	Electrochemical equivalent.	International atomic weight.	Corresponding value of a faraday.
Silver voltameter	0.00111798	107.88	96496
Iodine voltameter	0.00131502	126.92	96516
Cadmium voltameter	0.00058198	112.4	96569

These values of the faraday appear to be well within the possible variation of the atomic weights. For example, a direct conparison of the silver and cadmium voltameters indicates the atomic weight of cadmium to be 112.3, taking the atomic weight of silver as 107.88. The generally used value for the faraday is 96540. This number is most likely too high and it may be well to round it off to 96500 with a probable error of from 10 to 20.

V. Summary.

1. A special form of voltameter has been devised and used to determine the agreement between the amount of pure silver deposited at the cathode and dissolved at the anode. An agreement to within 7 parts per hundred thousand corrected for inclusions has been obtained. In the method used any error in the large amount of manipulation would tend to make the divergence greater, so that this figure represents a maximum.

2. An improved form of apparatus has been devised to measure the inclusions in the silver voltameter deposits and an accuracy of one part in a hundred thousand has been obtained.

3. The value of inclusion in deposits on a standard platinum cup voltameter has been found to be 6.7 parts per hundred thousand, giving 1.11798 as the value of the electrochemical equivalent of silver and 96496 as the value of the faraday.

4. The inclusions in deposits on silver are of the same value as those on platinum to within one part per hundred thousand, a value of 7.7 having been obtained.

5. The silver deposited on a silver wire in the special form of apparatus used for the anode loss and cathode gain comparison has been found to contain very large amounts of inclusions. The explanation for this abnormality is not yet forthcoming.

PRINCETON, N. J.

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

THE EFFECT OF FREEZING ON CERTAIN INORGANIC HYDROGELS. II.

BY H. W. FOOTE AND BLAIR SAXTON.

Received February 16, 1917.

In a previous article[1] we gave the results obtained up to the time of publication, regarding the structure and composition of certain inorganic hydrogels. It was shown, by freezing them in a dilatometer, that ordinary

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

moist hydrogels such as silicic acid, contain three kinds of water, (*a*) free water, which freezes sharply when the temperature is cooled slightly below 0°, (*b*) water which freezes gradually as the temperature is lowered, and (*c*) water which does not freeze. The water which freezes gradually with falling temperature was considered to be in the capillary condition, while the water which could not be frozen was called combined. The effect of conditions, such as time and previous freezing, on the capillary water was considered in some detail, but we were able to obtain but little reliable data on combined water. Our recent work, the results of which are given in the present article, has been concerned more particularly with determining combined water, *i. e.*, water which cannot be frozen.

Method.

As the dilatometer method, which we have used throughout the work, has been somewhat modified and improved during this time, it is desirable to give a description of the method as finally adopted. It consists essentially in freezing the precipitate, of known total water content, in a dilatometer and measuring the expansion caused by freezing free and capillary water. From the expansion, the amount of water frozen may be calculated and the amount of combined water obtained by difference.

The dilatometer had the usual straight form. It was made by sealing a piece of capillary tubing calibrated by means of a mercury thread and somewhat less than a meter long, to a piece of tubing having an inner diameter of about 12 mm. This latter piece, which was to serve as the bulb, was partially constricted some 10 cm. from the seal. The tube was cut two or three centimeters beyond the constriction. The portion beyond the constriction serves as a funnel and facilitates the introduction of the solid into the bulb. A small glass valve in the latter prevents any solid from entering the capillary when the bulb is being filled.

As we have had some trouble in filling the bulb properly, we shall give the details of the operation as finally carried out. The entire dilatometer with its glass valve, after thorough cleaning and drying, was weighed to 1 mg. It was then clamped, capillary end down, and the substance was introduced through the funnel end. The hydrogels were always moist and sticky but they could be pressed through the constricted part readily with a glass rod, while any material left sticking to the funnel end and in the constriction could be removed with a small swab of cotton. The apparatus was then weighed again to obtain the weight of material used. After sealing the bulb, this weight was checked repeatedly by the combined weight of the dilatometer and the funnel which was drawn off and the weights never varied over 1 mg., showing there was no appreciable loss of water in sealing the dilatometer.

Ligroin was used to fill the bulb. It has the advantage of high vapor pressure, making it possible to fill the bulb completely by the use of an ordinary water pump, and the solubility of water in this liquid is negligible. The bulb should be cold when it is evacuated and filled, to avoid a small loss of water vapor. We used for this purpose a bath at 0°, or even lower when there was no objection to freezing the hydrogel. Two dilatometers may be clamped to one meter scale for the heating and cooling observations. For temperatures as low as —20°, an ice-salt bath was used. For still lower temperatures, down to —36°, a mixture containing about equal weights of ice and crystallized calcium chloride was necessary.[1] In some cases, to insure complete freezing, the dilatometer was placed in a mixture of alcohol and solid carbon dioxide, which gives a temperature of about —78°. The two low temperature thermometers, which were used in measuring all temperatures down to that of calcium chloride and ice, had been calibrated with considerable care.

In practice, the temperature of the dilatometer was lowered gradually to about —20° in the ice-salt bath and then directly to about —30° or below in the calcium chloride. It was not practicable to lower the temperature gradually between —20° and —30°. The temperature could, however, be raised gradually from —30° by cautious addition of water. When carbon dioxide and alcohol was used, the dilatometer was lowered to about —30°, then to —78°, after which it was replaced in calcium chloride and gradually warmed.

The typical behavior of a hydrogel when subjected to this treatment has been described in our previous article.[2]

The main difficulty in determining combined water by the freezing method has been that capillary water freezes and melts throughout a considerable range of temperature, making it necessary to extrapolate our results in order to obtain its amount, and therefore the amount of combined water. Any treatment which cuts down the amount of capillary water in the hydrogel tends to shorten the extrapolation and may be expected to add to the accuracy with which combined water may be determined. A glance at any diagram will make these points clear. The less capillary water there is present, the more closely CD and DF approach DE.

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[1] The cryohydric temperature of calcium chloride has been given as —55° (Roozeboom, *Z. physik. Chem.*, 4, 42 (1889)). We have never been able to approximate this temperature, the minimum we have obtained, with both ice and the salt in excess, in a vacuum-walled jar, being about —36°. To obtain even this temperature, some care in the choice of calcium chloride is necessary. Crystallized calcium chloride as purchased is usually too moist for the purpose and we found it better to prepare our own. The dehydrated salt was dissolved and concentrated till the boiling point reached 130°, which is the boiling point of a solution having approximately the composition $CaCl_2.6H_2O$. The liquid was then transferred to a shallow tray where it solidified. This material is quite hard and we passed it through a grinder before use. In winter weather, when the laboratory air is dry, the material does not deliquesce in the open tray.

[2] *Loc. cit.*, pp. 591–592.

With none present, all three coincide in one straight line practically parallel with AB. This is the case, for instance, when a mixture of sand and water is frozen, and the first sample of alumina (Fig. 1) approximates this condition. We have already shown that freezing and time both tend to diminish capillary water. Our present investigation has shown that heating a hydrogel with water affects capillary water more than either long standing or freezing and this effect has therefore received much attention. We have also determined the amounts of combined water in several samples prepared under other conditions, and have duplicated some of our previous determinations where this seemed desirable.

The Expansion of Water to Form Ice.—It is necessary to know the expansion of water on freezing, with a considerable degree of accuracy in order to convert our measured values of expansion into the corresponding weights. This value has been determined by Bunsen and others and Bunsen's value was used in our first work. It has seemed best to determine this value anew under conditions similar to those which we have used. We have therefore made six determinations, using four different dilatometers. Sea sand which had been digested with hydrochloric acid and water, was washed and ignited and placed in dilatometers like those described. A weighed amount of water was introduced and the bulbs were then filled with ligroin, keeping them at about —10° while being filled to minimize any loss of water by evaporation. The object of the sand was to distribute the water and prevent it from freezing in a solid mass, tending to expand the dilatometer bulb. Freezing took place in the bulb at from —4° to —6° and the increase in volume could be determined by direct readings on the dilatometer. The following results were obtained:

No.	*a.* Water taken (g.).	*b.* Expansion due to freezing (cm.).	*c.* Volume of 1 cm. (corr.) (cc.).	Expansion of 1 g. of water (cc.). *bc/a.*
1....................	1.986	19.17	0.009622	0.09288
2....................	1.992	19.11	0.009786	0.09388
3....................	1.997	19.31	0.009622	0.09304
4....................	1.997	19.04	0.009786	0.09330
5....................	3.128	18.24	0.015960	0.09306
6....................	1.964	18.80	0.009748	0.09333
			Average,	0.09325

In the third and fourth determinations above, the ligroin had been dried over sodium, while in the other cases it was first saturated with water. The fact that the results agree closely shows that the solubility of water in ligroin is negligible. The mean of all six determinations is 0.0932. This result is 2.6% greater than Bunsen obtained. For our purposes, where similar conditions were used in freezing hydrogels, it is undoubtedly the better value. Our results on hydrogels have been calculated from the experimental data by the use of this value. We assume, therefore, that liquid water in the capillary conditions has essentially the same density as other water at the same temperature. This assumption appears justified from the results on capillary water in finely divided carbon given in a previous article.[1]

The Hydrogel of Alumina. *Sample I.*—This sample was precipitated from a warm solution of the chloride and washed free from chlorides. It was then digested on the steam bath with a large excess of water for twenty-four hours. The precipitate, after this treatment, passed through the filter. A few drops of ammonia coagulated it sufficiently, however, so that it could be filtered and washed. The material was exposed to the air until only slightly moist and then introduced into the dilatometer. Duplicate freezing curves, in different dilatometers, were obtained on this sample. They were of exactly the same type. One of the curves is plotted in Fig. 1. In this figure, as in all following, corrected readings of the dilatometer, in centimeters, are plotted as ordinates and temperatures as abscissas; observations taken on falling temperature are repre-

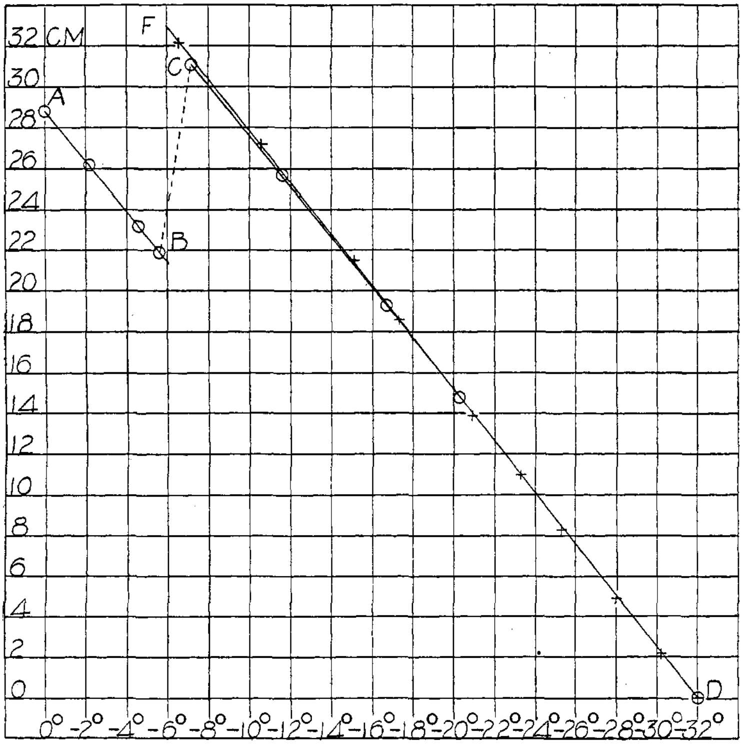

Fig. 1.—Alumina—Sample I.

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[1] THIS JOURNAL, 39, 627 (1917).

sented by circles, and on rising temperature, by crosses. The line CD shows the change in volume on falling temperature after freezing takes place, and DF, the corresponding change on rising temperature. The line DE, which is shown in most of the diagrams, is the extrapolation of the straight portion of DF from D and in the present case coincides with DF, which is a straight line. This figure is of considerable interest. It is almost of the type shown by sand and water since CD and DF are straight lines and nearly coincide. This shows that freezing took place in the hydrogel almost entirely at one temperature and that apparent capillary water is practically absent. Heating this hydrogel with water, like freezing or allowing it to stand, therefore removes capillary water, but is much more effective than the other means.

This material was particularly well suited to determine combined water as practically only two kinds—free and combined—were present. The data and results of the two determinations are given in Table I and will be discussed later.

Sample II.—This was part of material which had been used in our earlier work. It had been prepared much like Sample I, but at the time it was used had been standing about nineteen months, and it had not been heated with water. It was frozen four times. In the third and fourth freezings, after reaching the point D, the dilatometer was placed in a bath of alcohol and solid carbon dioxide merely to make sure that all

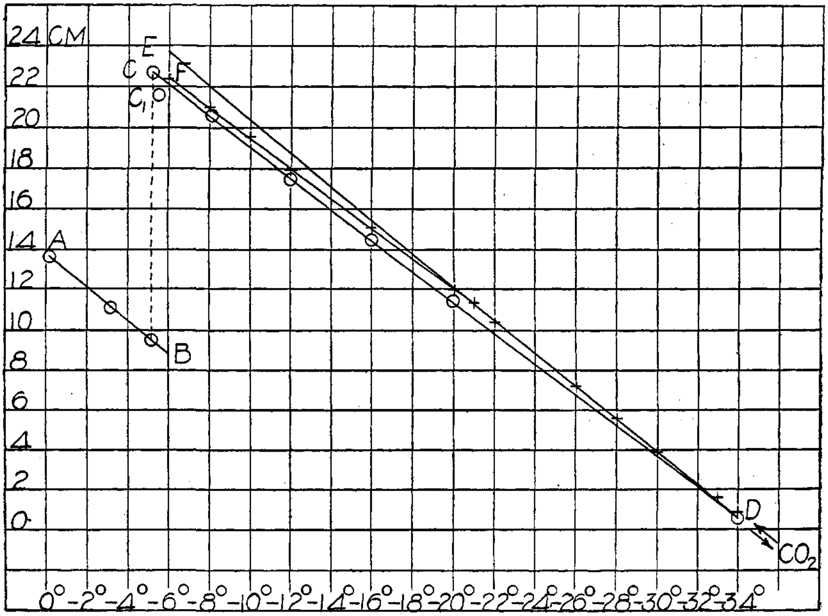

Fig. 2.—Alumina—Sample II.

capillary water was frozen. The apparatus was then replaced in the calcium chloride bath and the observations on DF were taken. The curves for the last two freezings were almost identical. To avoid confusion, only the curve for the fourth freezing is given in the diagram (Fig. 2), together with C_1 for the first freezing. The curve is of the usual type, showing the presence of some capillary water, which diminishes in amount after freezing. The data for combined water are given in Table I.

Sample III.—This was a fresh sample prepared by precipitating a cold, acid solution of the chloride with ammonia, and washing the precipitate free from chlorides. It had not been heated with water. The determinations on this sample were carried out in two dilatometers, freezing each twice, and using alcohol and carbon dioxide to complete the freezing. Both dilatometers gave similar curves. The curves of each freezing in one dilatometer are given in Fig. 3. CD for the second freezing practically coincides with DF, and therefore only one observation, C_2, in given on this curve. The quantitative data in Table I are from the second freezing in each case, though the first freezing gave practically the same result.

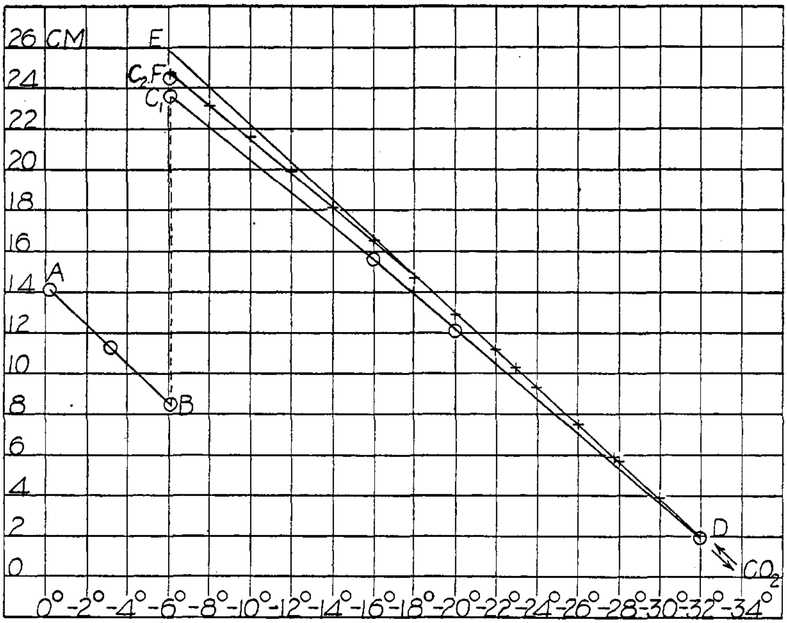

Fig. 3.—Alumina—Sample III.

Table I contains the five results on combined water in the three samples. The expansion due to freezing (Col. *c*) has been obtained graphically in all cases by plotting the results on a large scale. It is measured by the length of a vertical from B at —6° (any diagram) to DE and is due to freezing all free and capillary water. The other columns are self-explanatory.

TABLE I.—COMBINED WATER IN THE HYDROGEL OF ALUMINA.

No.	Sample.	a. Wt. of hydrogel.	b. Wt. of Al_2O_3.	c. Expansion due to freezing (cm.).	d. Volume of 1 cm. (cc.).	e. Wt. of H_2O frozen ($cd/0.932$).	f. Wt. of combined H_2O.	% of combined H_2O $100f/b+f$.
1	I	6.073	3.247	11.50	0.008058	0.994	1.832	36.07
2	I	6.962	3.723	13.75	0.007740	1.142	2.097	36.03
3	II	6.067	2.820	14.95	0.009622	1.543	1.704	37.67
4	III	6.277	2.796	17.30	0.009622	1.786	1.695	37.74
5	III	7.273	3.244	19.37	0.009786	2.034	1.995	38.08

The last column of this table gives the percentage of combined water found in each sample. Sample I, which had been heated with water before use, shows about 1.7% less combined water than the others. The compound $Al(OH)_3$ contains 34.6% of water. The samples therefore show an excess of from 1.5 to 3.2% of water above the amount required for this hydrate. The results are discussed later.

Apparent Capillary Water.—The amounts of what we have called "apparent capillary water," *i. e.*, water freezing below —6°, have been determined graphically. The expansion due to this kind of water is measured by the length of a vertical from C to E (any diagram) at —6°. Thus in Fig. 1, apparent capillary water is nearly zero, while in Fig. 2 it is entirely appreciable. The absolute amount of this type of water in any given case has no special interest in this place, but it is of interest to determine the effect of varying conditions on the amount. We give below (Table II) the results, showing in each case the amount of apparent capillary water per g. of Al_2O_3. The numbers and samples refer to those in Table I.

TABLE II.—APPARENT CAPILLARY WATER IN THE HYDROGEL OF ALUMINA.

No.	Sample.	Expansion CE (cm.).	Volume of 1 cm. (cc.).	Wt. of Al_2O_3.	Wt. of apparent capillary H_2O per g. Al_2O_3.
1	I	0.5	0.008058	3.247	0.013
2	I	0.35	0.007740	3.723	0.008
3 (1st freezing)	II	2.2	0.009622	2.82	0.081
3 (4th freezing)	II	1.85	0.009622	2.82	0.068
4 (1st freezing)	III	2.2	0.009622	2.796	0.081
4 (2nd freezing)	III	1.3	0.009622	2.796	0.048
5 (1st freezing)	III	1.9	0.009786	3.244	0.062
5 (2nd freezing)	III	0.45	0.009786	3.244	0.015

The results are discussed later.

The Hydrogel of Ferric Oxide.—It was shown in our earlier article that the hydrogel of ferric oxide as ordinarily prepared, contains an unusual amount of capillary water which freezes and melts at very low temperatures. On the heating curve, for instance, after cooling to —36°, it could be shown that melting began at —28°. For this reason, no accurate determination of combined water could be made. As capillary water in alumina is removed by heating the precipitate with water, it seemed probable that capillary water would behave similarly in the present case and a series of dilatometer determinations has been carried out on material which has been heated for varying periods on the steam bath with an excess of water.

Ferric hydroxide was prepared by precipitating a warm solution of the chloride, containing some hydrochloric acid, with ammonia. It was washed free from chlorides. The material was then digested on the steam bath with water as follows:

Sample I, 24 hours; Sample II, 3 days; Sample III, 12 days.

Sample I (Digested 24 hours).—After filtering, the material was partly air-dried. It contained 51.49% of water when ready for use. Two dilatometers were filled with this sample, and each was frozen twice, the second time using alcohol and carbon dioxide to make sure that freezing was complete. The Curve CD lies slightly lower in the first freezing in both cases, showing that a small amount of capillary water was eliminated in the operation. To avoid confusion, only the curve for the second freezing in one dilatometer is given in Fig. 4. By comparison with Fig. 13 of the previous article, it will be seen that capillary water has been markedly reduced in the present case, since CD lies much closer to DE.

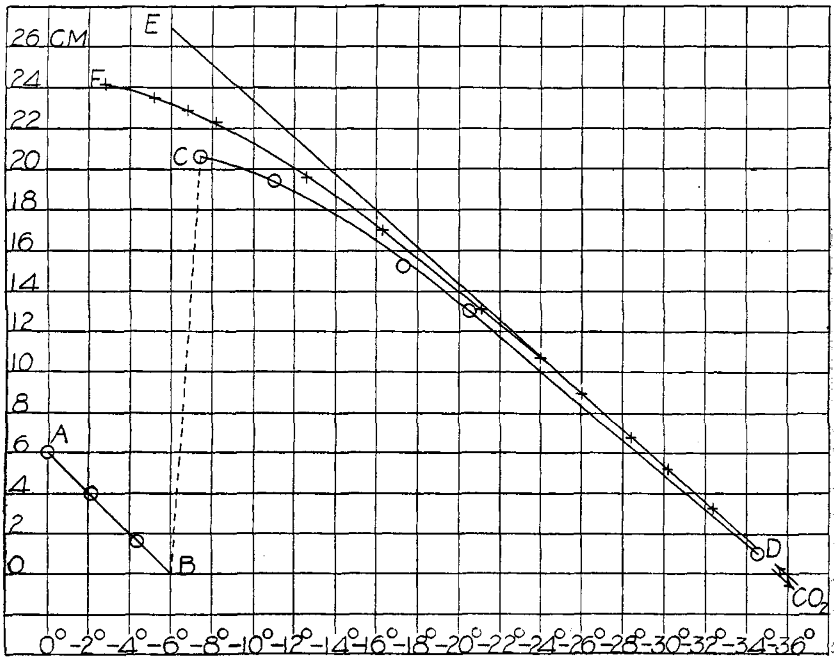

Fig. 4.—Ferric oxide—Sample I.

On the other hand, there is still much capillary water which freezes and melts at a low temperature, and on the heating curve, melting can be detected at about —21°. The five observations below this temperature lie in a straight line, however, and extrapolation should give reasonably good results. Combined water has been calculated from the four sets of observations. The results are given in Table III, Nos. 1–2. The average result on combined water is 21.3%, corresponding to the empirical formula $Fe_2O_3.2.4H_2O$.

Sample II (Digested 3 days).—This sample, when introduced into the dilatometer, had about the same pasty consistency as the first, but the percentage of total water (20.77) was much less. Two determinations in different dilatometers, gave similar results. Fig. 5 shows the results for one determination. The Curve CD runs fairly near DE, showing the amount of capillary water is small. The heating Curve DF begins to diverge from a straight line at —19° or —20°, showing that some capillary water still melts at a very low temperature. The results obtained are given in Table III, Nos. 3–4. Combined water has here fallen to an

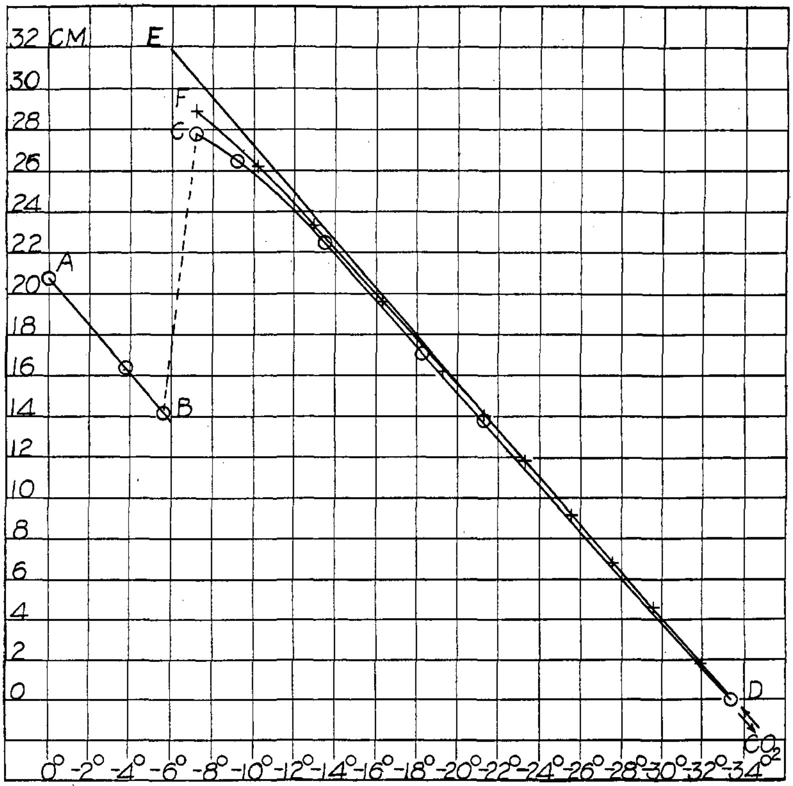

Fig. 5.—Ferric oxide—Sample II.

average of 5.62%, corresponding to the empirical formula $Fe_2O_3.0.53 H_2O$.

Sample III (Digested 12 days).—Digesting on the steam bath changed the color of all the precipitates of ferric oxide, but in the present case, the long treatment with water made the precipitate of such a character that it ran through the filter and could not be separated. We therefor coagulated it again with a few drops of ammonia, which caused it to separate in a somewhat bulky form. Although addition of ammonia undoubtedly affected the character of the precipitate, one determination was made in the dilatometer. The observations are plotted in Fig. 6.

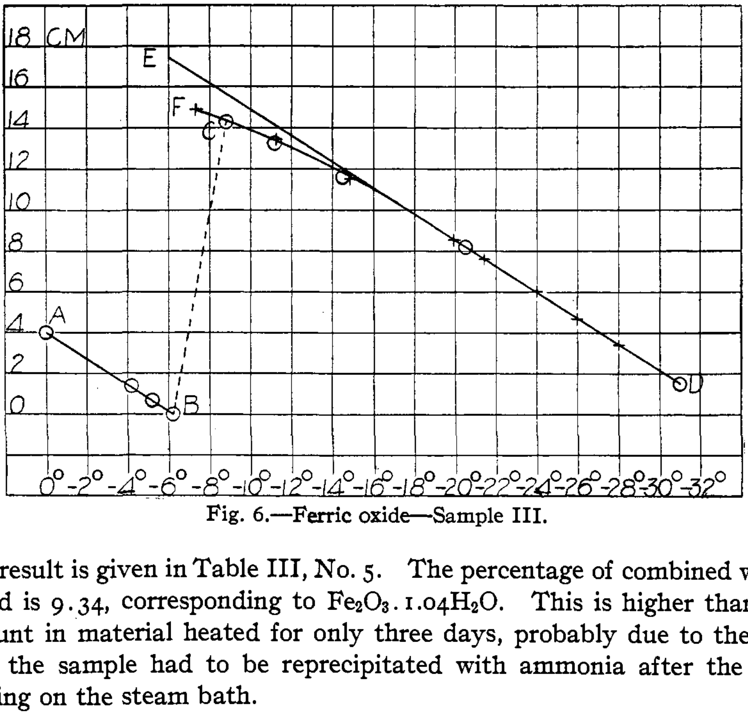

Fig. 6.—Ferric oxide—Sample III.

The result is given in Table III, No. 5. The percentage of combined water found is 9.34, corresponding to $Fe_2O_3.1.04H_2O$. This is higher than the amount in material heated for only three days, probably due to the fact that the sample had to be reprecipitated with ammonia after the long heating on the steam bath.

TABLE III.—COMBINED WATER IN THE HYDROGEL OF FERRIC OXIDE.

No.	Sample.	*a.* Wt. of hydrogel.	*b.* Wt. of Fe_2O_3.	*c.* Expansion due to freezing (cm.).	*d.* Volume of 1 cm. (cc.).	*e.* Wt. of H_2O frozen $cd/0.0932$.	*f.* Wt. of combined H_2O.	% of combined H_2O $100f/b+f$.
1 (1st freezing)......	I	6.900	3.347	15.65	0.01596	2.680	0.873	20.69
1 (2nd freezing).....	I	6.900	3.347	15.25	0.01596	2.611	0.942	21.96
2 (1st freezing)......	I	7.352	3.565	27.08	0.009748	2.832	0.954	21.11
2 (2nd freezing......	I	7.352	3.565	26.90	0.009748	2.814	0.972	21.42
3.................	II	9.538	7.557	18.10	0.008058	1.565	0.416	5.22
4.................	II	7.758	6.147	14.65	0.007740	1.217	0.394	6.02
5.................	III	14.698	10.693	16.95	0.01596	2.903	1.102	9.34

Apparent Capillary Water.—The necessary data and the results on apparent capillary water are given in Table IV. The numbers in Col. 1 refer to those in Table III.

TABLE IV.—APPARENT CAPILLARY WATER IN THE HYDROGEL OF FERRIC OXIDE.

No.	Sample.	Expansion CE (cm.).	Volume of 1 cm. (cc.).	Wt. of Fe_2O_3.	Wt. apparent capillary H_2O per g. Fe_2O_3.
1 (1st freezing).......	I	4.20	0.01596	3.347	0.215
1 (2nd freezing)......	I	3.40	0.01596	3.347	0.174
2 (1st freezing).......	I	7.0	0.009748	3.565	0.205
2 (2nd freezing)......	I	6.0	0.009748	3.565	0.176
3..................	II	3.4	0.008058	7.557	0.0389
4..................	II	2.85	0.007740	6.147	0.0385
5..................	III	2.1	0.01596	10.693	0.0336

The Hydrogel of Silica.—We have shown in our first article that silicic acid ordinarily contains much capillary water which is not decreased to any extent by freezing, differing very markedly from aluminium hydroxide in this respect. We have now investigated the effect on composition and structure of heating silicic acid with water, as we have done with the hydrogels of alumina and ferric oxide.

A sample of silicic acid was precipitated from a dilute acid solution of sodium silicate by treatment with ammonia. It was washed with dilute

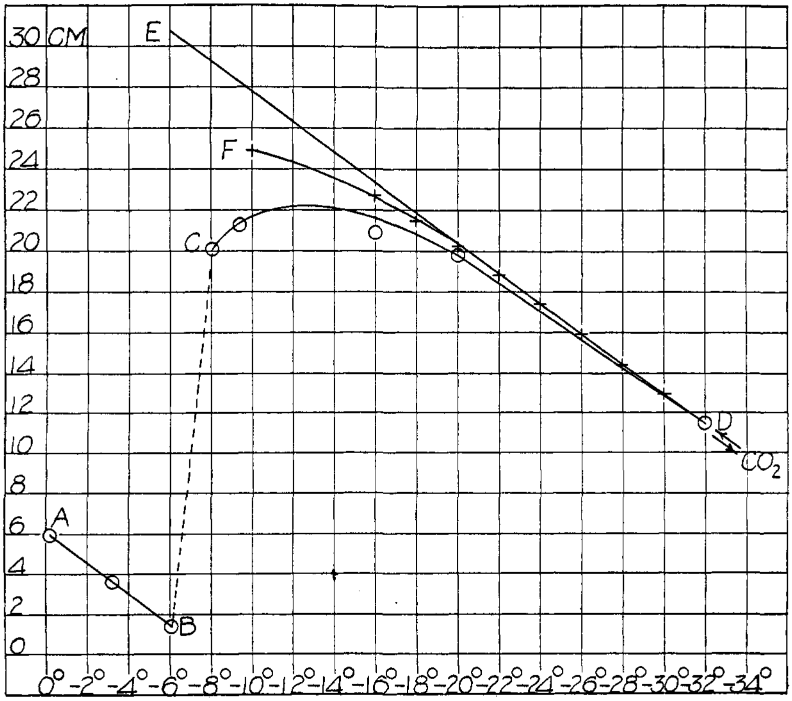

Fig. 7.—Silica—Sample I.

hydrochloric acid and then with water till free from chlorides. It was partly air-dried and used for the following samples:

Sample I. Used without further treatment.
Sample II. Digested with water for 24 hours.
Sample III. Digested with water for 7 days.

Sample I.—This was placed in the dilatometer and frozen, using alcohol and carbon dioxide to complete the freezing. This determination practically duplicated our previous ones on silicic acid, given in our former article, except that a much lower temperature was used. Duplicate determinations were made in two dilatometers. Three successive freezings gave almost identical results, the point C changing but slightly, showing that capillary water was but little affected, as we have previously observed. The curve for the last freezing in one determination is given in Fig. 7. The results are given in Table V, Nos. 1–2.

Sample II (Digested 24 hours).—After a partial air-drying, duplicate determinations were made in two dilatometers, each lot being frozen twice. The CD curves for each freezing nearly coincided below 15°, while the *DF* curves were practically identical throughout. The curve

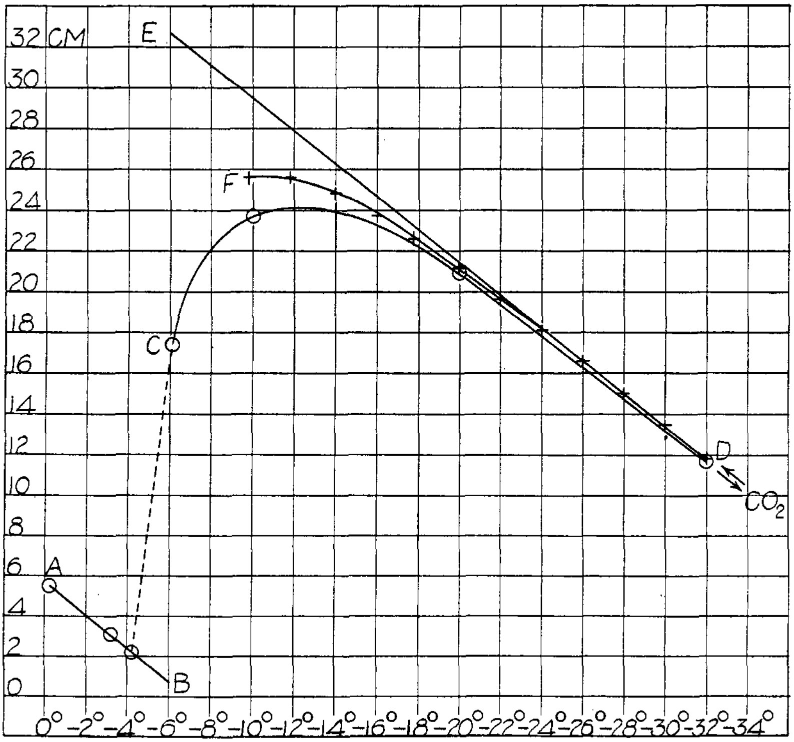

Fig. 8.—Silica—Sample II.

for the final freezing of one lot is given in Fig. 8. The results of the two determinations are given in Table V, Nos. 3–4.

Sample III (Digested 7 days).—After partial air-drying, as in Sample II, duplicate determinations were carried out in two dilatometers. Each was frozen but once. In the second determination, the material stood for about a month in a tightly-closed bottle before being placed in the dilatometer. The freezing curve for the first determination is given in Fig. 9. The results are given in Table V, Nos, 5–6.

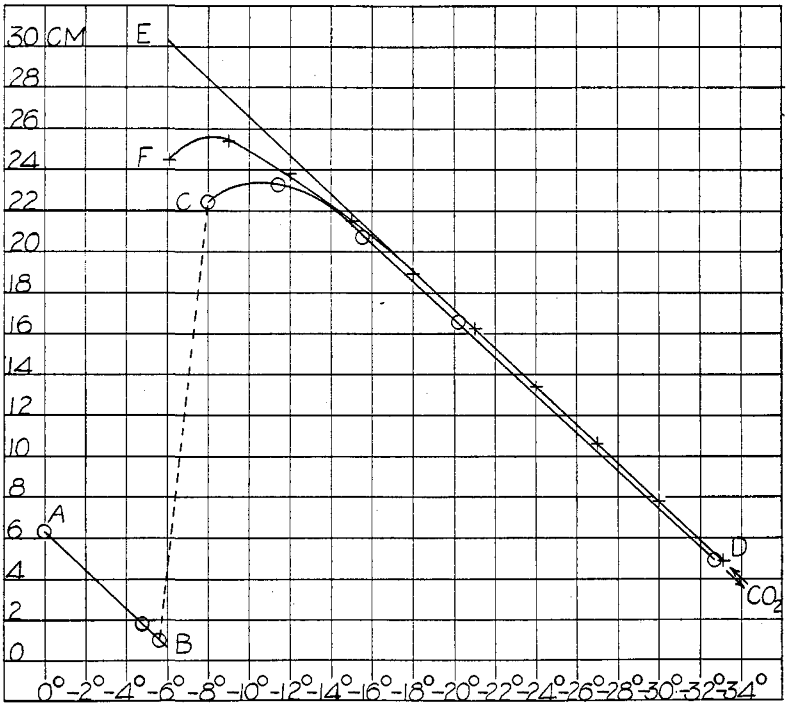

Fig. 9.—Silica—Sample III.

TABLE V.—COMBINED WATER IN THE HYDROGEL OF SILICA.

No.	Sample.	a. Wt. of hydrogel.	b. Wt. of SiO_2.	c. Expansion due to freezing (cm.).	d. Volume of 1 cm. (cc.).	e. Wt. of H_2O frozen $cd/0.0932$.	f. Wt. of combined H_2O.	% of combined H_2O $100f/b+f$.
1......	I	4.658	1.105	29.43	0.009622	3.060	0.493	30.8
2......	I	4.661	1.106	29.23	0.009786	3.069	0.486	30.5
3......	II	5.262	1.391	32.0	0.009622	3.304	0.567	28.9
4......	II	5.307	1.403	32.16	0.009786	3.377	0.527	27.3
5......	III	4.549	1.114	29.63	0.009748	3.099	0.336	23.17
6......	III	4.663	1.143	38.30	0.007740	3.181	0.339	22.87
7......	IV	2.186	0.695	13.7	0.008058	1.184	0.307	30.6

To determine whether the composition of the original silicic acid, before being heated with water, depended on its method of preparation, we have prepared a sample by hydrolyzing silicon fluoride. The latter was prepared in the usual manner from a mixture of calcium fluoride, powdered glass and sulfuric acid, and hydrolyzed by passing it into an excess of water. The resulting silicic acid was washed by decantation and on the filter. After air-drying sufficiently, the material, while still moist, was introduced into the dilatometer. This was called Sample IV. Silicic acid prepared by this method is very light and voluminous, and there was some difficulty in filling the dilatometer completely with ligroin. On the first freezing, the observations were irregular, in that CD lies above DF. The curve for the second freezing is given in Fig. 10. It will be noticed that CD and DF are very close together, but that DF is still very slightly

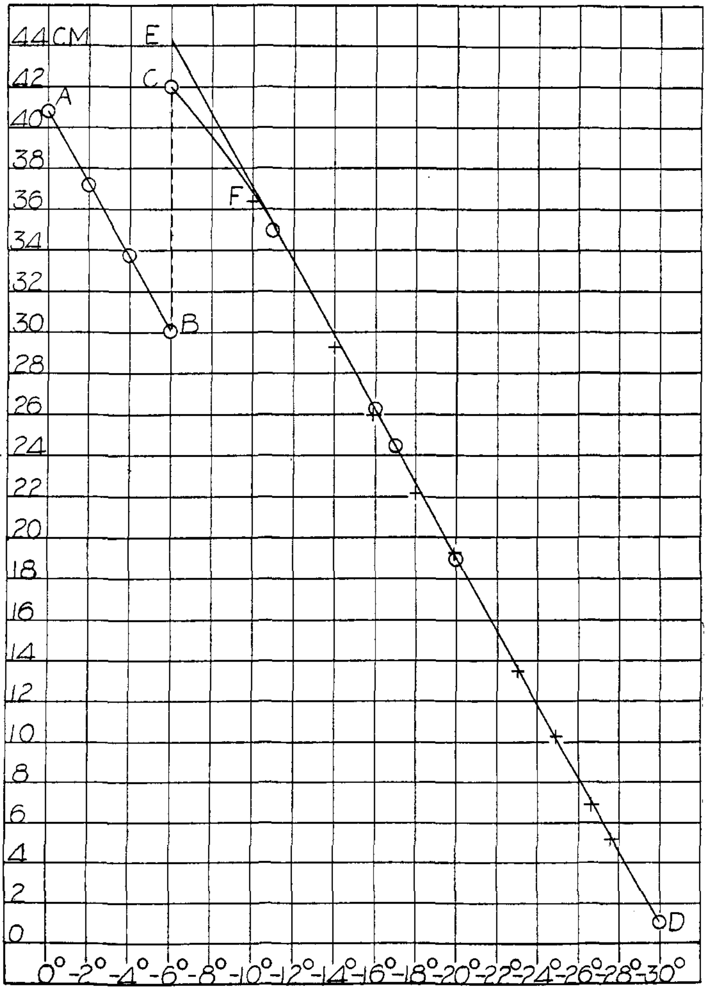

Fig. 10.—Silica—Sample IV.

below CD above —20°. We give the results on this determination in Table V, No. 7, with some reserve, as the character of the curve is unusual. There is very little capillary water, which is the more unexpected, as silicic acid prepared by this method is much more voluminous in appearance than when prepared by the other method, and we had therefore expected capillary water to be high.

We give below, in Table VI, a summary of the results obtained on combined water in silicic acid, together with the empirical formula of the material. We include the two results obtained in our previous work, which we have recalculated, using the new value for the expansion of water when freezing.

TABLE VI.

	I. Fresh.	II. Digested 24 hours.	III. Digested 3 days.	IV. Prepared from SiF_4.	Previous results. Fresh material.
Per cent. of combined water..	30.8	28.9	23.17		30.9
	30.5	27.3	22.87	30.6	32.9
Empirical formula (Av.)...	$SiO_2.1.48H_2O$	$SiO_2.1.31H_2O$	$SiO_2.1.0H_2O$	$SiO_2.1.48H_2O$	$SiO_2.1.57H_2O$

The freshly prepared material contains roughly 1.5 mols. of water, but this amount diminishes to 1 mol. when the hydrogel is heated with water for seven days.

In our previous work, we carried out one dilatometer determination on silicic acid which had previously been dehydrated over sulfuric acid and had then been rehydrated by standing over water. We were able to show that capillary water was still freezing at the lowest temperature obtained—about —33°. This demonstrated that capillary water in silicic acid thus treated was in much finer capillaries than in fresh samples which had not been dehydrated. This fact, however, prevented us from determining the amount of combined water, as all the capillary water could not be frozen. We have now made one further attempt with dehydrated material. A sample of silicic acid was allowed to come to nearly constant weight over concentrated sulfuric acid. It then contained 7.3% of water. Placed over water till practically saturated, the water content rose to 52.6%. This material was digested with water on the steam bath for three days, the object being to test the effect which this heating with water has on the exceedingly fine porous structure caused by dehydrating. The material, after digesting with water as above mentioned, was partly air-dried till it contained 53.9% H_2O, and then placed in the dilatometer. Fig. 11 gives the freezing curve. From the fact that CD and DF show no three points in a straight line, it is evident that freezing was still going on at —33°. The curve is similar to that of Fig. 12 of our previous article and corroborates the result obtained then. Heating the dehydrated material with water does not, therefore, noticeably affect its porous character. It is evident that combined water cannot be determined from this type of curve.

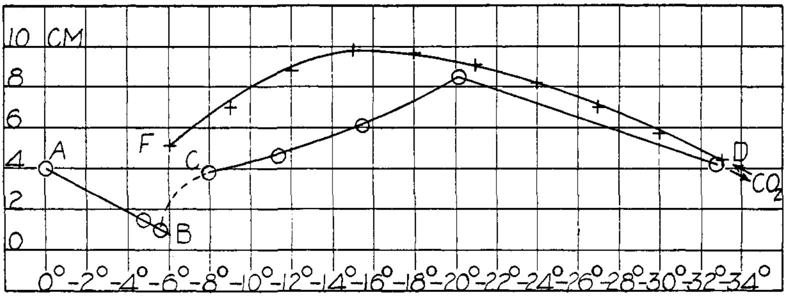

Fig. 11.—Silica and water. (Silica previously dehydrated.)

Apparent Capillary Water.—It is a difficult matter to determine the point C at —6° in the silicic acid diagram with any attempt at accuracy. Equilibrium is reached very slowly on freezing and in addition, the direction of the curve near C changes so rapidly that extrapolation is very uncertain. The results appear fairly regular at —10°, however, and we have therefore calculated the *apparent capillary water at —10°* instead of at —6°. The necessary data and the results are given in Table VII. The numbers in Col. 1 refer to those in Table V.

Table VII.—Apparent Capillary Water at —10° in the Hydrogel of Silica.

No.	Sample.	Expansion CE (cm.).	Volume of 1 cm. (cc.).	Wt. of SiO_2.	Wt. apparent capillary H_2O per g. SiO_2.
1	I	6.20	0.009622	1.105	0.58
2	I	5.95	0.009786	1.106	0.57
3	II	5.85	0.009622	1.391	0.43
4	II	6.15	0.009786	1.403	0.46
5	III	3.15	0.009748	1.114	0.295
6	III	4.0	0.007740	1.143	0.290
7	IV	0.4	0.008058	0.695	0.035

Discussion of the Results.

Combined Water.—It is evident that the results on combined water which have been given depend, for their accuracy, on freezing all capillary water present. If this is not completely frozen, the results on combined water will be high. The best evidence that practically all capillary water is frozen is shown when CD and DF (any diagram) nearly coincide in their lower portions, and DF, or its linear extrapolation, DE, is nearly parallel to AB. For if DF is parallel to AB, ice cannot be melting or the slope of DF would be less than that of AB; and if CD in its lower part coincides with DF, no ice can be forming or the slope of CD would be less than that of DF. The further the Curve DF follows and coincides with DE, which is merely the linear extrapolation of DF from D, the better, on the whole, the results on combined water should be, since the direction of DE is better fixed. An inspection of the diagrams (Figs. 1–10) will show how closely CD and DF coincide near D in the various determinations. To determine how closely DE is parallel to AB, we have calculated the ratios between the slopes of the lines DE and AB. If the lines are parallel, the ratio is evidently 1. If DE is more nearly horizontal than AB, the ratio is less than 1. The results are given in Table VIII. The numbers in the table refer to the corresponding determinations given previously in Tables I, III and V. Strictly, the lines should not be quite parallel, for, aside from any slight variation in the expansion of ligroin, at different temperatures, the expansion along AB is due essentially to ligroin and water, and along DE to ligroin and ice. The error from this source is, however, small and probably less than the errors of observation.

TABLE VIII.

Alumina.			Ferric oxide.			Silica.		
No.	Sample.	DE/AB.	No.	Sample.	DE/AB.	No.	Sample.	DE/AB.
1	I	0.99	1 (1st freezing)	I	0.92	1	I	0.99
2	I	0.98	1 (2nd freezing)	I	0.87	2	I	0.99
3	II	1.00	2 (1st freezing)	I	0.90	3	II	0.97
4	III	0.96	2 (2nd freezing)	I	0.86	4	II	0.97
5	III	0.96	3	II	0.93	5	III	0.99
			4	II	0.94	6	III	1.01
			5	III	0.96	7	IV	1.00

The ratios for alumina and for silica are all close to 1, showing that DE and AB are essentially parallel. The ratios for ferric oxide are not so good, making it probable that the values for combined water in alumina and silica are the best. Further evidence that practically all capillary water was frozen at D is furnished in those cases where the dilatometer was immersed in the alcohol-carbon dioxide bath before taking the heating curve. The volume at the temperature of D was increased but very slightly in any case, showing that no appreciable amount of ice formed in addition, even at this extreme temperature.

Obviously, combined water might be present as a definite hydrate (or mixture of hydrates) or as a solid solution of water in the oxide or some lower hydrate, and its actual behavior in the dilatometer would be the same in either case—that is, it would not freeze. From our results alone, therefore, we cannot determine definitely the condition of the combined water—whether hydrate or solid solution—but only its amount. From the amounts found, however, it may be fair to draw conclusions as to the condition.

Alumina.—The last column of Table I gives the results on combined water obtained for alumina. Sample I, which had been heated with water before use, shows about 1.7% less water than the others. Two other samples—one nineteen months old and the other fresh—show a nearly constant amount of combined water. The average is 37.83. The compound $Al(OH)_3$ contains 34.6% water. The three samples therefore show an excess of from 1.5 to 3.2% of water above the amount required for this hydrate. This can hardly be due entirely to experimental error. For instance, it would correspond to an error of 1.3 cm. expansion in the dilatometer on the first determination. Rather, the excess over 34.6% appears to be due to water in solid solution. For the condition of the rest of the water, we have no direct evidence. It is suggestive that of the minerals gibbsite, $Al_2O_3.3H_2O$, bauxite, $Al_2O_3.2H_2O$ and diaspore, $Al_2O_3.H_2O$, only the last commonly occurs in a well-crystallized condition, the others being usually amorphous deposits which are therefore probably of the same character as the hydrated material we have investigated, but containing less water.

Ferric Oxide.—If we consider all the results obtained for combined water in ferric oxide (Table III), it is difficult to avoid the conviction that no well-defined compound of precipitated ferric oxide and water exists, which contains more than 0.5 mol. of water. In our previous work, we found the combined water in a fresh sample of ferric hydroxide to be somewhat over 30%, the value being uncertain owing to the large proportion of capillary water freezing at low temperatures. The combined water found after heating the precipitate for 24 hours, 21.3%, corresponds to the empirical formula $Fe_2O_3.2.4H_2O$. After heating for three days, combined water was 5.6%, corresponding to $Fe_2O_3.0.53H_2O$, while when heated for twelve days and coagulated with ammonia, the precipitate contained 9.3% of water, corresponding to $Fe_2O_3.1.04H_2O$. In the latter case, the fresh precipitate which formed when ammonia was added undoubtedly increased the combined water, which happens to fall close to one mol. So far as the results show, combined water is slowly given off on heating the precipitate with water, with no tendency toward simple ratios between ferric oxide and water. When once dehydrated, the material shows no tendency to take up water to form definite hydrates, for the results of successive determinations of combined water in the dilatometer are practically constant. The evidence all points, rather, to a combination between ferric oxide and water in indefinite proportions, which is essentially a case of solid solution.

Silica.—The results on silicic acid which has not been heated, give fairly constant results, combined water amounting to somewhat over 30% (see Tables V and VI). On digesting with water, the amount of combined water falls off until after seven days it reaches one mol. It will be seen that the evidence, while not conclusive, strongly suggests that a part of the water in all three hydrogels is combined in indefinite proportions.

It appears to be possible, by combining the results which we have obtained with those obtained by others, to draw somewhat more definite conclusions as to the water which we have called combined. The results of van Bemmelen, Zsigmondy, and others, have shown that the vapor pressure of hydrogels is a continuous function of composition at a fixed temperature, and that dehydration does not in general take place in stages. The results show the behavior of the water as regards vapor pressure and these investigators have made it extremely probable that both capillary and combined water are present, but no conclusions as to the amounts of each can be drawn.[1] Our own results give the amounts of combined and of capillary water, but no information as to the behavior of the combined water. From both sets of results, however, the amount of combined water and its behavior can be obtained.

The data of others on vapor pressure cannot always be used in connection with ours on composition, since much of the work on vapor pressure has been done on material which had first been dehydrated to a large extent over sulfuric acid and then been rehydrated by standing over water. It is just this material which, as our results have shown (Fig. 11), retains its water in such fine capillaries that it is very difficult to freeze and no reliable data on combined water can be obtained. Bachmann and Anderson,[2] consider all water taken up in this way by silica as capillary in character. Vapor-pressure isotherms on material which had not been previously dehydrated have, however, been carried out by van Bemmelen for silicic acid[3] and for ferric hydroxide[4] and by Zsigmondy, Bachmann and Stevenson[5] and Anderson[2] on silicic acid. The isotherm for aluminium hydroxide does not appear to have been determined.

When a moist hydrogel is allowed to dry, it is obvious that free water will first be removed, since it has a higher vapor pressure than either capillary or combined water. When free water is removed, there appear to be two possibilities. Either (*a*) capillary water will be entirely removed, followed by combined water, or (*b*) capillary water will be partly removed followed by combined water. The first case is the simpler. It would obviously take place if the vapor pressure of all capillary water were greater than that of combined water. If this case were true, the vapor pressure due to capillary water would gradually fall as the material was dehydrated until only combined was left. The composition at this point could be found directly from our determinations. The form of the vapor-

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[1] We refer to the water in material which has not been previously dehydrated. In the case of silica, Bachmann (*Z. anorg. Chem.*, **79**, 202 (1913)) and Anderson (*Z. physik. Chem.*, **88**, 191 (1914)) have shown that when previously dehydrated over sulfuric acid, the water taken up again is probably all capillary in character.

[2] *Loc. cit.*

[3] *Z. anorg. Chem.*, **13**, 233 (1897).

[4] *Ibid.*, **20**, 185 (1899).

[5] *Ibid.*, **75**, 189 (1912).

pressure curve would then determine the character of the combined water. If horizontal, the vapor pressure is of the type shown by ordinary hydrates and we should be forced to conclude that such definite hydrates were present. If variable with composition, another degree of freedom is present, indicating a solid solution with but one solid phase. We were at first inclined to consider this case as the only one possible. There seems, however, to be no reason why capillary water should all have a higher vapor pressure than combined water as the two are entirely independent. It appears, therefore, entirely possible that combined water may begin to be removed before all capillary water is gone and in this case it is evident that our data on combined water will not show the composition in the vapor-pressure isotherm, where combined water begins to come off. However, in case the vapor pressure of the combined water exceeds that of the capillary, a part of the vapor pressure isotherm will be due to combined water only, and if definite hydrates exist, there should be a horizontal part of the curve, while if there are no definite hydrates, no part of the vapor-pressure curve should be horizontal. The fact is that all hydrogels of silica and of ferric hydroxide give a continuous curve of vapor pressure. Van Bemmelen showed, for silicic acid, that a part of the dehydration curve ran somewhat more nearly horizontal than the parts on either side of it, but he never regarded the curve as horizontal and subsequent investigations by Anderson,[1] and by Zsigmondy, Bachmann and Stevenson,[1] who used an improved method, have shown that this part of the curve is more inclined than van Bemmelen found it. The evidence all goes to show, therefore, that whether the vapor-pressure curve of combined water lies entirely below that of capillary water, or whether the two curves intersect, the form of the vapor pressure as determined precludes the existence of definite hydrates,[2] so that the combined water of silica and of ferric hydroxide is to be regarded as of the nature of water in solid solution. It ought to be stated that van Bemmelen repeatedly emphasized the conclusion, derived from his vapor-pressure curves, that definite hydrates do not exist, but his results did not show what part of the water was combined.

It has been shown by Tammann[3] that zeolites behave like hydrogels in that the vapor-pressure isotherm is a continuous function of composition. In this case, the original material is a crystalline compound of definite composition and Tammann considers that the partially dehydrated material is a solid solution of the hydrate and the anhydrous oxides. It may also be considered a solid solution of water in the anhydrous

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[1] *Loc. cit.*

[2] Vapor pressures are so low on material which is largely dehydrated that no conclusions can be drawn in regard to the existence of hydrates containing but little water.

[3] *Z. physik. Chem.*, 27, 323 (1898).

oxides. In the same way, hydrogels may be considered as solid solutions of a hydrate in the anhydrous oxide or—as we have done—as solid solutions of water in the oxide. This point cannot be decided. It is like the problem whether pyrrohotite is to be regarded as a solid solution of sulfur or of pyrite in ferrous sulfide; or whether the product obtained by heating iron at a high temperature with carbon is a solid solution of carbon or of iron carbide, in iron. In the case of hydrogels, however, there is no tendency to give a definite hydrate containing the maximum amount of water, which is the case with zeolites, and the simpler assumption appears the better.

Apparent Capillary Water.—Our observations on capillary water have mainly been incidental to the determination of combined water, but so far as they go, they confirm the results obtained in our former investigation and show, in addition, the effect of heating the hydrogels with water.

Alumina (Table II).—The capillary water remaining in the sample after heating with water is very small (Nos. 1–2). All samples when frozen more than once show a decrease in capillary water on the second freezing.

Ferric Oxide (Table IV).—The capillary water is decreased slightly by repeated freezing (Sample I) but long-continued heating decreases the amount to a much greater extent (Samples I–III). The value found for freshly precipitated ferric hydroxide in our first investigation, was 0.45 g. H_2O per g. of Fe_2O_3.[1] On heating twenty-four hours, the amount fell to 0.215 g. and finally to 0.0336 g. on much longer heating.

Silica (Table VII).—In general, capillary water is not eliminated by freezing. Instead, water appears to be reabsorbed when the ice has melted and the point C in the silica diagrams varies but little in successive freezings, differing in this way from aluminium and ferric hydroxides. The amount of capillary water per g. of silica is decreased by digesting on the steam bath. This is evident from the values in the last column of Table VII. The silica prepared from silicon fluoride (No. 7) contained but little capillary water and this was all frozen at —10°.

It appears probable that the freezing method which we have developed may be used to determine the condition of water—whether free, combined or capillary or absorbed—in substances other than inorganic hydrogels. Its most obvious application is to organic hydrogels whose solubility in water is small. Capillary water and water containing soluble substances behave similarly on freezing, so that solutions and hydrogels together offer a more complicated case. Its application to biological problems is suggested by the work of Miller-Thurgau[2] and Fischer[3] and his co-workers.

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[1] This value was not published but may be derived from the diagram.

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

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

Our method might also be used in investigating the conditions of water in soils.

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

NEW HAVEN, CONN.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF WISCONSIN.]

THE MEASUREMENT OF CRYOSCOPIC CONSTANTS AT ELEVATED TEMPERATURES.

BY J. HOWARD MATHEWS.

Received March 27, 1917.

All of the really accurate work on freezing-point constants to be found described in the literature has been limited to measurements made on substances having rather low melting points, where temperature control of the surroundings is easy. Obviously it is highly desirable that we have at our disposal a method capable of giving the same degree of accuracy in measurement for solvents which have comparatively high melting points.

While it is true that a considerable amount of cryoscopic work has been done with solvents having higher melting points, a critical examination of the methods used reveals the fact that no very high degree of accuracy can be claimed. In most cases the methods have been very crude indeed, while even in those where more care was taken it is evident that the methods used leave much to be desired in the way of precision. Brief mention will be made of some of the methods previously used.

Tolloczko[1] worked with antimony trichloride, whose melting point is 73.2°, using the ordinary form of Beckmann freezing-point apparatus the outside of the water mantle being wrapped with asbestos to keep the temperature constant. This is a fair example of the methods that have been used by a number of investigators. A considerable inprovement in experimentation was made by Auwers,[2] who reported a number of determinations in which the highest freezing point studied was that of benzil, which is 94°. He used the ordinary Beckmann apparatus, but surrounded it by a constant temperature bath, which was of course a great advance over the arrangement used by Tolloczko. Eykmann[3] made a large number of measurements with his depression bottle. This bottle, or "depressimeter," is not surrounded by a bath at constant temperature and has no device for stirrring the contents (except shaking by hand), yet its sponsor considered it to be accurate to 0.01°.

A considerable amount of cryoscopic work with organic solvents has

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[1] *Z. phys. Chem.*, **30**, 705 (1899).

[2] *Ibid.*, **18**, 595 (1895); **30**, 300 (1899); **32**, 55 (1900).

[3] *Z. phys. Chem.*, **2**, 964 (1888); **3**, 113 and 203 (1889); **4**, 497 (1889).