Calculations show that the fruitfulness of collisions between two nitrogen atoms to form a molecule is small. The temperature coefficient of the afterglow in nitrogen can be explained on the basis that only atoms possessing velocities below some critical value can combine on colliding.

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THE PROPERTIES OF PURE HYDROGEN PEROXIDE. VI

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The following paper is one of a series[1] that deals with the properties of pure hydrogen peroxide. In it several new freezing-point curves are described and the existence of compounds between hydrogen peroxide and a number of organic bases is investigated. The measurements of the heat of decomposition, the molecular weight in the vapor phase and the explosion temperature of pure hydrogen peroxide are described.

Pure hydrogen peroxide was prepared in much the same manner as was set forth in the first paper of this series with a few slight modifications. The concentration, by evaporation *in vacuo*, was carried out until the strength was about 98% by weight. The distillate produced in the final stages of evaporation was saved. The final purification was carried out as before by means of fractional crystallization.

Freezing-Point Curves.—This section of the experimental work deals with the solubility and freezing-point curves of various substances in pure hydrogen peroxide. These experiments are of interest in comparison with corresponding water systems. The apparatus employed consisted of a long test-tube set in a bath of ether in a transparent Dewar flask. A stirrer was provided in the tube and the bath was stirred by bubbling air through it. Its temperature could be controlled by adding carbon dioxide snow or by changing the rate of flow of air. The temperature was measured by a thermometer placed in the bath. The materials were added in the most convenient manner for each substance. The chemicals used were all carefully purified to remove foreign substances which might decompose the peroxide. The temperatures are those recorded just as the last crystals disappeared when the bath was slowly warmed.

In Table I the results are recorded for potassium chloride, sodium fluoride, potassium sulfate and methyl alcohol, and these systems are plotted in Figs. 1 and 2, with the corresponding water systems.

The data for the water curves are taken from the literature with the exception of the one for sodium fluoride, for which the following points

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

TABLE I

FREEZING POINTS IN HYDROGEN PEROXIDE

Potassium Chloride

Mole %	M. p., °C.
2.6	− 3.4 H_2O_2 solid phase
4.8	− 6.5
7.1	−10.4
9.4	−14.6
11.9	−20.2
13.9	−25.0
15.9	−31.4
17.0	−24.2 KCl solid phase
18.7	−16.0
20.5	− 7.0
22.1	− 1.0

Sodium Fluoride

Mole %	M. p., °C.
3.8	− 5.2 H_2O_2 solid phase
7.4	− 9.1
8.6	−10.6
9.8	−12.1
11.1	−13.9
12.3	−15.2 Eutectic

Potassium Sulfate

Mole %	M. p., °C.
0.87	− 2.0 H_2O_2 solid phase
2.27	− 4.8
3.68	− 8.2
5.3	−12.3
7.6	−17.5
8.4	−23.5
14.1	−11.0 K_2SO_4 in solid phase
15.9	+ 0.5

Methyl Alcohol

Mole %	M. p., °C.
5.6	− 1.7 H_2O_2 solid phase
13.2	− 6.4
18.4	−10.2
25.2	−15.3
28.3	−18.6
33.2	−22.2
43.8	−37.8
51.5	−49.3

were determined by the authors: 0.6%, −1.1° and 1.03%, −1.9° with ice as the solid phase. The eutectic was found to be at −2.9° for a per-

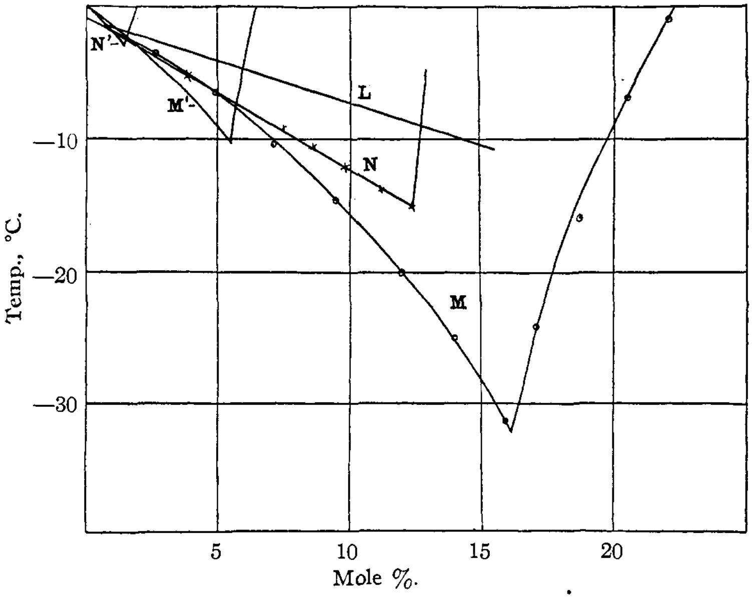

Fig. 1.—Freezing-point curves. L, Theoretical lowering in H_2O_2; M, H_2O_2–KCl; M', H_2O–KCl; N, H_2O_2–NaF; N', H_2O–NaF.

centage of 1.4. −5.6° was obtained by Guthrie as the eutectic,[2] but the authors found that the solution froze to a solid if cooled below −2.9°. The straight line L, plotted in each figure, represents the theoretical lowering of the freezing point in hydrogen peroxide caused by a substance which does not ionize or associate when dissolved.

In the potassium sulfate system no points could be recorded between the concentrations of 8.4 and 14.1% because the liquid froze to a glass. The same difficulty was encountered with methyl alcohol beyond 51.5%.

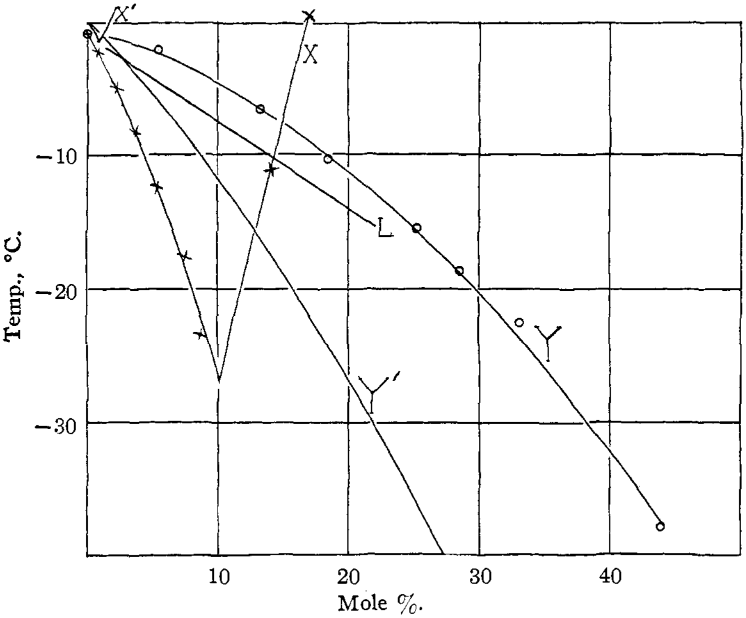

Fig. 2.—Freezing-point curves. L, theoretical lowering in H_2O_2; X, H_2O_2–K_2SO_4; X', H_2O–K_2SO_4; Y, H_2O_2–CH_3OH; Y', H_2O–CH_3OH.

From the figures it is apparent that the salts are dissociated in pure hydrogen peroxide whereas methyl alcohol is associated, all of which is indicated by the relative angles of the L curves and the freezing-point curves at infinite dilution. In every case, the eutectic in the hydrogen peroxide system occurs at a far higher concentration than in the corresponding water system, indicating a greater solubility in hydrogen peroxide than in water.

Potassium bromide was found to decompose hydrogen peroxide fairly rapidly, no matter how many times the salt had been purified by recrystallization.

When ether is added to hydrogen peroxide only a slight amount dissolves before a separate layer is formed. The peroxide is fairly soluble in this

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[2] Guthrie, *Phil. Mag.*, **5**, 640 (1878).

second layer, a considerable amount of heat being evolved during its solution. Freezing points which were obtained for the ether–hydrogen peroxide system are contained in Table II.

Table II

Freezing Points in Hydrogen Peroxide

Ethyl Ether

Weight, %	M. p., °C.	Weight, %	M. p., °C.
3.5	−1.2 (Two distinct layers)	47.8	− 6.0
41.6	... H_2O_2 layer nearly gone	59.2	−16.5
44.3	−4.8	66.5	−33.1
45.2	−5.1	71.5	−47.6

As long as there were two layers present, the freezing point of the lower layer was −1.2°. The freezing point of pure hydrogen peroxide is −0.9°,[3] that is, within 0.3° of the freezing point of the peroxide layer. Since the latter determination may be 0.2° too low on the absolute scale, the lower layer must have consisted of well-nigh pure peroxide. This shows that only a very slight amount of ether is soluble in pure hydrogen peroxide. When the peroxide layer had just disappeared the freezing point was still very high and the solid which crystallized out was filtered off at a low temperature and analyzed. The composition of the solid varied from 51.7% by weight of hydrogen peroxide to 45%, depending on the concentration of the solution. The composition of the ether layer varied with change of temperature when there were two layers in equilibrium, being 60.8% by weight of hydrogen peroxide at 0° and 64% at 20°, with complete miscibility somewhere in the neighborhood of 80°. The solid which is formed on cooling an ether solution may be a solid solution. The complete phase rule diagram is probably similar to that of succinic nitrile and water.

The system sulfuric acid–hydrogen peroxide was examined and where possible the freezing points were determined. The most convenient way of introducing definite quantities of anhydrous sulfuric acid was to add gaseous sulfur dioxide, which united with the peroxide, even when very cold, to form sulfuric acid. Table III contains the data thus obtained.

Table III

Freezing Points in Hydrogen Peroxide

SO_2, mole %	5.8	11.7	13.9	19.5	47.2	48.4	49.7	50.5
M. p., °C.	−5.3	−11.5	−18.0	−31.0	−10.0	−3.3	+2.4	+4.1

The solution was very viscous between 19.5 and 47.2% of sulfur dioxide and no crystals were obtainable. Between these percentages the solution solidified to a glass when the temperature was lowered below 25°. Toward the end of the addition a slight decomposition was noticed with the formation of ozone. This accounts for the lowering of the freezing point

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[3] Cuthbertson, Matheson and Maass, This Journal, **50,** 1120 (1928).

of the sulfuric acid formed, since at 50% sulfur dioxide the freezing point should have been 10°, that of pure sulfuric acid. The two portions of the curve obtained indicate that more than one eutectic is formed. This would show that some compound between sulfuric acid and hydrogen peroxide is formed. The great tendency to supercool prevented the isolation of crystals.

An apparatus has been described in a previous paper[4] for the examination of the ammonia–hydrogen peroxide system. An attempt was made to use this apparatus for the similar system phosphine–hydrogen peroxide. Great care was taken in the purification of the phosphine. It was found, however, that even in supercooled peroxide phosphine was soluble to an exceedingly slight extent.

The fact that ammonia formed a stable compound with the peroxide, whereas phosphine did not, seemed to indicate that the more basic the substance, the more readily would it combine with peroxide to form a stable compound. With this in view, the effect of a large number of organic bases was tried. It was found that the peroxide remained stable and the amine unoxidized when in contact at low temperatures, that is, below 0°. If the solutions were allowed to warm up to room temperature

Table IV

Freezing Points in Hydrogen Peroxide

Mole %	M. p., °C.	Mole %	M. p., °C.	Mole %	M. p., °C.	Mole %	M. p., °C.
Piperidine		39.6	− 9	13.3	−10.5	Di-*iso*butylamine	
5.6	−10.3	43.5	−11	16.6	− 3	2.24	− 2.5
11.1	−32.5	46.3	−13	21.9	+15.5	5.75	− 8.5
12.4	−43.0	51.4	−19	24.2	+21	8.5	−17
		56.0	−23	27.7	+25	10.9	−30
Diethylamine		59.5	−18	28.2	+24		
3.05	− 8.4	62.7	−12	31.2	+26	Tripropylamine	
11.3	−35.0	65.4	− 9.5	34.5	+23	3.0	− 4
		69.7	− 9	36.8	+20	9.1	−14.5
Mono-*n*-butylamine		71.4	−11	38.7	+16.5	12.1	−30
1.29	− 2.7	73.0	−13	39.9	+17		
4.61	− 9.0	75.8	−16.5	49.9	+17	Dimethylaniline	
8.37	−14.0	77.9	−20.5	53.1	+15.4	6.35	− 2.3
12.5	−29.0			55.5	+13.5	12.17	− 3.0
16.7	Froze to glass	*Tert.*-monobutylamine		58.5	+10	When warmed oil separated	
				60.8	+ 7		
20.7	Froze to glass	1.69	− 2	63.0	+ 8	Further addition gave two layers	
		3.82	− 5	65.0	+ 7.3		
23.0	0	5.47	− 7.5	66.6	+ 5.5		
24.0	− 2	8.40	−15	59.3	+ 5.0		
27.2	−10	9.22	−18	72.2	+ 1.5		
30.0	−10	12.7	−12	74.4	− 0.5		
33.6	− 8			76.4	− 5.0		

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[4] Maass and Hatcher, This Journal, **44**, 2473 (1922).

some of the amines caused decomposition of the peroxide, with oxidation of the amine to the nitro compound. Piperidine was the most active in producing decomposition, and when warmed to room temperature the heat of the reaction was sufficient to accelerate it progressively until the peroxide decomposed with explosive violence. The monobutylamine with the tertiary carbon atom attached to the nitrogen was the most stable of the amines tried, no decomposition taking place. The *iso*-normal-butylamine was next in the order of stability. In a test with the latter, less than 1% of peroxide decomposed after being in contact with various concentrations of this amine for eight hours, at temperatures below 0°.

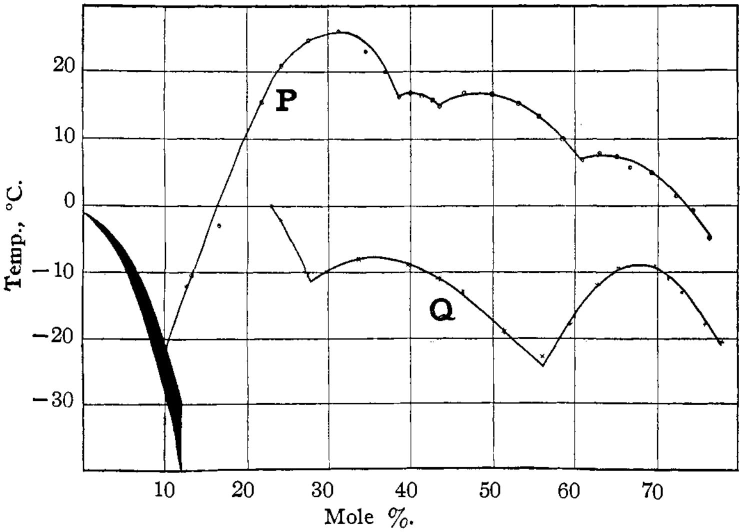

Fig. 3.—Freezing-point curves. Q, Mono *N*-butylamine–hydrogen peroxide. P, Mono butylamine–hydrogen peroxide.

In Table IV are given the freezing-point determinations made with the organic bases and hydrogen peroxide. Only in the case of the isomeric monobutylamines, the normal and tertiary, could a large part of the freezing-point curve be determined. In the case of all the others, no crystals could be formed at the higher concentrations of the organic base, since the mixture froze to a glass once the first eutectic had been passed.

Figure 3 represents all the points given in the above table. The depression of the freezing point of the peroxide was the same for all the bases, within experimental error, with the exception of the dimethylaniline. To prevent confusion the line is broadened to include all these points. In the case of the monobutylamine stable compounds were isolated. The compound having the composition $2H_2O_2{\cdot}C_4H_9NH_2$ was obviously the most stable. In the case of the *n*-butylamine a compound of the same molecular proportions was also isolated, with the indication, also, of a compound containing a greater proportion of hydrogen peroxide. As is well known this amine is oxidized to hydroxylamine at higher temperatures in aqueous solutions. This again illustrates the hypothesis that a molecular compound is generally formed between two substances before reacting and subsequent splitting up. Dimethylaniline, the only benzenoid amine investigated, behaved quite differently compared with the aliphatic amines. It was not as soluble in the peroxide and the small lowering of the freezing point of the peroxide indicated that it was associated in solution.

As it was not improbable that the other amines formed compounds which could not be crystallized out, due to supercooling, an entirely different method was resorted to in an attempt to isolate such compounds. This depended on the precipitation of an oil, from a mixture of anhydrous ether solutions of the amine and the hydrogen peroxide, with subsequent analysis of the resulting oil. This method had been found successful in the isolation of the ammonia compound.[4] The following will illustrate the procedure. When small portions of an ether solution of, for instance, diethylamine, were added to an ether solution of peroxide, successively, with vigorous stirring, at first an oil kept separating out. With further addition of amine this oil went back into solution. It was found that ether was not soluble in this oil, any more than in pure peroxide (see above). Hydrogen peroxide was soluble in the oil and could only be washed out by ether with great difficulty. Amine was also soluble in the oil but its far greater solubility in ether made it relatively easy to wash out the excess amine from the oil by means of anhydrous ether. The amine solution was therefore added until the maximum amount of oil had been precipitated and a slight amount more of amine was added, as indicated by the partial redissolving of the oil. The remaining oil was separated and could then be washed with ether. It was found that the composition of the oil was invariable, independent of the number of washings it had received. Furthermore, the analysis of the oil, in the case of all the amines tried, gave an exact molecular proportion of amine to peroxide.

Permanganate could not be used for titrating the peroxide in the presence of the organic bases. Hence the method used to analyze the oil was to dissolve a weighed portion of it in water and then add powdered manganese dioxide. The peroxide decomposed completely within a minute and the oxygen evolved was then measured.

Dimethylaniline, aniline, pyridine, phenylhydrazine, tripropylamine and di-*iso*butylamine did not give insoluble oils in ether. It cannot be taken for granted that because an oil does not separate on mixing ether solutions of organic bases and peroxide that no molecular compounds are formed. It was found that the more carbon atoms there were, to the amine, the greater was the solubility of the resulting oil in the ether; in the case of certain amines great care had to be taken to use concentrated ether solutions in order to get any oil at all. It seems probable, however, that some of the above bases do not form compounds with the peroxide. For example, dimethylaniline indicated this by its relative insolubility in the peroxide.

In Table V are given the results of the analyses of the oils that were formed, the percentages found and calculated being given in weight percentage of hydrogen peroxide. The exact agreement between the percentages found and calculated leaves little doubt as to the existence of these molecular compounds.

TABLE V

COMPOSITION OF OIL SEPARATING FROM ETHER

Base	Weight of H_2O_2 Found	Calcd.	Compound
Ammonia	66.7	66.7	$NH_3 \cdot H_2O_2$
Ethylamine	59.5	60.2	$2H_2O_2 \cdot C_2H_5NH_2$
n-Propylamine	53.2	53.7	$2H_2O_2 \cdot C_3H_7NH_2$
*Iso*butylamine	48.7	48.3	$2H_2O_2 \cdot C_4H_9NH_2$
n-Butylamine	48.5	48.3	$2H_2O_2 \cdot C_4H_9NH_2$
Tert.-monobutylamine	48.3	48.3	$2H_2O_2 \cdot C_4H_9NH_2$
Diethylamine	58.0	58.3	$3H_2O_2 \cdot (C_2H_5)_2NH$
Triethylamine	58.3	57.5	$4H_2O_2 \cdot (C_2H_5)_3N$
Piperidine	44.2	44.4	$2H_2O_2 \cdot C_5H_{10}NH$

Monobutylamine gave an oil which could be solidified at will, and having the same composition and freezing point as the stable compound indicated by the freezing-point curve. The same could be done in the case of the ammonia. All this indicates that the above method gives a reliable means of isolating those compounds which cannot be separated in the crystal form.

A feature of interest in the above table is the increase in the number of peroxide molecules taken up by the ethylamines with increase in substitution of the nitrogen hydrogens by ethyl groups. As a general conclusion, the possibility of forming a stable compound depends on the basicity of the base.

Heat of Decomposition of Hydrogen Peroxide

The heat of decomposition of hydrogen peroxide into water and oxygen was measured in an adiabatic calorimeter. The decomposition apparatus is shown in Fig. 4. It consisted essentially of two bulbs, A and B, which were joined by means of a ground-glass joint. This apparatus was submerged in the calorimeter water, leaving the two thin-walled glass tubes C and D protruding from the surface. Bulb A was filled with lumps of manganese dioxide which served to decompose any hydrogen peroxide carried over by entrainment. A quantity of peroxide was allowed to flow through a capillary funnel passing through Tube D into Bulb B. The amount which entered in this way was determined by weighing B before and after filling. A rubber tube was attached to C and led to a U-tube filled with pumice stone and sulfuric acid, outside of the calorimeter proper. The object of this was to catch any water vaporized during the decomposition and carried away with the oxygen, and thus to be able to correct for the heat of vaporization of this water. Actually it was found that this correction was very small, since, apparently, most of the water vapor with which the oxygen was saturated was reabsorbed in Bulb A.

After the apparatus had been put together, the calorimeter was brought to thermal equilibrium. The decomposition of the peroxide was started by dropping a small grain of manganese dioxide down Tube D, which was then immediately closed to force the oxygen along the other tubing. Most of the heat given off was transmitted through the walls of Bulb B, directly, from the liquid peroxide. The rate of reaction was controlled by the proper choice of the size of the initial grain of manganese dioxide. Toward the end, when the reaction slowed up, more manganese dioxide was added to increase the rate of decomposition. It was found that the reaction came to an abrupt end, as indicated by the sudden cessation of temperature change in the calorimeter. Throughout the whole process great care was taken to have complete adiabatic control. A sample calculation below gives an idea of the accuracy with which the determinations were made.

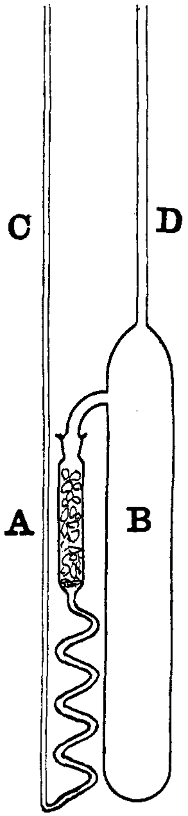

Fig. 4.—Heat of decomposition apparatus.

Sample Calculation

Concentration of peroxide = 38.05%
Weight of calorimeter + water = 1272.8 g.
Weight of calorimeter = 269.6 g.
Weight of water = 1003.2 g.

Water vapor carried out by oxygen

Weight of U-tube + water = 46.7191 g.
Weight of U-tube = 46.7176 g.
Weight of water vapor = 0.0015 g.

Weight of peroxide

Weight of Bulb B + H_2O_2 = 27.236 g.
Weight of Bulb B = 17.275 g.
Weight of H_2O_2 = 9.961 g.

Temperature change of calorimeter

Final reading = 3.784°
Initial reading = 1.345°
Change = 2.439°

The water equivalent of the calorimeter was made up as follows.

21.26 g. of glass: sp. ht. taken as 0.17 cal. Water equivalent = 3.62 cal.
9.38 g. of MnO_2: sp. ht. calculated from the atomic heats. Water equivalent = 1.16 cal.
298.2 g. of copper calorimeter and stirrer. Water equivalent = 24.70 cal.

Total water equivalent = 29.5 cal.

Heat change in water = 2444.4 cal.
Heat change in apparatus = 72.0 cal.
Heat carried off by water vapor = 0.9 cal.
Heat of residual water left in Bulb B = 19.8 cal

Total calories = 2537.1

Molecular heat of decomposition at 20° and concentration of 38.05% is

$$\frac{2537.1 \times 34.01 \times 100}{9.961 \times 38.05} = 22{,}714 \text{ cal.}$$

The heat of the reaction at 20° as represented by

$$H_2O_2(\text{liq.}) = H_2O(\text{liq.}) + \frac{1}{2}O_2(\text{ gas at atmos. press.}) + \text{Heat}$$

was found to be as follows. Two determinations of 97.15% peroxide gave 23,400 and 23,440 cal., respectively. Two determinations of 38.05% peroxide gave 22,746 and 22,714 cal., respectively. The heat of dilution between the above percentages is 690 cal. per mole, and the heat of decomposition of pure hydrogen peroxide averages 23,450 cal., which is considerably higher than values found in the literature.

The Molecular Weight of Hydrogen Peroxide in the Vapor State

The molecular weight of hydrogen peroxide in the vapor phase is difficult to determine because of its rapid decomposition at temperatures which would give measurable vapor pressures. A recent determination of the vapor pressure curve for pure hydrogen peroxide[5] indicated that such an experiment might, however, be carried out with success if the temperature was about 90°. At this temperature the vapor pressure of peroxide is about seven centimeters.

The apparatus used to carry out the experiment was of the Victor Meyer type. It is shown in Fig. 5. It consisted essentially of a large flask C with a long neck. It had a capacity of about 2400 cc. and the neck was 60 cm. long. The flask was sunk in the water-bath L which was stirred by the paddles N. The connecting tubing E was heated by means of nichrome wire embedded in asbestos. The current was regulated so that the temperature was about 5° above the bath temperature. A small tube F, filled with a few lumps of manganese dioxide, was inserted next to the manometer M. This served to protect it from the peroxide. A and B

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[5] Maass and Hubert, This Journal, **46**, 2693 (1924).

were outlets to a hydrogen reservoir and a vacuum pump, respectively. The magnetic device K for dropping the capsules of peroxide was fitted to the apparatus by means of a ground-glass joint.

The apparatus was made of pyrex glass but even so peroxide decomposed rapidly in it. It was found that if the glass surface was coated with a thin film of beeswax the decomposition was greatly reduced.

The procedure employed in using the apparatus was as follows. The bath was heated to 92° and at the same time the apparatus was thoroughly evacuated. Then it was filled to atmospheric pressure with dry hydrogen. The capsule with a weighed amount of pure hydrogen peroxide was inserted in the magnetic dropping device. This part of the apparatus was kept cool by blowing a current of air across it when the peroxide capsule was in it. The capsule was made of beeswax. A few drops of peroxide were poured into it and by difference in weight the amount of peroxide was known. The mouth of the capsule was closed after weighing until only a very fine opening was left. This was necessary to allow the air to escape when the pressure was reduced in order not to burst the capsule. When the capsule was in place the pressure was quickly lowered to one centimeter. At this pressure and room temperature the pure peroxide in the capsule was still far from its boiling point and not much could be lost by evaporation through the fine hole in the capsule. When the pressure had been reduced, two or three successive readings were taken on the manometer and then the capsule was dropped to the bottom of the flask C where the wax of the capsule melted and the peroxide was free to vaporize. Pressure readings were then taken at known intervals of time. At the same time the barometric pressure was observed in order to make corrections for its change. The object of the presence of the hydrogen gas was, of course, to prevent peroxide vapor from reaching the manometer. The dimensions of the flask and the narrow tube connections were chosen in order to reduce diffusion through the hydrogen as much as possible.

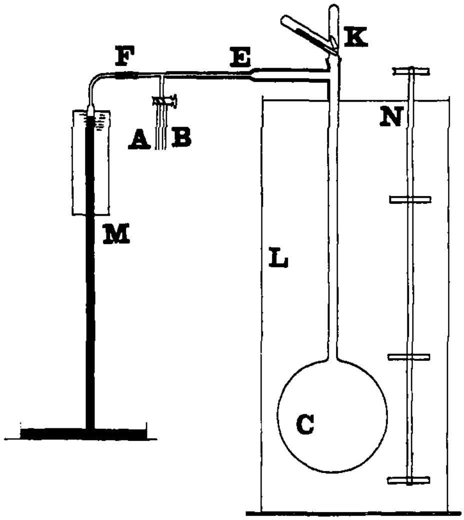

Fig. 5.—Vapor density apparatus.

The results obtained are given in the next table, VI, and plotted in Fig. 6. Experiment E was made with 56.6% peroxide instead of 100%, as in the case of the others.

TABLE VI

INCREASE IN PRESSURE (CM.) WITH TIME (MIN.)

Experiment	A	B	C	D	E
Weight of H_2O_2, g.	0.0774	0.0631	0.1052	0.0196	0.0468 (56.6%)
Temp., °C.	92	92	92	92	92
Time, min.	Pressure, cm.				
1	1.15	0.8	1.87	0.46	1.52
2	1.64	1.48	2.64	.52	1.74
3	2.00	1.74	2.96	.56	1.76
4	2.15	1.78	3.03	.57	1.77
5	..	1.79	3.07	.57	1.79
6	2.24	1.80	3.11	.57	1.81
7	2.25	1.82	3.13	.57	1.81
8	2.26	1.83	3.11	.57	1.81
9	2.29	1.84	3.13	.57	1.81
10	2.30	1.85	3.16	..	1.81
11	2.31	1.86	3.17	..	..
12	2.33	..	3.18	..	..
13	..	..	3.20	..	..
14	2.35	..	..	.60	..
16	2.38	1.90	..	..	..
18	2.42	..	3.28	..	..
19	..	..	..	.62	..
21	..	1.95	..	..	..
23	..	..	3.35	..	..
24	..	..	..	.64	..
28	..	..	3.40	..	..
29	..	..	..	.66	..
33	..	..	3.45	..	..
34	..	..	..	.68	..

A question that at once arose from the above curves was what portion was to be taken as the final pressure due to hydrogen peroxide vapor only. The answer for curves D and E, where only a small quantity of peroxide was used, was obviously the constant pressure portion. It seemed apparent from curve D that the action consisted, first, of a boiling of the peroxide to form a vapor and then a diffusion upward to the unwaxed portion of the system, the magnetic dropping device, where the peroxide decomposed. When a much larger quantity of peroxide was used the decomposition started before the boiling had finished and no constant pressure was reached. It did not appear correct, therefore, to extrapolate back to zero time and take that pressure as the correct one because the decomposition did not set in at the start. If six minutes from the start was taken as the point where evaporation ceased and decomposition just started, then the molecular weight determinations were as follows: A = 34.0; B = 34.3; C = 33.9; D = 34.0; mean = 34.0. Thus the molecular weight of hydrogen peroxide in the capor phase is 34.

If, on the other hand, the molecular weight is determined by extrapolation of the decomposition curve back to zero time, then the values are: A = 34.9; B = 34.5; C = 34.4; D = 35.2. From what has been said above these values are too high.

In Experiment E, in which 56.6% peroxide was used, the pressure was calculated which would be obtained if 34 were taken as the molecular weight of the peroxide and this pressure was compared with that observed. The observed pressure was $1^{1}/_{3}\%$ less than the theoretical. Experiments were carried out with water, under identical conditions of pressure and temperature, to check the apparatus. These gave molecular weights of slightly under 18.1.

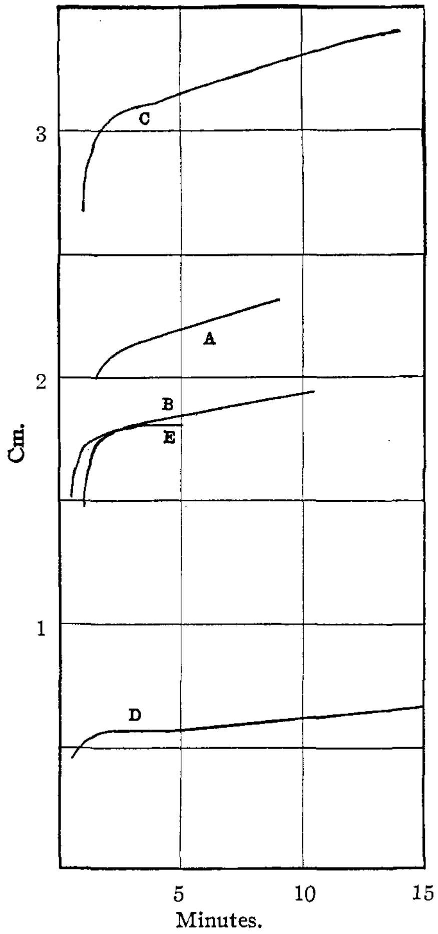

Fig. 6.—Increase of pressure with time.

The above experiments with peroxide have been repeated many times with the same conclusion that, like water vapor, it is unassociated in the vapor state.

The Explosion Temperature of Pure Hydrogen Peroxide

The minimum temperature of decomposition of hydrogen peroxide where the rate would be classed as explosive was investigated for a certain set of conditions. In these experiments the decomposition was called explosive when it made an audible report or "bang." The method of procedure was to drop about 0.05 to 0.3 g. of pure peroxide contained in a paraffin capsule into a tube about three centimeters in diameter. This tube was placed vertically in a deep oil-bath. The temperature of the oil-bath was taken with a mercury thermometer totally immersed in it. The results, which could be repeated every time quite independently of the quantity of peroxide used, were as follows: 146°, no explosion; 150°, dull explosion, barely audible; 151°, fairly sharp explosion; 153°, violent explosion; 159°, violent explosion of about the same intensity as at 153°.

The experiments were repeated with a saturated solution of potassium chloride in pure peroxide: 151°, no explosion; 160°, rapid decomposition to give a flame but no audible explosion.

At 160° a 95% solution of peroxide and water gave the same result as the potassium chloride solution at the same temperature.

From the results with the pure peroxide the nature of the explosion was seen to change rapidly between 150 and 153°. This indicates that the pure hydrogen peroxide explodes when it is heated to its boiling point. Dissolved potassium chloride or water, if anything, raise the explosion temperature.

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Summary

Melting-point curves were determined in pure hydrogen peroxide and a comparison was made with the analogous curves in water for potassium chloride, potassium sulfate, sodium fluoride and methyl alcohol. Curves were also obtained for ethyl ether and sulfuric acid in hydrogen peroxide.

Melting-point curves of *n*-butylamine and the monobutylamine (tertiary carbon) indicated the formation of compounds with hydrogen peroxide. These compounds are probably the first molecular complexes formed in the oxidation of amines to nitro compounds.

The oils which separate on mixing anhydrous ether solutions of amines and hydrogen peroxide were analyzed and shown to be molecular compounds of peroxide and the base.

An accurate determination of the heat of decomposition of hydrogen peroxide was carried out at 20° which gave the value 23,450 cal. for the molecular heat of decomposition into water and oxygen gas at atmospheric pressure.

A determination of the vapor density of hydrogen peroxide gave the molecular weight to be 34.

The decomposition of pure hydrogen peroxide was found to change rapidly in character about its boiling point, 151°, from that of a quiet reaction to a violent explosion. The addition of a little water or potassium chloride deadened the effect.

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