases, as might be expected if the assumption is correct that it is a capillary effect.

<sup>1</sup>Charcoal has been found to exert an enormous pressure upon a liquid with which its pores has been filled. It seems probable that a vapor within the pores might also be under greater pressure than the free vapor just outside the pores, with which it is in equilibrium. It is possible that data covering a wide range of temperatures and pressures, and using various vapors will throw considerable light upon the nature of the phenomena of occlusion of vapors by charcoal.

1. W. D. Harkins, Nat. Acad. Sci., Proc. 6. PP. 49-56, Feb, 1920.



Amount of Water Constant

- (1) 3.35 Grams
- (2-3) 2.70 ..
- (4) 2.00 ..
- (5) 0.57 ..

Pressure — cm. of Hg.

Temperature

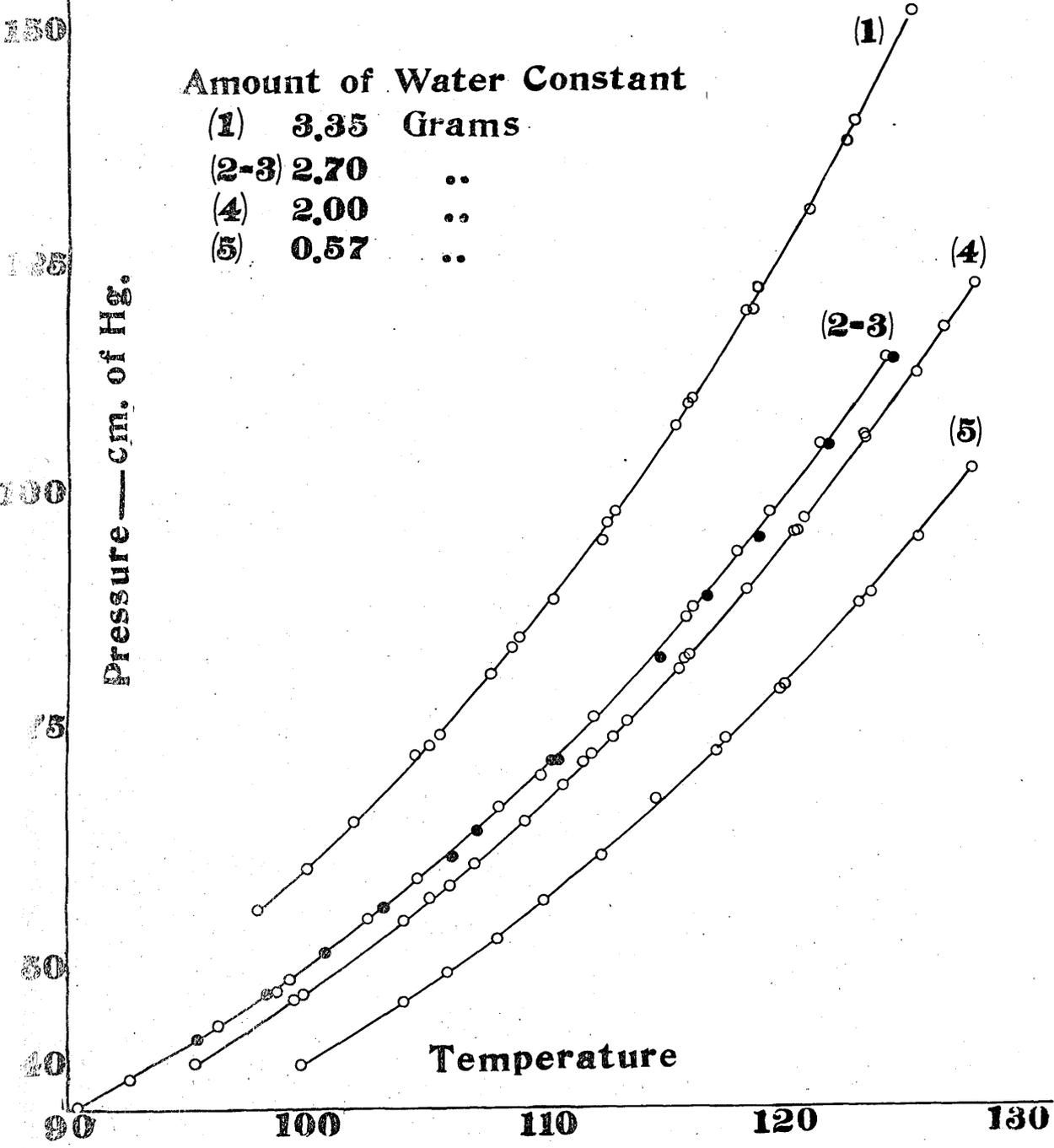


TABLE I.

Corrected Barometer Reading	Temp. °C, Reduced to correspond to pres. of 74.0 cm. of Hg.	Weight of water driven off- m.g.	Calculated weight of water retained by char- coal + what is retained at 220°C.
73.46	104.1	0	3463
73.40	111.95	1124	2339
73.20	120.2	1934	405
73.20	141.8	290	115
	220 ±	115	
73.07	102.65	0	3482
73.45	110.6	712	2770
73.68	115.6	2034	736
73.68	122.2	384	352
73.68	122.2	3	349
73.73	129	117	232
	220 ±	232	
74.02	101.3	0	3552
73.90	107.0	362	3190
73.77	113.2	1680	1510
73.84	117.3	892	618
	132.2	428	190
	200 ±	190	
73.60	101.35	0	3592
73.65	111.1	837	2755
73.57	115.15	1836	919
	132.2	729	190
	220 ±	190 #	

# The charcoal was in equilibrium at 132.2° C. the second time before baked out. One baking was made for the last two determinations.

Tabulation of data showing the relation between temperature and amount of water occluded by 8.5 grams of gas-mask charcoal.

TABLE II  
No. I

<u>Temp.</u> <u>o C.</u>	<u>Pres.</u> <u>Cm.Hg.</u>
110.2	89.0
108.5	83.8
105.5	74.65
112.5	97.15
116.0	110.2
118.5	119.9
121.2	131.4
123.2	140.4
125.7	152.4
122.9	138.3
118.8	120.0
115.6	107.5
112.3	95.2
107.6	81.0
105.0	73.3
101.8	65.25
99.9	60.4
97.9	56.2
104.4	72.4
108.8	84.8
112.8	98.4
116.2	110.7
119.0	122.6

No. 2

90.4	35.3
92.5	38.2
96.2	43.9
98.6	47.7
99.1	48.7
102.4	55.2
104.5	59.4
107.9	66.8
109.7	70.3
111.85	76.4
115.8	87.0
116.1	88.1
118.05	94.0
119.4	98.3
121.5	105.6
124.4	115.0

Table II shows the data for the set of curves expressing the relation between temperature and pressure.

No. 3

No. 4

Temp.	Pres.
<u>oC.</u>	<u>Cm.Hg.</u>
92.35	37.8
95.3	42.2
98.2	47.1
100.6	51.5
103.1	56.3
107.0	64.4
110.1	71.7
112.05	76.5
116.7	89.1
121.9	105.4
124.7	114.9
118.9	95.4
114.7	82.7
110.4	71.8
106.0	61.6

Temp.	Pres.
<u>oC.</u>	<u>Cm.Hg.</u>
109.0	65.5
105.9	58.65
111.6	71.7
113.3	76.0
116.0	83.0
118.4	90.0
120.8	97.6
123.6	106.5
125.7	113.45
128.2	122.8
120.5	96.2
115.5	81.5
112.7	74.3
110.6	69.2
116.9	60.9
103.9	54.9
99.3	46.5
95.2	39.8
99.7	47.1
105.0	57.3
111.8	72.5
115.7	82.85
120.4	96.1
123.5	106.2
126.9	118.3

TABLE II

No. 5

Temp. oC.	Pres. Cm. Hg.
117.7	74.2
120.0	79.8
123.2	88.5
125.7	95.6
128.1	102.8
123.7	89.6
119.8	79.3
117.1	72.8
114.5	67.7
112.2	61.7
109.8	57.0
107.8	53.0
105.8	49.6
103.9	46.3
99.6	39.75

Table III

Curve I			
P	P/P <sub>0</sub>	-logP/P <sub>0</sub>	h, meters
60.5	.796	.2281	3964
73.2	.807	.2144	3748
88.5	.823	.1948	3441
106.0	.835	.1803	3220
126.0	.845	.1680	3032
144.0	.852	.1601	2911

Curve II & III			
P	P/P <sub>0</sub>	-logP/P <sub>0</sub>	h, meters
43.4	.660	.4155	7127
50.3	.660	.4155	7189
60.2	.664	.4095	7159
71.5	.665	.4080	7244
84.5	.666	.4064	7257
99.7	.668	.4035	7283
113.5	.672	.3975	7227

P is the pressure of water vapor above charcoal and P<sub>0</sub> is the saturated vapor pressure of water at the same temperature.

h is calculated from the formula given on page 11.

TABLE III continued

## Curve IV

P	P/P <sub>0</sub>	-log P/P <sub>0</sub>	h, in meters
40.8	.621	.4764	8171
47.5	.625	.4700	8114
57.0	.625	.4700	8216
67.4	.627	.4668	8247
80.2	.631	.4604	8221
94.8	.635	.4541	8197
107.8	.636	.4525	8168
121.8	.637	.4510	8260

## Curve V

P	P/P <sub>0</sub>	-log P/P <sub>0</sub>	h, in meters
40.3	.530	.6349	1098
48.0	.529	.6367	1113
57.5	.534	.6273	1108
58.0	.535	.6255	1117
80.1	.537	.6217	1122
91.0	.538	.6199	1127
102.8	.537	.6217	1138

## CONCLUSION.

The relation between amount of water occluded by gas-mask charcoal and its temperature was determined. This determination was made at a pressure of 74 cm. of mercury. The relation between pressure and temperature, keeping the amount of water constant, was determined for different concentrations. These relations are shown by means of both tables and curves.

When it became evident that the phenomena observed could not be explained by capillarity other relations were sought. This led to the rather surprising similarity between the temperature-pressure relation of a solution and its vapor and the temperature-pressure relation determined in this experiment. From Raoult's law for ideal solutions,  $p_0 - p/p = n/N$ , we see that for a solution of fixed concentration,  $p/p_0 = K$ .  $p$  is the equilibrium vapor pressure of the solution at a temperature  $T$  and  $p_0$  is the saturated vapor pressure of the solvent at the same temperature. It seems significant that for all the temperature-pressure curves except no. (1) the tables show that the same relation, namely  $p/p_0 = K$ , holds to within a small percent variation. Indeed many concentrated solutions do not obey the law as well as does charcoal and water.

In conclusion I wish to express my thanks to Mr. George Lynn for making some of the special apparatus. And to Professor F.E. Kester, under whose direction this work was done. Professor Kester first proposed the problem and his many helpful suggestions enabled me to bring the work to its present state.

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January 29, 1921.