from any solution whose composition lies within the triangle formed by lines joining the compositions of these three phases.

These composition lines which have been drawn in Fig. 7 divide the diagram into 6 triangular areas. Each of these triangles represents all possible mixtures of those three compounds whose compositions are represented by the apices of the triangle. Though three certain, definite compounds can exist together in only one triangle, yet, as can be seen in the diagram, any one of these three compounds may be in a number of different triangles.

Summary.

The foregoing pages are a record of an investigation of the system CaO--Al_2O_3-MgO. This ternary system proved to be rather a simple one, there being no ternary compounds stable in contact with melt. The working out of this system, therefore, simply involved the equilibrium of the components (CaO, Al_2O_3, MgO) and the binary compounds ($3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO.Al_2O_3$, $3CaO.5Al_2O_3$, $MgO.Al_2O_3$) in ternary solutions.

The relations found to subsist between the components and compounds in binary systems and in the ternary system are exhibited in a series of concentration-temperature diagrams.

The optical and crystallographical properties of the components and pure compounds are given in the previous papers, but a few additional notes are made here on the compounds $5CaO.3Al_2O_3$ and $CaO.Al_2O_3$. A new form of Al_2O_3 has been described. The relation of this new form (β-Al_2O_3) to αAl-$_2O_3$ (corundum), the only form previously observed, could not be definitely established, although it would appear that β-Al_2O_3 is monotropic with respect to α-Al_2O_3. The relation of each of these forms, in the binary system MgO-Al_2O_3, involved solid solution, the extent of which was determined.

WASHINGTON, D. C.

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

THE EFFECT OF FREEZING ON CERTAIN INORGANIC HYDROGELS.[1]

BY H. W. FOOTE AND BLAIR SAXTON.

Received December 25, 1915.

The composition and nature of precipitated colloids or hydrogels, such as silicic acid and ferric hydroxide, have been the subjects of repeated investigations which have varied greatly in their results. In the earlier work, the composition of inorganic hydrogels was determined chiefly

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[1] Part of a dissertation presented by Blair Saxton to the Faculty of the Graduate School of Yale University, 1915, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

by drying the precipitates under fixed empirical conditions, and the results obtained were nearly as variable as the conditions of experiment. Later investigators have used other methods, of which the following are the chief: A dynamic method which consists in measuring the velocity of dehydration at constant temperature, which was used by Ramsay[1] and later by Tschermak;[2] a method depending on dehydration at gradually increased temperature, which was used by Carnelley and Walker,[3] and by Baikow;[4] a static method which consists in determining the vapor pressures during the course of dehydration, which was used by Van Bemmelen[5] and later by Zsigmondy and his co-workers;[6] a method devised by one of us[7] which consists in determining the composition of the hydrogel at the point where its vapor pressure falls below that of pure water; and lastly a thermal method used by Müller-Thurgau[8] and by Fischer[9] and his co-workers, in which the heat effect caused by the freezing of water in the hydrogels was measured. From that value, the amount of water frozen was calculated. This method has not been applied to inorganic colloids so far as we are aware.

Nearly all the methods of investigation have been based, directly or indirectly, on the vapor pressure exerted by the hydrogels, but it has been difficult to draw definite conclusions as to the condition of the water in hydrogels from a knowledge of the vapor pressure alone. This is due to the fact that water, no matter what its condition, always exerts a vapor pressure and any change in the condition of the water must be judged by changes in direction of the vapor-pressure curve or of curves derived from it, rather than from any absolute values. The work of Van Bemmelen and, in particular, of Zsigmondy and his co-workers,[10] has made it extremely probable that the water which evaporates from the hydrogel of silicic acid immediately after free water has been removed, and at a vapor pressure below that of pure water, is capillary in character, while the last of the water, coming off at the lower pressures, is combined or perhaps in solid solution.

In the present article, we shall give the results thus far obtained with

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[1] *J. Chem. Soc.*, **32**, 395 (1877).

[2] *Z. physik. Chem.*, **53**, 349 (1905); *Z. anorg. Chem.*, **63**, 230 (1909); *Monatsh.*, **33**, 1151 (1912).

[3] *J. Chem. Soc.*, **53**, 59 (1888).

[4] *Kolloid. Zeit.*, **2**, 374 (1907).

[5] *Z. anorg. Chem.*, **5**, 467 (1893); **13**, 233 (1897); **20**, 185 (1899).

[6] Zsigmondy, Bachman and Stevenson, *Ibid.*, **75**, 189 (1912); Bachman, *Ibid.*, **79**, 202 (1913); Anderson, *Z. physik. Chem.*, **88**, 191 (1914).

[7] THIS JOURNAL, **30**, 1388 (1908).

[8] See Fischer, *Beitr. Biol. Pflanz.*, 10, 200, 232 (1911).

[9] *Biochem. Z.*, **18**, 58 (1909); **20**, 143 (1909); *Beitr. Biol. Pflanz.*, 10, 133 (1911); *Kolloid. Zeit.*, **8**, 291 (1911).

[10] *Loc. cit.;* also *Z. anorg. Chem.*, **71**, 356 (1911); **73**, 158 (1911).

several inorganic hydrogels in an attempt to determine the water which can be separated from them by freezing. This is a determination of considerable interest, for it is to be expected that water which is present as a liquid can be converted into ice if the temperature is sufficiently lowered, even when the water is present in minute capillaries, while water which is combined as a solid hydrate cannot in general be separated by this means. A determination of the ice which can be produced in a hydrogel should therefore give a means of judging between capillary and combined water in a way which has not before been possible.

Since the method used in the present investigation is based on freezing the uncombined water in the hydrogels, we shall first consider previous observations on the effect of freezing on these precipitates. The earliest experiments on this subject are those of Limberger,[1] Wittstein[2] and Leroy,[3] all of whom stated that they obtained crystalline ferric hydroxide by freezing the amorphous precipitate. Van Bemmelen and Klobbie[4] repeated this experiment and showed that no crystalline hydrate was obtained. They found that freezing had little effect except to remove included water. Ruff[5] found that ferric hydroxide before and after freezing at —10° and —185° had the same composition, $Fe_2O_3 : 4.2H_2O$, when dried over 15% sodium hydroxide. The first important contribution is that of Lottermoser.[6] He froze silicic acid which appeared dry and found that water separated, leaving silicic acid as a granular mass. He explained this by assuming that water in the capillaries had expanded on freezing and broken the fine porous structure. It is interesting to note that he suggested freezing as a means of drying gelatinous precipitates of the silica type. Bruni[7] froze silicic acid and analyzed the residue, concluding that it has no constant composition. It should be pointed out, however, that it is very difficult to separate water, after melting, from the residue and constant results could hardly be expected. The heat evolved when water is frozen from a colloid has been used in calculating the amount of uncombined water in the substance. This method has been used by Müller-Thurgau and by Fischer.[8] The former measured the heat evolved directly while Fischer calculated it from the velocity of cooling. Their work was with organic hydrogels. A very complete bibliography on the effect of freezing on colloids, organized, organic and inorganic, may be found in Fischer's articles.

[1] *Jahresb.*, 1853, 370.

[2] *Ibid.*, 1853, 370.

[3] *Ibid.*, 1854, 363.

[4] *J. prakt. Chem.*, [2] 46, 497 (1892).

[5] *Ber.*, 34, 3417 (1901).

[6] *Ibid.*, 41, 3976 (1908).

[7] *Ibid.*, 42, 563 (1909).

[8] *Loc. cit.*

Method.

The method which we have used consists in freezing the precipitate, of known total water content, in a dilatometer and measuring the expansion caused by freezing the uncombined water. From the expansion, the amount frozen may be calculated and the amount of combined water obtained by difference.

The dilatometer had the usual form. The stem was calibrated by means of mercury. Ligroin was used to fill the bulb and mark changes in volume. It has the advantage of high vapor pressure, making it possible to fill the bulb completely by the use of an ordinary water pump. For temperatures as low as —20°, an ice-salt bath was used. For still lower temperatures, a mixture containing about equal weights of ice and calcium chloride was necessary. This mixture must be well protected against radiation. A convenient holder for our purpose consisted of a quart wide-mouthed thermos jar. In practice, the temperature of the dilatometer was lowered gradually in the ice-salt bath to about —20° and then directly to about —30° in the other. It was not practicable to lower the temperature gradually between —20° and —30°. The temperature could, however, be raised gradually from —30° by the cautious addition of water.

In carrying out a determination, the dilatometer readings at first show a regular decrease, as the temperature falls, due merely to contraction of the bulb and contents. At a temperature usually several degrees below zero, sudden expansion occurs, due to freezing. The water freezing in this first expansion consists of free water and that part of the capillary water whose freezing point has been reached. After the volume has become constant, a further lowering of temperature causes more capillary water to freeze and the volume usually expands somewhat farther. after which, contraction sets in, and, if the temperature is sufficiently lowered, the contraction finally becomes very nearly a linear function of the temperature, as it is before freezing occurs. On raising the temperature, the expansion is nearly linear for some distance but at a temperature still below 0° contraction sets in, due to melting, and the volume finally returns to its original value above 0°.

The following diagram (Fig. 1) illustrates the typical behavior. Dilatometer readings or volumes are plotted as ordinates and temperatures as abscissas. The line AB shows the normal contraction before freezing, BC the sudden expansion when freezing begins, CD the expansion and contraction on further cooling and DF the expansion and contraction as the temperature is raised. DE is the linear extension of the heating curve from D. Beginning at D the curve DF was found to be a straight line for a considerable distance, showing that capillary water, when once frozen, does not melt at as low a temperature as it freezes. The curve downward near F shows there is a decided tendency to melt at a temperature still somewhat below 0°. The extrapolated line DE gives the normal expansion if no melting occurred and the length of a vertical line between AB and DE gives the expansion due to freezing all free and capillary water. As AB and DE are very nearly, but not quite, parallel, we have chosen the length of the vertical at —6° as a measure of the expansion. Its length has been determined graphically from the plotted values. To convert the expansion due to ice formation, expressed in cubic centimeters, into the corresponding weight, we have used Bunsen's data that 1 g. of water at 0° expands 0.09070 cc. on freezing. In this way, the total weight of water which is frozen can be determined.

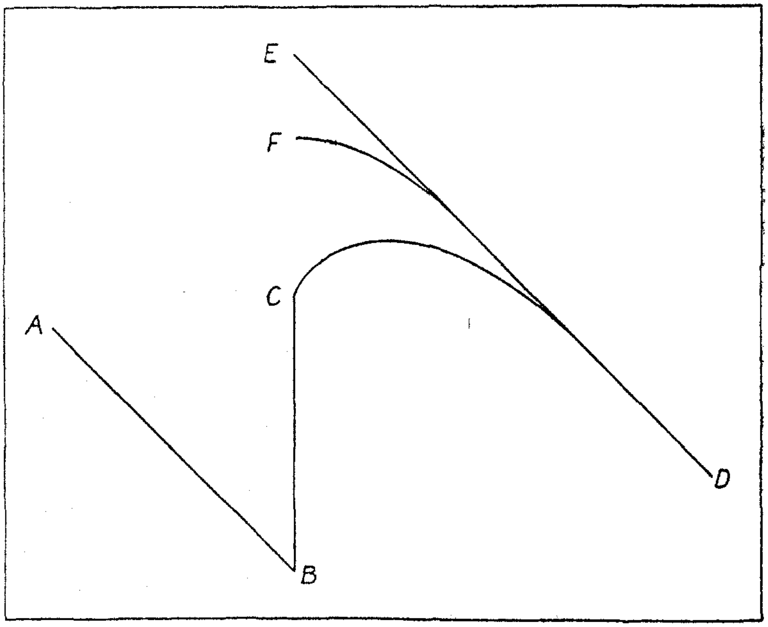

Fig. 1 (Diagrammatic).

It is not possible, from our results, to distinguish sharply between true capillary and free water, for the reason that supercooling always occurs in the dilatometer. If freezing occurred at 0°, the length of the vertical BC, measured at 0°, would give the free water, and of CE, the capillary. Where freezing occurs, as it does, several degrees below zero, the water freezing at this temperature is free water plus that capillary water whose freezing point has been reached. The length of BC therefore corresponds to free water and a part of the capillary water. It is possible, however, to determine with sufficient accuracy the capillary water separating below a certain temperature. We have chosen to determine the amount separating below —6° and shall call this the *apparent capillary water.* The actual capillary water is always greater in amount.

The chief uncertainty in the method appears to be whether, at D, all capillary water has frozen. This point will be discussed under "combined water in the hydrogel of alumina."

Preliminary Determinations.

We shall give first the results of several preliminary determinations in the dilatometer, which were carried out with such materials that we could draw conclusions in advance as to the nature of the water present—whether free, capillary, or combined. A mixture of sand and water was used to show the behavior of free water. The behavior of free and capillary water was illustrated with moist lampblack, while moist calcium hydroxide furnished an illustration of free and combined water. It was of course necessary to choose materials which were not soluble to any extent in water. Otherwise, there would be a lowering of freezing point due to dissolved substances as well as to capillarity, an unnecessary complication which we wished to avoid.

The mixture of sand and water in the dilatometer behaved as expected. In this case there was no question of capillary or combined water and the experiment was carried out chiefly to show how closely free water could be determined. Freezing occurred at —4° and all water froze sharply at this temperature. The contraction before and after freezing was entirely regular and dilatometer readings on falling and rising temperatures were practically identical. The observations are plotted in Fig. 2. In

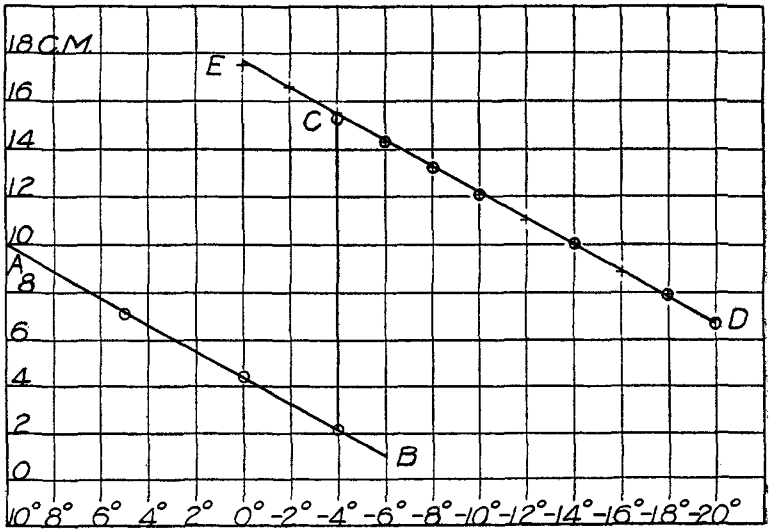

Fig. 2.—Sand and water.

this figure, as in all following, the corrected readings of the dilatometer in centimeters are plotted as ordinates; observations taken on falling temperature are represented by circles, and on rising temperature, by crosses. Necessary data and the result calculated from the observations are in the following table. The second column of the table gives the increase in volume due to freezing, measured in centimeters on the stem of the dilatometer. The third gives the corrected volume of 1 cm. of the dilatometer stem, expressed in cubic centimeters. The product gives the increase in volume due to ice formation, from which the weight of water found has been calculated.

SAND AND WATER.

Water taken. (g.).	Expansion due to freezing. (cm.).	Volume of 1 cm.. (cc.).	Water found. (g.).	Error.
1.404	13.3	0.009751	1.430	0.026

Lampblack was used in the next experiment. It had previously been intensely ignited. A weighed amount was moistened with water and allowed to stand for two days. The material was then nearly dry to the touch but contained over 40% of water. This material, when introduced into the dilatometer, required a temperature of —28° to complete the freezing. Its behavior was thus entirely different from that of sand and

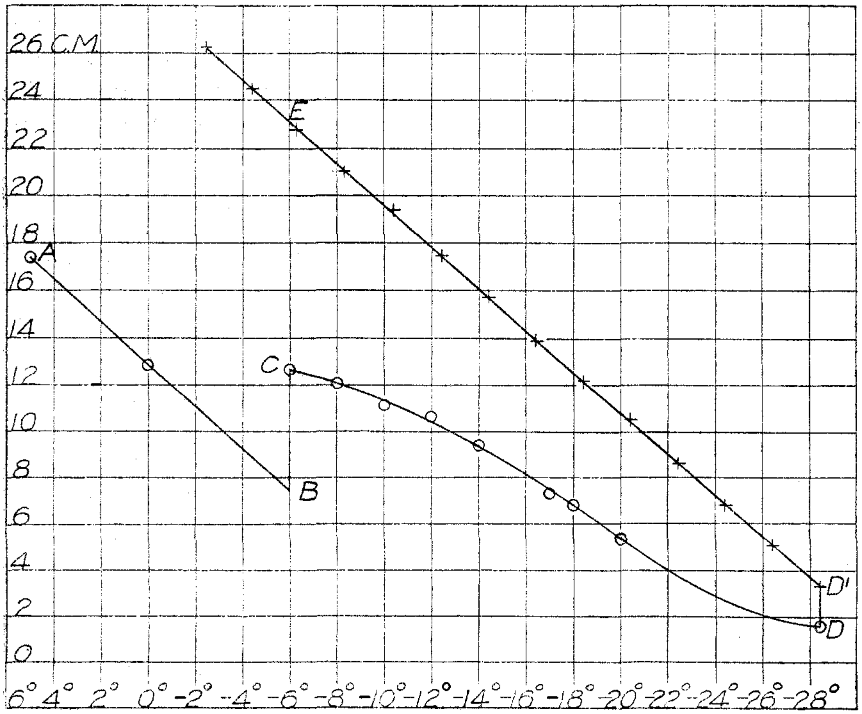

Fig. 3.—Lampblack and water.

water, due to the adsorbed or capillary water present. The observations are plotted in Fig. 3. Ice formed very slowly at the lower temperatures and when equilibrium had apparently set in at —28°, a further increase in volume occurred after two hours. This increase is represented in the figure by DD′. The results obtained are as follows:

LAMPBLACK AND WATER.

Lamp-black taken. (g.).	Water taken. (g.).	Total expansion due to freezing. (cm.).	Expansion due to freezing apparent capillary water. (cm.).	Volume of 1 cm.. (cc.).	Total water found. (g.).	Apparent capillary water found.	Error in total water. (g.).
2.530	1.834	15.7	10.35	0.01058	1.831	1.207	0.003

The result for apparent capillary water shows that lampblack adsorbed water equal to nearly half its own weight in such a manner that a temperature much below 0° was necessary to freeze it. A part of the water in the hydrogels which we have investigated is strikingly similar in its behavior to this adsorbed or capillary water of lampblack.

It seemed possible that filter paper might take up water as lampblack does and it was tested in the same manner. The water in this case, however, froze almost as sharply as in the mixture of sand and water, only a very small amount freezing gradually at a lower temperature. The results need not be given here. The total water found agreed closely with the amount taken.

For the mixture of calcium hydroxide and water, pure calcium oxide, prepared from the carbonate, was introduced into the dilatometer and warm, moist air, free from carbon dioxide, was passed over the oxide till the increase in weight showed a considerable excess of water over that required to convert the lime into calcium hydroxide. The freezing curve was determined as usual. The observations are plotted in Fig. 4. The results obtained are as follows:

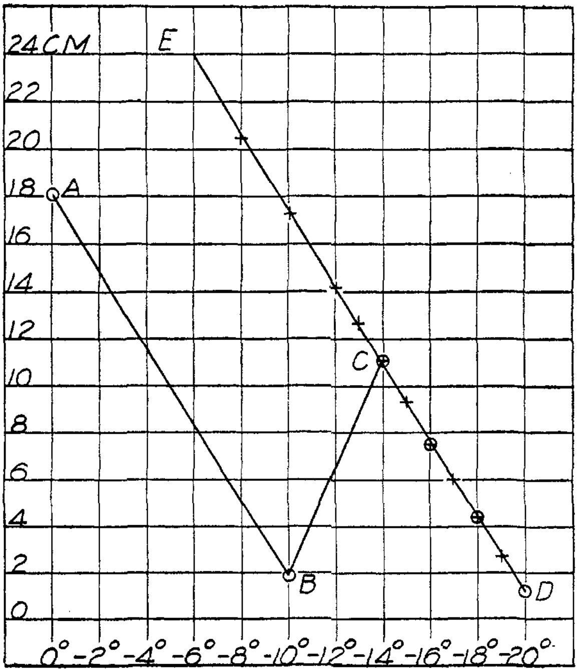

Fig. 4.—Calcium hydroxide and water.

CALCIUM OXIDE AND WATER.

CaO taken, (g.).	Total water taken, (g.).	Free and capillary water taken.	Expansion due to freezing. (cm.).	Volume of 1 cm.	Free and and capillary water found. (g.).	Error in free and capillary water.
3.921	2.510	1.251	16.0	0.006205	1.094	0.157

The amount of free water found is somewhat below the amount taken. The curve shows very well, however, the behavior of a hydrate containing very little capillary water, the curve CD being nearly a straight line and coinciding closely with DF.

The Hydrogel of Alumina.

In the dilatometer work on all the hydrogels, we have had two objects in mind: (1) to determine the general structure of the gels and how this varies with conditions; and (2) to determine, at least approximately, the amount of water which does not freeze and is therefore neither free nor capillary.

The hydrogel of alumina was the first with which we worked and many of the determinations were carried out using a minimum temperature of only —20°. These results serve to show the structure of the hydrogels and how it changes on freezing. It is probable, however, that not all the capillary water is removed at this temperature, so that the results on combined water in these determinations are undoubtedly high.

Four samples of aluminium hydroxide were prepared under varied conditions. It does not appear that the method of precipitation affects their character noticeably. All samples were washed free of chlorides. They were prepared as follows:

Sample A. Precipitated by ammonia from a cold dilute solution of the chloride. After washing, it was air-dried till it reached the composition desired.

Sample B. Precipitated by ammonia from a hot concentrated solution of aluminium chloride containing much ammonium chloride. It was air-dried after thorough washing.

Sample C. A part of Sample B before being dried in the air to any extent was thoroughly frozen. The granular residue remaining after melting was filtered and partly air-dried.

Sample D. Prepared like A but to hasten the drying it was frozen at a temperature a little below zero and remelted.

The dilatometer observations on these samples have been plotted in the curves which follow. The accompanying tables give other necessary data and also the results calculated from the observations.[1]

The first experiments show the effect on capillary water of varying amounts of free water in the hydrogel. For this purpose, Sample A was air dried and two samples were taken during the drying, containing

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[1] Tables of the values plotted in all figures are in the dissertation presented by Saxton.

decreasing percentages of water. The observations and results are shown in Figs. 5 and 6 and Table I.

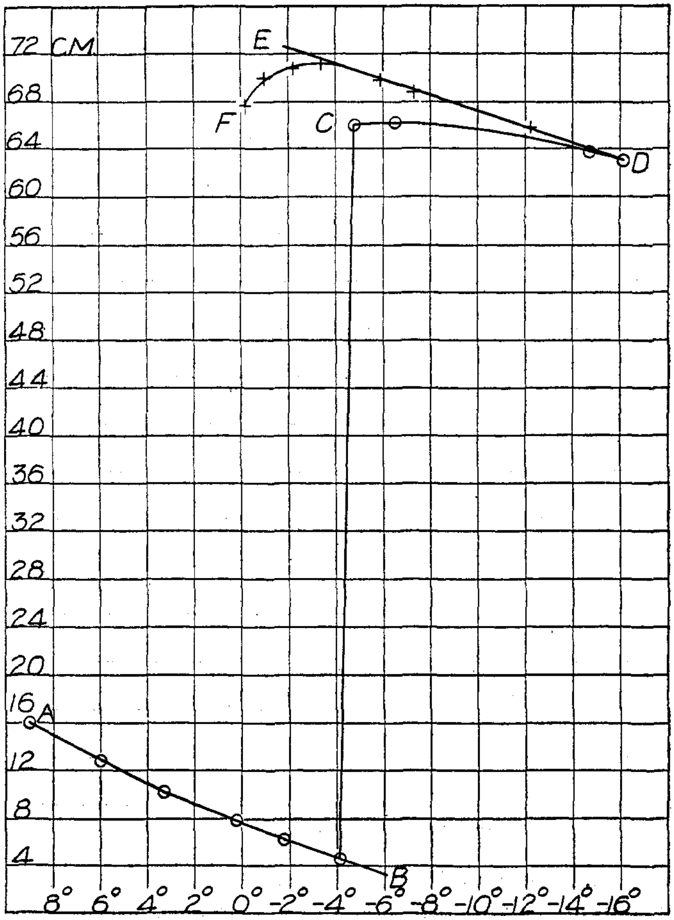

Fig. 5.—Alumina and water (75.2% water).

TABLE I.

Showing Effect of Water Content on the Capillary Water (Sample A).

No. of figure.	Wt. of hydrogel.	Per cent. H_2O in hydrogel.	Expansion due to apparent capillary water. (cm.).	Value of 1 cm. in cc.	Weight of apparent capillary water per g. Al_2O_3.
5	12.075	75.23	3.7	0.00920	0.1255
6	10.091	54.46	5.0	0.01058	0.1269

It is probable that the last of the capillary water was not frozen in either No. 5 or No. 6, but the results are comparable, as the lowest temperature in each case was about the same. Roughly, the difference between the two results shows in the figures from the lengths of BC; that is, No. 5 contains much the larger proportion of free water. The amounts of apparent capillary water, *i. e.*, water freezing below —6°, per gram of alumina, are shown in the last column. The results are practically identical and indicate that the amount of capillary water in the sample does not change as free water evaporates.

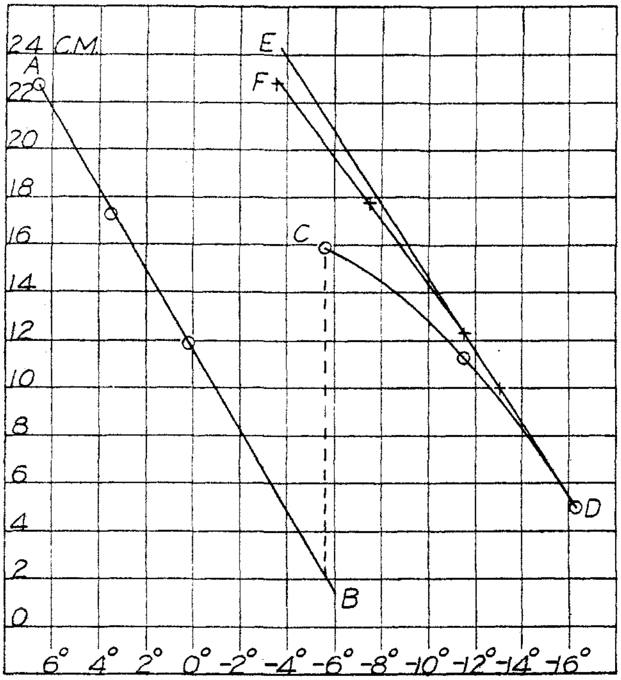

Fig. 6.—Alumina and water (54.46% water).

Another portion of Sample A was dried till it contained approximately the water content (38.18) corresponding to combined water alone. When cooled, the contraction in the dilatometer was entirely regular as far as the minimum temperature observed, —16.4°, and the dilatometer readings on falling and rising temperature lay on the same curve. Evidently, no water was frozen in this sample.

The change in appearance of alumina after freezing made it appear probable that the proportion of free water increased at the expense of capillary water by this process. To prove this, the same sample was frozen three times in the dilatometer. The observations on the first and the third freezing are plotted in Fig. 7. The contraction before freezing in both cases is represented by AB. The dotted lines show the results of the first freezing in this curve, as well as in all others where a precipitate has been frozen more than once. In order to avoid confusion in the diagram, the observations on the second freezing are not plotted The results obtained are in Table II.

TABLE II.

Determination of Free and Apparent Capillary Water, Showing Effect of Repeated Freezing.

Sample B. 58.09% H_2O. 8.655 g. substance. 1 cm. = 0.009751 cc.

No. of figure.	Treatment.	Expansion in cm. due to free and capillary water.	Wt. of free and capillary water.	Expansion in cm. due to apparent capillary water.	Wt. of apparent capillary water.	Wt. of apparent capillary water per g. Al_2O_3.
7	Air dried	21.6	2.322	3.9	0.4192	0.1156
	Once frozen	22.1	2.376	1.5	0.1612	0.0445
7	Twice frozen	22.1	2.376	1.0	0.1075	0.0296

The results in the last two columns show that capillary water is reduced by each successive freezing. On the other hand, the table shows that the weight of free and capillary water, representing all the water frozen, changes but little in successive freezings. Stated in a somewhat different way, repeated freezing appears to convert most of the capillary water into free water, while there is but little effect on combined water.

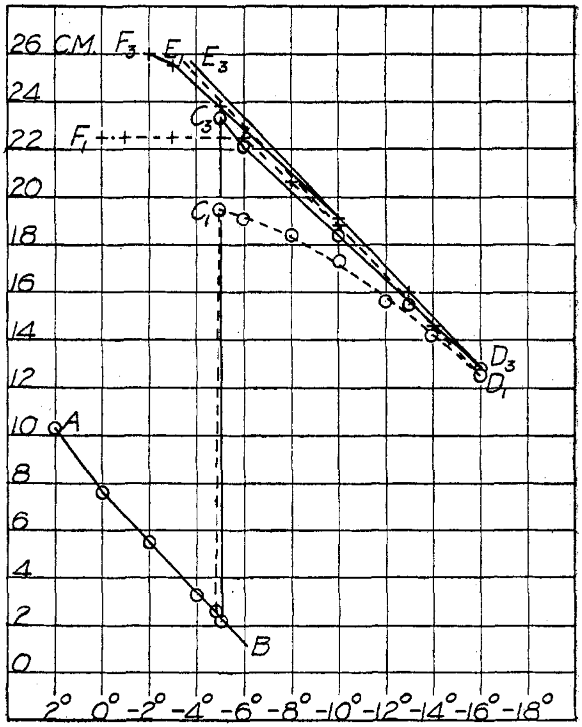

Fig. 7.—Alumina and water. (Effect of repeated freezing.)

The effect of freezing was also shown in another case. Sample B was thoroughly frozen, melted and partly air dried before placing it in the dilatometer. Two lots of this material (Sample C) were used in independent determinations. Both sets of observations are plotted in Fig. 8 and other data, with the results, are in Table III.

While the two curves are not identical, the capillary water is much less than in material which had not undergone previous freezing.

TABLE III.

Determination of Apparent Capillary Water after Previous Freezing.

Sample C. 59.09% H_2O.

No. of figure.	Wt. of hydrogel, (g.).	Expansion due to apparent capillary water, (cm.).	Volume of 1 cm., (cc.).	Wt. of apparent capillary water per g. Al_2O_3.
8*a*	4.401	0.05	0.009741	0.003
8*b*	5.996	1.4	0.009751	0.061

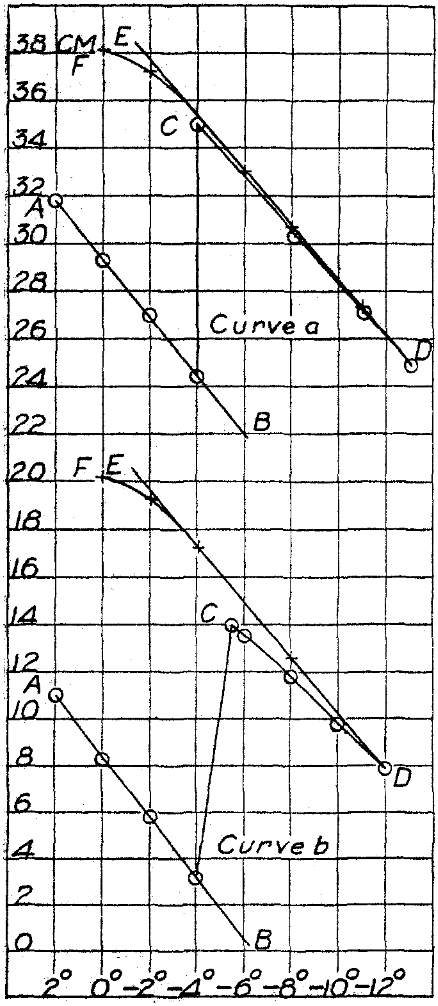

Fig. 8.—Alumina and water (material previously frozen).

The age of a hydrogel appears to affect it considerably. Sample D has been used to show this. The sample was frozen first by placing it out of doors at a freezing temperature before it was sealed in the dilatometer. The material was granular after freezing but the temperature was not sufficiently low to affect the apparent capillary water as will be seen below. A temperature of —6° is required to affect this. The sample was then frozen in the dilatometer and the curve shown by the dotted lines in Fig. 9 was obtained. After standing eight months the sample was frozen again twice, once to —20° and again to approximately —32°. The curves for these two freezings coincided so nearly that only the last one is shown in the figure. A comparison of the curves in Fig. 9 with the ones in Fig. 7, where the material was frozen repeatedly soon after preparation, will show at a glance the difference in the two cases. The apparent capillary water diminished in both cases after each freezing, but in Fig. 9, the total free and capillary water, after long standing, is considerably greater than that found when the same precipitate was fresh, as D_3E_3 lies well above D_1E_1. In Fig. 7, on the other hand, where the material was fresh, D_1E_1 and D_3E_3 are close together, showing that total free and capillary water has changed but little after each freezing. It will be noticed too, in Fig. 9, that the water freezing at —6° after long standing, represented by the length of BC_3, is greater than the total amount of free and capillary water freezing from the fresh material. There is evidently an appreciable amount of water in the fresh material which did not freeze at —18° and would therefore be counted as combined water, which does, however, freeze without difficulty after long standing. We shall discuss this point below in considering combined water. The quantitative data regarding free and capillary water in this sample are in Table IV. The

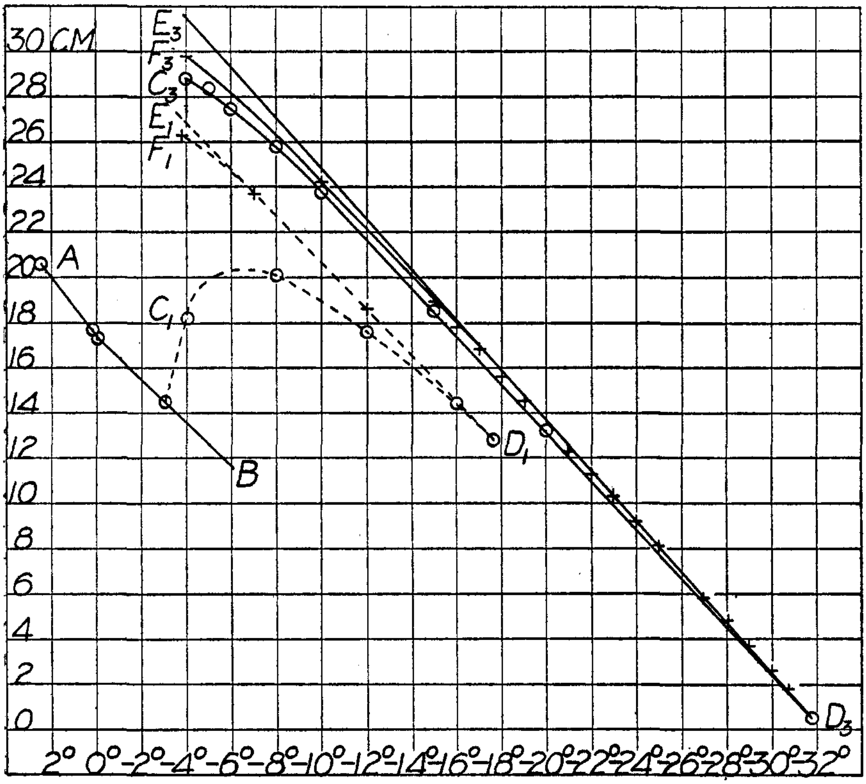

Fig. 9.—Alumina and water. (Effect of aging hydrogel.)

TABLE IV.

Determination of Free and Capillary Water, Showing Effect of Age on the Hydrogel.

Sample D. 51.90% H_2O. 5.179 g. substance. 1 cm. = 0.006288 cc.

No. of figure.	Treatment.	Expansion due to free and capillary water. (cm.).	Wt. of free and capillary water. (g.).	Expansion due to apparent capillary water. (cm.).	Wt. of apparent capillary water.	Wt. of apparent capillary water per gram Al_2O_3.
9	Fresh	13.6	0.9428	4.6	0.3189	0.1280
..	Stood 8 months	17.4	1.206	1.7	0.1179	0.0473
9	Stood 8 months	17.6	1.220	1.3	0.0901	0.0362

results show the character of the changes taking place, independent of whether all capillary water has been frozen or not.

The increase of free and capillary water is from 0.9428 g. to 1.220 g. while in Table II, the fresh sample, which was also frozen three times, showed but a slight increase in free and capillary water after each freezing. The change in apparent capillary water after each freezing is nearly the same in both samples.

Combined Water in the Hydrogel of Alumina.

An inspection of the diagrams for alumina will show that commonly the dilatometer readings near D are lower on the descending than on the ascending curve. This we interpret to mean that the temperature has not been sufficiently lowered in these cases and that freezing has taken place as far as D, so that on the curve for rising temperature, the volume is greater, due to the additional ice formed at lower temperatures. It is probable that in these cases, all capillary water has not been frozen even at D, and the results on capillary water are therefore low while combined water is correspondingly high. In general, of course, the lower the minimum temperature obtained, the more completely should capillary water be frozen. The results in Table IV and Fig. 9 have shown that a change occurs in the hydrogel on standing which increases the amount of water that can be frozen under the conditions we used. Whether this increase comes from water which was actually combined with alumina, or whether it was capillary water of too low a freezing point to appear earlier, our data do not show. Further work, particularly at much lower temperatures, will be necessary to decide this. It is, however, evident that the values for combined water in old material should represent equilibrium better than where fresh material was used.

We give in Table V the results thus far obtained on combined water. The necessary data have been taken from the previous tables and diagrams. The free and capillary water actually frozen in each determination is measured by the length of the vertical BE. As the total water is known, it is a simple matter to calculate the unfrozen. Where a sample has been frozen more than once, the results of the final freezing only are given in the table. The last column gives the percentage of unfrozen water

TABLE V.

No. of figure.	*a.* Wt. of hydrogel. (g.).	*b.* Wt. of Al_2O_3. (g.).	*c.* Total H_2O. (g.).	*d.* Free and capillary H_2O. (g.).	*e.* Unfrozen H_2O. (g.).	Per cent. of H_2O unfrozen $\frac{100e}{b+e}$.
5	12.075	2.991	9.084	6.755	2.329	43.8
6	10.091	4.595	5.496	2.251	3.245	41.4
7	8.655	3.627	5.028	2.376	2.652	42.2
8*a*	4.401	1.800	2.601	1.181	1.420	44.1
8*b*	5.996	2.453	3.543	1.537	2.006	45.0
9	5.179	2.491	2.688	1.220	1.468	37.1

remaining in the hydrogel, after deducting the water which has frozen. This is the same as the percentage of combined water in the hydrogel, if all capillary water is frozen.

The results vary considerably for reasons previously given. The last value, 37.1% of combined water, is undoubtedly the best. It was obtained on material which had been allowed to age for eight months and the lowest temperature of any was used in the freezing. There is the following evidence that all capillary water was frozen in this material. When frozen the first time after standing eight months, the temperature was lowered to only —20°. On the next freezing, the minimum temperature was nearly —32°. In spite of this difference of 12°, the line DE (Fig. 9) for the last freezing almost exactly covers the first (not shown in the diagram) which means that no additional ice formed below —20° in the last freezing. This is also shown by the fact that the curves CD and DF very nearly coincide for a considerable distance from D. It seems very probable therefore that all, or nearly all, free and capillary water was frozen in this sample and that the result, 37.1%, represents more closely than any of the others, the percentage of combined water in alumina. The calculated percentage of water in $Al(OH)_3$ is 34.6, a value 2.5% below the result found.

We have the following additional evidence that the result obtained above is nearly correct: A sample of alumina was dried over sulfuric acid till it contained 33.9% H_2O. It was then rehydrated over water till it contained 39.4%. This material, in the dilatometer, separated a little ice between —5° and —8°. Below this, the cooling and heating curves were straight lines and coincided exactly, the temperature being lowered to —31.4°. Allowing for the ice which separated, the residue contained 37.5% H_2O, a value very close to that given previously for combined water. The fact that below —6°, the cooling and heating curves coincide so exactly, is very strong evidence indeed that all free and capillary water was frozen. It follows that all of the water up by the partly dehydrated alumina which did not freeze, amounting to 3.2%, must have been recombined. As will be shown below, the water taken up by partly dehydrated silica behaves quite differently.

The Hydrogel of Silica.

Silicic acid was prepared from a dilute solution of sodium silicate. One hundred and twenty grams of this salt were dissolved in four liters of water and the solution acidified with hydrochloric acid. Silica was precipitated from this solution by the addition of ammonia. It was partly washed by decantation and then treated with hydrochloric acid to remove any basic oxides. Finally it was washed till chlorides were removed. The precipitate was divided into two parts, one of which, SiO_2 (I), was frozen and melted before placing it in the dilatometer while the other,

SiO_2 (II), was dehydrated in a current of dry air at ordinary temperature till dry in appearance. In freezing and melting SiO_2 (I), a considerable quantity of water was removed, leaving it granular in appearance. This is identical with the behavior observed by Lottermoser.[1] The water thus frozen out contained only a trace of chlorides. A third sample was prepared, starting with a part of SiO_2 (II). The latter was dried over concentrated sulfuric acid at room temperature and then rehydrated over water till saturated. This sample is called SiO_2 (II-*a*).

Dilatometer observations were taken like those on alumina except that lower temperatures were commonly used. In Fig. 10, the curves of SiO_2 (I) are given for the first and third freezings in the dilatometer.

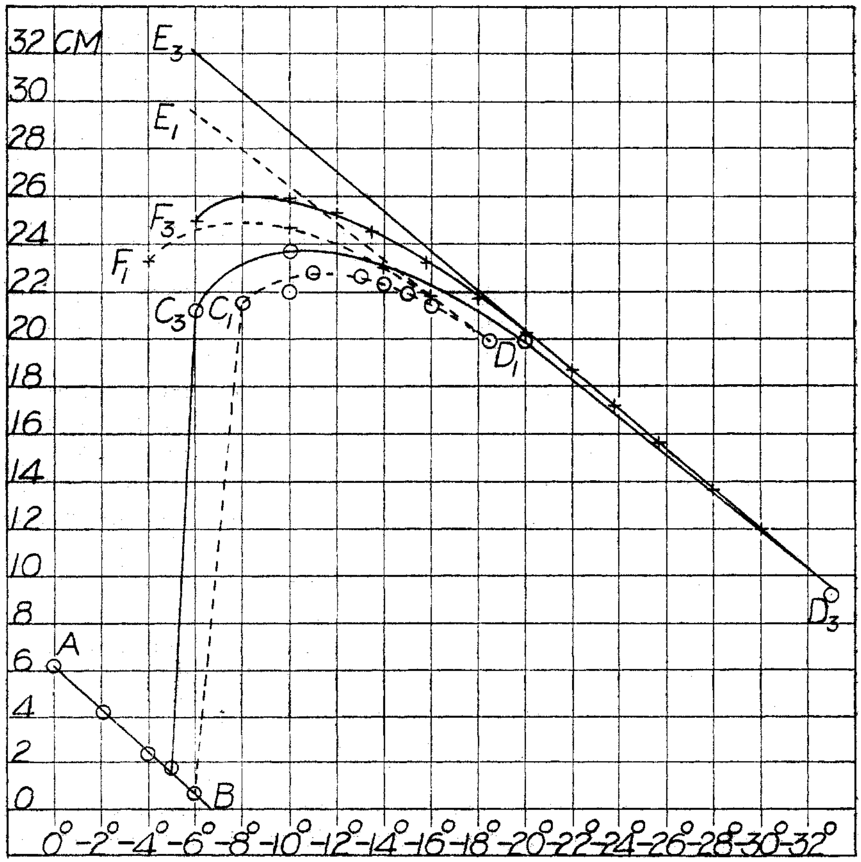

Fig. 10.—Silica and water (I).

The curve for the second freezing nearly coincides with that of the third and is not shown in the diagram. The minimum temperature on freezing

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[1] *Ber.*, 41, 3976 (1908).

the first time was not sufficiently low, as may be seen by inspecting the diagram, and only the results obtained from the second and third freezings are given (Table VI).

TABLE VI.

SiO_2 (I).—Results Obtained on Last Two Freezings.

71.18% H_2O. 6.131 g. hydrogel. 1 cm. = 0.01064 cc.

a. SiO_2 in hydrogel. (g.).	*b.* Expansion due to free and capillary water. (cm.).	*c.* Free and capillary water. (g.).	*d.* Expansion due to apparent capillary water. (cm.).	*e.* Apparent capillary water per g. SiO_2. (g.).	*f.* Unfrozen water. (g.).	*g.* Per cent. of unfrozen water $\frac{100f}{a+f}$.
1.767	31.3	3.672	12.3	0.817	0.692	28.1
1.767	31.3	3.672	10.8	0.717	0.692	28.1

SiO_2 (II) was frozen twice in the dilatometer. Both curves were identical except that they differed slightly on the initial expansion when freezing began, and only the second is given in Fig. 11. Freezing began at so low

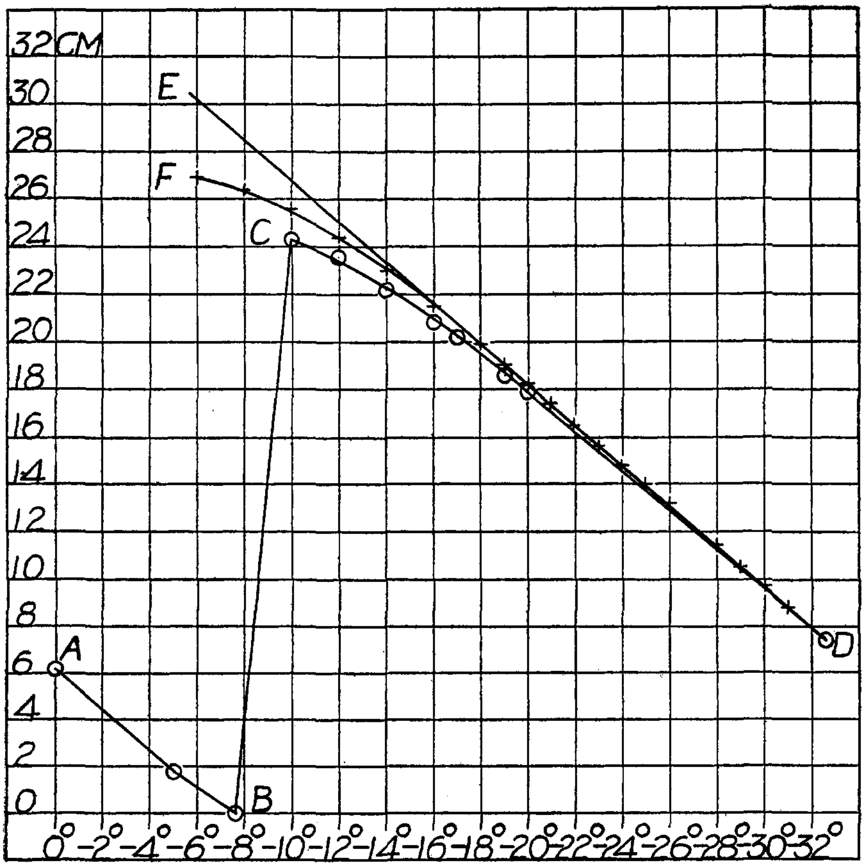

Fig. 11.—Silica and water (II).

a temperature that the result for apparent capillary water, by extrapolating to —6° has no value. The other results are given in Table VII.

TABLE VII.

SiO_2 (II).—Identical Results Obtained on Both Freezings.

78.36% H_2O. 4.903 g. hydrogel. 1 cm. = 0.01064 cc.

a.	b.	c.	d.	e.
SiO_2 in hydrogel (g.).	Expansion due to free and capillary water, (cm.).	Free and capillary water. (g.).	Unfrozen water, (g.).	Per. cent of unfrozen water. $\frac{100\ d}{a + d}$.
1.061	29.1	3.414	0.428	28.7

As may be seen from Fig. 10 and Table VI, the capillary water in silicic acid behaves quite differently from that in alumina. From Fig. 10, the lengths of BC and BC_3 are nearly equal, showing that the amounts of free and of capillary water have changed but little on successive freezings. It is evident, therefore, that silica reabsorbs capillary water after it has been frozen and melted, while we have shown previously that the amount of capillary water in alumina continually decreases on freezing and yields free water. The apparent capillary water, *i. e.*, water freezing below —6°, amounts to over 0.7 g. per gram of silica. This is nearly six times as much as any sample of alumina contained.

In both samples, the cooling and heating curves nearly coincide in their lower portion, near D, showing that very little ice forms as low as D. For instance, in SiO_2 (II), at —20°, the increase in volume on rising temperature is due to only 0.035 g. of water. This amount has frozen by lowering the temperature from —20° to —33°. It appears, therefore, that nearly all capillary water has been frozen and the unfrozen water represents true combined water fairly closely. In the two determinations given in the tables this amounts to 28.1 and 28.7%, corresponding to the empirical formulas $SiO_2.1.31H_2O$ and $SiO_2.1.35H_2O$. These results, like those for alumina, may well be somewhat high, though whether the unfrozen water forms a definite compound like H_2SiO_3 or a solid solution with a slight excess of water, must for the present remain unsettled.

These results on silicic acid, which show that over 25% of water remain unfrozen in the hydrogel, appear at first sight to contradict the results obtained by Bachmann[1] and Anderson,[2] who have shown that silicic acid, after being dehydrated over sulfuric acid, absorbs equal volumes of various liquids and that the liquids are not absorbed in any simple molecular proportion. This is very strong evidence indeed that all these liquids, including water, are absorbed in the capillary condition, and that water, for instance, on being taken up by the silica, does not combine with it. The silicic acid used in our work, however, is entirely different in character from that used by Bachmann and Anderson, as it has not been first de-

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[1] *Z. anorg. Chem.*, **79**, 202 (1913).

[2] *Z. physik. Chem.*, **88**, 191 (1914).

hydrated over sulfuric acid. It is evident that if the reaction between silica and water is not reversible, water may be combined originally and after dehydrating, it will only be taken up mechanically.

We have carried out one dilatometer experiment on silica which had first been largely dehydrated over sulfuric acid and then allowed to become saturated with water. The behavior of this material on freezing is quite different from that of silica which has not been previously dehydrated. The material SiO_2 (II-*a*) was dried over concentrated sulfuric acid till nearly constant in weight. It then contained 9.2% of water. It was then allowed to stand over water at room temperature till saturated. It then contained 50.96% of water. This material was frozen and melted twice. Cooling and heating curves were both taken the first time, while on the second freezing, only the heating curve, starting at —33°, was taken.

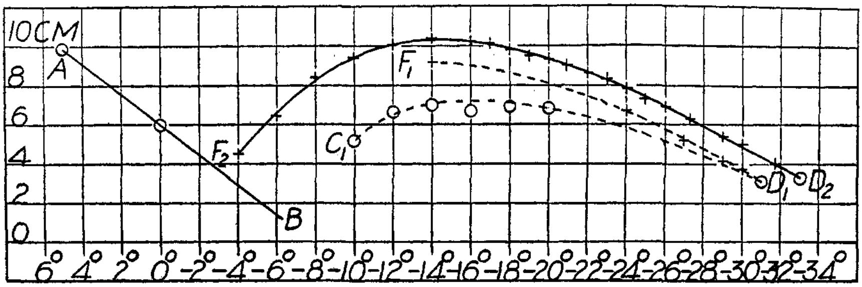

Fig. 12.—Silica and water. (Silica had previously been dehydrated.)

The observations are plotted in Fig. 12. The difference in character between these curves and those in Figs. 10 and 11, where the material had not been previously dehydrated, is quite striking. The curve C_1D_1 does not coincide with D_1F_1 in its lower part, showing that ice was still forming, as far as D_1. Also, D_1F_1 and D_2F_2 begin to curve immediately on leaving D_1 and D_2, showing that ice is melting at these extremely low temperatures. This is excellent evidence that water is present in much finer capillaries in this sample than in the others and supports the view that after dehydration, water reenters the silica in extremely fine capillaries. On account of the character of the curves, no quantitative data regarding capillary water can be derived from the diagram.

The Hydrogel of Ferric Oxide.

Ferric hydroxide was prepared by precipitating a solution of ferric chloride with ammonia. It was thoroughly washed by decantation and on the filter. Before use, it was frozen and melted. The water separated by this means was removed by filtering and the residue left exposed to the air till it appeared nearly dry. The sample was frozen twice in the dilatometer. Both series of observations are plotted in Fig. 13. The curves resemble somewhat those for alumina and silica and the presence of the three kinds of water in the precipitate can readily be shown. The form of the curve CD, however, differs from that of the corresponding curves of these hydrogels. Down to —14°, contraction is nearly regular after freezing begins. At this temperature, the ice separating increases and this continues to —20°. From this temperature, no observations could be made till D_1 or D_2 was reached, but the real course of the curve cannot be greatly different from that represented in the figure. The curve DF begins to slope away from DE at —28°, due to melting. The curves show that capillary water in this precipitate is held more firmly or in finer capillaries, than in the other colloids investigated. Apparent capillary water was found to be nearly the same on each freezing. It amounted to 0.449 g. per gram of ferric oxide on the first freezing, a value intermediate between the value for silica and alumina. The hydrogel resembles that of silica in there being but little change in capillary water caused by freezing.

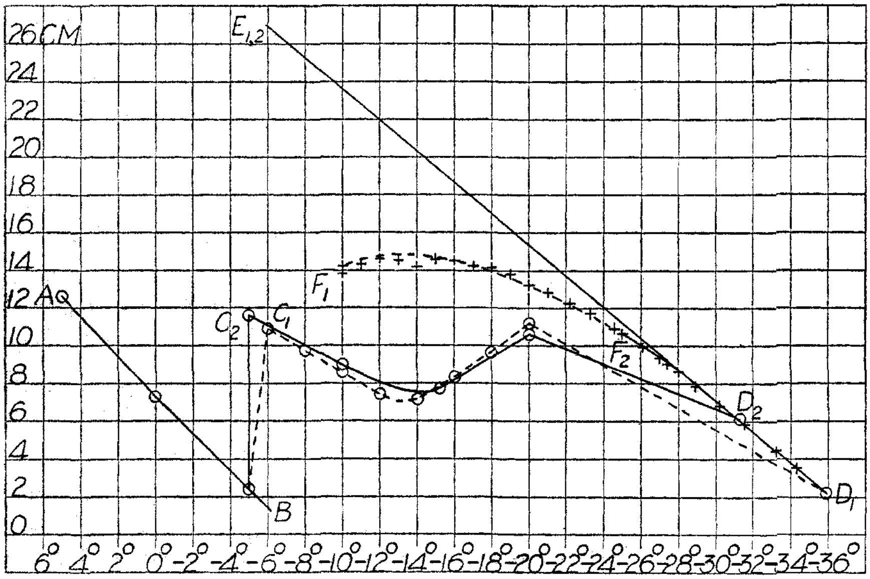

Fig. 13.—Ferric oxide and water.

The results obtained are in Table VIII. From the form of the curve, it is probable that the results are not as reliable as those for alumina and silica.

Table VIII.

Hydrogel of Ferric Oxide.

a. Weight of hydrogel, (g.).	b. Weight of Fe_2O_3 in hydrogel. (g.).	c. Expansion due to free and capillary water. (cm.).	d. Volume of 1 cm.. (cc.).	e. Free and capillary water. (g.).	f. Unfrozen water. (g.).	g. Per cent. of unfrozen water $\frac{100f}{b+f}$
9.190	4.178	25.3	0.01064	2.968	2.044	32.4

The percentage of water remaining unfrozen corresponds to the empirical formula $Fe_2O_3.4.25H_2O$.

In view of the results obtained above, which show quite definitely that considerable amounts of water can be frozen from colloidal precipitates after all water in its usual free condition has been removed, it is necessary to correct the conclusions which were drawn by one of us[1] (Foote) regarding the condition of water in hydrogels. A method was developed in the work referred to which showed the point where free water was just removed, and the water remaining was considered to be in solid solution. It is evident, however, that after free water is removed, it will be followed by capillary water, with its lower vapor pressure corresponding to lower freezing point, so that the method is one for determining the amount of combined and capillary water in a hydrogel instead of water in solid solution. For this purpose, the method probably gives more reliable data than any other. The results of the two methods are, however, not strictly comparable, the main reason being that the dilatometer method includes part of the capillary water in the free water, as previously explained, so that the "apparent capillary water" found is less than the capillary water which really exists.

We are indebted to Prof. W. G. Mixter of this laboratory for suggesting the use of lampblack and water in our work.

Work on the freezing of colloids is being continued in this laboratory.

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE JEFFERSON PHYSICAL LABORATORY OF HARVARD UNIVERSITY.]

FURTHER NOTE ON BLACK PHOSPHORUS.

BY P. W. BRIDGMAN.

Received November 26, 1915.

In a previous number of THIS JOURNAL[2] I have described a new black modification of phosphorus. It was produced by heating white phosphorus to 200° under a pressure of 12000 kg. or more; attempts to form it by other methods failed. Professor A. Smits, of Amsterdam, who had made such exhaustive studies of the relations between white and red phosphorus, has interested himself in the subject and has made measurements of the vapor pressure of black phosphorus. He has suggested in correspondence that it would be of interest to find the effect of high pressures on red phosphorus in the presence of iodine as a catalyzer. The purpose of this note is to describe this experiment and several others dealing with the same subject—the possibility of changing red to black phosphorus.

"Red" phosphorus is known not to be a definite substance, but varies

[1] THIS JOURNAL, 30, 1388 (1908); 31, 1020 (1909).

[2] *Ibid.*, 36, 1344 (1914).