

HYDROGEN PEROXIDE AND ITS ANALOGUES

II. PHASE EQUILIBRIUM IN THE SYSTEM HYDROGEN PEROXIDE - WATER¹

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Abstract

A precision freezing point apparatus with platinum resistance thermometer was used to investigate the system hydrogen peroxide - water over the whole concentration range. The freezing point of the purest sample of hydrogen peroxide obtained by repeated fractional crystallizations of a large quantity of 99.6% pure solution was found to be -0.461°C .; that of the dihydrate was -52.10°C . The two eutectics occur at concentrations of 45.2% and 61.2% H_2O_2 and at temperatures of -52.4° and -56.5°C . respectively. Contrary to what has been reported previously, water and hydrogen peroxide do not form solid solutions together. This was proved conclusively by applying the technique of radioactive tracers to the 'wet residue' method of Schreinemakers.

The purpose of this investigation was threefold. First, to redetermine the freezing point of pure hydrogen peroxide, with greater accuracy than heretofore (3). Second, to settle the question of solid solutions in the system hydrogen peroxide - water (6). Third, to use freezing point measurements for evaluating the degree of purity of very concentrated hydrogen peroxide. Indeed, the usual chemical methods of analysis are of little use for that purpose since the remaining traces of water cannot be determined directly (4). Other physical methods investigated so far are either not sensitive enough or subject to errors due to spontaneous decomposition. These three objectives are closely interconnected; for instance, the existence of solid solutions would render determinations of freezing point rather problematic. At the same time it could rule out the possibility of using this method for accurate analysis.

Experimental Methods and Results

Freezing Points

An apparatus similar to that originated by Mair (12) and perfected subsequently by Rossini and his collaborators (7, 13, 20) at the National Bureau of Standards was constructed for this purpose. The double-walled, silvered freezing tube had an internal diameter of 3 cm. and the rate of heat transfer was controlled by adjusting the pressure inside the annular space. The cold head was provided by a large Dewar flask filled with dry ice and acetone. The problem of stirring the sample presented some experimental difficulties since most materials catalyze the decomposition of hydrogen peroxide. Stirrers made of glass rods were too fragile. Aluminum or highly polished stainless steel has been recommended as suitable for this purpose (18); the latter was selected because of its greater strength. The stirrer was in the form of a double helix fashioned

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by winding a 1/16 in. rod first downwards on a wooden mandrel 9/16 in. diameter and then upwards on a cylinder 11/16 in. diameter over a 3 in. length. The stirrer was polished electrolytically (19) by making it the anode in a bath of 47% glycerol, 42% sirupy phosphoric acid, and 11% water. Electrolysis was carried out with a cathode of the same material in a bath at 125°C. with a current density of 0.2 amp. per sq. in. After a few trials, surfaces could be obtained that were completely inactive towards hydrogen peroxide. The stirrer was actuated by a windshield wiper type of motor with a reciprocating stroke of 2½ in. at the rate of two strokes per second. The apparatus was completed by a cork stopper covered with aluminum foil and through which the thermometer and stirrer were inserted, the latter guided by a length of glass tubing; two other inlets were provided, one for introducing crystals for seeding the sample and the other for blowing a stream of well dried air. This last precaution was necessary because concentrated hydrogen peroxide is very hygroscopic at low temperature.

The first few runs were made with a Beckmann thermometer, but it was soon realized that the time-temperature curves could not be followed long enough to give significant results, especially with the less concentrated solutions. A platinum resistance thermometer (Leeds and Northrup, type 8163) certified by the National Bureau of Standards was therefore used in conjunction with a Mueller bridge. The bridge was calibrated according to regular practice (15) against a 10 ohm Standard kept at 20.0°C. The ice point of the thermometer was determined after the method of Busse (2). Its resistance at 0°C. was 25.5188 international ohms. This value was again checked when the investigation was completed and perfect agreement obtained. The degree of reproducibility obtainable with this method and apparatus may be judged from the results in Table I.

TABLE I
TYPICAL RESULTS OF FREEZING POINT
DETERMINATIONS

Run No.	Weight % H ₂ O ₂	Freezing point, °C.
16	99.5 ₈	-0.869
17	99.5 ₈	-0.873
18	99.5 ₈	-0.876
33	99.7 ₄	-0.655
34	99.7 ₄	-0.655

Runs No. 33 and 34 were carried out on the same day, Nos. 16, 17, and 18 on successive days, the solution being kept at room temperature in the meantime. Although there was no evidence of streamers in the liquid it is likely that the slight drift in the freezing point is due to actual decomposition. Calculations show that the variation corresponds to a concentration change of 0.003% per day, which is far beyond the limit of accuracy of volumetric analysis in that concentration range. These observations confirm, therefore, the

superiority of freezing point measurement over chemical analysis for determining the purity of concentrated hydrogen peroxide.

The hydrogen peroxide used for these measurements was Becco's 90% solution. By fractional distillation through a 60 cm. glass column packed with Pyrex helices the concentration could easily be brought up to around 99.6%. Then it was subjected to fractional crystallization, the progress of concentration being followed by means of freezing point determinations. To be effective this last operation had to be carried out with great care. The solution to be concentrated was cooled in a stoppered flask and crystallization induced by seeding. It was then kept at -2°C . for several hours with occasional shaking. Then the two phases were separated by means of the device shown in Fig. 1. Flask *A* containing the partly frozen solution was inverted by rotating the connecting tube about ground joint *J*. By applying suction over flask *B* the liquid was filtered through the fritted glass plate. Thus any dilution from condensation of atmospheric moisture was avoided.

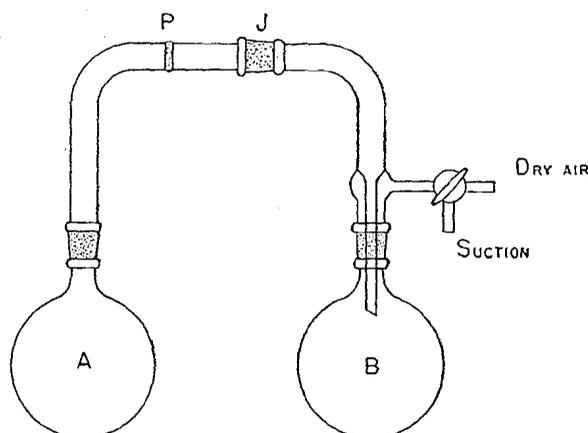


FIG. 1. Apparatus for concentrating hydrogen peroxide by fractional crystallization.

About 70 gm. of liquid was needed for a freezing point determination. In one series of determinations about 3 lb. of a 99.6% solution was recrystallized a number of times. The freezing point was measured when about two pounds was left and four times thereafter with at least two fractional crystallizations between successive measurements. The results shown in Table II are believed to be the most reliable to date. The measurements were carried out immediately after a recrystallization except in the case of Run No. 40 where the sample was left standing overnight, which may explain the slight discrepancy.

A second set of experiments was made starting with 1 lb. of concentrated solution, so that only three determinations could be made. The refractive index of the sample used for Run 39 was 1.40669 at 25°C ., in perfect agreement with the latest results from this laboratory (4).

TABLE II
FREEZING POINT OF PURE HYDROGEN PEROXIDE

Run No.	Weight % H ₂ O ₂ *	Freezing point, °C.
<i>1st series</i>		
29	99.7 ₉	-0.479
31	99.9 ₃	-0.465
38	100.0 ₃	-0.461
39	99.9 ₇	-0.461
40	99.9 ₃	-0.469
<i>2nd series</i>		
30	99.8 ₃	-0.500
32	99.9 ₃	-0.492
37	99.9 ₆	-0.461

* From volumetric analyses.

The method of W. P. White (21) for calculating the freezing point at zero impurity from time-temperature curves was applied to the above determinations assuming that traces of water were the only contaminant in the peroxide. The calculations were based on the portion of the cooling curve where from 1/10 to 1/3 of the sample was frozen. The results, summarized in Table III, are rather inconsistent as a whole, apparently owing to the fact that the system was very sluggish in reaching equilibrium. Other investigators (1) have reported that in the case of hydrocarbons equilibrium is attained within four or five minutes. In associated liquids, however, the high viscosity slows down diffusion considerably and this may lead to spurious results.

TABLE III
CALCULATED FREEZING POINT AT ZERO IMPURITY

Run No.	Fraction frozen	Temperature, °C.	Freezing point, °C. (at zero impurity)
30	1/10	-0.508	-0.428
"	1/5	-0.517	-0.432
31	1/5	-0.469	-0.448
"	1/3	-0.474	-0.447
32	1/10	-0.495	-0.468
"	1/5	-0.498	-0.468
"	1/4	-0.501	-0.465
37	1/5	-0.470	-0.425
"	1/4	-0.472	-0.428
39	1/10	-0.465	-0.425
"	1/5	-0.469	-0.429
40	1/5	-0.473	-0.451

Using the same apparatus and technique the freezing point curve of the system hydrogen peroxide-water was re-examined. Some twenty measurements covering the entire concentration range were carried out, particular attention being paid to the region between 40 and 60%. On the whole the results (Table IV) agree fairly well with those of previous investigators (6, 9, 11) except for the freezing point of the addition compound $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$. A comparison of the various values for this latter quantity and the co-ordinates of the two eutectic points is shown in Table V.

TABLE IV
FREEZING POINT OF HYDROGEN PEROXIDE SOLUTIONS

Run No.	Weight % H_2O_2	Freezing point, °C.
43	3.40	- 1.99 ₄
42	5.81	- 3.49 ₅
44	9.40	- 5.93 ₈
52	19.6 ₅	-14.3 ₁
51	28.1 ₅	-23.2 ₈
53	39.1 ₄	-39.9 ₇
55	44.6 ₅	-51.0 ₄
60	46.8 ₀	-52.1 ₈
62	48.5 ₁	-51.9 ₉
56	48.5 ₇	-52.1 ₀
59	48.6 ₄	-52.1 ₀
61	51.9 ₂	-52.4 ₀
50	57.7 ₇	-54.5 ₃
58	60.3 ₁	-56.1 ₂
54	70.9 ₄	-38.8 ₄
48	81.1 ₂	-23.0 ₁
46	91.0 ₄	-10.2 ₁
47	95.3 ₃	- 5.35 ₆
45	95.6 ₈	- 5.05 ₁
27	97.5 ₆	- 3.18 ₃

TABLE V
COMPOUND AND EUTECTICS

1st eutectic		Compound		2nd eutectic		Authors
Weight % H_2O_2	Temp., °C.	Weight % H_2O_2	Temp., °C.	Weight % H_2O_2	Temp., °C.	
45	-53	48.6	-51	59	-56	Maass and Herzberg Giguère and Maass Kubaschewski and Weber This work
46	-51.5	"	-50.3	60	-56.5	
45.8	-52.5	"	-50.3	59.0	-55.5	
45.2	-52.4	"	-52.10	61.2	-56.5	

Solid Solutions

The so-called 'wet-residue' method of Schreinemakers (17) was applied using potassium chloride for the third component. Indeed, it is soluble in both liquids and is easily determined; in addition it does not decompose hydrogen peroxide. Two experiments were done with dilute peroxide solutions and two with concentrated solutions. The ternary mixtures were placed in a constant temper-

ature bath (5) and crystallization was induced by seeding at a few degrees below the freezing point. Temperature was gradually lowered by about 10 degrees so that a good portion of the sample was solidified. After remaining at least 10 hr. at that temperature the two phases were separated as thoroughly as possible by siphoning the liquid through a filter stick. Both phases were then analyzed, potassium chloride being determined gravimetrically with silver nitrate, and hydrogen peroxide, by the usual titration with permanganate. The results of Table VI were plotted on a tricoordinate graph; the corresponding lines when extrapolated passed exactly through the apex in all four cases, thereby indicating that no solid solution existed on either side of the phase diagram.

TABLE VI
RESULTS OF THE 'WET RESIDUE' METHOD WITH POTASSIUM CHLORIDE

Filtration temperature, °C.	% Composition of mother liquor			% Composition of wet solid		
	KCl	H ₂ O ₂	H ₂ O	KCl	H ₂ O ₂	H ₂ O
-15	7.09	17.64	75.3	4.62	10.78	84.6
-15	11.38	15.49	73.13	7.16	9.98	82.9
-23.8	4.48	79.3	16.2	1.24	94.6 ₄	4.1 ₂
-23.8	2.12	79.9 ₅	17.9 ₃	0.93	93.7 ₈	5.9 ₂

An objection to the above method is that addition of a third component in the large amounts needed for significant analysis may disturb considerably the normal equilibrium between the two major components. A solution of this difficulty in the present case was discovered in the use of radioactive tracers. Because of the very minute quantity needed there can be no disturbing effect of such a third component; yet the techniques of radioactivity measurements and the availability of concentrated isotopes result in an accuracy considerably greater than that of conventional chemical analysis. Radioactive phosphorus P³² in the form of potassium dihydrogen phosphate was used for this purpose as it fulfilled a number of desirable conditions: solubility in both water and hydrogen peroxide; inertness towards the latter; only one type of particles (β) emitted, and with sufficient energy (1.7 Mev.), to allow use of thin walled glass counters; half life of the right order of magnitude (14.3 days) for the proposed experiments and at the same time presenting no serious problem of contamination. The isotope was obtained from the Atomic Energy Project of the National Research Council at Chalk River. The original sample weighing 0.028 gm. had an activity of 0.95 millicurie when shipped. It was diluted a 100-fold and an amount added to give a concentration of 0.00025 gm. per liter of peroxide solution.

Two determinations were made, one with a 7% and one with a 95% solution of hydrogen peroxide. The phase separation was effected at -10°C. as described above and the activity measured with a Geiger-Mueller counter (Tracerlab No. TGC-5). The plateau of this counter had a slope of the order of 5% per 100 volts; starting voltage, 825 v. The operating voltage was kept at 900 v. ±

0.1% by means of a stabilized power supply. The Geiger tube was mounted in an inverted position so that a test tube of appropriate size containing the solution could be placed around it. Care was taken that the liquid always reached the same level above the thin section of the counter. The latter was carefully cleaned between successive measurements and the background re-determined. This was kept at about 23 counts per minute with the help of a heavy shield of lead blocks. A scaler and a Cenco impulse counter completed the apparatus. The activities given in Table VII are corrected for background,

TABLE VII
RESULTS OF RADIOACTIVITY MEASUREMENTS

Wet solid			Mother liquor		
Weight of sample, gm.	Weight % H_2O_2	Activity, counts/min.	Weight of sample, gm.	Weight % H_2O_2	Activity, counts/min.
76.3	7.67	6911	25.5	15.38	13747
86.4	94.79	5021	70.4	79.23	19650

dead time of counter (100 μ sec.), and for decay of the radioactive material during experimentation. The calculations are as follows.

For the 7% solution the ratio of activities in the two phases is $6911/13747 = 0.5027$; therefore the per cent of water in the solid phase is:

$$\frac{(100 - 7.67) - 0.5027(100 - 15.38)}{(1 - 0.5027)} = 100.1\%$$

Similar calculations for the 95% solution yielded exactly the same result, thereby fully confirming the above conclusions.

Discussion

The freezing point of pure hydrogen peroxide was first reported as being $-1.7^\circ C.$ (10). This is still often quoted in spite of the fact that it was found later to be too low by about $0.8^\circ C.$ (3). More recent determinations (19) indicated definitely that the revised value, $-0.89^\circ C.$, was still too low. The present result, $-0.461^\circ C.$, is now believed to lie within a few thousandths of a degree from the true value for the following reasons: It is the highest freezing temperature observed in a direct determination; in addition it is the only result that could be duplicated to the limit of accuracy of the measurements (0.001°) and this with two different samples.

The results of calculations at zero impurity will not be considered since at least in one instance (Run No. 32) they lead to a lower temperature than the highest one obtained directly. If the correct freezing point were around $-0.43^\circ C.$ as suggested by runs No. 30, 37, and 39 (Table III), then the above result, $-0.461^\circ C.$, would correspond to a sample containing 0.03% water. Considering the difficulty of removing the last traces of water from hydrogen peroxide this is not a large quantity. However, there is no reason why exactly

the same amount of impurity should have been present in the three runs No. 37, 38, and 39 (Table II). The present investigation provides the most accurate and reliable method of ascertaining the purity of highly concentrated hydrogen peroxide. Its only drawback is the relatively large sample (70 cc.) necessary for a determination. It is planned to improve the apparatus in that respect, particularly along the lines adopted by Herington and Handley in their recent work (8).

At the time this work was begun the formation of solid solutions in the system hydrogen peroxide - water was considered an open question. In favor was the fact that fractional crystallization is extremely inefficient for concentrating hydrogen peroxide solutions. This observation, first made by Maass and Hatcher (10), has been verified repeatedly, in particular by Giguère and Maass (6), who applied the analytical, or phase separation method, and came to the conclusion that solid solutions were formed. In addition they pointed out that the freezing points of very concentrated peroxide solutions were appreciably higher than those calculated from Raoult's law.

On the other hand, these arguments were opposed by the following ones: the lattice constant of hydrogen peroxide is the same in frozen solutions (82 and 90%) as in the pure compound according to an X-ray investigation (16). More recently it has been observed in this laboratory that hydrogen peroxide solutions on cooling do not always solidify *completely* at temperatures below their corresponding eutectic, a result not easily reconciled with occurrence of solid solutions in the system (5). It is now obvious why these solutions can be supercooled with respect to the addition compound, $\text{H}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$; the limited stability of this hydrate is confirmed both by its low symmetry (16) and the flatness of its freezing point curve (Fig. 2).

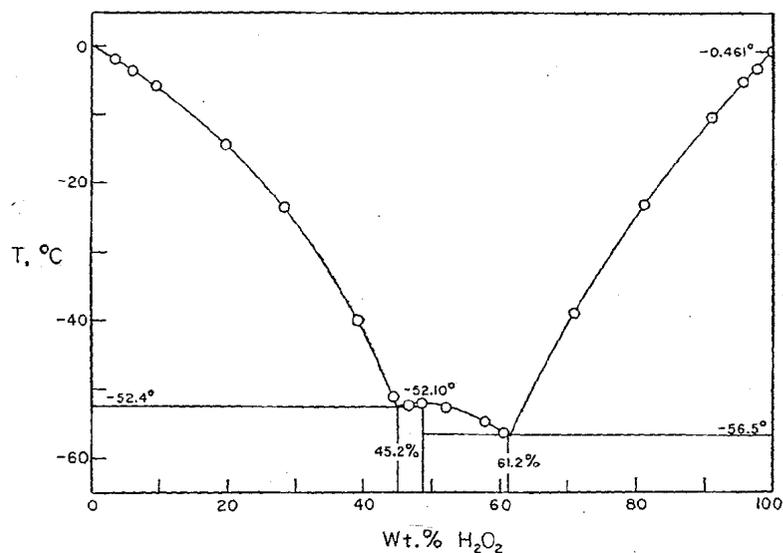


FIG. 2. Phase diagram of the system hydrogen peroxide - water.

From the present study and a similar one made on the system hydrazine-water (14) it must be concluded that the poor results obtained in attempting to freeze out the ice or the pure compound are due entirely to the difficulty of removing the mother liquor from the crystals. Calculations show that in most instances the solid still contained as much as its own weight of liquid although it looked quite dry. The so-called synthetic or 'wet residue' method is certainly superior to the analytical one for such investigations. In particular the use of radioactive tracers as described above should make it still more valuable and more widely applicable in the study of phase equilibria.

Finally there remained the question of deviation from Raoult's law; since dilute peroxide solutions show almost ideal behavior up to concentrations of 10% H_2O_2 it became questionable whether the accepted value, 74 cal. per gm., for the heat of fusion of hydrogen peroxide was not appreciably in error. A check of that datum by means of an ice calorimeter has yielded a value, 85.75 cal. per gm. which leads to very good agreement of the freezing point curve with Raoult's law. A description of this and other thermal measurements will be published shortly.

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