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

THE PARTITION COEFFICIENTS OF HYDROGEN PEROXIDE BETWEEN WATER AND CERTAIN ORGANIC SOLVENTS.

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The fact that hydrogen peroxide is soluble in ether and amyl alcohol has been recognized for a long time. It is not generally known, however, that a surprisingly large number of organic solvents dissolve this substance. A. Brann[1] carried out a series of semi-quantitative experiments in this laboratory, in which he agitated equal volumes of hydrogen peroxide solutions with various organic solvents at room temperature, and determined the amount of peroxide in each phase. The results of his experiments are incorporated in Table I. Brann found that the peroxide is also soluble in many other organic solvents, notably phenol and aniline. His experiments show that the solvents that dissolve water will also dissolve hydrogen peroxide.

TABLE I.

Solvent.	$\frac{\text{Conc. in solvent}}{\text{Conc. in water}}$.	Solvent.	$\frac{\text{Conc. in solvent}}{\text{Conc. in water}}$.
Ethyl acetate	2/5	Chloroform	1/600
Nitrobenzene	1/200	Benzene	1/200
Acetophenone	1/4	Isobutyl alcohol	1/3
Amyl acetate	1/8	Propyl formate	1/8
Ethyl isovalerianate	1/40	Isobutyl butyrate	1/50
Isoamyl propionate	1/12	Propyl butyrate	1/30

Measurements of the partition coefficients of hydrogen peroxide have been made by Calvert[2] with amyl alcohol and water and by Osipoff and Popoff[3] with water and ether at 17.5°.

The results obtained by the latter investigators are as follows:

Vol. ether	1	1	2	5	6	7	8	9	10
Vol. water	2	1	1	1	1	1	1	1	1
$\frac{\text{Conc. } H_2O_2 \text{ in water}}{\text{Conc. } H_2O_2 \text{ in ether}}$	17.4	16.8	16.7	16.7	13.3	13.5	14.9	14.3	13.9

Experimental.

The hydrogen peroxide used in these experiments was Merck's "Perhydrol," The organic liquids were the purest materials obtainable. These were redistilled once, and in some cases twice, and the constant boiling fractions used.

An electrically heated and controlled thermostat was constructed in which to carry on the experiments at constant temperature. Equal volumes of water and the given solvent, usually 15 cc. of each, and the de-

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[1] *Dissertation*, University of Wisconsin, **1914**.

[2] *Z. physik. Chem.*, **38**, 513 (1901).

[3] *J. Russ. Phys. Chem. Soc.*, **35**, 637 (1903).

sired volume of hydrogen peroxide were pipetted into glass stoppered bottles of about 60 cc. capacity. These bottles were then clamped in the bath in a shaking device. The liquids in the bottles were allowed to come to the temperature of the bath, and then were shaken until equilibrium was reached, about an hour being the usual period necessary. After equilibrium was reached, definite volumes of each layer were pipetted off and diluted. In general, 10 cc. of the aqueous layer were diluted to 200 cc. with distilled water. The layer of organic solvent was diluted with ethyl alcohol, either 5 or 10 cc. being made up to 100 cc., depending upon the ease of separation of the layers and upon the concentration of peroxide. Aliquot portions were then taken and the concentration of hydrogen peroxide in each solution was determined.

Two methods were employed for the estimation of the hydrogen peroxide. Whenever possible, it was titrated with standard potassium permanganate in dilute sulfuric acid solution. In these cases the sulfuric acid was added during dilution. In general 20 cc. portions were titrated,

TABLE II.

Partition Coefficients of Hydrogen Peroxide between Water and Certain Organic Solvents at 25°. Determined by Titration Method.

Solvent.	Solvent and water taken cc. of each.	Cc. 30% H_2O_2 taken.	Titration of 1 cc. of:		Partition coefficient $\frac{C_{aq.}}{C_s}$.
			Solvent C_s.[1]	Water C_{aq}.[1]	
Ethyl acetate	10.0	5.0	11.75	46.25	3.94
	10.0	5.0	13.77	53.84	3.92
	10.0	5.0	14.39	57.14	3.97
	10.0	5.0	14.25	57.24	4.01
	10.0	7.0	13.20	53.20	4.03
	15.0	5.0	10.01	39.68	3.97
	15.0	5.0	10.03	39.60	3.95
	15.0	7.0	13.28	54.44	4.10
	15.0	7.0	13.27	54.50	4.10
	15.0	7.0	13.00	53.51	4.11
Isobutyl alcohol	15.0	5.0	15.96	41.13	2.58
	15.0	7.0	20.18	52.30	2.59
	15.0	5.0	16.60	43.62	2.63
	15.0	7.0	21.05	54.13	2.58
Amyl acetate	15.0	5.0	3.64	47.75	13.1
	15.0	7.0	4.59	60.65	13.2
	15.0	10.0	5.90	76.80	13.0
Acetophenone	15.0	5.0	7.77	46.46	5.98
	15.0	7.0	9.82	59.47	6.06
	15.0	10.0	11.15	64.78	5.82
Ether	15.0	3.0	3.22	29.32	9.11
	15.0	5.0	5.05	44.22	8.76
	15.0	7.0	6.90	56.90	8.25

[1] C_s and $C_{aq.}$ represent concentration of H_2O_2 in 1 cc. of solvent and aqueous layers, respectively, expressed in terms of cubic centimeters of approximately 0.1 *N* $KMnO_4$.

so that the number of cubic centimeters of permanganate used gave the value for 1.0 cc. of the original aqueous layer.

In several cases permanganate could not be used because it oxidized the organic solvent. Consequently a gasometric method was devised to determine the concentration of peroxide. In this method an aliquot part of the solution was placed in a flask connected by a capillary tube to a water-jacketed gas buret. A capsule of manganese dioxide, held in the neck of the flask by a glass rod, was released, and allowed to drop into the liquid.[1] The manganese dioxide decomposed the hydrogen peroxide completely in about fifteen minutes. The volume of oxygen liberated was read on the gas buret. Errors of reading were decreased to the minimum by the use of large portions of the solution. Table II, preceding, gives the results obtained from use of the titration method with those liquids in which the hydrogen peroxide underwent no change of molecular weight.

In the above table it will be seen that the coefficient for ethyl acetate was determined a number of times more than for any of the other liquids. This was done to make sure that the method employed would give constant results. In the case of isobutyl alcohol, amyl acetate, and acetophenone, constant results were obtained. That the hydrogen peroxide does not undergo association in any of the solvents used in Table II is evidenced by the fact that the values $C_{aq.}/C_s$ for the different concentrations are constant.

The partition coefficients for water-ether are lower than the lowest value obtained by Osipoff and Popoff, 13.9. These investigators, however, worked at 17.5°, whereas the above measurements were carried out at 25°. In order to see whether or not this difference was due to the difference in temperature, partition coefficients were determined at 0°, with the following results:

Vol. ether.	Vol. water.	Vol. 30% H_2O_2.	$C_{aq.}$.	C_s.	$\frac{C_{aq.}}{C_s}$.
15 cc.	15 cc.	5 cc.	35.15 cc.	6.00 cc.	5.85
15 cc.	15 cc.	7 cc.	45.3 cc.	7.95 cc.	5.72

These results indicate that for lower temperatures the value of the partition coefficient decreases. Consequently the values obtained in this investigation are appreciably lower than those of Osipoff and Popoff.

A number of other organic solvents were used, but for various reasons quantitative results could not be obtained. Phenylhydrazine dissolves hydrogen peroxide, but it is rapidly oxidized with the formation of aniline as one of the oxidation products. With methyl iodide the solubility was so small that the buret readings were not reliable. By titration of the aqueous layer the $C_{aq.}/C_s$ was found to be approximately 200. *m*-Tolui-

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[1] Walton, *Z. physik. Chem.*, **47**, 2 (1904).

dine forms an addition product with the sulfuric acid. The titration of the aqueous layer gives a value of $C_{aq.}/C_s$ that is about 5. Aniline and phenol showed very little oxidation by the hydrogen peroxide, but were so rapidly oxidized by the permanganate that concordant results could not be obtained. The layers were consequently analyzed by the gasometric method already described. The results are given in Tables III and IV.

TABLE III.

Distribution of Hydrogen Peroxide between Water and Aniline. Temperature 25°.

Vol. aniline.	Vol. water.	Vol. 30% H_2O_2.	Oxygen from 2 cc. aniline C_s.	Oxygen from 2 cc. aqueous layer $C_{aq.}$.	$\frac{C_{aq.}}{C_s}$.
15 cc.	15 cc.	1 cc.	2.80 cc.[1]	11.40 cc.[1]	4.08
15 cc.	15 cc.	2 cc.	5.10 cc.	20.90 cc.	4.10

TABLE IV.

Distribution of Hydrogen Peroxide between Water and Phenol. Concentrations Expressed in Millimols per 10 cc. Temperature 25°.

H_2O_2 in phenol C_s.	H_2O_2 in aqueous layer $C_{aq.}$.	$\frac{C_{aq.}}{C_s}$.	$\frac{C_{aq.}}{\sqrt{C_s}}$.
105.7	459.1	4.35	44.7
182.1	839.0	4.61	62.1
250.5	1217.0	4.88	76.9
337.2	1868.0	5.55	102.0

The constancy of the values $C_{aq.}/C_s$ shows that the hydrogen peroxide does not undergo association when dissolved in aniline. The corresponding values obtained in Table IV, which gives the solubility of hydrogen peroxide in phenol, are far from constant, and indicate association. If the association consists in doubling all the molecules of hydrogen peroxide, the value $C_{aq.}/\sqrt{C_s}$ should be constant, but this is not the case.

TABLE V.

Distribution of Hydrogen Peroxide between Water and Quinoline. Concentrations are in Millimols per 10 cc.

Temp.	H_2O_2 in quinoline. C_s.	H_2O_2 in aqueous layer. $C_{aq.}$	$\frac{C_{aq.}}{C_s}$.	$\frac{C_{aq.}}{\sqrt{C_s}}$.
0°............	617	170.1	0.276	6.85
	1636	522.6	0.319	12.9
	2419	944.5	0.391	19.2
25°............	1118	408.0	0.365	12.2
	1456	635.0	0.435	16.6
	2181	1090.0	0.505	23.4
	2715	1538.0	0.559	29.5
	3361	2157.0	0.642	37.2
40°............	1330	686.0	0.516	18.7
	1993	1197.0	0.602	26.8

The solubility of hydrogen peroxide in quinoline is interesting because the partition coefficient is less than *one;* in other words, when quinoline

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[1] At 20° and 740 mm.

is agitated with an equal volume of hydrogen peroxide solution it removes more than half the hydrogen peroxide. The results of experiments with quinoline which are given in Table V point to association, for the ratio $C_{aq.}/C_s$ is not constant. The values of $C_{aq.}/\sqrt{C_s}$ and of $C_{aq.}/\sqrt[3]{C_s}$ have also been computed, but they do not give constants.

An examination of the data for the distribution at 0°, 25° and 40°, respectively (Table V), shows the existence of an appreciable temperature coefficient. For a given concentration of hydrogen peroxide, the lower the temperature the greater the percentage dissolved by the quinoline. A temperature effect of so great a magnitude is unusual for substances for which constant values of the partition coefficient can be obtained. Cases similar to the above have been found, however, by Hantzsch[1] and his co-workers. The large temperature coefficient, and the great change in distribution for a change in the concentration, indicate a combination of the solute with one of the solvents.[2] In the case of quinoline the existence of a compound of quinoline and hydrogen peroxide dissolved in the quinoline layer, and in equilibrium with uncombined hydrogen peroxide seems very probable, particularly when one recalls the basic properties of quinoline and the slightly acid properties of the peroxide. Quinoline, moreover, shows an unusual tendency to form addition products with a surprisingly large number of compounds. The results obtained from hydrogen peroxide and phenol are doubtless due to similar causes.

This investigation, and in particular the reactions of quinoline solutions of hydrogen peroxide, is being continued.

Summary.

1. Organic solvents that dissolve water will also dissolve hydrogen peroxide.

2. The partition coefficient of hydrogen peroxide between water and each of the following substances has been determined at 25°: ethyl acetate; isobutyl alcohol; amyl acetate; acetophenone; ethyl ether; aniline. The hydrogen peroxide does not undergo association in these solvents. The values obtained for ethyl ether do not agree with those of Osipoff and Popoff.

3. Hydrogen peroxide is soluble in phenol and in quinoline. The quinoline is not a solution of simple peroxide molecules, but probably consists of a compound of the solvent and hydrogen peroxide in equilibrium with hydrogen peroxide.

4. Quinoline is an unusually good solvent for hydrogen peroxide.

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[1] Hantzsch and Seboldt, *Z. physik. Chem.*, **30**, 258 (1899); Hantzsch and Vagt, *Ibid.*, **38**, 705 (1901).

[2] Herz, "Der Verteilungssatz," *Ahrens' Sammlung*, Vol. **15**, p. 17.

At 0° for certain concentrations of hydrogen peroxide the value $\frac{H_2O_2 \text{ in water}}{H_2O_2 \text{ in quinoline}}$ may be as low as 0.276.

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THE OXIDATION OF MANGANESE SOLUTIONS IN PRESENCE OF THE AIR.

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It is well known that manganous solutions when neutralized undergo hydrolysis, and that when such solutions are allowed to stand in contact with the air, oxidation takes place with the precipitation of hydrated manganese dioxide. In the presence of the common alkalies, manganous salts yield manganous hydroxide, which when exposed to the air undergoes oxidation with the formation of hydrated manganese dioxide.

The deposition of pyrolusite, the most plentiful of the manganese ores in nature, is doubtless the result of a series of reactions of neutralization and oxidation. Manganese is presumably transported in nature as bicarbonate, sulfate, or chloride. When a manganese-bearing solution comes in contact with such a substance as calcium carbonate which is so widely distributed in nature, the manganese salt is neutralized, hydrolysis takes place, the action of the oxygen of the air steps in and manganese dioxide is precipitated, the calcium carbonate serving to neutralize the free acid which is liberated in the reaction.

In studying the reactions incident to the deposition of manganese dioxide by the neutralization of manganese salts and the subsequent oxidation by means of air, a series of observations have been made by the writer which at first sight seemed to be examples of certain principles of positive and negative catalysis.

A large number of glass tubes were cleansed with the utmost care and in each tube was placed a 1% solution of pure manganous chloride, a piece of Iceland spar, and a piece of metal, mineral or metallic compound. The solution and solids filled about one-fourth of the tube; the remainder of the space was occupied by air. These tubes were then sealed and allowed to stand for a long time in order to allow the slow oxidation by the air to take place. Very striking differences in behavior are exhibited by the various metals under these conditions. Certain of the metals cause the production of manganese dioxide to be accelerated, while others cause its formation to be retarded, or in some cases to be actually inhibited. Lead and bismuth accelerate the deposition of manganese dioxide from a manganese chloride solution when calcite is present as a neutralizing agent.