THE PROPERTIES OF PURE HYDROGEN PEROXIDE. III

BY O. MAASS AND W. H. HATCHER

This paper deals with a further investigation of the properties of pure hydrogen peroxide. The procedure for the preparation of the pure peroxide has been described in THIS JOURNAL,[1] and was the same as that followed to obtain the samples used in the experiments described below.

Magnetic Susceptibility.—The determination of this constant is of some interest from the point of view of the strong paramagnetic character of oxygen. If the two oxygen atoms in peroxide are held together in any way resembling their arrangement in the oxygen molecule, then the diamagnetic character of water should be diminished and possibly reversed by the introduction of an oxygen atom into the water molecule. Very little attention has been paid in the past to magnetic susceptibility which is so highly constitutive in nature. Henrichson[2] showed that, as a general rule, unsaturation gives a diamagnetic tendency to the molecule.

The measurement of magnetic susceptibility in the case of a liquid may be carried out very conveniently by means of a method which may be credited to Quinque.

Two glass U-tubes, of exactly similar dimensions, were used, one filled with peroxide and the other with water. One arm of each U-tube was placed in the field of a powerful electromagnet, the 2 pole-pieces being such as to concentrate the field as uniformly as possible on the surfaces of the liquids in the U-tubes. The displacement of each liquid, when the field was turned on was measured by a microscope with scale; the positions of the tubes were reversed and the measurements repeated. Then

$$\frac{K_{H_2O_2} - K_{air}}{K_{H_2O} - K_{air}} = \frac{S_1 d}{S_2}$$

where K stands for the respective susceptibilities involved, S_1 the displacement of the peroxide whose density is d, and S_2 the displacement of the water.

Both water and peroxide were displaced in the same direction, that is, expelled from the field, the mean of a large number of measurements being $S_1 = 9.2 \pm 0.2$ scale divisions, and $S_2 = 10.9 \pm 0.2$ scale divisions. Taking K_{H_2O} as 7.2×10^{-7} and K_{air} as 0.25×10^{-7}, $K_{H_2O_2}$ has a value of 8.8×10^{-7}. These measurements were made at $10°$.

Thus, hydrogen peroxide is diamagnetic, and that to a greater extent than water.

Solubility in Organic Solvents.—Pure hydrogen peroxide is of course miscible with water in all proportions Samples of hydrogen peroxide ranging from 99.6% to 88% in strength were mixed with equal volumes of absolute alcohol and kept at $0°$. Complete miscibility occurred in each case.

Ether and pure peroxide are not miscible in all proportions as had been

[1] Maass and Hatcher, THIS JOURNAL, **42**, 2548 (1920).

[2] Henrichson, *Wied. Ann.*, **22**, 121 (1884); **34**, 180 (1888).

assumed by previous investigators, two layers existing up to a relatively high temperature.

A small volume of 99.4% peroxide was shaken for half an hour with an equal volume of anhydrous ether, the temperature being kept at 0°. The ether layer on analysis showed a content of 44% of peroxide. This layer was pipetted off and the same volume of fresh ether added; analysis again showed a 44% content of peroxide. A second sample of 96% peroxide, on treatment with an equal volume of ether, under conditions similar to those above, again showed 2 distinct layers, the volume of the ether being increased. Analysis of both layers showed that the ether had absorbed over half the hydrogen peroxide (55%), while the lower layer showed a 91% peroxide content; thus the peroxide must have taken up a small quantity of ether. The contents of the vessel were heated on a water-bath to 79°, when complete miscibility occurred; on cooling, the 2 layers again made their appearance.

The experiments on the system, hydrogen peroxide-ether, are incomplete. The conflicting data previously available[3,4] make it worth while to investigate the 3- component system, ether–hydrogen-peroxide–water, over the full range of concentrations. The present authors intend to do this in the near future.

In pure dry benzene pure hydrogen peroxide is quite insoluble, nor does complete miscibility occur on the addition of alcohol.

Solubility of Salts and Sugar.—The freezing-point curves of sodium chloride, sodium nitrate, sodium sulfate and sugar were determined in

TABLE I
SOLUBILITIES IN HYDROGEN PEROXIDE

Sodium Chloride		Sodium Sulfate	
Solute	Freezing pt.	Solute	Freezing pt.
%	° C.	%	° C.
1.08	−2.37	1.19	−2.17
3.14	−3.62	2.56	−2.87
5.42	−5.07	4.47	−3.12
8.61	−7.67	6.92	−4.27
11.81	−10.57	10.23	−5.52
15.63	−10.37	13.51	−6.77
17.00	above 0°	16.77	−9.02
Sodium Nitrate		19.47	−10.57
1.62	−2.47	22.64	+19.6
3.23	−2.82	23.59	29.1
5.11	−3.72	25.62	39.1
7.58	−4.72	Sugar	
10.11	−5.62	3.88	−1.97
13.19	−6.97	11.64	−2.60
16.66	−8.12	18.66	−3.47
20.19	−9.52	25.16	−4.72
22.25	−10.82	30.94	−5.70
25.22	+11.8	36.82	−7.57
28.25	32.3	42.86	−10.30
31.53	49.3	50.00	−14.32

[3] *J. Russ. Phys. Chem. Soc.*, **35**, 637 (1903).
[4] THIS JOURNAL, **38**, 633 (1916).

the usual way. Weighed quantities of solute were added to a weighed quantity of peroxide which was kept in a bath whose temperature could be regulated through small intervals, and the temperature was noted at which the last trace of solid disappeared. The results obtained are given in Table I.

Fig. 1 shows those values which could conveniently be represented graphically, together with the freezing-point curve of water in hydrogen
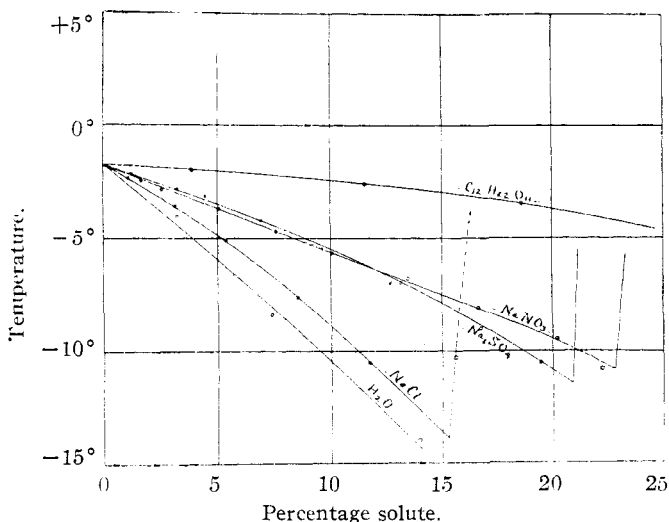

Fig. 1.—Solubility curves in H_2O_2.

peroxide.[5] For purposes of comparison the corresponding curves with water as solvent are shown in Fig. 2.

During the measurements only the sodium chloride solutions showed a tendency towards decomposition, and even this was slight. In all cases when the solute was the solid phase, decomposition occurred at the higher temperature, and this gave the upper limit of concentration to which measurements could be made.

Due to the marked tendency which hydrogen peroxide has towards supercooling, there is considerable difficulty in making accurate molecular weight determinations in it, but the above results will serve to show that salts are ionized in hydrogen peroxide. In Table II the first column gives the weight of dissolved substance M which in 100 g. of solution shows a lowering of $1°$; these values are obtained by taking the slope of the tangent at zero concentration, and are probably correct to only 10%. The second column gives M_0, the molecular weight calculated by using 1880 as the cryoscopic constant of hydrogen peroxide, calculated from the latent heat of fusion. The last column gives the ratio M_0/M of the calculated to the theoretical molecular weights.

[5] THIS JOURNAL, **42**, 2570 (1920).

TABLE II

MOLECULAR WEIGHTS OF SUBSTANCES IN HYDROGEN PEROXIDE

Solute	$M/100$	M_0	M_0/M
Water	1.27	22.8	1.26
Cane sugar	16.2	304	0.90
Sodium chloride	1.66	31.2	0.53
Sodium nitrate	2.55	48.0	0.56
Sodium sulfate	2.69	50	0.35

It will be seen that the molecular weight of sugar lies within the limits of experimental error, and that the 3 salts are dissociated probably to the same extent as they are in water.
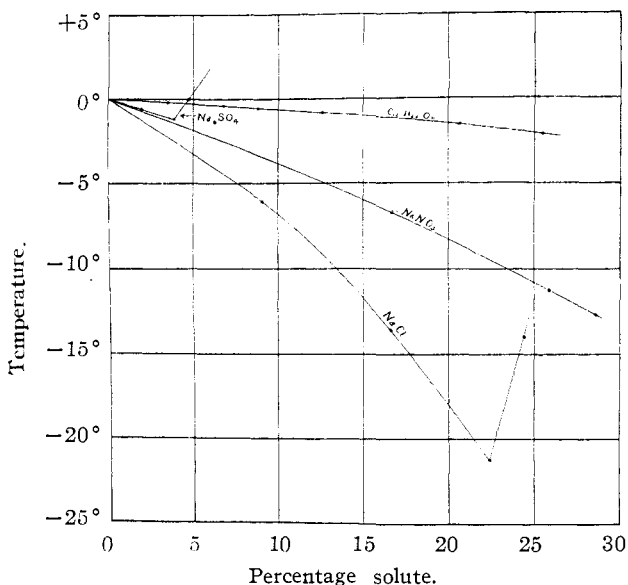

Fig. 2.—Solubility curves in H_2O.

The systems of hydrogen peroxide with sodium nitrate and with sodium chloride have eutectics at 22% and 15% as compared with 36.9% and 22.4%, the eutectics in the corresponding water systems; hence these salts are not so soluble in hydrogen peroxide as in water, nor do their solubilities increase with rise in temperature to the same degree as in water. After passing the eutectic, the solids precipitated from super-saturated solution were filtered off and dried with filter paper; on analysis they showed only a small indefinite content of peroxide, due to the diffi-culty of completely removing the solution from the crystals. No molec-ular compounds were found between hydrogen peroxide and either sodium chloride or sodium nitrate.

The curve for the system, sodium sulfate-hydrogen peroxide, differs more markedly from that of the corresponding water system, the eutectic

being reached at 21% as compared with 3.85% in the case of water. The solid separating from the supersaturated solution was filtered, dried and analyzed, and found to contain 31.5% of hydrogen peroxide, corresponding to the formula $Na_2SO_4.2H_2O_2$, for which the theoretical content is 32%.

In the case of the sugar-hydrogen peroxide system it was found impossible to continue the measurements beyond 50% concentration due to the viscosity of the solution, so that this eutectic could not be obtained. Evidently the curvature of the graph with higher concentrations points to the existence of complex sugar–hydrogen-peroxide molecules.

Action of the Halogens and Halogen Acids.—An attempt was made to dissolve hydrogen chloride and hydrogen bromide gases in anhydrous hydrogen peroxide.

The halogen acids were prepared and purified in the usual way, care being taken to dry them thoroughly. They were condensed in a glass bulb sealed to a gas buret containing mercury, which could be filled with definite volumes of the halogen hydride. A 2-way stopcock at the top of the buret made it possible to force out this volume of gas into a capillary tube, the end of which dipped into a tube of hydrogen peroxide immersed in a freezing mixture. A capillary T-piece served as an inlet tube through which air could be driven to wash out the gas remaining in the capillary.

When hydrogen chloride was slowly passed into the peroxide it apparently did not dissolve, the bubbles of gas passing through the liquid. A strong odor of chlorine made it evident that the hydrogen chloride had been oxidized. This was found to be the case even when the hydrogen peroxide was subcooled considerably below its freezing-point. In the case of hydrogen bromide a similar result was obtained, bromine being liberated in small globules which sank to the bottom of the liquid.

Chlorine and bromine are only slightly soluble in pure hydrogen peroxide (less so than in water); bromine gives just a faint color to the liquid. Iodine is also quite insoluble. Contact with any of the halogens causes the gradual decomposition of hydrogen peroxide. As a further test, pure chlorine was condensed on the top of solid peroxide and allowed to remain in contact with it for 24 hours with occasional shaking. Apparently no solution took place; at the end of the experiment the chlorine was poured off into a warm test-tube and allowed to evaporate, when a test showed that no hydrogen peroxide remained.

Dry hydrogen chloride was passed into hydrogen peroxide solutions of various strengths, and tests were made for the liberation of chlorine. Peroxide solutions of 87% and 70% showed the liberation of chlorine, whereas a 21% solution did not. In a 50% solution chlorine was liberated only after the hydrogen chloride had been passed in for some time. In the case of hydrogen bromide similar results were obtained, except that the concentrations of acid and peroxide necessary for reaction were of course much lower than in the case of hydrogen chloride. Pure hydrogen

peroxide liberates chlorine from the smallest trace of hydrogen chloride. In peroxide solutions the reaction depends on the concentration of the halogen acid; the more dilute the peroxide solution, the greater must be the concentration of hydrogen chloride before chlorine is liberated. These critical concentrations have been thoroughly investigated, and will form the subject of a separate paper.

The sodium and potassium salts of hydrobromic and hydriodic acids are violently acted upon by pure hydrogen peroxide and its concentrated aqueous solutions with the liberation of bromine and iodine. As has been mentioned before, sodium chloride does not act on anhydrous peroxide at low temperatures. At room temperature a slight decomposition of the peroxide occurs, but no chlorine is liberated.

Action of Ammonia.—Dry ammonia was passed into anhydrous hydrogen peroxide kept at $0°$. The gas dissolved readily and, after a considerable amount had gone into solution, white crystals formed. These were filtered off and dried with filter-paper; analysis showed that they had a composition corresponding to $NH_3.H_2O_2$. Use was then made of the apparatus by means of which the halogen hydrides had been added to peroxide.

Special care was taken to purify the ammonia, which was dried by means of potassium hydroxide sticks and liquefied by absorption in ammonium thiocyanate;[6] from this the gas was evaporated and condensed by a carbon-dioxide–ether mixture. By means of the gas buret, definite volumes of dry ammonia were added to a weighed quantity of peroxide so that the composition of the resulting solutions was accurately known. The freezing-points of these solutions were then determined.

At first the ammonia dissolved readily; no decomposition of the peroxide occurred and no odor of ammonia was noticed. When, however, the ammonia concentration reached a value of 30%, it was found that the latter had a considerable partial vapor pressure. Crystals deposited along the sides of the tube above the liquid where the agitation of the stirrer had spattered drops of the solution. These crystals were brought back into the solution only with great difficulty, and the partial vapor pressure of the ammonia was so high that the composition of the liquid could not be determined after ammonia had been added to a concentration of 33%. If the freezing-point is taken as the temperature at which the last trace of solid disappeared, the points from 28% up to 31% are slightly too high due to the conditions described above.

The pure compound had a melting point of $24.5°$ and a composition of 66.8% peroxide, corresponding to the theoretical value of the compound $NH_3.H_2O_2$. The freezing-points as determined are tabulated in Table III.

As it was of considerable interest to discover whether a compound of the formula $2NH_3.H_2O_2$ exists, the experimental method was changed.

[6] H. W. Foote and S. R. Brinkley, THIS JOURNAL, **43**, 1178 (1921).

A long glass freezing-tube, closed at both ends, was fitted with a stirrer moved by an electromagnet. A weighed quantity of hydrogen peroxide was introduced through a side tube which was then sealed. The freezing-tube was sealed by glass tubes to a vacuum pump and the ammonia supply. The peroxide was frozen by a mixture of carbon dioxide and ether and the whole apparatus thoroughly evacuated. Known volumes of ammonia were then condensed onto the peroxide and the latter brought into solution by vigorous stirring, the temperature meanwhile being gradually raised. A large amount of heat was developed during solution and the mixture had to be cooled down to —78° from time to time. No ammonia was lost at any time as mixing took place in an all-glass vessel. When complete solution had been effected, the freezing-point was determined by measuring the temperature of the surrounding bath which could be altered slowly in any desired direction. Ammonia was added and freezing-points taken until the volume of the liquid became too large. Then another procedure was adopted; a small quantity of peroxide was again sealed into the tube in the manner described above, and ammonia condensed on it to give a concentration of 68%. Crystals, at this high concentration of ammonia, formed only at liquid air temperature. Definite volumes of ammonia were then evaporated from the solution, so that the hydrogen peroxide concentration was increased to a known extent.

Crystals which formed from a 61% ammonia concentration melted below —78°, and two more points were taken at higher concentrations of peroxide. These points are shown in Section III of Table III.

TABLE III
NH₃-H₂O₂ FREEZING-POINTS

	NH₃ %	F. pt. °C.		NH₃ %	F. pt. °C.
1	0	− 1.72		48.6	+9
	3.41	−13		49.7	+1.5
	4.31	−18	II	50.7	0
	18.05	+ 5		51.8	−6
	19.6	+ 8		52.8	−9.5
	21.1	+15			
	23.9	+20		68.7	below −78
	25.2	+22		61.3	do
	26.4	+24	III	59.5	−53.5
	27.7	+25		56.7	−32
	28.8	do			
	31.1	do			
	31.2	do			
	33.2	do			

All of the freezing-points determined are plotted on the graph shown in Fig. 3. A compound of the formula, $2NH_3.H_2O_2$, would contain about 50% of each constituent and it is seen that such does not exist, particular care having been taken with this part of the curve. The same statement applies to a compound of the formula, $3NH_3.H_2O_2$, which would have a 60% ammonia content.

The ammonia-hydrogen peroxide compound melts at 24.5° to an oily liquid; it is quite stable and can be kept, provided that no trace of water is present. The presence of water causes decomposition of the hydrogen

peroxide; this increases the amount of water, which in turn raises the rate of decomposition. This is to be expected if the compound dissociates in water with the consequent formation of hydroxyl ions from the ammonium hydroxide. The solid compound is of course readily soluble in water; it dissolves in absolute alcohol to the extent of 18% without noticeable decomposition. In benzene it is insoluble, and in ether the solubility is of the order of only 1%.

A saturated solution of anhydrous peroxide in ether was prepared and ammonia gas passed in; oily globules separated until 2 layers formed. The ammonia dissolved readily until complete separation had taken place, the point where absorption ceased being very sharp. The upper layer on examination was found to be ether practically free from peroxide. The lower layer proved to be the subcooled compound whose melting point and composition were approximately the same as those of the compound prepared directly.

D'Ans and Wedig[7] on passing ammonia into an ethereal solution of hydrogen peroxide, found that solids separated corresponding to the formulas, $NH_3.H_2O_2$ and $2NH_3.H_2O_2$, and having melting points of 15° and —40°, respectively, decomposition taking place on melting. As the ether solution used by these investigators could not have been anhydrous, this is accounted for: the presence of water caused decomposition and the melting point registered for the first compound was far too low.

Fig. 3.—$NH_3 - H_2O_2$ system.

The compound to which D'Ans assigned the formula, $(NH_4)_2O_2$, does not form, and what he obtained may have been a complex molecule of ether, ammonia and hydrogen peroxide, as the analysis was based on peroxide content.
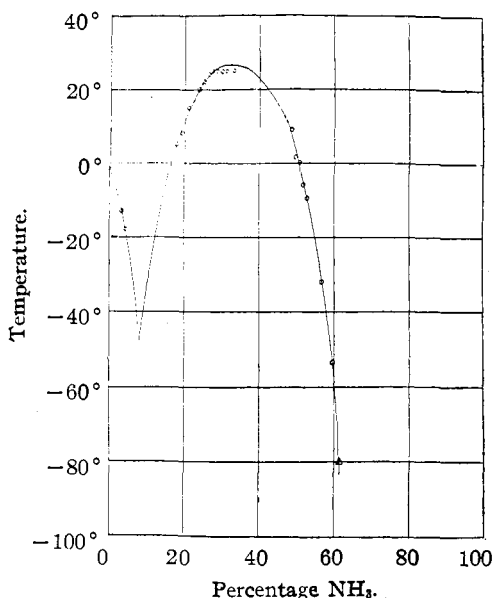
Summary

Hydrogen peroxide is diamagnetic, the susceptibility being 8.8×10^{-7}, which is more than that of water. This is evidence in favor of a structural formula in which the oxygen atoms are not connected in the same way as in the oxygen molecule.

[7] D'Ans and Wedig, *Ber.*, **46**, 3075 (1913).

The solubility of anhydrous peroxide was measured in various organic solvents.

The solubility curves of sodium chloride, sodium nitrate, sodium sulfate and sugar were determined. It was shown that in hydrogen peroxide the dissociation is of the same order as in water. The tendency towards molecular compound formation is less than in the case of water, there being evidence of only one compound, $Na_2SO_4.2H_2O_2$.

The action of the halogen hydrides on pure hydrogen peroxide and its aqueous solutions was examined, and conditions were indicated under which the oxidation of the halogen hydride occurs. The halogens were found to be less soluble in hydrogen peroxide than in water.

Ammonia is soluble in pure hydrogen peroxide, a crystalline compound being formed which melts at $24.5°$, and which is stable in the absence of water. This compound is slightly soluble in ether, and can be formed by passing ammonia into an anhydrous solution of peroxide in ether. It was shown that a compound corresponding to $2NH_3.H_2O_2$ does not form. The stability of the compound, $NH_3.H_2O_2$, shows that it is the hydroxyl ion which causes the decomposition of hydrogen peroxide. Water dissociates or possibly hydrolyzes it and, with the consequent formation of hydroxyl ions, the decomposition is cumulative. Whether this compound is an ammonium salt, NH_4O_2H, is not certain, but it is hoped that experiments with other alkalies will throw light on this point.

The vapor pressure and dielectric constant of hydrogen peroxide are being measured, as well as the conductivity of salts in anhydrous hydrogen peroxide.

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FREE AND TOTAL ENERGY CHANGES IN THE REDUCTION OF QUINONES

BY JAMES B. CONANT AND LOUIS F. FIESER

In a previous paper[1] we have dealt with the oxidation-reduction potentials of certain water-soluble anthraquinone derivatives and the change of these potentials with variations in the hydrogen-ion concentration. From the standpoint of the organic chemist one of the most interesting aspects of the subject of oxidation-reduction potentials is a comparison of the free energy of reduction of different classes of compounds and a study of the effects of substitution in a given class. We stated in our last paper that we should soon publish the results of our work on the oxidation-reduction potentials of certain derivatives of anthraquinone, naphthoquinone and benzoquinone together with the temperature coeffi-

[1] THIS JOURNAL, **44**, 1382 (1922).