## Summary

The freezing point–composition diagram of the system naphthalene–*m*-dinitrobenzene has been redetermined, the freezing points being measured by two methods which involve approaching the equilibrium from opposite sides. The resulting diagram is of the compound formation type and thus corroborates substantially the diagrams of Kremann[2] and of Olivari,[11] and disagrees with that of Puschin.[1] Exception is taken to the arguments of Puschin against compound formation in this system, and viscosity data are cited as further evidence showing that the system is not of the simple eutectic type as Puschin claims.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

# CONCENTRATION OF HYDROGEN PEROXIDE SOLUTIONS

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Numerous methods have been described for the concentration of hydrogen peroxide solutions to 60–90% strength, but apparently it is impossible to exceed 90–91% by evaporation or distillation methods. An efficient plan for such a process is that of Maass and Hatcher,[1] but in spite of its efficiency this method is made rather cumbersome by requiring an all-glass apparatus with ground-glass joints and also a sulfuric acid pump. Such special equipment detracts materially from the general usefulness of this process.

The method described in the present paper also is capable of concentrating hydrogen peroxide solutions rapidly to 90% strength, and the apparatus required is merely the simple equipment for distillation and for vacuum distillation. The essence of the method is to add an immiscible volatile liquid such as a hydrocarbon and to distil the mixture. This modified steam-distillation leaves a residue of concentrated hydrogen peroxide after the water and hydrocarbon have distilled away. The method is simple and by controlling the conditions one may obtain nearly any degree of concentration up to 90–91%. It is necessary only to mix about one volume of peroxide solution with two volumes of hydrocarbon. By ordinary distillation with xylene a 3% solution may be concentrated to about 30% strength, and by using *p*-cymene and distilling in a vacuum, a 30% solution may be concentrated to about 90%. A similar method was found to be very satisfactory for the concentration of hydrazine hydrate[2] solutions.

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[1] Maass and Hatcher, THIS JOURNAL, **42**, 2552 (1920).

[2] Hurd and Bennett, *ibid.*, **51**, 265 (1929).

Some of the results may be briefly summarized. With xylene as the hydrocarbon it was possible to effect a concentration of 3% to either 17% or to 25–30% by ordinary distillation. For the former, distillation was interrupted when the volume of the aqueous residue was about one-tenth its original volume. For the latter, the distillation was interrupted at one-twentieth the volume, and the yield of 30% peroxide by this method was about 60%. It.was found that 20–30% of the original peroxide was decomposed into oxygen gas, a decomposition which was caused by the high temperature (about 100°) of the distillation. Starting with 30% hydrogen peroxide, further concentration to a peroxide of 45–60% strength was attainable by another distillation but higher than 60% by this method was not realized. Vacuum distillation at 20–30 mm. with xylene effected a concentration of 30% hydrogen peroxide solution to only 44% (yield, 86%), so xylene was discontinued in favor of a higher-boiling hydrocarbon for the vacuum distillation studies.

*p*-Cymene and tetralin were both found to be satisfactory, but the residual concentrated hydrogen peroxide from tetralin always assumed a deep yellow color. The peroxide from cymene was colorless, and cymene was the most satisfactory of the three hydrocarbons tried. Indeed, it was found possible to start with 30% hydrogen peroxide and concentrate this to 89% strength in one operation in 60% yields merely by distilling it, admixed with cymene, in the vacuum of a water pump. The distillation temperature of the mixture when cymene was used at 25–32 mm. was 52–55°. Losses under these conditions were very small, since the total peroxide in the aqueous distillate and in the undistilled portion was 91–96% of the original quantity. The material of 88–91% purity which was produced crystallized readily in an ice–salt mixture and was thus capable of further concentration to pure hydrogen peroxide by the method of Maass and Hatcher, who found that several such recrystallizations were necessary before 100% purity was attained.

Since commercial solutions of hydrogen peroxide contain non-volatile preservatives, it is obvious that such substances, if originally present, will remain either in the residual concentrated peroxide solution or in the supernatant residual hydrocarbon layer. Most of our work was performed either with the 30% hydrogen peroxide of commerce or with the aqueous, peroxide-containing distillates from our own experiments. Such distillates necessarily contained no non-volatile preservatives, but the experiments with them seemed identical with the others. It is evident that a distilled peroxide solution should be used as a starting material whenever the presence of foreign material in the concentrated peroxide is objectionable.

## Experimental Part

**Materials Used.**—Both the 3% (Mallinckrodt) and the 30% (Merck's Superoxol) commercial solutions of hydrogen peroxide were used in this work. The former was stated to contain acetanilide (0.04%), whereas traces of acidic preservatives[3] (oxalic, no more than 0.035%; sulfuric, 0.015%; and lesser amounts of hydrochloric, hydrofluoric and phosphoric acids) were stated to be in the latter. In addition to these commercial sources of hydrogen peroxide solutions, several of the "aqueous distillates" which are mentioned below were also concentrated by the present method.

**Distillation of Hydrogen Peroxide with Xylene at Atmospheric Pressure.**—One volume of the peroxide solution was admixed with about two volumes of xylene in a pyrex distilling flask. The flask was attached in the usual way (cork stoppers) to a condenser and receiver. The flask was heated by an oil-bath and the distillation was continued until 80–90% of the xylene had distilled over. The temperature of the vapor was noted. The two layers of both the residue and the distillate were separated, measured and the aqueous portions analyzed by titration with standard permanganate. The data are summarized in Table I.

**Concentration of Hydrogen Peroxide Solutions by Vacuum Distillation with *p*-Cymene.**—The apparatus employed in this case was the customary one for organic vacuum distillations. Thus a Claisen flask was attached to a condenser, which in turn

TABLE I

DATA ON DISTILLATION EXPERIMENTS OF MIXTURES OF HYDROGEN PEROXIDE, WATER AND HYDROCARBONS

| Original $H_2O_2$ soln. Concn., % by wt. | Original $H_2O_2$ soln. Vol., cc. | Distn. temp., °C. | Press., mm. | Duration of distn., hrs. | Hydrocarbon Distillate, cc. | Hydrocarbon Residue, cc. | Aqueous distillate Vol., cc. | Aqueous distillate Concn., % by wt. | Residual $H_2O_2$ Vol., cc. | Residual $H_2O_2$ Concn., % by wt. | Residual $H_2O_2$ Yield, % | Recov. $H_2O_2$ (distillate + residue), g. | Recov. $H_2O_2$ (distillate + residue), % |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Xylene | | | | | | | | |
| 3 | 900 | 93 | 750 | 6 | 1870 | 127 | 835 | 0.3 | 59 | 25.1 | 60 | 18.5 | 68[a] |
| 3 | 900 | 93 | 750 | 6 | 1785 | 200 | 785 | 0.3 | 110 | 17.1 | 73 | 22.3 | 82 |
| 17.5 | 127 | 94 | 750 | 1 | 187 | 11 | 81 | 3.5 | 43 | 30.5 | 62 | 17.5 | 74 |
| 30 | 100 | 98 | 750 | 1 | 168 | 30 | 58 | 5.8 | 41 | 46.3 | 67 | 25.8 | 77 |
| 30 | 100 | 37 | 30 | 0.6 | 193 | 45 | 41 | 5.1 | 56 | 43.6 | 85 | 30.7 | 92 |
| 30 | 100 | 98 | 750 | 1 | 175 | 25 | 62 | 4.7 | 37 | 45.4 | 59 | 22.7 | 68 |
| 30 | 90 | 97 | 750 | 1.5 | 161 | 37 | 58 | 4.5 | 31 | 59.9 | 76 | 25.7 | 85 |
| 46 | 70 | 98 | 750 | 0.6 | 111 | 37 | 34 | 9.1 | 33 | 48.7 | 51 | 22.3 | 60 |
| 30 | 100 | 99 | 750 | 1.2 | 164 | 30 | 58 | 4.4 | 42 | 54.6 | 84 | 30.6 | 91 |
| | | | | | Cymene | | | | | | | | |
| 49 | 30 | 46 | 23 | 1 | 30 | 30 | 17 | 17.9 | 12 | 80.0 | 74 | 16.1 | 92 |
| 60 | 30 | 52 | 29 | 0.6 | 22 | 37 | 12 | 27.0 | 17 | 78.9 | 80 | 21.4 | 96 |
| 55 | 41 | 55 | 28 | 1 | 55 | 25 | 24 | 39.0 | 13 | 90.3 | 60 | 27.0 | 98 |
| 79 | 16 | 56 | 29 | 0.25 | 28 | 9 | 8 | 62.6 | 8 | 88.5 | 58 | 16.1 | 96 |
| 80 | 8 | 52 | 25 | 0.25 | 6 | 14 | 3 | 47.6 | 5 | 90.6 | 75 | 8.1 | 95 |
| 85.8 | 15 | 55 | 29 | 0.1 | 12 | 18 | 3 | 67.0 | 11 | 88.3 | 76 | 15.9 | 91 |
| 30 | 80 | 57 | 32 | 1 | 91 | 66 | 67 | 13.4 | 13 | 88.8 | 60 | 25.5 | 95 |
| 30 | 100 | 44 | 10 | 1.3 | 150 | 45 | 83 | 18.1 | 14 | 82.5 | 47 | 31.5 | 94 |
| | | | | | Tetralin | | | | | | | | |
| 60 | 61 | 52 | 27 | 0.5 | 15 | 83 | 30 | 29.0 | 30 | 84.3 | 76 | 44.1 | 97 |
| 87 | 13 | 38 | 7 | 0.2 | 4 | 24 | 3 | 70.7 | 9 | 90.2 | 73 | 14.1 | 91 |

[a] In this run 2900 cc. (26°, 750 mm.) of oxygen was collected. This is equivalent to 29% of the original hydrogen peroxide.

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[3] After reading the manuscript, the Referee commented that "the 30% peroxide now placed on the market contains salicylic acid."

was attached to a receiver, manometer and water pump. Rubber stoppers were satisfactorily used throughout, since they were not appreciably attacked by the hydrocarbon at the temperature employed. A water-bath, kept at 70–75°, was used to heat the Claisen flask. Since our experiments were designed to show the fate of all substances used, the receiver was kept in an ice-bath to minimize losses from the distillate. Were concentration of the peroxide the only goal, this ice-bath could be omitted. Usually, two volumes of cymene were placed in the Claisen flask with one volume of either 30 or 60% hydrogen peroxide solution. The distillation was stopped to analyze the various fractions before all of the cymene had distilled. These data also are collected in Table I.

Similar vacuum distillation experiments were also conducted with xylene and with tetralin. Some experiments with cymene and with tetralin were carried out with an oil pump, but no advantage was gained thereby. The concentrated hydrogen peroxide obtained when tetralin was used was always yellow in color. The cause of the coloration was not investigated.

## Summary

If hydrogen peroxide solutions are vacuum distilled with *p*-cymene, a peroxide of 88–91% strength may be obtained readily. The yield of this concentrated material which remains undistilled is 60–76% and most of the remaining peroxide is to be found in the distillate. Actual losses, therefore, are negligible since a 91–98% recovery was always realized when the distillation temperature was kept below 57°. The simplicity of the apparatus and the rapidity of the concentration are also very desirable features.

Tetralin behaves like cymene in this respect, but it imparts a yellow color to the concentrated peroxide. Xylene also was studied but its high vapor pressure, as compared to cymene, makes it undesirable for use at 25–30 mm. pressure. With distillation at atmospheric pressure the losses due to decomposition of the peroxide into oxygen become quite appreciable.

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# THE SENSITIVITY AND APPLICABILITY OF THE PICRIC ACID TEST FOR POTASSIUM

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The fact that an alcoholic solution of picric acid can be used as a reagent for potassium has been frequently noted in the literature of analytical chemistry. There exist, however, no quantitative data regarding either the sensitivity of this reagent toward the potassium ion or the allowable concentrations of other ions that can be present without causing interference. The present experiments were undertaken in order to determine these points and to find the optimum conditions for this reaction.

## Experimental Part

**Preparation of the Reagent.**—The reagent used in these experiments, and the one found most suitable, was prepared by drying the moist picric