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 5×10^3 bars and 0.3100 g. at 5×10^4 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.

PHILADELPHIA, PA.

SOME PROPERTIES OF CHARCOALS.

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

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:

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

TABLE I.

Time.	Weight of system in water. G.	Increase in Wt. G.	Volume change cu. mm. per g.
0...................	3.5602	....	....
5 min.............	3.5660	0.006	2.9
15 min.............	3.5732	0.013	4.2
1 hour.............	3.5854	0.0252	8.1
2 hours...........	3.5963	0.0361	11.7
9 hours...........	3.6130	0.053	17.1
19 hours...........	3.6177	0.0577	18.9
2 days............	3.6234	0.0634	20.4
5 days............	3.6285	0.0685	22.1
11 days...........	3.6313	0.0713	23.0
16 days...........	3.6315	0.0715	23.0

The final density of this charcoal was 1.850. By removing the external water from the pieces of charcoal, the weight less the mass of the charcoal gave the water in the capillaries, and the volume of these capillaries was found to be 0.42 cc. per g. In the case considered the "drift" was 5.5% of the capillary volume; other liquids have shown a drift of as much as 15% with this charcoal.

The charcoals were pumped out with a large Toepler pump arranged for drying with phosphorus pentoxide (Fig. 1). This pump collected the gases and also served as a MacLeod gage. The bulb held 1250 cc. and the fall tube was calibrated. It was possible to measure as little as 0.006 cc. under a pressure of 2 mm. in the upper part of this tube before it was run out. We thus knew the vacuum attained at any time. Most of the tubes were pumped out and sealed off at 445°, some at 218°, in the apparatus represented by Fig. 2, in connection with the determination of the moisture and gas content of
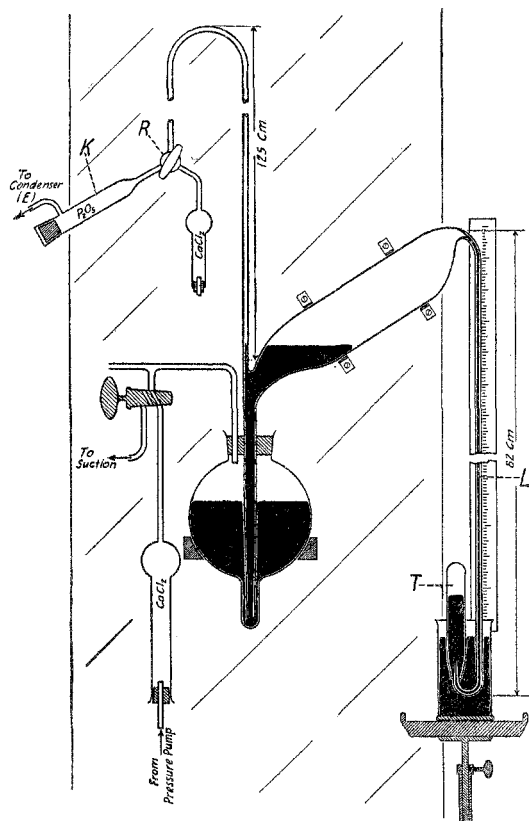

Fig. 1.

these charcoals. Some tubes were connected directly to the pump with good phosphorus pentoxide drying tubes and pumped out while being heated to 520° in an electric heater. Also some of the samples were put into quartz tubes heated to 1020°, thoroughly outgassed at this temperature, and sealed off; but there was no noticeable difference in the drift with these different treatments. Above 200° the absorbed gases and vapors were readily pumped off from the charcoals, but a trace of gas (mostly carbon dioxide and monoxide) was given off, slowly for an hour or so before there was a decrease whereupon the char was soon pumped down to very low pressures. When a char was satisfactorily out-gassed at any temperature it was found that increasing the temperature yielded more gas. Some work on another phase of the char-

Fig. 2.

coal problem, which we hope soon to publish, will give an explanation of this generally observed phenomenon. For the present we satisfied ourselves that there is no residual gas in our charcoals when opened under the liquids.

Figs. 1 and 2 will give the necessary details of the apparatus used in these experiments. The insert tube A (Fig. 2) was kept filled with solid carbon dioxide (—78°) so that any water froze immediately and was later removed and weighed in a special container. In order to manipulate the rods which carried the electrically heated wire, a rubber stopper was necessary. This stopper was sealed with marine glue into a ground glass collar B (Fig. 2) and was perfectly tight.

We have taken care to select well defined liquids and purify them, so as to avoid liquid mixtures or solutions which might readily permit of
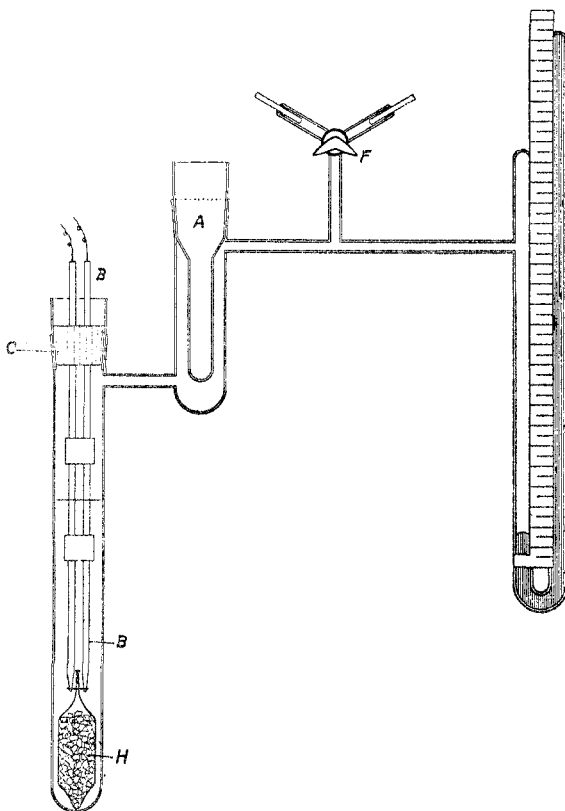
selective absorption of the heavier constituents and increase of weight with the time. We also paid particular attention to removing the dis-
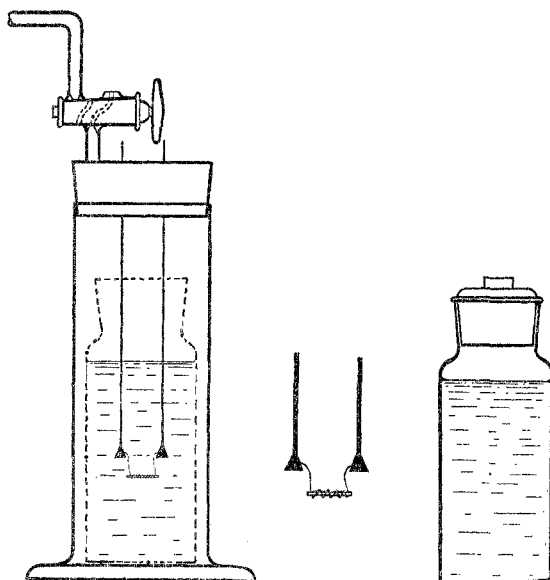
solved gases from these liquids. This difficult problem was handled as follows: The liquid to be used was put into the glass bottle (Fig. 3), this bottle and liquid placed in the vacuum cylinder B and the tiny spiral (electrically h e a t e d) caused the liquid to boil w h i l e i t w a s being pumped out. The cylinder was then opened and without disturbing the liquid the charcoal tube was introduced and the tip broken well down in the liquid. As soon as temperature effect had disappeared a fine, platinum wire was attached to the tube and weighings were made.

Fig. 3.

Charcoals and other Absorbent Materials Used.—Most of the work was done on a cocoanut charcoal, made for the Army gas-mask canisters at the Astoria plant. A 5-gallon sample (A 909) and samples of 4 to 6, 8 to 10 and 18 to 20 mesh sizes were obtained. We also prepared a sample of 100–200 mesh size. In order to obtain a very fine material, the char was ground in a ball mill (Fig. 4) and a slow current of dry air passed
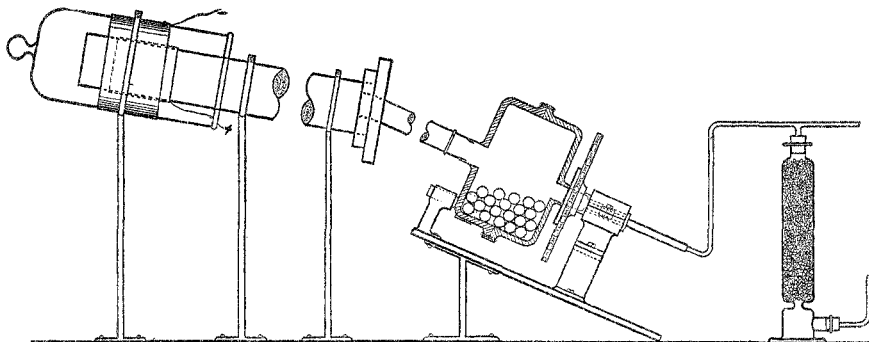
Fig. 4.

through the mill and controlled so that only the finest of the material suspended in the air was carried along. This material did not settle in the 4-ft. length of wide glass tubing, so it was necessary to use a Cottrell precipitator at the end. A microscopic examination of this deposit indicated that the largest pieces were about 0.001 mm. in diameter. A given sample could be put through this mill with but little loss. We also had available some British gas-mask charcoal made from birch wood and some German charcoal from unused canisters of a late date. We also worked with spongy platinum and precipitated gold, and with some silica gel furnished by Dr. W. A. Patrick.

The Drift.—The increase in weight of the charcoal with time when opened under a liquid, has been plotted in the form of curves (Fig. 5). In order to allow temperature effects to disappear, the first observation was generally taken some 10 to 15 minutes after opening the tube in the liquid. An inspection of the first part of these curves indicates that a considerable part of the drift had already taken place before the first reading was made. Evidently the drift is due to the liquid penetrating the grains of the charcoal, rapidly at first—then more slowly. The only other explanation of a changing weight, while immersed in the liquid, would be to attribute it to a change in the shape or size of the grains of charcoal, but there has been no suggestion of this in any of the work; indeed, in some of the experiments described later we have subjected the whole system to pressures of several thousand atmospheres, which resulted in completing the drift at once, but there was no observable effect on the size or appearance of the charcoal particles. If there had been a change in the size of the grains of the order of magnitude of the observed drift, there would have been some settling of the charcoal in the tube; that is, a change in the apparent density of several per cent. In the absence of this it must be concluded that the increase in weight is the result of a gradual penetration of the liquid into the grains of charcoal.

Many questions now presented themselves, and one of the first considered was as to the extent of the drift with liquids other than water. To study this effect we selected liquids which differed widely from water in surface tension, viscosity, molecular volume and other physical and chemical properties. The following observations (Table II) are typical of the results. They were obtained with a uniform sample of charcoal (A 909), 18 to 20 mesh, and are plotted in Fig. 5.

TABLE II.

Liquid.	Time of drift. Hrs.	Density after 15 min.	Density. Final.
H_2O	119	1.829	1.854
CS_2	362	1.915	1.984
C_6H_6	286	1.734	1.797
CCl_4	2856	1.596	1.647

It is seen that the amount of the drift, the extent in time of the drift
and the final density obtained vary widely with the 4 liquids under con-
sideration.   Other liquids tried showed values in the ranges here covered,
but these liquids have not been as yet so thoroughly investigated.
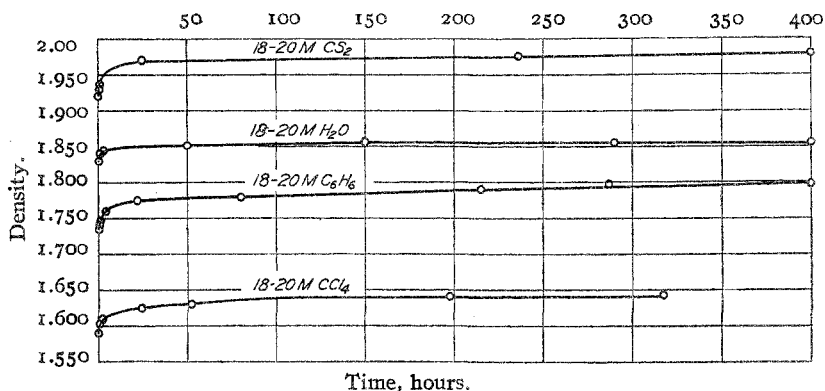

Fig. 5.

On opening a prepared tube of the char under a liquid the latter rushed
in and filled the voids at once and completely surrounded each grain of
charcoal.   Also, all large pores must have filled immediately but it seems
that the filling of the very fine pores is a slow process and is the main fac-
tor in the observed drift.   The maximum observed density of the carbon
of the char is above 1.9.   A gram of this char has shown a capillary volume
of 0.42 cc., so the block density of a grain of char would be about 1.07.
The first observation with carbon tetrachloride gave a density of 1.60,
some 70% of the 0.42 cc. of the capillaries had been filled, but this density
was taken 15 minutes after opening the tube and a considerable amount
of the drift had already taken place.   One experiment with water gave
many readings in the first part of the curve which permitted of extrap-
olation to zero time, indicating that about $1/5$ of the total drift takes
place in the first 15 minutes.   Vapor undoubtedly precedes the liquid
into the capillaries but it must be rapidly adsorbed by the clean carbon
surfaces in the capillaries of the charcoal and, in any event, could not im-
pede the entrance of the liquid.

The forces acting to fill the capillaries are atmospheric pressure and
capillary action.   We may calculate this latter force from the relation
between surface tension and the height to which a liquid will rise in a tube.[1]
Pores 0.001 mm. in diameter would have a capillary force corresponding
to 3 atmospheres, and 0.0001 mm. to 30 atmospheres, etc.   Whether we
are justified in extrapolating this relation to pores of molecular dimen-
sions is questionable, but obviously this force is far greater than atmos-

[1] Bigelow and Bartells, THIS JOURNAL, 31, 1197 (1909).

pheric pressure which, in our case, was constant, so we at once compared the surface tension of these liquids with the amount and extent of the penetration. Water has a surface tension of 72 absolute units while carbon disulfide shows only 34, but the latter showed much greater penetration and density. We must consider, however, that the viscosity of the liquid would be an important factor in the rate of penetration of these liquids into very fine capillaries and in determining the amount of penetration in experimentally realizable time. As a first approximation we have considered the penetration to be proportional to the surface tension of the liquid and inversely proportional to its viscosity, or more simply, to equal a constant times the product of surface tension and fluidity. The resulting numbers are: water, 7200; carbon disulfide, 9100; benzene, 4800; carbon tetrachloride, 2600. These numbers are entirely in accord with our observations on the drift and densities. The amyl alcohol number is 550 but we have only a few experiments with this substance as yet and they are around those of carbon tetrachloride. With capillaries of molecular dimensions the shape and size of the ultimate particles of the liquid must also be a factor, but this is the only relation we have as yet noticed between the drift and the physical properties of the liquids.

Attention may be next turned to the effect due to variation of the size of grains of the charcoal with a given liquid. Using this same A 909 charcoal, and water as a liquid, we secured the results given in Table
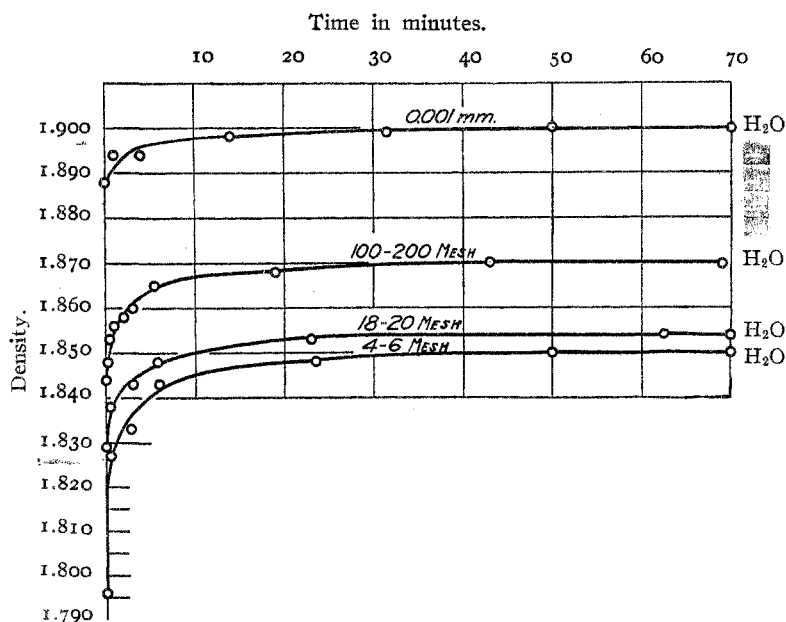

Fig. 6.—Drift in water.

III, and Figs. 6 and 7. For benzene with this same material the results
are given in Table IV.

TABLE III.

Size. Charcoal mesh.	Grain in mm.	Time of drift. Hrs.	Density after 15 min.	Density. Final.
6–10	1.95	227	1.751	1.845
18–20	0.71	119	1.829	1.854
100–200	0.165	74	1.844	1.870
	0.001	87	1.888	1.900

TABLE IV.

Benzene.

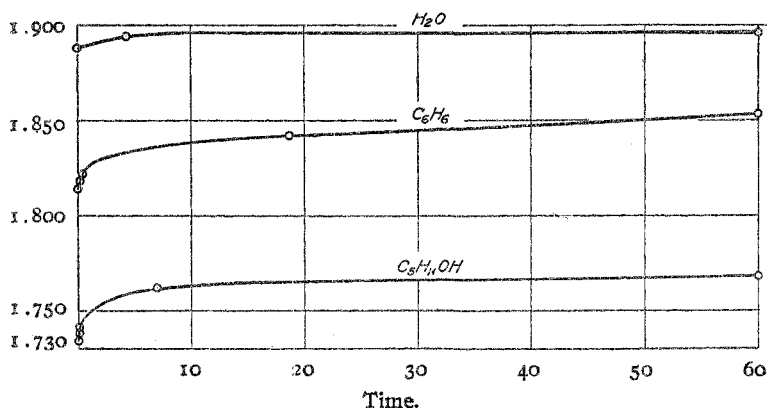| Size mesh.	Time of drift. Hrs.	Density after 15 min.	Density. Final.
6–10	743	1.695	1.785
18–20	286	1.734	1.797
0.001 mm.	210	1.814	1.866

Fig. 7.—0.001 mm. of substance.

It is noticeable in these results that the extent of the drift and its dura-
tion decreased markedly with the size of grain. Also the final density
increased with this factor. These effects have been noticeable with all
of the liquids. Such results may all be readily interpreted from the stand-
point that the liquids encounter mechanical difficulties in filling the small
pores. The value we have obtained for the volume of the capillary spaces,
0.42 cc. per g. for this char, has been found to be quite independent of this
size of the grains.[1]

Breaking up the grains increased the surfaces and number of pores
exposed per g. of char in the ratio of about 1 : 3 : 12 : 2000 for the

[1] This value was obtained first by using filter paper to remove the external water
from the grains of char which had been completely filled with water, thus getting the
weight of char filled with the liquid and subtracting the weight of the carbon. Later
we found that this could be more easily done by centrifuging in a Gooch crucible (8
cm. × 1000 r. p. m.). The results of different workers checked to 2%.

sizes 2 mm., 0.7 mm., 0.16 mm., and 0.001 mm. (6 to 10 mesh, 100 to 200 mesh and 0.001 mm.). The external surfaces of these size grains per g. are 0.003, 0.008, 0.034 and 5.6 square meters, respectively, while the surfaces in the capillaries are of quite another order of magnitude. Some results and calculations from vapor absorption work gives this area as less than 200 meters square per gram for this char. It will be seen, therefore, that the total surface available for adsorption is not materially affected by grinding, even when we were able to reduce the char to a powder whose largest grains were only 0.001 mm. in diameter. Our changes in drift and density are far more in accord with the changes in the external surfaces of the different sizes of grain than with the change in total surface of capillaries and external surfaces. Furthermore if 200 meters square per g. is the order of magnitude of the surfaces of the capillaries, a layer of liquid one molecule deep on this surface would represent a volume of some 20 cu. mm. If this adsorbed layer were in a condensed form and attained a greater density than the pure liquid, it still could lose only a part of its volume; if it enters into some chemical reaction with the carbon, due to residual valences, it would only contract to a portion of its volume as is evidenced by the decrease in volume when liquids and solids combine to form true compounds. Any explanation based on adsorption seems to offer little hope of explaining the drift which may, for this char, be as much as 50 to 100 cu. mm. Absorption may, however, play a secondary role. A calculation of the magnitude of the capillary force in causing the liquid to penetrate the pores showed that atmospheric pressure played only a secondary role in our experiments. Now, we have tried the experiment of applying external pressure to the liquid soon after the tubes were opened. We were not equipped for this work at Princeton, but the Geophysical laboratory of the Carnegie Institute most kindly allowed us to use their fine equipment for pressure work and we wish to take this opportunity to express our appreciation of the kindness and assistance of Messrs. L. H. Adams, E. D. Williamson and R. E. Hall in connection with the following experiments.[1]

Tubes were carefully prepared at Princeton and carried to Washington for the pressure experiments. One containing 3.9587 g. of charcoal A 909 was opened under water and the first part of the drift carefully followed; the observation gave sufficient points to extrapolate to zero time. The plot of the results is found in the first part of the curve of Fig. 8. Using the extrapolated value this char had shown a drift of 75 mg. in 32 minutes from the time the tube was opened. The system was then subjected to a pressure of 500 atmospheres and kept at this pressure for 30 minutes. On removing the pressure and weighing the tube and char,

an additional increase of 73 mg. was noted. The tube was now subjected to 1500 atmospheres pressure for 35 minutes which produced an increase of only 4.7 mg. The pressure was then raised to 9000 atmospheres, but there were indications of the water beginning to freeze, so the pressure was immediately lowered to 8600, which is below the freezing pressure of water for this temperature (19.5°), and this pressure was maintained for 50 minutes, but caused an increase in weight of only 3 mg.
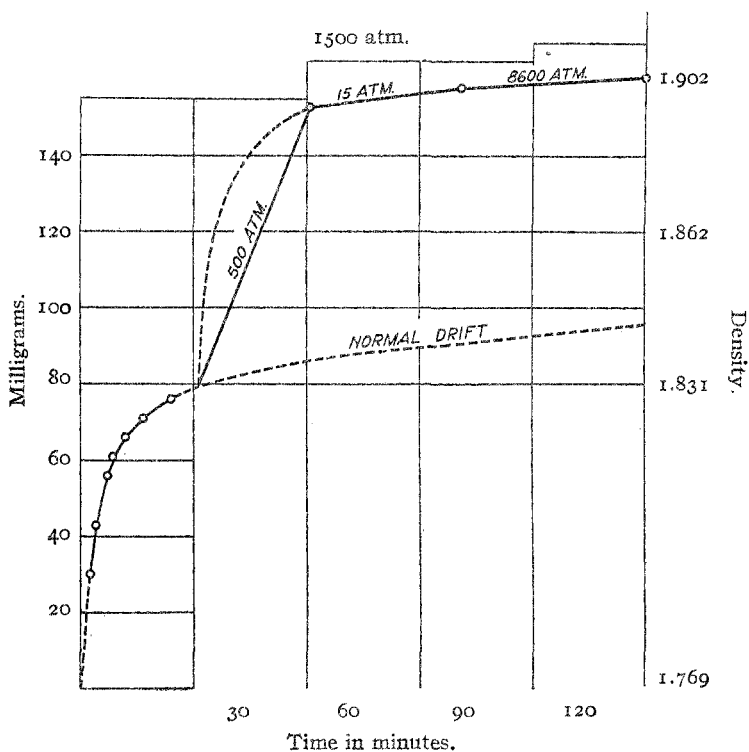

Fig. 8.

The dotted line (Fig. 8) presumably represents the drift while the tube was under a pressure of 500 atmospheres. It seems probable that the drift would have completed itself in a few hours under this pressure, and if further experiments confirm this supposition, moderate pressures will suffice to wipe out the drift in a few hours. This tube, immersed in water, was brought back to Princeton and weighed at intervals for 8 days but no further increase in weight was noted. The final density was 1.902 while we were getting for this charcoal immersed in water only 1.86 after 4 months. It would take years, at this rate, to reach the value obtained under pressure.

In some of the pressure experiments we weighed the charcoal in a few

minutes after the pressure was relieved and then at intervals for a few hours in order to detect a decrease in weight but in no case observed such a change, *i. e.*, water coming out of the char. In a few instances we did notice a slight increase in weight or still further drift. This happened when the pressure had not been applied long enough. A sample of this same char was opened under water and quickly subjected to a pressure of 3400 atmospheres for a half hour. This tube was then under observation for drift for 9 days but its weight under water did not change. We changed the temperature of this tube in water to $0°$ overnight and then to $50°$ for several hours, then on returning to room temperature the weight of the tube came back promptly to the previous weight. The water was now removed from this charcoal and it was pumped out and sealed off at $445°$. When this tube was opened under water it showed the normal drift, became practically constant in 10 days and then showed a density of 1.878, while the density was 1.83 after the first 15 minutes. It would seem, therefore, that pressure will quickly complete the drift and give a definite final condition, and that the pressure does not destroy the drift property or noticeably affect the properties of the charcoal. A few pressure experiments were made with other liquids. The benzene tube was over pressed, froze and broke the tube. The amyl alcohol tube and the carbon tetrachloride tubes came through all right and showed final densities of 1.70 and 1.67, respectively.

We wish again to thank the staff of the Geophysical Laboratory for their assistance in carrying out these experiments which have given us a good idea of the possibilities along this line. Now that it is possible to get final results in a short time instead of waiting months, it will be possible to investigate a larger number of liquids and materials and test out the relation of the penetration of different liquids to their surface tensions, viscosities and other properties. Where the capillaries are of molecular dimensions, the shape and size of the ultimate particles of the liquid must also be a factor.

The authors wish to thank Mr. B. Peyton for assisting in the preliminary work on this problem.

PRINCETON, N. J.