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THE PROPERTIES OF PURE HYDROGEN PEROXIDE. I.

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There are few chemicals which have found a greater variety of uses than hydrogen peroxide. Every year the literature becomes enriched with papers dealing with reactions in which hydrogen peroxide in dilute solution plays an important part. On the other hand, the properties, both physical and chemical, of pure hydrogen peroxide are for the greater part unknown and the accuracy of those properties which have been tabulated is subject to doubt. The present paper deals with the preparation of pure anhydrous hydrogen peroxide and the determination of some of its properties.

To treat hydrogen peroxide historically and describe its multitudinous reactions in dilute solution would fill several volumes and would not come within the scope of this paper. It will therefore be most convenient in the following account of the various steps in which hydrogen peroxide was purified and its properties investigated, to refer at each stage to any previously published work which suggests similarity to that being discussed.

What might be termed the "raw product" from which the pure hydrogen peroxide was to be derived consisted of a 3% solution prepared from commercial barium peroxide in the ordinary way. The principal impurities were sodium sulfate, phosphoric, sulfuric and hydrochloric acids and traces of several inorganic salts. This 3% solution was concentrated to 30% by means of the sulfuric acid concentrator[1] described in another paper, a yield of 95% being obtained. The details of various yields obtained under different conditions of temperature and pressure are of no particular scientific interest but may be made the subject of a separate paper in an industrial journal.

Subsequent purification of the hydrogen peroxide from the 30% solution was effected in 3 stages: (1) distillation to remove non-volatile impurities; (2) concentration of the 30% solution (now pure) to 90%; (3) separation of pure hydrogen peroxide out of this concentrated solution by fractional crystallization.

The first stage required considerable development as the 30% solution was found to be very unstable. This was due to the fact that all the impurities had been concentrated as well as the hydrogen peroxide. Generally, the decomposition at room temperature was found to average 1% per day so that, up to the moment when they were to be distilled, the solutions were kept at 0°, at which temperature the rate of decomposi-

[1] THIS JOURNAL, **42**, 2571 (1920).

tion is much less. A sulfuric acid pump[1] was used in the distillation in order that during this process the pressure might be kept at a minimum.

Fig. 1 is drawn to scale, and shows the relative sizes of Distilling Flask B, Receiver G and barrel of sulfuric acid Pump M. The volume of the latter is some 6 liters, this being more than 3 times the volume of all the rest of the apparatus to be evacuated. The sulfuric acid pump is regulated by a control valve[2] leading to J, O being connected to a Geissler water-pump, O N acting as a sulfuric acid seal. The reservoir K is filled with commercial sulfuric acid (95%), one filling being sufficient for innumerable distillations. D is a water condenser and is connected

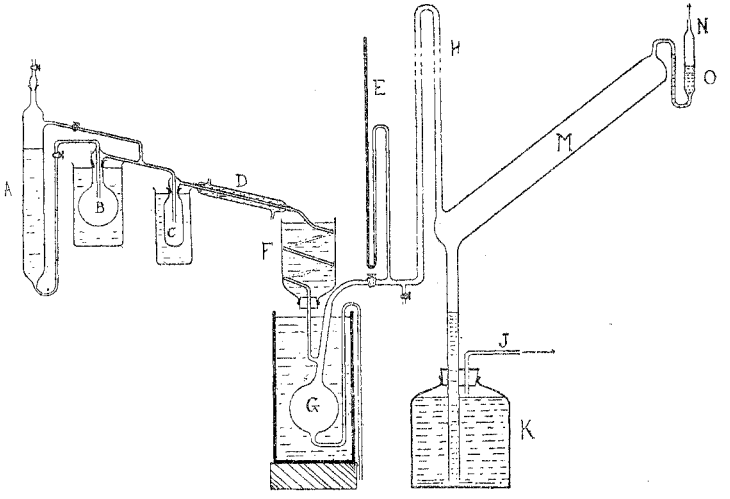


Fig. 1.

to a spiral, F, and a receiver, G, both of which are placed in vessels filled with ice. The tubing H connecting the receiver G to the sulfuric acid pump is about one cm. in diameter, the height of H being the barometric height in terms of sulfuric acid. A manometer, E, indicates the pressure at any moment. The distilling flask, B, with ground glass neck, has a volume of about 300 cc. and is heated by means of a water-bath. In the first experiments, 200 cc. of the 30% solution was placed directly in this flask at one time. The apparatus was constructed wholly out of glass tubing.

The sulfuric acid pump works automatically, going through one cycle in less than one minute with the aid of a small electric pre-evacuator connected through the valve to J. The water-bath is heated to about 60° so that this is the maximum temperature reached by the hydrogen

[1] O. Maass, THIS JOURNAL, 41, 53 (1919).
[2] *Ibid.*

peroxide solution during the distillation. At first the distillation takes place without a great loss of hydrogen peroxide due to decomposition. The solution gradually becomes more concentrated, the impurities concentrating more rapidly than the hydrogen peroxide, which, at the temperature of the distillation and under a pressure of one cm., vaporizes with the water and is condensed in the receiver. Towards the last, the impurities are concentrated to such an extent that they are precipitated in the solid form along the sides of the distilling flask. Then a certain amount of decomposition takes place. It is here that the value of the sulfuric acid pump becomes evident for it is possible to keep the pressure below one cm. of mercury in spite of the oxygen liberated. Any oxygen liberated is in an active form and mercury or any other metallic substance is corroded and the oil of a rotary pump thickens—another reason why the sulfuric acid pump is a desirable one to use.

For a while the distillations were carried out in the manner described above. Analysis of the distillate showed a 60% yield. It was found that the 40% loss was not due to decomposition alone, examination of the gelatinous residue in the distilling flask showed the presence there of a fairly large amount of hydrogen peroxide, suspected of being held in the form of hydrogen peroxide of crystallization by the sodium sulfate. It was found impossible to drive off this hydrogen peroxide without having to heat it to a temperature where vigorous decomposition resulted.

An attempt was made to increase the yield of hydrogen peroxide by what may be termed a vacuum steam distillation. A vessel, A, filled with water, was connected to the distilling flask B in the manner shown in the diagram. During the latter part of a distillation, when the solution had become very concentrated, the proper tap was opened slightly. The water entering the distilling flask was immediately vaporized, as the pressure in the apparatus was below the vapor pressure of water. Consequently a stream of water vapor was bubbled through the solution, the object being to displace the hydrogen peroxide. A fair measure of success attended this innovation, and the yields rose to 75%.

A further improvement was made by heating the empty distilling flask, B, to 65° and placing the hydrogen peroxide solution in A from which it was admitted into the heated flask drop by drop at the rate at which it evaporated. Thus the major portion of the distillate was kept cool during the greater part of the time of distillation. The yield was increased considerably, being over 90% in many cases. Three hours are required for the distillation of half a liter. Furthermore, it was found advisable to place a trap between distilling flask and the water condenser. This trap (C in Fig. 1), a thin-walled wash-bottle, was heated continuously to a temperature of 70°. This temperature, somewhat higher

than that in the distilling flask, prevented the condensation of any hydrogen peroxide. The function of the trap is of course to catch any small drops of liquid which might be carried along during the distillation.

A few further particulars of the precautions taken to insure the absolute purity of the hydrogen peroxide solution may be in place. The tap leading from A to the distilling flask B (by means of which the speed of entry of the hydrogen peroxide was regulated) was not greased. The same applies to the ground glass joints fitting into the tops of Flasks B and C. The latter were immersed in the heating water to such an extent that the ground glass joints were below the surface. The leak from the outside was negligible, as especially well-fitting joints had been chosen; the slight quantity of water working through was also distilled over, but the absence of tap-grease made certain that no organic impurity would find its way into the distillate. The bottom of Receiver G was connected to a glass tube as shown in the diagram, the end of the tube being sealed off before the distillation. After the distillation, this end of the tube was filed off and the peroxide forced out of the receiver by air pressure into the vessel in which it was to be stored. Thus, at no time during the distillation, or afterwards, was the peroxide brought into contact with any material except glass. Previous to a distillation, the whole apparatus was filled with chromic acid cleaning mixture by suction. The cleaning solution was removed after a few hours and the whole apparatus flushed out with distilled water until it was certain that no trace of the cleaning mixture remained.

A qualitative analysis of the distillate showed the absence of all non-volatile impurities. Sulfuric acid was also shown to be absent, but, in those cases where the original peroxide solutions contained large amounts of chloride, a small amount of hydrochloric acid was invariably present in the distillate. In order to prevent this, the concentrated peroxide solution was made slightly alkaline with sodium hydroxide before submitting it to distillation. This procedure removed the last impurity; it was found that the distillate was now absolutely pure, although the yield was cut down considerably.

The first stage in the purification of hydrogen peroxide may be summed up by saying that if the experimental methods described above are followed, it is possible to distil 30% impure peroxide solutions, the distillate being absolutely pure and corresponding to an 85% yield.

The second stage in the process of reaching 100% hydrogen peroxide is carried out as follows. The smaller of the 2 flasks in the sulfuric acid concentrator[1] was reserved for the concentration of the pure solutions. This flask had been especially cleaned with a hot chromic acid solution and had then been scrupulously washed out with distilled water. The

[1] THIS JOURNAL, 42, 2571 (1920).

concentration of *pure* hydrogen peroxide solutions can be carried out by means of the sulfuric concentrator without any loss whatever due to decomposition because concentrations can be rapidly carried out at low temperatures; attention was drawn to this factor in the description of the pump.

There is, however, an inevitable loss of hydrogen peroxide due to evaporation. As the solution becomes more concentrated in hydrogen peroxide, the partial vapor pressure of the peroxide itself, relative to the water-vapor pressure, becomes appreciable and, therefore, a portion finds its way into the sulfuric acid together with the water vapor. But this source of loss is also dependent on the temperature of concentration and therefore pressure. The lower the temperature, the greater is the difference, apparently, between the relative vapor pressures of water and hydrogen peroxide.

At this stage it might be well to refer to Wolffenstein,[1] who was the first to concentrate hydrogen peroxide by means of vacuum evaporation. Wolffenstein reported fairly large losses when concentrations were carried out to a high percentage concentration of peroxide in the concentration of pure solutions. Thus he obtained only a 28.3% yield when he concentrated 802 g. of 4.5% peroxide to 66.6%. The following example, taken at random from our experiments, shows in comparison what the sulfuric acid concentrator can do. 582 g. of 24.3% hydrogen peroxide was concentrated to 91.1%, 102 g. of this solution corresponding to a 65% yield being obtained. Thus, starting with a much larger quantity of peroxide (a solution containing 141 g. as compared to Wolffenstein's solution which contained 36 g.) 2.5 times the yield was obtained and the peroxide concentrated to a higher degree (91% as compared to 66%). The time required for the concentration in the example cited above was 4 hours, the temperature of the solution remaining below 0°.

The above is a typical example of the results obtained during this stage. The 30% pure peroxide solutions are concentrated to 90%, a yield of 65% being obtained. It is not advisable to try to concentrate the peroxide above this point as the loss becomes enormous. Around 98% the proportion of peroxide lost due to evaporation approaches the amount of water driven off, so that no gain is made. Apparently it is impossible in this way to dehydrate hydrogen peroxide completely.

There now remains a discussion of the last stage, which bears a similarity to a method employed by Ahrle[2] for obtaining strong concentrated solutions. Ahrle concentrated perhydrol (30% solution) to 85%, and some 50 g. of this solution was cooled to a temperature where the hydrogen peroxide crystallized out, the supernatant liquid was removed, the

[1] Wolffenstein, *Ber.*, **27**, 3307 (1894).

[2] Ahrle, *J. prakt. Chem.*, **79**, 129 (1909).

remaining crystals melted, and they were then subjected again to this same process. The quantity remaining was taken as being pure, and probably was sufficiently so for the purpose for which it was made, namely, the preparation of Caro's acid. Outside of the preparation of this acid, no further experiments were carried out by Ahrle with the hydrogen peroxide, and in view of the experiments to be described, it is doubtful if the hydrogen peroxide obtained in the above cited investigation was absolutely anhydrous.

After many attempts to obtain pure hydrogen peroxide from the 90% solution by crystallization, the following technique was devised. 100 g. of solution was placed in a large tube which was itself placed in a cooling mixture in a Dewar flask. A continuous stream of dried air was sent through a glass tube of small diameter leading through its cooling mixture to the bottom of the solution. The latter was thus kept stirred. The temperature indicated by a thermometer was then regulated to be one degree below the freezing point of the solution.[1] The latter was then inoculated with a crystal of hydrogen peroxide, and the temperature of the cooling bath was lowered until half the solution had solidified; the solution being stirred vigorously during this procedure. The crystals were finally allowed to settle, the supernatant liquid poured off, and the crystals and absorbed liquid transferred to another glass tube perforated by fine holes in the bottom. The transference was effected in a few seconds, crystals adhering to the side of the first test-tube having been melted by the warmth of the hand. The crystals were pulled out by a glass rod with a hook at the end.

A larger tube constituted an outer jacket for the perforated tube to which suction was applied by means of a side arm. Dried air entered the inner tube and carried the liquid adhering to the crystals into the outer jacket. The crystals meanwhile were pressed down by means of a glass rod flattened out at the bottom. The whole apparatus previous to the admission of the crystals was cooled in an ice-bath.

Vessel A, with the crystals, was then removed from B and was suspended in a beaker, and the crystals allowed to melt. The first few drops were added to the liquid collected in B to which was also added the supernatant liquid poured off from the crystals. The tube containing the melting crystals and the beaker into which they were melting were enclosed by a large bell jar containing also a desiccating agent; this precaution being necessary to prevent the solution from taking up moisture from the air during the time required for the crystals to melt.

The solution was thus separated into 2 portions—one concentrated and the other dilute. One might have expected that the concentrated solu-

[1] See freezing-point curve. O. Maass and O. W. Herzberg, THIS JOURNAL **42**, 2569 (1920).

tion, formed from the dry melted crystals, would approach 100%, but when carried out under the conditions described above, the concentration was only of the order of 4%, the solution having increased in concentration from 90 to 94%. This degree of concentration was still less without the precautions described above. The stirring of the solution during crystal formation was essential.

A number of results obtained may be worth while giving as showing the stepping up of the concentration of the solution.

% H_2O_2 in solution.	% H_2O_2 in melted crystals.	% H_2O_2 in mother liquor.
91.1	95.3	86.9
86.9	92.0	81.9
88.2	93.4	82.0
93.4	97.4	88.2
92.0	96.8	88.0
95.0	98.3	91.9
96.8	99.0	94.0
98.7	99.9	93.0

A systematic fractional crystallization was devised to utilize all available stock to obtain the highest percentage. Starting with 100 g. of 90% solution, 50 g. of 94% and 50 g. of 85% are obtained. This is repeated with another 100 g. of 90% solution. The 2 portions of 50 g. each of the 85% solution are united, and by crystallization 50 g. of 82% and 50 g. of 90% solution are obtained. The 2 portions of 94% are also united and give 50 g. of 97% and 50 g. of 90%, and so on. Thus 400 g. of 90% solution gave 50 g. of 100%, 50 g. of 97%, 50 g. of 94%, 50 g. of 90%, 50 g. of 86% and 150 g. of 82%. After having obtained these solutions, a fresh portion of 90% is separated completely into 2 end products 100% and 82%.

In practise, of course, the crystallizations are not controlled with the exactitude which the diagram would indicate, but a variation takes place due to the variation in relative amount of crystal and solution. However, the various solutions are united according to the scheme described above, which in the end results in the same thing.

Any impurities which may have found their way into the hydrogen peroxide will accumulate in the 82% solution. After a certain amount of this solution has been collected, it is distilled and then reconcentrated. There is no real loss in hydrogen peroxide during this third stage of the process except that sticking to the sides of the glass vessels.

Now that the various stages in the preparation of the anhydrous hydrogen peroxide have been described, it is possible to discuss the process as a whole. The limits of the various stages are not chosen in a haphazard manner, but were chosen with the object of obtaining the optimum yield, the time factor being taken into account. First, the impure 3% solutions are concentrated to 30%. If this concentration is carried further,

say to 50%, the impurities are concentrated to such an extent that a rapid decomposition sets in during the last part of the concentration. On the other hand, it is essential to have as small a bulk as possible when it comes to the actual distillation. If concentration is stopped at 10% instead of 30%, the time of distillation is increased and the decomposition during the distillation is tripled. It pays to carry out the first concentration to just about 30%. From the freezing-point curve it is evident that the concentration must be carried out to at least 80% before the crystallization procedure will give any results at all, and since it is the most cumbersome it is best to start crystallizing with solutions as highly concentrated as possible. On the other hand, concentrating a hydrogen peroxide solution above 90% is attended by high losses due to the vapor pressure of hydrogen peroxide itself so that 90% is perhaps the best concentration with which to end the concentration *in vacuo*.

The time required for the process is an important factor. The concentration of a liter of 3% solution requires 3 hours. The product of 4 such concentrations is distilled at one time, the distillation requiring about 3 hours. About 500 g. of the pure distillate is concentrated to 90%, 5 hours being allowed for the actual concentration. The crystallization is the most tedious, 4 or 5 sets of apparatus as described being required, so that several crystallizations may be carried out at once. The time for each crystallization may be put at 4 hours, the crystals taking a long time to melt completely.

The need of great cleanliness is essential throughout the work. The hydrogen peroxide solutions are allowed to come in contact only with glass. This glass, be it the receiver in the still or the thermometer used during crystallization, is treated with hot chromic acid solutions with subsequent washing with distilled water.

As regards the methods of analysis used, a few words may be in place. The silver test for chloride works in the presence of excess of nitric acid, the latter preventing the formation of silver oxide. The barium test can be used for the detection of sulfuric acid. Another qualitative test which is applied is the evaporation of the solution to dryness in a platinum evaporating dish to see if a non-volatile residue remains.

The amount of acid present in hydrogen peroxide solutions can be measured in the ordinary way with phenolphthalein as indicator, the hydrogen peroxide having no effect on the end-point up to 20% concentration.

The strength of hydrogen peroxide was measured by means of potassium permanganate solutions, carefully standardized by means of several samples of potassium tetra-oxalate of known purity. The use of potassium permanganate is objectionable in the presence of foreign substances, but gives perfect results in the case of pure aqueous solutions.

The experiments dealing with anhydrous hydrogen peroxide which will be described later on were carried out with a sample which had been obtained after many crystallizations as described above. The analysis of the final product, about 200 g., was carried out in this fashion. Portions weighing between 0.2 and 0.5 g. were transferred to a carefully weighed weighing bottle. This was weighed to 0.1 mg., the contents diluted with water and then transferred into an Erlenmeyer flask. The weighing bottle was washed out a number of times, the solution diluted to some 500 cc. and the requisite amount of sulfuric acid added. The permanganate solution was then added to the end-point, obtained under the same conditions as the conditions of standardization. One cc. of permanganate solution corresponded to 0.005070 g. of hydrogen peroxide, and hence the concentration could be determined to one part in 3000. The following percentages of hydrogen peroxide were obtained when the end product of all the crystallizations was analyzed: 100.02%, 99.89%, 99.91%, 99.90% and 99.94%. It may be stated here that it was the above sample which was used in the determination of the physical constants as will be described further on.

Brühl,[1] chiefly interested in determining its refractive index, prepared hydrogen peroxide by concentration alone (that is, continued evaporation *in vacuo*); his best sample, he claimed, showed 99.2% peroxide. Apart from the great losses attending this method, it is doubtful whether complete separation from water based on a fractional distillation method is possible; one need only draw attention to the futility of attempting to prepare anhydrous ethyl alcohol or anhydrous sulfuric acid by distillation. Brühl determined the refractive index, density and freezing point. These were the only properties of pure hydrogen peroxide known up to the present to which any reliability whatever could be attached, and the values obtained by Brühl will be referred to later on in comparison with those obtained by the authors.

The work described so far may be summed up as follows. Starting with commercial 3% hydrogen peroxide solutions, containing many impurities, it has been shown how the pure hydrogen peroxide can be isolated. The methods present several novel features, and a 50% yield of pure hydrogen peroxide is possible. In view of what has been said it is probable that the end product obtained was purer than any previous preparation.

Properties.

Freezing Point.—Brühl had found that the freezing point of his peroxide was —2.0°. The value found by the authors was 0.3° higher, namely, —1.70°. The determination was made by means of a Beckmann thermometer which was directly immersed in some of the pure peroxide

[1] Brühl, *Ber.*, **28**, 2854 (1895).

placed in a test-tube. The proximity of the freezing point of hydrogen peroxide to the freezing point of water made the calibration of the Beckmann thermometer a simple matter.

The freezing point of a 96.7% peroxide solution was also determined, and found to be —4.00°. Inserting these 2 values in the freezing-point curve, determined in a former piece of work,[1] it will be seen that dt/dc decreases with increased concentration.

Hydrogen peroxide can be supercooled more readily than water; a temperature of —30° has been reached before the solid phase separated out.

Density.—The density of liquid hydrogen peroxide was determined by the dilatometer method. A bulb having a capacity of about 10 cc. was blown at the end of a capillary tube which was graduated in mm. One cm. length of this capillary tube was found to correspond to a volume of 0.09627 cc. It was therefore easy to calibrate the volume of one part in 10,000. The position of a meniscus between two millimeter marks was found by means of a microscope with a scale and cross hair in the eye-piece, with an accuracy of one part in 20. The bulb and stem were immersed in a glass-walled thermostat whose temperature could be regulated to 0.1°. The reading of the meniscus was naturally taken while the bulb was immersed in the thermostat.

The calibration was carried out with water after the bulb had been well seasoned. Water was deemed preferable to mercury because of the exact similarity of its meniscus to that of hydrogen peroxide, thus making unnecessary any corrections. The bulb could be easily filled with liquid by means of a glass tube drawn out into a fine capillary.

The densities tabulated below were corrected to a vacuum. The total weight of the liquid in the bulb was 15.2575 g.

Temperature. °C.	Volume. Cc.	Density.
—12.13	10.3272	1.4774
— 9.80	10.3436	1.4751
— 8.38	10.3561	1.4733
— 6.23	10.3754	1.4705
— 2.85	10.3973	1.4674
— 0.53	10.4235	1.4638
+ 0.10	10.4295	1.4631
1.20	10.4379	1.4617
3.00	10.4523	1.4597
5.55	10.4716	1.4570
8.30	10.4928	1.4541
12.60	10.5294	1.4490
15.30	10.5476	1.4465
19.90	10.5814	1.4419

The graph (Fig. 2) shows the variation of the density with the temperature, the decrease in density per degree rise being 0.001075 on the

[1] See graph. O. Maass and O. W. Herzberg, THIS JOURNAL, **42**, 2570 (1920).

average. It is evident that the temperature coefficient is very large when compared to that of water. The possible source of error which at once suggests itself is a slight decomposition during the course of the measurement, the resulting bubbles of oxygen adhering to the sides of the tube. In the first place, not the smallest sign of such a bubble was visible. A large number of the density determinations were made at successive lower temperatures and a slight decomposition would result in a temperature coefficient smaller than the true one being found. The value at +0.1° was obtained first, and, after the other densities had been determined, the temperature was readjusted to the proximate temperature —0.53°. As is seen from the values of the 2 densities at these 2 temperatures no possible change in volume could have been caused by decomposition during the course of the experiments.

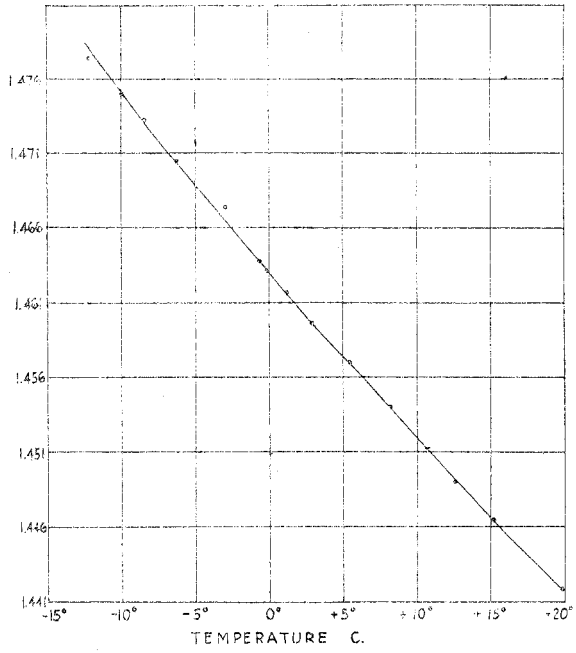


Fig. 2.

As was mentioned above, Brühl determined the density of his hydrogen peroxide. His value at 0° of 1.4584 is the closest to those obtained above, *viz.*, 1.4632 at 0°. His other determinations are obviously inexact.

Brühl's values.

Temperature. °C.	Density.
0	1.4584
14	1.3955
18.7	1.4262
19.6	1.4392
20.4	1.4371

It might be well to insert here the values for the densities of hydrogen peroxide—water mixtures; determined at a much later date with freshly prepared samples of hydrogen peroxide. The densities were determined at 2 temperatures, 0° and 18°, the method employed being the same as the one described above.

H_2O_2, %.	Density. 0°.	Density. 18°.	Temperature coefficient.
0.00	0.99987	0.99862	0.00007
10.57	1.0419	1.0372	0.000268
22.33	1.0894	1.0815	0.000437
40.14	1.1655	1.1552	0.000573
56.70	1.2404	1.2270	0.000744
61.20	1.2610	1.2465	0.000815
73.44	1.3235	1.3071	0.000921
84.86	1.3839	1.3662	0.000980
90.42	1.4144	1.3955	0.001050
98.89	1.4596	1.4404	0.001067

In Fig. 3 these results are shown graphically.

These data are of value in checking up the value for the density of 100% hydrogen peroxide for a calculation shows that 1.4633 at 0° and 1.4442 at 18° are the value for the anhydrous peroxide. It is seen also how the temperature coefficient increases uniformly from that of pure water 0.00007 to that of the pure peroxide 0.001075.

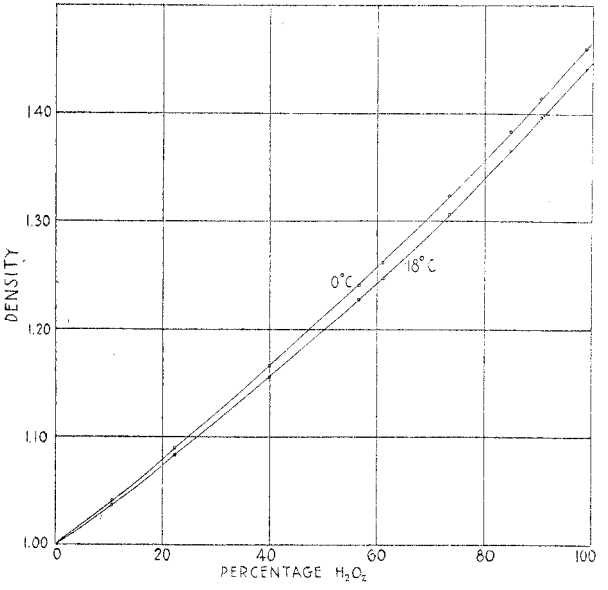


Fig. 3.

Density of Solid Hydrogen Peroxide.—Crystals of hydrogen peroxide sink to the bottom when formed in the liquid, and give the impression of being much denser than the liquid. The actual density of the solid determined as follows. The hydrogen peroxide in the dilatometer bulb was cooled until crystals formed. Most of these were allowed to melt and then the bottom of the bulb was gradually immersed in a freezing mixture kept at a constant temperature several degrees below the freezing point of the peroxide. The rate of immersion was timed to equal the rate of solid formation until all the bulb and a portion of the capillary were immersed in the freezing mixture. This insures the complete solidification without strain of the hydrogen peroxide in the bulb. The bulb was kept in the freezing mixture for one hour, the height to which the solid came in the capillary and the position of the meniscus of the liquid por-

tion in the capillary being carefully measured. The mean temperature of this liquid portion being known, its weight can be calculated because the volume it occupies in the capillary is known. The weight of that portion of the hydrogen peroxide which is in the solid form (by far the largest portion) is then found by difference, and as its volume is also known by the position of the top of the solid in the capillary, the density of the solid follows directly. The determinations were made *ab initio* at 2 temperatures of the freezing mixture.

Temperature of solid. ° C.	Density of solid.
—4.45	1.6434
—7.45	1.6437

There is, therefore, a contraction of about 11% on solidification.

Viscosity.—The impression seems to prevail that highly concentrated solutions of hydrogen peroxide are thick, viscous, syrupy liquids, although no measurements of viscosity had been made. It was therefore rather surprising to note the results obtained when the viscosity of pure hydrogen peroxide was measured with the aid of an Ostwald viscosimeter.

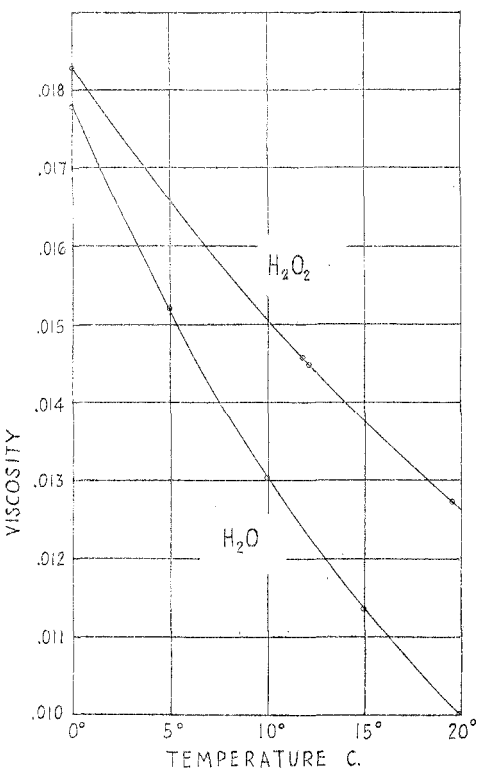


Fig. 4.—Viscosity-temperature curves for hydrogen peroxide and water.

The values of viscosity tabulated below are given in absolute units.

Temperature. ° C.	Viscosity.
0.04	0.01828
11.90	0.01456
12.20	0.01447
19.60	0.01272

The graph, Fig. 4, shows the variation of viscosity with the temperature. For purposes of comparison, the viscosity curve for water is plotted alongside that for hydrogen peroxide. At 0° the viscosity of hydrogen peroxide differs only slightly from that of water.

The viscosities of hydrogen-peroxide-water mixtures were also determined at a later date with the samples with which the densities of these mixtures had been determined. From the values obtained, it was seen that 0.01828 at 0° and 0.01307 at 18° were the correct values of 100% peroxide.

H_2O_2. %	Viscosity. 0°.	18°.
0.00	0.01778	0.01054
5.71	0.01762	0.01061
11.21	0.01740	0.01066
14.98	0.01734	0.01072
22.33	0.01758	0.01105
34.05	0.01805	0.01157
44.83	0.01846	0.01204
52.49	0.01876	0.01235
59.62	0.01900	0.01266
68.50	0.01938	0.01285
75.03	0.01929	0.01292
83.15	0.01909	0.01300
89.47	0.01873	0.01301
98.89	0.01828	.....

Fig. 5 shows these results graphically. It will be seen that at 0° there is a marked minimum at 15% and a maximum at 70%. At a higher temperature, this maximum and minimum degenerate into discontinuities. The molecular compound $2H_2O.H_2O_2$ has been shown to exist[1] but this corresponds to a 48.6% concentration. Certainly a study of binary mixtures does not seem to have established that a maximum or minimum in the viscosity curve indicates the existence of a compound of the composition indicated. The viscosity-concentration curve of *iso*-amyl alcohol-formamide[2] is an example of a system showing a similarity to the hydrogen-peroxide-water curve at 0°.

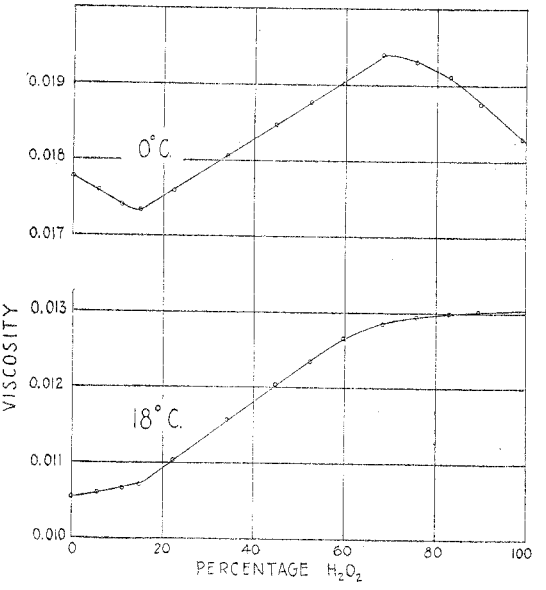


Fig. 5.

Surface Tension. — The principal interest attached to the determination of the surface tension of a substance in the past was not in the absolute value of this constant, but rather in its variation with the temperature in order that some clue might be found as to the molecular complexity of the liquid molecules. Recently some doubt has been thrown on the validity of this conception.

[1] O. Maass and O. W. Herzberg, THIS JOURNAL 42, 2570 (1910).

[2] Z. Drucker, *Z. physik. Chem.*, 76, 371 (1911).

The surface tension of hydrogen peroxide was measured by means of the capillary rise method, an apparatus being used similiar to the one described by Richards.[1] The wide arm of the tube was only 2.5 cm. in diameter so it was considered best to calibrate the capillary by measuring the surface tension of water. The angle of contact which hydrogen peroxide makes is very small; as far as could be judged by means of a microscope, the angle is zero.

Temperature. ° C.	Density.	Surface tension in dynes.
0.2	1.4630	78.73
6.2	1.4564	77.79
11.0	1.4512	77.51
13.9	1.4481	76.47
18.2	1.4434	75.94

The variations of surface tension with the temperature are plotted graphically (Fig. 6). For purposes of comparison, the surface tension of water and its variation with the temperature is plotted alongside.

On the assumptions made by Ramsay and Shields, the association of hydrogen peroxide would then be given by the following equation

$$\frac{78.73\left(\frac{34.02}{1.4630}\right)^{2/3} - 75.94\left(\frac{34.02}{1.4434}\right)^{2/3}}{18.2^\circ - 0.2^\circ} = 0.923.$$

x, the association of hydrogen peroxide is therefore $\left(\frac{2.12}{0.923}\right)^{3/2} = 3.48$. The value for water is 3.58.

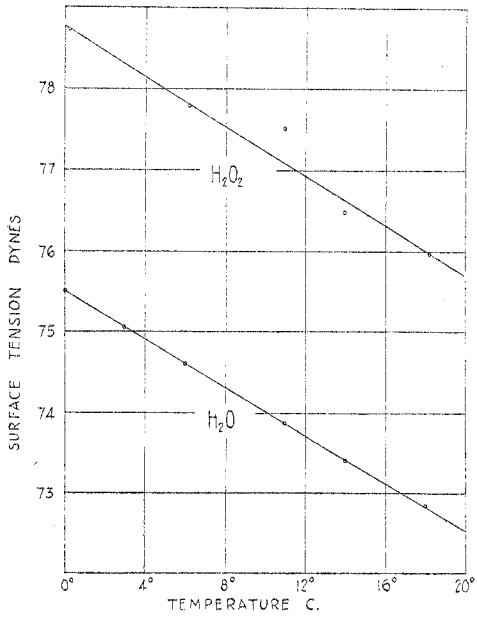


Fig. 6.

The surface tension of hydrogen peroxide is therefore, slightly greater than that of water and the association as calculated from the variation of surface tension with temperature is slightly less.

The similarity between the surface tensions of pure hydrogen peroxide and water has a certain significance in the light of recent work on surface tension by Langmuir[2] and Harkins.[3] Evidently the peroxide and water molecules are orientated in exactly the same way at the surface, and

[1] T. W. Richards and L. B. Coombs, THIS JOURNAL, **37**, 1656 (1915).

[2] I. Langmuir, *ibid.*, **39**, 1848 (1917).

[3] W. D. Harkins, E. C. H. Davies and G. L. Clark, *ibid.*, **39**, 541 (1917).

from that point of view also it might have been predicted, when their composition is taken into account, that pure hydrogen peroxide would have a slightly greater surface tension then water.

As a means of checking up the surface tension of pure hydrogen peroxide, the surface tensions of various concentrations were measured at 2 temperatures.

	H_2O_2. %	Surface tension (dynes).
At 0°.....	0.00	75.49
	12.54	75.91
	18.17	76.04
	27.22	76.26
	34.58	76.55
	56.06	77.31
	59.27	77.38
	86.31	78.30
At 18°.....	0.00	72.82
	12.78	73.22
	23.70	73.51
	28.14	73.67
	44.31	74.13
	59.27	74.67
	60.83	74.73
	79.01	75.29
	90.66	75.67

As Fig. 7 shows, the surface tensions vary in a regular expected manner, confirming the values of 78.76 dynes at 0° and 75.99 dynes at 18°, obtained from the pure 100% peroxide.

Specific Heat of Liquid Hydrogen Peroxide. Specific Heat of Solid Hydrogen Peroxide. Latent Heat of Fusion of Hydrogen Peroxide.—The measurement of the above constants of hydrogen peroxide presented certain experimental difficulties. Its chemical nature is such that it must not be allowed to come in contact with anything except glass. It was therefore decided to use the following method. A bulb, B (Fig. 8), was sealed at the end of a long glass tube, A, of small

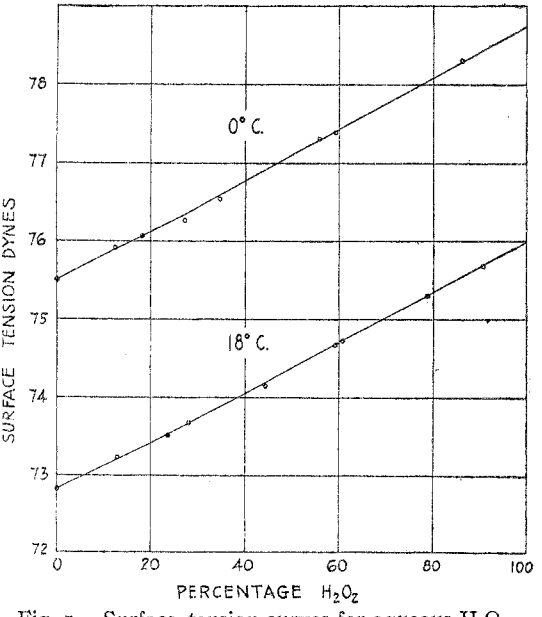


Fig. 7.—Surface tension curves for aqueous H_2O_2.

diameter, and, by means of a long drawn-out capillary, some 10 g. of peroxide was transferred into the bulb and weighed accurately. The bulb and a definite portion of the stem was then cooled to a known temperature by placing it in a metal Tube R, which latter was placed in a constant temperature mixture, H. Some phosphorus pentoxide placed at E and separated by a gauze from the bulb, B, presented the deposition of moisture on B. When sufficient time had elapsed for thermal equilibrium to set in, the bulb was quickly transferred into the inner vessel of a Richards' adiabatic calorimeter and the temperature changes measured in the usual way. It was considered advisable not to seal the hydrogen peroxide into a bulb so that if by chance any decomposition should occur, an explosion would be avoided.

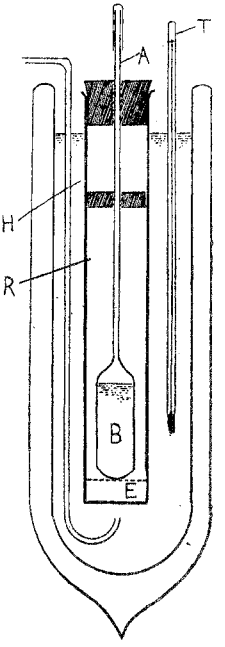


Fig. 8.

If H is the heat given by the calorimeter

$$H = ms(t - t') + k(t - t')$$

where s is the specific heat of the hydrogen peroxide, m its mass, t' the initial and t the final temperature, and k a constant involving the specific heat of the glass bulb and the mass of glass immersed in the calorimeter. The constant k was determined in 2 separate experiments by going through the procedure described above with the bulb empty. This value of k was also determined by filling the bulb with a substance having a known specific heat (water). All the values of k agreed to within a few per cent., the mean value coming out to be 2.19. Then finally to test the accuracy of the method a weighed quantity of water was frozen in the bulb and the latter placed in a carbon dioxide-ether bath (—78.2°). Taking the latent heat of ice as being 80 calories, the specific heat of ice came out to be 0.460, which is in fairly good agreement with the value 0.470 obtained by others for the specific heat of ice in that temperature range.

The values found for the specific heat of the liquid are given below.

Temperature range. °C.	Lowering of temperature in calorimeter. °C.	Specific heat.
0.0 to 18.5	0.3520	0.5730
0.0 to 18.5	0.3565	0.5841
—32.0 to 18.0	0.9480	0.5697

The figures for the lowering of the temperature in the calorimeter are given in order that the accuracy of the method may be judged. Evidently the experimental error is about 2%. In determining the last value given above the hydrogen peroxide was carefully cooled down in order to pre-

vent it from freezing. As constant temperature-bath, there was employed an ether-bath described elsewhere.[1]

The specific heat of the solid and latent heat of fusion of hydrogen peroxide were determined by means of the same apparatus. The hydrogen peroxide was first of all frozen and then kept for a long time at a constant temperature well below its freezing point. By varying this initial temperature, at which the frozen peroxide was kept, in a number of experiments it was possible to determine both specific heat and latent heat by combining the results of these several experiments.

The relation between the heat H given up by the calorimeter and the various factors governing the absorption of this heat by the bulb and contents is given by the following expression:

$$H = ms(t - t') + mL + ms'(t' - t'') + k(t' - t''),$$

where m is the weight of hydrogen peroxide in the bulb (8.995 g.)

s the specific heat of the liquid (0.579),

t the final temperature,

t' the melting point of hydrogen peroxide (—1.7°),

s' the specific heat of the solid,

k the constant of the bulb (2.19),

t'' the initial temperature at which the frozen hydrogen peroxide had been kept.

Number.	t''. °C.	Lowering of temperature in calorimeter. t. °C.	°C.	S'.	L.
1	—9.0	16.87	2.124	0.4636	74.28
2	—9.0	18.87	2.109	0.4767	73.55
3	—57.2	16.07	2.909	.....	.....
4	—30.5	16.47	2.556	.....	.....

By combining Experiments 1 and 3 and Experiments 2 and 4, two values of each of the constants S' and L can be calculated from the experimental data. The specific heat of the liquid is 0.579, that of the solid 0.470, and the latent heat of fusion 74 calories. These last 2 values are probably correct to within 4%.

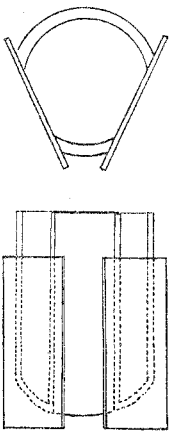


Fig. 9.

Refractive Index.—The refractive index of the pure hydrogen peroxide was determined last of all. Analysis of the purity of the sample showed that it was 99.91% pure. The method employed was the measurement of the "angle of least deviation."

For this purpose a special hollow prism was made. A thick-walled glass tube about 3 cm. long, 1.5 cm. diameter was rounded off at the bottom and 2 sides were ground out of the walls making an angle of about

[1] McIntosh and Maass, THIS JOURNAL, 35, 536 (1913).

60°. Two plates of optical glass edges were cemented on the outside so that the hydrogen peroxide did not come in contact with the cement. The accompanying diagram (Fig. 9) gives an idea of the prism when viewed from the top and the front (plan and elevation). Sodium light was used throughout the measurements.

Substance.	Temperature, °C.	Prism angle.	Angle of minimum deviation.	Refractive index.
Hydrogen peroxide.....	22	57° 54′	27° 54′	1.4140
Hydrogen peroxide.....	22	57° 54′	27° 53′	1.4138
Solution of hydrogen peroxide 96.81%.....	24	56° 58½′	27° 4¾′	1.4043
Water.....	25	56° 58½′	21° 55½′	1.3330

The prism was taken apart and cleaned after the first 2 experiments described above had been made; hence the slight change in the prism angle. The refractive index of water was measured in order that the accuracy of the measurements might be tested. The value 1.3330 obtained is in excellent agreement with the recognized value.

The refractive index was one of the few measurements which Brühl undertook to make; as a matter of fact, this measurement was really the sole object of his research. The values he obtained range from 1.4005 to 1.4069, indicating that his purest sample may have been only 98% at the time of measurement.

The interest in the refractive index lies principally in the fact that this physical property is both a constitutive and an additive one for atoms. That is, the property depends both on the atom and the nature of its linkages to other atoms. For purposes of comparison, the molecular refractive power of a substance is calculated by means of the Lorenz-Lorentz formula

$$R = \frac{n^2 - 1}{n^2 + 2} \frac{m}{d}$$

where R is the molecular refractive power, m the molecular weight, d the density and n the refractive index.

Substance.	Density.	Refractive index.	R.
Hydrogen peroxide.....	1.4403	1.4139	5.900
Water.....	0.9973	1.3330	3.715

Brühl of course obtained a lower value for R.

Following Brühl's reasoning in determining the constitution of hydrogen peroxide, but using the figures obtained by the author:

R for water, H.OH is 3.715
R for hydrogen, H is 1.050

R for hydroxyl, OH is 2.665

Hence, if hydrogen peroxide had the constitution given by

HO — OH

R for hydrogen peroxide would be 5.33. The fact that the experimental value is higher, points to unsaturation. Hence Brühl proposed the constitutional formula

$$HO \equiv OH$$

in which there are 2 quadrivalent oxygen atoms. Now, the value for the molecular refractive power of quadrivalent oxygen has been measured by Miss Homfray[1] in a number of salts of pyrone where oxygen is supposed to be quadrivalent. Miss Homfray's value for quadrivalent oxygen, R is 2.55 and, if this value is correct, the molecular refractive power of hydrogen peroxide containing 2 quadrivalent oxygen atoms would be much larger than the experimental value obtained.

Miscellaneous Facts about Anhydrous Peroxide.—An attempt was made to determine the crystal form of hydrogen peroxide. The crystals in contact with air take up moisture even at a temperature of —10°, so that a special apparatus is being built which will make it possible to measure the angles between 2 faces of a "growing" crystal.

The dielectric constant for hydrogen peroxide has been extrapolated by Calvert[2] from a value determined for a 45% solution. The accuracy of this extrapolation is very doubtful and the dielectric constant of the pure hydrogen peroxide is now being measured. An apparatus has also been devised by means of which the conductivity of pure hydrogen peroxide and of solutions of salts in hydrogen peroxide can be measured.

The impression seems to prevail that hydrogen peroxide is very soluble in ether and ether extraction has been used as a method of concentration. Brühl in his paper refers to his non-success in making use of this method of concentration. In this connection the interesting observation was made by the authors that apparently pure hydrogen peroxide and anhydrous ether are only slightly soluble in one another. In an experiment, a small amount of hydrogen peroxide was shaken up with a larger volume of ether without an appreciable visible change in the relative volumes.

Pure hydrogen peroxide dissolves various neutral salts readily, and at high temperatures it apparently acts on glass with resulting decomposition, this fact rendering the direct measurement of the boiling point impossible until a suitable container has been found.

Pure hydrogen peroxide coming in contact with wood decomposes. The presence of even a small amount of acid in the hydrogen peroxide causes this action to become so violent that the wood catches fire. Hydrogen peroxide also decomposes when brought in contact with most metals; the pure hydrogen peroxide does not do so explosively. However, a small piece of metallic sodium caused an "intense" explosion when brought in contact with a few drops of pure hydrogen peroxide.

[1] Miss Homfray, *J. Chem. Soc.*, **87**, 1443 (1905).

[2] Calvert, *Ann. chim. phys.*, **4**, 483 (1900).

Other observers have mentioned the effect of strong hydrogen peroxide solutions on the skin. The following observations were made when a drop of pure hydrogen peroxide was brought in contact with the skin of the hand. A violent decomposition of the peroxide occurred, and the skin became absolutely white. No blister was formed, but the skin had the appearance of being loose. No pain at all was felt although dilute solutions give burns accompanied by the sensation of pricking needles. But the most remarkable feature of all was that after 3 or 4 hours not a mark was left on the spot where the hydrogen peroxide had been applied, although, immediately after application, the appearance of the skin was sickening. Apparently the living tissue had not been hurt in the slightest. On the other hand, dead tissue is destroyed and removed by the pure peroxide.

As regards the decomposition of hydrogen peroxide solutions, experience has shown that pure aqueous solutions in a suitable container will keep indefinitely. Decomposition is caused by foreign substances getting into the solution and stronger solutions seem to be capable of destroying, in many cases, such impurities before they start the decomposition; hence, the stronger a solution is the better it "keeps." A "neutral" salt such as chemically pure sodium chloride does not in itself cause the slightest decomposition, but its presence seems to augment any decomposition caused by a second impurity. A salt consisting of a strong base and weak acid, or *vice versa*, causes decomposition to take place and the mechanism of many so-called catalyzers can be traced back to this cause. Anti-catalyzers were investigated and found to consist in every case of catalyzer-destroyers; that is, pure hydrogen peroxide does not decompose and the function of anti-catalyzers consists solely in destroying or rendering catalyzers innocuous.

Pure anhydrous hydrogen peroxide does not decompose when kept at 0°. Strong solutions even had the reputation of being highly explosive, but the apparent stability of the anhydrous substance soon caused the precautions which were initially taken to be relaxed. It must be stated, however, that in spite of the apparent stability of the pure hydrogen peroxide, all precautions are well worth taking.

An investigation of the chemical properties of anhydrous peroxide and of the physical properties indicated in the last few paragraphs is being carried out at the present time, and a discussion of the probable constitution of hydrogen peroxide had better be left until this investigation has been completed. In this paper the method of preparing absolute peroxide has been described and in conclusion, the peroxide's properties so far determined, compared to the corresponding ones of water, are tabulated.

Physical constant.	Hydrogen peroxide.	Water.
Freezing point	—1.70°	0°
Density of liquid at 0°	1.4633	0.99987
Mean coefficient of expansion —10° to +20°	0.00107	0.00000
Density of solid	1.644	0.9167
Specific heat of liquid	0.579	1.0
Latent heat of fusion	74 calories	80 calories
Specific heat of solid	0.470	0.472
Surface tension 0°	78.7 dynes	75.5 dynes
Association (Ramsay and Young) at 0°	3.48	3.58
Viscosity 0°	0.01828	0.01778
Refractive index (D) 22°	1.4139	1.3330
Molecular refractive power (D)	5.90	3.715

MONTREAL, CANADA.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF MCGILL UNIVERSITY.]

THE PROPERTIES OF PURE HYDROGEN PEROXIDE. II.

BY O. MAASS AND O. W. HERZBERG.

Received September 25, 1920.

This second paper deals solely with the freezing-point curve of solutions of hydrogen peroxide and water. These solutions were prepared by concentrating 3% hydrogen peroxide and purifying the resultant concentrated solution by means of a distillation. As the only volatile impurity contained by the original solution consisted of a trace of hydrochloric acid, the final product may be looked upon as having been pure except for a trace of this acid which found its way into the distillate. In this way an 86% solution was obtained.

In order to obtain the freezing points of hydrogen peroxide-water mixtures a weighed amount of this 86% peroxide solution was placed in a test-tube. A platinum thermometer, reading to 0.1°, was immersed in it. The temperature was lowered by means of a suitable freezing mixture until crystals formed. All but a few of these were allowed to melt and then the temperature was slightly lowered until crystallization again set in, the liquid in the meantime being vigorously stirred. The solution was then allowed to warm up slowly, the freezing point being taken as the temperature at which the last crystals melted under vigorous stirring. The solution was analyzed; an adequate amount of water, sufficient to dilute the solution a few per cent. was added, and then the whole procedure repeated. In this way the freezing points at various concentrations were determined.

The solutions between the concentrations 40% and 60% hydrogen peroxide had a tendency to supercool into a thick viscous mass, but when allowed to stand at a temperature of —90°[1] crystallization started after some time.

[1] Carbon dioxide-ether under a vacuum was used as freezing mixture in this case.