[CONTRIBUTION FROM THE SHEFFIELD CHEMICAL LABORATORY OF YALE UNIVERSITY.]

THE FREEZING OF WATER ABSORBED IN LAMPBLACK.

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In a previous article, concerned chiefly with the freezing of hydrogels,[1] we gave the results of one experiment to show the behavior of water absorbed in lampblack, when exposed to temperatures much below 0°. We found that the water does not all freeze sharply at one temperature, slightly below 0°, as for instance it does in a mixture of sand and water, but that it freezes gradually as the temperature is lowered, behaving in this respect much like a part of the water in hydrogels. On raising the temperature, after freezing has taken place, the ice does not melt until the temperature approaches zero.

By measuring, in a dilatometer, the increase in volume due to freezing, the amount of water could be determined, assuming that the density of this absorbed water was the same as that of other (liquid) water at the same temperature. In this way, the water found corresponded closely to the amount taken, showing that its density was essentially unchanged by absorption. Only one determination of this kind was made, and this comparatively early in our work when the technique of the operation was being developed. We have therefore made two further determinations of this kind, to corroborate the earlier result. This appeared quite necessary in view of the fact that in our work on hydrogels, we have assumed that the density of low-freezing or capillary water was the same as that of ordinary water, and this assumption was based largely on the single determination mentioned.

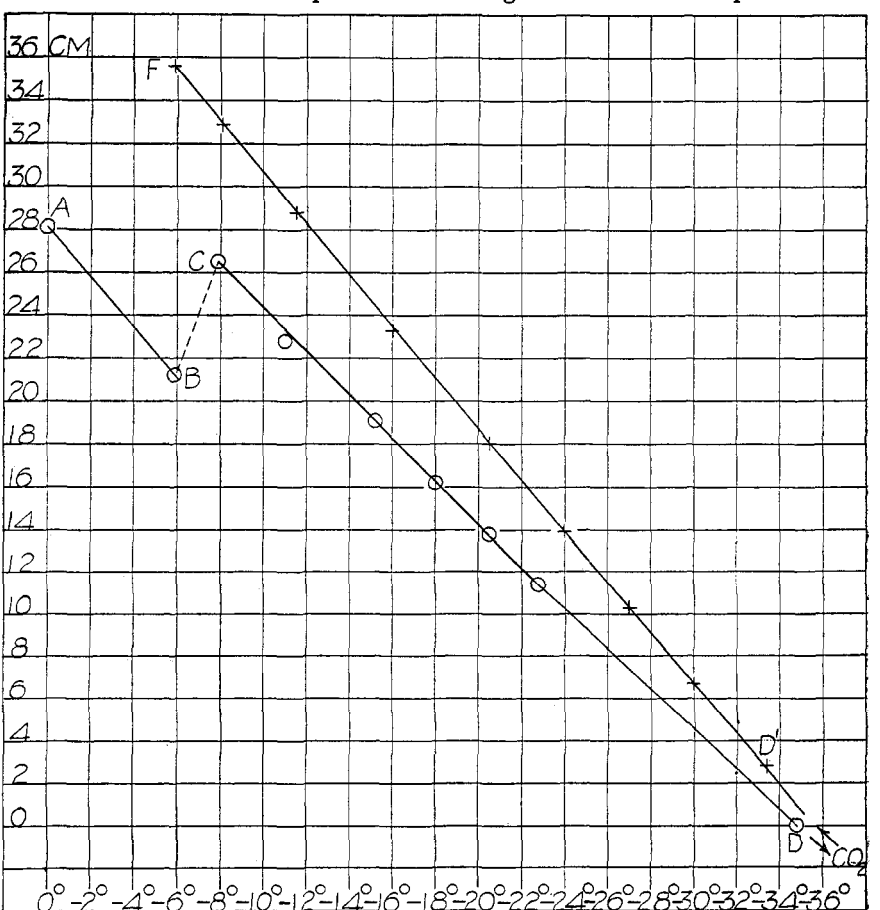
The lampblack used in the work was ignited at a red heat in a covered crucible to remove water, and introduced, while dry, into the dilatometers. For one determination, water was introduced by passing warm moist air through the dilatometer, keeping the bulb somewhat cool to ensure condensation. The amount of water was determined by weighing. This method required some little time, and in the second sample, water was introduced with a pipet directly into the dilatometer bulb containing lampblack. Water does not wet lampblack readily under these conditions and the mixture was allowed to stand about two days before filling the bulb with ligroin, to ensure a fairly uniform distribution of water. In filling with ligroin, the mixture of lampblack and water in the dilatometer was first cooled to about —8°, freezing part of the water. This had two

tellurium is 8.2. If, in accordance with the value of n' on the short horizontal line, a further subtraction of 2 were made from the residues starting at titanium—then the remainders as far as polonium would all be well within range, while an additional subtraction of 2 (which represents the raising of the short slope (iv) in the graph of n') would bring the last 5 elements into line.

[1] THIS JOURNAL, 38, 588 (1916).

advantages. It solidified the mixture, preventing any chance of mechanical loss in evacuating and filling the bulb with ligroin; and it lowered the vapor pressure, preventing loss of water by evaporation.

Each sample was frozen twice. The first time, the minimum temperature was about —35°. The shape of the freezing and melting curves showed that not all water was frozen even at this low temperature. In the second freezing, after cooling in a mixture of calcium chloride and ice to about —35°, the bulbs were placed for about two hours in a mixture of carbon dioxide and alcohol at a temperature of approximately —78° C. to make certain that no water remained unfrozen. The usual heating curve was then taken, beginning again with the calcium chloride-ice mixture. The two determinations, carried out in different bulbs and with different capillary tubes, gave curves of the same type when plotted. The results of one determination are plotted in the figure. Ordinates represent the



Lampblack and Water.

corrected dilatometer readings, expressed in centimeters. Temperatures are plotted as abscissas. The usual contraction of the bulb and its contents occurred along AB. Freezing then took place and the volume expanded to C, after which contraction set in as the bulb was cooled to D. After cooling in carbon dioxide and alcohol, the volume returned to D′ and from this point the observations on rising temperature lie very nearly on a straight line D′F. AB and D′F are very nearly parallel, and the length of a vertical line between them measures the increase in volume due to the formation of ice. Knowing the capacity of the capillary tube of the dilatometer, and the expansion caused by water in forming ice, the water found by freezing may be calculated and compared with the water taken. For the expansion caused by freezing 1 g. of water, we have taken the value 0.0932, this being the average of six closely agreeing determinations made on a mixture of sand and water under similar conditions, the results of which will be published later. The following results were obtained:

No.	*a.* Water taken.	*b.* Expansion due to freezing (cm.).	*c.* Volume of 1 cm. (cc.).	Wt. of water found.	Error.
1.....	1.066	6.32	0.01600	1.085	+0.019
2.....	1.241	14.30	0.008148	1.250	+0.009

The error in the first determination is a little less than 2% and would correspond to an error in the expansion due to freezing of about 1 mm. The error of the second determination is less than 1% and corresponds to about the same absolute error—1 mm.—in the expansion due to freezing. These differences may well be due to errors of observation. In the original determination,[1] the minimum temperature reached was only about —28°. Using the same method of calculating water found, that has been used above, there is an error of —0.049 g. This is to be expected in view of the later results, as the temperature was not sufficiently low to freeze all the water.

The experiments which have just been completed show that the density of water which has been absorbed or adsorbed by lampblack is essentially the same as that of other water at the same temperature, although the last of the water did not freeze until a temperature below —35° had been reached. This, we believe, justifies the assumption which has been made in our work on hydrogels, that the density of the water which freezes only at low temperatures is essentially the same as that of other water at the same temperature.

The freezing data are also sufficient to determine what, in the previous article, has been called "apparent capillary water," *i. e.*, water freezing below —6°. The amount is measured by the length of a vertical between CD and D′F at —6°. It has been obtained graphically after extrapola-

[1] *Loc. cit.*

ting CD to intersect the —6° ordinate. Following are the data for the two determinations:

No.	Lampblack taken (g.).	Expansion due to freezing apparent capillary water (cm.).	Volume of 1 cm. (cc.).	Apparent capillary water per g. of lampblack (g.).
1.....	0.969	4.27	0.01600	0.756
2.....	0.844	7.02	0.008148	0.727

The results show that apparent capillary water in this sample amounted to about three-fourths the weight of the carbon. The amount would undoubtedly vary with the sample of lampblack and with its treatment but it is much larger than we have found in any sample of hydrogel. It is also greater than that found previously in lampblack, but the sample used at that time contained a much smaller proportion of total water and was nearly dry to the touch, so that part of the capillary water had undoubtedly evaporated. There was sufficient water in both the present samples to make them distinctly moist, and the amounts found are probably as great as the sample is capable of absorbing.

In closing, we wish to call attention to the fact that the freezing curves for lampblack are similar to those of hydrogels. The curves differ materially in only one respect. In hydrogels, the line DF begins to curve ordinarily at a comparatively low temperature, often as low as —20°, showing that ice begins melting at this low temperature. In the curves for lampblack, the line D'F is straight as far as we have determined it, up to about —6°. In this case, therefore, ice when once formed does not melt again until the temperature approaches 0°.

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A DIRECT READING IONOMETER.[1]

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Owing to the numerous applications of the hydrogen electrode for both scientific and technical purposes it has seemed desirable to construct an apparatus for the determination of ion concentration which could be easily operated, which would be reasonably accurate, and which would give readings directly in terms of ion concentration.

Two different types of direct reading potentiometers have been described and used. An apparatus devised by McClendon[2] reads directly in terms of ion concentration and is similar in general principles to the apparatus herein described. With the Bovie apparatus[3] hydrogen ion

[1] The term potentiometer would be a misnomer for an apparatus of this type. Ion concentration and not potential values are determined.

[2] McClendon. *Am. J. Physiol.*, 38, 186 (1915).

[3] Bovie, *J. Med. Res.*, 33, 295 (1915).